Comprehensive Inorganic Chemistry

The Chemistry of

RUTHENIUM, RHODIUM, PALLADIUM, OSMIUM, IRIDIUM AND PLATINUM

Stanley E. Livingstone

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PREFACE

The excellent reception that has been accorded to *Comprehensive Inorganic Chemistry* since the simultaneous publication of the five volumes of the complete work has been accompanied by the plea that sections should be made available in a form that would enable specialists to purchase copies for their own use. To meet this demand the publishers have decided to issue selected chapters and groups of chapters as separate editions. These chapters will, apart from the corrections of misprints and the addition of prefatory material and individual indices, appear just as they did in the main work. Extensive revision would delay publication and greatly raise the cost, so limiting the circulation of these definitive reviews.

A. F. TROTMAN-DICKENSON
Executive Editor

43. THE SECOND- AND THIRD-ROW ELEMENTS OF GROUP VIII A, B AND C

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1. THE PLATINUM METALS

1.1. DISCOVERY AND EARLY HISTORY

The six elements ruthenium, osmium, rhodium, iridium, palladium, and platinum are known as the *platinum metals.*

In 1901 Berthelot[1] reported that a casket found at Thebes in Upper Egypt and dating from the seventh century BC, contained platinum. The casket was covered with hieroglyphs of metal; on one side the characters were of gold and on the other of silver. Berthelot found, on close examination, that one of the latter characters was not silver but native platinum containing a little gold and iridium. He suggested that it was doubtful whether the Egyptian craftsman had noticed the difference between this particular piece of metal and the silver used for the other characters. Although a few similar occurrences have been noted by Lucas[2] among ancient Egyptian objects, there is no substantial evidence that any of the platinum metals was known to the ancients.

Native platinum was used by the Indians of Ecuador before the arrival of the conquistadores and probably before the Inca conquest half a century earlier. These Indians made small articles of jewellery from native platinum or platinum alloyed with gold. Many of these objects, which were skilfully made, consisted of gold with a coating of platinum alloy on one side. In 1557 the Italian scholar and poet Scaliger made mention of an infusible metal from the mines of Honduras, a district between Mexico and Darien (Panamá). Although platinum does not occur in this region, it may well have been in the possession of persons in this part of the Spanish Indies. The first definite reference to platinum was made by de Ulloa, a Spanish naval officer and scientist, who accompanied an expedition sent by the Académie des Sciences in Paris to Quito in 1736 to measure the arc of the meridian at the equator. In his account of the expedition, published in 1748, de Ulloa described the occurrence of an unworkable metal called *platina* in the mines of the Chocó district of New Granada (Colombia). He reported that the separation of the platina from the gold, which occurred together as small grains in alluvial deposits, was tedious and costly such that a high content of platina rendered the ore virtually worthless.

The Spaniards first called the metal *platina del Pinto* (little silver of the Pinto), since it was first distinguished in the gravels of the Rio di Pinto, probably a tributary of the San

[1] M. Berthelot, *Compt. rend.* **132** (1901) 729.
[2] A. Lucas, *Ancient Egyptian Materials and Industries*, Edward Arnold, London (1934), p. 202.

Juan River in the Chocó district of the Bishopric of Popayan. Other names given to it were *oro blanco* (white gold) and *juan blanco*. It was also called the *eighth metal* in Europe, since only seven metals were recognized up to that time: namely, gold, silver, mercury, copper, iron, tin and lead; these seven had been known since classical times. When the elemental nature of *platina* was definitely established later in the eighteenth century, the neuter or masculine form gradually replaced the feminine: in Latin and English *platina* became platinum; in French *la platine* became *le platine*; in German *die Platina* became *das Platin*; in Spanish *la platina* became *el platino*. This change arose since minerals were usually regarded as feminine and elements were considered masculine or neuter.

The first samples of platinum to be investigated scientifically were brought to England in 1741 by Wood, a metallurgist from Jamaica, who obtained them in Cartagena in New Granada. The new metal aroused great interest in Europe where its properties were investigated by a number of able chemists in England, Sweden, Germany, France and Spain. Difficulty was experienced in working the metal because of its high melting point, and little progress was made with the problem of getting the product into malleable form because of the presence of iron and copper. By 1785 Chabeneau and Fausto de Elhuyar, who occupied chairs of physics and chemistry respectively at Vergara in Spain, evolved a method for producing malleable platinum in quantity. As a consequence, an ornate chalice, made entirely of platinum and weighing 55 oz, was presented by Charles III of Spain to Pope Pius VI in 1789; it is now in the Treasury at St. Peter's. The demand for platinum was such that in 1788 3820 lb of crude platinum were collected in the Chocó district and sent to the Spanish mints.

By 1805 Wollaston in London was producing malleable platinum by an improved process which involved hot forging of the purified metal. He was able to draw platinum into wire 0.00005 in. in diameter, and he manufactured platinum vessels for concentrating sulphuric acid; one such vessel held 30 gal and weighed 34 lb. During his researches on the purification of platinum, Wollaston in 1803 isolated *palladium* (named after the planet Pallas, discovered in 1802) from the mother liquor remaining after the precipitation of platinum as the chloroplatinate from its solution in aqua regia by the addition of ammonium chloride. In 1804 he isolated another new element from platinum ore; to this he gave the name *rhodium* (Gr. ῥόδον, rose) because of the red colour of its compounds.

In 1803 Collet-Descostils reported the isolation of a new element from the residue left after crude platinum had been treated with aqua regia. In the same year de Fourcroy and Vauquelin also reported the isolation of this new element. In the following year Tennant established that there were in fact not one but two new elements in the insoluble black powder remaining after treatment of crude platinum with aqua regia. To one he gave the name *iridium* (L. *iris*, rainbow—from the variety of colours of its salts) and to the other *osmium* (Gr. ὀσμή, smell—on account of the odour of its volatile oxide).

In 1827 Osann announced the discovery of three new elements, *pluran*, *ruthen* and *polin*, which he claimed to have isolated from the residues left after the dissolution of platinum ore from the Ural Mountains. In 1844 Klaus, Professor of Chemistry at the University of Kazan, showed that Osann's ruthenium oxide was very impure but that, nevertheless, it did contain a new element which out of respect for Osann he named *ruthenium* (L. *Ruthenia*, Russia). Klaus fused the osmiridium residues, obtained from previous platinum purifications, with potash and nitre in a silver crucible, dissolved the cooled melt in water and treated this solution with nitric acid, producing a black precipitate of the oxides of osmium and ruthenium. He distilled this precipitate with aqua regia and condensed the osmium

tetroxide. The residue, on treatment with ammonium chloride, yielded a precipitate of ammonium chlororuthenate which on being heated yielded 6 grams of ruthenium.

Numerous accounts of the history of the platinum metals have appeared since that given by Lewis[3] in 1763. An interesting and detailed history has been written recently by McDonald[4].

1.2. OCCURRENCE AND DISTRIBUTION

Estimates vary concerning the abundance of the platinum metals in the earth's crust but platinum is the most common with an abundance of about 10^{-2} g ton^{-1} (ppm); the abundances of the other metals in g ton^{-1} are approximately as follow: palladium, 10^{-3} to 10^{-2}; osmium and iridium, 10^{-3}; ruthenium and rhodium, 10^{-4}. These metals have also been found in meteorites.

The six metals usually occur associated together as indefinite alloys. Platinum mostly occurs native associated with one or more of the other platinum metals together with gold, iron, copper and chromium; the platinum content varies between 60 and 90%. It occurs in placer (alluvial) deposits as fine grains which are pale steel grey or silver white but sometimes black due to a layer of magnetite. The mother rock, from which the alluvial grains originally came, consists of basic or ultra-basic igneous rocks including the peridotites, pyroxenites and dunites. The peridotites and pyroxenites are composed of iron and magnesium silicates, pyroxene, and augite with hornblende, olivine, chromite, ilmenite and magnetite, while the dunites consist principally of olivine with some chromite. These rocks have been more or less altered to serpentine. In sedimentary rocks platinum is usually associated with quartz, copper, nickel, silver and palladium, whereas in alluvial deposits it is associated with chromite, magnetite, ilmenite, iridium and osmiridium. Platinum also occurs as *sperrylite* $PtAs_2$, *cooperite* PtS and *braggite* (Pt, Pd, Ni) S.

Alloys of osmium and iridium occur in placer deposits. These are known as *osmiridium* or *syserskite*—with less than 60% (usually *ca.* 50%) iridium and *ca.* 35% osmium—and *iridiosmium* or *nevyanskite*—with over 60% (usually *ca.* 70%) iridium and *ca.* 20% osmium. Small amounts of other platinum metals are present in these minerals. Osmiridium also occurs in gold ores on the Witwatersrand, Transvaal.

Until 1824 New Granada was the sole source of supply of the platinum metals. In 1819 osmiridium was found on the gold fields north of Ekaterinburg (Sverdlovsk) on the eastern watershed of the Ural Mountains in Russia. In 1824 platinum was found in gold placers in the Goroblagodat district north of Sverdlovsk. Within a year a dozen or more rich placers were found and over 1000 oz of platinum were collected in Russia. In 1825 even richer alluvial deposits were found in the nearby district of Nizhny-Tagil. The two areas Goroblagodat and Nizhny-Tagil in the Urals were the chief centres of the Russian platinum field which was to be the principal source of the world's supply for nearly a century. Other alluvial deposits of platinum were found in various countries, but in 1914 Russia was producing 93% of the world's supply. The average annual production (in troy ounces) of platinum for the 6 years 1909–14 was as follows[5]:

Russia	Colombia	Australasia	United States	Borneo	Burma	Canada
200,000	12,080	790	594	180	46	33

[3] W. Lewis, *Commercium Philosophico-technicum*, London (1763).

[4] D. McDonald, *A History of Platinum*, Johnson Matthey, London (1960).

[5] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, London (1937), Vol. 16, p. 14.

Production in Russia slumped due to the First World War and the Bolshevik Revolution. Platinum had been found to occur in sulphide ores: in the nickeliferous pyrrhotite and chalcopyrite at Sudbury, Ontario, and in the lead–zinc sulphide ores at Broken Hill, New South Wales. Much palladium in the form of arsenide and selenide is present in the nickel–copper ore at Sudbury. In 1909 refining of the Canadian platinum commenced in London, and by 1935 the Sudbury source had become the dominant factor in world supplies, although the Russian and Colombian outputs were substantial. In 1939 Sudbury produced 149,000 oz of platinum and 135,000 oz of other platinum metals.

Since 1947 the South African output has increased markedly, and by 1967 accounted for about half of the world's production. The chief source is from deposits of native platinum, sperrylite, braggite, *stibiopalladinite*, Pd_3Sb, and *laurite*, RuS_2, which occur in basic igneous rocks in the Merensky Reef of the extensive Bushveld outcrop in the Transvaal. The platinum metals, which occur to the extent of 4–10 g ton^{-1}, are associated with the nickel and copper sulphide ores, pyrrhotite, pentlandite and nickeliferous pyrite. The chief mining centre is at Rustenburg, west of Pretoria. Considerable quantities of platinum metals are also obtained from the gold ores of the Witwatersrand. Other sources of supply are Abyssinia, Japan, the Katanga area of the Congo and Alaska, where mining commenced at Goodnews Bay in 1934.

The average annual production (in troy ounces) of platinum metals over the 5 years 1956–60 for the chief producing countries is as follows[6]:

South Africa	Canada	USSR	United States	Colombia	Japan
500,000	400,000	350,000	19,000	18,000	12,000

About 75% of the total is platinum. In 1962 Canadian production of platinum metals was officially given as 453,566 oz while the outputs of South Africa and the USSR were estimated at about 350,000 oz each. Colombian, Alaskan and United States production together amounted to about 50,000 oz. The world output of platinum metals for 1962 has been estimated at 1,181,000 oz[7]. Accurate statistics for subsequent years are impossible to obtain because the production figures for both South Africa and the USSR are well-guarded secrets. Nevertheless, in 1966 Rustenburg Platinum Mines announced plans to increase their output of platinum metals to 850,000 oz by 1969; the annual production planned for 1973 is 1,200,000 oz of platinum.

1.3. PHYSICAL PROPERTIES

The atomic and physical properties of the platinum metals are listed in Table 1. Since minute traces of impurities, including other platinum metals, cause marked changes in some properties such as hardness, tensile strength and electrical resistance, it is of the utmost importance that high-purity specimens of the metals are used for the determination of physical properties. It has been pointed out[8] that the failure to achieve a high state of purity has led to lack of agreement on the values of the various physical properties as determined by different investigators.

[6] W. R. Jones, *Minerals in Industry*, 4th edn., Penguin, London (1963), p. 205.

[7] *Mining Journal Annual Review*, London (1963), p. 11.

[8] F. E. Beamish, A. E. McBryde and R. R. Barefoot, The Platinum Metals, in *Rare Metals Handbook*, 2nd edn. (C. A. Hempel, ed.), Reinhold, London (1961), p. 304.

TABLE 1. PHYSICAL PROPERTIES OF THE PLATINUM METALS

Property	Ru	Rh	Pd	Os	Ir	Pt
Atomic number	44	45	46	76	77	78
Electronic ground state	d^7s^1	d^8s^1	d^{10}	d^6s^2	d^7s^2	d^9s^1
Atomic weight [a]	101.07	102.905	106.4	190.2	192.2	195.09
Lattice structure [b]	c.p. hex.	f.c. cube	f.c. cube	c.p. hex.	f.c. cube	f.c. cube
Metallic radius: 12-coordination (Å) [b]	1.34	1.34	1.37	1.35	1.36	1.39
Specific gravity, 20°C [c]	12.45	12.41	12.02	22.61	22.65	21.45
Melting point (°C) [d]	2427	1967	1555	2697	2454	1769
Boiling point	4150 [e]	3877 [d]	3167 [d]	*ca.* 5300 [e]	*ca.* 4800 [e]	3827 [d]
Specific heat (cal g^{-1} $°C^{-1}$ at 0°C) [c]	0.055	0.059	0.058	0.031	0.031	0.031
ΔH fusion (kcal g-atom^{-1}) [d]	*ca.* 6.1	*ca.* 5.2	4.12	*ca.* 6.4	6.6	5.2
ΔH vaporization (kcal g-atom^{-1}) [d]	—	127	89	—	—	122
Entropy at 298°K (e.u.) [d]	6.9	7.6	8.9	7.8	8.7	10.0
First ionization potential (eV) [e]	7.7	7.7	8.3	*ca.* 8.7	8.7	8.88
Mass susceptibility, χ (cm^3 g^{-1} $\times 10^6$) [c]	+0.43	+0.99	+5.23	+0.05	+0.13	+0.97
Nuclear spin (I) [e]	Ru^{99} $\frac{5}{2}$ Ru^{101} $\frac{5}{2}$	Rh^{103} $\frac{1}{2}$	Pd^{105} $\frac{5}{2}$	Os^{187} $\frac{1}{2}$ Os^{189} $\frac{3}{2}$	Ir^{191} $\frac{3}{2}$ Ir^{193} $\frac{3}{2}$	Pt^{195} $\frac{1}{2}$
Nuclear magnetic moment μ [e]	Ru^{99} −0.63 Ru^{101} −0.69	Rh^{103} −0.088	Pd^{105} −0.57	Os^{187} 0.12 Os^{189} 0.651	Ir^{191} 0.16 Ir^{193} 0.17	Pt^{195} 0.60
Thermal neutron absorption cross-section (barns atom^{-1}) [f]	2.56±0.12	156±7	8.0±1.5	15.3±0.7	440±20	8.8±0.4
Electronegativity, Pauling scale	*ca.* 2.2	2.28 [g]	2.20 [g]	*ca.* 2.2	2.20 [g]	2.28 [g]
Coefficient of linear expansion, 20–100°C ($\times 10^6$) [c]	9.1	8.3	11.1	6.1	6.8	9.1
Resistivity (microhm-cm at 20°C) [c]	6.71	4.33	9.93	8.12	4.71	9.85
Temperature coefficient of resistance, 0–100°C ($\times 10^3$) [c]	4.2	4.6	3.8	4.2	4.3	3.9
Modulus of elasticity in tension (lb in^{-2} $\times 10^6$) [c]	60	46	17	81	75	25
Tensile strength—annealed (lb in^{-2}) [c]	—	100,000	25,000	—	160,000	18,000
Hardness—annealed (Hv) [c]	200–300	100–120	40–42	300–670	200–240	40–42
Hardness (Mho's scale) [h]	6.5	—	4.8	7.0	6–6.5	4.3

[a] International Atomic Weights (1961).
[b] A. F. Wells, *Structural Inorganic Chemistry*, 3rd edn., Clarendon Press, Oxford (1962), pp. 979, 984.
[c] *Platinum Metals Review*, Johnson Matthey, London (1963), **7**, 147.
[d] US Atomic Energy Commission Report ANL-5750.
[e] R. C. Weast (ed.), *Handbook of Chemistry and Physics*, 46th edn., Chemical Rubber Co., Cleveland (1965), p. E62.
[f] C. A. Hampel (ed.), *Rare Metals Handbook*, 2nd edn., Reinhold, London (1961), p. 320.
[g] A. L. Allred, *J. Inorg. Nucl. Chem.* **17** (1961) 215.
[h] Ref. e, p. F15.

TABLE 2. ISOTOPES OF THE PLATINUM METALS [a]

Metal	Atomic weight	Natural isotopes		Artificially produced isotopes	
		Isotope	Abundance (%)	Isotope	Half-life ($t_{\frac{1}{2}}$)
Ruthenium	101.07	$_{44}Ru^{96}$	5.5	$_{44}Ru^{93}$	50 s
		$_{44}Ru^{98}$	1.9	$_{44}Ru^{94}$	57 m
		$_{44}Ru^{99}$	12.7	$_{44}Ru^{95}$	99 m
		$_{44}Ru^{100}$	12.6	$_{44}Ru^{97}$	3 d
		$_{44}Ru^{101}$	17.1	$_{44}Ru^{103}$	40 d
		$_{44}Ru^{102}$	31.6	$_{44}Ru^{105}$	4 h
		$_{44}Ru^{104}$	18.6	$_{44}Ru^{106}$	1 y
				$_{44}Ru^{107}$	4 m
				$_{44}Ru^{108}$	4 m
Rhodium	102.905	$_{45}Rh^{103}$	100.0	$_{45}Ru^{96}$	10 m
				$_{45}Rh^{97}$	35 m
				$_{45}Rh^{98}$	9 m
				$_{45}Rh^{99}$	16 d
				$_{45}Rh^{100}$	21 h
				$_{45}Rh^{102}$	206 d
				$_{45}Rh^{104}$	42 s
				$_{45}Rh^{105}$	36 h
				$_{45}Rh^{106}$	30 s
				$_{45}Rh^{107}$	22 m
				$_{45}Rh^{108}$	17 s
				$_{45}Rh^{109}$	30 s
				$_{45}Rh^{110}$	4 s
Palladium	106.4	$_{46}Pd^{102}$	1.0	$_{46}Pd^{98}$	18 m
		$_{46}Pd^{104}$	11.0	$_{46}Pd^{99}$	22 m
		$_{46}Pd^{105}$	22.2	$_{46}Pd^{100}$	4 d
		$_{46}Pd^{106}$	27.3	$_{46}Pd^{101}$	9 h
		$_{46}Pd^{108}$	26.7	$_{46}Pd^{103}$	17 d
		$_{46}Pd^{110}$	11.8	$_{46}Pd^{107}$	7×10^6 y
				$_{46}Pd^{109}$	14 h
				$_{46}Pd^{111}$	22 m
				$_{46}Pd^{112}$	21 h
				$_{46}Pd^{113}$	1 m
				$_{46}Pd^{114}$	2 m
				$_{46}Pd^{115}$	45 s
Osmium	190.2	$_{76}Os^{184}$	0.02	$_{76}Os^{181}$	23 m
		$_{76}Os^{186}$	1.6	$_{76}Os^{182}$	22 h
		$_{76}Os^{187}$	1.6	$_{76}Os^{183}$	12 h
		$_{76}Os^{188}$	13.3	$_{76}Os^{185}$	94 d
		$_{76}Os^{189}$	16.1	$_{76}Os^{191}$	15 d
		$_{76}Os^{190}$	26.4	$_{76}Os^{193}$	32 h
		$_{76}Os^{192}$	41.0	$_{76}Os^{194}$	2 y
				$_{76}Os^{195}$	6 m
Iridium	192.2	$_{77}Ir^{191}$	37.3	$_{77}Ir^{182}$	15 m
		$_{77}Ir^{193}$	62.7	$_{77}Ir^{183}$	55 m
				$_{77}Ir^{184}$	3 h
				$_{77}Ir^{185}$	15 h
				$_{77}Ir^{186}$	5 h
				$_{77}Ir^{187}$	12 h
				$_{77}Ir^{188}$	41 h
				$_{77}Ir^{189}$	11 d

TABLE 2 (*cont.*)

Metal	Atomic weight	Natural isotopes		Artificially produced isotopes	
		Isotope	Abundance (%)	Isotope	Half-life ($t_{\frac{1}{2}}$)
Platinum	195.09	$_{78}Pt^{190}$*	0.01	$_{77}Ir^{190}$	11 d
				$_{77}Ir^{192}$	74 d
				$_{77}Ir^{194}$	19 h
				$_{77}Ir^{195}$	2 h
				$_{77}Ir^{197}$	7 m
				$_{77}Ir^{198}$	50 s
		$_{78}Pt^{192}$†	0.8	$_{78}Pt^{184}$	3 h
		$_{78}Pt^{194}$	32.9	$_{78}Pt^{186}$	2 h
		$_{78}Pt^{195}$	33.8	$_{78}Pt^{187}$	2 h
		$_{78}Pt^{196}$	25.3	$_{78}Pt^{188}$	10 d
		$_{78}Pt^{198}$	7.2	$_{78}Pt^{189}$	11 h
				$_{78}Pt^{191}$	3 d
				$_{78}Pt^{193}$	< 500 y
				$_{78}Pt^{197}$	20 h
				$_{78}Pt^{199}$	30 m
				$_{78}Pt^{200}$	12 h

* Radioactive, $t_{\frac{1}{2}}$, 7×10^{11} y.
† Radioactive, $t_{\frac{1}{2}}$, *ca.* 10^{15} y.
s = seconds; m = minutes; h = hours; d = days; y = years.
[a] R. C. Weast (ed), *Handbook of Chemistry and Physics*, 46th edn., Chemical Rubber Co., Cleveland (1965), p. B–4.

As with other metals, hardness and other mechanical properties depend on the amount of cold working or annealing to which the metallic specimen has been subjected. By heavy cold work, the hardness of platinum can be increased from 40 in the annealed state to 120 Hv. Similarly, the tensile strength of platinum increases from 18,000 lb in^{-2} in the annealed condition to approximately 30,000 lb in^{-2} after severe cold working[8].

1.4. ISOTOPES

A list of the naturally occurring and the artificially produced isotopes of the platinum metals is given in Table 2.

The relative abundance of the naturally occurring isotopes and the half-life period of the radioactive isotopes are also given in the table. A more complete set of data for each nuclide has been published[9].

The nuclear reactions for producing isotopes frequently involve neutron bombardment of the target material. Bombardment by α-particles, deuterons, protons, electrons, γ-rays and X-rays is also used. If the resulting nuclide is isotopic with the parent atom, it is necessary to employ some method of separation: the techniques used include gaseous diffusion,

[9] D. Strominger, J. M. Hollander and G. T. Seaborg, *Rev. Mod. Phys.* **30** (1958) 585.

thermal diffusion, mass spectrometry and fractional distillation. Large electromagnetic separators are frequently employed. If the bombardment results in transmutation so that the nuclide produced is not isotopic with the parent atom, chemical as well as physical methods may be required to separate the isotopes.

The types of nuclear reactions used to produce isotopes and the separation techniques employed have been discussed in considerable detail in books devoted to nuclear chemistry[10, 11].

1.5. EXTRACTION AND PURIFICATION

The methods used to extract and purify the platinum metals are quite complex and vary according to the type of ore. A detailed description of the published refining procedures has been given by Beamish, McBryde and Barefoot[8], who point out that the refiners of the platinum metals have long been reluctant to disclose the details of their operations and consequently other (unpublished) methods may also be in use.

The platinum metals occur in the Cu–Ni sulphide ore from Sudbury, Ontario, to the extent of 0.5 g ton^{-1}. The ore is first crushed and finely ground and then treated by flotation and magnetic methods to separate the sulphide minerals. The sulphides are further separated by flotation to yield a nickel concentrate which contains most of the platinum metals. The nickel concentrate is heated with coke and sodium bisulphate to dissolve the copper sulphide in preference to the nickel sulphide. During the slow cooling of the Bessemer matte, two layers separate; the copper sulphide remains in the top layer while the bottom layer contains the nickel sulphide. The oxidation of the sulphur is controlled to produce a small proportion of metallic nickel. The bulk of the platinum metals is in this metallic fraction which, being magnetic, can be separated magnetically. This fraction is further concentrated by being heated with sulphur to convert most of the nickel to sulphide. The enriched nickel–platinum alloy is then refined electrolytically, whereupon the platinum metals are deposited in the anode slimes.

The platinum ores from the Merensky Reef in the Transvaal are subjected to a different treatment to that used for the Sudbury ore. After being crushed and ground, the ore is concentrated by gravity to give a product containing over 20% platinum metals as metal or as sulphide. The tailings from the gravity separation are treated by flotation methods to yield a product containing the platinum metal sulphides together with the sulphides of copper, nickel and iron. This product is smelted and the resulting matte is blown to remove the iron. This matte is then smelted with coke and sodium bisulphate, as described above for the Sudbury ore. The copper sulphide "tops" are separated from the nickel sulphide "bottoms". The latter are roasted to oxidize the nickel sulphide to oxide, which is reduced with coal in a reverbatory furnace. The resulting crude nickel is cast into anodes and refined electrolytically; the platinum metals accumulate in the anode slimes.

The platinum concentrates from the Sudbury process are smelted with litharge, fluxes and charcoal to remove silica and base metals. The litharge is reduced to lead which acts as a collector for the precious metals. The lead is oxidized by cupellation to give an ingot of an alloy with a high concentration of platinum metals. This alloy is treated with concentrated sulphuric acid which dissolves practically all the silver and about one-third of the

[10] G. Friedlander and J. W. Kennedy, *Nuclear and Radiochemistry*, Wiley, New York (1955), ch. 4, p. 91.
[11] M. Haïssinsky, *La Chimie nucleaire et ses applications*, Masson, Paris (1957), ch. 9, p. 198.

palladium as their sulphates, leaving a residue of the platinum metals and gold. The silver is recovered and refined electrolytically by the Moebius process[12] and the palladium is recovered from the anode slimes.

The concentrates are now extracted with aqua regia which dissolves most of the gold, palladium and platinum and leaves a residue containing ruthenium, rhodium, iridium and silver chloride. Ferrous sulphate is added to the filtrate to precipitate the gold which is purified by the Wohlwill electrolytic process[12]. The solution is next treated with ammonium chloride which precipitates the platinum as ammonium hexachloroplatinate(IV), $(NH_4)_2PtCl_6$. This precipitate is dried and ignited to platinum which is then dissolved in aqua regia. This solution is evaporated in the presence of sodium chloride and hydrochloric acid. The resulting salt Na_2PtCl_6 is dissolved in hot water and treated with sodium bromate in order to convert any iridium, rhodium, or palladium to oxidation states which produce filterable hydroxides. The filtered solution now contains only platinum which is precipitated with ammonium chloride; this second precipitate of ammonium hexachloroplatinate(IV) upon slow ignition at 1000°C yields a pure platinum sponge.

The filtrate from the first precipitation with ammonium chloride is treated with an excess of ammonia, then with hydrochloric acid in order to precipitate palladium as yellow *trans*-dichlorodiamminepalladium(II), $Pd(NH_3)_2Cl_2$. This product is purified by dissolution in ammonia and reprecipitation with hydrochloric acid. The reprecipitated $Pd(NH_3)_2Cl_2$ is slowly ignited at 1000°C to produce a pure palladium sponge.

The insoluble residue from the aqua regia treatment is mixed with soda ash, borax, litharge and charcoal, and the mixture is smelted. Silica, alumina and some base metals are removed in the slag, while the precious metals remain in the lead alloy which is cupelled to remove most of the lead as litharge. The resulting alloy is treated with nitric acid to remove lead and silver.

The residue from the parting with nitric acid contains rhodium, iridium, ruthenium and a little osmium. This residue is fused with sodium bisulphate to dissolve the rhodium as a Rh(III) sulphato complex, while iridium, ruthenium and osmium remain unaffected. The cooled melt is extracted with water and, after filtration, the solution is treated with sodium hydroxide. The precipitate of Rh(III) hydroxide is dissolved in hydrochloric acid and treated with sodium nitrite to convert the rhodium to sodium hexanitrorhodate(III). Base metals are removed as hydroxides after the addition of alkali, in which $Na_3[Rh(NO_2)_6]$ is soluble. Ammonium chloride is then added to precipitate $(NH_4)_3[Rh(NO_2)_6]$ which is digested with hydrochloric acid to convert the rhodium to the $[RhCl_6]^{3-}$ anion. Impurities are removed by a cationic exchange resin, and formic acid is added to reduce the rhodium from the trivalent state to the metal, which is obtained as a finely divided black powder. This is then heated in a hydrogen atmosphere at 1000°C to give a pure rhodium sponge.

The insoluble residue from the sodium bisulphate fusion contains ruthenium and iridium and from negligible to appreciable amounts of osmium. It is treated to remove lead sulphate and then fused with potassium hydroxide and potassium nitrate or with sodium peroxide. The ruthenium is oxidized to potassium or sodium ruthenate(VI), K_2RuO_4 or Na_2RuO_4, and the iridium is oxidized to insoluble Ir(IV) oxide, IrO_2. The cooled melt is extracted with water and the solution is treated with chlorine. Heating of this solution causes ruthenium tetroxide, RuO_4, to distil off; it is collected in a mixture of dilute hydrochloric acid and methyl alcohol, which reduces ruthenium from the octavalent

[12] J. L. Bray, *Non-ferrous Production Metallurgy*, 2nd edn., Wiley, New York (1947), pp. 268, 433.

to the quadrivalent state. Upon evaporation, the solution yields Ru(IV) oxychloride, $RuOCl_2$. Ignition of this compound in an atmosphere of hydrogen yields ruthenium sponge.

If osmium is present in any quantity, it will contaminate the ruthenium which can be freed from osmium by the use of one of several procedures. One method is to catch the volatile RuO_4 and OsO_4 in an hydrochloric-acid trap. The solution in the trap is boiled and the osmium tetroxide distils off. Warm hydrochloric acid reduces the ruthenium to the trivalent state. The addition of ammonium chloride precipitates the ruthenium as ammonium hexachlororuthenate(III), $(NH_4)_3RuCl_6$, which is collected and heated in hydrogen at 1000°C to give ruthenium sponge. The volatilized OsO_4 is absorbed in alcoholic sodium hydroxide and the solution is digested with ammonium chloride; this causes the precipitation of the osmium as $OsO_2(NH_3)_4Cl_2$. Ignition of this complex in hydrogen yields osmium metal. Another method consists of the treatment of the aqueous extract of the potassium hydroxide–potassium nitrate fusion with alcohol which precipitates the ruthenium as RuO_2. After the ruthenium has been removed, the osmium is isolated from the filtrate by the addition of excess potassium hydroxide which precipitates potassium osmate(VI), K_2OsO_4.

The insoluble Ir(IV) oxide from the potassium hydroxide–potassium nitrate fusion is dissolved in aqua regia. The addition of ammonium chloride precipitates ammonium hexachloriridate(IV), $(NH_4)_2IrCl_6$. The impure salt is either recrystallized several times or dissolved in dilute ammonium sulphide solution which precipitates impurities as sulphides. In the latter case the solution is treated with nitric acid and ammonium chloride in order to precipitate pure $(NH_4)_2IrCl_6$, which is heated at 1000°C under hydrogen to produce pure iridium powder.

The flow sheet for the International Nickel Company's process for the recovery of the platinum metals at the Acton refinery, London, is given in Fig. 1.

Alluvial deposits of the platinum metals are usually subjected to a wet separation which begins with the treatment of the ore with aqua regia, and is similar to that described above.

The methods used by the US Bureau of Standards for the production of each of the platinum metals in the pure state have been published[13].

1.6. FABRICATION

Melting

When European scientists began to investigate the properties of platinum in the years subsequent to 1741, difficulties were encountered in working the metal. All attempts to melt platinum had failed until 1758 when Macquer and Baumé in Paris brought about partial fusion of a small sample by concentrating the sun's rays on the ore by means of a large concave "burning mirror". Attention was recently drawn[14] to a passage in the *Memoirs of Casanova*. The famous adventurer records that when in Paris in 1757 he visited a wealthy woman, the Marquise d'Urfé, who was interested in alchemy. She showed Casanova samples of platinum which she melted by means of a "burning mirror". It is noteworthy that Casanova did not write his memoirs until 1792, by which time the technique of melting platinum was well known. However, since Casanova's other statements on the chemistry of platinum are correct, there is no reason to doubt his story.

[13] R. Gilchrist, *Chem. Rev.* **32** (1943) 277.
[14] *Platinum Metals Rev.* **6** (1962) 28.

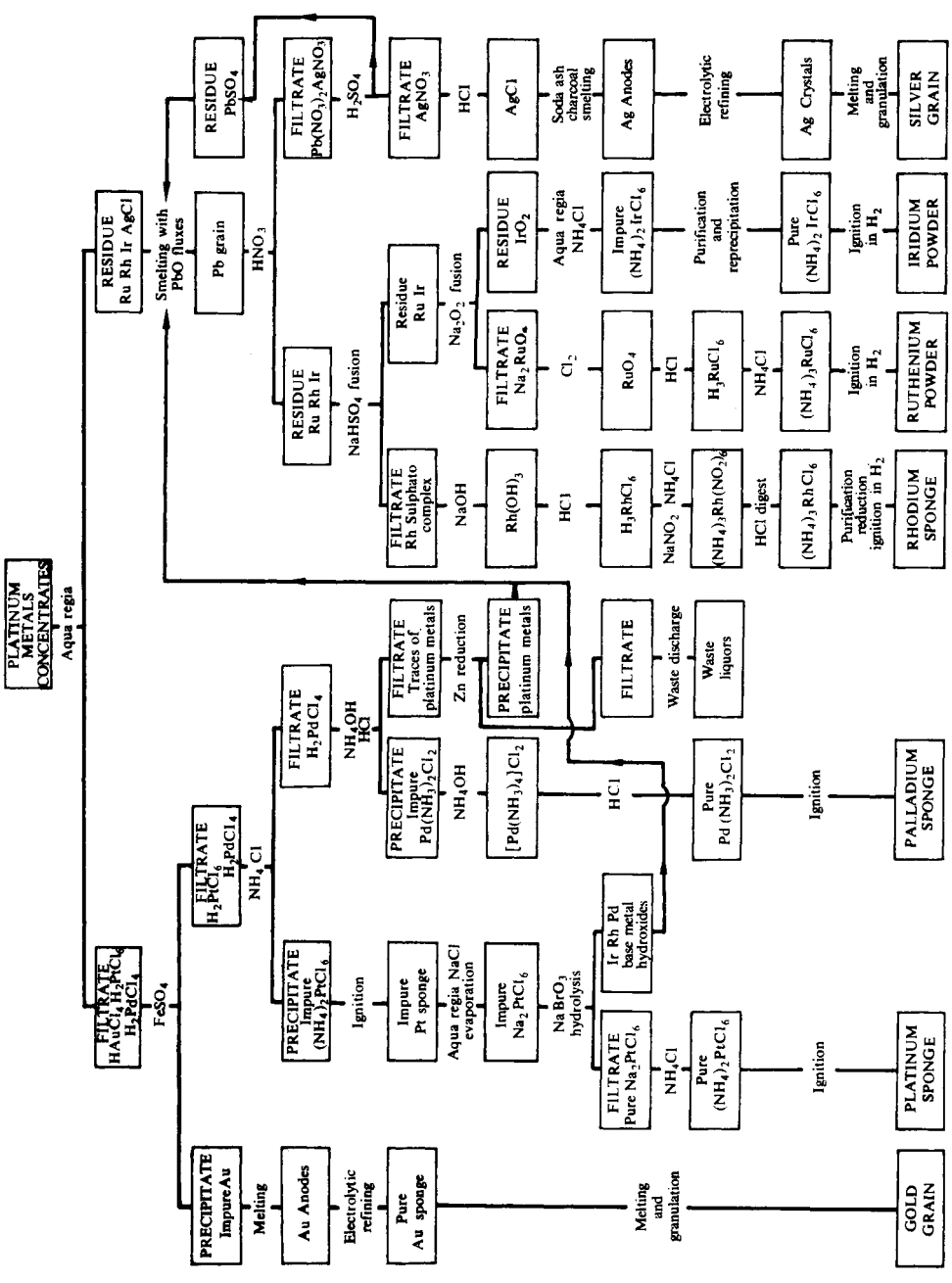

FIG. 1. Flow sheet for the recovery of the platinum metals at the Acton refinery. (Courtesy of the International Nickel Company.)

The first complete melting of platinum was achieved in 1783 by Lavoisier, who heated small particles of the metal on charcoal in a blast of oxygen. However, he only succeeded in melting quantities less than 15 grains.

Earlier, Baumé had shown that platinum could be consolidated like iron by forging at a high temperature, but often when this technique was applied to the alluvial grains they failed to cohere, due to the presence of small amounts of alloyed iron which oxidized on the surface to produce magnetite when the grains were heated. Consequently it was recognized that the iron would have to be removed before welding would take place. The arsenic process was developed by the French goldsmith Janety. It consisted of heating the ore with an oxidizing mixture containing potash and white arsenic which removed the iron and produced an alloy which, when cast into thin discs and heated carefully below the melting point, lost the arsenic by volatilization. This method was used to prepare the four original platinum standard metres which are still kept in Paris. However, the arsenic process was slow and dangerous.

An alternative method was developed in 1786 by de Elhuyar and Chabaneau. They dissolved the ore in aqua regia, precipitated the platinum with ammonium chloride, then calcined the $(NH_4)_2PtCl_6$ to a sponge of platinum metal which was then heated to the highest possible temperature and forged. However, the product varied in quality and sometimes failed mechanically. In 1800 Wollaston developed an improved process, the details of which were published in 1828. An account of his work on the production of malleable platinum has been recently published[15]. The essential details of Wollaston's process are as follows. (i) The aqua regia should be diluted with an equal volume of water so as to avoid dissolving the iridium. (ii) The precipitate of $(NH_4)_2PtCl_6$ must be well washed and then pressed before being subjected to just sufficient heat to produce the platinum sponge. Wollaston recognized the need to preserve a certain virginity in the surfaces, thus anticipating the recognition of the principles of powder metallurgy by over a century. (iii) The sponge should be ground to a uniform fine powder by hand rubbing and then washed with water. (iv) The water is pressed out and then the mass is pressed to a hard cake. (v) The cake is then heated strongly and forged. Between 1800 and 1821 Wollaston produced 36,000 oz (i.e. over a ton) of malleable platinum by this method.

An historical account of the development of improved methods for the melting of platinum has been given by McDonald[16]. The invention in 1801 by Hare of the oxy-hydrogen blowpipe led to the development of a commercial method for melting platinum. In 1836 Hare melted platinum, rhodium and iridium by means of the oxy-hydrogen blowpipe. In 1842 Bishop used Hare's method on a commercial scale at Malvern, Pennsylvania. In 1857 Deville in Paris melted platinum in a lime crucible with a coal gas–oxygen flame introduced through a hole in the top of the crucible. From 1857 melted platinum was used in fabrication, gradually replacing the forging technique. In 1862 Deville and Debray showed that platinum could be hardened by the addition of *ca.* 10% iridium. This alloy could most readily be produced by fusion.

Lime is used for the crucible material since, being porous, it absorbs the small amount of base metals. Clay, graphite or silica are unsuitable, since they cause contamination with silicon or carbon, rendering the metal brittle due to the formation of a low-melting grain-boundary constituent. However, there are certain disadvantages associated with the

[15] D. McDonald, *Platinum Metals Rev.* **10** (1966) 101.
[16] D. McDonald, *Platinum Metals Rev.* **2** (1958) 55.

limeblock method. Firstly, it is difficult to obtain suitable lime which will withstand the high temperatures without cracking. Secondly, precise control of the gas mixture is necessary. Thirdly, under even slightly reducing conditions the metal takes up impurities in the form of calcium and magnesium. If the composition of the gases errs on the oxidizing side, the metal contains inclusions which affect its mechanical properties.

In 1920 Northrup invented the high-frequency electric induction furnace, and a furnace of this type with zirconia as the refractory was first used to melt platinum in 1922; this type of heating is more commonly used in industry. One advantage of the induction furnace is that the current promotes a vigorous electromagnetic rotation in the molten metal and thus produces efficient mixing. Furthermore, the melting can be carried out *in vacuo* or in an inert atmosphere.

More recently the vacuum arc furnace has been used for research into alloy development where small quantities are used. For the production of platinum metals of high purity the melting can be done in an atmosphere of argon in a vacuum arc furnace with a water-cooled copper crucible and a tungsten electrode[8].

The melting of palladium is somewhat more difficult than that of platinum. Palladium melted under oxidizing conditions contains gas occlusions, whereas melting in a reducing environment produces ingots that are hot short and brittle. The use of hydrogen as a deoxidizer during the melting of palladium results in very dense ingots, although violent gassing and attendant spattering occurs. Other disadvantages associated with the use of hydrogen are reduction of the crucible material with concomitant contamination of the metal, steam formation which causes pitting of the castings, and blister formation which occurs when the strip is heated in air. The use of carbon monoxide as a deoxidizer yields the best results[17].

Rhodium is usually melted by induction heating under an inert atmosphere. Iridium is generally consolidated by arc-melting or by induction heating, both in an argon atmosphere, or powder-metallurgical techniques, but it can be melted in lime crucibles with an oxy-hydrogen flame[17].

Ruthenium and osmium are usually consolidated by powder metallurgy, although arc melting has been used. An inert atmosphere must be used with osmium because of the volatility of the oxide. Arc-melted ruthenium has a poorer workability than the metal which has been produced by powder metallurgy[17].

Working

Mention has been made of Wollaston's method for the forging and fabrication of platinum. Platinum, palladium and their alloys are not particularly difficult to work. Platinum and palladium are very ductile and can be worked hot or cold. The ingots are usually hot forged with a power hammer. Wire is cold rolled or swaged and then drawn through tungsten carbide or diamond dies. Both platinum and palladium withstand drastic cold working and can be beaten into thin leaf like gold. Platinum can be drawn into wire 0.00005 in. diameter by the Wollaston method (i.e. with a silver jacket which is afterward removed with nitric acid). Platinum is easily hammer-welded by gentle hammering at 1000°C. By heavy cold working the Vickers hardness can be increased from 40 in the

[17] R. W. Douglass, F. C. Holden and R. I. Jaffee, *High Temperature Properties and Alloying Behaviour of the Refractory Platinum-group Metals*, US Department of the Navy Office of Naval Research Technical Phase Report PB 161823 (1959).

annealed state to 120–125 for platinum and to *ca.* 105 for palladium, and the tensile strength can be increased from 10 to 15 tons in^{-2} for platinum and from 12 to 20 tons in^{-2} for palladium. Both metals require annealing in an inert atmosphere at a temperature between 800 and 1000°C in order to obtain maximum ductility with a short anneal. An investigation of the most suitable atmosphere for the annealing of palladium showed that helium and argon are the most satisfactory, followed by carbon dioxide, steam and nitrogen. Air is unsuitable because oxygen reacts with hydrogen to produce blisters[17].

Rhodium and iridium are harder and more brittle than platinum and palladium. Rhodium powder may be consolidated either by powder-metallurgical techniques or by melting. If compacts of high density are required, careful control of the physical properties of the powder is necessary since the compacting pressure and the sintering temperature are dependent on the particle size. The sintering is usually carried out at 1200°C and may be done in air, hydrogen, or *vacuo*. The metal can be rolled to strip or swaged to wire down to 1 mm diameter. Working is initially done at 1200°C but subsequently the temperature may be dropped. Wrought rhodium needs to be annealed at 800°, preferably in an inert atmosphere, since a superficial oxide film is formed below 1000°C. Complete annealing should be avoided as recrystallized rhodium is less ductile than the metal having a fibrous structure. Moderate cold working may be given between stress-relief anneals; frequent annealing is necessary, since rhodium work hardens rapidly at room temperature. Single crystals of rhodium prepared by electron-beam zone melting are more ductile and can withstand more cold working without anneal[18].

Iridium powder may be consolidated by powder metallurgical techniques or by melting. Sintering may be done in air at 1500°C. Initial working is done at 1200–1500°C. Subsequent drawing into wire is done at 600–750°C. Drawing at lower temperatures leads to an increase in hardness and lower ductility. Iridium cannot be cold rolled at all. Strip can be produced by rolling at 600–750°C, but rolling can be carried out at 1200–1500°C [19].

Ruthenium powder is consolidated by powder metallurgy or by argon-arc melting. Ruthenium is difficult to work but improvements in its ductility and working behaviour have recently been achieved enabling its valuable properties, such as its high resistance to corrosive materials, to be utilized. Ruthenium may be worked to strip or rod by hot forging, swaging or rolling. Swaging is carried out at 1150–1500°C, but rolling is best done in the range 1050–1250°C. Once reduced to 0.02 in. thickness, hot-rolled strip can be cold rolled down to 0.003 in. Wire can now be drawn down to 0.020 in. in diameter[20].

Osmium has not as yet been worked successfully. The fabrication of osmium is rendered dangerous because of the toxic nature of its volatile oxide. Accordingly all working at elevated temperatures must be done in an inert atmosphere.

Electrodeposition

Among the platinum metals only rhodium, platinum and palladium have been electrodeposited on a commercial scale. Although some success has been claimed for the electrodeposition of ruthenium on a laboratory scale, it appears that no satisfactory aqueous electrolyte for the deposition of iridium plate of technically useful thicknesses has been yet developed[21]. Rhodium has been most extensively used because of the brilliant finish,

[18] *Rhodium*, International Nickel Ltd., London (1965).
[19] *Iridium*, International Nickel Ltd., London (1964).
[20] *Ruthenium*, International Nickel Ltd., London (1964).
[21] F. H. Reid, *Metall. Rev.* **8** (1963) 167.

reflectivity and hardness of the deposit. It has been used for jewellery and decorative purposes, since it is capable of imparting a tarnish-resistant finish to silver and silver-plated cutlery. More recently, electrodeposited rhodium has been used for electrical contacts.

Rhodium can be deposited directly on silver, copper, nickel, brass, phosphor–bronze and certain copper alloys. If it is required to deposit rhodium on tin, lead, zinc, cadmium, aluminium, iron or steel, a preliminary deposit, preferably of silver, must be applied. The thickness of the rhodium deposit depends upon the purpose for which it is required. The thickest recommended deposit is 0.002 in., while for protection against tarnish a thickness of 0.00002 in. is usually adequate.

A comprehensive review of the details concerning the electrodeposition of the platinum metals and a list of the relevant papers and patents has been published by Reid[21]. Thin or "flash" coatings of rhodium, platinum and palladium can be produced relatively easily from a number of electrolytes, but thicker deposits of platinum and palladium are more difficult to produce because of cracking of the deposit. Methods have now been developed for the deposition of relatively thick deposits (10^{-4} to 10^{-3} in.) for industrial applications such as electrical contacts.

For electrodeposition of palladium an electrolyte solution containing dinitrodiammine-palladium(II), $Pd(NH_3)_2(NO_2)_2$, "palladium P salt", is most commonly employed. The solutions used for platinum plating contain one of the following: (i) chloroplatinic acid, H_2PtCl_6, (ii) $Pt(NH_3)_2(NO_2)_2$, "platinum P salt", (iii) sodium hexahydroxyplatinate(IV), $Na_2[Pt(OH)_6]$, (iv) various nitroplatinum(II) complexes. Electrolytes for rhodium plating are based on sulphate and/or phosphate-containing solutions. The rhodium is probably present partly as the anionic complex $[Rh(SO_4)_3]^{3-}$, but cationic species such as $[Rh(H_2O)_6]^{3+}$, [RhOH aq]$^{2+}$ and $[Rh(OH)_2$ aq$]^+$ are doubtless present also.

1.7. ALLOYS

Alloys of the platinum metals are used when greater hardness, strength and resistance to corrosion are required than are obtainable with the pure metal.

Hume-Rothery[22] has interpreted the alloying behaviour of the platinum metals with a number of transition metals in terms of "electron concentration" principles. At the ends of the second and third transition series, the elements have the sequence of structures shown in Table 3.

TABLE 3. CRYSTAL STRUCTURES OF METALS OF GROUPS VA–IB IN THE SECOND AND THIRD TRANSITION SERIES

Group	Metal	Crystal structure
VA, VIA	Nb, Ta, Mo, W	Body-centred cubic
VIIA, VIIIA	Tc, Re, Ru, Os	Close-packed hexagonal
VIIIB, VIIIC	Rh, Ir, Pd, Pt	Face-centred cubic
IB	Ag, Au	Face-centred cubic

[22] W. Hume-Rothery, *Platinum Metals Rev.* **10** (1966) 94.

In the metals of Groups VA, VIA, VIIA and VIIIA the electrons are in hybrid *spd* states, but the proportion in *d* states falls rapidly from Group VIIIA to Group VIIIC. Hume-Rothery suggests that in the body-centred cubic structures of the Group VIIA and VIIIA elements the bonding forces are more directional than has been supposed. While the face-centred structures become more stable in passing from Group VIIIB to Group IB, the proportion of *s* function also increases. Palladium, and to a lesser extent platinum, can provide the electrons with *s* character required by silver and gold, which, when acting as solutes, can adjust themselves to the lattices of palladium and platinum respectively. Gold and palladium are freely miscible but silver and platinum are not. The reason for this behaviour seems to be that the higher valency of platinum compared with palladium renders it more difficult for a univalent metal to give the high proportion of *d* function required by platinum. The greater polarizability of the gold $(5d)^{10}$ ion compared with the silver ion $(4d)^{10}$ allows the gold atom to supply more *d* function to platinum; this explains why gold is freely miscible with platinum whereas silver is not.

Silver and gold are almost immiscible with rhodium and iridium, apparently because in rhodium and iridium the proportion of *d* function is so high that the Group IB metal cannot provide electrons of the required characteristics.

Equilibrium diagrams of palladium and platinum with first-row transition metals such as iron, cobalt and nickel show effects which can be attributed to the more easily polarizable electron cloud of platinum compared with that of palladium.

Hume-Rothery[22] points out that it is convenient to refer to the average group number (AGN) of an alloy. Group numbers of 8, 9 and 10 are allotted to the elements of Groups VIIIA, VIIIB and VIIIC respectively. Thus an equiatomic alloy of rhodium and palladium has an AGN value of 9.5, and equilibrium diagrams can be drawn in terms of AGN values. In general, body-centred cubic, close-packed hexagonal and face-centred phases occur over characteristic ranges of AGN values. For example, face-centred cubic solid solutions in palladium, platinum and rhodium formed by preceding transition metals extend backwards to a characteristic AGN value of about 8.4. These AGN principles for transition metal alloys correspond to the electron concentration principles of the Cu–Zn and Cu–Ga systems. These principles apply to the alloys of the later elements of the second and third transition series. They do not apply to alloys of elements of the first transition series with those of the later transition series because the sizes of the ions are not comparable.

Several binary alloys of platinum, palladium or rhodium with metals of the first transition series are known to develop *superlattice* structures when the alloys are carefully annealed, but no cases of this type of structure have been reported in binary systems containing two platinum metals.

Platinum Alloys

Alloys of platinum with other platinum metals, with gold and with base metals such as molybdenum, tungsten, cobalt, nickel and copper are in use. Iridium is most widely used for enhancing the mechanical properties of platinum. The commercial alloys contain from 10 to 30% of iridium. With up to about 20% of iridium the alloys are quite ductile, but with 30% or more fabrication becomes difficult. The use of Pt–Ir alloys above 800°C is not recommended because of the development of a black oxide film. Ruthenium has a more marked effect than iridium on the hardness and resistivity of platinum alloys: the addition of 30% iridium to platinum increases the resistivity from 10 to 33 (microhm-cm

at 20°C) and the Vickers hardness (annealed) from 40 to 285, while platinum containing 10% ruthenium has a resistivity of 42 and a Vickers hardness of 200.

The addition of rhodium to platinum has a less pronounced effect on the mechanical properties than the addition of iridium, but the rhodium alloys are more stable at high temperatures. Alloys containing from 5 to 40% rhodium are used commercially. As with iridium, a high rhodium content (>40%) renders fabrication very difficult. Platinum hardens gold considerably, while platinum crucibles containing a few per cent gold have greater strength and a finer grain structure than those made from pure platinum.

Beamish *et al.*[8] have listed the comparative alteration in the physical properties by various alloying metals as follows:

Hardness: Ni > Ru > Cu, Au > Ir > Rh

Resistivity: Cu > Ag > Ru > Ir, Au > Rh

Tensile strength, annealed: Ru > Au > Ir > Rh

Cobalt–platinum alloys possess strong ferromagnetic properties. Alloys having a composition of approximately 50 at.% are subject to ordering on cooling below 825°C, and, after heat treatment which produces partial ordering, these alloys have pronounced magnetic properties. The exact magnetic properties can be varied appreciably by minor alterations in composition and heat treatment. The annealed alloy has good workability. One commercially available alloy when fully magnetized has a remanence of 6400 gauss, a coercive force of 4800 oersted, and an energy product (BH_{max}) of 9.2×10^6 gauss-oersted[23].

Critical reviews on the constitution and properties of Pt–Rh and Pt–Au alloys have been written by Darling[24].

Palladium Alloys

The most widely used alloys of palladium are those with copper, silver and gold. The 40% copper alloy when annealed has a Vickers hardness of 145 but can be readily worked. The 40% silver alloy, which does not tarnish in air, is used for electrical contacts and resistance windings. The gold alloys are somewhat more resistant to corrosion than pure palladium. The 50% gold alloy has a Vickers hardness of 85. Ruthenium has the most marked effect on the hardness of palladium. Ruthenium and rhodium are often used together to increase the hardness and mechanical strength of palladium for use in jewellery.

Rhodium Alloys

The most important alloys are those with platinum. Platinum and rhodium form solid solutions when alloyed in any proportions, and no solid-state phase changes are known to occur. Alloys of platinum and rhodium in all proportions can be fabricated. Platinum–rhodium alloys are used when improved mechanical properties are required at high temperatures, e.g. in contact with molten glass in the glass industry. Platinum containing 20% rhodium is used for furnace windings, while the 10 and 13% rhodium alloys are used in conjunction with platinum as thermocouples in industry.

Palladium and rhodium form a continuous series of solid solutions above 845°C, but below this temperature there is a miscibility gap. Rhodium increases the resistance of palladium to corrosion.

Iridium–rhodium alloys—with either 40 or 60% iridium—are used with iridium as

[23] R. A. Mintern, *Platinum Metals Rev.* **5** (1961) 82.

[24] A. S. Darling, *Platinum Metals Rev.* **5** (1961) 58, 97; **6** (1962) 60, 106.

thermocouples for very high temperature work. At high temperatures rhodium and iridium in all proportions form solid solutions. Since ruthenium and osmium crystallize in a different crystal system from rhodium, it is impossible for these metals to form a continuous series of solid solutions with rhodium.

The mutual solubility in the solid state of rhodium with gold and silver is slight. Rhodium–gold and Rh–Ag alloys have no industrial application. However, the mechanical properties of Pd–Rh alloys are improved markedly by the addition of from 2.5 to 10% of gold[25].

Small additions—up to 3%—of titanium or zirconium increase substantially the tensile strength of rhodium. Rhodium improves the corrosion resistance of titanium and chromium to non-oxidizing acids. The Rh–Fe alloy containing equiatomic proportions has an ordered body-centred cubic structure and displays the phenomenon of an anti-ferromagnetic to ferromagnetic change at 87°C in a zero external field, but in a field of 120,000 gauss the change occurs at −51°C [26].

Iridium Alloys

Iridium and osmium occur as a natural alloy osmiridium, containing between 30 and 65% osmium with small amounts of other platinum metals. The iridium-rich solid solution extends to 35% osmium but at higher compositions a hexagonal close-packed osmium-rich single phase occurs. However, in cast Ir–Os alloys, containing between 38 and 79% osmium, a two-phase structure occurs, indicating the existence of a miscibility gap between the two terminal solid solutions[17].

Iridium is used to harden platinum and palladium and to increase their resistance to corrosion. Alloys of platinum and iridium form a continuous series of solid solutions at high temperatures. However, at lower temperatures a miscibility gap with a maximum at 50% platinum and 975°C extends over nearly the whole composition range.

Iridium forms a continuous series of solid solutions with rhodium. The addition of a few per cent of ruthenium raises the melting point of iridium by several hundred degrees. The addition of tungsten (*ca.* 5%) markedly increases the tensile strength of iridium particularly at high temperatures, and iridium–tungsten alloys have been used for springs required to operate at high temperatures.

The intermetallic compounds Ti_3Ir, $ThIr_2$, $ZrIr_2$, Nb_3Ir and Th_7Ir_3 are superconductors[19].

Ruthenium Alloys

Ruthenium is a very effective hardener for both platinum and palladium. Platinum–ruthenium alloys containing up to 14% ruthenium have been used for electrical contacts. High ruthenium content alloys (30–70% ruthenium) containing other platinum metals or base metals are used for severe wear and corrosion resistance applications. The 50 at.% Rh–Mo alloy is a superconductor below 10.6°K [20].

Osmium Alloys

The Os–Pt system, like the Os–Ir system, shows the existence of a miscibility gap between the terminal solid solutions. Osmiridium and alloys containing about 60% osmium, some

[25] A. A. Rudnitskii and A. N. Khotinskaya, *Zh. Neorg. Khim.* **5** (1960) 2781.
[26] M. Fallot and R. Hocart, *Rev. Sci.* **77** (1939) 498.

ruthenium and the remainder other platinum metals, are used for instrument pivots and tips of fountain pens where great hardness is required. Alloys of osmium with a few metals such as nickel and molybdenum have been investigated but, apart from the uses already mentioned, osmium alloys have not found wide application.

More detailed information on the alloys formed by the platinum metals can be found in works by Mellor[27], Vines[28], Hansen[29] and Raub[30] and in the references already cited[17–20, 24].

1.8. PRINCIPAL USES

The industrial applications of the platinum metals are based on their high resistance to corrosion.

Platinum

The principal uses may be broadly classified as (i) chemical engineering, including catalytic applications, (ii) electrical engineering, (iii) jewellery, (iv) dental, medical and laboratory, (v) temperature measurement. Platinum and its alloys are used in the chemical industry for components subjected to corrosive materials and high temperatures. Platinum has an outstanding resistance to fluorine compounds, including hydrofluoric acid, at high temperatures. Platinum-clad electrodes are finding increasing application. Platinum is also used for high-pressure vessels and laboratory apparatus which is subjected to much heating; in the latter case a 3% rhodium alloy is used. The heaviest demand for platinum is as a catalyst, especially in petroleum reforming. Platinum alloys are used in the glass industry, as they are the only metallic materials which will withstand exposure to molten glass in a non-reducing atmosphere. Large vessels of pure platinum are used for the manufacture of optical and special glasses.

Platinum alloys are used in electrical engineering as contact materials, particularly where reliability of operation is essential, because of their freedom from film formation. The pronounced ferromagnetic properties of certain cobalt–platinum alloys make them of considerable importance as materials for permanent magnets.

Alloys containing 5–10% iridium or 5% ruthenium are used for jewellery. The purest platinum is used for resistance thermometers and thermocouples. The platinum resistance thermometer is used to define the International Temperature Scale from −182.97°C (the boiling point of oxygen) to 630.5°C (the melting point of antimony). The platinum:platinum–rhodium thermocouple is widely used in industry for the accurate measurement of temperatures above 1000°C.

Palladium

Palladium is often used as a substitute for the more expensive platinum. Palladium alloys are used for contacts in electrical relays and in dental alloys to a greater extent than

[27] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, London (1937), Vol. 15, pp. 642, 750; Vol. 16, p. 194.
[28] R. F. Vines, *The Platinum Metals and Their Alloys*, International Nickel Co. Inc., New York (1941).
[29] M. Hansen, *Constitution of Binary Alloys*, 2nd edn., McGraw-Hill, London (1958).
[30] E. Raub, *J. Less-Common Metals* **1** (1959) 3.

platinum. Palladium alloys containing 4% ruthenium and 1% rhodium are much used in jewellery, while "white gold" is a Au–Pd alloy.

The principal use of palladium in the chemical industry is as a catalyst (see section 1.9), but it is also used as a constructional material for protective sheaths and linings.

Rhodium

In addition to its use as a constituent of platinum alloys, rhodium finds considerable application as an electrodeposited coating because of the hardness and high reflectivity of the deposit. It is also used for electrical contacts in components of radio-frequency circuits.

Iridium

Iridium is used as an additive to harden platinum and palladium and for extrusion dies for high-melting glasses. Iridium is highly resistant to attack by a wide range of molten metals and molten salts and oxides. Iridium crucibles are used in the preparation of single crystals of high-melting salts such as barium titanate and calcium tungstate.

Ruthenium

Ruthenium is mainly used to harden palladium and platinum alloys and as an additive for osmium alloys. It is also used as a catalyst for specific reactions.

Osmium

Alloys with *ca.* 60% osmium content are used where extreme hardness is required such as for instrument pivots.

1.9. CATALYTIC APPLICATIONS

In 1820 Edmund Davy discovered that chemically reduced platinum black has the power to promote the oxidation of alcohol. In the following year the reaction was further investigated by Döbereiner who found that not only was the alcohol entirely oxidized to acetic acid but the platinum remained unchanged and available for more work. In 1823 Döbereiner discovered that platinum sponge will ignite a premixed stream of hydrogen and air. This discovery was quickly developed into the Döbereiner lamp which tended to replace the tinder box until the lamp itself was replaced by the phosphorus match. Phillips (1831) and Döbereiner (1832) independently discovered the power of platinum to assist in the oxidation of sulphur dioxide to the trioxide. The phenomenon was given the name *catalysis* by Berzelius in 1835.

The platinum metals have been used as catalysts for the following reactions: (i) hydrogenation of olefins, acetylenes and aromatics; (ii) oxidation of sulphur dioxide in the manufacture of sulphuric acid, although platinum has been largely superseded by vanadium pentoxide for this purpose; (iii) the preparation of oxides of nitrogen for use in the Chamber process for the manufacture of sulphuric acid; (iv) oxidation of ammonia to nitric acid; (v) the reformation of petroleum to produce branched-chain and aromatic compounds with high octane rating; (vi) the electrolytic oxidation of hydrocarbons in fuel cells.

Although carbonyl and other π-bonded complexes of the platinum metals are finding increasing application in homogeneous catalysis, only those catalytic reactions which

involve the use of the Group VIII elements in their metallic state will be discussed in this section. However, it should be borne in mind that in hydrogenation reactions the effective catalyst must often be regarded as the hydrided metal rather than the pure metal.

For hydrogenation reactions two quantities have been recognized as determining catalytic activity, namely the electronic and geometric factors. These factors have been explained as follows[31]. For the ready chemisorption of gases on a metallic surface, the metal must have vacant *d* orbitals which can accept electrons from the reactants. However, when the number of vacant *d* orbitals is large, as with the metals of Groups IIIA to VIIA, the gases are strongly chemisorbed and their removal is thus rendered difficult. The metals of Group IB have no vacant *d* orbitals, consequently chemisorption will not occur to any extent and the catalytic activity will be small. The maximum activity is to be expected for those metals which possess the smallest number of vacant *d* orbitals, namely the metals of Group VIII. This is the electronic factor. The metal atoms in the surface should be spaced such that the transition-state complex has the lowest possible energy. It follows that the activation energy must be small and the reaction must take place at a relatively low temperature. This second requirement is known as the geometric factor. Both factors are optimal for catalysis in the Group VIII metals.

Pauling[32] has calculated the percentage *d* character (δ) of metal–metal bonds in the solid metals. The values of δ range from about 20% for Group IIIA metals to 40% for the triad, iron, cobalt and nickel, and 44–50% for the platinum metals. The quantity $(100-\delta)$ gives a measure of the number of vacant *d* orbitals. Ruthenium and rhodium, with values of 50% for $(100-\delta)$ and 1.34 Å for the metallic radius, and osmium (51%, 1.35 Å) and iridium (51% and 1.36 Å) should be more active than the more commonly used palladium (54% and 1.37 Å) and platinum (56% and 1.39 Å).

Fischer and Tropsch[33] found that the order of activity for the formation of methane from carbon monoxide and hydrogen was

$$\text{Ru} > \text{Ir} > \text{Rh} > \text{Os} > \text{Pt} > \text{Pd}$$

All the platinum metals can be used as catalysts for the hydrogenation of acetylenes and di-olefins. Metals which produce high yields of mono-olefin are termed highly selective, by reference to the definition[34]:

$$\text{Selectivity} = \frac{\text{yield of mono-olefin}}{\text{yield of mono-olefin} + \text{paraffin}}$$

Selectivity is characteristic of the metal and is largely independent of the physical form of the catalyst and of the multiply-unsaturated hydrocarbon undergoing hydrogenation. However, selectivity decreases with increasing hydrogen pressure and decreasing temperature. The selectivity sequence is

$$\text{Pd} > \text{Rh} > \text{Pt} > \text{Ru} > \text{Os} > \text{Ir}$$

The tendency for the selectivity to decrease from the second to the third transition is common for all the platinum metals. The degree of specificity, e.g. for *cis*-but-2-ene formation from the hydrogenation of dimethylacetylene, increases from left to right across each

[31] G. C. Bond, *Platinum Metals Rev.* **1** (1957) 87.
[32] L. Pauling, *Proc. Roy. Soc.* A, **196** (1949) 343.
[33] F. Fischer, H. Tropsch and P. Dithey, *Brennstoff-Chem.* **6** (1925) 265.
[34] P. B. Wells, *Platinum Metals Rev.* **7** (1963) 18.

series and decreases from the second to the third series[35]. Furthermore the sequence of isomerization activity is[35]

$$Pd > Rh > Ru > Os \gg Pt \simeq Ir$$

The chemisorption of olefins probably occurs by the formation of an olefin–metal complex[36]. Similar π-complexes are probably formed by acetylenes. If this is so, it follows that the geometric factor is of minor importance in catalysis. This view is supported by the close similarity between the catalytic activity of the close-packed hexagonal metals, ruthenium and osmium, and the activity of the other platinum metals, which have face-centred cubic structures. The chemisorption of acetylene by the formation of two σ-bonds to the metal would involve only the longer interatomic spacings and, although these exist in the c.p.h. metals, they are less commonly available than in the f.c.c. metals. Consequently the c.p.h. metals would be expected to show lower activity for acetylene hydrogenation than the f.c.c. metals; however, this is not the case[35].

The stability of π-complexes usually increases from ruthenium to osmium, rhodium to iridium and palladium to platinum. If the same order of stability holds for the transition-state complexes in catalytic reactions, it follows that the greater ability of the second-row metals to promote isomerization and olefin exchange compared to that of the third-row metals can be attributed to the lower stabilities of the olefin complexes formed by the second-row metals, since the less stable the complex the more readily will desorption of the reacted olefin occur[35].

Similarly, the lower selectivity of the third-row metals can be explained if π-complex formation is assumed. The selectivity will depend on the readiness of the olefin to desorb rather than remain and undergo further hydrogenation to an alkane.

Although Kuhlmann in 1839 produced nitric acid by passing an air–ammonia mixture over heated platinum and dissolving the oxides of nitrogen in water, the principle was not used on a commercial scale until 1909. A 10% rhodium–platinum alloy is generally used, since rhodium increases the conversion of ammonia to oxides of nitrogen and improves the mechanical properties of the gauze. At a pressure of 10 atm a preheated mixture of air and ammonia burns on the rhodium–platinum gauze. The reaction begins at 600° and is optimum at 940° to yield about 9% NO. The loss of catalyst is claimed to be less than 0.005 oz platinum per ton of 100% nitric acid.

Since 1950 increasingly larger quantities of platinum have been used in the petroleum industry as *platforming* catalysts. Platforming is a method of catalytically reforming petroleum naphthas to improve their anti-knock properties, i.e. to produce branched chain and aromatic compounds with high octane numbers. Highly selective *duofunctional* catalysts are used. These contain platinum as one of the functional agents; the other function is provided by the acidity of the specially prepared catalyst support which varies according to the purpose for which it is required.

Catalytic reforming involves four main types of reaction: (a) dehydrogenation of naphthenes to aromatics; (b) dehydrocyclization of paraffins to aromatics; (c) hydrocracking of higher to lower boiling point paraffins; (d) isomerization of paraffins to highly branched products. The platinum function promotes the hydrogenation and dehydrogenation. The acid function promotes isomerization, cracking and cyclization. The two functions are dispersed on an alumina support which contains from 0.2 to 0.75% platinum.

[35] G. Webb, *Platinum Metals Rev.* **8** (1964) 60.
[36] J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939; J. J. Rooney, *J. Catalysis* **2** (1963) 53.

The reactions are carried out at temperatures of from 475° to 550°C under hydrogen pressures of 18–36 atm. The process is also used to convert benzene to cyclohexane used to make adipic acid for the manufacture of nylon.

The high catalytic activity and resistance to corrosion displayed by the platinum metals form the basis for their use in fuel cells. The principal obstacle to the commercial use of these fuel cells is the high cost of the platinum metal required. The cells can use as fuel hydrogen, ammonia, hydrazine or hydrocarbons. The platinum metals provide the best electrocatalysts for fuel cells designed to operate at ambient temperature and to use simple hydrocarbon or partially oxygenated hydrocarbon fuels. The metals are used in diffusion-type electrodes in the form of high area blacks supported on various types of substrate. Palladium and palladium alloys have been used as the anodes in fuel cells. The palladium acts as a membrane to separate the gaseous and liquid phases. The hydrogen diffuses through the membrane and is electrochemically oxidized at the diffusion interface with the electrolyte.

While platinum and palladium are principally used industrially, other platinum metals are finding catalytic applications for specific reactions[18, 20].

Rhodium supported on alumina has been found to be superior to ruthenium, platinum and palladium in the catalytic hydrogenation of benzene; a similar catalyst is suitable for the hydrogenation of aromatic and heterocyclic compounds at room temperature.

Ruthenium has proved to be more selective than other platinum metals for a number of reactions. Ruthenium will catalyse the reduction of sugars and, at high temperatures and pressures, polysaccharides to polyhydroxy alcohols. Ruthenium catalysts have been shown to display *synergism*, i.e. their activity is improved when mixed with palladium, platinum or rhodium. More active catalysts have been found by making use of this property for the hydrogenation of aromatic and aliphatic nitro compounds, ketones, nitriles and pyridine.

Because of its low selectivity, iridium has found little use in catalysis. However, use has been made of the synergistic effect of iridium with other platinum metals.

1.10. ANALYTICAL CHEMISTRY

The analytical chemistry of the six platinum metals has been fully discussed in two recent publications[37, 38], while that of ruthenium is the subject of a separate monograph which is available in English translation[39]. Only a brief outline will be given here.

When several precious metals are present in the sample, the analytical procedure is not simple. The platinum metals, along with silver and gold, are usually separated from base metals and then the more difficult separation of the noble metals is undertaken. The most suitable method to be used[37] to get the metals into solution will depend on the nature of the sample: ore, alloy, combustible-containing scrap, used catalyst material or metal complex.

The platinum metals can be determined by most of the accepted analytical procedures: gravimetric, volumetric, spectrophotometric, polarographic, optical and X-ray emission spectroscopy and X-ray fluorescence.

[37] T. J. Walsh and E. A. Hausman, The Platinum Metals, in *Treatise on Analytical Chemistry*, Part II, Vol. 8 (I. M. Kolthoff and P. J. Elving, eds.), Wiley Interscience, New York (1963), p. 379.

[38] F. E. Beamish, *Analytical Chemistry of the Noble Metals*, Pergamon Press, Oxford (1966).

[39] T. D. Avtokratova, *Analytical Chemistry of Ruthenium*, Israel Programme for Scientific Translations, Jerusalem (1963).

Gravimetric Methods

Beamish[38] has stated: "Although the separational value of precipitation methods will eventually give way to such techniques as ion-exchange separation, it is unlikely in the foreseeable future that either the platinum metal industries or the research analyst will be able to dispense with good gravimetric methods." The author concurs with this statement.

Coordination complexes containing rhodium, iridium, palladium or platinum can be analysed by direct ignition to the metal provided the complex does not contain phosphorus, arsenic or antimony, since these elements alloy with the noble metal, in particular palladium and platinum. Alkali metals must also be absent. The sample is placed in a silica crucible and heated very gently until decomposition is complete. The crucible is then heated strongly in air until all the carbon has been oxidized. Palladium forms a layer of oxide which can be reduced by allowing the crucible to cool well below red heat, then holding a piece of filter paper moistened with methyl alcohol in the mouth of the crucible until the metal sponge ceases to glow and remains silver-grey on cooling.

There is no specific gravimetric reagent for ruthenium and all the gravimetric methods yield non-stoichiometric precipitates which must be converted to the metal. However, ruthenium, along with osmium, can be separated from the other platinum metals and base metals by distillation of the volatile tetroxide. The distillation separation is effected by treatment of a strongly alkaline solution with chlorine, followed by the addition of nitric acid to remove osmium as Os(VIII) oxide, the oxidation of ruthenium with sodium bromate and the collection of the Ru(VIII) oxide in a reducing solution containing hydrochloric acid and alcohol. The solution is adjusted to pH 6 and boiled. The hydrated ruthenium oxide, which is quantitatively precipitated, is filtered off, washed, dried and ignited in air, then reduced in hydrogen at 750°C and cooled in an inert atmosphere to yield the metal. Alternatively, the trap solution is evaporated to dryness and the residue is dissolved in dilute hydrochloric acid. The solution is buffered with sodium acetate and the ruthenium is precipitated with an excess of sodium sulphide. The precipitated ruthenium sulphide is coagulated by boiling, then filtered off and ignited to the oxide, which is reduced to the metal as described above.

The gravimetric determination of osmium by the hydrolytic method is similar to that described above for ruthenium. The Os(VIII) oxide is collected in 1:1 hydrochloric acid saturated with sulphur dioxide. The sulphur dioxide is removed by boiling the solution, which is then adjusted to pH 4 by the addition of sodium bicarbonate. Under these conditions hydrated Os(IV) oxide is quantitatively precipitated. The precipitate is filtered into a porcelain filtering crucible and washed with 1% ammonium chloride solution and then covered with a layer of ammonium chloride to avoid loss by deflagration. The mixture is heated under hydrogen in a quartz ignition tube, gently at first until the ammonium chloride is volatilized, then strongly for 1 hr. The metal is allowed to cool in hydrogen for 5 min, then in carbon dioxide or nitrogen for 15 min.

1,2,3-Benzotriazole can be used for the gravimetric determination of osmium. The reagent is added to a solution of Os(VIII) oxide in dilute sodium hydroxide solution containing a little ethyl alcohol. The solution is then heated and the pH adjusted to 3 with acetic acid. The precipitated complex is filtered off, washed with hot water, dried at 110°C and weighed as $Os(OH)_3(C_6H_4N_2NH)_3$.

As with ruthenium, there are no specific gravimetric reagents for rhodium or iridium and all precipitates, because of their non-stoichiometric nature, must be converted to the

metal. Rhodium is quantitatively precipitated by hydrogen sulphide from dilute acid solution at the boiling point. The precipitate of Rh(III) sulphide is washed with dilute acid and ignited in air to the oxide which is reduced to the metal by heating in hydrogen.

Iridium is best determined by the precipitation of Ir(IV) oxide which is subsequently reduced to the metal. The iridium solution is treated at the boiling point with 10% sodium bromate solution. The pH is adjusted to 6 by the addition of sodium bicarbonate. The precipitated iridium oxide is filtered off, washed thoroughly with 1% ammonium chloride solution and ignited in air. The oxide is then reduced by heating in hydrogen at 700°C for 30 min and the metal is cooled in carbon dioxide. Determination of iridium by sulphide precipitation is not recommended.

There are over fifty gravimetric reagents for the determination of palladium. The most important of these are the oximes, of which dimethylglyoxime, nioxime and salicylaldoxime are the most commonly used. Salicylaldoxime gives a quantitative separation of palladium in the presence of ruthenium, iridium, platinum, gold, nickel, iron and lead. The selectivity of nioxime is about the same as that of dimethylglyoxime. The dimethylglyoxime method is the one most widely employed. Gold is the only metal which causes interference and it must be removed—e.g. by reduction with oxalate. An alcohol solution of the reagent is added to the palladium solution in dilute hydrochloric acid. An excess of dimethylglyoxime should be avoided. The yellow precipitate is allowed to stand for 1 hr, then it is filtered off and washed with water. Drying and weighing of the complex is not recommended. The precipitate is carefully ignited until all the filter paper and organic matter have been burnt, and then the residue is strongly heated. The oxide film is reduced with methanol vapour, as described earlier in this section. Despite some statements in the literature about possible loss of palladium during ignition, the author has found that this method gives excellent results.

As there are no known specific reagents for platinum, the metal must be separated from other elements which interfere. Precipitation with ammonium chloride has been used for over two centuries. The platinum must be in the quadrivalent state and nitrates should be absent: accordingly the solution obtained by dissolution in aqua regia must be evaporated several times with hydrochloric acid to remove nitrate. Palladium can be removed with dimethylglyoxime; ruthenium and osmium can be removed by distillation; rhodium and iridium are removed by the hydrolytic procedure. The solution should be fairly concentrated and ammonium chloride is added as a saturated solution. The precipitate of $(NH_4)_2PtCl_6$ is washed with 20% ammonium chloride solution and ignited to the metal.

Reducing agents such as zinc, magnesium and sodium formate have been used to reduce platinum in solution to the metal. Of these the formate method is preferred. Reduction can also be effected by the addition of hydrazine sulphate to a hot acidic solution, followed by an excess of alkali. The precipitated metal is filtered off, washed well and ignited.

Volumetric Methods

In general, volumetric methods for the determination of the platinum metals are not satisfactory. They are usually only applicable to solutions of the purified metal salts. The nature of the species in solution often depends upon the pH, the pretreatment of the solution and the attainment of equilibrium, which is often slow, particularly with osmium, iridium and platinum.

Spectrographic Methods

Spectrographic methods are often useful, especially when the metals are present in small or trace amounts. Thiourea and its derivatives are most commonly used for ruthenium and osmium. Stannous halides, in particular the bromide, are used for rhodium. The intense absorption at 488 mμ by $[IrCl_6]^{2-}$ ion can be used to determine iridium. Stannous bromide is also used for iridium but rhodium, palladium and platinum must be absent.

Since the separation of palladium from the other noble metals is the most easily effected, colorimetric methods for the determination of palladium have little advantage over the gravimetric estimation with dimethylglyoxime. Nevertheless, some fifty colorimetric reagents for palladium have been described: thiocyanate ion, *p*-nitrosoaniline derivatives, 8-mercaptoquinoline and other thiols are among the better known reagents.

Stannous chloride and *p*-nitrosodimethylaniline are used for platinum.

Detailed reviews on the colorimetric determination of the platinum metals have been published[38, 40].

Spectrochemical Methods

Spectrochemical analysis has found successful application for the determination of: (i) low and trace concentrations of the platinum metals; (ii) trace impurities in refined platinum metals; (iii) intermediate or high concentrations of platinum metals in alloys or other materials. Optical emission spectrography is used for the determination of low concentrations of platinum metals in ores and rocks and of impurities in refined platinum metals. X-ray emission spectrometry is principally used for high concentrations.

Atomic Absorption Spectrometry

The technique consists essentially of measuring the atomic vapour of the element at a selected wavelength. Dissociation of the compound into atoms is achieved thermally in a gas flame. The only limitation on the type of sample is that it must be capable of giving a solution of the metal in either an aqueous or an organic solvent.

The literature on atomic absorption spectrometry has expanded rapidly since 1960; among the more recent reviews are those by Walsh and Willis[41] and by Elwell and Gidley[42]. The application of the technique for the analyses of rhodium, palladium and platinum has been reported[43, 44]. The sensitivity for ruthenium, rhodium and palladium is less than 1 ppm (μg ml^{-1}), and 8 ppm for platinum.

Other Methods

Polarography has proved to be a suitable method of analysis in only a few cases where the conditions favour the stabilization of a particular complex.

X-ray fluorescence spectroscopy has been used for the determination of rhodium, iridium, palladium and platinum[45].

[40] F. E. Beamish and W. E. A. McBryde, *Anal. Chim. Acta* **9** (1953) 349; **18** (1958) 551.

[41] A. Walsh and J. B. Willis, Atomic Absorption Spectrometry, chap. 6 in *Standard Methods of Chemical Analysis*, 6th edn., Vol. 3A (F. J. Welcher, ed.), Van Nostrand, Princeton, N.J (1966), p. 105.

[42] W. T. Elwell and J. A. F. Gidley, *Atomic Absorption Spectrophotometry*, 2nd edn., International Series of Monographs on Analytical Chemistry, Vol. 6, Pergamon, New York (1966).

[43] R. Lockyer and G. E. Hames, *Analyst*, **84** (1959) 385.

[44] V. L. Ginzburg, D. M. Livshits and G. I. Satarina, *Zh. Analit. Khim.* **19** (1964) 1089.

[45] W. M. MacNevin and E. A. Hakkila, *Anal. Chem.* **29** (1957) 1019.

1.11. GENERAL CHEMICAL TRENDS

Mendeléeff's placing of three elements of each period in Group VIII has over-emphasized their similarity to one another; this resemblance is not much closer than between any three consecutive transition elements. Sidgwick[46] has suggested that it would be more accurate to divide the group vertically into three triads which would be called Groups VIIIA, IXA and XA, since the elements of each triad have respectively 8, 9 and 10 electrons more than the preceding rare gas. However, the convention of placing the nine elements in one group is too well established to be changed[46].

The Group VIII elements have the smallest atomic volumes in each of the three long periods. Consequently these elements display a pronounced tendency to form covalent bonds, the effect being more marked for the second and third transition series. Whereas iron, cobalt and nickel readily form the hydrated ions $[M(H_2O)_6]^{2+}$, the six platinum metals show little tendency to do so. Aqua ions of Ru(II), Rh(III) and Pd(II) are known to exist in solution but only in the absence of anions which are capable of forming complex ions. Aqua ions do not appear to be formed by the heavier metals, osmium, iridium and platinum. Apart from binary compounds, such as oxides, halides, sulphides, etc., the compounds formed by the platinum metals are complex.

Because of this difference between iron, cobalt and nickel, on the one hand, and the platinum metals on the other, it must not be overlooked that the relationships within Group VIII are vertical. Correlations can be found; a few examples are listed below. Iron, ruthenium and osmium form the monomeric carbonyls $M(CO)_5$, the very stable complexes $[M(CN)_6]^{4-}$, $[M(phen)_3]^{2+}$ and $[M(bipy)_3]^{2+}$ (M = Fe, Ru, Os); alkali metal salts of the anion $[MO_4]^{2-}$ can be prepared, although the iron compound is easily reduced. Cobalt, rhodium and iridium form the complex anions $[M(CN)_6]^{3-}$, $[M(NO_2)_6]^{3-}$ and $[M(C_2O_4)_3]^{3-}$, and the dimeric carbonyls $M_2(CO)_8$ (M = Co, Rh, Ir). Nickel, palladium and platinum form the very stable $[M(CN)_4]^{2-}$ (M = Ni, Pd, Pt) and neutral complexes with a large number of oximes, the best known being dimethylglyoxime which is used for the quantitative estimation of nickel and palladium.

The stability of the higher oxidation states increases down each triad: Fe < Ru < Os; Co < Rh < Ir; Ni < Pd < Pt, and decreases across each period: Ru > Rh > Pd and Os > Ir > Pt. The maximum oxidation state is 8 for ruthenium and osmium, 6 for rhodium, iridium and platinum, and 4 for palladium. The lowest oxidation states yet reported are: −2 for ruthenium, −1 for rhodium and iridium, and 0 for osmium, palladium and platinum.

2. RUTHENIUM

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In Group VIII the second and third members of each triad resemble each other more closely than they do the first member; consequently ruthenium resembles osmium more than it does iron. Ruthenium is a hard, white metal which occurs in four modifications with the transitions:

$$\alpha \xrightarrow{1030\text{–}1040^\circ} \beta \xrightarrow{1200^\circ} \gamma \xrightarrow{ca.\ 1500^\circ} \delta$$

It is virtually unaffected by mineral acids but it can be got into solution by fusion with sodium peroxide which oxidizes ruthenium to sodium ruthenate(VI), Na_2RuO_4. If the

[46] N. V. Sidgwick, *The Chemical Elements and their Compounds*, Clarendon Press, Oxford (1950), p. 1316.

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[46] N. V. Sidgwick, *The Chemical Elements and their Compounds*, Clarendon Press, Oxford (1950), p. 1316.

aqueous extract is treated with chlorine and heated, ruthenium tetroxide, RuO_4, distils off. Hydrochloric acid reacts with RuO_4 in the presence of potassium chloride to yield red $K_4[Ru_2OCl_{10}]$, formerly assigned the formula $K_2[RuCl_5OH]$.

TABLE 4. ELECTRODE POTENTIALS FOR RUTHENIUM [a, b]

Reaction	Potential (V)
$RuCl_5^{2-} + 3e = Ru + 3Cl^-$	0.4
$RuCl_5^{2-} + e = Ru(II) + 5Cl^-$	−0.08
$RuCl_5OH^{2-} + H^+ + 4e = Ru + 5Cl^- + H_2O$	0.6
$RuCl_5OH^{2-} + H^+ + e = RuCl_5^{2-} + H_2O$	0.86
$RuO_4^{2-} + 8H^+ + 6e = Ru + 4H_2O$	1.19
$RuO_4^- + e = RuO_4^{2-}$	0.6
$RuO_4^{2-} + 4H^+ + 2e = RuO_2 + 2H_2O$	2.01
$RuO_4^- + 7H^+ + 5Cl^- + 3e = RuCl_5OH^{2-} + 3H_2O$	1.78
$RuO_4 + 4H^+ + 4e = RuO_2 + 2H_2O$	1.39
$RuO_4 + e = RuO_4^-$	0.95

[a] W. M. Latimer, *Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd edn., Prentice-Hall, Englewood Cliffs, New Jersey (1952), p. 228.

[b] T. J. Walsh and E. A. Hausman, *The Platinum Metals* in *Treatise on Analytical Chemistry*, Part II, Vol. 8 (I. M. Kolthoff and P. J. Elving, eds.), Wiley Interscience, New York (1963), p. 397.

The electrode potentials for ruthenium are given in Table 4. Ruthenium is remarkable in that it displays ten oxidation states; these, together with representative compounds, are given in Table 5. Ruthenium(VIII) is less stable than Os(VIII) and is represented by only one compound, viz. RuO_4. The septavalent state occurs only in the perruthenate ion $[RuO_4]^-$. Fewer Ru(VI) compounds are known than is the case for Os(VI). Ruthenium(V) is represented only by the pentafluoride and some complex fluorides. Quadrivalent ruthenium is more easily reduced than Os(IV). The trivalent state is the most stable oxidation state and Ru(III) resembles Rh(III) and Ir(III) somewhat more than it does Os(III). Ruthenium(II) shows some similarity to Fe(II) and is remarkable for the large number of

TABLE 5. OXIDATION STATES OF RUTHENIUM

Oxidation state	Examples
Ru^{-II}	$[Ru(CO)_4]^{2-}$
Ru^0	$Ru(CO)_5$, $Ru(CO)_3(PPh_3)_2$
Ru^I	$[RuCOBr]_n$
Ru^{II}	$[Ru(bipy)_3]^{2+}$, $Ru(\pi\text{-}C_5H_5)_2$, $[RuNOCl_5]^{2-}$
Ru^{III}	$RuCl_3 \cdot 3H_2O$, $[Ru(NH_3)_6]^{3+}$ $[RuNOCl_5]^{2-}$
Ru^{IV}	$K_2[RuCl_6]$, RuO_2
Ru^V	RuF_5, $K[RuF_6]$
Ru^{VI}	$K_2[RuO_4]$, $K_2[RuO_2Cl_4]$
Ru^{VII}	$K[RuO_4]$
Ru^{VIII}	RuO_4

nitrosyl complexes which it forms. The lower oxidation states (+I, 0, −II) are confined to carbonyls, carbonyl halides and phosphine complexes.

Thermodynamic data for ruthenium and some of its compounds are listed in Table 6.

TABLE 6. THERMODYNAMIC DATA ON RUTHENIUM AND ITS COMPOUNDS [a]

Substance	State	$\Delta H°$	$\Delta F°$	$S°$
Ru	g	160	149	44.57
Ru	c	0	0	6.9
$RuCl_3$	c	−63	−46.9 [b]	
RuO_2	c	−52.5	−40.7 [b]	
RuS_2	c	−48.1	−44.1	

$\Delta H°$ = standard heat of formation at 25° (kcal mole^{-1}).
$\Delta F°$ = standard free energy of formation at 25° (kcal mole^{-1}).
$S°$ = entropy at 25° (cal deg^{-1}).
g = gaseous; c = crystalline.

[a] Unless otherwise indicated, values are from the US National Bureau of Standards Circular 500, *Selected Values of Thermodynamic Properties* (1952).

[b] W. M. Latimer, *Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, 2nd edn., Prentice-Hall, Englewood Cliffs, New Jersey, (1952), p. 229.

2.2. BINARY COMPOUNDS

The halides and chalcogenides, along with their known physical properties, are listed in Table 7.

Halides

The hexafluorides of the platinum metals show decreasing stability in the order: Os > Ir > Pt, Ru > Rh. Ruthenium hexafluoride can be prepared by the action of fluorine on the metal; it is octahedral and the solid is isostructural with the other platinum metal hexafluorides[47]. The compound is thermally unstable and highly reactive, reacting vigorously with water. The pentafluoride RuF_5 can be obtained by heating the metal in fluorine at 300° or by the reaction of bromine trifluoride on the metal. It is tetrameric with a non-linear fluoro bridge between each pair of ruthenium atoms; it is sensitive to moisture and fumes in air. The tetrafluoride can be obtained by the reaction:

$$10RuF_5 + I_2 \xrightarrow{\Delta} 10RuF_4 + 2IF_5$$

The reaction of chlorine on $RuCl_3$ at 750° is said to yield the tetrachloride $RuCl_4$, which can be condensed at −30° [48]. The action of hydrochloric acid on the tetroxide RuO_4 produces the hydrated tetrachloride $RuCl_4 \cdot 5H_2O$, which occurs as red hygroscopic crystals, and the reddish-brown hydroxotrichloride $RuOHCl_3$, depending on the conditions. The latter compound can be obtained by the evaporation of a solution of RuO_4 in

[47] H. H. Claassen, H. Selig, J. G. Malm, C. L. Chernick and B. Weinstock, *J. Am. Chem. Soc.* **83** (1961) 2390.

[48] N. I. Kolbin, A. N. Ryabov and V. M. Samoilov, *Russ. J. Inorg. Chem.*, Eng. Transl., **8** (1963) 805.

TABLE 7. HALIDES AND CHALCOGENIDES OF RUTHENIUM

Compound	Colour/form	M.p.	B.p.	Structure	ΔH (kcal mole^{-1})	ΔS (cal mole^{-1} deg^{-1})	μ (BM)
RuF_6	Dark brown crystals	54°		Octahedral			
$[RuF_5]_4$	Dark green crystals	85.6	227°	Tetrameric with F bridges; octahedral coordination [a]	15.23 [b]	30.4 [b]	3.60
RuF_4	Yellow crystals						3.04
RuF_3	Brown powder			Distorted hexagonal lattice [c]			
$RuCl_4$	Vapour above 750°				-22.3 ± 4 [d]	-20.4 ± 4 [d]	
$RuCl_3$	Dark brown			Tetrahedral [e]	13.4 ± 3 [d]	8.3 ± 3 [d]	2.07
$RuCl_2$	Brown						
$RuBr_3$?	Brown			Hexagonal lattice [f]			
$RuBr_2$	Black crystals						
RuI_3	Black powder			Hexagonal lattice [f]	38.2 ± 1.4 [g]		
RuI_2	Blue						
RuO_4	Yellow crystals	25.4	40	Tetrahedral	-46.7 ± 5 [h]	-39.3 ± 5 [h]	
RuO_3	Vapour at 1200°				-18.0 ± 4 [h]	-16.6 ± 4 [h]	
RuO_2	Deep blue crystals			Rutile	-72.2 ± 2 [h]	12.5 ± 2	0.78
RuS_2	Grey crystals	d. 1000		Pyrites			
$RuSe_2$	Greyish black crystals			Pyrites			
$RuTe_2$	Bluish grey crystals			Pyrites			

[a] J. H. Holloway, R. D. Peacock and R. W. H. Small, *J. Chem. Soc.* 1964, 644.
[b] J. H. Holloway and R. D. Peacock, *J. Chem. Soc.* 1963, 527.
[c] M. A. Hepworth, K. H. Jack, R. D. Peacock and G. J. Westland, *Acta Cryst.* **10** (1957) 63.
[d] W. E. Bell, M. C. Garrison and U. Merten, *J. Phys. Chem.* **65** (1961) 517.
[e] J. M. Fletcher, W. E. Gardner, E. W. Hooper, K. R. Hyde, F. H. Moore and J. L. Woodhead, *Nature* **199** (1963) 1089.
[f] H. G. von Schnering, K. Brodersen, F. Moers, H. K. Breitbach and G. Thiele, *J. Less-Common Metals* **11** (1966) 288.
[g] S. A. Schukarev, N. I. Koblin and A. N. Ryabov, *Russ. J. Inorg. Chem., Eng. Transl.* **4** (1959) 763.
[h] W. E. Bell and M. Tagami, *J. Phys. Chem.* **67** (1963) 2432.

hydrochloric acid[49]. It is very soluble in water and can be reduced to $RuCl_3$ by the action of stannous chloride. The structures of these compounds are not known and the compounds are probably complex.

The trifluoride RuF_3 can be obtained by reduction of RuF_5 with iodine at 250° [50]. It has a rhombohedral lattice with the fluorine atoms arranged octahedrally about the metal atom; the octahedra are joined by sharing corners only. Variations occur in the unit-cell dimensions due to deviations from stoichiometry caused by the presence of cations with valencies other than three[51].

The anhydrous trichloride occurs in two forms: brown β-$RuCl_3$, which is soluble in alcohol, and black α-$RuCl_3$, which is insoluble in water and alcohol. The β-form is best prepared by the action of a 3:1 mixture of chlorine and carbon monoxide on ruthenium sponge at 330°; it can also be obtained by the evaporation of alcoholic solutions of Ru(IV) chloro complexes. It is converted into the α-form by heating in a current of chlorine at 700° [52]; the irreversible transition occurs at 450°. α-$RuCl_3$ becomes antiferromagnetic at low temperatures with the Néel temperature of 30°K [53]; β-$RuCl_3$ has a lower magnetic susceptibility at all temperatures[53]. The α-form has a layer lattice and is isomorphous with violet $CrCl_3$. The β-form has been reported as having tetrahedral coordination[53], but more recently[54] as octahedral with the rather close Ru–Ru distance of 2.83 Å.

Evaporation of a solution of RuO_4 in aqueous hydrochloric acid in a stream of hydrogen chloride yields a red product usually regarded as $RuCl_3 \cdot 3H_2O$. Commercial hydrated ruthenium chloride is impure and may contain polymeric chloro and hydroxy-chloro complexes of Ru(IV). The deep red solution darkens on standing due to hydrolysis. The commercial product can be reduced with mercury in dilute hydrochloric acid to give solutions containing Ru(III) which are oxidized by air to Ru(IV). The species $[Ru(H_2O)_6]^{3+}$, $[Ru(H_2O)_5Cl]^{2+}$ and *cis*- and *trans*-$[Ru(H_2O)_4Cl_2]^+$ have been identified in the reduced solution.

The tribromide has been obtained only as an impure product from the evaporation of solutions of RuO_4 and RuO_2 in hydrobromic acid. The hygroscopic crystals are soluble in water to give a brown solution which gives bromo complexes upon the addition of bromide ions. The black triiodide RuI_3 is precipitated from Ru(III) chloride solutions by the addition of potassium iodide. It is insoluble in water and is easily oxidized with the liberation of iodine.

The only definite dihalide appears to be $RuBr_2$. Blue solutions which probably contain $RuCl_2$ can be obtained by hypophosphite or electrolytic reduction of $RuCl_3$. This blue colour was reported by Fourcroy and Vauquelin in 1804. Catalytic reduction of an alcoholic solution of $RuBr_3$ with hydrogen gives a bluish-violet solution from which black crystals of $RuBr_2$ can be obtained[55]. Similar reduction of RuI_3 in alcohol yields a blue solution which may contain RuI_2 [55]. The spectra of the blue solutions of Ru(II) in HCl have been

[49] G. Brauer, *Handbook of Preparative Inorganic Chemistry*, Academic Press, New York (1965), p. 1597.
[50] E. E. Aynsley, R. D. Peacock and P. L. Robinson, *Chem. Ind.* 1952, 1002.
[51] M. A. Hepworth, K. H. Jack, R. D. Peacock and G. J. Westland, *Acta Cryst.* **10** (1957) 63.
[52] K. R. Hyde, E. W. Hooper, J. Waters and J. M. Fletcher, *J. Less-Common Metals* **8** (1965) 428.
[53] J. M. Fletcher, W. E. Gardner, E. W. Hooper, K. R. Hyde, F. H. Moore and J. L. Woodhead, *Nature* **199** (1963) 1089.
[54] G. N. Schrauzer, V. Mayweg, H. W. Finck, U. Müller-Westerhoff and W. Heinrick, *Angew. Chem.* **3** (1964) 381.
[55] H. Gall and G. Lehmann, *Ber.* **59** (1926) 2856.

interpreted as being indicative of planar $[RuCl_4]^{2-}$ ions[56]. The solutions are oxidized by water to Ru(III) and the kinetics have been studied[57].

The monohalides RuCl, RuBr and RuI have been reported to exist in aqueous solutions of the trihalides when treated with hypophosphorous acid[58]; however, no solid compounds have been isolated.

Oxides

The thermochemistry of the oxides of ruthenium has been reviewed[59].

The tetroxide RuO_4 is produced when acidified solutions of ruthenium are heated with strong oxidizing agents such as $KMnO_4$, HIO_4, Ce(IV) or Cl_2. It can be prepared from the metal by heating ruthenium with sodium peroxide or a fused mixture of potassium hydroxide and potassium nitrate, then treating the leached melt with Cl_2 or $KMnO_4$ in acid. It forms yellow crystals which are sparingly soluble in water (2.03 g per 100 g H_2O at 20°) but very soluble in carbon tetrachloride. Because of its volatility (b.p. 40°), toxicity and irritant effect on the eyes, it should be handled with great care. It has a tetrahedral configuration and is less stable than OsO_4 and can explode if heated above 180°, giving RuO_2 and oxygen. The tetroxide is a powerful oxidizing agent and is reduced by HCl to Ru(IV) and by alkali to Ru(VI), giving the ruthenate ion $[RuO_4]^{2-}$. Carbon tetrachloride solutions have been used for specific oxidation reactions in organic chemistry[60, 61]. Donor molecules such as NH_3, pyridine, PF_3 and NO form black hygroscopic adducts with RuO_4. Among these are $RuO_4 \cdot PF_3$, $(RuO_4)_2 \cdot PF_3$ and $RuO_4(NO)_2$; their structures are not known.

The trioxide RuO_3 has been shown to exist in the vapour state at 1200°, but it has not been isolated in the solid state. The deep blue dioxide RuO_2 can be prepared by heating the metal or $RuCl_3$ in oxygen at 1000°. It is usually contaminated with Ru_2O_3. It is unattacked by acids in the cold. The low magnetic moment, 0.78 at 298°K, compared to the values of 2.8–3.0 BM found for most Ru(IV) compounds, suggests some metal–metal interaction, but the Ru–Ru distance (3.11 Å) is not exceptionally short[62]. Reduction of aqueous RuO_4 by hydrogen yields the monohydrate $RuO_2 \cdot H_2O$ or $RuO(OH)_2$, which can also be obtained by heating RuO_2 in a current of hydrogen.

The oxides Ru_2O_5, Ru_2O_3 and RuO have been claimed to have been prepared, but it is doubtful if any of these oxides have been obtained in anything like a pure condition in the solid state. The black hydroxide $Ru(OH)_3$ is said to be precipitated by the addition of alkali to solutions of ruthenium trichloride, but it is difficult to wash the precipitate free from alkali and the product is very unstable, being easily oxidized by air to Ru(IV).

Compounds of Sulphur, Selenium, Tellurium and Phosphorus

The compounds RuS_2, $RuSe_2$ and $RuTe_2$ can be prepared by heating the metal with the appropriate chalcogen. All have the pyrites structure. The sulphide occurs as the mineral *laurite*, which contains a small amount of osmium. Prolonged passage of hydrogen sulphide through a solution of $RuCl_3$ yields RuS_2 as a yellowish-brown deposit. It is

[56] C. K. Jørgensen, *Acta Chem. Scand.* **10** (1956) 518.
[57] G. A. Rechnitz and H. A. Catherino, *Inorg. Chem.* **4** (1965) 112.
[58] W. Manchot and J. Düsing, *Z. anorg. allgem. Chem.* **212** (1933) 29.
[59] A. B. Nikol'skii and A. N. Ryabov, *Russ. J. Inorg. Chem.* **12** (1965) 1.
[60] C. Djerassi and R. R. Engle, *J. Am. Chem. Soc.* **75** (1953) 3838.
[61] H. Nakata, *Tetrahedron* **19** (1963) 1959.
[62] F. A. Cotton and J. T. Mague, *Inorg. Chem.* **5** (1966) 317.

more easily obtained as a black precipitate by treating a solution of K_2RuCl_6 with H_2S at 80°. The sulphides RuS_3 and RuS_6 have been reported as being precipitated from ruthenium solutions by H_2S at 0°, but these are polysulphides or, more probably, mixtures of RuS_2 and free sulphur.

The diphosphide RuP_2 is formed from the elements at temperatures above 650° and is stable in the presence of phosphorus vapour at 1 atm up to 900° [63]. It has the marcasite structure. The lower phosphides Ru_2P and RuP are known; these are isostructural with Co_2P and FeP, respectively.

The ternary compounds RuAsS, RuAsSe, RuAsTe, RuSbS, RuSbSe and RuSbTe have been prepared by sintering pressed pellets of the intimately mixed components at 700–900°. They have a similar structure to arsenopyrite FeAsS and are diamagnetic, semiconducting and non-metallic[64].

2.3. OXO- AND HYDROXO-HALIDES

A number of oxo- and hydroxo-halides have been reported. Pale green crystals of $RuOF_4$ can be prepared by treating ruthenium metal with a mixture of bromine trifluoride and bromine[65]. The dark brown hydroxotrichloride $RuOHCl_3$ can be prepared from RuO_4 and hydrochloric acid[66]. Ru_2OCl_6 and Ru_2OCl_5 can be obtained by treating a solution of $RuCl_3$ with chlorine[53]. The violet colour which is produced when a solution of Ru(IV) in perchloric acid is treated with chloride ion is said to be due to $Ru(H_2O)_2(OH)_2Cl_2$, which may be trimeric[67]. The hydroxodichloride $RuOH(H_2O)Cl_2$ has been obtained from the hydrolysis of $K_2[RuCl_5H_2O]$.

2.4. COMPLEXES OF RUTHENIUM(−II)

Tetrahedral Ru(−II) has the electronic configuration of the next inert gas and should be thermodynamically stable. The known complexes of Ru(−II) are confined to the anions $[Ru(CO)_4]^{2-}$, $[Ru(P\text{–}P)_2]^{2-}$ (P–P = $Me_2PCH_2CH_2PMe_2$) and $[Ru(PF_3)_4]^{2-}$. The former is best prepared by the action of sodium on $Ru_3(CO)_{12}$ in liquid ammonia; evaporation of this solution yields a buff residue, presumably $Na_2[Ru(CO)_4]$ [68]. Treatment of this solid with phosphoric acid yields the hydride $H_2Ru(CO)_4$. The complex $[Ru(P\text{–}P)_2]^{2-}$ has been obtained as an intermediate in the synthesis of *cis*-$[H_2Ru(P\text{–}P)_2]$ [69]. The trifluorophosphine complex $K_2[Ru(PF_3)_4]$ is also known.

2.5. COMPLEXES OF RUTHENIUM(0)

Carbonyls

Ruthenium pentacarbonyl, $Ru(CO)_5$, and triruthenium dodecacarbonyl, $Ru_3(CO)_{12}$, were first reported in 1936. The former can be prepared in rather poor yield (10%) by

[63] W. Blitz and H. Ehrhorn, *Z. anorg. Chem.* **240** (1939) 117.
[64] F. Hulliger, *Nature* **201** (1964) 381.
[65] J. H. Holloway and R. D. Peacock, *J. Chem. Soc.* 1963, 527.
[66] R. Charronat, *Ann. chim.* (*Paris*) **16** (10) (1931) 40, 68.
[67] P. Wehner and J. C. Hindman, *J. Phys. Chem.* **56** (1952) 10.
[68] M. I. Bruce, J. D. Cotton and F. G. A. Stone, *J. Chem. Soc.* A, 1968, 2162.
[69] J. Chatt and J. M. Davidson, *J. Chem. Soc.* 1965, 843.

heating ruthenium powder at 180° under carbon monoxide at a pressure of 200 atm [70]. It can also be obtained by heating a mixture of RuI_3 and excess silver powder at 170° for 24 hr with carbon monoxide at 450 atm. The volatile $Ru(CO)_5$ can be recovered from the gases by trapping it at low temperature; the $Ru_3(CO)_{12}$ formed by this reaction can be extracted with benzene[70]. The pentacarbonyl is a colourless liquid (m.p. −22°) readily soluble in organic solvents. It is considered to have a trigonal bipyramidal structure on the basis of its infrared spectrum[71].

The dodecacarbonyl, originally reported as $Ru_2(CO)_9$, can be prepared as described above or by heating $Ru(CO)_5$ in benzene, or by treating a solution of $RuCl_3$ in methanol with zinc and carbon monoxide (10 atm) at 65°; the yield is 75%. It forms orange crystals (m.p. 154–155°), moderately soluble in organic solvents. It is isomorphous and isostructural with $Os_3(CO)_{12}$, which is a metal cluster with the three metal atoms at the corners of an equilateral triangle and with all the CO groups terminal. The reactions of $Ru_3(CO)_{12}$ have been recently reviewed[72].

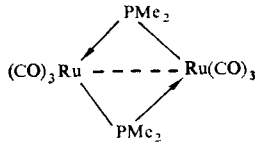
The polymeric carbonyl $[RuCO]_n$ is produced in low yield along with $Ru_3(CO)_{12}$ from $Ru(CO)_5$. It forms green crystals which are soluble in alcohol; its structure is unknown. The mixed carbonyls $Fe_2Ru(CO)_{12}$, $FeRu_2(CO)_{12}$, $Ru_2Os(CO)_{12}$ and $RuOs_2(CO)_{12}$ are known.

The cluster carbonyl $Ru_6(CO)_{18}$ and the related "carbonyl carbide cluster" compounds $Ru_6C(CO)_{17}$ and $Ru_6C(CO)_{14}$ arene are known[72]. A structure determination of the mesitylene derivative shows that the carbide atom lies close to the centre of a slightly distorted octahedron of ruthenium atoms, which are all 8-coordinate. The covalent radius for Ru(0) is 1.45 (cf. 1.42 Å in $Ru_3(CO)_{12}$) [73].

Phosphine and Arsine Carbonyl Complexes

The complexes $Ru(CO)_3(PPh_3)_2$ and $Ru(CO)_3(AsPh_3)_2$ can be obtained by treatment of $Ru(CO)_2Cl_2L_2$ (L = PPh_3, $AsPh_3$) with zinc dust and CO. The compounds are soluble in organic solvents and do not trimerize. There is evidence to support a trigonal bipyramidal structure with the three CO groups in equatorial positions. The complexes undergo oxidation reactions with halogen with the loss of one CO group to give $Ru(CO)_2X_2L_2$ (X = Cl, Br) [74]. $Ru(CO)_3(PPh_3)_2$ reacts with HgX_2 (X = Cl, Br) to give $[Ru(CO)_3(PPh_3)_2X]X$ and $[Ru(CO)_3(PPh_3)_2HgX]HgX_3$ [75].

The dodecacarbonyl $Ru_3(CO)_{12}$ reacts with PR_3 (R = Ph, Bu^n, OC_6H_5) to give $Ru_3(CO)_9(PR_3)_3$ [76, 77], but with Me_2PPMe_2 the dimeric complex (I) is produced[76].



(I)

[70] W. Manchot and W. J. Manchot, *Z. anorg. allgem. Chem.* **226** (1936) 385.
[71] F. Calderazzo and F. l'Eplattenier, *Inorg. Chem.* **6** (1967) 1220; **7** (1968) 1290.
[72] M. I. Bruce and F. G. A. Stone, *Angew. Chem.*, Int. Edn., **7** (1968) 427.
[73] R. Mason and W. R. Robinson, *Chem. Communs.* 1968, 468.
[74] J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.* **87** (1965) 4008.
[75] J. P. Collman and W. R. Roper, *Chem. Communs.* 1966, 244.
[76] J. P. Candlin, K. K. Joshi and D. T. Thompson, *Chem. Ind. (London)* 1966, 1960.

$Ru_3(CO)_9(PPh_3)_3$ reacts with halogen to give $Ru_2X_4(CO)_2PPh_3$ and $RuX_2(CO)_2(PPh_3)_2$, and with CO (150 atm, 150°) to give $Ru(CO)_4PPh_3$, which is highly reactive[77].

Reaction of $Ru_3(CO)_{12}$ with the quadradentate ligands $[o\text{-}Ph_2PC_6H_4]_3P$ (QP) and $[o\text{-}Ph_2AsC_6H_4]_3As$ (QAS) yields RuCO(QP) and RuCO(QAS) [72]. The compound *trans*-$[P(OCH_2)_3CEt]_2Ru(CO)_3$ is known[78].

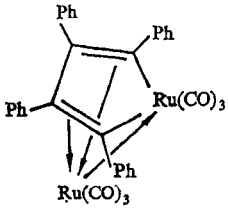
Phosphine Complexes

The complexes $Ru(PF_3)_5$ [79] and $Ru(P\text{–}P)_2$ (P–P = $Me_2PCH_2CH_2PMe_2$) [69] are known; the former can be regarded as a derivative of $Ru(CO)_5$ in which all the CO groups have been substituted by PF_3. The latter is in tautomeric equilibrium with the 6-coordinate Ru(II) hydrido complex $RuH(CH_2PMeCH_2CH_2PMe_2)(P\text{–}P)$, but the reactions are those of the Ru(0) complex $Ru(P\text{–}P)_2$ [69].

π-Complexes

The bonding of the olefin or aromatic nucleus to the metal atom in these complexes is generally attributed to interaction between the π-electrons of the organic ligand and the metal orbitals. The olefin complexes cyclo-octa-1,3,5-trienebicyclo-octa-2,4-dieneruthenium $C_8H_{10}RuC_8H_{10}$, cyclo-octa-1,5-dienecycloheptatrieneruthenium $C_8H_{12}RuC_7H_8$, norborna-dienecycloheptatrieneruthenium $C_7H_8RuC_7H_8$ and benzenecyclohexa-1,3-diene $C_6H_6RuC_6H_8$ are known[80, 81].

There are many examples of Ru(0) carbonyl complexes containing unsaturated hydrocarbons; the following compounds have been reported[72]: $C_8H_{12}Ru_3(CO)_{10}$ (C_8H_{12} = cyclo-1,3-octadiene), $C_6H_8Ru(CO)_3$ (C_6H_8 = cyclo-1,3-hexadiene), $(R_4C_4CO)Ru(CO)_3$ (R_4C_4CO = tetra-substituted cyclopentadienone; R = Ph or CF_3), $C_8H_8Ru(CO)_3$ (C_8H_8 = cyclo-octatetraene), $C_8H_8Ru_2(CO)_6$, $C_8H_8Ru_2(CO)_5$ and $(C_8H_8)_2Ru_3(CO)_4$. The following complexes have been prepared from diphenylacetylene (Ph_2C_2): $(Ph_2C_2)Ru_3(CO)_9$, $(Ph_2C_2)_2Ru_2(CO)_6$, $(Ph_2C_2)Ru_2(CO)_6$, $(Ph_2C_2)_2Ru_3(CO)_8$, $(Ph_2C_2)_2Ru_2(CO)_7$ and $(Ph_2C_2)_2Ru(CO)_4$. The structures of several of these compounds are similar to those of the analogous iron complexes; accordingly it has been suggested that $(Ph_2C_2)_2Ru_2(CO)_6$ has the structure (II) [72]. 4,4′-Dichlorophenylacetylene gives $[(ClC_6H_4)_2C_2]_3Ru_3(CO)_9$ and



(II)

[77] F. Piacenti, P. Pino, M. Bianchi, G. Braca and G. Sbrana, *Progress in Coordination Chemistry* (M. Cais, ed.), Elsevier, Amsterdam (1968), p. 54.
[78] M. I. Bruce, M. Cooke and M. Green, *J. Organomet. Chem.* **13** (1968) 227.
[79] T. Kruck, *Angew. Chem.* **6** (1967) 53.
[80] J. Muller and E. O. Fischer, *J. Organomet. Chem.* **5** (1966) 277.
[81] D. Jones, L. Pratt and G. Wilkinson, *J. Chem. Soc.* 1962, 4458.

$[(ClC_6H_4)_2C_2]_2Ru_3(CO)_8$. The cyclo-octatetraene complex $C_8H_8Ru(CO)_3$ undergoes 1,2-addition reactions with hexafluoroacetone and other active molecules, whereas diene systems usually undergo 1,4-addition reactions with these reagents[82].

2.6. COMPLEXES OF RUTHENIUM(I)

The polymeric compounds $[RuCOBr]_n$ and $[Ru(CO)_xI]_n$ have been obtained by the reaction of the Ru(III) halides with carbon monoxide under pressure[83,70]. The cyclopentadienyl complex $[C_5H_5Ru(CO)_2]_2$ can be prepared from $Ru(CO)_2I_2$ and sodium cyclopentadienide[84]. The carbonyl hydrides $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ have been described; their infrared spectra are consistent with the presence of a Ru–H–Ru bridge[85]. The nitrosyl complexes which contain the ligand NO^+, $[RuNOX_2]_n$ (X = Br, I), $RuNOI_2py_2$, $RuNOI_2bipy$ and $RuNOI_2Ph_2MeAs$ have been reported[86].

2.7. COMPLEXES OF RUTHENIUM(II)

Ruthenium(II) forms a large number of complexes some of which are extremely stable; they are almost invariably 6-coordinate. All the complexes are diamagnetic, indicating that Ru(II) has the low-spin $(t_{2g})^6$ configuration. They are usually prepared by the reduction of Ru(III) chloride or Ru(III) or Ru(IV) halogeno complexes in the presence of the appropriate ligand. The aqua-ion $[Ru(H_2O)_6]^{2+}$ can be isolated as the BF_4^- or *p*-toluene-sulphonate salt, but ClO_4^- is reduced. The value of E_0 for Ru(III)/Ru(II) is -0.25 V [87].

Complexes are formed by Cl^-, CN^-, NH_3, en, *N*-heterocycles and tertiary phosphines, arsines and stibines. Many cationic, neutral and anionic nitrosyl complexes are known; indeed, more than for any other element. Numerous carbonyl and hydrido compounds have been characterized. Of especial interest are the recently discovered complexes containing N_2 as a ligand.

Halide and Cyanide Complexes

The very stable complex $K_4[Ru(CN)_6]$ can be obtained by the action of KCN on K_2RuO_4 or Ru(III) chloride. A few chloro complexes containing the anions $[RuCl_4]^{2-}$ and $[RuCl_5H_2O]^{3-}$ have been reported but these have not been well characterized.

Complexes with Nitrogen Ligands

The hexammine-type complexes $[Ru(NH_3)_6]Cl_2$ [88], $[Ru\ en_3]Br_2$ [89], $[Ru\ bipy_3]X_2 \cdot nH_2O$ (X = Cl, Br, I, ClO_4, NO_3, $n = 6$; X = OH, $n = 8$; $2X = CO_3$; $n = 10$) [90], $[Ru\ phen_3]Cl_2$ [90], $[Ru\ terpy_2]Cl_2$ [91], $[Ru(NH_3)_2phen_2]I_2$, $[Ru\ en\ phen_2]I_2$,

[82] M. Green and D. C. Wood, *Chem. Communs.* 1967, 1062.
[83] W. Manchot and E. Enk, *Ber.* **64** (1931) 2673.
[84] F. A. Cotton and G. Yagupsky, *Inorg. Chem.* **6** (1967) 15; R. D. Fischer, A. Vogler and K. Noack, *J. Organomet. Chem.* **7** (1967) 135; K. Noack, *J. Organomet. Chem.* **7** (1967) 151.
[85] B. F. G. Johnson, R. D. Johnston, J. Lewis and B. H. Robinson, *Chem. Communs.* 1966, 851.
[86] W. Manchot and H. Schmid, *Ber.* **64** (1931) 2673; R. J. Irving and P. G. Laye, *J. Chem. Soc.* A, 1966, 161.
[87] E. E. Mercer and R. R. Buckley, *Inorg. Chem.* **4** (1965) 1692.
[88] F. M. Lever and A. R. Powell, *Chem. Soc.*, Spec. Publ. No. 13, 1959, 135.
[89] A. D. Allen and C. V. Senoff, *Can. J. Chem.* **43** (1965) 888.
[90] F. H. Burstall, *J. Chem. Soc.* 1936, 173.
[91] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.* 1937, 1654.

$[Rupy_2\ phen_2](ClO_4)_2$, $[Ru(NH_3)_2py_2bipy](ClO_4)_2$, [Ru py bipy terpy]$(ClO_4)_2$, [Ru py_4 bipy]$(ClO_4)_2$ [92] and $[Ru(o\text{-}C_5H_4N\cdot CH_2NH_2)_3]Cl_2$ [93] are known. The red complex $[Ru\ bipy_3]Cl_2$ is extremely stable, being unaffected by heating at 300° or by boiling HCl or 50% KOH. Its optical isomers do not racemize in the cold and only slowly at 90°. The cation *cis*-$[Ru\ py_2\ phen_2]^{2+}$ has been resolved into antimers from which optically active monosubstituted complexes have been prepared[94].

With the exception of $Ru(NH_3)_2Cl_2H_2O$ [95], the complexes with less than six NH_3 groups contain either NO (see Nitrosyl Complexes, p. 1200), or the groups SO_2, HSO_3^- or SO_3^{2-}, which behave as unidentate ligands. The latter are prepared by the action of $NaHSO_3$ on Ru(III) ammine complexes; they include $[Ru(NH_3)_5SO_3]\cdot 2H_2O$, $[Ru(NH_3)_5SO_2]X_2$ (X = Cl, Br, NO_3, $\frac{1}{2}SO_4$), $[Ru(NH_3)_4(SO_3H)_2]$, $[Ru(NH_3)_4SO_2X]X$ (X = Cl, Br) and $Na_4[Ru(NH_3)_2(SO_3)_2(SO_3H)_2]$ [95].

The following complexes of 1,10-phenanthroline and 2,2′-bipyridyl have been described: $[Ru\ bipy_2X_2]$ (X = Cl, Br, I, $\frac{1}{2}C_2O_4$) [96], $[Ru\ phen_2X_2]$, [Ru py_3bipyCl]Cl, [Ru py_2X_2chel] (X = Cl, Br, I, SCN; chel = bipy, phen), [Ru pyClphen$_2$]ClO_4, [Ru $py_2(C_2O_4)$bipy], [Ru terpy bipy Cl]ClO_4, [Ru chel $(acac)_2$], [Ru phen$_2$acac]ClO_4, [Ru py_2acac bipy]ClO_4, [Ru $py(H_2O)phen_2](ClO_4)_2$ [92], and $[Ru\ bipy_2(CN)_2]$ [97]. The bis(aniline) adduct of Ru(II) phthalocyanine is known[98]. The anti-bacterial activity of a number of Ru(II) complexes of 1,10-phenanthroline and its derivatives has been investigated[99].

The pentammine complex $[Ru(NH_3)_5H_2O]^{2+}$ reacts with gaseous N_2 in aqueous solution to yield $[Ru(NH_3)_5N_2]^{2+}$, in which the N_2 is bound end-on as is CO in carbonyls. NH_3, NH_2NH_2 and N_3^- have also been used as a source of the N_2 ligand[100]. This complex can be transformed into the dimeric ion $[(NH_3)_5Ru\text{–}N_2\text{–}Ru(NH_3)_5]^{4+}$; both complexes are more resistant to oxidation than Ru(II) ammines. Oxidation leads to quantitative release of N_2. The Ru(II) complexes are the only N_2 complexes which can be reduced with borohydride to produce NH_3. This makes them the closest known analogues of biological nitrogen fixation systems. Nitrogenase is probably a metallo-enzyme in which the metal atom is the active site; molecular N_2 complexes to the metal ion and is then reduced to NH_3 which leaves the complex so that more N_2 can coordinate[101]. The benzonitrile complex $[Ru(NH_3)_5(NCPh)]Br$ is analogous to the N_2 complex in that both contain the system Ru–N≡; the compound can be oxidized to the corresponding Ru(III) complex[102].

Phosphine, Arsine and Stibine Complexes

These are quite numerous; those which contain CO or H are discussed under Carbonyl Complexes (p. 1201) and Hydride Complexes (p. 1203). Monodentate ligands yield the

[92] F. P. Dwyer, H. A. Goodwin and E. C. Gyarfas, *Austral. J. Chem.* **16** (1963) 42, 544.
[93] F. G. Nasouri, M. W. Blackmore and R. J. Magee, *Austral. J. Chem.* **20** (1967) 1291.
[94] B. Bosnich and F. P. Dwyer, *Austral. J. Chem.* **19** (1966) 2229.
[95] K. Glen, W. Breuel and K. Rehm, *Z. anorg. Chem.* **235** (1938) 201, 211.
[96] C. F. Liu, N. C. Liu and J. C. Bailar, *Inorg. Chem.* **3** (1964) 1085; J. E. Fergusson and G. M. Harris, *J. Chem. Soc.* A, 1966, 1293.
[97] A. A. Schilt, *Inorg. Chem.* **3** (1964) 1323.
[98] I. M. Keen and B. W. Malerbi, *J. Inorg. Nucl. Chem.* **27** (1965) 1311.
[99] A. Shulman and F. P. Dwyer, *Chelating Agents and Metal Chelates* (F. P. Dwyer and D. P. Mellor, eds.), Academic Press, New York (1964), p 415.
[100] D. E. Harrison and H. Taube, *J. Am. Chem. Soc.* **89** (1967) 5706; J. Chatt and J. E. Fergusson, *Chem. Communs.* 1968, 126.
[101] A. D. Allen and F. Bottomley, *Progress in Coordination Chemistry* (M. Cais, ed.), Elsevier, Amsterdam (1968), p. 5; J. Chatt, J. E. Fergusson and R. L. Richards, *ibid.*, p. 40.
[102] P. C. Ford and R. E. Clarke, *Chem. Communs.* 1968, 1109.

complexes $[RuX_2(MR_3)_4]$ (X = Cl, Br; M = P, As) [103], the dimeric chloro bridged species $[Ru_2Cl_3(PR_3)_6]Cl$ [103], and the 5-coordinate compounds $RuCl_2(MPh_3)_3$ (M = P, Sb) [104]. The latter have a square-pyramidal configuration with the vacant sixth octahedral position blocked by a phenyl ring. The bidentate ligands $R_2PCH_2CH_2PR_2$ (R = Me, Et, Ph) and o-$C_6H_4(PPh_2)_2$ form *cis*- and *trans*-$RuCl_2(P\text{–}P)_2$ (P–P = diphosphine) [103], while o-$C_6H_4(AsMe_2)_2$ forms *trans*-$RuX_2(As\text{–}As)_2$ (As–As = diarsine) [105].

Nitrosyl Complexes

The RuNO group occurs in cationic, anionic, and neutral octahedral complexes and is exceptionally stable towards acid and oxidizing agents; its presence is indicated by a strong band in the infrared spectrum in the range 1930–1845 cm^{-1} [106]. The nitrosyl group is considered to act as the positively charged ligand NO^+—it is assumed that the neutral NO group donates an electron to Ru(III), thus yielding a Ru(II) complex containing NO^+. The short Ru–N distance, which has been found to vary from 1.70–2.07 Å depending on the complex, is consistent with the formulation of the bonding as $Ru{=}\overset{+}{N}{=}O$. The NO group is π-bonded and has a high *trans*-effect[107]. The reagents used to prepare nitrosyl complexes include HNO_3, KNO_2, NO_2 and NO. The colours of the complexes range from yellow through orange, red and brown to black.

The number of known nitrosyl complexes of Ru(II) exceeds a hundred; a complete list of the types of compounds and references is given by Griffith[108]. Only one NO group is found in these complexes; the associated ligands cover a wide range: charged ligands include Cl^-, Br^-, I^-, SCN^-, CN^-, NO_3^-, NO_2^-, OH^-, SO_4^{2-}, oxalate, acetylacetonate and dialkyl dithiocarbamate, while neutral ligands include H_2O, NH_3, py, en, bipy, phen, terpy, PR_3, AsR_3, SbR_3 and R_3PO. The dark red $K_2[RuNOCl_5]$ was prepared by Claus in 1847; it can be obtained by heating ruthenium with KOH and KNO_3 and dissolving the product in HCl. Similar complexes $K_2[RuNOX_5]$ (X = Br, I, SCN, CN) and the oxalato complexes $K_2[RuNO(C_2O_4)_2Cl]$ and $K_2[RuNO(C_2O_4)I_3]$ are known. The full range of chloro species from $[RuNOCl(H_2O)_4]^{2+}$ to $[RuNOCl_5]^{2-}$ has been characterized and the infrared spectra have been studied[109]. The main types of complex are $[RuNO(H_2O)_5]^{3+}$ [110], $[RuNO(NH_3)_5]^{3+}$ [111], $[RuNO(NH_3)_4X]^{2+}$ (X = Cl, Br, I, NO_3, NO_2) [112], $[RuNOCl_3L_2]$ (L = PR_3, AsR_3, SbR_3; 2L = diarsine, bipy, phen) [113] and $[RuNOX_3]_n$ [112].

In the compounds $[RuNONO_2L_2OH]$ the strength of the Ru–N bond decreases with increase in the donor properties of L: $H_2O < NH_3 <$ py $< Bu^n_3PO$ [114]. An X-ray structure determination on the diethyl dithiocarbamate complex $[RuNO(S_2CNEt_2)_3]$ showed that

[103] J. Chatt and R. G. Hayter, *J. Chem. Soc.* 1961, 896; 1963, 6017; J. Chatt, B. L. Shaw and A. E. Field, *J. Chem. Soc.* 1964, 3466.

[104] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.* **28** (1966) 945.

[105] R. S. Nyholm and G. J. Sutton, *J. Chem. Soc.* 1958, 567.

[106] D. M. Adams, *Metal–Ligand and Related Vibrations*, Arnold, London (1967).

[107] O. E. Zvjagintsev, N. M. Sinitsyn and V. N. Pitchkov, *Proc. VIIIth Int. Conf. Coord. Chem. Vienna*, Springer-Verlag (1964), p. 142.

[108] W. P. Griffith, *The Chemistry of the Rarer Platinum Metals*, Wiley Interscience, New York (1967).

[109] E. E. Mercer, W. M. Campbell and R. M. Wallace, *Inorg. Chem.* **3** (1964) 1018.

[110] R. M. Wallace, *J. Inorg. Nucl. Chem.* **20** (1961) 283.

[111] K. Gleu and I. Buddecker, *Z. anorg. allgem. Chem.* **268** (1952) 202.

[112] A. Joly, *Compt. rend.* **108** (1889) 854, **111** (1890) 964; A. Werner, *Ber.* **40** (1907) 2614.

[113] J. Chatt and B. L. Shaw, *J. Chem. Soc.* A, 1966, 1811; M. B. Fairy and R. J. Irving, *J. Chem. Soc.* A, 1966, 475.

[114] V. N. Pickov, A. E. Zvjagintsev and N. M. Sinitsyn, *Zh. Neorg. Khim.* **13** (1966) 2560.

the metal atom is not 7-coordinate but octahedral with one dithiocarbamate group, which is *cis* to the NO group, behaving as a unidentate ligand[115].

Carbonyl Complexes

Most of the carbonyl complexes of Ru(II) contain covalently bound halide; however, other negatively charged ligands such as dialkyl dithiocarbamate yield carbonyl complexes. Carbonyl chloride complexes are readily formed, usually by the action of CO, followed by the ligand, on alcoholic solutions of commercial $RuCl_3 \cdot 3H_2O$. In some cases the CO can be derived from formic acid: e.g. a 1:1 mixture of hydrochloric and formic acid reacts with Ru(III) chloride to give $[Ru(CO)_2Cl_2]_n$. A list of the types of carbonyl complexes is given in Table 8. The compounds are mostly yellow, although some are colourless, while others are orange or brown.

Compounds of the type $[Ru(CO)_2X_2]_n$ are polymeric with halogen bridges; the iodo complex reacts with a variety of ligands to give monomeric species $Ru(CO)_2I_2L_2$. The compound $Ru(CO)_4I_2$ has been shown to be *cis*, and *cis* and *trans* isomers of $Ru(CO)_2X_2(PR_3)_2$ have been prepared. Some carbonyl complexes containing Ru–M bonds (where M = Hg, Si or Sn) are known[72].

π-Complexes

In addition to CO other π-bonding ligands form complexes with Ru(II). Ruthenocene, $Ru(C_5H_5)_2$, can be prepared from Ru(III) chloride and sodium cyclopentadienide in tetrahydrofuran; it is pale yellow and melts at 200°. Its heats of fusion, vaporization and sublimation are 4.75, 12.9 and 17.6 kcal $mole^{-1}$ respectively[116]. Unlike ferrocene, ruthenocene has the cyclopentadienyl rings eclipsed and not staggered. Acetylruthenocenes and acylruthenocenes can be prepared by Friedel–Craft synthesis; diacetylruthenocene and dibenzoylruthenocene have the eclipsed configuration of ruthenocene. Trimethylsilylruthenocene, $C_5H_5RuC_5H_4SiMe_3$, undergoes acid-cleavage of the C–Si bond at a greater rate than the analogous osmium and iron compounds. The kinetics of the solvolysis of the α-ruthenocenyl ethyl acetate have been studied. The chemistry of ferrocene, ruthenocene and osmocene has been recently reviewed[116].

The cyclopentadienyl compounds $C_5H_5Ru(CO)_2X$ (X = Br, I) can be prepared by the action of halogen on $[C_5H_5Ru(CO)_2]_2$ [84]. The compounds $[C_5H_5Ru(CO)_2C_2H_4]^+$ and $C_5H_5Ru(CO)_2R$ (R = Me, Et) are also known[84,117]. The bis(indenyl) complex $Ru(C_9H_7)_2$ can be hydrogenated to bis(tetrahydroindenyl)ruthenium(II) $Ru(C_9H_{11})_2$. Spectroscopic studies show that in both complexes the five-membered ring is π-bonded to the metal atom[118]; the crystal structure of $Ru(C_9H_7)_2$ has been determined[119].

The yellow benzene and mesitylene complexes $[(C_6H_6)_2Ru](ClO_4)_2$ and $[(C_6H_3Me_3)_2Ru](ClO_4)_2$ can be made by Friedel–Crafts synthesis; the former, when treated with $LiAlH_4$, yields a mixture of dicyclohexadienylruthenium(II) $Ru(C_6H_7)_2$ and the isomeric Ru(0) complex $C_6H_6RuC_6H_8$ [120].

[115] A. Domenicano, A. Vaciago, L. Zambonelli, P. D. Loader and L. M. Venanzi, *Chem. Communs.* 1966, 476.

[116] M. Rosenblum, *Chemistry of the Iron Group Metallocenes*, Wiley, New York (1965).

[117] A. Davison, J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.* 1963, 1133.

[118] H. P. Fritz and C. G. Kreiter, *J. Organomet. Chem.* **4** (1965) 198; J. H. Osiecki, C. J. Hofmann and D. P. Hollis, *ibid.* **3** (1965) 107.

[119] N. C. Webb and R. E. Marsh, *Acta Cryst.* **22** (1967) 382.

[120] E. O. Fischer and R. Böttcher, *Z. anorg. allgem. Chem.* **291** (1957) 305; E. O. Fischer, C. Elschenbroich and C. G. Kreiter, *J. Organomet. Chem.* **7** (1967) 481.

TABLE 8. CARBONYL COMPLEXES OF RUTHENIUM(II)

Compound	References
$Ru(CO)_4X_2$ (X = Cl, I)	E. R. Corey, M. V. Evans and L. F. Dahl, *J. Inorg. Nucl. Chem.* **24** (1962) 926; L. Porri, M. C. Gallazzi, A. Colombo and G. Allegra, *Tetrahedron Letters* 1965, 4187.
$[Ru(CO)_2X_2]_n$ (X = Cl, Br, I, NO_2)	W. Manchot and E. König, *Ber.* **57** (1924) 2130; J. P. Candlin, K. K. Joshi and D. T. Thomson, *Chem. Ind. (London)* 1966, 1960; J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.* **87** (1965) 4008.
$[Ru(CO)_2Cl_4]^{2-}$	J. Halpern, B. R. James and A. L. W. Kemp, *J. Am. Chem. Soc.* **88** (1966) 5142.
$[Ru(CO)_2X_2(SnX_3)_2]^{2-}$ (X = Cl, Br)	T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.* **28** (1966) 945; J. V. Kingston, J. W. S. Jamieson and G. Wilkinson, *ibid.* **29** (1967) 133.
$Ru(CO)_2(R_2NCS)_2$	J. V. Kingston and G. Wilkinson, *J. Inorg. Nucl. Chem.* **28** (1966) 2709.
$RuCO(R_2NCS_2)_2$	J. P. Candlin *et al.*, *op. cit.*
$Ru(CO)_3I_2PPh_3$	*Idem.*, *ibid.*
$Ru(CO)_3IPMe_2$	R. J. Irving, *J. Chem. Soc.* 1956, 2879.
$Ru(CO)_2I_2L_2$ (L = NH_3, py, PPh_3, $AsMePh_2$)	
$Ru(CO)_2X_2(MPh_3)_2$ (X = Cl, Br, I; M = P, As, Sb)	R. J. Irving, *op. cit.*; T. A. Stephenson and G. Wilkinson, *op. cit.*
$Ru(CO)_2X_2L_2$ (X=Cl, I; L = py, β-pic, PR_3)	*Ibid.*
$RuCOX_2(PR_3)_3$ (X = Cl, Br, I, SCN)	J. Chatt, B. L. Shaw and A. E. Field, *J. Chem. Soc.* 1964, 3466; J. M. Jenkins, M. S. Lupin and B. L. Shaw, *J. Chem. Soc.* A, 1966, 1787.
$Ru(CO)_2X_2(PR_3)_3$ (X = Cl, Br, I)	J. M. Jenkins *et al.*, *op. cit.*
$[RuCO(S_2CNR_2)_2]_n$	J. V. Kingston and G. Wilkinson, *op. cit.*
$Ru(CO)_2X_2L_2$ (X = Cl, Br; L = $PhNH_2$; 2L = phen, bipy)	J. V. Kingston *et al.*, *op. cit.*
$Ru(CO)_2(o\text{-}SC_6H_4NH_2)$	*Ibid.*
$[Ru(CO)_2(SEt_2)_3SnCl_3]^+$	*Ibid.*
$[Ru(CO)_2X_2(SnX_3)_2]^{2-}$ (X = Cl, Br)	*Ibid.*
$[Ru(CO)_3(PPh_3)_2HgX]HgX_3$ (X = Br, I)	J. P. Collman and W. R. Roper, *Chem. Communs.* 1966, 244.
$C_5H_5Ru(CO)_2Br$	E. O. Fischer and J. Müller, *Ber.* **96** (1963) 3217.
RuCO diene Cl_2 (diene = C_7H_8, C_8H_{12})	S. D. Robinson and G. Wilkinson, *J. Chem. Soc.* A, 1966, 300.
$RuCOCl_2py_3$	*Ibid.*
$(Me_3Sn)_2Ru(CO)_4$	M. I. Bruce and F. G. A. Stone, *Angew. Chem.*, Int. Edn., **7** (1968) 427.
$Ru(CO)_2(PR_3)_2(MMe_3)_2$ (M = Si, Sn)	*Ibid.*

A number of diene complexes are known: $[C_8H_{12}RuCOCl_2]_2$ (C_8H_{12} = cyclo-octa-1,5-diene), $[C_8H_{12}RuX_2]_n$ (X = Cl, Br, I), $C_8H_{12}RuCl_2p\text{-}NH_2C_6H_4Me$, $[C_7H_8RuCl_2]_n$ (C_7H_8 = norbornadiene), $C_7H_8RuCl_2p\text{-}NH_2C_6H_4Me$ and $C_7H_8Ru(PPh_3)_2X_2$ (X = Cl, Br) [121].

[121] M. A. Bennett and G. Wilkinson, *Chem. Ind. (London)* 1959, 1516; R. G. Guy and B. L. Shaw, *Adv. Inorg. Chem. Radiochem.* **4** (1962) 77; S. D. Robinson and G. Wilkinson, *J. Chem. Soc.* A, 1966, 300.

Hydride Complexes

Hydride complexes of transition metals contain covalent M–H bonds which have little tendency to ionize or undergo hydrolysis. They are mostly of the type MH_xL_y (L = CO, X^-, cyclopentadienyl, PR_3). It is noteworthy that L must possess a high ligand field strength in order to stabilize the hydride complex of the metal which is in a low oxidation state—generally 2 for ruthenium. The hydride complexes are usually obtained by reduction or protonation of suitable complexes. The resonance of the hydrogen nucleus attached to a transition metal shows a very high positive chemical shift (τ-value) in the n.m.r. spectrum as compared to hydrogen atoms attached to non-transition elements. The infrared spectra show strong bands due to M–H stretching and bending modes in the regions 2250–1700 cm^{-1} and 850–660 cm^{-1} respectively, although in the carbonyl hydrides the bands are sometimes difficult to identify. The substitution of PPh_3 for CO increases markedly the stability of the hydrides in respect to temperature and oxidation. Transition metal hydrides have recently been reviewed[122].

TABLE 9. HYDRIDE COMPLEXES OF RUTHENIUM(II)

$H_2Ru(CO)_4$ [a]	
$H_2Ru_3(CO)_{12}$ [a]	
$H_2Ru_4(CO)_{13}$ [a]	
$H_4Ru_4(CO)_{12}$ [a]	
cis- and *trans*-$H_2Ru(P\text{–}P)_2$* [c]	
trans-$HRuX(P\text{–}P)_2$ [c]	(X = Cl, Br, I, SCN)
cis- and *trans*-$HRuR(P\text{–}P)_2$	(R = Me, Et, Ph)
$HRuX(CO)(PR_3)_3$ [b]	(X = Cl, Br, I; R = Ph, Et_2Ph)
$HRu(CO)_2(C_5H_5)$ [b]	
$HRuCl(PPh_3)_3$ [b]	
$[H\{Ru(CO)_2(C_5H_5)\}_2]^+$ [b]	
$H_2Ru(CO)_2(PR_3)_2$ [a]	(R = Et, Ph)

*(P–P) = diphosphine $R_2PCH_2CH_2PR_2$ or *o*-$C_6H_4(PEt_2)_2$.

[a] M. I. Bruce and F. G. A. Stone, *Angew. Chem.*, Int. Edn. 7 (1968) 427.

[b] J. Chatt, *Science* **160** (1968) 723.

[c] J. Chatt and R. G. Hayter, *J. Chem. Soc.* 1961, 2605; 1963, 6017.

A list of the hydride complexes of Ru(II) is given in Table 9. Although $H_2Fe(CO)_4$ has been known for a long time, the ruthenium analogue $H_2Ru(CO)_4$ has been reported only recently[68]. It is a very unstable colourless liquid which rapidly decomposes to a reddish-brown solid, probably $H_2Ru_3(CO)_{12}$, at temperatures above $-40°$. The hydride $H_2Ru(CO)_4$ exhibits a high field proton resonance at $\tau = 17.6$ in its n.m.r. spectrum and a Ru–H stretching frequency at 1980 cm^{-1}. It reacts with phosphines to give the complexes $H_2Ru(CO)_2(PR_3)_2$ (R = Et, Ph) which are more conveniently prepared by reduction of $Ru(CO)_2Cl_2(PR_3)_2$ with $LiAlH_4$. These hydrides undergo reaction with chlorinated solvents such as CCl_4 to give the halides $Ru(CO)_2Cl_2(PR_3)_2$ [72]. The polynuclear carbonyl hydride $H_4Ru_4(CO)_{12}$ can be prepared by the action of CO and hydrogen on carbonylated $RuCl_3$ solutions in the presence of silver powder[72].

[122] J. Chatt, *Science* **160** (1968) 723.

The cyclopentadienyl hydride complex $HRu(CO)_2(C_5H_5)$ can be obtained as a colourless liquid from the reaction of sodium borohydride with $(C_5H_5)Ru(CO)_2I$. Treatment of the hydride with sodium amalgam in tetrahydrofuran gives the sodium salt $Na[(C_5H_5)Ru(CO)_2]$, which reacts with alkyl iodide to yield the alkyl derivatives $(C_5H_5)Ru(CO)_2R$ (R = Me, Et) [117].

The hydrides $HRuCl(CO)(PR_3)_3$ were prepared by the reaction:

$$[Ru_2Cl_3(PR_3)_6]Cl + 2KOH + 2C_2H_5OH \rightarrow 2HRuCl(CO)(PR_3)_3 + 2CH_4 + 2KCl + 2H_2O$$

From n.m.r. and dipole moment studies it was concluded that the CO group is *trans* to chlorine[103]. *Trans*-$HRuX(P\text{–}P)_2$ can be prepared from *cis*- or *trans*-$RuX_2(P\text{–}P)_2$ by reaction with $LiAlH_4$. *Trans*-$HRuR(P\text{–}P)_2$ can be prepared from $RuClR(P\text{–}P)_2$ (R = Me, Et, Ph) by reduction with $LiAlH_4$ [103]. *Cis*-$HRuR(P\text{–}P)_2$ (R = Ph, 2-naphthyl) can be obtained from *cis*- or *trans*-$RuCl_2(P\text{–}P)_2$ by reaction with arene ions in tetrahydrofuran solution[69].

2.8. COMPLEXES OF RUTHENIUM(III)

Trivalent ruthenium forms a large number of complexes which are more numerous and stable than those formed by Os(III). Indeed Ru(III) resembles Rh(III) and Ir(III) more than either Os(III) or Fe(III). The coordination number is nearly always 6, and where it appears to be otherwise no structural data are available. All complexes of Ru(III) are low-spin—as are those of Ru(II)—and with the exception of K_2RuCl_5 (see below) have room-temperature magnetic moments within the range 1.8–2.2 BM. On the assumption of approximately octahedral symmetry of the ligand field, the electronic configuration is $(t_{2g})^5$.

Ligands found in Rh(III) complexes include halide, hydroxide, carboxylate, sulphite, alkyl sulphide, ammonia, amines, nitrogen heterocycles, and other nitrogen ligands, tertiary phosphines and arsines, CO, and cyclopentadienyl. One fluoro complex, $[RuF_6]^{3-}$, and several chloro complexes are known; the bromo complexes are not well characterized, while iodo and cyano complexes are unknown, although iodide can occur as a ligand in ammine or phosphine complexes. No salts of the aqua-ion $[Ru(H_2O)_6]^{3+}$ have been isolated, but evidence has been obtained for its existence in reduced solutions of Ru(IV) perchlorate and in oxidized solutions of $[Ru(H_2O)_6]^{2+}$ [87, 123].

Halide and Cyanide Complexes

The fluoro complex $K_3[RuF_6]$ can be prepared by treatment of $RuCl_3$ with molten KHF_2; it is insoluble in water but dissolves in dilute acid, apparently without decomposition. The Ru(III) chloro-aquo system has been studied and the following species have been identified in solution: $[RuCl(H_2O)_5]^{2+}$, *cis*- and *trans*-$[RuCl_2(H_2O)_4]^+$, $[RuCl_3(H_2O)_3]$, $[RuCl_4(H_2O)_2]^-$, $[RuCl_5H_2O]^{2-}$ and $[RuCl_6]^{3-}$ [124]. Complexes have been isolated with Cl:Ru ratio of 4, 5, 6 or 7. The compound $K_2[RuCl_5H_2O]$ can be obtained as red crystals by the reduction with alcohol of a solution of RuO_4 in HCl [124]. $K_2[RuCl_6]$ can be made by treating $K_2[RuCl_5H_2O]$ with hydrogen chloride; its electronic spectrum has been discussed[125]. Compounds of the type $[NR_4]_2[RuCl_5]$ and $[NR_4]_4[RuCl_7]$ have been

[123] D. K. Atwood and T. de Vries, *J. Am. Chem. Soc.* **83** (1961) 1509.

[124] R. E. Connick, in *Advances in the Chemistry of the Coordination Compounds* (S. Kirschner, ed.), Macmillan, New York (1961), p. 15; D. Connick and D. A. Fine, *J. Am. Chem. Soc.* **83** (1961) 3414; **82** (1960) 4187.

[125] C. K. Jørgensen, *Mol. Phys.* **2** (1959) 309.

reported[126]. The former probably contains a dimeric chloro-bridged anion and the latter may be $[NR_4]_3[RuCl_6]\cdot NR_4Cl$, but the structures are not known. $K_2[RuCl_5]$ can be obtained as brown crystals when $K_2[RuCl_5H_2O]$ is heated at 200°. The magnetic susceptibility ranges from 1.14 at 80°K to 1.64 BM at 300°K; this suggests some metal–metal interaction and the anion is probably dimeric with chloro-bridges[127]. It slowly aquates to give $K_2[RuCl_5H_2O]$ and adducts are known with ammonia and pyridine. The tetrachloro complexes $M_2[RuCl_4(H_2O)_2]$ (M = NH_4, Rb, Cs) can be prepared by treatment of RuO_4 with HCl and $SnCl_2$, followed by the alkali halide.

The bromo complexes $K_2[RuBr_5H_2O]$, $K_2[RuBr_5]$, $[NR_4]_2[RuBr_5]$, $[NR_4]_4[RuBr_7]$ and $NH_4[RuBr_4(H_2O)_2]$ have been reported[126] but no iodo complexes are known.

The complex $[Ru(CN)_6]^{3-}$, analogous to ferricyanide, is not known, although $Ru(CN)_3$, $Ru_2(CN)_5H_2O$ and $Ru(CN)_3(NH_3)_2H_2O$ have been described[128].

Complexes of Oxygen Ligands

Tris complexes are formed with acetylacetone (acac), benzoylacetone, dibenzoylmethane and other β-diketones. The p.m.r. spectrum of $Ru(acac)_3$ indicates that ligand to metal charge transfer predominates over M → L transfer[129]. Some complex oligomeric species, which probably contain Ru(II) and Ru(III), are formed with carboxylic acids[130]. Ethylenediaminetetra-acetic acid (H_4EDTA) gives the complexes $Ru(HEDTA)H_2O$ and $RuCl(H_2EDTA)H_2O$. The oxalato species $[Ru(C_2O_4)_3]^{3-}$, $[Ru(C_2O_4)_2Cl_2]^{3-}$ and *cis*- and *trans*-$[Ru(C_2O_4)_2py_2]^-$ are known. Attempts to resolve the potassium salt $K_3[Ru(C_2O_4)_3]$ were unsuccessful, and it has been suggested that rapid racemization via 7- or 8-coordinated aqua-species may occur[131].

Sulphito Complexes

Sulphite ion coordinates to Ru(III), but the compounds reported—e.g. $Ru_2(SO_3)_3$ and $K_2[Ru_2(OH)_2(SO_3)_3]\cdot 3H_2O$—have not been well characterized.

Complexes of Nitrogen Ligands

Ammines are formed with from 6 to 3 NH_3 groups. The colourless hexammine $[Ru(NH_3)_6]^{3+}$ is best prepared by oxidation of $[Ru(NH_3)_6]^{2+}$; it is stable to acid but not to alkali. The pentammines $[Ru(NH_3)_5H_2O]^{3+}$, $[Ru(NH_3)_5X]^{2+}$ (X = Cl, Br, I, NO_3, OH), and $[Ru(NH_3)_5S_2O_3]^+$, the tetrammines *cis*- and *trans*-$[Ru(NH_3)_4X_2]^+$ and $[Ru(NH_3)_4(OH)X]^+$ and the triammines $[Ru(NH_3)_3X_3]$ (X = Cl, Br, I) are known[132,108]. Treatment of the hexammine with boiling HCl converts it to the yellow pentammine $[Ru(NH_3)_5Cl]Cl_2$, which, when treated with NH_4OH followed by careful acidification, yields yellow $[Ru(NH_3)_5H_2O]Cl_3$. The base hydrolysis of $[Ru(NH_3)_5Cl]^+$ is 10^6 times faster than acid hydrolysis, as is the case for the analogous Co(III) complex but not for Cr(III) and Rh(III) [133].

[126] A. Gutbier and F. Krauss, *J. prakt. Chem.* **91** (2) (1915) 103.
[127] A. Earnshaw, B. N. Figgis, J. Lewis and R. S. Nyholm, *Nature* **179** (1957) 1121.
[128] F. Krauss and G. Schrader, *Z. anorg. allgem. Chem.* **173** (1928) 63.
[129] D. R. Eaton, *J. Am. Chem. Soc.* **87** (1965) 3097.
[130] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.* **28** (1966) 2285.
[131] F. P. Dwyer and A. M. Sargeson, *J. Phys. Chem.* **60** (1956) 1331.
[132] N. V. Sidgwick, *The Chemical Elements and Their Compounds*, Clarendon Press, Oxford (1950), pp. 1468, 1479.
[133] J. A. Broomhead, F. Basolo and R. G. Pearson, *Inorg. Chem.* **3** (1964) 826.

The aerial oxidation of $[Ru(NH_3)_6]Cl_3$ gives rise to an intensely coloured solution, first reported by Joly in 1892 and known as "ruthenium red". Weak oxidizing agents render the acidified solution yellow, but the red colour is restored by strong reducing agents such as Ti(III). A diamagnetic red complex has been isolated and assigned the structure[134]:

$$[(NH_3)_5Ru^{III}\text{–}O\text{–}Ru^{IV}(NH_3)_4\text{–}O\text{–}Ru^{III}(NH_3)_5]^{6+}$$

Oxidation of ruthenium red with Ce(IV) yields a paramagnetic brown complex, assigned the structure[134]:

$$[(NH_3)_5Ru^{IV}\text{–}O\text{–}Ru^{III}(NH_3)_4\text{–}O\text{–}Ru^{IV}(NH_3)_5]^{7+}$$

The following amine and pyridine complexes have been reported: $[Ru(EtNH_2)_4Cl_2]Cl$, $[Ru\ en_2Cl_2]Cl$, $[Ru\ en_2(OH)X]X$ (X = Cl, I), $[Ru\ py_4Cl_2]Cl$, $[Ru\ py_4(OH)Cl]Cl$, $[Ru\ py_3Cl_3]$ [135]. A number of complexes of 2,2′-bipyridyl and 1,10-phenanthroline are known, viz.[92]: $[Ru(phen)_3]Cl_3$, $[Ru(chel)_2Cl_2]ClO_4$ (chel = phen, bipy), K[Ru chel X_4], [Ru chel Cl_2 acac], [Ru bipy $(acac)_2$]Cl, [Ru bipy $Cl_3(H_2O)$] and [Ru bipy Cl terpy].

Excess 1,2-dicyanobenzene reacts with $RuCl_3$ to yield the phthalocyanine complex $PcRuClC_6H_4(CN)_2$ from which $PcRuClpy_2$ can be obtained ($PcH_2 = C_{32}H_{18}N_8$) [98].

No nitro or nitrosyl complexes of Ru(III) are known: the complex originally reported as $K_2[Ru^{III}(NO_2)_5]$ has been shown to be $K_2[Ru^{II}NO(OH)(NO_2)_4]$.

Phosphine and Arsine Complexes

Unidentate phosphines and arsines form the brown complexes $RuX_3(MR_3)_3$ (X = Cl, Br; M = P, As) [103b, 136] and the green complex $[RuCl_4(PR_3)_2]^-$ [130]. The diarsine $o\text{-}C_6H_4AsMe_2$ (As–As) yields the green complexes *trans*-$[Ru(As\text{–}As)_2X_2]^+$ (X = Cl, Br, I), $[Ru(As\text{–}As)_2X_2][Ru(As\text{–}As)X_4]$ (X = Cl, Br) and $[Ru(As\text{–}As)_3][Ru(As\text{–}As)I_4]$ [105]. The binuclear chloro-bridged complexes $Ru_2Cl_6(PBu^n_3)_4$ and $Ru_2Cl_5(PBu^n_3)_4$ have been reported; the latter contains Ru(II) and Ru(III) [137].

Carbonyl Complexes

Only a few carbonyl complexes of Ru(III) have been reported: these include $Ru(CO)Br_3(PPh_3)_2$ [104], $[Ru(CO)_2\{(PhCH_2)_2NCS_2\}_2]Cl$ [138] and $[Ru(CO)Cl_5]^{2-}$. Solutions of $[RuCl_5(H_2O)]^{2-}$ absorb CO to give $[Ru(CO)Cl_5]^{2-}$, which can be reduced to $[Ru(CO)Cl_4(H_2O)]^{2-}$; the latter acts as a catalyst for the hydration of acetylene[139].

π-Complexes

Ruthenocene can be oxidized anodically to yield the pale yellow $[Ru(C_5H_5)_2]X$ (X = I, ClO_4) [116].

[134] J. M. Fletcher, B. F. Greenfield, C. J. Hardy, D. Scargill and J. L. Woodhead, *J. Chem. Soc.* 1961, 2000.

[135] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.* 4 (1963) 43; J. Soucek, *Collection Czech. Chem. Communs.* 27 (1962) 960; J. A. Broomhead and L. A. P. Kane-Maguire, *J. Chem. Soc.* A, 1967, 546.

[136] F. P. Dwyer, J. E. Humpoletz and R. S. Nyholm, *J. Proc. Roy. Soc. NS Wales* 80 (1946) 217.

[137] J. K. Nicholson, *Angew. Chem.* 79 (1967) 273.

[138] J. V. Kingston and G. Wilkinson, *J. Inorg. Nucl. Chem.* 28 (1967) 2709.

[139] J. Halpern, J. F. Harrod and B. R. James, *J. Am. Chem. Soc.* 88 (1966) 5150.

2.9. COMPLEXES OF RUTHENIUM(IV)

Quadrivalent ruthenium forms relatively few complexes none of which is cationic. The most important are with halide ion, but a few complexes are known with oxygen donors and nitrogen heterocycles. As might be expected, ligands which are effective in stabilizing low oxidation states—viz. phosphines, arsines and CO—do not appear to form complexes with Ru(IV).

The complexes are octahedral and have room-temperature moments in the range 2.7–3.0 BM which is normal for the $(t_{2g})^4$ configuration. However, at lower temperatures the moments decrease as the square root of the absolute temperature. The values of μ_{eff} for K_2RuX_6 (X = F, Cl, Br) are ~2.85 BM at room temperature but fall to ~0.5 BM at 80°K [140]. This behaviour is attributed to the relatively high value of the spin–orbit coupling constant for Ru(IV); the value of the spin–orbit coupling constant is much greater for Os(IV) which displays abnormally low magnetic moments (1.2–1.7 BM) at room temperature.

Halide Complexes

These are of the type $[RuX_6]^{2-}$ (X = F, Cl, Br) and $[Ru_2OX_{10}]^{4-}$ (X = Cl, Br); no iodo complexes are known. The yellow fluoro complex $K_2[RuF_6]$ has been obtained by treating $K[RuF_6]$ with water[141]. It is hydrolysed slowly in cold but rapidly in hot water to hydrated RuO_2. The dark brown chloro complex $K_2[RuCl_6]$ can be prepared by fusing ruthenium powder with potassium chlorate and adding potassium chloride to the leached melt. It is isomorphous with the corresponding Os, Ir, Pd and Pt salts. The caesium salt forms purple crystals which are almost insoluble in water. The potassium salt gives a yellow solution which soon darkens due to hydrolysis; the electronic spectrum of $[RuCl_6]^{2-}$ has been discussed[125]. The bromo complex $K_2[RuBr_6]$ can be prepared by oxidation with bromine of $K_2[RuBr_5H_2O]$. It forms black crystals and is more readily hydrolysed than the chloro complex.

The deep red complex $K_4[Cl_5Ru–O–RuCl_5]$, which was formerly thought to be $K_2[RuCl_5OH]$, can be obtained by the action of HCl on RuO_4 or by the reduction of K_2RuO_4 with alcohol in the presence of HCl. The compound is soluble in hot water to give a reddish-brown solution which slowly decomposes yielding a black residue. If it is dissolved in concentrated HCl the hexachloride K_2RuCl_6 crystallizes out. X-ray structure analysis showed the compound to be binuclear with a linear Ru–O–Ru bridge. The diamagnetism, which was difficult to account for since Ru(IV), is a d^4 ion, has been explained on the basis of a molecular orbital interpretation of the bonding: three-centred molecular orbitals are formed from the d_{xz} orbitals on each ruthenium atom and the p_z orbital on the oxygen atom; similarly the d_{yz} orbitals interact with the p_y orbital of the oxygen, and there are no unpaired electrons[142]. The black bromo complex $K_4[Ru_2OBr_{10}]$, which is doubtless similar, can be prepared from $RuBr_4$ and KBr in aqueous solution.

The Ru(IV)–Cl system in aqueous solution is complicated; when chloride ions are added to Ru(IV) perchlorate in dilute acid solution, the following colour changes are observed: reddish → yellow → violet → yellow. Various species have been postulated to account for these colour changes; however, there is some doubt as to the exact nature of the species present.

[140] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.* **6** (1965) 37.
[141] M. A. Hepworth, R. D. Peacock and P. L. Robinson, *J. Chem. Soc.* 1954, 1197.
[142] J. Dunnitz and L. E. Orgel, *J. Chem. Soc.* 1953, 2594.

Complexes of Oxygen Ligands

Strontium and barium ruthenites $MRuO_3$ can be prepared by heating ruthenium metal with the alkaline earth carbonate. In $BaRuO_3$ the ruthenium atoms have six oxygen atoms arranged octahedrally and the Ru–Ru distance is quite short (2.55 Å) [143].

There is some evidence for the existence of the hexaqua ion $[Ru(H_2O)_6]^{4+}$ in solutions of Ru(IV) perchlorate obtained by dissolving RuO_4 in $HClO_4$ and reducing the solution with H_2O_2. However, it is readily converted into hydrolysed species such as $[RuO\ aq]^{2+}$. The black oxalato complex $K_2[Ru(C_2O_4)_3]$ has been prepared by oxidation of $K_3[Ru(C_2O_4)_3]$ with H_2O_2. A bright red solution of Ru(IV) sulphate can be obtained by treating $BaRuO_3$ with H_2SO_4; it is almost certainly complex but its structure is unknown.

Complexes of Nitrogen Ligands

No ammine complexes have been definitely established but the following complexes are known with nitrogen heterocycles: [Ru py_2 Cl_4] (yellow), [Ru bipy Cl_4] (purple) and [Ru phen Cl_4] (purple)[92].

2.10. COMPLEXES OF RUTHENIUM(V)

The only definite complexes of quinquevalent ruthenium are the salts of $[RuF_6]^-$. The potassium compound $K[RuF_6]$ is made by the action of BrF_3 and Br_2 on $RuBr_4$ in the presence of KBr [141]. The fluororuthenates(V) are decomposed by water to $[RuF_6]^{2-}$ with the liberation of oxygen. The magnetic moments of $K[RuF_6]$ and $Cs[RuF_6]$ are 3.5 and 3.6 BM, respectively, and are independent of temperature[140].

2.11. COMPLEXES OF RUTHENIUM(VI)

Potassium ruthenate, K_2RuO_4, is made by fusing ruthenium with KOH and KNO_3. It forms hygroscopic black crystals with a green lustre which are soluble in water to give a deep orange solution. The $[RuO_4]^{2-}$ ion is unstable in neutral or acid solution but is moderately stable to alkali; it is reduced by organic compounds. The compound is paramagnetic with two unpaired electrons. Other alkali and alkaline earth salts are known. When K_2RuO_4 is treated with ammonia, a substance is obtained with the composition of $(NH_4)_2RuO_4$, but its properties are quite different from those of the other ruthenates. It has been suggested that its structure is $[RuO_2(NH_3)_2(OH)_2]$. A similar compound $[Et_3NH]_2RuO_4$ is obtained with ethylamine[132].

The action of Cl_2 and HCl on $RuCl_4$ yields the acid $H_2[RuO_2Cl_4]\cdot 3H_2O$ which forms brown hygroscopic crystals very soluble in water and alcohol. The compound is hydrolysed in dilute solution, while concentrated HCl converts it to H_2RuCl_6. The caesium salt $Cs_2[RuO_2Cl_4]$ can be prepared by adding CsCl to a solution of RuO_4 in HCl. It forms deep reddish-purple crystals which are readily hydrolysed. The complex is diamagnetic, which is surprising since Ru(VI) is a d^2 ion. Infrared evidence suggests that the oxo groups are *trans*. The rubidium salt is similar.

[143] P. C. Donohue, L. Katz and R. Ward, *Inorg. Chem.* 4 (1965) 306.

2.12. COMPLEXES OF RUTHENIUM(VII)

Septavalent ruthenium occurs only in the perruthenates which resemble the permanganates and the perrhenates. Potassium perruthenate, $KRuO_4$, is the primary product of the fusion of ruthenium with KNO_3 and an excess of KOH. It can be prepared by passing chlorine into a concentrated alkaline solution of $KRuO_4$ until the orange solution turns green. It can also be obtained by collecting RuO_4 in ice cold 1 M KOH. The compound forms black crystals which are stable when dry. It is isomorphous with $KOsO_4$ and KIO_4 but not $KMnO_4$. The yellowish-green solutions of RuO_4^- are reduced by alkali to RuO_4^{2-}. The electronic spectrum has been assigned[144].

3. OSMIUM

3.1. GENERAL CHEMISTRY

Osmium resembles ruthenium in its chemistry, particularly in regard to the number of oxidation states; as is to be expected, the higher valency states become more stable with osmium. In its higher oxidation states osmium tends to resemble rhenium more than ruthenium.

Osmium is a bluish-white metal with a high specific gravity (22.61) which is exceeded only by that of iridium (22.65). The metal is easily oxidized to the volatile tetroxide OsO_4. The ease of oxidation depends on the state of division: the finely powdered metal is slowly oxidized by air at room temperature, since a faint smell of the tetroxide can be detected but in massive form the metal is not attacked by air below 400°. It is attacked by fluorine and chlorine above 100° but is unaffected by mineral acids, including aqua regia. It is best dissolved by alkaline oxidizing fusion: with sodium hydroxide and sodium peroxide or potassium chlorate. Potassium osmate $K_2[OsO_2(OH)_4]$, which is a useful starting material for the preparation of osmium complexes, is best prepared by reduction with alcohol of potassium perosmate $K_2[OsO_4(OH)_2]$, which can be obtained by treating OsO_4 with cold KOH [145]. Ammonium hexachloroosmate(IV), $(NH_4)_2[OsCl_6]$, can be prepared by dissolving OsO_4 in concentrated HCl and reducing the solution with $FeCl_2$ [146].

The electrode potentials for osmium are given in Table 10. Osmium, like ruthenium, displays ten oxidation states; these are listed in Table 11. Simple aqua-ions do not appear to be formed by osmium in any of its oxidation states. The octavalent state is more stable than that of ruthenium; it occurs in the tetroxide OsO_4, the perosmate $[OsO_4(OH)_2]^{2-}$, the difluoroperosmate $[OsO_4F_2]^{2-}$ and the osmiamate $[OsO_3N]^-$. It is significant that all these compounds contain Os=O bonds. The septavalent state is represented by OsF_7, $OsOF_5$ and $[OsO_5]^{3-}$. Osmium(VI) occurs in the hexafluoride OsF_6, potassium osmate $K_2[OsO_2(OH)_4]$ and in a large number of oxo species, e.g. $[OsO_2Cl_4]^{2-}$ and $[OsO_2(NH_3)_4]^{2+}$. Osmium(V), like Ru(V), is a rare oxidation state, and the only well established compounds are OsF_5 and $K[OsF_6]$. The quadrivalent state is the most common for osmium and occurs in the oxide OsO_2, the halides OsX_4 (X = F, Cl, Br) and the hexahalogenoosmates(IV) $[OsX_6]^{2-}$ (X = F, Cl, Br, I); the latter are among the most important osmium compounds. Complexes of Os(III) are less numerous than those of Ru(III), but complexes of nitrogen

[144] A. Viste and H. B. Gray, *Inorg. Chem.* 3 (1964) 1113.
[145] E. Fritzmann and L. Tchugaev, *Z. anorg. allgem. Chem.* **172** (1938) 213.
[146] F. P. Dwyer and J. W. Hogarth, *Inorg. Syntheses*, McGraw-Hill, New York (1957), Vol. 5, p. 206.

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Osmium is a bluish-white metal with a high specific gravity (22.61) which is exceeded only by that of iridium (22.65). The metal is easily oxidized to the volatile tetroxide OsO_4. The ease of oxidation depends on the state of division: the finely powdered metal is slowly oxidized by air at room temperature, since a faint smell of the tetroxide can be detected but in massive form the metal is not attacked by air below 400°. It is attacked by fluorine and chlorine above 100° but is unaffected by mineral acids, including aqua regia. It is best dissolved by alkaline oxidizing fusion: with sodium hydroxide and sodium peroxide or potassium chlorate. Potassium osmate $K_2[OsO_2(OH)_4]$, which is a useful starting material for the preparation of osmium complexes, is best prepared by reduction with alcohol of potassium perosmate $K_2[OsO_4(OH)_2]$, which can be obtained by treating OsO_4 with cold KOH [145]. Ammonium hexachloroosmate(IV), $(NH_4)_2[OsCl_6]$, can be prepared by dissolving OsO_4 in concentrated HCl and reducing the solution with $FeCl_2$ [146].

The electrode potentials for osmium are given in Table 10. Osmium, like ruthenium, displays ten oxidation states; these are listed in Table 11. Simple aqua-ions do not appear to be formed by osmium in any of its oxidation states. The octavalent state is more stable than that of ruthenium; it occurs in the tetroxide OsO_4, the perosmate $[OsO_4(OH)_2]^{2-}$, the difluoroperosmate $[OsO_4F_2]^{2-}$ and the osmiamate $[OsO_3N]^-$. It is significant that all these compounds contain Os=O bonds. The septavalent state is represented by OsF_7, $OsOF_5$ and $[OsO_5]^{3-}$. Osmium(VI) occurs in the hexafluoride OsF_6, potassium osmate $K_2[OsO_2(OH)_4]$ and in a large number of oxo species, e.g. $[OsO_2Cl_4]^{2-}$ and $[OsO_2(NH_3)_4]^{2+}$. Osmium(V), like Ru(V), is a rare oxidation state, and the only well established compounds are OsF_5 and $K[OsF_6]$. The quadrivalent state is the most common for osmium and occurs in the oxide OsO_2, the halides OsX_4 (X = F, Cl, Br) and the hexahalogenoosmates(IV) $[OsX_6]^{2-}$ (X = F, Cl, Br, I); the latter are among the most important osmium compounds. Complexes of Os(III) are less numerous than those of Ru(III), but complexes of nitrogen

[144] A. Viste and H. B. Gray, *Inorg. Chem.* 3 (1964) 1113.
[145] E. Fritzmann and L. Tchugaev, *Z. anorg. allgem. Chem.* **172** (1938) 213.
[146] F. P. Dwyer and J. W. Hogarth, *Inorg. Syntheses*, McGraw-Hill, New York (1957), Vol. 5, p. 206.

TABLE 10. ELECTRODE POTENTIALS FOR OSMIUM [a, b]

Reaction	Potential (V)
$OsCl_6^{3-} + 3e = Os + 6Cl^-$	0.71
$OsCl_6^{2-} + e = OsCl_6^{3-}$	0.85
$OsO_4^{2-} + 8H^+ + 6e = Os + 4H_2O$	0.99
$OsO_4^{2-} + 4H^+ + 2e = OsO_2 + 2H_2O$	1.61
$HOsO_5^- + 9H^+, + 8e = Os + 5H_2O$	0.85
$HOsO_5^- + H^+ + 2e = OsO_4^{2-} + H_2O$	0.71
$OsO_{4(g)} + 6Cl^- + 8H^+ + 4e = OsCl_6^{2-} + 4H_2O$	1.0
$OsO_{4(g)} + 2e = OsO_4^{2-}$	0.46

[a] W. M. Latimer, *Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, 2nd edn., Prentice-Hall, Englewood Cliffs, New Jersey (1952), p. 202.

[b] T. J. Walsh and E. A. Hausman, The Platinum Metals, in *Treatise on Analytical Chemistry*, Part II, Vol. 8 (I. M. Kolthoff and P. J. Elving, eds.), Wiley Interscience, New York (1963), p. 397.

TABLE 11. OXIDATION STATES OF OSMIUM

Oxidation state	Examples
Os^{-II}	$[Os(CO)_4]^{2-}$
Os^0	$Os(CO)_5$, $Os_3(CO)_{12}$, $Os(CO)_3(PPh_3)_2$
Os^I	$[Os(CO)_4Br]_2$, $Os(C_5H_5)(CO)_2Br$
Os^{II}	$[Os(phen)_3]^{2+}$, $[Os(CN)_6]^{4-}$, $Os(CO)_4Cl_2$, $[HOsCl(CO)(PR_3)_3]$, $[HOsCl(P-P)_2]$ [a]
Os^{III}	$[Os(bipy)_3]^{3+}$, $[OsCl_6]^{3-}$, $Os(PR_3)_3X_3$
Os^{IV}	[Os bipy Cl_4], $[OsCl_6]^{2-}$, $[Os(As-As)_2X_2]^{2+}$ [b]
Os^V	OsF_5, $[OsF_6]^-$
Os^{VI}	OsF_6, $OsOCl_4$, $[OsO_2(OH)_4]^{2-}$, $[OsO_2Cl_4]^{2-}$
Os^{VII}	OsF_7, $OsOF_5$
Os^{VIII}	OsO_4, OsO_3F_2, $[OsO_4(OH)_2]^{2-}$, $[OsO_3N]^-$

[a] (P–P) = diphosphine $R_2PCH_2CH_2PR_2$.

[b] (As–As) = diarsine o-$C_6H_4AsMe_2$.

ligands—e.g. $[Os(NH_3)_6]^{3+}$ and $[Os(bipy)_3]^{3+}$—and with phosphines and arsines are probably the most important. Osmium(II) complexes are octahedral and diamagnetic with the rather stable $(t_{2g})^6$ configuration and are usually kinetically inert. The bivalent state occurs in cationic species such as $[Os(phen)_3]^{2+}$ and anionic species such as $[Os(CN)_6]^{4-}$. A large number of phosphine, arsine and carbonyl complexes occur; hydrido complexes containing phosphines or CO groups are also known. Osmium(I) is represented by the very stable carbonyl halides $[Os(CO)_4X]_2$ and a cyclopentadienyl complex $[Os(C_5H_5)(CO)_2]_2$. Osmium(0) occurs only in carbonyls and Os(−II) in the carbonyl anion $[Os(CO)_4]^{2-}$.

Thermodynamic data for osmium and some of its compounds are given in Table 12.

TABLE 12. THERMODYNAMIC DATA ON OSMIUM AND ITS COMPOUNDS [a]

Substance	State	$\Delta H°$	$\Delta F°$	$S°$
Os	g	174	163	45.97
Os	c	0	0	7.8
OsO_4	g	−79.9	−67.9	65.6
OsO_4 (white)	c	−91.7	−70.5	34.7
OsO_4 (yellow)	c	−93.4	−70.7	29.7
OsO_4	aq		−68.6	
OsS_2	c	−35		
H_2OsO_5	aq	−54.96	−37.60	−2.5

[a] US Bureau of Standards Circular 500, *Selected Values of Thermodynamic Properties* (1952).

Magnetochemistry

Ions of the first transition series usually have magnetic moments close to the "spin-only" value and hence the moment gives an indication of the number of unpaired electrons, which in turn often indicates the oxidation state and, in some cases, the stereochemistry. For ions of the second and third transition series this is not always so, since these ions tend to be "spin-paired" so that if there is an odd number of electrons there may only be one unpaired electron and if there is an even number of electrons, the compounds are often diamagnetic. Moreover, the observed magnetic moment is often less than that calculated by means of the "spin-only" formula. The reasons for this behaviour are as follows. Firstly, the 4*d* and 5*d* orbitals are larger than the 3*d* orbitals, so that there is less interelectronic repulsion between two electrons occupying the same orbital. Secondly, the ligand-field splittings for 4*d* orbitals are up to 50% and for 5*d* orbitals up to 70% greater than for 3*d* orbitals with the same ligand. Thirdly, the heavier ions have high values for the spin–orbit coupling constant (λ). When λ is much greater than kT, the magnetic moment may be well below the "spin-only" value even at room temperature. The d^4 ions Cr(II) and Mn(III) have values of λ of approximately 90 and 170 cm^{-1} respectively; these values are comparable to kT at room temperature ($\sim 200\ cm^{-1}$). Consequently, at room temperature low-spin octahedral Cr(II) and Mn(III) lie on the flat portion of the Kotani curve (μ vs. $-kT/\lambda$), and their moments are ~ 3.6 BM, due to the presence of two unpaired electrons, which give rise to a moment of 2.83 BM plus a fairly large orbital contribution which is to be expected for the spin-paired $(t_{2g})^4$ configuration. On the other hand, Os(IV) has a very high value for λ ($\sim 3600\ cm^{-1}$), and even at room temperature kT/λ is quite small so that Os(IV) falls on the steep part of the Kotani curve and a moment of about 1.2 BM is to be expected. The moments of Os(IV) complexes at room temperature lie in the range 1.2–1.7 BM and are temperature-dependent. The value of λ for Ru(IV) is 800 cm^{-1}, and Ru(IV) complexes have practically normal moments (2.7–2.9 BM) at room temperature. Osmium(IV) moments decrease as the square root of the absolute temperature. In the case of low-spin d^5 ions, the moments should be temperature-independent, except for very low values of kT/λ, and even then the temperature-dependence is only

TABLE 13. MAGNETIC MOMENTS OF OSMIUM COMPLEXES

Oxidation state	Electron configuration	Complex	μ (BM) at room temperature	Comment
Os(VII)	t_{2g}^1	OsF_7	1.08 (195°K)	$\chi \propto T^{-1}$; μ constant with T
Os(VI)	t_{2g}^2	OsF_6	1.50	$\chi \propto (T+\theta)^{-1}$; μ fairly constant with T
		$OsOCl_4$	diam.	
		$K_2[OsO_4]$	diam.	
		$Cs_2[OsO_4]$	diam.	
		$K_2[OsNCl_5]$	diam.	
		$K_2[OsO_3(NO_2)_2]\cdot 3H_2O$	diam.	
Os(V)	t_{2g}^3	$[OsF_5]_4$	2.06	μ falls with decrease in T
		$Na[OsF_6]$	3.05	$\chi \propto T^{-1}$; μ constant with T
		$K[OsF_6]$	3.34	$\chi \propto T^{-1}$; μ constant with T
		$Cs[OsF_6]$	3.23	$\chi \propto T^{-1}$; μ constant with T
Os(IV)	t_{2g}^4	$K_2[OsF_6]$	1.31	$\mu \propto T^{\frac{1}{2}}$
		$Cs_2[OsF_6]$	1.50	$\mu \propto T^{\frac{1}{2}}$
		$K_2[OsCl_6]$	1.51	$\mu \propto T^{\frac{1}{2}}$
		$Cs_2[OsCl_6]$	1.66	$\mu \propto T^{\frac{1}{2}}$
		$K_2[OsBr_6]$	1.20	$\mu \propto T^{\frac{1}{2}}$
		$Cs_2[OsBr_6]$	1.76	$\mu \propto T^{\frac{1}{2}}$
		$(NH_4)_2[OsBr_6]$	1.51	$\mu \propto T^{\frac{1}{2}}$
		$K_2[OsI_6]$	1.38	$\mu \propto T^{\frac{1}{2}}$
		$Cs_2[OsI_6]$	1.65	$\mu \propto T^{\frac{1}{2}}$
		$[Os(As\text{–}As)_2X_2](ClO_4)_2$ (X = Cl, Br, I)	1.16–1.25	a
Os(III)	t_{2g}^5	OsI_3	1.8	a
		$[Os(NH_3)_6]Br_3$	1.8	a
		$[Os(NH_3)_6]I_3$	2.2	a
		$[Os(NH_3)_6][OsBr_6]$	1.76	a
		$[Os(NH_3)_5Br]Br_2$	2.1	a
		$[Os(NH_3)_5Br]I_2$	1.6	a
		$[Os(en)_3]I_3$	1.60	a
		$[Os(terpy)_2](ClO_4)_3$	1.67	a
		$Os(acac)_3$	1.81	a
		$Os(Ph_2MeAs)_3Br_3$	1.95	$\chi \propto (T+\theta)^{-1}$
		$[Os(As\text{–}As)_2X_2]X$ (X = Cl, Br, I)	1.85–1.93	a a

[a] χ measured at room temperature only.

slight; this has been found for Os(III) complexes. A fuller discussion of the magnetic behaviour of *5d* and *6d* ions has been given by Figgis and Lewis[140].

The magnetic moments found for osmium complexes are listed in Table 13.

3.2. BINARY COMPOUNDS

The halides and chalcogenides of osmium are listed in Table 14.

Halides

With the higher oxidation states Os(VII), Os(VI) and Os(V), only the fluorides are known, whereas with the lower oxidation states Os(II) and Os(I), only the iodides are known. The octafluoride OsF_8 was reported by Ruff in 1913, and for over 40 years was quoted as the only known example of a binary compound of the type AB_8. However, it has been shown that the yellow crystals reported by Ruff were in fact crystals of the hexafluoride OsF_6 [147,148]. Until recently the only known example of a compound of the type AB_7 was IF_7, but now both ReF_7 and OsF_7 are known. The heptafluoride OsF_7 was prepared by the action of fluorine on osmium metal at 600° and 400 atm. Its infrared spectrum is consistent with a pentagonal bipyramidal structure[149]. Osmium hexafluoride OsF_6 is the most stable of the platinum metal hexafluorides, but it is readily hydrolysed by water. This compound has been investigated by infrared and Raman spectroscopy and X-ray diffraction, while an electron-diffraction study has been made on the vapour[150]. The magnetic moment has been determined over the temperature range 81–297°K and the moment obeys the Curie–Weiss law but with a large value of θ (66°); the value of μ is 1.50 BM at 297°K. Osmium pentafluoride OsF_5 can be obtained from OsF_6 by treatment with I_2 in IF_5 or by reduction with $W(CO)_6$; the latter gives a mixture of OsF_5 and OsF_4 which can be separated by vacuum distillation[151]. Osmium pentafluoride forms blue crystals which on melting give a green liquid, but the vapour is colourless. These colour changes are probably due to polymerization in the solid and liquid states. The crystals are isomorphous with $[RuF_5]_4$, and thus in the solid state the compound is probably tetrameric with fluoro bridges like $[RuF_5]_4$. In the vapour state the compound is probably 5-coordinate and monomeric. The magnetic moment is 2.06 BM at room temperature, but it drops to 1.73 at 101°K [151]. Osmium(V) has the $(t_{2g})^3$ configuration and the low value for the moment suggests that there is some antiferromagnetism arising from metal–metal interaction. The compound $OsIF_4$ has been reported as a product of the reaction of OsF_6 with I_2 [151]; it is a black solid but nothing is known of its structure. The tetrafluoride OsF_4 can be prepared by the reduction of OsF_6. It is a non-volatile yellow solid; the structure is unknown but, like OsF_5, the compound is probably polymeric. It is readily soluble in water but is slowly hydrolysed.

Heating of osmium metal with chlorine gives a mixture of $OsCl_4$ and $OsCl_3$, but with excess chlorine above 650° the pure tetrachloride is obtained. The red crystals sublime at 450°. Osmium tetrachloride dissolves in water and alcohol with decomposition to $OsO_2 \cdot nH_2O$, but is insoluble in non-polar solvents. The heat of formation of the solid

[147] B. Weinstock and J. G. Malm, *J. Am. Chem. Soc.* **80** (1958) 4466.
[148] G. B. Hargreaves and R. D. Peacock, *Proc. Chem. Soc.* 1959, 85.
[149] O. Glemser, H. W. Roesky, K. H. Hellberg and H. U. Werther, *Ber.* **99** (1966) 2652.
[150] B. Weinstock, H. H. Claassen and J. G. Malm, *J. Chem. Phys.* **32** (1960) 181.
[151] G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.* 1960, 2618.

TABLE 14. HALIDES AND CHALCOGENIDES OF OSMIUM

Compound	Colour/form	M.p. (°)	B.p. (°)	Structure	μ (BM)
OsF_7	Yellow solid			Pentagonal bipyramid [a]	1.08 [a]
OsF_6	Yellow solid	32	46	Octahedral; body-centred cubic lattice [b, c]	1.50 [b]
OsF_5	Blue crystals	70	226	Probably tetrameric with F bridges but monomeric in vapour state [b]	2.06 [b]
OsF_4	Yellow solid	230		Probably polymeric [b]	
$OsCl_4$	Red crystals		450		
$OsBr_4$	Black crystals		d. 350	Cubic symmetry [d]	
$OsCl_3$	Dark grey powder		d. 450	Tetrahedral	
$OsBr_3$	Dark grey powder		d. 450		
OsI_3	Black amorphous powder				1.8 [e]
OsI_2	Black amorphous powder				0.6 [e]
OsI	Grey powder				0.5 [e]
OsO_4	Pale yellow solid	40	131	Tetrahedral [f]	
OsO_2	Dark brown crystals			Rutile [g]	
OsS_2	Black solid			Pyrites [h]	
$OsSe_2$	Black solid			Pyrites [i]	
$OsTe_2$	Black solid			Pyrites [i]	

[a] O. Glemser, H. W. Roesky, K. H. Hellberg and H. U. Werther, *Ber.* **99** (1966) 2652.
[b] G. B. Hargreaves and R. D. Peacock, *Proc. Chem. Soc.* 1959, 85; *J. Chem. Soc.* 1960, 2618.
[c] B. Weinstock and J. G. Malm, *J. Am. Chem. Soc.* **80** (1958) 4466.
[d] I. N. Semenov and N. I. Kolbin, *Russ. J. Inorg. Chem.* **6** (1961) 638.
[e] J. E. Fergusson, B. H. Robinson and W. R. Roper, *J. Chem. Soc.* (1962) 2113.
[f] T. Ueki, A. Zalkin and D. H. Templeton, *Acta Cryst.* **19** (1965) 157.
[g] F. Krauss and G. Schrader, *Z. anorg. Chem.* **176** (1928) 394.
[h] A. K. Meisel, *Z. anorg. Chem.* **219** (1934) 141.
[i] L. Thomassen, *Z. Physikal. Chem.* **B2** (1929) 349.

from its elements, ΔH°_{298} is -60.9 ± 2.8 kcal mole^{-1} [152]. Osmium tetrabromide, $OsBr_4$, is obtained by heating the elements in a sealed tube. It forms black crystals which are insoluble in water and acid[152]. The compound Os_2Br_7 was also described[152]. The tetraiodide OsI_4 was reported in 1893 to be formed by the action of hydriodic acid on OsO_4, but recent work has shown that the product of this reaction is $(H_3O)_2[OsI_6]$.

The trihalides OsX_3 (X = Cl, Br, I) are known but not the trifluoride. Osmium trichloride, $OsCl_3$, can be prepared by heating the tetrachloride at 470° in an atmosphere of chlorine[152]. It is insoluble in water, acids and organic solvents, and is isomorphous with α-$RuCl_3$. The tribromide $OsBr_3$ can be made by heating the tetrabromide; it is similar to $OsCl_3$. The triiodide OsI_3 can be obtained by the thermal decomposition of $(H_3O)_2[OsI_6]$ or by heating the diiodide with iodine. The magnetic moment is 1.8 BM.

The only dihalide appears to be the black amorphous diiodide OsI_2 which is obtained by heating $(H_3O)_2[OsI_6]$. A reinvestigation of the product, reported as $OsCl_2$, obtained by heating $OsCl_3$ *in vacuo* or in chlorine, showed that $OsCl_2$ is not obtained in this way and that $OsCl_3$ is decomposed to give the metal only[151].

Osmium monoiodide, OsI, has been reported as another of the products obtainable from the thermal decomposition of $(H_3O)_2[OsI_6]$; the moment is 0.5 BM suggesting Os–Os interaction.

Oxides

Osmium tetroxide, OsO_4, is the most important compound of osmium and is the product of the heating of the metal in air and of the oxidation of osmium solutions with nitric acid. On the other hand, RuO_4 is not obtained by oxidation of ruthenium solutions with nitric acid alone. Osmium tetroxide is a pale yellow solid with a low melting point (40°). The Os–O distance has been determined as 1.74 Å in the solid[153] and as 1.71 Å in the vapour[154]. Evidence obtained from electron diffraction, infrared and Raman studies indicate that the molecule is tetrahedral; the dipole moment in benzene is practically zero. The compound is diamagnetic—Os(VIII) is d^0—and the electrical conductivity in the liquid state is $< 10^{-11}$ mho. The standard enthalpy ΔH°_{298} for the reaction

$$Os(g) + 2O_2 \rightarrow OsO_4(g)$$

is -79.9 kcal mole^{-1} [59]. The solubility of OsO_4 in water at 25° is 7.24 g per 100 g water, and in carbon tetrachloride is 250 g per 100 g CCl_4 at 20°. The compound behaves as a non-associated substance in both solvents. The aqueous solution has a slight but perceptible conductivity due to the formation of the weak perosmic acid $H_2[OsO_4(OH)_2]$ for which K_1 has a value of approximately 8×10^{-13}. Osmium tetroxide dissolves in cold alkali to give $[OsO_4(OH)_2]^{2-}$ from which the potassium, rubidium, caesium and NH_4 salts have been isolated.

Polarographic studies have been carried out on solutions of OsO_4 [155]. Both OsO_4 and RuO_4 are strong oxidizing agents but OsO_4, being more stable than RuO_4, is the weaker

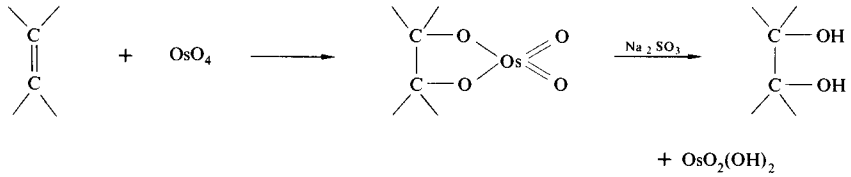
[152] I. N. Semenov and N. I. Kolbin, *Russ. J. Inorg. Chem.* **7** (1962) 111; N. I. Kolbin, I. N. Semenov and Y. M. Shutov, *ibid.* **8** (1963) 1270; **9** (1964) 108.

[153] T. Ueki, A. Zalkin and D. H. Templeton, *Acta Cryst.* **19** (1965) 157.

[154] H. M. Seip and R. Stølevik, *Acta Chem. Scand.* **20** (1966) 385.

[155] R. E. Cover and L. Meites, *J. Am. Chem. Soc.* **83** (1961) 4706; J. Perichon, S. Palous and R. Buvet, *Bull. soc. chim. France* 1963, 982; K. Fulop and L. J. Csányi, *Acta Chim. Acad. Sci. Hung.* **38** (1963) 193.

oxidant. It is reduced by hydrochloric acid with a density greater than 1.6 with the formation of $H_2[OsCl_6]$ and Cl_2 but not by dilute hydrochloric acid, which reduces RuO_4. Osmium tetroxide is used as an oxidant in organic chemistry, since in solution in ether, benzene or cyclohexane it will add to olefinic double bonds to give cyclic Os(VI) esters which can be reduced by sodium sulphite to *cis*-diols:



The tetroxide can be used as a catalyst for similar hydroxylation reactions involving aqueous solutions of silver or barium chlorate or hydrogen peroxide in t-butyl alcohol. The subject of olefin hydroxylation by means of OsO_4 has been reviewed[156].

Because of its ready reduction by organic matter to OsO_2 or even the metal, OsO_4 has been used in dilute aqueous solution as a biological stain. It has a powerful and objectionable odour and is very toxic. It is particularly harmful to the eyes, nose and throat. However, there is no evidence that it is a cumulative poison. Because of the ready oxidation of osmium compounds to the tetroxide and of the volatility of OsO_4, care must be exercised in working with osmium compounds: a good fume cupboard is the minimum precaution. The toxicology of OsO_4 has been discussed[157].

The trioxide does not seem to be stable in the solid state and has not been isolated; however, it has been detected in the gaseous phase by mass spectrometry. The dioxide OsO_2 can be made by heating the metal in a stream of nitric oxide at 650° or in a stream of OsO_4 at 600° [158]. It is readily oxidized by heating in air to the tetroxide and dissolves in hydrochloric acid to give $[OsCl_6]^{2-}$. The black hydrated oxide $OsO_2 \cdot 2H_2O$ can be made by reducing a solution of the tetroxide or by treating $K_2[OsCl_6]$ with K_2CO_3. The sesquioxide Os_2O_3 was described by Deville and Debray in 1859, the hydroxide $Os(OH)_2$ was reported by Berzelius in 1829 and the monoxide OsO was described by Claus in 1847; yet these compounds have not been definitely established, and the dioxide OsO_2 must be regarded as the lowest oxide of osmium.

Compounds of Sulphur, Selenium, Tellurium and Phosphorus

The disulphide OsS_2 is the only sulphide formed by osmium. It can be prepared by heating the elements above 600° or by treating a solution of $K_2[OsCl_6]$ with hydrogen sulphide. It is insoluble in alkali or sodium sulphide solution and in acids other than nitric acid which oxidizes it to OsO_4. The diselenide $OsSe_2$ and ditelluride $OsTe_2$ can be made from the elements at 800° and resemble OsS_2. All three compounds possess the pyrites structure, so, strictly, these compounds should be regarded as containing Os(II).

The diphosphide OsP_2 is formed when the elements are heated above 500°; it has the marcasite structure. It is stable *in vacuo* to 1000° at about which temperature it decomposes

[156] F. D. Gunstone, *Advances in Organic Chemistry*, Interscience, New York (1960), Vol. 1, p. 110.
[157] D. Hunter, *J. Pharm. Pharmacol.* **5** (1953) 149.
[158] L. Wöhler and L. Metz, *Z. anorg. Chem.* **149** (1925) 301.

into its elements. It is unattacked by acid or aqueous alkali but dissolves in alkali on fusion.

The ternary compounds OsPS, OsAsS, OsSbS, OsPSe, OsAsSe and OsAsTe have been prepared from the elements at 700–900°. They are similar to the corresponding ruthenium compounds, being diamagnetic, semi-conducting and non-metallic, and having the arsenopyrite structure[64].

3.3. OXO- AND HYDROXO-HALIDES

The established oxo-halides of osmium are listed in Table 15. The action of BrF_3 on OsO_4 gives the Os(VIII) oxofluoride OsO_3F_2 [159]. Its structure is unknown, but its high melting point suggests that it may be dimeric with fluoro bridges. The Os(VII) oxofluoride $OsOF_5$ can be made by the action of fluorine on OsO_2 at 200° [160]; it is isomorphous with UF_6. The Os(VI) compound $OsOF_4$ was obtained during the preparation of OsF_6; it is diamagnetic[151]. The corresponding oxochloride $OsOCl_4$ can be made by the reaction of a mixture of chlorine and oxygen on osmium at 400°; it is also diamagnetic[159].

TABLE 15. OXO-HALIDES OF OSMIUM

Compound	Colour	M.p. (°)	Structure
OsO_3F_2	Orange	170	Dimeric with F bridges (?)
$OsOF_5$	Emerald green	60	Octahedral
$OsOF_4$	Golden yellow	90 (subl.)	Dimeric with F bridges (?)
$OsOCl_4$	Dark brown	32	Dimeric with Cl bridges (?)

The reddish-brown hydroxochloride $Os(OH)Cl_3$ can be prepared by passing hydrogen chloride gas into a solution of OsO_4 in hydrochloric acid; it is hygroscopic. The hydroxobromide $Os(OH)Br_3$ can be obtained as dark red crystals from a solution of OsO_4 in hydrobromic acid. It is very soluble in water and in alcohol. Both compounds react with alkali halides to give $M[Os(OH)X_5]$ (X = Cl, Br) [161].

3.4. COMPLEXES OF OSMIUM(−II)

The carbonyl anion $[Os(CO)_4]^{2-}$ is produced when the carbonyl $Os_3(CO)_{12}$ is treated with sodium in liquid ammonia. $K_2[Os(PF_3)_4]$ has been isolated as colourless crystals, stable to air[79].

3.5. COMPLEXES OF OSMIUM(0)

Carbonyls

Two carbonyls are known: osmium pentacarbonyl $Os(CO)_5$ and triosmium dodecacarbonyl $Os_3(CO)_{12}$. The pentacarbonyl can be prepared by treating OsI_3 with CO at

[159] M. A. Hepworth and P. L. Robinson, *J. Inorg. Nucl. Chem.* **4** (1957) 24.
[160] N. Bartlett, N. I. Jha and J. Trotter, *Proc. Chem. Soc.* 1962, 277.
[161] F. Krauss and D. Wilken, *Z. anorg. allgem. Chem.* **137** (1924) 349.

200–300 atm and 150–300° in the presence of copper or silver powder which act as halogen acceptors. However, the best method of preparation is the dry reduction of the tetroxide by carbon monoxide itself:

$$OsO_4 + 9CO \rightarrow Os(CO)_5 + 4CO_2$$

The reaction was carried out at 300° and 300 atm and gave a quantitative yield of the carbonyl[162]. Osmium pentacarbonyl is a colourless monomeric liquid (m.p. −15°). Infrared evidence is in accordance with a pentagonal bipyramidal structure, as has been found for $Fe(CO)_5$ [162].

The dodecacarbonyl $Os_3(CO)_{12}$, which was previously erroneously formulated as $Os_2(CO)_9$, is formed along with $Os(CO)_5$ when Os(III) halides are treated with CO under pressure with a halogen acceptor, as described above, but the yields are usually ~5%. The compound can be prepared in 70% yield by heating OsO_4 in xylene at 175° under CO at 120 atm[163]. Yields of up to 85% have been reported with the reaction of OsO_4 in methanol with CO under a variety of conditions of temperature and pressure[164]. $Os_3(CO)_{12}$ forms yellow crystals (m.p. 224°) which are readily soluble in hydrocarbon solvents. X-ray analysis has definitely established the trimeric structure: the three osmium atoms are in an equilateral triangular arrangement, and each has four terminal CO groups; there are no bridging CO groups; the average Os–Os distance is 2.88 Å. The infrared spectrum shows the expected four bands in the terminal CO region but no bands which can be attributed to bridging CO groups[162].

Mass spectrometric investigations have shown that the following reaction takes place:

$$Os_3(CO)_{12} \rightarrow Os_3(CO)_n + (12 - n)CO \qquad n = 0\text{–}11$$

There is no evidence of any monomeric or dimeric species being formed in the mass spectrometer. The metal cluster of three osmium atoms remains intact even when all the carbonyl groups have been removed. The stability of the metal cluster in the compounds $M_3(CO)_{12}$ decreases in the order Os > Ru > Fe [85, 165]. There are significant differences in the reactivities of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ towards halogens. The metal cluster in $Ru_3(CO)_{12}$ is cleaved to give the monomeric *cis*-$Ru(CO)_4X_2$, followed by the repolymerization of the mononuclear species to give $Ru_3(CO)_{12}X_6$. On the other hand, $Os_3(CO)_{12}$ yields $Os_3(CO)_{12}X_2$ without rupture of the metal–metal bonds[166].

Other Complexes

The 5-coordinate carbonyl phosphine complex $Os(CO)_3(PPh_3)_2$ can be prepared by the reaction of CO at 140° and 4 atm on $OsCl_2(CO)_2(PPh_3)_2$ in the presence of zinc powder. The compound reacts with HX to give $OsX_2(CO)_2(PPh_3)_2$ and with X_2 to give $[OsX(CO)_3(PPh_3)_2]X$ (X = Br, I) [167]. The phosphorus trifluoride complex $Os(PF_3)_5$ was obtained as colourless crystals from the reductive fluorophosphination of $OsCl_3$ in the absence of hydrogen[79].

[162] I. Wender and P. Pino, *Organic Syntheses via Metal Carbonyls*, Wiley Interscience, New York (1968).
[163] C. W. Bradford and R. S. Nyholm, *Chem. Communs.* 1967, 384.
[164] B. F. G. Johnson, J. Lewis and P. A. Kilty, *Chem. Communs.* 1968, 180.
[165] B. F. G. Johnson, R. D. Johnson, J. Lewis and B. H. Robinson, *J. Chem. Soc.* A, 1967, 341.
[166] B. F. G. Johnson, R. D. Johnson, J. Lewis, I. G. Williams, R. Mason and V. Duckworth, *Proc. Ist Internat. Symposium on New Aspects of the Chemistry of Metal Carbonyls, Venice* (1968), p. A1.
[167] J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.* **88** (1966) 3504.

The unstable hexammineosmium(0) $Os(NH_3)_6$ has been reported as being formed by the reduction of $[Os(NH_3)_6]Br_3$ by potassium in liquid ammonia[168]. However, it is possible that this compound is a hydride of Os(I) or Os(II).

The arene–olefin complex, benzenecyclohexa-1,3-dieneosmium(0) $(C_6H_6)Os(C_6H_8)$ has been prepared[169].

The complex $Os_3(CO)_{12}OsO_4$ can be isolated from the reaction of OsO_4 and CO (200 atm, 150°, 15 hr). It is soluble in organic solvents, and the frequencies of the CO stretching modes are significantly different from those of $Os_3(CO)_{12}$ [170].

3.6. COMPLEXES OF OSMIUM(I)

The bright yellow hexammine complex $[Os(NH_3)_6]Br$ has been made by reduction of $[Os(NH_3)_6]Br_3$ with potassium in liquid ammonia; its magnetic moment is 1.5 BM [168]. The yellow dimeric carbonyl halides $[Os(CO)_4X]_2$ (X = Br, I) are quite stable; they are halogen-bridged and may contain metal–metal bonds.

A number of carbonyl hydrides have been recently prepared. The dodecacarbonyl $Os_3(CO)_{12}$ reacts with base or sodium amalgam to give the tetranuclear hydrides $H_4Os_4(CO)_{12}$ and $H_2Os_4(CO)_{13}$; the trinuclear hydride $H_2Os_3(CO)_{10}$ was also isolated. Reaction of OsO_4 with CO in methanol under a variety of conditions yields $Os_3(CO)_{12}$ but the hydrides $HOs_2(CO)_{10}OH$ and $HOs_3(CO)_{10}OMe$ and the methoxy derivative $Os_3(CO)_{10}(OMe)_2$ are also produced [164, 165].

The diamagnetic cyclopentadiene complex $[C_5H_5Os(CO)_2]_2$ is known[171].

3.7. COMPLEXES OF OSMIUM(II)

Whereas iron readily forms the aqua ion $[Fe(H_2O)_6]^{2+}$ and $[Ru(H_2O)_6]^{2+}$ can be isolated as the BF_4^- salt, Os(II) does not appear to form the hexa-aqua ion. Iron(II) gives both spin-free and spin-paired compounds but Os(II), like Ru(II), gives only spin-paired diamagnetic compounds with the $(t_{2g})^6$ configuration. They are usually kinetically inert, and the coordination number is invariably 6. Bivalent osmium is stabilized by ligands which have relatively strong π-acceptor properties. Complexes are formed with CN^-, nitrogen heterocycles such as pyridine, 1,10-phenanthroline, 2,2′-bipyridyl, 2,2′,2″-terpyridyl, phosphines, arsines, stibines, CO and cyclopentadienyl ion; all these ligands are good π-acceptors. The complexes are usually prepared by reduction of $[OsCl_6]^{2-}$ or Os(III) halides in the presence of the ligand, which in many cases serves as the reducing agent.

Some nitrosyl complexes, containing the ligand NO^+, are known but they are not as numerous as for Ru(II). One cationic complex containing molecular nitrogen is known—viz. $[Os(NH_3)_5N_2]^{2+}$. No doubt other complexes containing N_2 as a ligand will be discovered in the future. The various types of Os(II) complexes are discussed below.

Halide and Cyanide Complexes

The chloro complex ion $[OsCl_6]^{4-}$ may be present in the blue solutions obtained by reduction of $[OsCl_6]^{3-}$, but it has not been isolated. No other halide complexes are

[168] G. W. Watt, E. M. Potrafke and D. S. Klett, *Inorg. Chem.* **2** (1963) 868.
[169] E. O. Fischer and J. Muller, *Ber.* **96** (1963) 3217.
[170] B. F. G. Johnson, J. Lewis, I. G. Williams and J. Wilson, *Chem. Communs.* 1966, 391.
[171] E. O. Fischer and A. Vogler, *Angew. Chem.* **4** (1965) 700.

known. The colourless complex cyanide $K_4[Os(CN)_6]\cdot 3H_2O$ can be prepared by fusing $(NH_4)_2[OsCl_6]$ with KCN or by evaporation of a solution containing KCN and K_2OsO_4. The electronic spectra of $K_4[Os(CN)_6]$ and other hexacyano complexes have been discussed in the light of molecular-orbital theory[172]. The anhydrous acid $H_4[Os(CN)_6]$ can be obtained as colourless crystals by the addition of hydrochloric acid and ether to $K_4[Os(CN)_6]$. Infrared data suggest that the solid compound contains asymmetric hydrogen bonds[173]. Various other salts of $[Os(CN)_6]^{4-}$ are known[174].

Sulphito Complex

The dark brown complex $Na_4[Os(SO_3)_3]\cdot 6H_2O$ has been prepared by the action of Na_2SO_3 on esters of osmic acid[174].

Complexes with Nitrogen Ligands

There is some evidence for the existence of $[Os(NH_3)_6]^{2+}$ in a solution of $[Os(NH_3)_6]^{3+}$ in liquid ammonia which has been treated with potassium. The nitrogen complexes $[Os(NH_3)_5N_2]X_2$ (X = Cl, Br, I, ClO_4, BF_4, BPh_4) have been prepared; they are diamagnetic. The chloride was obtained as a pale yellow powder from $(NH_4)_2[OsCl_6]$ in hydrazine hydrate under reflux. The chloride and bromide are stable to air but the other salts decompose slowly, especially in strong light. The chloride, when heated strongly, gave 87% of the theoretical quantity of N_2. The $\nu(N\equiv N)$ mode occurs at 2064–2010 cm^{-1}; this lowering of $\sim 300\ cm^{-1}$ upon coordination, denotes a strong Os–N_2 bond. The $\nu(Os–N_2)$ band occurs at 546–520 cm^{-1} [175]. Treatment of $[Os(NH_3)_5N_2]I$ with HI in the presence of a mild oxidizing agent gives a high yield of $[Os(NH_3)_5I]^{2+}$; this reaction provides an improved synthetic route to the Os(III) acidopentammines[175]:

$$[Os(NH_3)_5N_2]I_2 \xrightarrow{HI+[O]} [Os(NH_3)_5I]^{2+} \xrightarrow{HX} [Os(NH_3)_5X]^{2+}$$

Dwyer and his co-workers[176,177] have prepared a large number of complexes with pyridine, 1,10-phenanthroline, 2,2′-bipyridyl and 2,2′,2″-terpyridyl; the complexes are listed in Table 16. The tris-ligand complexes [Os bipy$_3$]Cl_2 and [Os phen$_3$]I_2 and the terpyridyl complex [Os terpy$_2$]Cl_2 were prepared from $[OsCl_6]^{2-}$ an excess ligand which apparently acts as the reducing agent. The complex ions [Os phen$_3$]$^{2+}$, [Os bipy$_3$]$^{2+}$, [Os py$_2$phen$_2$]$^{2+}$ and [Os bipy phen$_2$]$^{2+}$ have been resolved. The compounds can be reversibly oxidized and reduced without loss of optical activity[177]. Electron-transfer reactions involving [Os bipy$_3$]$^{2+}$ have been studied and found to be very fast[178]. The dimeric mono-imino bridged complex $[Os_2bipy_4Cl_2NH_2]ClO_4$ and the di-imino bridged complex $[Os_2bipy_4(NH_2)_2]$ are known.

[172] H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.* **85** (1963) 2922.
[173] D. F. Evans, D. Jones and G. Wilkinson, *J. Chem. Soc.* 1964, 3164.
[174] N. V. Sidgwick, *The Chemical Elements and Their Compounds*, Clarendon Press, Oxford (1950), pp. 1490 *et seq.*
[175] A. D. Allen and J. R. Stevens, *Chem. Communs.* 1967, 1147.
[176] W. W. Brandt. F. P. Dwyer and E. C. Gyarfas, *Chem. Rev.* **54** (1954) 959.
[177] D. A. Buckingham, F. P. Dwyer, H. A. Goodwin and A. M. Sargeson, *Austral. J. Chem.* **17** (1964) 315, 325; D. A. Buckingham, F. P. Dwyer and A. M. Sargeson, *ibid.* **17** (1964) 622.
[178] B. M. Gordon, L. L. Williams and N. Sutin, *J. Am. Chem. Soc.* **83** (1961) 2061.

TABLE 16. COMPLEXES OF OSMIUM(II) WITH NITROGEN HETEROCYCLES[177]

Complex		Colour
trans-[Os py_4X_2]	(X = Cl, Br)	Dark red
[Os $chel_3]X_2$ [a]	(chel = bipy, phen; X = Cl, I, ClO_4)	Green
[Os $terpy_2]X_2$ [b]	(X = Cl, I)	Green
[Os en $chel_2]I_2$		Dark brown
[Os $py_2chel_2]X_2$	(X = I, ClO_4)	Dark green
[Os py_2phen bipy]I_2		Dark brown
[Os py bipy terpy]X_2	(X = I, ClO_4)	Dark brown
[Os γ-pic bipy terpy]$(ClO_4)_2$		Dark brown
[Os py_4bipy]X_2	(X = I, ClO_4)	Dark green
[Os$(NH_3)_2bipy_2]I_2$		Dark green
[Os $bipy_2$phen]X_2	(X = I, ClO_4)	Black
[Os bipy $phen_2]X_2$	(X = I, ClO_4)	Black
[Os py_3bipy X]X	(X = Cl, Br, I)	Dark brown
[Os $chel_2C_2O_4$]		Crimson
[Os $bipy_2$gly]I		Dark brown
[Os $phen_2$acac]Cl		Dark purple
[Os $bipy_2$acac]X	(X = Cl, ClO_4)	Brown
[Os phen bipy acac]Cl		Dark purple
[Os $chel_2Cl_2$]		Purple
[Os phen bipy Cl_2]		Dark violet
[Os py $chel_2$X]X	(X = Cl, Br, I)	Brown
[Os NH_3bipy_2Cl]X	(X = Cl, I)	Dark brown
[Os py_2terpy Cl]X	(X = Cl, I, ClO_4)	Dark brown
[Os bipy terpy X]X	(X = Cl, Br, I, SCN)	Black
[Os bipy terpy NO_2]I		Brown
[$Os_2bipy_4Cl_2NH_2$]ClO_4		Brown
[$Os_2bipy_4(NH_2)_2$]		Brown

phen = 1,10-phenanthroline; bipy = 2,2′-bipyridyl; terpy = 2,2′,2″-terpyridyl; py = pyridine; γ-pic = γ-picoline; acac = acetylacetonate; gly = glycinate.

[a] F. H. Burstall, F. P. Dwyer and E. C. Gyarfas, *J. Chem. Soc.* 1950, 953.

[b] G. Morgan and F. H. Burstall, *J. Chem. Soc.* 1937, 1649.

Nitrosyl Complexes

Osmium(II), like Ru(II), forms nitrosyl complexes, but fewer are known with osmium. The complexes are all diamagnetic. The yellow $K_2[Os(NO)(OH)(NO_2)_4]$ can be obtained by the prolonged action of KNO_2 on $K_2[OsCl_6]$. Heating of this complex with halogen acids yields the deep reddish purple compounds $K_2[Os(NO)X_5]$ [179].

Phosphine, Arsine and Stibine Complexes

The known complexes of Os(II) with phosphines, arsines and stibines are listed in Table 17. The binuclear complexes $[Os_2(PR_3)_6Cl_3]Cl$ probably contain three chloro bridges. The compounds reported as $Os(PPh_3)_3Br_2$ and $Os(AsR_3)_3I_2$ are probably dimeric with halogen bridges and are listed in Table 17 as $[Os_2(PPh_3)_6Br_4]$ and $[Os_2(AsR_3)_6I_4]$. Complexes are known with several diphosphines and a diarsine; these ligands form strong π-bonds and are effective in stabilizing low oxidation states. The diphosphine complexes are known in both *cis* and *trans* forms.

[179] P. Gans, A. Sabatini and L. Sacconi, *Inorg. Chem.* **5** (1966) 1877.

TABLE 17. COMPLEXES OF OSMIUM(II) WITH PHOSPHINES, ARSINES AND STIBINES

Compound		Colour	Ref.
$[Os_2(PR_3)_6Cl_3]Cl$	(R = Ph_2Et, Ph_2Me, $PhEt_2$)	Yellow	a
$[Os_2(PPh_3)_6Br_4]$		Green	b
cis- and *trans*-$[Os(P\text{–}P)_2X_2]$ *	(X = Cl, I)	Yellow	a
cis- and *trans*-$[Os\{C_2H_4(PPh_2)_2\}_2ClMe]$		Yellow	a
trans-$[Os\{C_2H_4(PPh_2)_2\}_2ClEt]$		Yellow	a
cis-$[Os\{C_2H_4(PPh_2)_2\}_2R_2]$	(R = Me, Et)	Yellow	a
$[Os(AsR_3)_4X_2]$	(X = Cl, Br; R = $MePh_2$, Me_2Ph)	Yellow	c
$[Os_2(AsR_3)_6I_4]$	(R = Me_2Ph, $MePh_2$)	Red	c
trans-$[Os(As\text{–}As)_2X_2]$ †	(X = Cl, Br, I, SCN)	Purple	d
$[Os(SbPh_3)_4Br_2]$		Orange	b
$[OsNO(SbPh_3)_2Cl_3]$		Red	e

* (As–As) = *o*-$C_6H_4(AsMe_2)_2$.
† (P–P) = *o*-$C_6H_4(PEt_2)_2$, $C_2H_4(PPh_2)_2$, $CH_2(PPh_2)_2$.
[a] J. Chatt and R. G. Hayter, *J. Chem. Soc.* 1961, 896; 1963, 6017.
[b] L. Vaska, *Chem. Ind. (London)* 1961, 1402.
[c] F. P. Dwyer, R. S. Nyholm and B. T. Tyson, *J. Proc. Roy. Soc. N.S. Wales* **81** (1947) 272.
[d] R. S. Nyholm and G. J. Sutton, *J. Chem. Soc.*, 1958, 572; J. Lewis, R. S. Nyholm and G. A. Rodley, *ibid.*, 1965, 1483.
[e] A. Araneo and C. Bianchi, *Gazzetta* **97** (1967) 885.

If the Os(III) complex $[Os(SbPh_3)_3Cl_3]$ is treated with NO, the red Os(II) nitrosyl complex $[OsNO(SbPh_3)_2Cl_3]$ is produced.

Carbonyl and hydride complexes containing phosphines are discussed below under Carbonyl Complexes and Hydride Complexes.

TABLE 18. CARBONYL COMPLEXES OF OSMIUM(II)

$[Os(CO)_6]Cl_2$ [a]		$OsCl(RCO_2)(CO)_2(PR'_3)_2$ [c]	(R = Me, Et; R' = Ph, C_6H_{11})
$Os(CO)_4X_2$ [b]	(X = Cl, Br, I)		
$[Os(CO)_3X_2]_2$ [b]	(X = Cl, Br, I)	$[Os(CO)_4(PR_3)_2]^{2+}$ [c]	(R = Ph, OPh)
$[Os(CO)_2X_2]_n$	(X = Br, I)	$OsX_2(CO)_2(PPh_3)_2$ [d]	(X = Cl, Br, I)
$OsCl_2(CO)_2(PR_3)_2$ [c]	(R = Ph, OPh)	$[OsX(CO)_3(PPh_3)_2]^+$ [d]	(X = Br, I)
$OsCl_2(CO)(SbPh_3)_3$ [f]		$Os(C_5H_5)(CO)_2Br$ [e]	
cis- and *trans*-$OsCl_2(CO)_2(SbPh_3)_2$ [f]			

[a] W. Hieber and T. Kruck, *Angew. Chem.* **73** (1961) 580.
[b] W. Hieber and H. Stallmann, *Ber.* **75** (1942) 1472.
[c] W. Hieber and V. Frey, *Z. Naturforsch.*, Ser. B, **21** (1966) 704.
[d] J. P. Collmann and W. R. Roper, *J. Am. Chem. Soc.* **88** (1966) 3504.
[e] E. O. Fischer and A. Vogler, *Z. Naturforsch.*, Ser. B, **17** (1962) 421.
[f] A. Araneo and C. Bianchi, *Gazzetta* **97** (1967) 885.

Carbonyl Complexes

The carbonyl complexes of Os(II) are listed in Table 18. The reaction of CO at 160° and 200 atm on $OsCl_3$ yields the colourless monomeric carbonyl chloride $Os(CO_4)Cl_2$. The carbonyl halides $Os(CO)_4X_2$ (X = Br, I) can be prepared in a similar manner from Os_2Br_9 and $H_2[OsI_6]$. The latter are known in two forms, one colourless the other yellow; these may be *cis* and *trans* isomers. The dimeric carbonyl halides $[Os(CO)_3X_2]_2$ have been made from osmium halides and CO under pressure; these complexes probably contain bridging halide groups. The polymeric compounds $[Os(CO)_2X_2]_n$ (X = Br, I) have been obtained by heating either the monomeric or the dimeric carbonyl halides; their structures are unknown but they are probably polymeric with halide bridges.

The cationic complex $[Os(CO)_6]Cl_2$ was prepared by treating $Os(CO)_4Cl_2$ with CO at 400 atm in the presence of $AlCl_3$.

The reaction of $[Os(CO)_3Cl_2]_2$ with tertiary phosphines in boiling benzene yields $Os(CO)_2(PR_3)_2Cl_2$ in which the chlorine atoms are *cis* and the phosphine ligands are *trans*. Reaction of this compound with CO at 300 atm in the presence of $AlCl_3$ gives *trans*-$[Os(CO)_4(PR_3)_2][AlCl_4]_2$. The chloro compound $Os(CO)_2(PPh_3)_2Cl_2$ can be prepared from $OsCl_3$, CO and PPh_3. The bromo compound $Os(CO)_2(PPh_3)_2Br_2$ can be prepared in a similar manner from $(NH_4)_2[OsBr_6]$, but the analogous iodo complex was prepared from $Os(CO)_3(PPh_3)_2$ and HI. The reaction of mercuric halides with $Os(CO)_3(PPh_3)_2$ yields the cationic complexes $[Os(CO)_3(PPh_3)_2X]X$ and $[Os(CO)_3(PPh_3)_2(HgX)]HgX_3$ (X = Br, I); the latter contains a Hg–Os bond[75]. Treatment of $OsCl_3(SbPh_3)_3$ with CO in chloroform yields the pale green $OsCl_2(CO)(SbPh_3)_3$, and the colourless *cis* and the yellow *trans* isomers of $OsCl_2(CO)_2(SbPh_3)_2$.

The cyclopentadienyl complex $[Os(C_5H_5)(CO)_2Br]$ is prepared by treatment of $[Os(C_5H_5)(CO)_2]_2$ with Br_2 [171].

Hydride Complexes

The types of hydride complexes are given in Table 19. The carbonyl hydride $H_2Os(CO)_4$ has been obtained in high yield from the reaction of OsO_4 in heptane with CO and H_2 at 180 atm and 160°. It can also be obtained from the reaction of $Os(CO)_5$ and H_2 at 80 atm and 100°. The infrared spectrum is consistent with a *cis*-configuration. The carbonyl hydride reacts with PPh_3 to give *cis*-$H_2Os(CO)_3PPh_3$ and with carbon tetrahalides to give $OsX_2(CO)_4$ (X = Cl, Br)[180]. The halogenohydridocarbonyls $HOsX(CO)(MR_3)_3$ (M = P, As) are obtained by treating $(NH_4)_2[OsX_6]$ with the phosphine or arsine in an alcohol solvent, usually 2-methoxyethanol or ethylene glycol. The reaction can be carried out in the presence of KOH: e.g. $HOsCl(CO)(PEt_2Ph)_3$ was obtained by treating $OsCl_3(PEt_2Ph)_3$ with KOH in boiling ethyl alcohol. The carbon atom of the carbonyl group is derived from the alcohol or glycol. The compound $HOsBr(CO)(PPh_3)_3$ has been shown by an X-ray structural investigation to have an octahedral configuration with the bromine atom *trans* to the carbonyl group and the three PPh_3 groups and the hydrido group in the equatorial plane. The Os–P distance for the phosphine *trans* to the hydrogen atom is 2.56 Å, compared to 2.34 Å for the two other phosphine groups[181]. The osmium phosphine carbonyl hydrides are among the most stable hydride complexes, being unaffected by air at room temperature. The complex $HOsCl(CO)(PPh_3)_3$ has been found to display catalytic activity: e.g. it catalyses the reduction by hydrogen of acetylene to ethylene. It has been suggested that the process involves the formation of the 8-coordinate Os(IV) hydride $H_3OsCl(CO)(PPh_3)_3$ which reacts with acetylene[182]:

$$H_3OsCl(CO)(PPh_3)_3 + HC{\equiv}CH \rightarrow HOsCl(CO)(PPh_3)_3 + H_2C{=}CH_2$$

The complexes *trans*-$HOsX(P{-}P)_2$ are obtained by reduction of *cis*- or *trans*-$OsX_2(P{-}P)_2$ with $LiAlH_4$. Further reduction of $HOsCl(P{-}P)_2$ with $LiAlH_4$ gives *trans*-$H_2Os(P{-}P)_2$. Similarly, reduction of *trans*-$OsClR(P{-}P)_2$ with $LiAlH_4$ gives the hydrides $HOsR(P{-}P)_2$ (R = Me, Et).

TABLE 19. HYDRIDE COMPLEXES OF OSMIUM(II)

$H_2Os(CO)_4$ [a]	
cis-$H_2Os(CO)_3PPh_3$ [a]	
$HOs(CO)X(PPh_3)_3$ [b]	(X = Cl, Br)
$HOs(CO)X(AsPh_3)_3$ [b]	(X = Cl, Br)
trans-$H_2Os(P{-}P)_2$ [c]	(P–P = *o*-$C_6H_4(PEt_2)_2$)
trans-$HOsX(P{-}P)_2$ [c]	(X = Cl, Br, I, SCN; P–P = *o*-$C_6H_4(PEt_2)_2$ or $C_2H_4(PR_3)_2$, R = Me, Et, Ph)
trans-$HOsR(P{-}P)_2$ [c]	(R = Me, Et; P–P = $C_2H_4(PPh_2)_2$

[a] F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.* **6** (1967) 2092.
[b] L. Vaska, *J. Am. Chem. Soc.* **86** (1964) 1943.
[c] J. Chatt and R. G. Hayter, *J. Chem. Soc.* 1961, 2605; 1963, 6017.

[180] F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.* **6** (1967) 2092.
[181] P. O. Orioli and L. Vaska, *Proc. Chem. Soc.* 1962, 333.
[182] L. Vaska, *Inorg. Nucl. Chem. Letters* **1** (1965) 89.

π-Complexes

These include osmocene and its derivatives and a few olefin complexes. Osmocene $Os(C_5H_5)_2$ can be prepared in 20% yield from $OsCl_3$ and sodium cyclopentadienide. Whereas ferrocene is orange and ruthenocene is yellow, osmocene forms colourless crystals (m.p., 229°; b.p., 311°). The heats of fusion, vaporization and sublimation are respectively 7.0, 11.0 and 18.0 kcal mole^{-1}. In osmocene, as in ruthenocene, the two cyclopentadienyl rings are eclipsed and not staggered as in ferrocene. Proton magnetic resonance measurements in carbon tetrachloride solution show that the τ values decrease from ferrocene (5.96) to osmocene (5.29). The diamagnetic Os(IV) complexes $[(C_5H_5)_2Os(OH)]^+$ and $[(C_5H_5)_2OsI]^+$ can be prepared by oxidation of osmocene. Acylosmocenes and alkylosmocenes can be prepared by Friedel–Crafts synthesis[116]. Trimethylsilylosmocene has been prepared; the first-order rate coefficients for the cleavage of the C–Si bond in $(C_5H_5)M(C_5H_4SiMe_3)$ (M = Fe, Ru, Os) in methanol solution containing HCl fall in the sequence: Ru > Os > Fe [183].

The olefin complex $OsCl_2(C_8H_{12})(PEtPh_2)_2$ (C_8H_{12} = cycloocta-1,5-diene) has been prepared by the reaction of the diene with $[Os_2Cl_3(PEtPh_2)_6]Cl$ [103]. The compound $[Os(C_6H_6)I_2]_n$ is also known[184]. An interesting complex of formula $(C_8H_8)Os_2(CO)_6$ has been prepared by the reaction of $Os_3(CO)_{12}$ with 2,3-dimethylbuta-1,3-diene[185]. The X-ray structure determination revealed that there is a metal–metal bond (2.74 Å) between the two octahedrally coordinated osmium atoms, which each has three carbonyl groups attached. However, one osmium atom is bivalent, since it forms two σ-bonds to the terminal carbon atoms of the butadiene. The other osmium atom is zerovalent, being π-bonded to the two C=C groups of the diene[186].

3.8. COMPLEXES OF OSMIUM(III)

Osmium(III) appears to be less stable than Ru(III) and fewer complexes are known with Os(III) than with Ru(III). Trivalent osmium forms the halogeno complexes $[OsX_6]^{3-}$ (X = Cl, Br) and an acetylacetone complex. A few complexes are known with sulphur donors. Complexes are formed with ammonia and nitrogen heterocycles and with tertiary phosphines, arsines and stibines. Carbonyl and hydride complexes apparently are not formed by Os(III), although a few carbonyl complexes are known with Ru(III). All Os(III) complexes are octahedral and low-spin with the $(t_{2g})^5$ configuration. Low-spin d^5 ions have normal magnetic behaviour except when kT/λ becomes very small. For Os(III) λ is quite large (~ 5000 cm^{-1}), yet the moments lie in the range 1.6–2.2 BM (see Table 13) and can be considered to be essentially "normal".

Halide Complexes

The hexachloro complex $K_3[OsCl_6]$ can be obtained by the action of chlorine on a mixture of the metal and KCl above 600° or by treating potassium osmiamate $K[OsO_3N]$ with hydrochloric acid. It forms red crystals which are very soluble in water and alcohol, but the solutions decompose on standing. A trihydrate is also known[174]. The bromo

[183] G. Marr and D. E. Webster, *J. Organomet. Chem.* **2** (1964) 99.
[184] G. Winkhaus, H. Singer and M. Kricke, *Z. Naturforsch.*, Ser. B, **21** (1966) 1109.
[185] E. O. Fischer, K. Bittler and H. P. Fritz, *Z. Naturforsch.*, Ser. B, **18** (1963) 83.
[186] R. P. Dodge, O. S. Mills and V. Schomaker, *Proc. Chem. Soc.* (*London*) 1963, 380.

complex $K_3[OsBr_6]$ can be obtained as brown crystals by the electrolytic reduction of a solution of $K_2[OsBr_6]$ in an atmosphere of carbon dioxide[187]. The spectra of these complexes have been discussed[125]. The iodo complex $[OsI_6]^{3-}$ has been obtained in solution and the cyano complex has been detected by polarography but no salts have been isolated.

Acetylacetone Complex

The compound $Os(acac)_3$ can be prepared by treating a solution of $[OsBr_6]^{3-}$ with the β-diketone; the moment is 1.8 BM [188].

Complexes of Sulphur Ligands

The complex $[Os\{CS(NH_2)_2\}_6]Cl_3$ can be prepared from $[OsCl_6]^{2-}$ and thiourea; it is probably S-bonded[189]. The complex of 5-chloro-8-mercaptoquinoline has also been reported[190].

Complexes of Nitrogen Ligands

The hexammines $[Os(NH_3)_6]X_3$ can be made from $(NH_4)_2[OsX_6]$ (X = Cl, Br) and ammonia under pressure at 290°; along with the hexammine, the halogenopentammines $[Os(NH_3)_5X]X_2$ are formed in low yield[168]. The hydroxopentammine $[Os(NH_3)_5OH]Cl_2$ has been obtained by the hydrolysis of $[Os(NH_3)_5Cl]Cl_2$. The anionic complex $K_2[Os(NH_3)Cl_5]$ can be made by reduction of $K_2[OsNCl_5]$ with $SnCl_2$ [191].

The ethylenediamine complex $[Os\ en_3]I_3$ was obtained by reduction of $[Os(en–H)en_2]^{3+}$ [192]. It reacts with potassium amide to give diamagnetic products which were formulated as the Os(III) species $[Os(en–H)en_2]^{2+}$, $[Os(en–H)_2en]^{+}$ and $[Os(en–H)_3]$ [192].

As for Os(II), a large number of complexes are known with the nitrogen heterocycles, pyridine, 2,2′-bipyridyl, 1,10-phenanthroline and 2,2′,2″-terpyridyl; these compounds are listed in Table 20. Most of the complexes were prepared by oxidation of the corresponding Os(II) complexes with Cl_2 or Ce(IV). Oxidation of $[Os\ bipy_2(NH_3)Cl]Cl$ with Ce(IV) yields the dark brown imido-bridged complex $[Cl\ bipy_2Os–NH–Os\ bipy_2Cl]^{2+}$ which was isolated as the perchlorate[177]. The *d* and *l* forms of $[Os\ phen_3](ClO_4)_3$ were prepared from the *d* and *l* isomers of $[Os\ phen_3]^{2+}$; they can be reduced to the Os(II) complexes without loss of optical activity[177]. The oxidation potential for $[Os\ phen_3]^{3+}/[Os\ phen_3]^{2+}$ is 0.859 V in 0.1 N HCl, while the potential for the bipyridyl system is 0.877 V in neutral solution[176].

The dark blue phthalocyanine complex Os pc Cl $C_6H_4(CN)_2$ (pc = $C_{32}H_{16}N_8^{2-}$) was prepared by the action of 1,2 dicyanobenzene on $(NH_4)_2[OsCl_6]$; the moment is 1.1 BM [193].

Phosphine, Arsine and Stibine Complexes

The red or purple complexes $[Os(MR_3)_3X_3]$ (MR_3 = $PEtPh_2$, $AsPh_3$, $AsMe_2Ph$, $AsMePh_2$, $SbPh_3$; X = Cl, Br) have been prepared from $(NH_4)_2[OsX_6]$ and MR_3 in ethanol[194, 195]. The complex $[Os(PBu^n_2Ph)_3Cl_3]$ is more resistant to oxidation than the

[187] W. R. Crowell, R. K. Brinton and R. F. Evenson, *J. Am. Chem. Soc.* **60** (1938) 1105.
[188] F. P. Dwyer and A. M. Sargeson, *J. Am. Chem. Soc.* **77** (1955) 1285.
[189] R. D. Sauerbrann and E. B. Sandell, *J. Am. Chem. Soc.* **75** (1953) 3554.
[190] J. Bankovskis, G. Mezarups and A. Levins, *Latvijas PSR Zinatnu Akad Vēstis* 1962, 323; 1964, 135.
[191] W. P. Griffith, *J. Chem. Soc.* 1966, 899.
[192] G. W. Watt, J. T. Summers, E. M. Potrafke and E. R. Birnbaum, *Inorg. Chem.* **5** (1966) 857.
[193] I. M. Keen, *Platinum Metals Rev.* **8** (1964) 143.

TABLE 20. COMPLEXES OF OSMIUM(III) WITH NITROGEN HETEROCYCLES [177]

Complex		Colour
$[Ospy_3Cl_3]$		Brown
$[Os\ chel_3]X_3$	(chel = bipy, phen; X = Cl, ClO_4)	Red
$[Os\ terpy_2]Cl_3$		Brown
$[Os\ chel_2X_2]X$	(chel = bipy, phen; X = Cl, Br)	Brown
$[Os\ phen_2bipy](ClO_4)_3$		Brown
$[Os\ bipy_2phen](ClO_4)_3$		Brown
$[Os\ py_2chel_2](ClO_4)_3$	(chel = bipy, phen)	Brown
$[Os\ bipy(H_2O)Cl_3]$		Brown
$[Os\ terpy\ bipy\ X]^{2+}$	(X = Cl, Br, I, SCN, NO_2)	Brown
$[Os\ chelCl_4]^-$	(chel = bipy, phen)	Brown
$[Os\ bipyCl_2acac]$	(acac = acetylacetonate)	Brown
$[Os\ bipyCl_2gly]$	(gly = glycinate)	Brown
$[Os\ bipy\ acac_2]I$		Brown
$[Os\ bipy\ gly_2]I$		Brown
$[Os\ terpy\ py_2Cl]^{2+}$		Brown
$[Os_2bipy_2(NH)Cl_2](ClO_4)_2$		Brown
$[Os_2bipy_2Cl_4(OH)_2]$		Brown
$[Os_2O\ bipy_2terpy_2](ClO_4)_4$		Blue

rhenium compound, which is oxidized by CCl_4, but the osmium complex in dry boiling CCl_4 under N_2 is oxidized to the yellow-brown $[OsCl_4(PBu_2^nPh)_2]$ [196]. The tertiary diarsine complexes $[Os(As–As)_2X_2]^+$ were obtained by the oxidation of the Os(II) complexes $[Os(As–As)_2X_2]$; their infrared spectra are consistent with a *trans* configuration[197]. Their moments are given in Table 13.

3.9. COMPLEXES OF OSMIUM(IV)

The most important are the halogeno complexes $[OsX_6]^{2-}$ which are frequently used as starting materials for the preparation of complexes of Os(IV) and Os(III). The only amine complexes are [Os chel X_4] (chel = phen, bipy) and a series of diamagnetic ethylenediamine complexes in which one or more ethylenediamine moieties have been deprotonated. A few complexes with tertiary arsines and an interesting phosphine hydrido complex are known. The complexes are octahedral with the $(t_{2g})^4$ configuration which is associated with anomalous magnetic behaviour (see discussion in section 3.1). The magnetic moments of Os(IV) complexes lie in the range 1.2–1.8 BM, which is well below the spin-only value (2.83 BM) for two unpaired electrons expected for the $(t_{2g})^4$ configuration. The *d–d* transitions in Os(IV) complexes have not been satisfactorily elucidated, since the ligand field bands in the spectra are usually overshadowed by strong charge-transfer bands.

Halide Complexes

The hexahalide complexes $[OsX_6]^{2-}$ are known with all four halogens. The fluoro complex $K_2[OsF_6]$ can be obtained as pale yellow crystals by treating a solution of

[194] F. P. Dwyer, R. S. Nyholm and B. T. Tyson, *J. Proc. Roy. Soc. NS Wales* **81** (1947) 272.
[195] L. Vaska, *Chem. Ind. (London)* 1961, 1402.
[196] J. Chatt, G. J. Leigh, D. M. P. Mingos and R. J. Paske, *Chem. Ind. (London)* 1967, 1324.
[197] J. Lewis, R. S. Nyholm and G. A. Rodley, *J. Chem. Soc.* 1965, 1483.

$K[OsF_6]$ with KOH [198] or from OsF_4 and KF. The compound has a hexagonal structure[198] and is only sparingly soluble (1.2 g per 100 g of water at 20°), while the caesium salt is less soluble (0.7 g at 20°). The caesium salt displays three bands at 23,500, 30,000 and 33,000 cm^{-1}. The band at 23,500 cm^{-1} has been assigned as the spin-forbidden $^3T_{1g} \rightarrow {}^5E_g$ transition which is allowed because the spin selection rules have been relaxed by spin–orbit coupling[199].

Potassium hexachloroosmate(IV), $K_2[OsCl_6]$, can be made by heating a mixture of osmium and KCl in a stream of chlorine or by adding KCl and alcohol to a solution of OsO_4 in hydrochloric acid. It forms red crystals which are isomorphous with $K_2[PtCl_6]$ and are stable in air to 600°. The sodium, ammonium, rubidium, caesium, silver, thallium and barium salts have been prepared. They vary from orange (Cs) through red (K, NH_4) to olive green (Tl) and brown (Ag), but solutions of $[OsCl_6]^{2-}$ are yellow. A convenient method for the preparation of $(NH_4)_2[OsCl_6]$ is by the reduction of a solution of OsO_4 in HCl with $FeCl_2$, followed by the addition of NH_4Cl [200]. The infrared and Raman spectra of $[OsCl_6]^{2-}$ have been discussed[201]. The kinetics of aquation of $[OsCl_6]^{2-}$ to give $[OsCl_5(H_2O)]^-$ and $[OsCl_4(H_2O)_2]$ have been studied[202].

Potassium hexabromoosmate(IV), $K_2[OsBr_6]$, which can be obtained by the addition of KBr to a solution of OsO_4 in hydrobromic acid, forms black crystals which are isomorphous with $K_2[OsCl_6]$ and $K_2[PtCl_6]$. Numerous salts are known but, with the exception of the sodium salt, they are sparingly soluble in water to give dark purple solutions. A method for the preparation of $(NH_4)_2[OsBr_6]$ from OsO_4, HBr and NH_4Br has been published[200]. The iodo complex $K_2[OsI_6]$ can be prepared by the action of hydriodic acid on $K_2[OsO_2(OH)_2(NO_2)_2]$. It forms dark violet crystals, slightly soluble in water but more so than $K_2[OsCl_6]$ and $K_2[OsBr_6]$. The aqueous solution decomposes on being heated even in the presence of hydriodic acid. Mixed halide complexes of the type $[OsCl_nBr_{6-n}]^{2-}$ have been isolated[203,204]. The electronic spectra of $[OsX_6]^{2-}$ (X = Cl, Br, I) have been measured and assignments have been made for the ligand-field and charge-transfer transitions[205].

The dark brown compound $(NH_4)_4[Os_2OCl_{10}]$ can be obtained by reduction with ferrous sulphate of an aqueous solution containing OsO_4 and NH_4Cl [202]. It has the same structure as $K_4[Ru_2OCl_{10}]$ [206]. The potassium salt, formulated as $K_2[OsCl_5OH]$, is no doubt similar. The complexes $(CH_3NH_3)_2[OsCl_3BrOH]$ and $(CH_3NH_3)_2[OsBr_5OH]$ probably have similar dimeric anions[206].

Complexes with Oxygen Ligands

The species $[Os(OH)_6]^{2-}$ probably exists in reduced alkaline solutions of osmium tetroxide[207]. A considerable number of sulphito complexes have been reported[208]; they

[198] M. A. Hepworth, P. L. Robinson and G. J. Westland, *J. Chem. Soc.* 1954, 4269; 1958, 611.
[199] D. H. Brown, D. R. Russell and D. W. A. Sharp, *J. Chem. Soc.* A, 1966, 18.
[200] F. P. Dwyer and J. W. Hogarth, *Inorg. Synth.* **5** (1957) 204.
[201] L. A. Woodward and M. J. Ware, *Spectrochim. Acta* **20** (1964) 711.
[202] R. R. Miano and C. S. Garner, *Inorg. Chem.* **4** (1965) 337.
[203] F. Blasius and W. Preetz, *Z. anorg. allgem. Chem.* **335** (1965) 16.
[204] W. Preetz, *Angew. Chem.* **4** (1965) 710.
[205] C. K. Jørgensen, *Absorption Spectra and Chemical Bonding in Complexes*, Pergamon, Oxford (1962), p. 284.
[206] D. Hewkin and W. P. Griffith, *J. Chem. Soc.* A, 1966, 472.
[207] L. Meites, *J. Am. Chem. Soc.* **79** (1957) 4631.

are of the following types: $Na_8[Os(SO_3)_6]\cdot 8H_2O$ (brown), $K_6[Os(SO_3)_5(H_2O)]\cdot 4H_2O$ (colourless), $Na_7[Os(SO_3)_5Cl]\cdot 6H_2O$ (pale violet), $Na_6[Os(SO_3)_4Cl_2]\cdot 10H_2O$ (purple) and $K_8[Os(SO_3)_4Cl_4]$ (brown). They were prepared from $[OsCl_6]^{2-}$ and sodium or potassium sulphite under various conditions. The compounds have been little investigated and their structures are not known; the sulphito group is no doubt unidentate and probably O-bonded rather than S-bonded, since osmium has a low affinity for sulphur ligands[209].

Complexes of Nitrogen Ligands

The diamagnetic nitrido complexes $[Os_2N(NH_3)_8X_2]X_3$ (X = Cl, Br) have been prepared by treatment of $[OsX_6]^{2-}$ with ammonia under pressure[210]. Infrared evidence suggests that the structure is $[X(NH_3)_4Os\cdots N\cdots Os(NH_3)_4X]X_3$ with a linear Os–N–Os bond, similar to the M–O–M bond in the diamagnetic anionic complexes $K_4[Ru_2OCl_{10}]$ and $(NH_4)_4[Os_2OCl_{10}]$ [206]. The compound Os_2NCl_5 can be obtained by the reaction of $(NH_4)_2[OsCl_6]$ with Cl_2 at *ca.* 400° [152]. Its diamagnetism and its infrared spectrum suggest that it also possesses a Os–N–Os arrangement[206], but otherwise its structure is not known.

No ammines of Os(IV) have been isolated but some ethylenediamine complexes are known in which at least one ethylenediamine ligand has been deprotonated. The complexes $[Os(en–H)_2en]X_2$ (X = Br, I) (pink), $[Os(en–H)en_2]X_3$ (green) and $[Os(en–H)_2en_2]I_2$ (pink) have been reported[211]. The complexes [Os chel Cl_4] (chel = phen, bipy) have been obtained by pyrolysis of $K(phenH)[OsCl_6]$ and $(bipyH_2)[OsCl_6]$ [177].

Phosphine and Arsine Complexes

Few complexes of Os(IV) are known with tertiary phosphines or tertiary arsines, although it would seem that others could be prepared. The complex $Os(AsPh_3)_2Br_4$ was prepared from $(NH_4)_2[OsBr_6]$ [195]. The complexes $[Os(As–As)_2X_2](ClO_4)_2$ (As–As = *o*-$C_6H_4(AsMe_2)_2$; X = Cl, Br, I) were obtained by oxidation of $[Os(As–As)_2X_2]^+$ with nitric acid[197]; the moments of these compounds are listed in Table 13. When $[OsCl_3(PBu_2^nPh)_3]$ is treated with dry boiling CCl_4 under nitrogen for 72 hr, the yellowish-brown Os(IV) complex $[OsCl_4(PBu_2^nPh)_2]$ is obtained. However, heating of $[OsCl_3(PBu_2^nPh)_3]$ with moist CCl_4 in air under reflux for 3 hr gave a high yield of the Os(IV) hydrido complex $HOsCl_3(PBu_2Ph)_2$ (μ, 1.5 BM). Presumably water is the source of the hydride ligand but it is remarkable that it occurs along with oxidation. Three isomers of the Os(III) hydrido complex $HOsCl_2(PBu_2^nPh)_3$ were reported[196].

Cyclopentadiene Complexes

Oxidation of osmocene with ferric ion yields $[Os(C_5H_5)_2OH]^+$ which can be isolated as the $[PF_6]^-$ salt. The complex $[Os(C_5H_5)_2I]I$ was also prepared. These compounds are diamagnetic[212].

[208] A. Rosenheim and E. A. Sasserath, *Z. anorg. allgem. Chem.* **21** (1899) 132; A. Rosenheim, *ibid.* **24** (1900) 420.
[209] S. E. Livingstone, *Quart. Rev.* **19** (1965) 386.
[210] F. P. Dwyer and J. W. Hogarth, *J. Proc. Roy. Soc. NS Wales* **85** (1951) 113.
[211] F. P. Dwyer and J. W. Hogarth, *J. Am. Chem. Soc.* **77** (1955) 6152.
[212] E. O. Fischer and H. Grubert, *Ber.* **92** (1959) 2302.

3.10 COMPLEXES OF OSMIUM(V)

The only complexes which have been definitely established are $K[OsF_6]$ and other metal salts containing the $[OsF_6]^-$ anion. The potassium salt was prepared from $OsBr_4$, KBr and BrF_3 [198]. An X-ray structure determination shows that the complex has a distorted caesium chloride type structure containing K^+ ions and somewhat distorted octahedral $[OsF_6]^-$ ions[213, 214]. The potassium and caesium salts have magnetic moments of ~3.3 BM and obey the Curie–Weiss law (see Table 13). Assignments of the bands in the electronic spectrum of solid $Cs[OsF_6]$ have been made[199].

The ethylenediamine complex $[Os(en\text{–}H)_3en]I_2$ has been reported[211]; further work is necessary to establish whether this compound contains 8-coordinate Os(V).

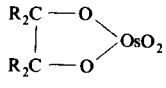
3.11. COMPLEXES OF OSMIUM(VI)

Osmium(VI) has a high affinity for oxygen and forms a considerable number of diamagnetic osmyl complexes containing the O=Os=O grouping with the two oxygen atoms mutually *trans*. The Os–O bond length is 1.75 Å (cf. 1.72 Å in OsO_4), indicating a double bond[215]. There are a group of nitrido complexes containing an Os≡N triple bond.

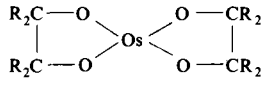
Oxo Complexes

Potassium osmate, originally formulated as $K_2OsO_4 \cdot 2H_2O$, has the octahedral structure $K_2[OsO_2(OH)_4]$ with the two oxo groups *trans* with the Os–O distance 1.77 Å. The four hydroxyl groups lie in the equatorial plane with an Os–O bond length of 2.03 Å [216]. The compound can be prepared by reduction of $K_2[OsO_4(OH)_2]$ with alcohol or KNO_2 [174]. The sodium and barium salts are also known: all are reddish-purple. The dry salts are stable in the cold but decompose when heated in air, forming OsO_4. In solution they slowly decompose. They react with halogen acids to give $[OsO_2(OH)_2X_2]^{2-}$, $[OsO_2X_4]^{2-}$ and $[OsX_6]^{2-}$.

Cyclic esters of the types (III) and (IV) can be made by the action of OsO_4 on unsaturated hydrocarbons such as indene and dihydronaphthalene[217] (see also section 3.2).



(III)



(IV)

The compounds $Na_4[OsO_5]$, $Li_6[OsO_6]$, and $M_2M'[OsO_6]$ (M = Ca, Sr; M′ = Mg, Ca, Sr, Zn, Cd) have been prepared at an elevated temperature (800°) [218].

A list of osmyl complexes is given in Table 21. It has been suggested that the diamagnetism of these osmyl complexes is due to the tetragonal distortion from octahedral symmetry caused by the strongly π-donating oxo groups. This distortion causes further

[213] R. D. Kemmitt, D. R. Russell and D. W. A. Sharp, *J. Chem. Soc.* 1963, 4408.
[214] M. A. Hepworth, K. H. Jack and G. J. Westland, *J. Inorg. Nucl. Chem.* **2** (1956) 79.
[215] F. H. Kruze, *Acta Cryst.* **14** (1961) 1035.
[216] N. A. Porai-Koshits, L. A. Atovyman and V. G. Adrianov, *J. Struct. Chem. USSR*, Engl. transl., **2** (1960) 686.
[217] R. Criegee, *Angew. Chem.* **51** (1938) 519.
[218] R. Scholder and G. Schatz, *Angew. Chem.* **70** (1958) 591.

splitting of the e_g level into two singlets $d_{x^2-y^2}$ and d_{z^2} and of the t_{2g} level into a singlet (d_{xy}) and a doublet (d_{xz}, d_{yz}). Since the d_{xy} orbital lies in the equatorial plane, it cannot take part in π-bonding with the oxo groups, hence it will have the lowest energy. If the distortion along the z axis is sufficiently large, as it is in this case due to the short Os=O bonds, then spin pairing of the two t_{2g} electrons will occur in the d_{xy} orbital[219]. The broad band at *ca.* 500 mμ in the spectrum of $K_2[OsO_2(OH)_4]$ is considered to arise from the forbidden $t_{2g} \rightarrow e_g$ transitions[219].

TABLE 21. OSMYL COMPLEXES

Compound		Colour
$K_2[OsO_2X_4]$ [a]	(X = Cl, Br)	Red
$K_2[OsO_2(CN)_4]$ [b]		Red
$K_2[OsO_2(C_2O_4)_2]$ [a]		Brown
$Na_2[OsO_2(SO_3)_4]$ [c]		Yellow
$K_2[OsO_2(OMe)_4]$ [d]		Brown
$K_2[OsO_2(NO_3)_2(NO_2)_2]$ [a]		Orange
$K_2[OsO_2(OH)_2(NO_2)_2]$ [a]		Brown
$K_2[OsO_2(OH)_2X_2]$ [a]	(X = Cl, Br)	Brown
$K_2[OsO_2(OH)_2(C_2O_4)]$ [a]		Black
$OsO_2(NH_3)_2Cl_2$ [e]		Brown
OsO_2(phthalocyanine) [f]		Blue

[a] L. Wintrebert, *Ann. Chim. Phys.* **28** (7) (1903) 15, 54, 86.
[b] F. Krauss and G. Schrader, *J. prakt. Chem.* **120** (1929) 36.
[c] A. Rosenheim and E. A. Sasserath, *Z. anorg. allgem. Chem.* **21** (1899) 132.
[d] R. Criegee, *Ann.* **522** (1936) 75.
[e] L. Gibbs, *Am. J. Chem.* **3** (1881) 233.
[f] I. M. Keen, *Platinum Metals Rev.* **8** (1964) 143.

The osmyl complexes have mostly been prepared from the tetroxide. The complex $K_2[OsO_2(NO_3)_2(NO_2)_2]$, originally formulated as $K_2[OsO_2(NO_2)_4]$, can be obtained by the action of NO on an aqueous solution containing OsO_4 and KNO_2. The compound $K_2[OsO_2(OH)_2(NO_2)_2]$ can be isolated as slightly soluble brown crystals from a solution of the tetroxide in KNO_2. It is a useful starting material for the preparation of other osmyl complexes. It is converted by halogen acids successively into $K_2[OsO_2(OH)_2X_2]$, $K_2[OsO_2X_4]$ and $K_2[OsX_6]$ (X = Cl, Br). The cyano complex $K_2[OsO_2(CN)_4]$ is obtained from KCN and OsO_4. It is remarkably stable and is not decomposed by hot HCl or H_2SO_4.

Complexes of Nitrogen Ligands

The nitrido complex $K_2[OsNCl_5]$ can be obtained as reddish-purple crystals by reacting hydrochloric acid with potassium osmiamate $K[OsO_3N]$ [220]; it is quite soluble but is readily hydrolysed in the absence of acid. X-ray crystallographic studies have shown that the four equatorial chlorine atoms are at 2.40 Å, while the apical chlorine atom, which is

[219] K. A. K. Lott and M. R. C. Symons, *J. Chem. Soc.* 1960, 973.
[220] A. P. Clifford and C. S. Kobayashi, *Inorg. Synth.* **6** (1960) 204, 206, 207.

trans to the nitride group, is at a much shorter distance (2.16 Å), although the ligand in the apical site in $K_2[OsNBr_5]$ shows the "*trans* effect"[221]. The ν(Os–N) mode occurs at 1081 cm^{-1} [222]. Two red nitrido bromo complexes $K_2[OsNBr_5]$ and $K[OsN(H_2O)Br_4]$ have been isolated from the reaction of $K[OsO_3N]$ with hydrobromic acid. In the aqua complex the water molecule is *trans* to the nitrido group[221]. The nitrido complexes $K[OsN(H_2O)(CN)_4]$, $K[OsN(H_2O)(C_2O_4)_2]$, $K[OsN(H_2O)F_2(OH)_2]$ and $K[OsN(H_2O)(C_2O_4)(OH)_2]$ have been reported. The infrared spectra indicate that the aqua group is *trans* to the nitrogen atom. The compounds are diamagnetic[222].

The tetrammines $[OsO_2(NH_3)_4]X_2$ (X = Cl, NO_3, NO_2; 2X = C_2O_4) have been prepared by the reaction of $K_2[OsO_2(OH)_4]$ and ammonium salts in solution[223]. The diamagnetic ethylenediamine complex $[Os(en–H)_4]I_2$ has been described[211]. The pyridine complex $Ospy_2O_3$ has been obtained by the addition of pyridine and alcohol to a solution of OsO_4 in cyclohexane. Its structure is not known but cyclic esters containing the $>OsO_2py_2$ moiety have been prepared from it[224].

3.12. COMPLEXES OF OSMIUM(VII)

The complexes of Os(VII) are confined to a few oxo complexes which have been recently reported. The compound $K_3[OsO_5]$ has been made; it decomposes in water to OsO_4 and $K_2[OsO_2(OH)_4]$ [225]. The compound $Na_5[OsO_6]$ and the corresponding lithium and barium salts were also made. The compounds were prepared at elevated temperatures. All are black. The complex $LiBa_2[OsO_6]$ was reported to have a moment of 1.44 BM. This suggests that the compound does contain Os(VII) and is not a lattice compound of Os(VIII) and Os(VI).

3.13. COMPLEXES OF OSMIUM(VIII)

The oxofluoro complexes $M[OsO_3F_3]$ (M = K, Cs, Ag) have been prepared by the action of BrF_3 on OsO_4 and the metal halide[159]. The yellow complexes $M_2[OsO_4F_2]$ (M = Rb, Cs) were obtained by adding OsO_4 to a cold saturated solution of MF [226].

Potassium perosmate $K_2[OsO_4(OH)_2]$ can be obtained as deep red crystals, very soluble in water, by the addition of OsO_4 to a concentrated solution of KOH at $-10°$ [145,226]. The infrared spectrum is consistent with a *trans* arrangement of the OH groups[227]. The ammonium, caesium and barium salts are also known; they are unstable in air, losing OsO_4.

Potassium osmiamate $K[OsO_3N]$ was first reported in 1847. It is prepared by adding aqueous ammonia to a solution of $K_2[OsO_4(OH)_2]$; it forms pale yellow crystals, slightly soluble in water. The rubidium and caesium salts are less soluble but the sodium, barium and zinc salts are very soluble. The constitution of the osmiamates was established in 1901 by Werner[228], who showed that the proposed structure $[OsO_2(NO)]^-$ was unlikely on

[221] L. A. Atovyman and G. B. Bokii, *J. Struct. Chem. USSR*, Engl. transl., **1** (1960) 468.
[222] W. P. Griffith, *J. Chem. Soc.* 1965, 3694.
[223] L. Wintrebert, *Ann. chim. Phys.* **28** (7) (1903) 15.
[224] R. Criegee, *Ann.* **522** (1936) 75.
[225] R. Scholder and G. Schatz, *Angew. Chem.* **2** (1963) 264.
[226] F. Krauss and D. Wilken, *Z. anorg. allgem. Chem.* **145** (1925) 151.
[227] W. P. Griffith, *J. Chem. Soc.* 1964, 245.
[228] A. Werner and K. Dinklage, *Ber.* **34** (1901) 2698.

account of (a) the ease of formation of osmiamates, (b) potassium osmiamate liberates nitrogen *in vacuo* above 200°, and (c) $K[OsO_3N]$, upon treatment with halogen acid, is converted to $K[OsNX_5]$ (X = Cl, Br). An X-ray crystal structure determination of $K[OsO_3N]$ showed that the three oxygen atoms and the nitrogen atom lie at the corners of a tetragonal bisphenoid, i.e. a distorted tetrahedron[229]. The infrared and Raman spectra are consistent with this structure[230,231]. The ν(Os–N) mode occurs at 1021 cm^{-1}, indicating that an Os≡N triple bond is present. Similar nitrido complexes are known with Mo(VI) and Re(VII), viz. $[MoO_3N]^{3-}$ and $[ReO_3N]^{2-}$.

The action of t-butylamine on OsO_4 in hexane yields yellow crystals of $O_3Os{=}NC(CH_3)_3$[220]. The orange addition compounds $OsO_4 \cdot NH_3$, $OsO_4 \cdot py$ and $2OsO_4 \cdot C_6H_{12}N_4$ ($C_6H_{12}N_4$ = hexamethylenetetramine) have been reported, but their structures are not known.

4. RHODIUM

4.1. GENERAL CHEMISTRY

Rhodium is a fairly soft, ductile, silver-white metal which is insoluble in aqua regia unless in the form of sponge. It is attacked by fused sodium bisulphate to give a water-soluble sulphate complex which, upon treatment with alkali, yields a precipitate of $Rh(OH)_3$ or, more correctly, the hydrated sesqui-oxide. The hydroxide is soluble in hydrochloric acid; the addition of NH_4Cl to the solution precipitates $(NH_4)_3[RhCl_6]$ which can be reduced to the metal.

The electrode potentials for rhodium are given in Table 22. The oxidation states are listed in Table 23. The valency states I and III are the most important; the other oxidation states are rare and, in some cases, only one compound is known. The trivalent state is the most common. The yellow aqua ion $[Rh(H_2O)_6]^{3+}$ occurs and can be isolated as the perchlorate

TABLE 22. ELECTRODE POTENTIALS FOR RHODIUM [a, b]

Reaction	Potential (V)
$RhCl_6^{3-} + 3e = Rh + 6Cl^-$	0.43
$RhCl_6^{4-} + e = RhCl_6^{3-}$	*ca.* 1.2
$RhO_4^{2-} + 8H^+ + 3e = Rh(III) + 4H_2O$	0.80
$RhO_4^{2-} + 4H^+ + 2e = RhO_2 + 2H_2O$	2.01

[a] W. M. Latimer, *Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd edn., Prentice-Hall, Englewood Cliffs, New Jersey (1952), p. 215.

[b] T. J. Walsh and E. A. Hausman, The Platinum Metals, in *Treatise on Analytical Chemistry*, Part II, Vol. 8 (I. M. Kolthoff and P. J. Elving, eds.), Wiley Interscience, New York (1963), p. 397.

229 F. M. Jaeger and J. E. Zanstra, *Proc. Acad. Sci. Amsterdam* **35** (1932) 610.
230 J. Goubeau, *Angew. Chem.* **5** (1966) 571.
231 L. A. Woodward, J. A. Creighton and K. A. Taylor, *Trans. Faraday Soc.* **56** (1960) 1267.

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The electrode potentials for rhodium are given in Table 22. The oxidation states are listed in Table 23. The valency states I and III are the most important; the other oxidation states are rare and, in some cases, only one compound is known. The trivalent state is the most common. The yellow aqua ion $[Rh(H_2O)_6]^{3+}$ occurs and can be isolated as the perchlorate

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[a] W. M. Latimer, *Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd edn., Prentice-Hall, Englewood Cliffs, New Jersey (1952), p. 215.

[b] T. J. Walsh and E. A. Hausman, The Platinum Metals, in *Treatise on Analytical Chemistry*, Part II, Vol. 8 (I. M. Kolthoff and P. J. Elving, eds.), Wiley Interscience, New York (1963), p. 397.

229 F. M. Jaeger and J. E. Zanstra, *Proc. Acad. Sci. Amsterdam* **35** (1932) 610.
230 J. Goubeau, *Angew. Chem.* **5** (1966) 571.
231 L. A. Woodward, J. A. Creighton and K. A. Taylor, *Trans. Faraday Soc.* **56** (1960) 1267.

TABLE 23. OXIDATION STATES OF RHODIUM

Oxidation state	Coordination number	Examples
Rh(−I)	4	$[Rh(CO)_4]^-$, $[Rh(CO)_2(PPh_3)_2]^-$
	5 (?)	$[Rh(NO)_2Cl]_n$
Rh(0)	6	$Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$
Rh(I)	4	$[Rh(CO)_2Cl]_2$, $Rh(AsPh_3)_2(CO)Cl$, $[Rh(C_2H_4)_2Cl]_2$
	5	$HRh(diphos)_2$, $HRh(PF_3)_4$
Rh(II)	4	$[Rh(MNT)_2]^{2-}$*
	5	$[Rh(OAc)_2]_2$, $[HRh(bipy)_2]^+$
Rh(III)	6	$[Rh(H_2O)_6]^{3+}$, $[Rh(NH_3)_6]^{3+}$, $Rhpy_3Br_3$, $[Rh(NO_2)_6]^{3-}$
Rh(IV)	6	$K_2[RhF_6]$, $Cs_2[RhCl_6]$
Rh(V)	6	$[RhF_5]_4$
Rh(VI)	6	RhF_6

* MNT = maleonitriledithiolate, $C_4N_2S_2^-$.

and in alums. The complexes, especially those with nitrogen donors, resemble those of Co(III). Rhodium(I) occurs with ligands which are π-acceptors. The Rh(I) complexes are mostly square-planar, but some 5-coordinate species are known. Many of the square-planar complexes are of importance in catalysis, since the metal atom can increase its coordination number by accepting ligands in the apical sites.

Thermodynamic data for rhodium and some of its compounds are listed in Table 24.

TABLE 24. THERMODYNAMIC DATA ON RHODIUM AND ITS COMPOUNDS [a]

Substance	State	$\Delta H°$	$\Delta F°$	$S°$
Rh	g	138	127	44.39
Rh	c	0	0	7.6
Rh_2O	c	−22.7	−19.1 [b]	
RhO	c	−21.7	−16.0 [b]	
Rh_2O_3	c	−68.3	−50.0 [b]	
RhCl	c	−16	−12.4 [b]	
$RhCl_2$	c	−36	−26.4 [b]	
$RhCl_3$	c	−56	−39.6 [b]	
$RhCl_6^{3-}$	aq	−207.8	−158.3 [b]	

$\Delta H°$ = standard heat of formation at 25° (kcal mole^{-1}).
$\Delta F°$ = standard free energy of formation at 25° (kcal mole^{-1}).
$S°$ = entropy at 25° (cal deg^{-1}).
g = gaseous; c = crystalline; aq = aqueous solution.

[a] Unless otherwise indicated, values are from the US National Bureau of Standards Circular 500, *Selected Values of Thermodynamic Properties* (1952).

[b] W. M. Latimer, *Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd edn., Prentice-Hall, Englewood Cliffs, New Jersey (1952), p. 215.

4.2. BINARY COMPOUNDS

The halides and chalcogenides are listed in Table 25.

TABLE 25. HALIDES AND CHALCOGENIDES OF RHODIUM

Compound	Colour	Remarks
RhF_6	Black	Melting point 70° [a]
$[RhF_5]_4$	Dark red	Tetrameric, isomorphous with $[RuF_5]_4$, $[OsF_5]_4$ and $[IrF_5]_4$; μ, 2.93 BM [b]
RhF_4	Purplish red	μ, 1.1 BM [c]
RhF_3	Red	Insoluble, very stable; hexagonal close-packed structure [d]
$RhCl_3$	Red	Insoluble; isostructural with $AlCl_3$ [e]
$RhBr_3$	Reddish brown	Insoluble
RhI_3	Black	Insoluble
Rh_2O_3	Brown	Stable to >1000°; corundum lattice
Rh_2S_5	Greyish black	Chemically inert [f]
RhS_2	Greyish black	Pyrites structure [g]
$RhSe_2$	Greyish black	Pyrites structure [h]
$RhTe_2$	Greyish black	Pyrites (at low temp.), $Cd(OH)_2$ (at high temp.) [i]
Rh_2Te_3	Greyish black	Orthorhombic [j]
RhTe	Greyish black	NiAs structure [i]

[a] C. L. Chernick, H. H. Claassen and B. Weinstock, *J. Am. Chem. Soc.* **83** (1961) 3165.
[b] J. H. Holloway, P. R. Rao and N. Bartlett, *Chem. Communs.* (1965) 306.
[c] A. G. Sharpe, *J. Chem. Soc.* 1950, 3444; R. S. Nyholm and A. G. Sharpe, *ibid.* 1952, 3579.
[d] M. A. Hepworth, K. H. Jack, R. D. Peacock and G. J. Westland, *Acta Cryst.* **10** (1957) 63.
[e] H. Barnighausen and K. B. Handa, *J. Less-Common Metals* **6** (1964) 226.
[f] R. Juza, O. Hulsmann, K. Meisel and W. Blitz, *Z. anorg. allgem. Chem.* **225** (1935) 380.
[g] L. Thomassen, *Z. physik. Chem. (Frankfurt)* **4** (1929) 277.
[h] F. Hulliger, *Nature* **204** (1964) 644.
[i] S. Geller, *J. Am. Chem. Soc.* **77** (1955) 2641.
[j] W. H. Zachariasen, *Acta Cryst.* **20** (1966) 334.

Halides

The hexafluoride RhF_6 can be prepared by the reaction fluorine on the metal. It is the least stable hexafluoride of the platinum metals and will react with glass even when dry. The pentafluoride RhF_5 is isomorphous with $[RuF_5]_4$ and is almost certainly tetrameric. It can be obtained by the action of fluorine on RhF_3 under pressure at 400°. The tetrafluoride RhF_4 can be prepared by the reaction of BrF_3 on $RhCl_3$ or $RhBr_3$. It forms an adduct $RhF_4 \cdot 2BrF_3$ which, on being heated, yields the tetrafluoride. It reacts violently with water. The trifluoride RhF_3 can be obtained by the direct fluorination of $RhCl_3$ or RhI_3 at 500–600°. It is quite stable and is not attacked by water, acid or alkali. The hydrates $RhF_3 \cdot 6H_2O$ and $RhF_3 \cdot 9H_2O$ can be isolated from solutions of Rh(III) containing hydrofluoric acid. They are soluble in water and the yellow colour of the solution suggests the presence of the aquated ion $[Rh(H_2O)_6]^{3+}$.

The trichloride $RhCl_3$ is prepared by the action of chlorine on the metal at 300°; the red crystals can be sublimed at 900°. The compound has a structure identical with that of aluminium chloride. It is insoluble in water. However, a water-soluble anhydrous form can be obtained by heating $RhCl_3 \cdot 3H_2O$ at 180° in a stream of dry hydrogen chloride. The trihydrate $RhCl_3 \cdot 3H_2O$ is the most useful starting material for the preparation of

rhodium compounds. A convenient method of preparation is as follows[232]. Rhodium sponge and KCl (2 equiv.) are finely ground together and heated at 550° in a stream of chlorine for 60 min. The red product is extracted with water and the filtered solution of $K_2[Rh(H_2O)Cl_5]$ is treated with just sufficient KOH to precipitate $Rh(OH)_3$, which is washed and dissolved in a minimum of HCl. The solution on evaporation to dryness on a steam bath yields wine red crystals of $RhCl_3 \cdot 3H_2O$.

The tribromide $RhBr_3$ can be obtained from the elements at 300°. Like $RhCl_3$ it is insoluble in water. The soluble dihydrate can be obtained by treating rhodium sponge with HBr and bromine. The triiodide RhI_3 can be obtained by treating $RhBr_3 \cdot 2H_2O$ with potassium iodide.

There is some evidence for the existence of the dichloride $RhCl_2$. It has been reported to be formed when $RhCl_3$ is heated at 950° in a stream of chlorine. Although both the dibromide and diiodide have been reported their existence is doubtful.

Oxide and Hydroxide

The only definite oxide is the sesquioxide Rh_2O_3 which can be obtained by heating the metal or the trichloride in oxygen at 600°. The hydroxide, actually the hydrated sesquioxide $Rh_2O_3 \cdot 5H_2O$, is precipitated from Rh(III) solutions by alkali. The green hydrated dioxide $RhO_2 \cdot 2H_2O$ can be obtained by the addition of alkali to an anodically oxidized solution of Rh(III). Its composition is variable and it may be a peroxide. It dissolves in alkali.

Compounds of Sulphur, Selenium and Tellurium

These are listed in Table 25. They are obtained by heating the elements, or in the case of Rh_2S_5 by heating $RhCl_3$ with sulphur. The latter compound is quite inert and is not attacked by strong acids.

Phosphide

The phosphide RhP_3 has the $CoAs_3$ structure with a planar ring of four phosphorus atoms.

4.3. OXO- AND HYDROXO-HALIDES

The so called "basic rhodium chloride" $Rh(OH)_2Cl \cdot aq.$ can be prepared by the action of hydrochloric acid on $Rh_2O_3 \cdot 5H_2O$; its structure is not known. The hydroxo-fluoride $Rh(OH)_2F$ and the hydroxo-bromide $Rh(OH)_2Br \cdot 2H_2O$ are also known.

4.4. COMPLEXES OF RHODIUM(−I)

The compound $Na[Rh(CO)_2(PPh_3)_2]$ can be obtained by treating $Rh(CO)Cl(PPh_3)_2$ with sodium amalgam[233]. Salts of $[Rh(PF_3)_4]^-$ can be obtained from the hydride $HRh(PF_3)_4$. It is possible that the Rh(−I) anions $[Rh(diphosphine)_2]^-$ and $[Rh(CO)_4]^-$ may be produced from $HRh(diphosphine)_2$ and $HRu(CO)_4$. The nitrosyl complexes $[Rh(NO)_2X]_n$ (X = Cl, Br, I; n = 2 or 4) have been obtained from the reaction of nitric oxide on

[232] S. N. Anderson and F. Basolo, *Inorg. Synth.* 7 (1963) 214.
[233] J. P. Collmann, F. D. Vastine and W. R. Roper, *J. Am. Chem. Soc.* **88** (1966) 5035.

$[Rh(CO)_2X]_2$ [234, 235]; they are probably halogen-bridged. The monomeric nitrosyl complexes $Rh(NO(MPh_3)_3$ (M = P, As, Sb) are also known[234].

4.5. COMPLEXES OF RHODIUM(0)

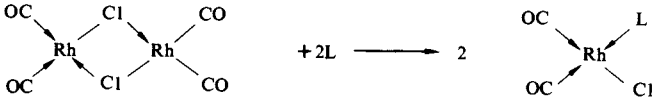
Carbonyls

Rhodium apparently forms three carbonyls: $Rh_2(CO)_8$ (orange; m.p. 76° with decomp.), $Rh_4(CO)_{12}$ (red; decomp. 150°) and $Rh_6(CO)_{16}$ (black; decomp. 220°). There is some doubt about the existence of $Rh_2(CO)_8$ about which there have been no reports apart from that of the discoverers[236]. It can apparently be obtained only when finely divided rhodium (prepared from Na_3RhCl_6 and hydrogen at below 150°) is treated with CO at 280 atm and 200°. Both $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ can be obtained by heating anhydrous $RhCl_3$ and CO at 200 atm for 15 hr in the presence of copper[236]. The temperature appears to have an important effect on the nature of the product. At 50–80° the tetramer is formed, whereas in the range 80–230° the product is $Rh_6(CO)_{16}$.

The infrared spectrum of $Rh_4(CO)_{12}$ displays a band at 1885 cm^{-1}, indicative of bridging CO groups. Preliminary X-ray data show that the structure is similar to that of $Co_4(CO)_{12}$—the metal atoms are at the apices of a tetrahedron; there are two terminal CO groups per metal atom while the remaining four CO groups form bridges between the metal atoms. The hexanuclear carbonyl $Rh_6(CO)_{16}$, originally formulated as $Rh_4(CO)_{11}$, has been shown by an X-ray study[237] to have the rhodium atoms situated at the corners of an octahedron. Each metal atom has two terminal CO groups, while each of the remaining four CO groups bridges three rhodium atoms.

4.6. COMPLEXES OF RHODIUM(I)

The complexes of Rh(I) are quite numerous, but almost exclusively they involve π-bonding ligands. The majority are square-planar but there are also some 5-coordinate complexes. Rhodium(I) complexes are usually prepared by reaction of $RhCl_3 \cdot 3H_2O$ with the ligand. The reducing agent may be the ligand itself, the alcoholic solvent or a specific reducing agent such as stannous chloride. The chloro-bridged carbonyl $[Rh(CO)_2Cl]_2$ is often used as a starting material for the preparation of Rh(I) complexes. The bridge is cleaved by donor ligands:



Carbonyl replacement can occur without splitting of the bridge:

$$[Rh(CO)_2Cl]_2 + 2diene \rightarrow [Rh(diene)Cl]_2$$

An important reaction of square-planar Rh(I) complexes is their ability to add molecules such as H_2 to give octahedral Rh(III) complexes. The complex $RhClCO(PPh_3)_2$ is the

[234] W. Hieber and K. Heinicke, *Z. Naturforsch.* **14B** (1959) 819; *Z. anorg. allgem. Chem.* **316** (1962) 321.
[235] W. P. Griffith, J. Lewis and G. Wilkinson, *J. Chem. Soc.* 1959, 1775.
[236] W. Hieber and H. Lagally, *Z. anorg. allgem. Chem.* **251** (1943) 96.
[237] E. R. Corey, W. Beck and L. F. Dahl, *J. Am. Chem. Soc.* **85** (1965) 1202.

most effective known catalyst for hydroformylation reactions; the reaction may involve a Rh(III) dihydride as an intermediate. The most effective catalyst for the homogeneous hydrogenation of olefins and acetylenes is $RhCl(PPh_3)_3$. The mechanism has been discussed[238]; in solution the complex loses a PPh_3 group to form $RhCl(PPh_3)_2 \cdot$solvent which takes up molecular hydrogen to form *cis*-$H_2RhCl(PPh_3)_2$; the olefin becomes attached in the vacant sixth coordination position and is thereby activated for hydrogenation to occur. The hydrogenated olefin falls off to yield $RhCl(PPh_3)_2 \cdot$solvent. The reactions and catalytic properties of rhodium complexes in solution have been the subject of a review[239].

Complexes of Nitrogen Ligands

The complex $Rh(C_2H_5N)_3I$ (C_2H_5N = ethyleneimine) has been reported to be formed by the reaction of $Rh(C_2H_5N)_3Cl_3$ with silver oxide and iodide ion[240]. Reduction of [Rh $bipy_2Cl_2$]NO_3 with sodium borohydride gives paramagnetic [Rh $bipy_2$]NO_3 (μ, 1.86 BM); however, it may well be a Rh(II) hydride [HRh $bipy_2$]NO_3 [241].

Nitrosyl Complexes

The complexes $Rh(NO)(PPh_3)_2Cl_2$ and $Rh(NO)(OAc)_2$ have been reported[242].

Complexes of Phosphines, Arsines and Stibines

These are numerous and the various types are listed in Table 26. Phosphine complexes containing carbonyl or hydrido groups are discussed under Carbonyl Complexes (p. 1239) and Hydride Complexes (p. 1242), respectively. Of especial interest is the complex $Rh(PPh_3)_3Cl$ which can be obtained by treating $RhCl_3 \cdot 3H_2O$ with triphenylphosphine in alcohol. The complex dissociates in solution:

$$Rh(PPh_3)_3Cl \rightleftarrows Rh(PPh_3)_2Cl + PPh_3$$

The reactivity of this complex in solution and its use in catalysis have been discussed above. In solution the compound undergoes substitution reactions to give $Rh(PPh_3)_2LCl$ (L = py, DMSO, MeCN, C_2H_4, CO); e.g. carbon monoxide reacts readily to yield $RhCO(PPh_3)_2Cl$, which can also be obtained by reaction with aldehydes, dimethylformamide and acetic acid, the CO being abstracted from the organic molecule. In dichloromethane solution it reacts with molecular oxygen to form $Rh(PPh_3)_2(O_2)Cl \cdot \frac{1}{2}CH_2Cl_2$. The analogous arsine complex $Rh(AsPh_3)_2(O_2)Cl$ has also been isolated. In ethereal solution Grignard reagents react to give the organometallic compounds $Rh(PPh_3)_3R$ (R = Me, Ph). The compound $Rh(PPh_3)_3Cl$ also undergoes electrophilic addition reactions: e.g. with methyl iodide it forms the 6-coordinate complex $RhCH_3(PPh_3)_2ClI(CH_3I)$, in which CH_3I is coordinated through the iodine atom. With gaseous HCl it forms $HRh(PPh_3)_2Cl_2$.

It is noteworthy that the diphosphine complex $[Rh(Ph_2PCH_2CH_2PPh_2)_2]Cl$ is inactive and does not react with CO or H_2 under ambient conditions. However, $[Rh(Me_2PCH_2CH_2PMe_2)_2]Cl$ reacts with H_2 in tetrahydrofuran to give

$$cis\text{-}[H_2Rh(Me_2PCH_2CH_2PMe_2)_2]Cl$$

238 J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, *J. Chem. Soc.* A, 1966, 1711.
239 B. R. James, *Coordination Chem. Revs.* **1** (1966) 505.
240 J. Scherzer, K. Phillips, L. B. Clapp and J. O. Edwards, *Inorg. Chem.* **5** (1966) 847.
241 B. Martin, W. R. McWhinnie and G. M. Waind, *J. Inorg. Nucl. Chem.* **23** (1961) 207.
242 W. Hieber and K. Heinicke, *Z. anorg. allgem. Chem.* **316** (1962) 321; S. A. Johnson, H. R. Hunt and H. M. Neumann, *Inorg. Chem.* **2** (1963) 960.

and with CO to give $[RhCO(Me_2PCH_2CH_2PMe_2)_2]Cl$ from which the CO group is easily removed by oxidative addition, as in the following reactions[243]:

$$[RhCO(Me_2PCH_2CH_2PMe_2)_2]Cl + X_2 \rightarrow \textit{trans}\text{-}[(Rh(Me_2PCH_2CH_2PMe_2)_2X_2]Cl$$
$$[RhCO(Me_2PCH_2CH_2PMe_2)_2]Cl + HX \rightarrow \textit{trans}\text{-}[HRh(Me_2PCH_2CH_2PMe_2)_2X]Cl$$

The chloro-bridged complex of pentafluorophenylphosphine, $[Rh\{P(C_6F_5)_3\}_2Cl]_2$ reacts with CO to give $RhCO\{P(C_6F_5)_3\}_2Cl$.

TABLE 26. PHOSPHINE, ARSINE AND STIBINE COMPLEXES OF RHODIUM(I)

Compound		Colour
$Rh\{P(OR)_3\}_3X$ [a]	(X = Cl, Br, I; R = *p*-MeC_6H_4, *p*-ClC_6H_4)	Yellow
$[Rh\{P(OR)_3\}_2SCN]_2$ [a, b]	(R = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4)	Yellow
$Rh\{P(OPh)_3\}_3SCN$ [b]		Yellow
$Rh(PPh_2H)_3Cl$ [c]		Yellow
$Rh(MPh_3)_3X$ [d, e]	(M = P, As, Sb; X = Cl, Br, I)	Orange, red, brown
$Rh(MPh_3)_3SCN$ [b]	(M = P, As, Sb)	Yellow
$[Rh(PPh_3)_2Cl]_2$ [d]		Pink
$[Rh(PPh_3)_2CN]_4$ [f]		Yellow
$[Rh\{P(C_6F_5)_3\}_2Cl]_2$ [g]		Green
$[Rh(Ph_2PCH_2CH_2PPh_2)_2]Cl$ [h]		Yellow
$[Rh(Me_2PCH_2CH_2PMe_2)_2]Cl$ [i]		Yellow
$Rh(NO)(MPh_3)_2Cl_2$ [j]	(M = P, As)	
$Rh(PPh_3)_2LCl$ [d]	(L = py, DMSO, MeCN, C_2H_4)	Yellow
$Rh(PPh_3)_3R$ [k]	(R = Me, Ph)	Orange
$Rh(MPh_3)_2(O_2)Cl$ [l]	(M = P, As)	Light brown
$Rh(PPh_3)_3(SnCl_3)$ [m]		Red
$Rh(PR_3)_2(1\text{-naphthyl})_2Br$ [n]	(PR_3 = PPr^n_3, PEt_2Ph)	Cream
Rh(QAS)X [o] *	(X = Cl, Br, I)	

* QAS = tris(*o*-diphenylarsinophenyl)arsine.
[a] L. Vallarino, *J. Chem. Soc.* 1957, 2473.
[b] M. A. Jennings and A. Wojcicki, *Inorg. Chem.* 6 (1967) 1854.
[c] R. G. Hayter, *Inorg. Chem.* 3 (1964) 301.
[d] J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, *J. Chem. Soc.* A, 1966, 1711.
[e] J. T. Mague and G. Wilkinson, *J. Chem. Soc.* A, 1966, 1736.
[f] D. N. Lawson, M. J. Mays and G. Wilkinson, *J. Chem. Soc.* A, 1966, 52.
[g] R. D. W. Kemmitt, D. I. Nichols and R. D. Peacock, *Chem. Communs.* 1967, 599.
[h] A. Sacco and R. Ugo, *J. Chem. Soc.* 1964, 3274.
[i] J. Chatt and S. A. Butter, *Chem. Communs.* 1967, 501.
[j] W. Hieber and K. Heinicke, *Z. anorg. allgem. Chem.* **316** (1962) 321.
[k] W. Keim, *J. Organometallic Chem.* **8** (1967) P25.
[l] M. C. Baird, D. N. Lawson, J. T. Mague, J. A. Osborn and G. Wilkinson, *Chem. Communs*, 1966, 129.
[m] J. F. Young, R. D. Gillard and G. Wilkinson, *J. Chem. Soc.* 1964, 5176.
[n] J. Chatt and A. E. Underhill, *J. Chem. Soc.* 1963, 2088.
[o] R. J. Mawby and L. M. Venanzi, *Experienta*, Suppl. No. 9 (1964) 240.

Carbonyl Complexes

A list of the known carbonyl complexes is given in Table 27. Three types of carbonyl halide are known. The dimeric carbonyls $[Rh(CO)_2X]_2$ are obtained from the reaction of

[243] J. Chatt and S. A. Butter, *Chem. Communs.* 1967, 501.

TABLE 27. CARBONYL COMPLEXES OF RHODIUM(I)

$[Rh(CO)_2X]_2$ [a]	(X = Cl, Br, I)
$[Rh(CO)_2X]_2$ [b]	(X = NO_3, SCN, RCO_2, $\frac{1}{2}SO_4$)
$[Rh(CO)_2X_2]^-$ [b, c]	(X = Cl, Br, I)
$[RhCOX_2]_2^{2-}$ [c]	(X = Br, I)
$Rh(CO)_2LCl$ [b]	(L = amine)
$Rh(CO)_2$β-diketone [d]	
$RhCO(RNC)_2X$ [e]	(R = aryl; X = Cl, Br)
$[Rh(CO)_2SR]_2$ [f]	(R = Et, Ph)
$RhCO(MR_3)_2X$ [a, g]	(M = P, As, Sb; R = Et, Ph; X = Cl, Br, I, SCN)
$RhCO(SbPh_3)_2Cl$ [h]	
$RhCO(SbPh_3)_3Cl$ [i]	
$RhCO(SbPh_3)_4X$ [j]	(X = Cl, Br)
$RhCO\{P(C_6F_5)_3\}_2Cl$ [k]	
$RhCO\{P(OR)_3\}_2Cl$ [l]	(R = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4)
RhCO(diphos)Cl [m]	
$RhCO(PPh_3)_2SR$ [f]	(R = Et, Ph)
$RhCO(SO_2)(PPh_3)_2Cl$ [n]	
$[Rh(CO)_2(MPh_3)_2]^+$ [m]	(M = P, Sb)
$RhCO(SbPh_3)_3Cl$ [m]	
$RhCO(SbPh_3)_3$β-diketone [d]	
$[Rh(CO)_2PPh_2]_n$ [m]	
$RhCO(M_2Ph_4)_2Cl$ [m]	(M = P, As)
$[RhCOClAsPh_2]_2$ [m]	
$Rh(CO)_2L$ [o]	(L = MeCO═CHC(Me)═NR; R = Ph, *p*-MeC_6H_4, 1-naphthyl)
$Rh(CO)_2(S_2NCR_2)$ [p]	(R = Me, Et)
[RhCO(QAS)]Cl [q]	
$Rh(CO)_2$(fulvene)Cl [r]	
$RhCO(RC{\equiv}CR)Cl$ [s]	(R = Et, Ph)
$Rh(CO)X(MPh_3)_2BX_3$ [t]	(M = P, As; X = Cl, Br)
$[RhCO(SnCl_3)_2Cl]^{2-}$ [u]	

QAS = tris(*o*-diphenylarsinophenyl)arsine.

[a] J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.* 1964, 4200; *Inorg. Synth.* **8** (1966) 211; W. Hieber and H. Lagally, *Z. anorg. allgem. Chem.* **251** (1943) 96.

[b] D. N. Lawson and G. Wilkinson, *J. Chem. Soc.* 1965, 1900.

[c] L. Vallarino, *Inorg. Chem.* **4** (1965) 161.

[d] F. Bonati and G. Wilkinson, *J. Chem. Soc.* 1964, 3156.

[e] R. Ugo and F. Bonati, *Rend. Ist. Lombardo Sci. Lettere A* **98** (1964) 548.

[f] W. Hieber and K. Heinicke, *Z. Naturforsch.* **14B** (1959) 819.

[g] J. Chatt and B. L. Shaw, *Chem. Ind. (London)* 1961, 290; *J. Chem. Soc.* A, 1966, 1437; L. Vallarino, *J. Chem. Soc.* 1957, 2287.

[h] J. T. Mague and G. Wilkinson, *J. Chem. Soc.* A, 1966, 1736.

[i] W. Hieber, H. Heusinger and O. Vohler, *Ber.* **90** (1957) 2425.

[j] R. Ugo, F. Bonati and S. Cenini, *Rend. Ist. Lombardo Sci. Lettere A* **98** (1964) 627.

[k] R. D. W. Kemmitt, D. I. Nichols and R. D. Peacock, *Chem. Communs.* 1967, 599.

[l] L. Vallarino, *J. Chem. Soc.* 1957, 2473.

[m] W. Hieber and F. Volker, *Ber.* **99** (1966) 2614; **100** (1967) 148.

[n] L. Vaska and S. S. Bath, *J. Am. Chem. Soc.* **88** (1966) 1333.

[o] F. Bonati and R. Ugo, *J. Organomet. Chem.* **7** (1967) 167.

[p] F. A. Cotton and J. A. McCleverty, *Inorg. Chem.* **4** (1964) 1398.

[q] R. J. Mawby and L. M. Venanzi, *Experienta*, Suppl. No. 9 (1964) 240.

[r] J. Altman and G. Wilkinson, *J. Chem. Soc.* (1964) 5654.

[s] P. M. Maitlis and S. McVey, *J.Organomet. Chem.* **4** (1965) 254.

[t] P. Powell and H. Nöth, *Chem. Communs.* 1966, 637.

[u] J. F. Young, J. A. Osborn, F. H. Jardine and G. Wilkinson, *Chem. Communs.* 1965, 860.

CO on Rh(III) halides. When treated with HX they yield the anionic carbonyls $[Rh(CO)_2X_2]^-$ which were isolated as the NR_4^+ salts. From this reaction the binuclear anionic species $[RhCOX_2]_2^{2-}$ can be isolated. Treatment of $[Rh(CO)_2Cl]_2$ with AgX yields $[Rh(CO)_2X]_2$ (X = NO_3, SCN, RCO_2, $\frac{1}{2}SO_4$). The red $[RhCOCl_2]_2$ has a chloro-bridged structure in which the planes of the two square-planar coordinated rhodium atoms are inclined at 124°. This structure presumably persists in solution, since the dipole moment has been reported as 1.64*D*. The marked reactivity of this compound has been utilized in the preparation of other Rh(I) complexes (see above).

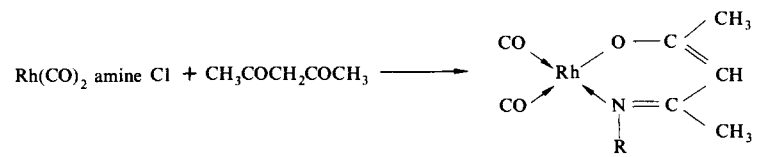
The phosphine, arsine and stibine complexes (Table 27) are obtained by the action of MR_3 (M = P, As, Sb) on $[Rh(CO)_2Cl]_2$ or from MR_3 and $RhCl_3 \cdot 3H_2O$ in alcohol or dimethylformamide. Triphenylstibine gives the octahedral complex $Rh(CO)(SbPh_3)_4X$ (X = Cl, Br). The yellow $RhCO(PPh_3)_2Cl$ has a *trans* configuration and, like $Rh(PPh_3)_3Cl$, is a good catalyst for hydroformylation reactions.

The red–violet acetylacetone complex $Rh(CO)_2$acac can be prepared by refluxing a solution of $RhCl_3 \cdot 3H_2O$ and the β-diketone in dimethylformamide. It reacts with PPh_3 to give $RhCOacacPPh_3$ [244].

The planar complex $Rh(CO)_2$acac is dichroic, suggesting weak metal–metal interaction; a crystal structure determination shows that the Rh–Rh distance is 3.27 Å [245]. Other β-diketone complexes $Rh(CO)_2$β-diketone have been prepared from $[Rh(CO)_2Cl]_2$. They also react with phosphines and arsines with loss of CO to give $RhCOMPh_3$β-diketone (M = P, As). However, $SbPh_3$ gives octahedral complexes $RhCO(SbPh_3)_3$β-diketone. Diolefines such as cycloocta-1,5-diene replace the CO groups in $Rh(CO)_2$β-diketone to give Rh(diene)β-diketone.

Isocyanides and dithiocarbamates react with $[Rh(CO)_2Cl]_2$ to give $RhCO(RNC)_2X$ and $Rh(CO)_2(S_2NCR_2)_2$ respectively. The cationic species $[Rh(CO)_2(RNC)_2]^+$ is also known.

Complexes of ketoimines can be prepared by the following reaction:



However, the reaction is complicated and other products are also formed.

Boron trihalides react with carbonyl phosphine and arsine complexes to give stable, presumably 5-coordinate adducts $RhCOX(MPh_3)_2BX_3$ (M = P, As; X = Cl, Br).

Thiocarbonyl Complexes

The phosphine complex $Rh(PPh_3)_3Cl$ reacts with carbon disulphide at the boiling point to give the orange thiocarbonyl complex $Rh(CS)(PPh_3)_2Cl$ in 50% yield. The latter has a square-planar configuration with the CS ligand bound through the carbon atom. The C–S distance is 1.54 Å, while the Rh–C distance of 1.79 Å indicates π-bonding between metal

[244] Yu. S. Varshavskii and T. G. Cherkasova, *Zh. Neorg. Khim.* **12** (1967) 1709.
[245] N. A. Bailey, E. Coates, G. B. Robertson, F. Bonati and R. Ugo, *Chem. Communs.* 1967, 1041.

and carbon; this is supported by the infrared spectrum. The analogous bromo complex can also be prepared. The complexes yield $Rh(CS)(PPh_3)_2X_3$ (X = Cl, Br) by oxidative addition of halogen in dichloromethane solution at 0°. The C–S stretching frequency occurs at 1298 cm^{-1} in the Rh(I) complexes but shifts to 1355–1362 cm^{-1} in the Rh(III) complexes[246].

Hydride Complexes

These are not very numerous; all are apparently 5-coordinate. The unstable carbonyl hydride $HRu(CO)_4$ (pale yellow, m.p. −10°) was reported to be formed when $RhCl_3 \cdot 3H_2O$ is heated with CO (200 atm, 200°) for 24 hr [236]. Its existence is doubtful.

The trifluorophosphine hydride $HRh(PF_3)_4$ can be prepared by treating a mixture of $RhCl_3$ and copper with PF_3 and H_2 at 170°. The reaction of $Ph_2PCH_2CH_2PPh_2$ (diphos) with $[Rh(CO)_2Cl]_2$ gives $[Rh(diphos)_2]Cl$ which will react with $LiAlH_4$ to give the air-sensitive orange hydride $HRh(diphos)_2$ [247]. The dipole moment of 4.35*D* suggests a trigonal bipyramidal structure similar to that of $HCo(CO)_4$.

The triphenylphosphine hydride $HRhCO(PPh_3)_3$ can be made by treating $RhCO(PPh_3)_2Cl$ with PPh_3 and hydrazine in alcohol[248]. A structure determination showed that this compound has a distorted trigonal bipyramidal configuration; the Rh–C distance is 1.83 Å and the Rh–H distance is 1.60 Å [249]. The compound displays catalytic activity for the hydrogenation of ethylene.

Cyanide Complexes

Only two Rh(I) cyano complexes have been definitely established: a blue polymeric complex $[Rh(CO)_2CN]_n$, prepared from $[Rh(CO)_2Cl]_2$ and KCN, and $[Rh(PPh_3)_2CN]_4$, obtained by treatment of $[Rh(CO)_2CN]_n$ with PPh_3 [250].

π-Complexes

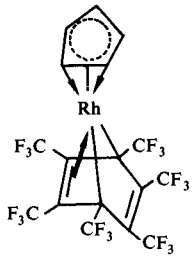
(a) *Cyclopentadienyl complexes.* Three carbonyl complexes are known: viz. $(C_5H_5)Rh(CO)_2$, $[(C_5H_5)Rh(CO)]_3$ and $(C_5H_5)_2Rh_2(CO)_3$, although there is some evidence for the existence of the red dimer $[(C_5H_5)Rh(CO)_2]_2$. The orange monomer $(C_5H_5)Rh(CO)_2$ melts at −11°; it is prepared by the reaction of C_5H_5Na with $[Rh(CO)_2Cl]_2$ [251]. Irradiation of the monomer gives $(C_5H_5)_2Rh_2(CO)_3$, which has one bridging CO group, and $[(C_5H_5)RhCO]_3$. The structure of the trimer is such that the three CO groups bridge the metal atoms, which form an equilateral triangle (Rh–Rh dist., 2.62 Å); the three π-bonded cyclopentadienyl rings are on the opposite side of the triangle to the three CO groups[251].

The brownish-black diamagnetic hydride $HRh_3(C_5H_5)_4$, which is air-stable and soluble in organic solvents, was isolated in low yield from the reaction of $RhCl_3$ with C_5H_5MgBr. The metal atoms form an equilateral triangle; one cyclopentadienyl group is attached to each rhodium atom as in $[(C_5H_5)RhCO]_3$. The fourth cyclopentadienyl ring lies nearly

[246] M. C. Baird and G. Wilkinson, *Chem. Communs.* 1966, 267; 1967, 92; J. L. de Boer, D. Rogers, A. C. Shapski, and P. G. H. Troughton, *ibid.* 1966, 756.
[247] A. Sacco and R. Ugo, *J. Chem. Soc.* 1964, 3274.
[248] S. S. Bath and L. Vaska, *J. Am. Chem. Soc.* **85** (1963) 3501.
[249] Th. Kruck and W. Lang, *Angew. Chem.*, Int. Edn., **4** (1965) 870.
[250] D. N. Lawson, M. J. Mays and G. Wilkinson, *J. Chem. Soc.* A, 1966, 52.
[251] E. O. Fischer and K. Bittler, *Z. Naturforsch.* **16B** (1961) 225; O. S. Mills and E. F. Paulus, *Chem. Communs.* 1966, 815.

parallel to the rhodium triangle on the opposite side to the three other π-bonded C_5H_5 rings. The Rh–Rh distance (2.72 Å) is longer than in $[(C_5H_5)RhCO]_3$ but shorter than in $Rh_6(CO)_{16}$ [252].

The bis(ethylene) complex $(C_5H_5)Rh(C_2H_4)_2$ and the 1,5-hexadiene complex $(C_5H_5)Rh(C_6H_{10})$ are known[253]; in the latter compound the diene behaves as a 2π-ligand. Of a different type are the diene complexes $(C_5H_5)Rh(diene)$ (diene = cyclopentadiene C_5H_6, cyclopentadienylcyclopentadiene $C_5H_5 \cdot C_5H_5$, phenylcyclopentadiene PhC_5H_5, tetrakistrifluoromethylcyclopentadienone $C_5(CF_3)_4O$ and hexakistrifluoromethylbenzene). From physical data it has been inferred that in these complexes the diene behaves as a $(\pi+2\sigma)$ rather than a 2π-ligand[254]. In the case of $(C_5H_5)RhC_6(CF_3)_6$ this was confirmed by an X-ray structure determination which showed that the complex has the structure (V), so that, in effect, it is a Rh(III) complex[255].



(V)

(b) *Arene complexes.* The cationic hexamethylbenzene complex $[Rh(C_6Me_6)_2]^+$, the dimeric 2,3,5,6-tetramethyl-1,4-benzoquinone (tbq) complex $[Rh(tbq)Cl]_2$ and the indene complex $(C_9H_7)Rh(CO)_2$ are known[256].

(c) *Mono-olefin complexes.* The complexes $[Rh(C_2H_4)_2Cl]_2$, $[Rh(C_3H_6)_2Cl]_2$, $Rh(C_2H_4)_2acac$ and $Rh(C_2H_4)(MPh_3)_2Cl$ (M = P, As) are known[238, 253, 257]. Both $[Rh(C_2H_4)_2Cl]_2$ and $Rh(C_2H_4)_2acac$ act as catalysts for the dimerization of ethylene to butenes[258]. The complexes $[Rh(olefin)_2Cl]_2$ (olefin = cyclooctene, cycloheptene and norbornene) have been prepared from $[Rh(C_2H_4)_2Cl]_2$ [259].

(d) *Diolefin complexes.* The diene complexes $[Rh(diene)Cl]_2$ (diene = cycloocta-1,5-diene, cyclooctatetraene, norbornadiene, 1,5-hexadiene, cyclohexa-1,3-diene, dicyclopentadiene, cyclodeca-1,6-diene and 2,5-dimethylhexa-1,5-diene) can be prepared by heating $RhCl_3 \cdot 3H_2O$ with the diolefin[253, 259–262]. The bromo and iodo analogues of the

[252] E. O. Fischer, O. S. Mills, E. F. Paulus and H. Wawersik, *Chem. Communs.* 1967, 643.

[253] R. B. King, *Inorg. Chem.* **2** (1963) 528; R. Cramer, *J. Am. Chem. Soc.* **86** (1964) 217.

[254] R. J. Angelici and E. O. Fischer, *J. Am. Chem. Soc.* **85** (1963) 3733; R. S. Dickson and G. Wilkinson, *J. Chem. Soc.* 1964, 2699.

[255] M. R. Churchill and R. Mason, *Proc. Chem. Soc. (London)* 1963, 365.

[256] E. O. Fischer and H. H. Lindner, *J. Organomet. Chem.* **1** (1964) 307; H. P. Fritz and C. G. Kreiter, *ibid.* **4** (1965) 198; S. McVey and P. M. Maitlis, *Can. J. Chem.* **44** (1966) 2429.

[257] J. F. Harrod and A. J. Chalk, *J. Am. Chem. Soc.* **86** (1964) 1776.

[258] R. Cramer, *J. Am. Chem. Soc.* **87** (1965) 4717; **88** (1966) 2272.

[259] G. Winkhaus and H. Singer, *Ber.* **99** (1966) 3593, 3602, 3610.

[260] J. Chatt and L. M. Venanzi, *J. Chem. Soc.* 1957, 4735.

[261] E. W. Abel, M. A. Bennett and G. Wilkinson, *J. Chem. Soc.* 1959, 3178.

[262] J. C. Trebellas, J. R. Olechowski, H. B. Jonassen and D. W. Moore, *J. Organomet. Chem.* **9** (1967) 153.

cycloocta-1,5-diene complex $[Rh(C_8H_{12})Cl]_2$ have also been prepared[260]. The complex $[Rh(C_8H_{12})Cl]_2$ has a chloro-bridged structure but, unlike in $[Rh(CO)_2Cl]_2$, the two square-coordinated rhodium atoms lie in the same plane. The chloro-bridge is split by donor ligands to give products such as $Rh(C_8H_{12})(C_5H_5)$, $Rh(C_8H_{12})$acac and $[Rh(C_8H_{12})$diamine$]^+$ [260].

An interesting reaction is that of diphenylacetylene with $[Rh(CO)_2Cl]_2$: the product is a complex of 2,3,4,5-tetraphenylcyclopentadienone, viz. $[(Ph_4C_5O)RhCl]_2$, from which $[(Ph_4C_5O)Rh(CO)Cl]_2$, (Ph_4C_5O)RhpyCl, (Ph_4C_5O)Rhacac and $(Ph_4C_5O)RhPPh_3Cl$ were prepared[263].

The 5-coordinate butadiene complex $Rh(C_4H_6)_2Cl$ was obtained from $RhCl_3$ and butadiene in alcohol[264]. The fluoro-olefin complexes $Rh(C_2F_4)(MPh_3)_2Cl$ (M = P, As) have been described[265].

The reaction of cyclohexa-1,3-diene with $[Rh(CO)_2Cl]_2$ yields an addition complex $Rh_2(CO)_4Cl_2$(diene) in which the diene acts as a bridge[259].

(e) *Acetylene complexes.* The complexes $Rh(RC{\equiv}CR)(CO)Cl$ (R = Et, Ph), $Rh(PhC{\equiv}CPh)(MPh_3)_2Cl$ (M = P, As) and $Rh(F_3CC{\equiv}CCF_3)(PPh_3)_2Cl$ have been reported[265, 266].

(f) *Allyl complexes.* Allyl alcohol reacts with $RhCl_3 \cdot 3H_2O$ to give $Rh_2Cl_2(CH_2{=}CHCH_2OH)_4$, which catalyses the decomposition of allyl alcohol to propene and propionaldehyde. The complexes $Rh(MPh_3)_3X$ (M = As, Sb) react with allyl halides under nitrogen to yield $Rh_2(MPh_3)_2X_2(C_3H_4R)$ (R = H, Me; X = Cl, Br) [267].

Complexes with Metal–Metal Bonds

The yellow halogen-bridged anionic complexes $[NEt_4]_4[Rh_2X_2(SnCl_3)_4]$ have been prepared. The presence of Rh–Sn bonds is confirmed by the infrared spectra: whereas the ν(M–X) modes shift to lower frequencies when X is changed from Cl to Br, the band at 209 cm^{-1} remains unaltered and this band has been assigned as ν(Rh–Sn) [268].

The 5-coordinate complexes $Rh(C_7H_8)_2(SnCl_3)$ (C_7H_8 = norbornadiene), $Rh(C_7H_8)(MPh_3)_2(SnCl_3)$ (M = P, As, Sb) [269] and $Rh(CO)_2(PPh_3)_2(SnMe_3)$ have been reported[233]. The complexes $(C_5H_5)Rh(C_8H_{12})$ and $(C_5H_5)Rh(C_7H_8)$ form 1:1 adducts with HgX_2 (X = Cl, Br) [270].

4.7. COMPLEXES OF RHODIUM(II)

Rhodium(II) has the d^7 configuration; consequently the complexes would be expected to be paramagnetic. The number of genuine Rh(II) complexes is small; earlier reports of pyridine complexes of Rh(II) have been shown to be in error.

Complexes of Oxygen Ligands

Hydrated Rh_2O_3 reacts with carboxylic acids to form deep green diamagnetic complexes $[Rh(RCO_2)_2]_2$. Their diamagnetism indicates strong metal–metal interaction. The acetato

[263] P. M. Maitlis and S. McVey, *J. Organomet. Chem.* 4 (1965) 254.
[264] L. Porri, A. Lionetti, G. Allegra and A. Immirzi, *Chem. Communs.* 1965, 336.
[265] J. T. Mague and G. Wilkinson, *J. Chem. Soc.* A, 1966, 1736.
[266] J. Mays and G. Wilkinson, *J. Chem. Soc.* 1965, 6629.
[267] H. C. Volger and K. Vrieze, *J. Organomet. Chem.* 9 (1967) 527, 537.
[268] D. M. Adams and P. J. Chandler, *Chem. Ind. (London)* 1965, 269.
[269] J. F. Young, R. D. Gillard and G. Wilkinson, *J. Chem. Soc.* 1964, 5176.
[270] D. J. Cook, J. L. Dawes and R. D. W. Kemmitt, *J. Chem. Soc.* A, 1967, 1547.

complex $[Rh(CH_3CO_2)_2H_2O]_2$ has been shown to have the copper acetate structure[271]. The complexes readily add two ligand molecules—with π-bonding ligands such as PPh_3 the adducts are orange to red but with water and other oxygen ligands the adducts are green or blue.

The halogeno-acetates $[Rh(RCO_2)_2EtOH]_2$ (R = Cl_3C, $ClCH_2$, F_3C, F_2ClC, $BrCH_2$ and Cl_2CHCH_2) are also known. Some of the compounds lose alcohol at 120° and will readily form $[Rh(RCO_2)_2L]_2$ (L = py, PPh_3) [272]. The green formato complex $[Rh(HCO_2)_2]_2 \cdot \frac{1}{2}H_2O$ readily forms adducts with NH_3 and pyridine[273].

Complexes of Sulphur Ligands

These are confined to the green square-planar complexes $[NR_4]_2[Rh(MNT)_2]$ (MNT = maleonitriledithiolate) which are paramagnetic (μ, 1.9 BM). The complexes formally contain Rh(II), but the assignment of a definite oxidation state to the metal atom in dithiolate complexes is not very meaningful because of the special nature of these ligands[209].

Complexes of Nitrogen Ligands

The paramagnetic compound, originally formulated as $[Rh(bipy)_2]NO_3$, may be the Rh(II) hydride $[HRh(bipy)_2]NO_3$ [241]. Some complexes of dimethylglyoxime (DMGH) have been reported; however, there exists the possibility that they may be hydride complexes of Rh(III). Among these are $H_2[Rh(DMG)_2Cl_2]$ and $[Rh(DMG)_2PPh_3]_2$; both are diamagnetic[274].

Phosphine Complexes

The paramagnetic blue–green, air-stable complex $Rh\{P(o\text{-}MeC_6H_4)_3\}_2Cl_2$ (μ, 2.3 BM; θ, 10°) is isomorphous with the corresponding palladium compounds[275].

π-Complexes

Rhodocene $Rh(C_5H_5)_2$ has been prepared but it is unstable[276]. The red cationic complex $[Rh(C_6Me_6)_2]^{2+}$ can be isolated as its $[PtCl_6]^{2-}$ and $[PF_6]^-$ salts; they are weakly paramagnetic (μ, 1.3 BM) and quite stable[256].

4.8. COMPLEXES OF RHODIUM(III)

The trivalent state is the most common for rhodium and, indeed, until recently few compounds in other oxidation states had been established with certainty. The complexes resemble those of Co(III), being almost invariably octahedral; on the other hand, except in a few instances, they differ from those of Co(III) in that they cannot be reduced to

[271] M. A. Porai-Koshits and A. S. Antsyshkina, *Proc. Acad. Sci. USSR Chem. Sect.*, Engl. transl., **146** (1962) 902.

[272] G. Winkhaus and P. Ziegler, *Z. anorg. allgem. Chem.* **350** (1967) 51.

[273] I. I. Chernyaev, E. V. Shenderetskaya, A. G. Maiorova and A. A. Koryagina, *Zh. Neorg. Khim.* **11** (1966) 2575.

[274] S. A. Shchepinov, E. N. Sal'nikova and M. L. Khidekel, *Izvest. Akad. Nauk SSSR, Ser. Khim.*, 1967, 2129.

[275] M. A. Bennett, R. Bramley and P. A. Longstaff, *Chem. Communs.* 1966, 806.

[276] E. O. Fischer and H. Wawersik, *J. Organomet. Chem.* **5** (1966) 559.

Rh(II) complexes. Rhodium(III) has the d^6 configuration and all the compounds are diamagnetic, including $K_3[RhF_6]$, whereas the analogous cobalt complex is high spin. The electronic (visible) spectra of Rh(III) complexes display two bands toward the blue end of the spectrum, although in many instances only the first spin-allowed ligand-field band ($^1A_{1g} \rightarrow {}^1T_{1g}$) is observed, since the second band is often obscured by charge-transfer transitions. The bands are responsible for the yellow, red or reddish-brown colours of Rh(III) compounds.

The yellow aqua ion is formed from hydrated Rh_2O_3 and acid and the yellow perchlorate $[Rh(H_2O)_6](ClO_4)_3$ can be obtained by evaporation of solutions of $RhCl_3$ in $HClO_4$. The compound is isomorphous with $[Co(NH_3)_6](ClO_4)_3$. The aqua ion also occurs in the yellow sulphate $Rh_2(SO_4)_3 \cdot 18H_2O$ and in Rh(III) alums.

Halide, Thiocyanate and Cyanide Complexes

The ions $[RhX_6]^{3-}$ are known where X = F, Cl, Br, SCN and CN but apparently not for X = I. Other ions of the type $[RhX_5]^{2-}$, $[RhX_7]^{4-}$, $[Rh_2X_9]^{3-}$ and $[Rh_2X_{10}]^{4-}$ (X = Cl or Br) have been reported.

The insoluble fluoro complex $K_3[RhF_6]$ can be made by fusing $K_3[Rh(NO_2)_6]$ with KHF_2. In the solid-state reflectance spectrum the ligand field bands are not obscured by charge-transfer absorption. The two principal bands in the range 20,000–30,000 cm^{-1} are the two expected spin-allowed transitions ($^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$), while a third transition appears as a shoulder at 37,000 cm^{-1} [277]. The compound $K_2[RhF_5]$ can be obtained by fusion of $K_3[RhF_6]$ with KHF_2; the anion is probably either dimeric or polymeric.

The red sodium, potassium and caesium salts of $[RhCl_6]^{3-}$ have been prepared in a variety of ways. When $[Rh(H_2O)_6]^{3+}$ is heated with dilute HCl, various chloro-aqua species $[RhCl_n(H_2O)_{6-n}]^{(3-n)+}$ are formed; the spectra and the kinetics have been studied[278]. The pentachloro complex $K_2[RhCl_5]$—which is most probably the chloro-bridged dimer $K_4[Rh_2Cl_{10}]$—can be obtained by heating $K_2[RhCl_5(H_2O)]$ at 250°. The complex $[NMe_4]_3[Rh_2Cl_9]$ can be obtained as brown crystals[279]; the anion probably has a tris-μ-chloro-bridged structure. The red aqua salts $M_2[RhCl_5(H_2O)]$ (M = K, Rb, Cs, NH_4) have also been obtained.

The reddish-brown $K_3[Rh_2Br_9]$ appears to be the principal product obtained from solutions of $RhBr_3$ and KBr. The species $[RhBr_6]^{3-}$ has been isolated only as the sodium salt $Na_3[RhBr_6] \cdot 12H_2O$. With solutions of $RhBr_3$ other alkali metal bromides and organic bases yield salts of $[Rh_2Br_9]^{3-}$ and $[RhBr_5]^{2-}$ or $[Rh_2Br_{10}]^{4-}$; other less well-characterized species have been reported[280]. The green complex $Cs_2[RhBr_5(H_2O)]$ is also known[280].

The red thiocyanato complex $K_3[Rh(SCN)_6]$ has been shown by ^{14}N magnetic resonance, infrared and X-ray studies to contain *S*-bonded thiocyanato groups[209]. The orange $Rh(SCN)_3 \cdot nH_2O$ is precipitated by KCN from acid solutions of $RhCl_3$. The pale yellow $K_3[Rh(CN)_6]$ has been obtained by fusion of KCN with $(NH_4)_3[RhCl_6]$. It cannot be obtained by the action of KCN on $RhCl_3 \cdot nH_2O$ or on a solution of $RhCl_3$.

[277] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam (1968).

[278] W. C. Wolsey, C. A. Reynolds and J. Kleinberg, *Inorg. Chem.* **2** (1963) 463; W. Robb and G. M. Harris, *J. Am. Chem. Soc.* **87** (1965) 4472.

[279] A. Gutbier and H. Bertsch, *Z. anorg. allgem. Chem.* **129** (1923) 67.

[280] P. Poulenc, *Ann. Chim.* **4** (11) (1935) 567, 648.

Complexes of Oxygen Ligands

Apart from the aqua ion (mentioned above), a number of complexes are known with oxygen donors. The rhodites $M^{II}Rh_2O_4$ (M^{II} = Mg, Mn, Cu, Zn, Cd) and $M^{III}RhO_3$ (M^{III} = Fe, Cr) have been obtained by high-temperature reactions. The former have spinel and the latter have ilmenite structures.

The red nitrate $(Rh(NO_3)_3 \cdot 2H_2O$ was reported in 1860 to be obtained from $Rh_2O_3 \cdot nH_2O$ and HNO_3; nothing is known of its structure but it is probably complex. Various yellow hydrates of $Rh_2(SO_4)_3$ are known. The red sulphate $Rh_2(SO_4)_3 \cdot 6H_2O$, obtained by evaporation of the yellow solutions at 100°, gives no precipitate with $BaCl_2$ and is no doubt complex. Repeated evaporations of a solution of Cs–Rh alum yields $Cs[Rh(SO_4)_2] \cdot H_2O$ which is probably also complex. Treatment of acid solutions of $Rh_2(SO_4)_3$ with $NaBiO_3$ yields a blue solution which has been claimed to contain Rh(IV) but no definite product was isolated. Selenates are also known in red and yellow forms.

No Rh(III) formate or acetate has been definitely established; the only compounds of rhodium containing these anions involve Rh(II). Various complexes of ethylenediaminetetraacetic acid are known and some have been resolved into their optical antimers; the circular dichroism of $[Rh(PDTA)(H_2O)]^-$ ($PDTAH_4$ = 1,2-propylenediaminetetraacetic acid) has been studied[281].

Alkali metal salts of the tris-oxalato anion $[Rh(C_2O_4)_3]^{3-}$ can be obtained from the reaction of oxalates on solutions of $RhCl_3$. The potassium salt $K_3[Rh(C_2O_4)_3] \cdot 4\frac{1}{2}H_2O$ has been optically resolved and from proton magnetic resonance data it has been concluded that the solid compound is actually $K_6[Rh(C_2O_4)_2(C_2O_4H)(OH)][Rh(C_2O_4)_3] \cdot 8H_2O$ and that the OH^- and $C_2O_4H^-$ groups are mutually *cis* and hydrogen-bonded[282].

Yellow *cis*- and *trans*-$K[Rh(C_2O_4)_2(H_2O)_2]$ are known. The green *cis*-$K_3[Rh(C_2O_4)_2Cl_2]$ can be obtained by treating the *cis*-diaqua complex with KCl and the orange *trans*-$K_3[Rh(C_2O_4)_2Cl_2]$ can be obtained by heating a solution of the *cis*-dichloro isomer[283].

Complexes of Rh(III) have been reported with citric, tartaric, aspartic and glutamic acids[284].

The acetylacetonato complex $Rh(acac)_3$ has been resolved chromatographically and the optical antimers upon chlorination, bromination, nitration and acetylation, were found to retain their optical activity[285]. The complex of trifluoroacetylacetone has also been resolved. The compound $RhCl(hfa)_2 \cdot 3H_2O$ (hfaH = hexafluoroacetylacetone) upon sublimation yields the chloro-bridged dimer $[Rh(hfa)_2Cl]_2$ [286]. Tris(β-diketone) complexes of dibenzoylmethane and *p,p'*-dinitrodibenzoylmethane have been prepared by heating $Rh(acac)_3$ with the β-diketone in a high-boiling solvent[287]. The tropolone complex $Rh(C_7H_5O_2)_3$ has been described[288].

[281] F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.* **82** (1960) 4823; R. D. Gillard and G. Wilkinson, *J. Chem. Soc.* 1964, 1368; R. D. Gillard, *Spectrochim. Acta* **20** (1964) 1431.

[282] A. L. Porte, H. S. Gutowsky and G. M. Harris, *J. Chem. Phys.* **34** (1961) 66.

[283] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.* 1964, 870.

[284] F. Pantani, *Ric. Sci. Rend.*, Ser. A, **4** (1964) 41; H. Frye, C. Luschak, and D. Chinn, *Z. Naturforsch.* **22b** (1967) 268.

[285] J. P. Collman, R. P. Blair, R. L. Marshall and L. Slade, *Inorg. Chem.* **2** (1963) 577; J. P. Collman, R. L. Marshall, W. L. Young and C. T. Sears, *J. Org. Chem.* **28** (1963) 1449.

[286] S. C. Chattoraj and R. E. Sievers, *Inorg. Chem.* **6** (1967) 408.

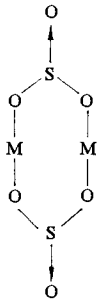
[287] L. Wolf, E. Butter and H. Weinelt, *Z. anorg. allgem. Chem.* **306** (1960) 87.

[288] E. L. Muetterties and C. M. Wright, *J. Am. Chem. Soc.* **87** (1965) 4706.

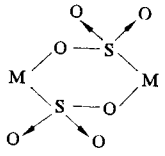
The dimethylsulphoxide complexes $RhX_3(DMSO)_3$ (X = Cl, I) are known. It has been found that $RhCl_3$ catalyses the aerial oxidation of dimethylsulphoxide to dimethylsulphone. However, the complex $H[RhCl_4(DMSO)_2]\cdot 2DMSO$ is more active than $RhCl_3$ itself[289].

Complexes of Sulphur and Selenium Ligands

The thiocyanate complex has already been mentioned. The sulphito complex $K_3[Rh(SO_3)_3]\cdot 2H_2O$ can be obtained by treating $K_3[RhCl_6]$ with $KHSO_3$. The infrared spectra of this and the analogous Co(III) complex indicate that bridging sulphito groups



(VI)



(VII)

are present as in (VI) or (VII), although structure (VII) seems more likely. However, when the SO_3 group is unidentate, as in $[Rh(NH_3)_3(SO_3)_3]^{3-}$ and $[Rh(NH_3)_2(SO_3)_4]^{5-}$, it is *S*-bonded[209]. The fact that amine-sulphito complexes of Co(III) are yellow and those of Rh(III) and Ir(III) are colourless, indicates that SO_3^{2-} has a high position in the spectrochemical series, comparable with that of NH_3 [209].

The thiosulphato complex $Na_3[Rh(NH_3)_2(S_2O_3)_3]$ can be prepared from $[RhCl_6]^{3-}$, $Na_2S_2O_3$ and ammonia. Treatment of *trans*-$[Rhen_2Cl_2]Cl$ with $Na_2S_2O_3$ yields $Na[Rhen_2(S_2O_3)_2]$. In these compounds the thiosulphato group is almost certainly unidentate and *S*-bonded as in other heavy metal complexes[209].

Thiourea has been claimed to stabilize Rh(IV) in solution, but this seems unlikely since thiourea reduces Cu(II) to Cu(I), Au(III) to Au(I), Pt(IV) to Pt(II) and Te(IV) to Te(II). The Rh(III) complexes $[Rh(thu)_6]Cl_3$, $[Rh(thu)_5Cl]Cl_2$ and $[Rh(thu)_3Cl_3]$ can be obtained by heating a solution of $[RhCl_6]^{3-}$ with thiourea (thu)[209].

The dialkyl sulphide and selenide complexes $RhX_3(SEt_2)_3$, (X = Cl, Br, I), $Rh_2Br_6(SEt_2)_4$, $RhCl_3(SMe_2)_3$ and $RhCl_3(SeR_2)_3$ (R = Me, Et) have been prepared[209].

A number of complexes are known with bidentate sulphur ligands. The monothio derivative of dibenzoylmethane, viz. 3-mercapto-1,3-diphenylprop-2-en-1-one, PhC(SH)=CHCOPh(LH), forms the stable red complex RhL_3; the M–O stretching mode occurs at 498 cm^{-1} and ν(M–S) at 389 cm^{-1} [290]. Complexes of dialkyl and diaryl dithiophosphates, $Rh\{(RO)_2PS_2\}_3$ (R = alkyl, aryl), diethyldiselenophosphate $Rh\{(RO)_2PSe_2\}_3$, thiosemicarbazide $Rh\{HN{=}C(S)NHNH_2\}_3$, dithiocarbamates $Rh(R_2NCS_2)_3$ (R = Me, Et, Bu^n) and 2,2′-di(aminoethyl)sulphide $[Rh\{S(CH_2CH_2NH_2)_2\}_2]^{3+}$

[289] Trocha-Grimshaw and H. B. Henbest, *Chem. Communs.* 1968, 1035.
[290] S. H. H. Chaston and S. E. Livingstone, *Austral. J. Chem.* **20** (1957) 1065.

have been prepared and their electronic spectra have been discussed[291]. Quinoline-8-thiol gives the stable $Rh(C_9H_6NS)_3$ [292]. The dithiooxalate complex $KCa[Rh(C_2S_2O_2)_3]$ has been resolved and is optically stable[209].

1,2-Dithiocyanatoethane forms the halogen-bridged complexes $RhX_3(SCNCH_2CH_2NCS)$ (X = Cl, Br, I), in which the ligand is *S*-bonded. The bridges are readily split by unidentate ligands[293].

Complexes of Nitrogen Ligands

The ammine complexes of Rh(III) are quite numerous; the coordination number is always 6 and the complexes are of every type from the hexammine $[Rh(NH_3)_6]^{3+}$ to $[RhNH_3X_5]^{2-}$, the series being completed by the hexahalides $[RhX_6]^{3-}$.

Hexammines. The colourless $[Rh(NH_3)_6]Cl_3$ can be made by heating $[Rh(NH_3)_5Cl]Cl_2$ with aqueous ammonia in a sealed tube; salts of other anions have been also prepared. However, the corresponding pyridine complex is not known. The diamine complexes $[Rhen_3]Cl_3$, $[Rhpn_3]Cl_3$ (pn = 1,2-diaminopropane), and the corresponding tris-complexes of 1,2-diaminopentane, 1,2-diaminohexane, 1,2-diaminocyclopentane and 1,2-diaminocyclohexane are known. The ethylenediamine complex $[Rhen_3]^{3+}$ was among the first 6-coordinate complexes to be resolved into their optical antimers by Werner in 1912 [294]. The 2,2′-bipyridyl complex $[Rhbipy_3](ClO_4)_3$ is known[294] but not the phenanthroline complex. Bis-ligand complexes are known with the tridentate nitrogen donors 1,2,3-triaminopropane[294], diethylenetriamine[295] and 2,2′,2″-terpyridyl[296].

Pentammines. The complexes $[Rh(NH_3)_5X]^{2+}$ (X = Cl, Br, I, SCN, NCS, N_3, NO_3, ONO, NO_2, OH and RCO_2), $[Rh(NH_3)_5SO_4]^+$ and $[Rh(NH_3)_5H_2O]^{3+}$ are known; they range from colourless to orange (X = I). The chloropentammine $[Rh(NH_3)_5Cl]Cl_2$ can be prepared by heating a solution of $RhCl_3$ with ammonium chloride and ammonia or ammonium carbonate. It is but sparingly soluble in water and almost insoluble in strong hydrochloric acid. Consequently, it can be used to separate rhodium from palladium, iridium and platinum. The aquapentammine can be obtained by the action of silver oxide on $[Rh(NH_3)_5Cl]^{2+}$. The colourless nitrosopentammine $[Rh(NH_3)_5ONO]Cl_2$ can be obtained from $[Rh(NH_3)_5H_2O]Cl_3$ and nitrous acid at 0°; it isomerizes to the colourless nitro complex $[Rh(NH_3)_5NO_2]Cl_2$.

Tetrammines. The complexes $[Rh(NH_3)_4Cl_2]Cl$, $[Rhpy_4X_2]X$, $[Rhbipy_2X_2]X$ (X = Cl, Br) and $[Rhphen_2Cl_2]Cl$ are known; all are *trans*. The complex *trans*-$[Rhbipy_2Br_2][RhbipyBr_4]$ is also known. Both *cis*- and *trans*- isomers of $[RhL_2Cl_2]Cl$ (L = en, bipy, tetramethylethylenediamine, ½ triethylenetetramine) have been isolated and their rates of hydrolysis in acid and alkaline solution have been measured[297]. The tetradentate N_4 ligands 1,4,7,10-tetraazacylododecane and 1,4,8,11-tetraazaundecane form *cis*-$[RhLCl_2]^+$ (L = tetramine)[298].

The pyridine complex *trans*-$[Rhpy_4Cl_2]Cl$ is readily prepared by the addition of alcohol and pyridine to an aqueous solution of $[RhCl_6]^{3-}$. It is a useful starting material for the

[291] C. K. Jørgensen, *J. Inorg. Nucl. Chem.* **24** (1962) 1571; *Mol. Phys.* **5** (1962) 485.
[292] J. Bankovskis, G. Mezarups and A. Ievins, *Zh. Anal. Khim.* **17** (1962) 721.
[293] D. C. Goodall, *J. Chem. Soc.* A, 1967, 203.
[294] N. V. Sidgwick, *The Chemical Elements and their Compounds*, Clarendon Press, Oxford (1950), p. 1522.
[295] G. W. Watt and B. J. McCormick, *Inorg. Chem.* **4** (1965) 143.
[296] C. M. Harris and E. D. McKenzie, *J. Inorg. Nucl. Chem.* **25** (1963) 171.
[297] S. A. Johnson, F. Basolo and R. G. Pearson, *J. Am. Chem. Soc.* **85** (1963) 1741.
[298] B. Bosnich, R. D. Gillard, E. D. McKenzie and G. A. Webb, *J. Chem. Soc.* A, 1966, 1331.

preparation of *trans*-$[RhL_4Cl_2]^+$ (L = neutral unidentate ligand). The kinetics of formation of *trans*-$[Rhpy_4Cl_2]^+$ in the presence of a catalyst have been studied. All the reagents which catalyze the reaction are reducing agents capable of producing Rh(III) hydrides and it has been suggested that the active intermediate is *trans*-$[HRhpy_3Cl_2]$, which reacts with pyridine to give *trans*-$[Rhpy_4Cl_2]^+$ [229], and not a Rh(I) complex, as had been proposed by earlier workers.

A study of *N*-, *NN'*-, *NN*-, *NNN'*- and *NNN'N'*-methyl substituted ethylenediamine complexes of Rh(III) showed that substitution of more than one methyl group gave only bis-*trans*-dichloro species, due to steric effects of the methyl groups. A correlation was found between the nephelauxetic series and ν(Rh–N) [300].

Sulphamide $(NH_2)_2SO_2$ readily loses two protons to form the anionic complex $Na[Rh\{(NH)_2SO_2\}_2(H_2O)_2]$, which was resolved through its α-phenylethylamine salt and shown to possess a *cis*-configuration[294].

Triammines. The triammine type complexes $Rh(NH_3)_3X_3$ (X = Cl, Br, I, NO_2), $Rh(RNH_2)_3Cl_3$ (R = Et, Ph), $Rhpy_3Cl_3$ (X = Cl, Br, I, NO_3, NO_2, SCN), $RhpyX(C_2O_4)$ (X = Cl, Br) and $Rh(C_2H_4NH)_3X_3$ (C_2H_4NH = ethyleneimine; X = Cl, Br) are known. The colours range from yellow to red, except that the nitro compounds are colourless. Geometric isomerism is possible and the 1,2,3- and 1,2,6- isomers of $Rhpy_3X_3$ (X = Cl, Br, SCN) and $RhdienCl_3$ (dien = diethylenetriamine) have been obtained[301, 302].

Diammines. The diammine series is represented by $Na_3[Rh(NH_3)_2(S_2O_3)_3]$—in which one thiosulphato group is presumably bidentate—*cis*- and *trans*-$pyH[Rhpy_2Cl_4]$, $pyH[Rhpy_2Br_4]$, $NH_4[Rhpy_2(NO_2)_4]$, *cis*- and *trans*-$Ag[Rhpy_2Cl_3NO_3]$ and *cis*- and *trans*-$[Rhpy_2Cl_3H_2O]$[280, 294].

Monoammines. These are confined to the red $K_2[RhNH_3Cl_5]$ and $(pyH)_2[RhpyBr_5]$ which are not very stable[280, 294]. The red acetonitrile complex $M_2[Rh(MeCN)Cl_5]$ (M = NH_4, Cs, Ag) can be obtained from $Na_3[RhCl_6]$, NH_4Cl and acetonitrile[303].

Complexes containing deprotonated ethylenediamine and diethylenetriamine, viz. $[Rhen_2(en–H)]I_2$, $[Rhen(en–H)_2]I$, $[Rh(en–H)_3]$, $[Rh(dien–H)_2]I$ and $[Rh(dien–H)(dien–H)_2]$, have been prepared by the reaction of KNH_2 on $[Rhen_3]I_3$ and $[Rhdien_3]I_3$ in liquid ammonia[295, 304].

Some complexes are known with the α-diimine ligands 2,2'-bipyridyl, 2,2',2''-terpyridyl and 1,10-phenanthroline. The colourless $[Rh(bipy)_3]Cl_3$ and $[Rh(terpy)_2]Cl_3$ have been obtained by fusion of $RhCl_3$ with the heterocyclic base. Other salts of these cations have also been prepared. The complexes $[Rh(bipy)_2Cl_2]Cl$, $[Rh(bipy)_2Br_2]Br$, $[Rh(bipy)_2I_2]I$ and $[Rh(phen)_2Cl_2]Cl$ are known; they have the *trans* configuration[296]. The tris-phenanthroline complex is not known.

The colourless hexanitro complex $K_3[Rh(NO_2)_6]$ can be obtained by heating a solution containing $K_3[RhCl_6]$ and KNO_2. Other alkali metal salts are known. No nitrosyl complexes of Rh(III) have been established with certainty.

The dimethylglyoxime (DMGH) complexes $[Rh(DMG)_3]$ and $NH_4[Rh(DMG)_2X_2]$ (X = Cl, Br, I) and some other less well-established complexes have been reported[305].

[299] R. D. Gillard, J. A. Osborn, P. B. Stockwell and G. Wilkinson, *Proc. Chem. Soc.* 1964, 284.
[300] G. W. Watt and P. W. Alexander, *J. Am. Chem. Soc.* **89** (1967) 1814.
[301] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.* 1964, 1224; 1965, 1951.
[302] H. H. Schmidtke, *Z. anorg. allgem. Chem.* **339** (1965) 103.
[303] B. F. G. Johnson and R. A. Walton, *J. Inorg. Nucl. Chem.* **28** (1966) 1901.
[304] G. W. Watt and J. K. Crum, *J. Am. Chem. Soc.* **87** (1965) 5366.
[305] F. P. Dwyer and R. S. Nyholm, *J. Proc. Roy. Soc. NS Wales* **78** (1944) 266; **79** (1945) 126.

The blue phthalocyanine complex RhPcCl ($PcH_2 = C_{32}H_{18}N_8$) was obtained by fusing $RhCl_3$ with phthalonitrile[193]. Other Rh(III) porphyrins have been prepared from $[Rh(CO)_2Cl]_2$ [306].

Phosphine and Arsine Complexes

Tertiary phosphines and arsines react with $RhCl_3$ in alcohol to give the yellow neutral complexes $Rh(MR_3)Cl_3$ (M = P, As; R = alkyl, aryl) [307]. The values of the dipole moments (~ 7 *D*) indicate that these compounds have the 1,2,6 or *trans* configuration. However, both *cis* (1,2,3) and *trans* (1,2,6) isomers of $Rh(PR_3)_3Cl_3$ (R = PEt_2H, PPh_2H) have been prepared[308]. The bromo complex *trans*-$Rh(PPr^n_3)_3Cl_3$ was also isolated[307]. The dimeric complexes $Rh_2(MEt_3)_4Cl_6$ (M = P, As) and $Rh_2(AsEt_3)_3X_6$ (X = Cl, Br) can also be obtained[307]. No doubt the former possess a dichloro-bridged structure, but whether the latter contain a trihalogeno bridge is less certain.

The diarsine complexes $[Rh\{o\text{-}C_6H_4(AsMe_2)_2\}X_2]X$ (X = Cl, Br, I) have been prepared[309], but the only diphosphine complex reported is the hydride $[HRh(Ph_2PCH_2CH_2PPh_2)_2Cl]Cl$ [247]. The tridentate ligand *bis*(*o*-diphenylarsinophenyl)-phenylarsine (TAS) and the quadradentate tris(*o*-diphenylarsinophenyl)arsine (QAS) form the complexes $[Rh(TAS)Cl_3]$ and $[Rh(QAS)X_2]X$ (X = Cl, Br, I) [309].

The arsenic–sulphur ligand dimethyl-*o*-methylthiophenylarsine, *o*-$MeSC_6H_4AsMe_2$ (As–S), forms the complexes $[Rh(As\text{–}S)_2X_2][Rh(As\text{–}S)X_4]$ and $[Rh(As\text{–}S)_2I_2]^+$ [310]. The arsenic–nitrogen ligand *o*-dimethylaminophenyldimethylarsine, *o*-$Me_2NC_6H_4AsMe_2$ (As–N), and the arsenic–oxygen ligand *o*-methoxyphenyldimethylarsine, *o*-$MeOC_6H_4AsMe_2$ (As–O), give the octahedral complexes $[Rh(As\text{–}N)_2Cl_3]$ and $[Rh(As\text{–}O)_2Cl_3]$ in which one arsine ligand is bidentate and the other is unidentate, being coordinated via the arsenic atom only. In the former the Rh–As (chelated) distance is 2.34 Å, while the Rh–As (unidentate) distance is considerably longer (2.53 Å) [311].

Carbonyl Complexes

The dimeric carbonyl fluoride $[Rh(CO)_2F_3]_2$ has been prepared by the reaction of RhF_4 with CO [312]. The carbonyl iodide $[NBu_4][Rh(CO)I_4]$ was obtained by heating a solution of $[NBu_4][Rh(CO)_2I_2]$ with HI in methanol[313]. Quite a number of carbonyl complexes of Rh(III) containing phosphines, arsines, or stibenes are known. The Rh(I) carbonyl $Rh(CO)Cl(MR_3)_2$ (M = P, As, Sb; R = aryl) can be oxidized by treatment with halogen in carbon tetrachloride solution to yield the octahedral Rh(III) carbonyls $Rh(CO)Cl(MR_3)_2X_2$ (X = Cl, Br, I) [313, 314]. The tribromo carbonyl $Rh(CO)Br_3(PPh_3)_2$ can be obtained in a similar manner. The Rh(I) carbonyl $Rh(CO)Cl(PBu_3)_2$ will undergo oxidative addition with methyl chloride or iodide to give $Rh(CO)Me(PBu_3)_2ClX$ (X = Cl, I) [315]. Similarly, acetyl bromide reacts with $Rh(CO)Br(PEt_2Ph)_2$ to give $Rh(CO)Br_2(PEt_2Ph)_2(CH_3CO)$ [314].

[306] E. B. Fleischer and N. Sadasivan, *Chem. Communs.* 1967, 159.
[307] J. Chatt, N. P. Johnson and B. L. Shaw, *J. Chem. Soc.* 1964, 2508.
[308] R. G. Hayter, *Inorg. Chem.* **3** (1964) 301.
[309] R. J. Mawby and L. M. Venanzi, *Experientia*, Suppl. No. 9, 1964, 240.
[310] B. Chiswell and S. E. Livingstone, *J. Chem. Soc.* 1960, 3181.
[311] G. Bombieri, R. Graziani, C. Panattoni and L. Volponi, *Chem. Communs.* 1967, 977, 1284.
[312] D. W. A. Shap, *Proc. Chem. Soc.* (*London*) 1960, 317.
[313] L. Vallarino, *Inorg. Chem.* **4** (1965) 161; *J. Inorg. Nucl. Chem.* **8** (1958) 288.
[314] J. Chatt and B. L. Shaw, *J. Chem. Soc.* A, 1966, 1437.
[315] R. F. Heck, *J. Am. Chem. Soc.* **86** (1964) 2796.

Thiocarbonyl Complexes

The Rh(I) thiocarbonyl complexes $Rh(CS)X(PPh_3)_2$ can be oxidized by halogen to give $Rh(CS)X_3(PPh_3)_2$ [246].

Hydride Complexes

The complex *trans*-$K_2[HRh(CN)_4H_2O]$ can be obtained by the action of excess KCN on $[Rh(CO)_2Cl]_2$ [250]. The Rh(I) complexes $Rh(MPh_3)_3Cl$ (M = P, As, Sb) will undergo oxidative addition of HCl in solution to give the Rh(III) hydrides $HRh(MPh_3)_3Cl_2$ [316].

The reaction of hydrogen gas on $Rh(PPh_3)_3X$ (X = Cl, Br, I) in chloroform solution produces the dihydrides $H_2Rh(PPh_3)_2X$ [238, 316]. It has been suggested that the complexes are octahedral in solution with a solvent molecule attached to the sixth coordination site. The arsine and stibine complexes $H_2Rh(AsPh_3)_2Cl$ and $H_2Rh(SbPh_3)_2Cl$ can also be prepared. The chloro-bridged dimer $[H_2Rh(PPh_3)_2Cl]_2$ can be obtained by passing hydrogen into a solution of $[Rh(PPh_3)_2Cl]_2$ in dichloromethane[238].

Alkyl and Aryl Complexes

The Rh(I) complex $Rh(PPh_3)_3Cl$ undergoes an unusual addition reaction with methyl iodide to give the Rh(III) complex $RhMe(PPh_3)_2ClI(MeI)$ in which the methyl iodide is coordinated through the iodine atom. The MeI ligand can be replaced by CO [317]. The dimethyl sulphide complex $Rh(SMe_2)_3Cl_3$ reacts with the Grignard reagent in benzene to give $Rh_2Me_4I_2(SMe_2)_3$ which has an iodo-bridged structure; it has been suggested that one SMe_2 group is bridging but this seems rather unlikely. The cyclopentadienyl complex $Rh(C_5H_5)Me_2(SMe)$ was also obtained[318]. The similar phosphine complex $Rh(C_5H_5)Me(PPh_3)$ has been reported[319]. The compound $RhClIMe(PBu^n_3)_2CO$ is known; it takes up CO to give the acetyl complex $RhClI(MeCO)(PBu^n_3)_2CO$ [315]. The ethyl complex $Cs[RhEtCl_3(H_2O)_2]$ has been reported[258].

Reaction of perfluoroalkyl iodides RI (R = CF_3, C_2F_5, C_3F_7) with cyclopentadienyl rhodium carbonyl $Rh(C_5H_5)(CO)_2$ yields the octahedral Rh(III) compounds $Rh(C_5H_5)R(CO)I$. The monomeric presumably 5-coordinate species $Rh(\alpha\text{-naphthyl})_2Br(PR_3)_2$ and some acyl phosphine-carbonyl complexes are also known[314, 315].

π-Complexes

(a) *Cyclopentadienyl complexes.* The bis-cyclopentadienyl Rh(III) ion $[Rh(C_5H_5)_2]^+$ occurs as the nitrate and perchlorate. The dimeric $[Rh(C_5H_5)Br_2]_2$ reacts with pyridine to give $[Rh(C_5H_5)Br_2py]$ [254]. The carbonyl complex $Rh(C_5H_5)(CO)_2$ undergoes oxidative addition of iodine to give $Rh(C_5H_5)(CO)_2I_2$ [320].

(b) *Olefin complexes.* Few olefin complexes of Rh(III) are known and they are not very stable.

(c) *Allyl complexes.* The tris-allyl complex $Rh(C_3H_5)_3$ has the allyl groups π-bonded to the metal. The delocalized allylic system $CH_2{:::}CH{:::}CH_2$, like NO, acts as a three-electron

[316] A. Sacco, R. Ugo and A. Moles, *J. Chem. Soc.* A, 1966, 1670.
[317] M. C. Baird, D. N. Lawson, J. T. Mague, J. A. Osborn and G. Wilkinson, *Chem. Communs.* 1966, 129.
[318] H. P. Fritz and K. E. Schwartzhans, *J. Organomet. Chem.* **5** (1966) 283.
[319] A. Kasahara, T. Izumi and K. Tanaka, *Bull. Chem. Soc. Japan* **40** (1967) 699.
[320] R. B. King, *Inorg. Chem.* **1** (1962) 82.

donor, or if considered as an anion, as a four-electron donor. Consequently the allyl group behaves in a similar manner as the six-electron donor cyclopentadienyl ion. Other known π-allyl complexes include $Rh(RC_3H_4)Cl_2(PPh_3)_2$ (R = H, Me), $[Rh(C_3H_5)_2py_2]^+$, $Rh(C_5H_5)(C_3H_5)_2$ and $Rh(C_5H_5)Cl(C_3H_5)$. The complex $Rh(C_5H_5)(C_3H_5)_2$ is considered to contain a π- and a σ-bonded allyl group[321].

The reaction of acetylene with $HRhCl_2(PPh_3)_3$ yields the σ-vinyl complex $Rh(CH{=}CH_2)Cl_2(PPh_3)_2$ which will react with CO to give $Rh(CH{=}CH_2)Cl_2(CO)(PPh_3)_2$[317].

Complexes with Metal–Metal Bonds

Some air-stable compounds containing Rh–Hg bonds have been prepared from $HRh(AsMePh_2)_3X_2$ (X = Cl, Br) and mercuric salts. They are of the type $YHgRh(AsMePh_2)_3X_2$ (Y = F, Cl, Br, I, OAc)[322].

4.9. COMPLEXES OF RHODIUM(IV)

The quadrivalent state is not common for rhodium and few compounds are known, whereas iridium forms a considerable number of compounds in this oxidation state.

The complex halides $K_2[RhF_6]$ and $Cs_2[RhCl_6]$ are known. The former is prepared by the action of F_2 or BrF_3 on $K_3[RhCl_6]$. The rubidium and caesium salts have also been prepared. Their magnetic moments are *ca.* 2.0 BM at room temperature, showing the presence of one unpaired electron $(t_{2g})^5$. These yellow salts are completely hydrolysed by water[323].

The dark green paramagnetic chloro complex $Cs_2[RhCl_6]$ is precipitated when a solution of $Cs_3[RhCl_6]$ is treated with ceric sulphate. It is decomposed by water to Rh(III) with the liberation of chlorine.

Sodium rhodate(IV) Na_2RhO_3 can be obtained by heating rhodium metal with sodium carbonate.

4.10. COMPLEXES OF RHODIUM(V)

The only complex known is the dark red fluoro compound $Cs[RhF_6]$ which was obtained from $[RhF_5]_2$ and CsF in iodine pentafluoride solution[324].

4.11. COMPLEXES OF RHODIUM(VI)

Although the trioxide has not been isolated, potassium rhodate(VI), K_2RhO_4, was reported by Claus in 1860 to be produced by the action of chlorine on a solution of RhO_2 in concentrated potassium hydroxide. The compound was isolated as blue crystals. The existence of this compound has not been fully established.

[321] J. Powell and B. L. Shaw, *Chem. Communs.* 1966, 236, 323.
[322] R. S. Nyholm and K. Vrieze, *J. Chem. Soc.* 1965, 5331.
[323] E. Weise and W. Klemm, *Z. anorg. allgem. Chem.* **272** (1953) 211.
[324] J. H. Holloway, P. R. Rao and N. Bartlett, *Chem. Communs.* (1965) 306.

5. IRIDIUM

5.1. GENERAL CHEMISTRY

Iridium has the distinction of having the highest specific gravity of all the elements, being just slightly more dense than osmium. It is brittle and considerably harder than platinum, but its hardness when annealed is inferior to that of osmium (see Table 1, p. 1167). It is quite noble and is not attacked by aqua regia. The powdered metal reacts with oxygen at red heat to form the dioxide, but in massive form only a film of the dioxide is formed. Iridium is attacked by chlorine at red heat and by a mixture of potassium hydroxide and potassium nitrate on fusion, the latter treatment giving the dioxide IrO_2. If chlorine is passed over a heated mixture of iridium sponge and potassium chloride, black crystals of $K_2[IrCl_6]$ are produced. The metal is attacked by hydrochloric acid only in the presence of a strong oxidizing agent such as $NaClO_3$ at 120°.

A few electrode potentials for iridium are given in Table 28. Examples of compounds in the various oxidation states are listed in Table 29. As with rhodium, the valency states I and III are important, but in addition iridium forms a number of stable compounds with halogen and oxygen donors in which the oxidation state is IV. The other valency states are confined to a few compounds. With few exceptions, phosphorus, arsenic and sulphur donors reduce Ir(IV) to Ir(III).

TABLE 28. ELECTRODE POTENTIALS FOR IRIDIUM [a, b]

Reaction	Potential (V)
$IrC_6^{3-} + 3e = Ir + 6Cl^-$	0.77
$IrC_6^{2-} + e = IrCl_6^{3-}$	1.02
$IrO_4^{2-} + 8H^+ + 3e = Ir(III) + 4H_2O$	1.16
$IrO_4^{2-} + 4H^+ + 2e = IrO_2 + 2H_2O$	1.61

[a] W. M. Latimer, *Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd edn., Prentice-Hall, Englewood Cliffs, New Jersey (1952), p. 217.

[b] T. J. Walsh and E. A. Hausman, The Platinum Metals, in *Treatise on Analytical Chemistry*, Part II, Vol. 8 (I. M. Kolthoff and P. J. Elving, eds.), Wiley Interscience, New York (1963), p. 397.

Unlike rhodium, iridium does not form an aquated cation. Iridium(III) forms cationic, neutral and anionic complexes with a variety of ligands; the coordination number is invariably 6. All Ir(III) complexes are kinetically inert, whereas most anionic complexes of Rh(III) are labile.

Square-planar Ir(I) complexes resemble those of Rh(I) and occur with carbon monoxide, olefins and tertiary phosphines and arsines as ligands. These complexes are able to undergo oxidative addition reactions to give 6-coordinate Ir(III) complexes. Of particular importance is the compound $Ir(CO)Cl(PPh_3)_2$, which will undergo a variety of reactions,

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[a] W. M. Latimer, *Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd edn., Prentice-Hall, Englewood Cliffs, New Jersey (1952), p. 217.

[b] T. J. Walsh and E. A. Hausman, The Platinum Metals, in *Treatise on Analytical Chemistry*, Part II, Vol. 8 (I. M. Kolthoff and P. J. Elving, eds.), Wiley Interscience, New York (1963), p. 397.

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TABLE 29. OXIDATION STATES OF IRIDIUM

Oxidation state	Coordination number	Examples
Ir(−II)	3 (?)	$Ir(NO)_2PPh_3$
Ir(−I)	4	$K[Ir(PF_3)_4]$
Ir(0)	4 (?)	$Ir_4(CO)_{12}$
Ir(I)	4	$Ir(CO)Cl(PPh_3)_2$
	5	$HIr(CO)(PPh_3)_3$
Ir(II)	4	$Ir(CO)_2Cl_2$
	5	$[Ir(CO)_2I_3]^-$
Ir(III)	5	$H_3Ir(AsPh_3)_2$
	6	$[Ir(NH_3)_5Br]^{2+}$, $[IrCl_6]^{3-}$, $H_3Ir(AsPh_3)_3$
Ir(IV)	6	$[IrCl_6]^{2-}$
Ir(V)	6	$[IrF_6]^-$
Ir(VI)	6	IrF_6

many of which are important in catalysis, e.g. the homogeneous reduction of acetylene by molecular hydrogen.

Thermodynamic data for iridium and some of its compounds are listed in Table 30.

TABLE 30. THERMODYNAMIC DATA ON IRIDIUM AND ITS COMPOUNDS [a]

Substance	State	$\Delta H°$	$\Delta F°$	$S°$
Ir	g	165	154	46.25
Ir	c	0	0	8.7
IrCl	c	−22.3	−19.8 [b]	
$IrCl_2$	c	−42.8	−33.7 [b]	
$IrCl_3$	c	−61.5	−45.6 [b]	
$IrCl_6^{3-}$	aq	−186.4 [b]	−134.7 [b]	
$IrCl_6^{2-}$	aq	−155.0	−111.2 [b]	
IrF_6	liq	−130		
IrO_2	c	−40.1	−28.0 [b]	
IrS_2	c	−30	−30.4 [b]	
Ir_2S_3	c	−51	−49.8 [b]	34.3 [b]

[a] Unless otherwise indicated, values are from the US National Bureau of Standards Circular 500, *Selected Values of Thermodynamic Properties* (1952).

[b] W. M. Latimer, *Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd edn., Prentice-Hall, Englewood Cliffs, New Jersey (1952), p. 217.

5.2. BINARY COMPOUNDS

The halides and chalcogenides are listed in Table 31.

TABLE 31. HALIDES AND CHALCOGENIDES OF IRIDIUM

Compound	Colour	Remarks
IrF_6	Yellow	Melting point 44°; boiling point 53°; octahedral; μ 2.90 BM
$[IrF_5]_4$	Yellow	Melting point 104°; isomorphous with $[RuF_5]_4$; μ 1.3 BM
IrF_3	Black	Hexagonal close packed structure
$IrCl_3$	Red	Octahedral; from $Ir+Cl_2$ at 500°
$IrBr_3$	Reddish brown	
IrI_3	Dark brown	From Ir_2O_3+HI
IrCl (?)	Dark red	
IrBr (?)	Dark brown	
IrI (?)	Black	
IrS_3	Greyish black	From $IrCl_3+S$ at 600° (sealed tube)
$IrSe_3$	Greyish white	From $IrCl_3+Se$ at 600° (sealed tube)
$IrTe_3$	Dark grey	From $IrCl_3+Te$ at 700° (sealed tube)
IrO_2	Black	Rutile lattice; stable to 1100°
IrS_2	Grey	By heating Ir+S; pyrites type lattice
$IrSe_2$	Grey	From $IrSe_3+H_2$ at 600°
$IrTe_2$	Grey	From $IrTe_3+H_2$ at 600°
Ir_2O_3	Brown	By heating $K_2[IrCl_6]+Na_2CO_3$; dec. > 400°
Ir_2S_3	Brown	From $Ir_2O_3+H_2SO_4+H_2S$
Ir_2Se_3	Black	From $IrCl_3+H_2Se$
IrS (?)	Deep blue	By heating IrS_2 in CO_2

Halides

The hexafluoride IrF_6 can be prepared by direct fluorination of iridium metal at 270°; it is isomorphous with OsF_6 [325]. The magnetic moment is 2.90 BM at room temperature and 2.7 BM at 90°K. The compound is decomposed by water with the liberation of ozone. The pentafluoride is tetrameric and is isomorphous with $[RuF_5]_4$. It was prepared by reaction of fluorine and iridium at 380°. The moment is 1.3 BM at 293° but falls to 0.7 BM at 90°K [326]. The tetrafluoride does not seem to exist, although it had been reported, but the product was actually the pentafluoride. Reports of the other tetrahalides IrX_4 (X = Cl, Br, I) are also probably erroneous. The trifluoride IrF_3 can be prepared by reducing the hexafluoride with iridium metal[51].

The trichloride $IrCl_3$ can be obtained by heating the metal in a stream of chlorine at a temperature above 450°. Two red forms of the compound have been reported[327]. Both forms are insoluble in water and dissolve only with difficulty in aqua regia to form $[IrCl_6]^{2-}$. Water-soluble hydrates are known. The dark green $IrCl_3 \cdot 3H_2O$ has been used as a starting material for various complexes. It can be obtained by heating the oxychloride $Ir(OH)Cl_2 \cdot 3H_2O$ in hydrogen chloride[328]. When dissolved in water the hydrated trichloride gives an acidic dark green solution.

[325] G. J. Westland and P. L. Robinson, *J. Chem. Soc.* 1956, 4481.
[326] N. Bartlett and P. R. Rao, *Chem. Communs.* 1965, 253.
[327] D. Babel and P. Deigner, *Z. anorg. allgem. Chem.* **339** (1965) 57.
[328] F. Krauss and H. Gerlach, *Z. anorg. allgem. Chem.* **143** (1925) 125, 268, 277.

The reddish-brown anhydrous tribromide $IrBr_3$ has been obtained by treating the so called "dibromide" with bromine[328]. An improved method for the preparation of anhydrous $IrBr_3$ has been recently reported: iridium metal is heated with bromine in sealed ampoules at 8 atm and 570°; the product is a greyish-brown powder[329]. Various hydrated forms of the tribromide have been reported; the composition of these products seems a little uncertain. If the hydrated sesquioxide $Ir_2O_3 \cdot nH_2O$ is dissolved in hydrobromic acid, a blue solution is produced from which the olive-green tetrahydrate $IrBr_3 \cdot 4H_2O$ can be obtained. The water is lost at 100° [328]. The monohydrate $IrBr_3 \cdot H_2O$ and the compounds $IrBr_3 \cdot 3HBr \cdot 3H_2O$ and $IrBr_3 \cdot HBr \cdot H_2O$ have also been reported. The latter two compounds may be the free acids $(H_3O)_3[IrBr_6]$ and $H_3O[IrBr_4]$, but their structures are unknown.

If the sesquioxide $Ir_2O_3 \cdot nH_2O$ is treated with hydriodic acid, the deep yellow trihydrate $IrI_3 \cdot 3H_2O$ is obtained. This compound is converted at 120° into the monohydrate $IrI_3 \cdot H_2O$ which when heated *in vacuo* at 200–250° yields the anhydrous triiodide as dark brown crystals. The anhydrous compound is only slightly soluble in water but dissolves in hot alkaline solution[328].

The dibromide $IrBr_2$ was reported to be formed by heating $IrBr_3$ in a stream of HBr at 440°. The product is a reddish-brown powder, insoluble in water and acids[328]. Similarly, the diiodide IrI_2 was reported to be formed when IrI_3 is heated in HI at 330° [328]. It is doubtful whether these products are actually Ir(II) halides and further work is necessary to establish their existence. The Ir(I) halides IrX (X = Cl, Br, I) have also been reported and, although their existence has not been unequivocally established, it seems likely that they are genuine Ir(I) compounds. The chloride IrCl was reported to be formed as a sublimate when the trichloride is heated to 770°; it forms copper-red crystals (sp.gr. 10.18) which sublime in chlorine at 790° and above 798° decompose to yield the metal. The compound is insoluble in acids and alkalis[330]. The monobromide IrBr is obtained by heating $IrBr_3$ in an atmosphere of HBr to 485°. It is dark brown and stable in the cold and can be sublimed at 500°. It is very slightly soluble in water, acids and alkalis[328]. The monoiodide IrI is prepared by heating IrI_3 or IrI_2 in an atmosphere of HI to 355°. It is black and resembles IrBr[328]. In view of the low oxidation state of iridium in these compounds, their stability is surprising, and a further investigation of these monohalides is warranted.

Chalcogenides

The only definitely established oxides are the dioxide IrO_2 and the sesquioxide Ir_2O_3. The tetroxide IrO_4 has been reported as the final oxidation state of the metal, but no definite compound was isolated; its existence seems very unlikely. The trioxide IrO_3 was reported to be able to be made by heating the metal with KOH and KNO_3 or with Na_2O_2. However, the product could never be obtained free from alkali and the oxygen content was always less than the theoretical. It is a powerful oxidizing agent and the substance may well be a peroxide. The evidence suggests that IrO_3 does not exist in the solid state but can exist in the vapour state at *ca.* 1200° [331].

The dioxide IrO_2 can be obtained by heating iridium powder in air or oxygen. It can also be obtained by treating a solution of $[IrCl_6]^{2-}$ with alkali and then dehydrating the product. The pure dioxide and its hydrate were obtained by the careful addition of alkali

[329] N. I. Kolbin and V. M. Samoilov, *Zh. Neorg. Khim.* **12** (1967) 2526.
[330] L. Wöhler and S. Streicher, *Ber.* **46** (1913) 1577.
[331] W. E. Bell, M. Tagami and R. E. Inyard, *J. Phys. Chem.* **70** (1966) 2048.

to a boiling solution of $[IrCl_6]^{2-}$ until the brown solution just turned blue. The resulting blue precipitate can be dried *in vacuo* to a bluish-black powder which corresponds to $Ir(OH)_4$ or $IrO_2 \cdot 2H_2O$. Under nitrogen this product is completely dehydrated at 350° to yield black IrO_2 [328]. The hydroxide $Ir(OH)_4$ is insoluble in alkali but dissolves in HCl to form $[IrCl_6]^{2-}$ and in HBr to give $[IrBr_6]^{2-}$.

The anhydrous sesquioxide can be obtained in the anhydrous form by heating $K_3[IrCl_6]$ with sodium carbonate. The hydroxide $Ir(OH)_3$ is precipitated by the addition of potassium hydroxide to a solution of $K_3[IrCl_6]$ in an atmosphere of carbon dioxide. The precipitate ranges in colour from yellowish green to bluish black and tends to be colloidal. The sesquioxide is less stable than the dioxide and cannot be obtained quite pure, since the hydrated form always retains some adsorbed alkali and oxygen begins to be evolved above 400° and a mixture of IrO_2 and the metal results. The hydroxide is slightly soluble in alkali and dissolves in mineral acids but nitric acid oxidizes it to the dioxide.

The compounds IrS_3, $IrSe_3$ and $IrTe_3$ have been obtained by heating $IrCl_3$ with excess chalcogen in evacuated tubes[332]. The sulphide is particularly inert and is unaffected by aqua regia. The selenide and telluride are attacked only slowly by boiling aqua regia. It is open to question whether these compounds can be regarded as containing Ir(VI) since S–S, Se–Se and Te–Te bonds may be involved.

The disulphide IrS_2 can be prepared from the elements, while the diselenide $IrSe_2$ and the ditelluride $IrTe_2$ have been prepared by reduction of $IrSe_3$ and $IrTe_3$ with hydrogen at 600° [332]. Iridium sesquisulphide Ir_2S_3 can be obtained by heating the disulphide or as a precipitate obtained by passing hydrogen sulphide into an acid solution of Ir_2O_3. The sesquiselenide Ir_2Se_3 can be made from the elements at red heat or by the passage of hydrogen selenide into a hot solution of $IrCl_3 \cdot 3H_2O$. It is particularly stable, being unattacked by nitric acid and dissolving but slowly in aqua regia.

The monosulphide IrS has been reported as a deep blue inert substance obtained by heating the disulphide in carbon dioxide[333]. The arsenide $IrAs_3$ has the $[CoAs_3]_4$ structure with four arsenic atoms in a ring; $IrSb_3$ is similar.

5.3. OXO- AND HYDROXO-HALIDES

The Ir(VI) oxofluoride $IrOF_4$ was reported to be formed in small amounts when IrF_6 came into contact with glass or traces of moisture. However, later work showed that the product was a mixture and almost certainly does not contain $IrOF_4$ [325].

The deep blue Ir(IV) compound $Ir(OH)_3Cl$ is reported to be formed by the hydrolysis of $[IrCl_6]^{2-}$ [334].

When gaseous hydrogen chloride reacts with $Ir(OH)_4$ at room temperature, the product is a dark green hygroscopic solid $Ir(OH)Cl_2 \cdot 3H_2O$, which can be dehydrated to the monohydrate $Ir(OH)Cl_2 \cdot H_2O$ by heating in a stream of hydrogen chloride at 210° [328]. These hydrates readily dissolve in water to give an acidic dark green solution which may contain the acid $H_3O[IrCl_2(OH)_2(H_2O)_2]$. The corresponding bromo compounds $Ir(OH)Br_2 \cdot 3H_2O$ and $Ir(OH)Br_2 \cdot H_2O$ are known; they are green[328].

[332] L. Wöhler, K. Weald and H. G. Krall, *Ber.* **66** (1933) 1638.
[333] U. Anthony, *Gazz. chim. ital.* **23** (1893) 143, 190.
[334] E. Ogawa, *J. Chem. Soc. Japan* **50** (1929) 239.

5.4. COMPLEXES OF IRIDIUM(−II)

The action of nitric oxide on the hydride $H_3Ir(PPh_3)_2$ yields the violet nitrosyl complex $Ir(NO_2)PPh_3$, which has a magnetic moment of 1.4 BM [335]. If the nitrosyl group is considered as NO^+, then this compound formally contains Ir(−II).

5.5. COMPLEXES OF IRIDIUM(−I)

The trifluorophosphine complex $K[Ir(PF_3)_4]$ can be obtained by treating the hydride $HIr(PF_3)_4$ with potassium amalgam in ether[79, 249].

Several diamagnetic nitrosyl complexes have been reported[335]. The brown compounds $Ir(NO)_2X(PPh_3)_2$ (X = Cl, Br, I) were obtained by the reaction of the Ir(−II) complex $Ir(NO)_2(PPh_3)_2$ with lithium halide. The low frequency for ν(N–O) (1540–1490 cm^{-1}) suggest that in these three complexes the NO groups may be bridging. Treatment of $[H_2Ir(PPh_3)_3]ClO_4$ with NO yields the violet cationic nitrosyl complex $[Ir(NO)_2(PPh_3)_2]ClO_4$. Triphenylphosphine will replace one of the NO groups in this compound to give the orange neutral complex $Ir(NO)(PPh_3)_3$. When the hydride $HIr(CO)(PPh_3)_3$ is treated with NO, the orange nitrosyl carbonyl $Ir(NO)(CO)(PPh_3)_2$ is produced[335].

5.6. COMPLEXES OF IRIDIUM(0)

The zerovalent state occurs in carbonyls and in the rather curious compound $Ir(NH_3)_5$, if this be the correct formulation.

Pentammineiridium(0) has been reported to be formed as a yellow substance when $[Ir(NH_3)_5Br]Br$ is treated with potassium in liquid ammonia[336]. Its diamagnetism suggests that it may be the Ir(I) hydride $HIr(NH_3)_5$.

Two carbonyls have been reported: viz. $[Ir(CO)_4]_n$, where n is probably 2, and $Ir_4(CO)_{12}$. These carbonyls were first prepared by the carbonylation of Ir(III) halides for 24 to 48 hr at 350 atm. Temperatures of 140°, 120° and 100° were required for the chloride, bromide and iodide respectively. The copper lining of the autoclave acted as a halogen acceptor. When $[IrX_6]^{3-}$ and $[IrX_6]^{2-}$ salts were used, temperatures of 170–200° and the addition of excess copper or silver were required. A mixture of the two carbonyls was always obtained. Separation was effected by use of the greater solubility of $[Ir(CO)_4]_n$ in ether and carbon tetrachloride[337].

The tetracarbonyl $[Ir(CO)_4]_n$ is greenish yellow. Although its existence has been questioned, an improved method for its preparation has been described[338]. It appears to be unstable and little is known about it. However, it has been suggested that, unlike $Co_2(CO)_8$, $[Ir(CO)_4]_n$ contains only a metal–metal bond and no bridging CO groups[339].

The yellow tricarbonyl $Ir_4(CO)_{12}$ sublimes at 210° in an atmosphere of carbon dioxide. It is tetrameric with the iridium atoms occupying the corners of a tetrahedron; there are no bridging carbonyl groups[339]. The infrared spectrum is in accordance with a structure having no bridging CO groups[162].

[335] L. Malatesta, M. Angoletta and G. Caglio, *Angew. Chem.*, Int. Edn., **2** (1963) 739.
[336] G. W. Watt, E. P. Helvenston and L. E. Sharif, *J. Inorg. Nucl. Chem.* **24** (1962) 1067.
[337] W. Hieber and H. Lagally, *Z. anorg. allgem. Chem.* **245** (1940) 321.
[338] N. S. Imyanitov and D. M. Rudkovskii, *J. Gen. Chem. USSR*, Engl. Transl., **33** (1963) 1041.
[339] E. R. Corey and L. F. Dahl, *J. Am. Chem. Soc.* **83** (1961) 2203; C. H. Wei and L. F. Dahl, *ibid.* **88** (1966) 1821.

The tricarbonyl reacts with trialkyl and triaryl phosphites to give the dimeric compounds $[Ir(CO)_2P(OR)_3]_2$ (R = Et, Ph, *p*-tolyl). Their infrared spectra indicate the presence of bridging CO groups. They react with iodine to give the Ir(III) complexes $[Ir(CO)I_3P(OR)_3]_2$ [340].

5.7. COMPLEXES OF IRIDIUM(I)

There is an extensive chemistry for Ir(I), but the complexes are not quite as numerous as those of Rh(I). As with Rh(I), they involve ligands which are capable of π-bonding. These ligands include NO, phosphines, CO and dienes. These d^8 complexes are mostly square-planar, but 5-coordinate complexes are known with the hydride ligand and with $SnCl_3^-$. The rather unusual complex $Ir(CO)(SO_2)Cl(PPh_3)_2$ has been shown to possess a square-pyramidal configuration.

Some of the square-planar d^8 complexes, like their Rh(I) analogues, undergo oxidative addition reactions to yield octahedral d^6 complexes. The interesting and important complex $Ir(CO)Cl(PPh_3)_2$ readily reacts with H_2, Cl_2, HCl and O_2 to give octahedral Ir(III) complexes. It reacts with azides to give the Ir(I) complex $Ir(N_2)Cl(PPh_3)_2$ and with SO_2 to yield the 5-coordinate adduct $Ir(CO)(SO_2)Cl(PPh_3)_2$ mentioned above.

The phosphine complexes $Ir(CO)Cl(PPh_3)_2$ and $HIr(CO)(PPh_3)_2$ act as hydrogenation catalysts; the mechanism involves homolytic splitting of molecular hydrogen with the concomitant formation of an octahedral Ir(III) complex. However, these two compounds are less effective hydrogenation catalysts than the Rh(I) complex $RhCl(PPh_3)_3$, since the Rh–H bond is more labile than the Ir–H bond.

Several Ir(I) complexes are known with Ir–M bonds (M = Sn, Au, Hg).

Nitrosyl Complexes

The reddish-brown compounds $Ir(NO)X_2(PPh_3)_2$ (X = Cl, Br, I) have been obtained by the reaction of HX on $[Ir(NO)_2(PPh_3)_2]ClO_4$ [335]. Since the nitrosyl stretching frequencies are low (*ca.* 1560 cm^{-1}), these compounds may contain bridging NO groups.

Phosphine Complexes

The trifluorophosphine complex $Ir(PF_3)_4I$ was obtained from the Ir(−I) compound $K[Ir(PF_3)_4]$ by reaction with iodine at −80° [79]. The diphosphine complex $[Ir(diphos)_2]Cl$ (diphos = $Ph_2PC_2H_4PPh_2$) was obtained by treating $Ir(CO)_3Cl$ with the diphosphine[341]. It will react with various ligands to give the 5-coordinate complexes $[Ir(diphos)_2L]^+$ (L = CO, PF_3, O_2, SO_2) [342]. Other phosphine complexes are known with carbonyl and/or hydrido groups (see below).

Carbonyl Complexes

The carbonyl halides $IrX(CO)_3$ (X = Cl, Br, I) were prepared by the action of CO on Ir(III) halides at atmospheric pressure and 150°. They are monomeric and range in colour from light to deep brown[162,343]. The anionic carbonyl halides $[AsPh_4][Ir(CO)_2X_2]$ (X = Br, I) are yellow. The bromo compound was obtained by carbonylation of $[AsPh_4]_3[IrBr_6]$ at

[340] F. Zingales, F. Canziani and U. Sartorelli, *Rend. Ist. Lombardo Sci. Lettere* **A96** (1962) 771.
[341] A. Sacco, M. Rossi and C. F. Nobile, *Chem. Communs.* 1966, 589.
[342] L. Vaska and D. L. Catone, *J. Am. Chem. Soc.* **88** (1966) 5324.
[343] W. Hieber, H. Lagally and A. Mayr, *Z. anorg. allgem. Chem.* **246** (1941) 138.

200° and 200 atm [344]. The iodo compound was prepared by reduction of $[AsPh_4][Ir(CO)_2I_4]$ with zinc[344]. The infrared spectra suggest a *cis* configuration for these anionic complexes. The brown binuclear anionic complex $[AsPh_4][Ir_2(CO)_4Br_3]$ was also isolated[344].

TABLE 32. CARBONYL AMINES, PHOSPHINES, ARSINES AND STIBINES OF IRIDIUM(I)

$Ir(CO)Cl(PEt_3)_3$ [a]	
$Ir(CO)X(PPh_3)_2$ [b, c, d]	(X = Cl, Br, I)
$Ir(CO)Cl\{P(OPh)_3\}_2$ [c]	
$Ir(CO)_2XMPh_3$ [b]	(M = P, As; X = Cl, Br)
$[Ir(CO)_2(MPh_3)_2]^+$ [b]	(M = P, As)
$Ir(CO)_2XL$ [b]	(L = *p*-toluidine; X = Cl, Br)
$Ir(CO)_2ClL_2$ [c]	(L = py, *p*-toluidine, ½ phen, ½ bipy)
$Ir(CO)Cl(MPh_3)_2$ [c]	(M = As, Sb)
$[Ir(CO)_2(SbPh_3)_3]^+$ [c]	
$[Ir(CO)(diphos)_2]^+$ [d, e]	
$Ir(CO)_2Cl(diphos)$ [c]	
$Ir(CO)(RCO_2)(SbPh_3)_3$ [e]	(R = Me, Et)
$Ir(CO)(SO_2)Cl(PPh_3)_2$ [f]	
$Ir(CO)(H_2S)Cl(PPh_3)_2$ [f]	
$[Ir(CO)_3(PR_3)_2]^+$ [g]	(R_3 = Ph_3, Ph_2Me)

diphos = $Ph_2PC_2H_4PPh_2$.

[a] J. Chatt and B. L. Shaw, *Chem. Ind. (London)* 1960, 931.

[b] M. Angoletta, *Gazz. chim. ital.* **89** (1959) 2359.

[c] W. Hieber and F. Volker, *Ber.* **99** (1966) 2607; J. A. J. Jarvis, R. H. B. Mais, P. G. Owston and K. A. Taylor, *Chem. Communs.* 1966, 906.

[d] L. Vaska and J. W. di Luzio, *J. Am. Chem. Soc.* **83** (1961) 2784.

[e] W. Hieber and F. Volker, *Ber.* **99** (1966) 2614; W. Hieber and R. Kummer, *Ber.* **100** (1967) 148.

[f] L. Vaska and S. S. Bath, *J. Am. Chem. Soc.* **88** (1966) 1333; L. Vaska, *ibid.*, p. 5325.

[g] M. J. Church and M. J. Mays, *Chem. Communs.* 1968, 435.

There are numerous carbonyl complexes containing phosphines, arsines or stibines; these are listed in Table 32. Complexes containing one, two and three carbonyl groups are known. Various methods of preparation have been used. The compounds $Ir(CO)X(PPh_3)_2$ can be prepared from hydrated $IrCl_3$ and PPh_3 with 2-methoxyethanol or dimethylformamide and methanol as the carbonylating agent. Most of the other compounds listed in Table 32 were prepared from Ir(I) or Ir(III) carbonyls. It is noteworthy that quite a few of these compounds are 5-coordinate.

Of especial interest is the monocarbonyl $Ir(CO)Cl(PPh_3)_2$. It readily adds on two ligands to form octahedral Ir(III) complexes. Although the dipole moment indicates a *trans* arrangement of the two phosphine groups, there is evidence that the incoming ligands take up *cis* positions since the chloride ligand moves out of the plane of the square[345]. The uptake of hydrogen, oxygen and sulphur dioxide is reversible. The kinetics of these addition reactions have been discussed[345]. Whereas most of these reactions involve oxidative addition to yield octahedral Ir(III) complexes, azides, hydrogen sulphide and sulphur dioxide

[344] L. Malatesta and F. Canziani, *J. Inorg. Nucl. Chem.* **19** (1961) 81; L. Malatesta, L. Naldini and F. Cariati, *J. Chem. Soc.* 1964, 961.

[345] R. S. Nyholm, *Congress on Catalysis (Amsterdam)* **1** (1965) 74.

react to give Ir(I) complexes: viz. $Ir(N_2)Cl(PPh_3)_2$, $Ir(CO)(H_2S)Cl(PPh_3)_2$ and $Ir(CO)(SO_2)Cl(PPh_3)_2$. An X-ray structure determination on the SO_2 adduct shows that the complex has a square-pyramidal structure with the sulphur atom at the apex. The Ir–S distance is rather long (2.49 Å) indicating a weak Ir–S bond; the two phosphine groups are mutually *trans*[346]. The catalytic property of $Ir(CO)Cl(PPh_3)_2$ has been discussed above.

The complexes $Ir(CO)Cl(PPh_3)_2$ and $Ir(CO)Cl(PPh_2Me)_2$ in the presence of sodium perchlorate in acetone solution react with CO under ambient conditions to form the tricarbonyl cationic complexes $[Ir(CO)_3(PR_3)_2]ClO_4$, which have a *trans* configuration. These 5-coordinate Ir(I) complexes react with hydrogen at less than 1 atm to form $[H_2Ir(CO)_2(PR_3)_2]ClO_4$ [347].

Carbonyl complexes of the type $Ir(CO)_2(\beta$-diketone) have been prepared; the β-diketones include acetylacetone, trifluoroacetylacetone, hexafluoroacetylacetone, benzoylacetone and dibenzoylmethane. These complexes undergo substitution reactions with phosphines to yield $Ir(CO)(\beta$-diketone)PR_3. Complexes of the type $Ir(CO)_2Cl$ (Schiff base) were also prepared[348].

Hydride Complexes

The carbonyl hydride $HIr(CO)_4$ was reported to be formed if traces of moisture are present during the preparation of $[Ir(CO)_4]_n$ and $Ir_4(CO)_{12}$ [337]. Its existence has not been confirmed and little is known about it.

The reaction of Ir(III) halides with phosphorus trifluoride under pressure yields $HIr(PF_3)_4$. It is a colourless liquid (b.p. 95°) [79].

The phosphine hydride $HIr(CO)(PPh_3)_2$ was obtained by the reaction of $Ir(CO)Cl(PPh_3)_2$ with hydrazine[248]. The arsine analogue $HIr(CO)(AsPh_3)_2$ has been reported to have a *cis* configuration[349]. The 5-coordinate complex $HIr(CO)(PPh_3)_3$ was prepared from $Ir(CO)Cl(PPh_3)_2$ and sodium borohydride[350]. It is isostructural with $HRh(CO)(PPh_3)_3$ [349] which has a trigonal bipyramidal structure with the three phosphine ligands in the equatorial plane. The iridium complex is a catalyst for the hydrogenation of acetylene, being more efficient than the rhodium analogue [351].

π-Complexes

The cyclopentadienyl complex $Ir(C_5H_5)(C_5H_6)$ has been described[352]. If the cyclopentadiene is behaving as a 2π donor, then the complex can be regarded as containing 5-coordinate Ir(I). If, however, the C_5H_6 ligand acts as a $(2\sigma+\pi)$ donor, then the complex contains 6-coordinate Ir(III). A similar complex, $Ir(C_5H_5)$(duroquinone) has been prepared; from infrared and electronic spectral data it was concluded that the duroquinone ring is π-bonded[353]. The carbonyl compound $Ir(C_5H_5)(CO)_2$ and the corresponding π-indenyl complex $Ir(C_9H_7)(CO)_2$ have been reported[256, 354].

[346] S. J. La Placa and J. A. Ibers, *Inorg. Chem.* **5** (1966) 405.
[347] M. J. Church and M. J. Mays, *Chem. Communs.* 1968, 435.
[348] F. Bonati and R. Ugo, *Chim. Ind. (Milan)* **46** (1964) 1339, 1486; *J. Organomet. Chem.* **7** (1967) 167.
[349] F. Canziani, U. Sartorelli and F. Zingales, *Rend. Ist. Lombardo Sci. Lettere* **A96** (1962) 21.
[350] M. Angoletta and G. Caglio, *Rend. Ist. Lombardo Sci. Lettere* **A97** (1963) 823.
[351] L. Vaska and R. E. Rhodes, *J. Am. Chem. Soc.* **87** (1965) 4970.
[352] E. O. Fischer and U. Zahn, *Ber.* **92** (1959) 1924.
[353] G. N. Schrauzer and K. C. Dewhirst, *J. Am. Chem. Soc.* **86** (1964) 3265.
[354] E. O. Fischer and K. S. Brenner, *Z. Naturforsch.*, Ser. B, **17B** (1962) 774.

Olefin complexes. A number of olefin complexes are known. Ethylene reacts with $Ir(CO)Cl(PPh_3)_2$ to give an unstable adduct $Ir(CO)Cl(PPh_3)_2(C_2H_4)$ [351]. However, tetrafluoroethylene gives the octahedral Ir(III) complex $Ir(CO)Cl(PPh_3)_2(C_2F_4)$ in which the olefin behaves as a 2σ donor[355]. On the other hand, hexafluorobut-2-yne gives the complex $Ir(CO)Cl(PPh_3)_2(C_4F_6)$ which is very stable and is considered to be a π-bonded olefin complex of Ir(I) on the basis of its fluorine magnetic spectrum[355].

Reaction of $Na_2[IrCl_6]$ with cycloocta-1,5-diene and norbornadiene yields the dimeric chloro complexes $[Ir(C_8H_{12})Cl]_2$ and $[Ir(C_7H_8)Cl]_2$, whereas with cyclohexa-1,3-diene the monomeric bis-diene complex $Ir(C_6H_8)_2Cl$ is produced. Triphenylphosphine reacts with these products to give Ir(diene)Cl(PPh_3) (diene = cyclooctadiene or norbornadiene) and $Ir(C_6H_8)Cl(PPh_3)_2$. 2,3-Dimethyl-1,3-butadiene reacts with $Na_2[IrCl_6]$ to give $Ir(diene)_2Cl$. The mono-olefin complexes $Ir(olefin)_3(CO)Cl$ (olefin = cycloheptene or cyclooctene) have been described[259].

Complexes Containing Metal–Metal Bonds

When the phosphine carbonyl $Ir(CO)ClPPh_3$ is reduced with sodium amalgam in tetrahydrofuran, one of the species in solution is considered to be $[Ir(CO)_3PPh_3]^-$. This will react with $AuCl(PPh_3)$, R_3SnCl, Me_2SnCl_2 and $Hg(CN)_2$ to give $(PPh_3)AuIr(CO)_3(PPh_3)$, $R_3SnIr(CO)_3(PPh_3)$, $(PPh_3)(CO)_3Ir(SnMe_2)Ir(CO)_3(PPh_3)$ and $(PPh_3)(CO)_3IrHgIr(CO)_3(PPh_3)$ [233].

The 5-coordinate compounds $Ir(SnCl_3)(diene)(MPh_3)_2$ (diene = cycloocta-1,5-diene; M = P, As) and $Ir(SnCl_3)(diene)_2$ (diene = cycloocta-1,5-diene and norbornadiene) are also known[269].

5.8. COMPLEXES OF IRIDIUM(II)

This is not a common oxidation state for iridium and the compounds which have been shown to contain bivalent iridium are of rather special types. Many of the compounds which have been reported to contain Ir(II) are probably Ir(III) hydrides or Ir(III) compounds containing a σ Ir–C bond and not a π-bond as was supposed. Bivalent iridium has the d^7 configuration, hence the compounds would be expected to be paramagnetic.

Some sulphito complexes such as $[Ir(SO_3)_4]^{6-}$ were reported over 90 years ago, but their formulation is probably incorrect and it is unlikely that they contain Ir(II). One established compound, which can formally be regarded as an Ir(II) complex, is the nitrosyl $Ir(NO)Br_3(PPh_3)_2$ which is paramagnetic (μ 1.34 BM) [335].

There are several carbonyl halides which must be regarded as Ir(II) compounds. They are diamagnetic and it has been suggested that some type of metal–metal interaction is involved. The compounds which have been reported are: $[Ir(CO)_2X_2]_n$ (X = Cl, Br, I), $Ir(CO)X_2$(*p*-toluidine)$_2$ (X = Cl, Br), $[AsPh_4][Ir(CO)X_3]$ (X = Br, I), $[AsPh_4]_2[Ir(CO)I_4]$ $K_2[Ir_2(CO)_4I_6]$; their colours range from yellow to brown[343, 344].

Reaction of the Ir(III) cyclopentadienyl complex $[Ir(C_5H_5)]^+$ with sodium gives a complex $Ir_2(C_5H_5)_4$. However, it seems that the latter is an Ir(III) complex. A dimeric

[355] G. W. Parshall and F. N. Jones, *J. Am. Chem. Soc.* **87** (1965) 5356.
[356] S. Ahrland, J. Chatt and N. R. Davies, *Quart. Rev.* **12** (1958) 265.
[357] E. N. Sloth and C. S. Garner, *J. Am. Chem. Soc.* **77** (1955) 1440.
[358] O. W. Haworth, R. E. Richards and L. M. Venanzi, *J. Chem. Soc.* 1964, 3335.
[359] L. H. Jones, *J. Chem. Phys.* **41** (1964) 856.

structure has been proposed involving a bridging dicyclopentadiene group which is bound to each metal atom by one π- and two σ-bonds. Since the remaining cyclopentadienyl groups (one to each iridium atom) act as $(\sigma+2\pi)$ donors, each iridium atom is thus trivalent[276].

5.9. COMPLEXES OF IRIDIUM(III)

Iridium(III) is a d^6 ion with the $(t_{2g})^6$ configuration; consequently all its complexes are diamagnetic. The coordination number is almost always 6. Whereas Ir(IV) is an (a) class acceptor[209, 356], forming complexes almost exclusively with the electronegative donor atoms fluorine, oxygen, chlorine and bromine, Ir(III) is a (b) class acceptor, forming complexes with the "soft" ligands[209] carbon monoxide, phosphines, arsines, stibines, thioethers and iodide ion. Complexes are known with the ligands Cl^-, Br^-, I^-, CN^-, SO_4^{2-}, SO_3^{2-}, SCN^-, NO_2^-, MR_3 (M = P, As, Sb), R_2S and CO. There are a large number of hydride complexes containing phosphines, arsines or stibines; quite a few of these complexes contain one carbonyl group. The aquated ion $[Ir(H_2O)_6]^{3+}$ is not known and, apart from a few monoaquachloro complexes, no solid complexes containing coordinated water have been isolated.

Halide, Thiocyanate and Cyanide Complexes

The only fluoro complexes are the rather unusual nitrosonium and nitronium compounds $(NO)_2[IrF_5]$ and $(NO_2)_2[IrF_5]$, which were obtained by heating the Ir(IV) compounds $(NO)_2[IrF_6]$ and $(NO_2)_2[IrF_6]$, respectively[325]. The complexes $[IrX_6]^{3-}$ (X = Cl, Br, I, SCN, CN) are all known.

The olive-green potassium chloroiridate(III) $K_3[IrCl_6]$ can be obtained by reduction of $K_2[IrCl_6]$; oxalate or alcohol can be used as the reducing agent. The potassium and ammonium salts are moderately soluble in water, but the rubidium and caesium salts are only sparingly soluble. The crystal-field parameter ($10Dq$) for $[IrCl_6]^{3-}$ is 25,000 cm^{-1} [277]. It has been shown that exchange of ^{192}Ir between $[IrCl_6]^{3-}$ and $[IrCl_6]^{2-}$ is rapid in dilute acid solution. The bromo complex $K_3[IrBr_6]$ can be made by reduction of an aqueous solution of $K_2[IrBr_6]$ with sulphur dioxide. It is also olive green. The green iodo complex $K_3[IrI_6]$ can be prepared from $IrI_3 \cdot 3H_2O$ and potassium iodide.

The thiocyanato complex $[Ir(SCN)_6]^{3-}$ can be obtained from $[IrCl_6]^{3-}$ and thiocyanate ion. Nuclear magnetic resonance spectroscopic data showed that this complex contains *S*-bonded thiocyanate. In *S*-bonded complexes the ^{14}N resonance is shifted slightly downfield compared to the free SCN^- ion, whereas in *N*-bonded complexes it is shifted upfield by a comparatively large amount[358].

The colourless cyanide complex $K_3[Ir(CN)_6]$ is obtained by fusing $(NH_4)_2[IrCl_6]$ with KCN. The infrared and Raman spectra of $[Ir(CN)_6]^{3-}$ indicate that the metal–carbon stretching force constants decrease in the order Ir > Rh > Co, suggesting that iridium forms the strongest bond to carbon[359].

Complexes of Oxygen Ligands

Hydroxo species such as $[Ir(OH)_6]^{3-}$ and $[Ir(OH)_5(H_2O)]^{2-}$ may be present in alkaline solutions of Ir_2O_3.

A number of oxalato complexes have been reported viz.:

$K_3[Ir(C_2O_4)_3]_nH_2O$ (n = 0, 2, 4½), $KH_2[Ir(C_2O_4)_3]\cdot 4H_2O$
$K[Ir(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$, $K_2[Ir(C_2O_4)_2(H_2O)OH]\cdot 2H_2O$
$M_3[Ir(C_2O_4)_2Cl_2]\cdot nH_2O$
$M_3[Ir(C_2O_4)(NO_2)_2Cl_2]\cdot nH_2O$ (M = Li, Na, K, Rb, Cs, NH_4)
$K_3[Ir(NO_2)(C_2O_4)Cl_3]\cdot 2H_2O$
$M_3[Ir(C_2O_4)Cl_4]$ (M = Na, Rb, Cs, NH_4) [360]

The compound $K_3[Ir(C_2O_4)_2Cl_2]$ is known in *cis* and *trans* isomeric forms; the *cis* isomer is a trihydrate and the *trans* isomer is a tetrahydrate. The reddish-orange tris-oxalato complex $K_3[Ir(C_2O_4)_3]\cdot 4\frac{1}{2}H_2O$ can be prepared from $K_3[IrCl_6]$ and $K_2C_2O_4$. It has been resolved into optical antimers which do not racemize in boiling water. The exchange of ^{14}C labelled oxalate ion with $[Ir(C_2O_4)_3]^{3-}$ is slow[361]. The circular dichroism of this complex has been studied and discussed[362]. The free acid $H_3[Ir(C_2O_4)_3]\cdot nH_2O$ has been made. Both *cis* and *trans* forms of $K_3[Ir(C_2O_4)_2Cl_2]$ are red, the colour of the *cis* isomer being deeper. The *cis* form has been optically resolved; it is converted to the *trans* isomer upon being heated in potassium chloride solution for an hour. The dark red oxalatotetrachloro complex $Na_3[Ir(C_2O_4)Cl_4]$ was obtained from $Na_2C_2O_4$ and $Na_3[IrCl_6]$; it is converted into the dichloro complex $Na_3[Ir(C_2O_4)_2Cl_2]$ by the addition of $Na_2C_2O_4$.

Several sulphato complexes have been reported; some of these have not been well characterized. Iridium(III) sulphate $Ir_2(SO_4)_3\cdot$aq can be obtained by dissolving $Ir_2O_3\cdot nH_2O$ in sulphuric acid in the absence of air. It is yellow and sparingly soluble; it is, no doubt, complex but its structure is not known. The yellow alums $MIr(SO_4)_2\cdot 12H_2O$ (M = K, Rb, Cs, NH_4, Tl) have been prepared. The tris-sulphato complex $K_3[Ir(SO_4)_3]$ has been made by the fusion of iridium salts with $KHSO_4$. Other sulphato complexes of more complex formulation have been reported.

A nitrato complex $[Ir(NO_3)_6]^{3-}$ has been claimed[363]. A number of poorly characterized phosphato complexes have been described. These include such compounds as $IrCl_3(H_3PO_3)_3$ and $K_3[IrCl_3(H_2PO_3)_3]$ [360]. These formulations are open to question.

The yellow acetylacetonate $Ir(acac)_3$ can be obtained in low yield when $Ir_2O_3\cdot 3H_2O$ is treated with acetylacetone; like most inner complexes of acetylacetone it is soluble in benzene.

Complexes of Sulphur and Selenium Ligands

Several sulphito complexes have been reported. Those in which the sulphito group is unidentate are: $Na_7[Ir(SO_3)_4Cl_2]$, $Na_3[Ir(SO_3)_3(NH_3)_3]$, $Na_5[Ir(SO_3)_2Cl_4]$ and $Na_2[Ir(SO_3)_2(NH_3)_3Cl]$. Infrared data indicate that the sulphito group is *S*-bonded[364]; this is in keeping with the (b) class character of Ir(III) [209]. In the complexes $K_4[Ir(SO_3)_2Cl_3]$ and $Na[Ir(SO_3)_2(NH_3)_3]$ the infrared spectra indicate that one of the sulphito groups is bidentate, being coordinated through two oxygen atoms. Potassium nitrite reacts with $K_3[Ir(SO_3)_2Cl_4]$ to give $K_4[IrSO_3(NO_2)_5]$ from which the SO_3 group cannot be replaced by NO_2, indicating that the *trans* effect of the former is greater than that of the latter[365].

[360] H. Gmelin, *Handbuch der anorganischen Chemie*, Verlag Chemie, Weinheim.
[361] R. W. Oliff and A. L. Odell, *J. Chem. Soc.* 1964, 2467.
[362] R. D. Gillard, *J. Chem. Soc.* 1963, 2092.
[363] A. Ferrari and C. Colla, *Gazz. chim. ital.* **63** (1933) 507.
[364] A. Babaeva, Y. Y. Kharatonov and Z. M. Novozhenyuk, *Zh. Neorg. Khim.* **6** (1961) 2263, 2281.
[365] I. I. Chernyaev and Z. M. Novozhenyuk, *Russ. J. Inorg. Chem.* **6** (1961) 1247.

The complex $K_4[Ir(SO_3)_2(NO_2)_2Cl]$ has also been reported[365].

The following thiourea complexes have been reported:[366]

$[Ir(thu)_6]Cl_3$ (yellow), $[Ir(thu)_5Cl]Cl_2$ (olive green)
$[Ir(thu)_4Cl_2]Cl$ (red), $[Ir(thu)_3Cl_3]$ (golden yellow)
$NH_4[Ir(thu)_2Cl_4]$ (orange), $(NH_4)_2[Ir(thu)Cl_5]$ (orange)

Thus the full range of complexes is known.

With dimethylsulphoxide (DMSO) both *cis* (1,2,3) and *trans* (1,2,6) isomers of $[IrCl_3(DMSO)_3]$ and of $H[IrCl_4(DMSO)_2]\cdot 2DMSO$ have been obtained. These complexes display catalytic activity for hydrogen-transfer reactions[367].

The diethyl sulphide complexes $Ir(Et_2S)_3Cl_3$ can be obtained in two forms: yellow (m.p. 131°) and red (m.p. 165°). Measurements of their dipole moments, electrical conductivity, electronic and n.m.r. spectra showed that the yellow form is *cis*-(1,2,3)-$[Ir(Et_2S)_3Cl_3]$ and that the red form is *trans*-$[Ir(Et_2S)_4Cl_2]$*trans*-$[Ir(Et_2S)_2Cl_4]$ [368]. The complexes $[Ir(Et_2S)_2pyCl_3]$, $[Ir(Et_2S)py_2Cl_3]$ and $[Ir(Et_2S)(NH_3)_5]Cl_3$, have been reported[369]. The dialkyl selenide complexes $[Ir(R_2Se)_3Cl_3]$ (R = Me, Et) have been prepared from $(NH_4)_2[IrCl_6]$ and the dialkyl selenide[370].

Dithiocyanatoethane forms the halogen-bridged complexes $Ir_2(SCNC_2H_4NCS)_2X_6$ (X = Cl, Br, I); the halogen bridges are readily split by unidentate ligands. In these complexes the ligand is bidentate, being coordinated through both sulphur atoms[293].

The inner complexes $[Ir(dtp)_3]$, $[Ir(dsep)_3]$ and $[Ir(tscz)_3]$ (dtp = diethyldithiophosphate, $\{EtO\}_2PS_2^-$; dsep = diethyldiselenophosphate, $\{EtO\}_2PSe_2^-$; tscz = thiosemicarbazide, $H_2NC\{S^-\}{=}NNH_2$) have been prepared. The values of $10Dq$ for $[Ir(dtp)_3]$ and $[Ir(dsep)_3]$ are 26,700 and 25,000 cm^{-1} respectively. These values place these two ligands in an early position (between Cl^- and F^-) in the spectrochemical series. On the other hand, these ligands occupy a late position in the nephelauxetic series, dsep coming after I^- [209, 291].

Although a dithiooxalato complex of Rh(III) is known, no corresponding complex of Ir(III) appears to have been reported. No dithiocarbamato complex has been reported.

Complexes of Nitrogen Ligands

A considerable number of complexes are known with ammonia, pyridine and other amines such as ethylamine and ethylenediamine. Detailed lists of the complexes and their methods of preparation are to be found in the comprehensive treatises by Gmelin[360] and Mellor[5]. A summary of the types of complexes is given here. The ammine complexes are particularly stable, being more stable than the corresponding ammines of trivalent cobalt. The compounds can be boiled with alkali without decomposition.

Hexammines. The colourless hexammine $[Ir(NH_3)_6]Cl_3$ can be made by treating $[Ir(NH_3)_5Cl]Cl_2$ with ammonia under pressure in a sealed tube at 140°. The bromide, iodide, nitrate and carbonate are known. The value of $10Dq$ for $[Ir(NH_3)_6]^{3+}$ is 41,200 cm^{-1} [277]. As with Rh(III), no hexapyridine complex is known.

Pentammines. The aquapentammines $[Ir(NH_3)_5(H_2O)]X_3$ (X = Cl, Br, I) are made by the action of boiling potassium hydroxide on the halogenopentammines $[Ir(NH_3)_5X]X_2$.

366 W. W. Lebedinskii, E. S. Schapiro and I. P. Kassaltkina, *Izvest. Inst. Izuc. Plat.* **12** (1935) 79.
367 Y. M. Y. Haddad, H. B. Henbest, J. Husbands and T. R. B. Mitchell, *Proc. Chem. Soc.* 1964, 361.
368 G. B. Kauffmann, J. H. Tsai, R. C. Fay and C. K. Jørgensen, *Inorg. Chem.* **2** (1963) 1233.
369 P. C. Rây and N. Adhikari, *J. Ind. Chem. Soc.* **9** (1932) 251; **11** (1934) 517.
370 E. K. Fritzmann and W. Krinitskii, *J. Appl. Chem. USSR*, Engl. transl. **11** (1938) 1610.

The value of $10Dq$ for $[Ir(NH_3)_5Cl]Cl_2$ is 40,400 cm^{-1} [277]. The chloride $[Ir(NH_3)_5(H_2O)]Cl_3$ loses water at 100° and is converted to the chloropentammine. The yellow chloropentammine $[Ir(NH_3)_5Cl]Cl_2$ is prepared by heating $[IrCl_6]^{3-}$ with aqueous ammonia; other salts (Cl, Br, I, NO_3, SO_4, etc.) of this cation are known. The bromopentammine $[Ir(NH_3)_5Br]Br_2$ and the iodopentammine $[Ir(NH_3)_5I]I_2$ can be obtained by the reaction of $[Ir(NH_3)_5(H_2O)]^{3+}$ with the halogen acids. The rate of exchange of bromide ion with $[Ir(NH_3)_5Br]^{2+}$ is less than 2% of that with $[Rh(NH_3)_5Br]^{2+}$ [371]. The colourless hydroxopentammine $[Ir(NH_3)_5(OH)]Cl_2$ can be prepared by treating the aquapentammine with aqueous ammonia.

Heating of $[Ir(NH_3)_5(H_2O)](NO_3)_3$ at 100° gives the colourless nitratopentammine $[Ir(NH_3)_5NO_3](NO_3)_2$. The nitrosopentammine $[Ir(NH_3)_5ONO]Cl_2$ and the nitropentammine $[Ir(NH_3)_5NO_2]Cl_2$ are known; both are colourless. The nitroso complex was prepared from $[Ir(NH_3)_5(H_2O)]Cl_3$, $NaNO_2$ and HCl at 0°. It isomerizes to give the nitro complex and the rate of isomerization has been studied[372]. Irradiation of the nitro complex with ultraviolet light produces the nitroso isomer[372].

The rates of acid-catalysed hydrolysis of the acetatopentammines

$$[Ir(NH_3)_5(RCO_2)](ClO_4)_2 \ (R = Me, CMe_3 \text{ and } CF_3)$$

have been measured; the rate of hydrolysis is dependent upon the acid concentration[373].

Both *N*-bonded and *S*-bonded thiocyanatopentammine complexes

$$[Ir(NH_3)_5NCS](ClO_4)_2$$

and $[Ir(NH_3)_5SCN](ClO_4)_2$ as well as the azidopentammine $[Ir(NH_3)_5N_3](ClO_4)_2$ have been recently reported[374].

Although no pyridine complex is known with more than four pyridine ligands per iridium atom, some mixed pyridine–ammonia species are known, viz. $[Ir(NH_3)_4pyCl]Cl_2$, $[Ir(NH_3)_3py_2(OH)]Cl_3 \cdot 3H_2O$ and $[Ir(NH_3)_3py_2Cl]Cl_2$. The yellow ethylamine complex $[Ir(EtNH_2)_5Cl]Cl_2$ is also known[360].

Tetrammines. The orange dichlorotetrammine $[Ir(NH_3)_4Cl_2]Cl$ and the colourless dinitrotetrammine $[Ir(NH_3)_4(NO_2)_2]Cl$ are known, each only in one form which is probably *trans*. However, *cis* and *trans* forms of $[Irpy_4Cl_2]Cl$ have been prepared[375, 376]. The mixed ligand complexes $[IrNH_3py_3Cl_2]Cl$ and $[Ir(NH_3)_2py_2Cl_2]Cl$ and the ethylamine complex $[Ir(EtNH_2)_4Cl_2]Cl$ have been reported.

Triammines. The compounds in this class include the insoluble yellowish orange trichlorotriammine $[Ir(NH_3)_3Cl_3]$, the colourless trinitrotriammine $[Ir(NH_3)_3(NO_2)_3]$ and the pyridine complexes *cis*- and *trans*-$[Irpy_3X_3]$ (X = Cl, Br), $[Irpy_2(H_2O)Cl_3]$, $[Irpy_2(H_2O)OHCl_2]$, $[Irpy_2(H_2O)Br_3]$, $[Irpy_2(Et_2S)Cl_3]$ and $[Irpy(Et_2S)_2Cl_3]$.

Diammines. The known complexes of this type contain pyridine or picoline but not ammonia. The reaction of pyridine on $K_3[IrCl_6]$ yields $K[Irpy_2Cl_4]$, which is known in a yellow *cis* form and an orange *trans* form. The bromo-complex $pyH[Irpy_2Br_4]$ is also known. The yellow chlorooxalato complex $K[Irpy_2Cl(C_2O_4)(H_2O)]$ was prepared from $K_3[Ir(C_2O_4)_3]$.

[371] G. B. Schmidt, *Z. phys. Chem.* **41** (1964) 26.
[372] F. Basolo and G. S. Hammaker, *Inorg. Chem.* **1** (1962) 1.
[373] F. Monacelli, F. Basolo and R. G. Pearson, *J. Inorg. Nucl. Chem.* **24** (1962) 1241.
[374] H. H. Schmidtke, *Inorg. Chem.* **5** (1966) 1682.
[375] E. König and H. L. Schafer, *Z. physik. Chem. (Frankfurt)* **26** (1960) 371.
[376] R. D. Gillard and B. T. Heaton, *Chem. Communs.* 1968, 75.

Monoammines. The monoammine complex $K[Ir(NH_3)Cl_5]$ was prepared by boiling $K_2[IrCl_6]$ with ammonium acetate solution. The corresponding pyridine compound $K_2[IrpyCl_5]$ was made from $K_2[Ir(H_2O)Cl_5]$ and pyridine. The oxalato-complex $K_2[IrpyCl_3(C_2O_4)]$ is known in two isomeric forms, one with a chloro group *trans* to pyridine and the other with an oxygen atom *trans* to pyridine. Both are orange.

Ethylenediamine Complexes. The tris-chelated complex $[Iren_3]I_3$ was obtained by heating $Na_3[IrCl_6]$, ethylenediamine and sodium iodide at 140°. The value of $10Dq$ (41,400 cm^{-1}) shows that the ligand field is almost identical with that in $[Ir(NH_3)_6]^{3+}$ (41,200 cm^{-1}). The ion was resolved by Werner into its optical antimers. More recently, measurements of the Cotton effect have established the absolute configuration[377]. The salts $[Iren_3]X_3$ (X = Br, NO_3, ClO_4) have been isolated. *Cis*-$[Iren_2(NO_2)_2]I$ was obtained by heating $Na_3[Ir(NO_2)_4Cl_2]$ with ethylenediamine at 170°, followed by the addition of potassium iodide. It was also resolved. Recently the *cis* and *trans* isomers of $[Iren_2Cl_2]Cl$ were reported[378]. The light yellow *cis* isomer was obtained by treating a solution of $[IrCl_6]^{3-}$ with ethylenediamine at pH3. Heating of the reddish-orange $K[IrenCl_4]$ with ethylenediamine at 100° for 2 hr gave the very soluble orange *trans* isomer.

Treatment of $[Iren_3]^{3+}$ with potassium amide in liquid ammonia gives the deprotonated species [Ir(en–H)$_2$en]I and $K_2[Ir(en–2H)(en–H)]$ [379]. The diethylenetriamine complex $[Ir(dien)_2]Br_3$ was similarly deprotonated to give [Ir(dien–H)(dien–2H)] [295].

α-Diimine complexes. The yellow bipyridyl complex $[Ir(bipy)_3](ClO_4)_3$ can be obtained from $K_3[IrCl_6]$, the ligand and perchlorate ion[380]. The phenanthroline complex $[Ir(phen)_3](ClO_4)_3 \cdot 5H_2O$ was prepared by fusion of $(NH_4)_3[IrCl_6]$ with 1,10-phenanthroline, followed by treatment of the aqueous extract of the melt with $NaClO_4$. The compound can be obtained colourless after recrystallization[381]. The chloride, bromide and iodide were prepared in a similar way. The reddish-brown salts $[Ir(phen)_2X_2][IrphenX_4]$ (X = Cl, Br, I) can be isolated from the reaction of $[IrX_6]^{3-}$ with 1,10-phenanthroline in hot water. The yellow *cis*-$[Ir(phen)_2Cl_2]Cl \cdot 3H_2O$ and the orange *cis*-$[Ir(phen)_2Br_2]Br$ were obtained by heating $(NH_4)_2[IrX_6]$ (X = Cl, Br) with phenanthroline at 220° for 14 hr, followed by extraction of the melt with water[381]. The *cis* configuration was confirmed by resolution of $[Ir(phen)_2Cl_2]Cl$ by means of sodium arsenyl tartrate[382].

The only terpyridyl complex which seems to have been reported is $[IrterpyCl_3]$ [383].

Di-2-pyridylamine (dipyram), although somewhat similar to 2,2′-bipyridyl, does not contain the α-diimine grouping —N=C–C=N— and is thus more flexible. This ligand forms the tris-chelated complexes $[Ir(dipyram)_3]X_3$ (X = Cl, Br, I) [384].

Biguanide complex. Biguanide, $HN{=}C(NH_2)NHC(NH_2){=}NH$ (big) forms complexes containing the tris-chelated cation $[Ir(big)_3]^{3+}$, which has been resolved into its optical antimers[385].

Dimethylglyoxime complexes. Several complexes of dimethylglyoxime (DMGH) have been isolated; they include the anionic complexes $[Ir(DMG)_2Cl_2]^-$, $[Ir(DMG)_2(NO_2)_2]^-$,

[377] J. H. Dunlop, R. D. Gillard and G. Wilkinson, *J. Chem. Soc.* 1964, 3160.
[378] S. Kida, *Bull. Chem. Soc. Japan* **39** (1966) 2415.
[379] G. W. Watt, L. E. Sharif and E. P. Helvenston, *Inorg. Chem.* **1** (1962) 6.
[380] B. Martin and G. M. Waind, *J. Chem. Soc.* 1958, 4284.
[381] B. Chiswell and S. E. Livingstone, *J. Inorg. Nucl. Chem.* **26** (1964) 47.
[382] J. A. Broomhead and W. Grumley, *J. Inorg. Nucl. Chem.* **29** (1967) 2126.
[383] G. Morgan and F. H. Burstall, *J. Chem. Soc.* 1937, 1649.
[384] G. C. Kulasingham and W. R. McWhinnie, *J. Chem. Soc.* 1965, 7145.

$[Ir(DMG)_2(NO_2)Cl]^-$ and $[Ir(DMG)_2(NO_2)SCN]^-$, and the cationic diammine complex $[Ir(DMG)_2(NH_3)_2]Cl$ [386].

Nitro complexes. The colourless hexanitro complex $K_3[Ir(NO_2)_6]$ can be obtained by the action of KNO_2 on $K_3[IrCl_6]$ in solution[360]. Other alkali metal salts are known. The infrared and Raman spectra have been discussed[387]. The yellow dichlorotetranitro complex $K_3[Ir(NO_2)_4Cl_2]$ was prepared by treating a solution of $[IrCl_6]^{3-}$ with KNO_2. The yellow tetrachlorodinitro complex $K_3[Ir(NO_2)_2Cl_4]$ was also isolated from the action of $[IrCl_6]^{3-}$ with nitrite ion. Other salts of these anions were also prepared. The mononitropentachloro-complex $K_3[IrNO_2Cl_5]$ can be obtained by treating a solution of $Na_3[Ir(NO_2)_4Cl_2]$ with KCl. The neutral complex $[Ir(NH_3)_3(NO_2)_3]$ was prepared by the action of aqueous ammonia on $Na_3[IrCl_2(NO_2)_4]$ in a sealed tube[360]. Other ammine complexes containing the nitro group and the oxalato-complexes $K_3[Ir(NO_2)_2Cl_2(C_2O_4)]$ and $K_3[Ir(NO_2)Cl_3(C_2O_4)]$ have been mentioned above.

Nitrosyl complexes. Two nitrosyl complexes of Ir(III) are known. The reaction of KNO_2 with $K_3[IrBr_6]$ in acid solution yields the golden coloured compound $K[Ir(NO)Br_5]$ [388]. The infrared spectrum of this complex has been measured and discussed[179]. The phosphine nitrosyl complex $[Ir(NO)Cl_3(PPh_3)_2]ClO_4$ has been prepared from the Ir(−I) nitrosyl $[Ir(NO)_2(PPh_3)_2]ClO_4$ by oxidation with chlorine[335].

Phosphine, Arsine and Stibine Complexes

Some phosphorus trihalide complexes were reported nearly 80 years ago[360]. The compounds $Ir(PX_3)_3X_3$ (X = Cl, Br) and $Ir(PCl_3)_2(SCl_2)Cl_3$ are probably monomeric. The structures and even the formulation of the compounds $Ir(PX_3)_2X_3$ are uncertain but they may be halogen-bridged dimers.

The number of known complexes of Ir(III) with tertiary phosphines, arsines and stibines is considerable. They are mostly yellow or orange. No complex is known with more than four phosphorus or arsenic atoms per metal atom, and in the case of unidentate ligands none is known with more than three. Their most outstanding property is the ready solubility in many organic solvents.

Tertiary phosphines, arsines and stibines react with $[IrX_6]^{3-}$ to give $[Ir(MR_3)_3X_3]$ (M = P, As, Sb; R = alkyl or aryl; X = Cl, Br, or I) [389–393]. Dipole moment measurements on the phosphine and arsine complexes indicate that these compounds have the symmetrical *trans* (1,2,6) configuration[389]. Both *cis* (1,2,3) and *trans* (1,2,6) forms of $[Ir(SbPh_3)_3Cl_3]$ have been obtained[394]. Dimeric halogen-bridged species $Ir_2(PEt_3)_4Cl_6$ and $Ir_2(SbPh_3)_4Br_6$ have been obtained[389, 392]. The bromo bridge in the latter is split by unidentate ligands to give $[Ir(SbPh_3)_2Br_3L]$ (L = NH_3, py, CO) [392]. The anionic complexes $Na[Ir(SbPh_3)_2Cl_4]$ and $K[Ir(SbPh_3)_2Br_4]$ have also been obtained from the reaction of triphenylstibine with $[IrX_6]^{3-}$ in alcohol[392, 394].

[385] S. P. Ghosh and A. I. P. Ghosh, *J. Inorg. Nucl. Chem.* **26** (1964) 1703.
[386] W. W. Lebedinskii and I. A. Federov, *Izvest. Inst. Izuc. Plat.* **12** (1935) 87; **18** (1945) 23.
[387] M. Postollec, J-P. Mathieu and H. Poulet, *J. Chim. Phys.* **60** (1963) 1319.
[388] L. Malatesta and M. Angoletta, *Angew. Chem.*, Int. Edn., **2** (1963) 155.
[389] J. Chatt, A. E. Field and B. L. Shaw, *J. Chem. Soc.* 1963, 3371.
[390] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* 1965, 1407, 6789.
[391] M. Angoletta, *Gazz. chim. ital.* **93** (1963) 1343.
[392] A. Araneo and S. Martinengo, *Gazz. chim. ital.* **95** (1965) 61, 825.
[393] F. P. Dwyer and R. S. Nyholm, *J. Proc. Roy. Soc. NS Wales* **77** (1943) 116; **79** (1945) 121.
[394] A. Araneo, S. Martinengo and F. Zingales, *Gazz. chim. ital.* **95** (1965) 1435.

The catalytic activity of some Ir(III) phosphine complexes has been studied[395]. It appears to be less than that of the analogous Rh(III) complexes.

The infrared spectra of many of the complexes have been measured, and it has been found that the frequency of the metal–chlorine stretching mode depends markedly on the nature of the ligand *trans* to chlorine but is little affected by the ligands in the *cis* positions. The frequency of ν(Ir–Cl) occurs in the range 320–303 cm^{-1} when the *trans* ligand is chlorine, 278–262 cm^{-1} when it is PR_3 or AsR_3 and 249–246 cm^{-1} when it is hydrogen. This shows that the "*trans* effect" decreases in the order $H^- > AsR_3 \simeq PR_3 > Cl^-$ [390].

The chelating ligand dimethyl-*o*-methylthiophenylarsine, *o*-MeS·C_6H_4·$AsMe_2$ (As–S), forms the complexes $Ir(As–S)_2X_3$. The colours range from yellow (X = Cl) through orange (X = Br) to yellowish brown (X = I). The complexes are monomeric and virtually non-electrolytes in nitrobenzene. However, the iodo complex behaves as a uni-univalent electrolyte in nitromethane and acetone, indicating that in these more polar solvents it exists as $[Ir(As–S)_2I_2]I$. The chloro and bromo complexes have low conductivities in these solvents indicating that the species in solution is mostly in the form $[Ir(As–S)_2X_3]$. It is possible that these complexes contain 7-coordinate Ir(III) or, alternatively, one arsine ligand is unidentate, being coordinated through the arsenic atom only[310].

Hydride Complexes Containing Phosphines, Arsines or Stibines

These complexes are very numerous and, indeed, trivalent iridium forms more complexes of this type than any other element. They can be divided into three main types: trihydrides, dihydrides and monohydrides. They have been prepared by a variety of methods, mostly involving Ir(III) halides or Ir(III) halide complexes. The source of the hydride ligand can be sodium borohydride, lithium aluminium hydride, ethanol, or stannous chloride and acid.

Trihydrides. Both 6- and 5-coordinate compounds are known: $H_3Ir(MR_3)_3$ and $H_3Ir(MR_3)_2$ (M = P, As; R = alkyl, Ph). The compounds $H_3Ir(PPh_3)_3$ and $H_3Ir(AsPh_3)_3$ have been prepared in *cis* and *trans* forms[390, 396, 397]. Data obtained from dipole moment measurements and n.m.r. spectra indicate that the compounds $H_3Ir(PR_3)_2$ have a *trans* trigonal bipyramidal configuration[397].

Dihydrides. The known types of 6-coordinate dihydrides are: $H_2Ir(MR_3)_3X$ (M = P, As; X = Cl, Br or I) [390, 396–8], $H_2Ir(PPh_3)_3L$ (L = CN, NO_2, OAc) [391], $H_2Ir(PPh_3)_2(acac)$ [399], $[H_2Ir(AsPh_3)_4]^+$ [396], and $[H_2Ir(diphos)_2]^+$ [341]. There are also the 5-coordinate species $[H_2Ir(MPh_3)_3]ClO_4$ (M = P, As) [396].

Monohydrides. The 6-coordinate monohydrides are of the types $HIr(MR_3)_3X_2$ (M = P, As, Sb; X = Cl, Br or I) [390–2, 394–7], and $HIr(PPh_3)_2X_2L$ (X = Cl, Br; L = NH_3, py, MeCN) [399]. One 4-coordinate species $[HIr(PPh_3)_2]^{2+}$ is known[399].

Carbonyl Complexes

Carbonyl complexes of Ir(III) are of the types $Ir(CO)_3I_3$, $[Ir(CO)_2I_3]_2$, $K[Ir(CO)_2X_4]$ (X = Br, I) and $K_2[Ir(CO)X_5]$ (X = Cl, Br, I); they were prepared from IrI_3 or $K_2[IrBr_6]$ by carbonylation with CO at 200–250 atm and 100–250° [344].

[395] J. K. Nicholson and B. L. Shaw, *Tetrahedron Letters* 1965, 3533.

[396] M. Angoletta, *Gazz. chim. ital.* **92** (1962) 811; M. Angoletta and A. Araneo, *Rend. Ist. Lombardo Sci. Lettere* **A97** (1963) 817; F. Canziani and E. Zingales, *ibid.* **96** (1962) 513.

[397] J. Chatt, R. S. Coffey and B. L. Shaw, *J. Chem. Soc.* 1965, 7391.

[398] L. Vaska, *J. Am. Chem. Soc.* **83** (1961) 756.

[399] A. Araneo, S. Martinengo and P. Pasquale, *Rend. Ist. Lombardo Sci. Lettere* **A99** (1965) 797.

In addition there are many carbonyl complexes known containing phosphine, arsine, or stibine ligands. These have been prepared by (a) treatment of $[IrCl_6]^{3-}$ with CO and MR_3, or (b) oxidative addition of halogen to 4-coordinate Ir(I) carbonyl phosphines. The compounds $Ir(CO)(MR_3)_2X_3$ (M = P, As, Sb; X = Cl, Br) have been obtained in *cis* and *trans* isomeric forms[400]. Other types include $Ir(CO)(MR_3)_2X_3$ (M = P, As, Sb; X = Cl, Br or I) [390, 392, 401, 402], $Ir(CO)_2(AsPh_3)I_3$ [402] and $[Ir(CO)\{P(OR)_3\}I_3]_2$ [340].

Of particular interest is the oxygen complex $Ir(O_2)(CO)(PPh_3)_2Cl$ which can be obtained by the action of oxygen on the Ir(I) carbonyl phosphine complex $Ir(CO)(PPh_3)_2Cl$; the addition of oxygen is reversible. The compound is diamagnetic and can be considered to contain Ir(III) and the peroxo group –O–O–. An X-ray structure determination shows that the two phosphine groups occupy apical sites in an octahedral structure which contains the two oxygen atoms, the chlorine atom and the carbonyl group in the equatorial plane. The O–O distance (1.30 Å) is longer than that of molecular oxygen (1.21 Å) but considerably shorter than that of the peroxide ion (1.45 Å) [403].

Carbonyl Phosphine Hydrides

These are numerous and as with the phosphine and arsine hydrides mono-, di- and trihydrides are known. The trihydrides $H_3Ir(CO)(MPh_3)_2$ (M = P, As) were prepared by carbonylation of $H_3Ir(MPh_3)_3$ [349, 350, 396]. The dihydrides include the 6-coordinate complexes $H_2Ir(CO)(PPh_3)_2Cl$ and $[H_2Ir(CO)(PPh_3)_3]ClO_4$ and the 5-coordinate complex $[H_2Ir(CO)(PPh_3)_2]ClO_4$ [355,402]. The monohydrides contain two halide groups and are of the type $HIr(CO)(MR_3)_2X_2$ (X = Cl, Br; M = P, As). Infrared, n.m.r., and dipole moment measurements have been made on many of these hydrides[350, 392, 400, 402].

Alkyl and Aryl Complexes

The trimethyl complexes 1,2,3-$IrMe_3(PR_3)_3$ have been obtained by reaction of $Ir(PR_3)_3Cl_3$ and the Grignard reagent[404]. Treatment of $Ir(CO)Cl(PPh_3)_2$ with arylsulphonyl chlorides gives $Ir(CO)Cl_2(PPh_3)_2(RSO_2)$ which lose sulphur dioxide to give the aryl compounds $Ir(CO)Cl_2(PPh_3)_2R$ [405]. On the other hand, treatment of $Ir(CO)Cl(PPh_3)_2$ with an alkyl halide yields the alkyl compounds $IrR(CO)Cl(PPh_3)_2I$ (R = alkyl) [315].

A crystal structure determination of the chloro-bridged dimer $[Ir(CO)_2MeCl_2]_2$ shows that there is weakening of the Ir–Cl bonds *trans* to the methyl groups: the Ir–Cl bond *trans* to Me is 2.52 Å, while the Ir–Cl bond *trans* to CO is 2.38 Å [406]. Compounds of the type $IrX_n(Me)_{3-n}MPhMe_2$ (X = Cl, Br; M = P, As) have been prepared and their infrared have been measured. The Ir–C stretching frequency occurs at 488–543 cm^{-1}. The frequency of ν(Ir–Cl) is sensitive to the group *trans* to Cl. When the *trans* group is chlorine, ν(Ir–Cl) occurs at 315 cm^{-1}, when it is phosphine ν(Ir–Cl) occurs at 276 cm^{-1}, and when it is Me, ν(Ir–Cl) occurs at 254 cm^{-1}, indicating that the methyl group has the strongest "*trans* effect" [407].

[400] J. Chatt, N. P. Johnson and B. L. Shaw, *J. Chem. Soc.* 1964, 1625, 1662.
[401] M. Angoletta, *Gazz. chim. ital.* **90** (1960) 1021.
[402] L. Vaska and J. Di Luzio, *J. Am. Chem. Soc.* **83** (1961) 2784; **84** (1962) 679.
[403] S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.* **87** (1965) 2581.
[404] J. Chatt and B. L. Shaw, *J. Chem. Soc.* A, 1966, 1836.
[405] J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.* **88** (1966) 180.
[406] N. A. Bailey, C. J. Jones, B. L. Shaw and E. Singleton, *Chem. Communs.* 1967, 1051.
[407] B. L. Shaw and A. C. Smithies, *J. Chem. Soc.* A, 1967, 1047.

Tetrafluoroethylene reacts with $Ir(CO)Cl(PPh_3)_2$ to give $Ir(CO)Cl(PPh_3)_2C_2F_4$ in which the C_2F_4 forms 2σ-bonds to iridium such that the complex is an alkyl complex of Ir(III) and not a π-complex of Ir(I) [355].

The compound $Ir(Me_2SO)_2Cl_2$(benzylacetophenone) contains a metal–carbon σ-bond. The two Me_2SO groups are *S*-bonded and the deprotonated benzylacetophenone is chelated through the ketonic oxygen and the β-carbon atom[408].

π-Complexes

The cyclopentadienyl complex $[Ir(C_5H_5)_2]^+$ can be made by oxidation of $(C_5H_5)Ir(C_5H_6)$. The duroquinone (dqu) complexes $HIrCl_2(dqu)$ and $HIrCl_2(dqu)_2$ have been prepared from $IrCl_3$ and duroquinone[353].

There are few olefin complexes known containing Ir(III). However, the complexes $[HIr(diene)X_2]_2$ (diene = cycloocta-1,5-diene; X = Cl, Br, I) can be prepared from $K_3[IrCl_6]$, KX and the diene[272].

Complexes with Metal–Metal Bonds

The silyl complexes $HIr(CO)Cl(PPh_3)_2(SiCl_3)$ and $Ir(CO)EtCl(PPh_3)_2(SiCl_2H)$ were prepared by the reaction of $SiCl_3H$ and $EtSiCl_2H$ on $Ir(CO)Cl(PPh_3)_2$ [409]. The stannous chloride complexes $HIr(CO)Cl(PPh_3)_2(SnCl_3)$, $H_2Ir(CO)(PPh_3)_2(SnCl_3)$,

$$HIrCl(PPh_3)_3(SnCl_3)$$

and $H_2Ir(PPh_3)_3(SnCl_3)$ have prepared[410]. The reaction of HgX_2 with $Ir(CO)Cl(PPh_3)_2$ gives the compounds $XHgIrXCl(CO)(PPh_3)_2$ (X = Cl, Br, I, SCN, CN, OAc) [411].

5.10 COMPLEXES OF IRIDIUM(IV)

Halide Complexes

The hexahalogeno complexes $[IrX_6]^{2-}$ are known when X = F, Cl and Br, but not when X = I. The potassium salt of the fluoro complex $K_2[IrF_6]$ is red and can be obtained by heating iridium metal with $K_2[PbF_6]\cdot KHF_2$ or by treating $K[IrF_6]$ with KOH [198]. Salts of the ions Na, NH_4, Rb, Cs and Ba have been prepared and also the nitrosonium and nitronium salts $(NO)_2[IrF_6]$ and $(NO_2)_2[IrF_6]$ [412, 413].

Iridium metal is attacked by chlorine at elevated temperatures, especially in the presence of alkali metal chlorides; the optimum temperature appears to be *ca.* 625° [414]. A mixture of iridium powder and sodium chloride is heated in a stream of chlorine at 625° for 15–30 min. The melt is extracted with hot water, then boiled with aqua regia to oxidize any $[IrCl_6]^{3-}$. The addition of NH_4Cl precipitates the sparingly soluble $(NH_4)_2[IrCl_6]$ [414]. The potassium salt can be made similarly from the solution of the more soluble sodium salt. The salts form dark reddish-black crystals with a green reflex. The hydrated acid $H_2[IrCl_6]\cdot 6H_2O$ can be obtained by treatment of the ammonium salt with aqua regia;

[408] M. McPartlin and R. Mason, *Chem. Communs.* 1967, 545.
[409] A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.* **87** (1965) 16.
[410] R. C. Taylor, J. F. Young and G. Wilkinson, *Inorg. Chem.* **5** (1966) 20.
[411] R. S. Nyholm and K. Vrieze, *J. Chem. Soc.* 1965, 5337.
[412] N. Bartlett, S. P. Beaton and N. K. Jha, *Chem. Communs.* 1966, 168.
[413] P. L. Robinson and G. J. Westland, *J. Chem. Soc.* 1956, 4481.
[414] G. B. Kauffmann and L. A. Teter, *Inorg. Synth.* **8** (1966) 223.

it is soluble in ether. The hexabromides $M_2[IrBr_6]$ (M = Na, K, Rb, Cs, NH_4) can be prepared from $IrO_2 \cdot nH_2O$, HBr and MBr. They are bluish black. The solution of the free acid $H_2[IrBr_6]$, on standing, turns green and evolves bromine. All five species of the type $[IrCl_nBr_{6-n}]^{2-}$ have been isolated[203].

Although both $K_2[IrI_6]$ and $K[IrI_5]$ have been briefly reported, these reports need confirmation.

Some chloroaqua and chlorohydroxo species have been reported to occur in solution, but no solid complexes have been isolated. The species $[Ir(H_2O)_3Cl_3]^+$, $Ir(H_2O)_2Cl_4$, $[Ir(H_2O)Cl_5]^-$, $[Ir(OH)_2Cl_4]^{2-}$ and $[Ir(OH)_4Cl_2]^{2-}$ have been postulated[415].

The magnetic susceptibility of $(NH_4)_2[IrCl_6]$ is 1.8 BM and that of $(NH_4)_2[IrBr_6]$ is 2.1 at 300°K, but both drop to 1.4 BM at 78°K. The Curie–Weiss law is obeyed by the chloro complex above 190°K but not by the bromo complex below 300°K [416]. Electron spin resonance measurements on $K_2[IrCl_6]$ showed the presence of spin–spin interaction between iridium atoms even in a magnetically dilute environment, i.e. in crystals of $K_2[PtCl_6]$ containing a relatively small amount of $K_2[IrCl_6]$ [417]. The electronic spectra of $[IrX_6]^{2-}$ ions have been discussed[205].

Complexes with Oxygen Donors

Sodium iridate(IV) Na_2IrO_3 is obtained when iridium powder is fused with sodium carbonate. The calcium salt $CaIrO_3$ is known in two crystalline forms—hexagonal and orthorhombic. In the latter form there is a distorted octahedral arrangement of the oxygen atoms about the iridium atom with four long (Ir–O, 2.06 Å) and two short (1.94 Å) bonds[418].

Two trinuclear sulphato species appear to have been established with some certainty. They are salts of $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ and $[Ir_3O(SO_4)_9]^{10-}$. The nitrido complex contains one Ir(III) and two Ir(IV) atoms per trinuclear unit, while the oxo species contains two Ir(III) and one Ir(IV) atoms. It has been suggested that the three iridium atoms form an equilateral triangle with the nitrogen or oxygen atom at the centre. Each structure is assumed to contain three bridging sulphato groups[420].

The oxalato complexes $Cs_2[IrCl_4(C_2O_4)]$ and $K[IrCl_3bipy(C_2O_4)]$ have been prepared by oxidation of Ir(III) oxalato complexes with chlorine[421].

Complexes with Nitrogen Ligands

These are not very numerous, but cationic, neutral and anionic species are known: $[Ir(NH_3)_4Cl_2]Cl_2$, $[Ir(NH_3)_2py_2Cl_2]Cl_2$ [419], IrL_2Cl_4 and $[IrLCl_5]^-$ (L = py, α- or γ-picoline) [422, 423].

[415] J. C. Chang and C. S. Garner, *Inorg. Chem.* **4** (1965) 209.
[416] V. Norman and J. C. Morrow, *J. Phys. Chem.* **31** (1959) 455.
[417] E. A. Harris and J. Owen, *Proc. Roy. Soc.* A, **289** (1965) 122.
[418] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.* 1965, 4997.
[419] M. Delépine, *Z. Physik. Chem. (Frankfurt)* **130** (1927) 227; *Ann. chim. (Paris)* 1959, 1115, 1131.
[420] C. K. Jørgensen and L. E. Orgel, *Mol. Phys.* **4** (1961) 215.
[421] M. Inamura, *Bull. soc. chim. France* 7 (5) (1940) 750.
[422] G. B. Kauffmann, *Inorg. Synth.* 7 (1963) 220.
[423] F. Larèze, *Compt. rend.* **256** (1963) 2396.

5.11. COMPLEXES OF IRIDIUM(V)

The only complexes are those containing the $[IrF_6]^-$ anion. The potassium salt $K[IrF_6]$ can be made by treating a mixture of $IrBr_3$ and KBr with BrF_3. Other alkali metal salts are known[198]. The compounds $[NO][IrF_6]$, $SeF_4 \cdot IrF_5$ and $SeF_4(IrF_5)_2$ are also known[412,413].

6. PALLADIUM

6.1. GENERAL CHEMISTRY

Palladium is a silver-white ductile metal which has a great affinity for hydrogen, being able to absorb that gas to a greater degree than any other metal. When in the form of sponge or powder, the metal can absorb up to 900 times its own volume of hydrogen. The amount absorbed decreases with increase in temperature for a given pressure. The absorption is accompanied by expansion of the solid and the lattice constant may increase by as much as 5%. At the same time the electrical conductivity and magnetic susceptibility fall. These data and the shape of the pressure–concentration isotherm suggest the existence of definite hydrides below 300°C. Below this temperature the isotherm exhibits a horizontal pressure–invariant portion in which the so-termed α- and β-phase hydrides coexist. Although it has been suggested that the stoichiometric compound Pd_2H is formed, it is now accepted that the composition of the hydride phase varies continually with temperature and that there is no simple ratio of hydrogen atoms to palladium atoms in either the α- or the β-phase. Hydrogen and deuterium are able to diffuse through heated massive palladium. This is specific for hydrogen and deuterium; helium, for example, has no such power.

It has been suggested that interaction between hydrogen and palladium atoms or ions could yield Pd–H or $Pd–H^+$ entities which could be considered equivalent to an equal number of silver atoms or ions, since Pd–H is isoelectronic with Ag. This hypothesis is supported by evidence that the solubility of hydrogen in Pd–Ag alloys decreases more or less linearly with silver content. However, any approximation to a linear dependence of hydrogen solubility on silver content breaks down over substantial ranges of reference pressure when the solubility of hydrogen is more rigorously defined with reference to the pressure of hydrogen gas in equilibrium.

Another hypothesis which has been proposed is that the hydrogen is dissolved as protons which are located in interstitial positions in the lattice without being specifically bound to a particular metal atom. The effects of the electrons from the absorbed hydrogen on the structure of palladium were then considered. Until 1965 it had been accepted that the magnetic susceptibility data were consistent with there being 0.6 "holes" per palladium atom in the 4*d* band, and it was proposed that for values of H:Pd up to 0.6, these holes were filled by electrons from the hydrogen atoms. Furthermore, since the value of H:Pd can, under certain circumstances, exceed 0.6, it was proposed that the additional electrons were accommodated in the 5*s* band. However, a recent theoretical analysis of the palladium band structure suggests that there are only 0.36 holes in the 4*d* band per metal atom. If the hydrogen is absorbed as protons, it is behaving as an alloying metal and this would account for the retention of thermal and electrical conductivity and malleability.

Analogies to the Pd–H system are provided by the M–H systems for the Group V metals (M = V, Nb, Ta), where with absorption of hydrogen there is still a retention of

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Analogies to the Pd–H system are provided by the M–H systems for the Group V metals (M = V, Nb, Ta), where with absorption of hydrogen there is still a retention of

considerable electrical conductivity; there are also similarities in the pressure–concentration relationships. From a consideration of the changes in lattice parameters, it has been suggested that the hydrogen in these Group V metal–hydride systems is present as negative hydride ions. Consequently it is a distinct possibility that in the Pd–H system also the hydrogen is present as hydride ions.

Another proposal, which is supported by various lines of evidence, is that the hydrogen is present as PdH_4 molecular units with a tetrahedral rather than a square-planar configuration. At the present time the exact nature of the manner in which hydrogen is absorbed by palladium is still not established. The Pd–H system has been extensively studied for over a century and the subject has been recently reviewed[424].

Palladium is more readily attacked by oxidizing agents than the other platinum metals. It is dissolved by nitric acid and is attacked by fluorine and chlorine at red heat. When heated in air to dull red heat, the metal acquires a violet film of oxide, whereas platinum does not.

Potassium chloropalladate(II) $K_2[PdCl_4]$ is the most convenient starting material for the preparation of palladium complexes; it can be prepared as follows. A weighed amount of palladium sponge is treated with aqua regia (3 parts HCl, 1 part HNO_3) in a conical beaker covered with a watch-glass. The contents of the beaker are warmed on a hot plate whereupon a vigorous reaction occurs and the whole of the palladium is dissolved within a minute or less (difference from platinum). The dark reddish-brown solution is carefully heated to dryness. Sufficient concentrated hydrochloric acid is added to dissolve the residue and the solution taken to dryness; this process is repeated twice more in order to remove all traces of nitric acid and oxides of nitrogen. The residue is dissolved in the minimum amount of boiling water containing a few drops of hydrochloric acid. Two molecular equivalents of potassium chloride are added with stirring. The mixture is cooled in ice and the yellowish-brown crystals of $K_2[PdCl_4]$ are separated by filtration and recrystallized from water containing a few drops of HCl. Potassium bromopalladate(II) $K_2[PdBr_4]$ can be prepared

TABLE 33. ELECTRODE POTENTIALS FOR PALLADIUM [a, b]

Reaction	Potential (V)
$Pd(H_2O)_4^{2+} + 2e = Pd + 4H_2O$	0.99
$PdCl_4^{2-} + 2e = Pd + 4Cl^-$	0.62
$PdBr_4^{2-} + 2e = Pd + 4Br^-$	0.60
$Pd(OH)_2 + 2e = Pd + 2OH^-$	0.07
$PdCl_6^{2-} + 2e = PdCl_4^{2-} + 2Cl^-$	1.29
$PdO_2 + 4H^+ + 2H_2O + 2e = Pd(H_2O)_4^{2+}$	1.19

[a] W. M. Latimer, *Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd edn., Prentice-Hall, Englewood Cliffs, New Jersey (1952), p. 202.

[b] T. J. Walsh and E. A. Hausman, The Platinum Metals, in *Treatise on Analytical Chemistry*, Part II, Vol. 8 (I. M. Kolthoff and P. J. Elving, eds.), Wiley Interscience, New York (1963), p. 397.

[424] F. A. Lewis, *The Palladium–Hydrogen System*, Academic Press, London (1967).

similarly by dissolving palladium sponge in a mixture of nitric and hydrobromic acids. However, since it is much more soluble than $K_2[PdCl_4]$, the solution must be concentrated to small bulk.

TABLE 34. OXIDATION STATES OF PALLADIUM

Oxidation state	Coordination number	Stereochemistry	Examples
Pd(0)	?	?	$Pd(PhNC)_2$, $Pd(PPh_3)_3$
	4	Tetrahedral	$[Pd(CN)_4]^{4-}$, $[Pd(PF_3)_4]$, $[Pd\{C_6H_4(AsMe_2)_2\}_2]$
Pd(I)	?	?	$[PdCl(CO)]_x$
	4	?	$PdCl(CO)(PPh_3)_2$
Pd(II)	4	Square-planar	$[Pd(NH_3)_4]^{2+}$, $[PdenCl_2]$, $[PdCl_4]^{2-}$
	5	Square pyramidal	[Pd(As–As–As–As)Cl]ClO_4 [a]
	6	Distorted octahedral	$[Pd\{C_6H_4(AsMe_2)_2\}_2I_2]$
Pd(IV)	6	Octahedral	$[Pd(NH_3)_2Cl_4]$, $[PdCl_6]^{2-}$

[a](As–As–As–As) = *o*-phenylenebis(*o*-dimethylarsinophenylmethylarsine).

Some electrode potentials for palladium are given in Table 33. The oxidation states are listed in Table 34. Palladium is much closer to platinum than to nickel in its chemistry. Indeed, the similarity between palladium and platinum is more marked than that between any other two platinum metals. This is particularly so for the bivalent state which is the most important for palladium. In this oxidation state both palladium and platinum display pronounced (b) class behaviour[356]. Stable complexes are formed with ligands containing the "soft" donors CN^-, P, As, Sb, S, Se and Te. A great many complexes are known with nitrogen ligands. On the other hand, relatively few complexes are known with oxygen ligands and none at all with fluorine, apart from PdF_2. π-Allylic complexes are readily formed. Palladium(II) complexes are moderately labile, while those of Pt(II) are inert. Only a few instances of *cis-trans* isomerism are known for Pd(II), whereas there are numerous examples of this type of isomerism among complexes of square-planar Pt(II) and octahedral Pt(IV).

The oxidation state IV is much less important for palladium than it is for platinum. The complexes are confined to $[PdX_6]^{2-}$ (X = F, Cl, Br), $[Pd(amine)_2X_4]$ (X = Cl, Br) and a few others such as $[Pd(diarsine)_2Cl_2]^{2+}$.

The zerovalent state is well established and a number of phosphine, arsine and isocyanide complexes of Pd(0) have been characterized. Although the cyanide complex $[Pd(CN)_4]^{4-}$ has been prepared, the isoelectronic carbonyl $Pd(CO)_4$, analogous to $Ni(CO)_4$, is not known.

The existence of Pd(I) has not been established with certainty, although a few compounds such as $PdCl(CO)PPh_3$ have been reported. Several complexes for which the stoichiometry suggests an oxidation state of III are known to contain Pd(II) and Pd(IV). Consequently it is doubtful if the trivalent state occurs at all for palladium.

Thermodynamic data for palladium and some of its compounds are listed in Table 35.

Since papers dealing with palladium complexes are legion, in this section reference will be made in many instances to *Gmelin's Handbuch*, annual reports of the Chemical Society London, or a review article where the original reference is cited.

TABLE 35. THERMODYNAMIC DATA ON PALLADIUM AND ITS COMPOUNDS [a]

Substance	State	$\Delta H°$	$\Delta F°$	$S°$
Pd	g	93	84	39.91
Pd	c	0	0	8.9
$PdCl_2$	c	−45.4		
$PdCl_4^{2-}$	aq	−128.3	−96.7	41
$PdBr_2$	c	−24.9	−21.8 [b]	
$Pd(CN)_2$	c	52.1		
PdO	c	−20.4	−14.4 [b]	
$Pd(OH)_2$	c	−92.1	−72	
$Pd(OH)_4$	c	−169.4	−126	
$PdCl_6^{2-}$	aq	−156.7	−99.6 [b]	
Pd_2H	c	−8.9		

[a] Unless otherwise indicated, values are from the US National Bureau of Standards Circular 500, *Selected Values of Thermodynamic Properties* (1952).

[b] W. M. Latimer, *Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd edn., Prentice-Hall, Englewood Cliffs, New Jersey (1952), p. 203.

6.2. BINARY COMPOUNDS

The halides and chalcogenides are listed in Table 36.

TABLE 36. HALIDES AND CHALCOGENIDES OF PALLADIUM

Compound	Colour	Remarks
PdF_4	Brick red	Eight-coordinate structure similar to UCl_4
PdF_2	Pale violet	Octahedral structure; μ 2.9 BM
$PdCl_2$	Dark red	Infinite chain structure; square-planar coordination
$PdBr_2$	Reddish black	Structure not known
PdI_2	Black	Insoluble; structure not known
$PdO_2 \cdot nH_2O$	Dark red	Indefinite composition; loses O_2 at 200° [a]
PdS_2	Greyish black	From $PdCl_2$ + excess S at 400–500° [a]
$PdSe_2$	Olive grey	From $PdCl_2$ + excess Se at 600° [a]
$PdTe_2$	Silver grey	From $PdCl_2$ + large excess Te at 700° [a]; CdI_2 structure
PdO	Black	From $PdCl_2 + Na_2CO_3$ (fusion); insoluble in acids [a]
PdS	Greyish black	From heating Pd + S [a]
PdSe	Dark brown	From heating $[Pd(NH_3)_2Cl_2]$ + Se [a]
PdTe	Yellow	From heating Pd + Te [a]

[a] *Gmelin's Handbuch der Anorganischen Chemie*, Vol. 65, Verlag Chemie, Berlin (1942).

Halides

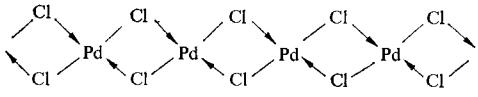
The only halide of Pd(IV) is the diamagnetic tetrafluoride PdF_4, which was obtained by direct fluorination (7 atm F_2 at 150°) of "palladium trifluoride". The tetrafluoride is violently hydrolysed by water. The metal atom is 8-coordinate, being at the centre of two flattened tetrahedra. The supposed palladium trifluoride has been shown not to contain Pd(III) but Pd(II) and Pd(IV), the correct formulation being $Pd^{II}[Pd^{IV}F_6]$ [425]. The paramagnetism is not due to the d^7 configuration of Pd(III), as was originally supposed, but to the high-spin d^8 configuration of Pd^{2+}. The Pd^{2+} ion also occurs in $Pd[PtF_6]$, $Pd[SnF_6]$ and $Pd[GeF_6]$. The "trifluoride" $Pd[PdF_6]$ is obtained by treating $PdBr_2$ with BrF_3. This yields the adduct $Pd_2F_6 \cdot 2BrF_3$, which on being heated to 180°, loses BrF_3 to give $Pd[PdF_6]$. The platinum, tin and germanium compounds are obtained by the reaction of BrF_3 on mixtures of $PdBr_2$ and MBr_4 (M = Pt, Sn, Ge) [425]. The values of the magnetic moment of Pd^{2+} in these compounds are: $Pd[PdF_6]$, 2.88 BM, $Pd[PtF_6]$, 2.72 BM, $Pd[SnF_6]$, 2.98 BM, $Pd[GeF_6]$, 2.82 BM. The palladium complex $Pd[PdF_6]$ obeys the Curie–Weiss law with $\theta = 28°$.

Palladium difluoride PdF_2 was obtained by refluxing $Pd[PdF_6]$ with selenium tetrafluoride[425]:

$$Pd^{II}[Pd^{IV}F_6] + SeF_4 \rightarrow 2PdF_2 + SeF_6$$

It is the only binary compound of Pd(II) which is paramagnetic and the moment (μ 2.9 BM) is consistent with the observed octahedral coordination in the rutile type structure. The compound is hydrolysed in moist air.

Palladium dichloride $PdCl_2$ can be made from the elements at red heat. At about 600° it begins to sublime and dissociate into its elements; the dissociation pressure is 1 atm at 738°. It can also be prepared by heating $H_2[PdCl_4] \cdot aq$, obtained by dissolving palladium in aqua regia (see above). When prepared in this way, the anhydrous compound is insoluble in water and dissolves only with difficulty in hydrochloric acid. It forms red crystals which contain infinite flat chains (VIII) in which the coordination around the palladium atom is square-planar (Pd–Cl distance, 2.31 Å) [426,427]. Another form of $PdCl_2$ has been reported recently; it is isomorphous with $PtCl_2$ and contains discrete Pd_6Cl_{12} units [428].



(VIII)

The dihydrate $PdCl_2 \cdot 2H_2O$ can be obtained from aqueous solution as dark red hygroscopic crystals. Palladium dichloride is easily reduced to the metal; hydrogen effects the reduction in the cold, while ethyl alcohol and ethylene will reduce $PdCl_2$ in a warm solution. Many hydroaromatic compounds, such as cyclohexane, cyclohexanol, hydroquinolines and hydrocarbazoles, are converted into their aromatic cogeners by boiling with a 2% aqueous solution of $PdCl_2$ with concomitant deposition of metallic palladium[427].

Palladium dibromide $PdBr_2$ can be prepared in a similar manner to that used for $PdCl_2$: the metal is dissolved in a mixture of nitric and hydrobromic acids and the dark mass of

[425] N. Bartlett and M. A. Hepworth, *Chem. Ind.* 1956, 1425; N. Bartlett and P. R. Rao, *Proc. Chem. Soc.* 1964, 393.

[426] *Gmelin's Handbuch der Anorganischen Chemie*, Vol. 65, Verlag Chemie, Berlin (1942).

[427] N. V. Sidgwick, *The Chemical Elements and their Compounds*, Clarendon Press, Oxford (1950), p. 1553.

$H_2[PdBr_4]\cdot aq$, obtained on evaporation of the solution, on being heated, loses HBr to give fine dark reddish-brown crystals of $PdBr_2$. Palladium diiodide PdI_2 is obtained as a black precipitate when KI is added to a solution of $K_2[PdCl_4]$. It is insoluble in water and only slightly soluble in the presence of excess iodide ions. The crystal structures of $PdBr_2$ and PdI_2 have not been investigated.

Chalcogenides

The hydrated Pd(IV) oxide $PdO_2\cdot nH_2O$ is said to be precipitated upon the addition of alkali to a solution of the Pd(IV) chloro-complex $K_2[PdCl_6]$. It is dark red and a strong oxidizing agent. It slowly evolves oxygen at room temperature and is converted to the monoxide PdO at 200°. It has not been well characterized.

The disulphide PdS_2, the diselenide $PdSe_2$ and the ditelluride $PdTe_2$ have been prepared[426]. However, as with similar compounds of the other platinum metals, it is questionable whether these compounds actually contain the metal in the quadrivalent state. The disulphide has been prepared by heating $PdCl_2$ and sulphur in an evacuated tube at 450°. The product was extracted with carbon disulphide to remove the excess sulphur. The disulphide can also be obtained by heating $K_2[PdCl_6]$ with sulphur at 210° in the absence of air or by acidification of a solution of the complex sulphide Na_2PdS_3.

The olive-grey diselenide was obtained by heating $PdCl_2$ with a large excess of selenium in a stream of carbon dioxide; the reaction product was ground to a powder, mixed with a large excess of selenium, and heated at 600° in an evacuated tube. The excess selenium was removed as KSeCN by heating the powdered product with KCN solution.

The ditelluride was prepared by heating $PdCl_2$ with a large excess of tellurium at 750° in a stream of carbon dioxide; the reaction product was powdered and heated with excess tellurium in an evacuated tube at 700°. The excess tellurium was removed with concentrated KOH solution. The compound crystallizes in the hexagonal system with the cadmium iodide type structure.

Palladium(II) oxide PdO can be obtained by heating the metal in oxygen or by fusing $PdCl_2$ with $NaNO_3$ at 600°[427]. It is obtained as a black powder insoluble in acids. The dissociation pressure of oxygen is 1 atm at 875°. It glows on contact with hydrogen at room temperature, being reduced to the metal. It has been used as a catalyst for reduction by hydrogen, the CHO group being reduced to CH_3. The hydrated oxide $PdO\cdot nH_2O$ can be obtained as a gelatinous yellowish-brown precipitate by the hydrolysis of Pd(II) nitrate. Unlike the anhydrous oxide, it is soluble in acids. It loses water in air and goes brown and loses more water on being heated but cannot be completely dehydrated without loss of oxygen. It has been reported that $Pd(OH)_2$, obtained by hydrolysis of $[PdCl_4]^{2-}$, differs from the product $PdO\cdot H_2O$, resulting from the action of heat on an acid solution of $Pd(NO_3)_2$. The latter is said to contain molecules of water within the PdO lattice[429].

Palladium(II) sulphide PdS can be obtained as a brown precipitate by passing hydrogen sulphide into a solution of $[PdCl_4]^{2-}$. It can be obtained as a greyish-black crystalline powder by heating palladium and sulphur together; the melting point is $970\pm5°$. The palladium atom is surrounded by four sulphur atoms in a slightly distorted square-planar arrangement.

[428] H. Schafer, U. Wiese, K. Rinke and K. Brendel, *Angew. Chem.*, Int. Edn., **6** (1967) 253.
[429] O. Glemser and G. Peuschel, *Z. anorg. Chem.* **281** (1955) 44.

Palladium selenide PdSe can be obtained as a dark brown precipitate by the addition of a solution of $PdCl_2$ to a saturated solution of hydrogen selenide. It can also be obtained by heating *trans*-$[Pd(NH_3)_2Cl_2]$ with selenium and borax.

The telluride PdTe is precipitated by the addition of sodium telluride to a solution of $[PdCl_4]^{2-}$. It can be made in the dry way by heating the elements in the correct proportion in the absence of air.

Compounds with Other Non-metals

The reactions of palladium with the non-metals boron, silicon, phosphorus, arsenic and antimony have been investigated[426]. The systems are complex. The stoichiometric compounds Pd_2Si, PdSi, PdP_2 and $PdAs_2$ have been reported.

Other Simple Compounds

Palladium nitrate. If palladium is dissolved in nitric acid and the solution is concentrated, brown crystals are obtained. Most texts state that the product is $Pd(NO_3)_2$. However, if the product is collected, pressed almost dry, and dried *in vacuo* over NaOH, it analyses for $Pd(NO_3)_2(H_2O)_2$ [430]. The infrared spectrum indicates coordinated unidentate nitrato groups: the asymmetric NO_2 stretch and the symmetric NO_2 stretch occur at 1502 and 1274 cm^{-1} respectively, while the NO stretch occurs at 988 cm^{-1} [430]. The brown volatile anhydrous nitrate $Pd(NO_3)_2$ has been prepared by the reaction of liquid N_2O_5 on $Pd(NO_3)_2(H_2O)_2$ at room temperature. The difference of 460 cm^{-1} between $\nu_{as}NO_2$ (1630 cm^{-1}) and $\nu_{sym}NO_2$ (1170 cm^{-1}) indicate bridging nitrato groups[431].

It has been claimed that the infrared and n.m.r. spectra of $Pd(NO_3)_2(H_2O)_2$ indicate that it is in fact a Pd(IV) compound, viz. $Pd(NO_3)_2(OH)_2$ [432]. This seems doubtful since it is unlikely that OH groups could be produced in strong acid solution.

If the hydrated nitrate is treated with N_2O_4 at $-78°$ and the mixture is allowed to reach room temperature, a brown viscous liquid is produced. After 24 hr brown crystals of palladium(IV) nitrate $Pd(NO_3)_4$ are obtained. The compound oxidizes I^- but not Fe^{2+} [432]. Palladium is the first element known to yield anhydrous nitrates in two oxidation states.

Palladium nitrite. This compound has not been prepared pure, but if palladium nitrate is reacted with NO, a product is obtained with composition near to $Pd(NO_2)_2$ [426].

Palladium sulphate. The reddish-brown dihydrate $PdSO_4 \cdot 2H_2O$ and an olive-green monohydrate $PdSO_4 \cdot H_2O$ have been reported. Both are deliquescent and easily hydrolysed. If palladium is dissolved in nitric acid and the solution is then taken to dense fumes with sulphuric acid, dark red crystals of the anhydrous sulphate $PdSO_4$ are obtained.

Palladium selenate. Palladium selenate $PdSeO_4$ can be isolated as dark brown crystals from the solution obtained by dissolving palladium in a mixture of nitric and selenic acids[426].

Palladium cyanide. A yellow precipitate of $Pd(CN)_2$ is obtained when mercury cyanide is added to a solution of $Pd(NO_3)_2$ [426].

Palladium thiocyanate. A red precipitate of $Pd(SCN)_2$ is produced if KSCN is added to a solution of $K_2[PdCl_4]$. With excess KSCN a red solution of $K_2[Pd(SCN)_4]$ is produced.

[430] B. M. Gatehouse, S. E. Livingstone and R. S. Nyholm, *J. Chem. Soc.* 1957, 4222.
[431] B. O. Field and C. J. Hardy, *J. Chem. Soc.* 1964, 4428.
[432] C. C. Addison and B. G. Ward, *Chem. Communs.* 1966, 155.

6.3. COMPLEXES OF PALLADIUM(0)

The zerovalent state of palladium is stabilized by soft ligands such as cyanide ion, isocyanides, acetylides, nitrosyl, phosphines and arsines. In the Pd(0) d^{10} system metal to ligand charge transfer (d_π–d_π or d_π–π^* bonding) must be important in order to reduce the high formal negative charge on the metal atom produced by the donation of a pair of electrons from the ligand (σ-bond). If the ionization potentials of gaseous nickel, palladium and platinum are considered, it follows that palladium and platinum, because of their high ionization potentials (*ca.* 8.3 eV), should be much less effective in forming metal–ligand π-bonds than nickel with its lower ionization potential (5.8 eV). However, this is not so, since the coordinative abilities of Ni(0), Pd(0) and Pt(0) are very similar. However, many authors have pointed out that a more important factor is the promotion of $(n-1)d$ electrons to np orbitals. The promotion energies for $(n-1)d^{10} \rightarrow (n-1)d^9np$ are: Ni, 1.72, Pd, 4.23 and Pt, 3.28 eV.

These d^{10} systems can stabilize coordinatively unsaturated species, such as $Pd(PhNC)_2$ and $Pt(PPh_3)_2$, which can be compared to an atom on a metal surface. The d^8 complexes of Ru(0), Rh(I) and Ir(I) also display a tendency toward coordinative unsaturation or, like $Rh(PPh_3)Cl$, dissociate in solution to give coordinatively unsaturated species in solution. This tendency accounts, at least in part, for their marked reactivity and catalytic activity. Many Pd(0) and Pt(0) complexes undergo reactions involving either coordinative dissociation or coordinative addition[433]. There have been little structural data on Pd(0) compounds.

Cyanide Complex

The yellow cyanide complex $K_4[Pd(CN)_4]$ has been obtained by reduction of the Pd(II) complex $K_2[Pd(CN)_4]$ with potassium in liquid ammonia. It is readily oxidized[427]. The corresponding Ni(0) complex $[Ni(CN)_4]^{4-}$ is isoelectronic with $Ni(CO)_4$ but $Pd(CO)_4$ has not been prepared.

Isocyanide Complexes

The Pd(II) isocyanide complexes $PdX_2(RNC)_2$ cannot be reduced by strong reducing agents in acid, neutral, or weakly alkaline solution, but reduction occurs spontaneously in strongly alkaline solution but then only if more than 2 moles of isocyanide are used. With slightly less than 2 moles of isocyanide not even a trace of the Pd(0) complexes $Pd(RNC)_2$ are obtained, whereas with 2.6 moles a 50% yield is obtained. The iodo-complexes $PdI_2(RNC)_2$ are the most convenient starting materials because of their ease of preparation[434].

The diamagnetic brown complexes $Pd(RNC)_2$ (R = Ph, *p*-tolyl, *p*-anisyl) are known. They react with iodine to give the Pd(II) compounds $PdI_2(RNC)_2$. With phosphines and triarylphosphites partial or complete displacement of the isocyanide ligand occurs; the course of the reaction and the products obtained vary with the nature of the substituting ligand. Colourless compounds such as $Pd(RNC)\{P(p\text{-}ClC_6H_4O)_3\}_3$ have been isolated[434].

Cyclohexylisonitrile and isopropylisonitrile react with π-cyclopentadienylcyclohexenyl-palladium $(C_5H_5)Pd(C_6H_9)$ to give the yellow diamagnetic compounds bis (cyclohexylisonitrile)palladium(0) and bis(isopropylisonitrile)palladium(0) [435].

[433] R. Ugo, *Coordination Chem. Rev.* **3** (1968) 319.
[434] L. Malatesta, *Prog. in Inorg. Chem.* **1** (1959) 283.
[435] D. Nicholls, *Ann. Rep. Chem. Soc. London* **59** (1962) 152.

Acetylide Complexes

Palladium(II) acetylide complexes $K_2[Pd(CN)_2(C{\equiv}CR)_2]$ can be prepared by the reaction of the potassium acetylide on $K_2[Pd(CN)_4]$. The complexes can be reduced by potassium in liquid ammonia to the Pd(0) compounds $K_2[Pd(C{\equiv}CR)_2]$. These Pd(0) derivatives are diamagnetic and are readily oxidized[435]. The structures are not known.

Nitrosyl Complexes

There are a few nitrosyl complexes which, if we consider the nitrosyl group as NO^+, formally contain zerovalent palladium. The complex $Pd(NO)_2Cl_2$ has been isolated from the reaction of NO on $PdCl_2$ in methanol. It is diamagnetic and presumably tetrahedral. It is unstable and evolves NO in moist air or on being heated[436]. The compound Pd(NO)Cl has been obtained from the reaction of NO on $PdCl_2$ in the presence of water[437].

The reddish-brown monomeric nitrosyl (π-C_5H_5)PdNO was obtained by the reaction of Pd(NO)Cl with sodium cyclopentadienyl in pentane[438].

Phosphine and Arsine Complexes

Treatment of Pd(0) isocyanide complexes $Pd(RNC)_2$ with phosphines yields three types of Pd(0) phosphine complex $Pd(RNC)L_3$, PdL_3 and PdL_4 (L = PPh_3 or $P(OR)_3$, R = aryl). The coordinatively saturated compound $Pd(PPh_3)_4$ is largely dissociated in benzene solution to give $Pd(PPh_3)_3$ [434].

A number of Pd(0) complexes containing chelating tertiary phosphines and arsines have been reported. They were prepared by reduction of Pd(II) phosphine or arsine complexes with a variety of reducing agents; however, aqueous sodium borohydride was found to be the most suitable reducing agent. These compounds cannot be hydrides since no absorption attributable to ν(Pd–H) occurs in the infrared spectra. When the ligands are predominantly aliphatic, the complexes tend to be colourless and readily oxidized by air, becoming more

TABLE 37. PALLADIUM (0) COMPLEXES OF CHELATING TERTIARY PHOSPHINES AND ARSINES[439]

Compound	M.p. (°)	Colour	Dipole moment (*D*)
[Pd{PhP(*o*-$C_6H_4PEt_2$)$_2$}(PPh_3)]	175–178	Dark red	—
[Pd{$C_2H_4(PMe_2)_2$}$_2$]	182–183	White	1.6
[Pd{*o*-$C_6H_4(PEt_2)_2$}$_2$]	229–230	Yellow	~0
[Pd{*o*-$C_6H_4(AsMe_2)_2$}$_2$]	188–189*	Yellow	—
[Pd{$CH_2(PPh_2)_2$}$_2$]	195–210*	Scarlet	—
[Pd{$C_2H_4(PPh_2)_2$}$_2$]	234	Yellow	1.6
α-[Pd{$MeC(CH_2PPh_2)_3$}$_2$]	246–247	Dull yellow	~0
β-[Pd{$MeC(CH_2PPh_2)_3$}$_2$]	194–195	Bright yellow	2.25
[Pd{*o*-$C_6H_4(PEt_2)_2$}{*o*-$C_6H_4(AsEt_2)_2$}]	184–186	Yellow	0.95
[Pd{*o*-$C_6H_4(PEt_2)_2$}{*o*-$C_6H_4(AsMe_2)_2$}]	141	Orange	—
[Pd{*o*-$C_6H_4(PEt_2)_2$}{$C_2H_4(PPh_2)_2$}]	207–208	Yellow	2.1
[Pd{*o*-$C_6H_4(PEt_2)_2$}{$MeC(CH_2PPh_2)_3$}]	200–201	Bright yellow	3.1

* With decomposition.

[436] A. G. Sharpe and D. W. A. Sharp, *Ann. Rep. Chem. Soc. London* **56** (1959) 130.
[437] A. G. Sharpe and D. W. A. Sharp, *Ann. Rep. Chem. Soc. London* **57** (1960) 137.
[438] D. Nicholls, *Ann. Rep. Chem. Soc. London* **60** (1963) 204, 222.

orange and less readily oxidized as the aromatic nature of the ligands increases[439]. The complexes are listed in Table 37. The tritertiary phosphine complex $[Pd\{MeC(CH_2PPh_2)_3\}_2]$ occurs in two isomeric forms. The isomers are readily interconvertible; the α-form passes into the β-form on recrystallization from benzene-methanol and the β-form goes over to the α-isomer when heated or when recrystallized from light petroleum. The two isomers of the analogous Ni(0) complex behave similarly. Since the α-form has zero dipole moment, it was concluded that the phosphine ligands are tridentate and that this form has an octahedral configuration. It seems that the β-isomer has a lower coordination number—4 or 5—with one or both phosphine ligands bidentate.

The diphosphine–triphosphine complex $[Pd\{o\text{-}C_6H_4(PEt_2)_2\}\{MeC(CH_2PPh_2)_3\}]$ could be 4- or 5-coordinate. Its relatively high dipole moment (3.1*D*) suggests that it may be 5-coordinate with a square-pyramidal configuration.

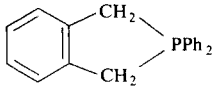
The trifluorophosphine complex $Pd(PF_3)_4$ has been obtained as a volatile liquid (m.p. *ca.* −100°) by the reaction of PF_3 on $Pd(CO)_2Cl_2$ under pressure; the complex is rather unstable[440].

The reactivity of phosphine complexes of Ni(0), Pd(0) and Pt(0) has been recently reviewed[433]. The reactions of the Pd(0) complexes have not been investigated as extensively as those of Pt(0). The complex $Pd(PPh_3)_3$ reacts with halogen acids HX to yield $PdX_2(PPh_3)_2$ and hydrogen; the reaction probably proceeds via an unstable hydride intermediate. Alkynes react with $Pd(PPh_3)_4$ to give $Pd(PPh_3)_2$(alkyne) which are considered to contain Pd(0). However, it is possible that the alkyne is attached to the metal atom by two σ-bonds, thus making the palladium bivalent. Oxygen addition occurs with $Pd(PPh_3)_3$ to give $Pd(PPh_3)_2O_2$, which decomposes above 20° but is more stable than the analogous nickel complex yet considerably less stable than the platinum complex.

6.4. COMPLEXES OF PALLADIUM(I)

The occurrence of univalent palladium is still in doubt, although a few compounds purporting to contain Pd(I) have been reported.

2-Phenylisophosphindoline (IX) forms the colourless complex $Pd(C_{14}H_{13}P)_2Cl$ which is dimorphic and melts to a scarlet liquid. Its solutions in warm ethanol or acetone are bright yellow but at the boiling point become bright red. Molecular weight determinations in boiling solvents indicate that the compound is a hexamer[441].



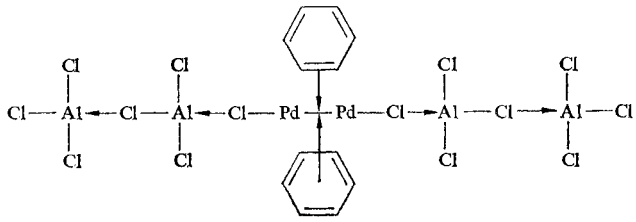
(IX)

A polymeric reddish-violet carbonyl halide $[PdCl(CO)]_x$ can be obtained from $Pd(CO)Cl_2$. It is insoluble in organic solvents[442].

A bisarene metal complex $[PdAl_2Cl_7(C_6H_6)]_2$ has been prepared from palladium

[439] J. Chatt, F. A. Hart and H. R. Watson, *J. Chem. Soc.* 1962, 2537.
[440] G. F. Svatos and E. E. Flagg, *Inorg. Chem.* **4** (1965) 422.
[441] F. G. Mann, I. T. Millar and F. H. C. Stewart, *J. Chem. Soc.* 1954, 2833.
[442] F. J. Kohl and J. Lewis, *Ann. Rep. Chem. Soc. London* **63** (1966) 209.

chloride, aluminium, aluminium chloride and benzene. The compound has the structure (X) in which the two palladium atoms are contained between two benzene rings.



(X)

6.5. COMPLEXES OF PALLADIUM(II)

Palladium(II) has the d^8 configuration and all the complexes are diamagnetic. The great majority of Pd(II) complexes are square-planar; the earlier evidence for the square-planar configuration of Pd(II) and Pt(II) has been reviewed[444]. However, weaker bonds may be formed in the apical sites to give a tetragonally distorted octahedral configuration. There is evidence that these apical positions may be occupied by solvent molecules[445, 446], and in ligand displacement and catalytic reactions the initial attack probably occurs by displacement of the solvent molecules in these axial sites. There are a considerable number of solid complexes in which the coordination around the palladium atom probably exceeds 4 [447, 448], although verification from a crystal structure determination has been obtained in only a few cases. There are also several compounds, such as $Pd(DMG)_2$ and $[Pd(NH_3)_4][PdCl_4]$, in which there is axial interaction between the square-planar units in the crystal lattice[449]. A trigonal bipyramidal structure occurs in the quadradentate arsine complex [Pd(QAS)X]X [450].

The aqua ion $[Pd(H_2O)_4]^{2+}$ is formed when PdO dissolves in dilute nitric, perchloric, or sulphuric acids. If palladium is dissolved in concentrated nitric acid and the solution is taken to fumes with perchloric acid, brown crystals of $[Pd(H_2O)_4](ClO_4)_2$ are deposited when the solution cools[451]. The compound is readily hydrolysed by water. The aqua ion is stable in solution only at a low pH and in the absence of any ligand capable of coordinating to palladium[451].

Halide, Thiocyanate and Cyanide Complexes

The complexes $[PdX_4]^{2-}$ (X = Cl, Br, I, SCN, CN) can easily be prepared. The corresponding fluoro complex is not known; however, if a suspension of PdF_2 in SeF_4 is treated

[443] F. J. Kohl and J. Lewis, *Ann. Rep. Chem. Soc. London* **62** (1965) 188.
[444] D. P. Mellor, *Chem. Rev.* **33** (1943) 137.
[445] C. M. Harris, S. E. Livingstone and I. H. Reece, *J. Chem. Soc.* 1959, 1505.
[446] S. E. Livingstone and B. Wheelahan, *Austral. J. Chem.* **17** (1964) 219.
[447] C. M. Harris and S. E. Livingstone, *Rev. Pure Appl. Chem.* **12** (1962) 16.
[448] A. D. Westland, *J. Chem. Soc.* 1965, 3060.
[449] J. R. Miller, *Adv. in Inorg. Chem. and Radiochem.* **4** (1962) 133.
[450] L. M. Venanzi, *Angew. Chem.*, Int. Edn., **3** (1964) 453.
[451] S. E. Livingstone, *J. Chem. Soc.* 1957, 5091.

with CsF, the complex $CsPdF_3$ can be isolated; its structure is not known[452]. The colours of these complexes are: chloro, yellowish brown; bromo, dark reddish-brown; iodo, black; thiocyanato, bright red; cyano, colourless. The chloro complex was the first Pd(II) complex for which the square planar arrangement was established by a crystal structure determination; the Pd–Cl distance is 2.30 Å and the Pd–Pd distance is 4.10 Å; which is too long for any metal–metal interaction. The sodium salt $Na_2[PdCl_4]$ is deliquescent, very soluble in water and soluble in alcohol. Salts of NH_4, Rb, Cs, Ca, Ba and heavy metals have been prepared[453].

The absorption spectrum of an aqueous solution of $[PdCl_4]^{2-}$ changes with time due to hydrolysis and the formation of aqua species. The chloro-aqua system has been investigated spectrophotometrically by measurements on solutions of $[Pd(H_2O)_4]^{2+}$ containing sufficient perchloric acid to repress hydrolysis. Evidence was obtained for the existence of all species from $PdCl^+$ to $[PdCl_6]^{4-}$ [454]. A continuous variation spectrophotometric study on mixtures of $[NEt_4]_2[PdBr_4]$ and NEt_4Br in nitrobenzene showed the existence of the $[PdBr_6]^{4-}$ ion in solution[447, 455]. The formation of a similar higher bromo complex in methanol and in water has been observed[456, 457].

The halogen-bridged anionic complexes $[Pd_2X_6]^{2-}$ (X = Cl, Br, I) can be isolated as their quaternary ammonium or arsonium salts from solutions of $K_2[PdX_4]$ (X = Cl, Br) in water or $Na_2[PdI_4]$ in ethanol by the addition of $[AsPh_3Me]Cl$ or $[NR_4]X$ (X = Br, I; R_4 = Et_4, $PhMe_3$) [458]. An X-ray powder photograph of $[NEt_4]_2[Pd_2Br_6]$ showed that the structure must be similar to that of $[NEt_4]_2[Pt_2Br_6]$ for which the dimeric bromo-bridged structure was established by X-ray crystal analysis[458].

Spectrophotometric evidence has been obtained for the solvation of the ions $[PdX_4]^{2-}$ (X = Cl, Br) and $[Pd_2X_6]^{2-}$ (X = Cl, Br, I) by various polar solvents. The spectra of the solutions display a progressive shift of the maxima towards higher frequencies if the solvents are arranged in the order: nitrobenzene < acetic anhydride < nitromethane < acetone < methanol < acetonitrile < water. This was attributed to the formation of 6-coordinate solvated species, particularly since the maxima occur at considerably lower frequencies in the spectra of the solid compounds. It was concluded that this order indicates the order of increasing strength of attachment of the solvent molecules to the palladium atom[456].

The electronic spectra of $[PdX_4]^{2-}$ have been discussed and compared with the spectra of other square-planar ions, viz. $[PtX_4]^{2-}$ and $[AuX_4]^-$ (X = Cl, Br) [459]. The spectra display three spin-allowed *d–d* bands of medium intensity and two metal → ligand charge-transfer bands of high intensity ($\varepsilon > 10{,}000$).

Point dipole and molecular orbital calculations suggest that in these complexes the *d* orbital energy level sequence is:

$$d_{xy}, d_{yz} < d_{z^2} < d_{xy} < d_{x^2-y^2}$$

[452] A. G. Sharpe and D. W. A. Sharp, *Ann. Rep. Chem. Soc. London* **58** (1961) 103.
[453] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, London (1936), Vol. 15.
[454] A. K. Sundaram and E. B. Sandell, *J. Am. Chem. Soc.* **77** (1955) 855.
[455] C. M. Harris, S. E. Livingstone and I. H. Reece, *Austral. J. Chem.* **10** (1957) 282.
[456] C. M. Harris, S. E. Livingstone and I. H. Reece, *J. Chem. Soc.* 1959, 1505.
[457] A. A. Grinberg and N. V. Kisileva, *Zh. Neorg. Khim.* 1958, 1804.
[458] C. M. Harris, S. E. Livingstone and N. C. Stephenson, *J. Chem. Soc.* 1958, 3697.
[459] H. B. Gray, *Transition Metal Chemistry* (R. Carlin, ed.), Edward Arnold, London (1965), Vol. 1, p. 239.

With halogen ligands the d_{xz}, $d_{yz}(e_g)$ and $d_{xy}(b_{2g})$ orbitals are π-antibonding. The d_{xz} and d_{yz} orbitals interact with the two p_z orbitals on pairs of halogens mutually *trans*, while the d_{xy} orbital interacts with all four halogens, using the p_x and p_y orbitals. Since the p orbitals are filled, the d_{xy} orbital lies at a higher energy than the d_{xz}, d_{yz} orbitals, because of its greater interaction[277].

Three spin-allowed transitions are to be expected; these correspond to the transitions:

$$d_{xy}(b_{2g}) \rightarrow d_{x^2-y^2}(b_{1g})[^1A_{1g} \rightarrow {}^1A_{2g}] = \Delta_1 - C$$
$$d_{z^2}(a_{1g}) \rightarrow d_{x^2-y^2}(b_{1g})[^1A_{1g} \rightarrow {}^1B_{1g}] = \Delta_1 + \Delta_2 - 4B - C$$
$$d_{xz},\, d_{yz}(e_g) \rightarrow d_{x^2-y^2}(b_{1g})[^1A_{1g} \rightarrow {}^1E_g] = \Delta_1 + \Delta_2 + \Delta_3 - 3B - C$$

B and C are the Racah parameters.

The two charge-transfer bands are the two $\pi \rightarrow d_{x^2-y^2}$ transitions, which occur at approximately the same energy and the $\sigma \rightarrow d_{x^2-y^2}$ transition, which occurs at the higher frequency and has the highest intensity. The frequencies of the observed bands and their assignments are given in Table 38.

TABLE 38. ELECTRONIC SPECTRAL BANDS OF PALLADIUM(II) HALIDE COMPLEXES [456, 459]

$K_2[PdCl_4]$ (cm^{-1})	$K_2[PdBr_4]$ (cm^{-1})	$[NEt_4]_2[Pd_2I_6]$ (cm^{-1})	Assignment
16,700 [a]	16,000 [a]	13,700 [a]	$^1A_{1g} \rightarrow {}^1A_{2g}$
21,500 [a]	20,000 [a]	17,100 [a]	$^1A_{1g} \rightarrow {}^1B_{1g}$
23,500 [a]	26,000 [a]	21,000 [a]	$^1A_{1g} \rightarrow {}^1E_{1g}$
36,000 [b]	30,100 [b]	27,000 [a]	$^1A_{1g} \rightarrow {}^1A_{2u}, {}^1E_u$
44,900 [b]	40,500 [b]	38,000 [a]	$^1A_{1g} \rightarrow {}^1E_u$

[a] Solid-state spectrum.
[b] Absorption spectrum of aqueous solution containing excess halide ion.

From pure quadrupole resonance of the halogen atoms in $K_2[PdX_4]$ and $K_2[PdX_6]$ (X = Cl, Br) it was concluded that the M–X bonds have 40% covalent character in the Pd(II) complexes and 60% in the Pd(IV) complexes[435]. The overall stability constant ($\log \beta_4$) for $[PdCl_4]^{2-}$ is 12.3 and for $[PdBr_4]^{2-}$ is 13.1 [460].

The interaction of various unidentate ligands with the halogen-bridged anionic complexes $[NEt_4]_2[M_2X_6]$ (M = Pd, Pt; X = Br, I) in acetone solution has been investigated. The halogen bridges are readily split, but whereas with $[NEt_4]_2[Pt_2X_6]$ the compounds $[NEt_4][PtLX_3]$ (L = NH_3, amine, $AsMePh_2$, Et_2S) were obtained, only one such palladium compound, viz. $[NEt_4][Pd(Et_2S)Br_3]$, could be isolated. In all other cases PdL_2X_2 or a mixture of products was obtained[461].

In general the thiocyanate ion coordinates to (a) class metals through nitrogen, and to (b) class metals through sulphur, but the nature of the other ligands in the complex and also

[460] A. E. Martell and L. G. Sillén, *Stability Constants of Metal-ion Complexes*, Chem. Soc. Special publ. No. 17 (1964).
[461] S. E. Livingtone and A. Whitley, *Austral. J. Chem.* **15** (1962) 175.

steric factors may determine the way in which the thiocyanato group is bound. Infrared spectral data indicate *S*-bonding in $[M(SCN)_4]^{2-}$ and $[M(NH_3)_2(SCN)_2]$ but *N*-bonding in $[M(PR_3)_2(NCS)_2]$ (M = Pd, Pt; R = Et, Ph). The change from M–S to M–N bonding in these complexes of (b) class metals has been explained on the basis that strong π-electron acceptors, such as tertiary phosphines, can make the d_ε orbitals of the metal less available for bonding with the π-orbitals of the sulphur atom. However, steric factors can influence the manner of attachment of the thiocyanato group, since the steric requirements for M–SCN are greater than for the linear M–NCS: e.g. $[Pd(dien)SCN]^+$ is *S*-bonded but $Pd[(Et_4dien)NCS]^+$ is *N*-bonded. Since $Pd(\gamma\text{-pic})_2(SCN)_2$ is *S*-bonded and $Pdpy_2(NCS)_2$ is *N*-bonded, it seems that electronic effects are also important[209]. Both linkage isomers of *trans*-$[Pd(AsPh_3)_2(SCN)_2]$ and *trans*-$[Pd(bipy)_2(SCN)_2]$ have been isolated; the reaction of $[Pd(SCN)_4]^{2-}$ with $AsPh_3$ or bipyridyl at 0° yields the *S*-bonded isomers which rearrange to the *N*-bonded isomers at 150° [438].

The cyanide complex $[Pd(CN)_4]^{2-}$ is colourless and among the most stable of palladium complexes. The potassium salt $K_2[Pd(CN)_4]$ occurs as a mono- and a tri-hydrate. The alkaline earth metal salts $M[Pd(CN)_4]\cdot nH_2O$ (M = Ca, Sr, n = 5; M = Ba, n = 4) are isomorphous with their nickel and platinum analogues. The square-planar configuration of the ion has been established by crystal structure analysis[426].

The electronic spectrum of $[Pd(CN)_4]^{2-}$ in aqueous solution shows three closely spaced charge-transfer bands. Whereas the order of increasing energy of the first allowed charge-transfer band in the planar halide complexes is

$$[AuBr_4]^- < [PdBr_4]^{2-} < [AuCl_4]^- < [PdCl_4]^{2-} < [PtBr_4]^{2-} < [PtCl_4]^{2-}$$

in the planar cyanide complexes the order is

$$[Ni(CN)_4]^{2-} < [Pt(CN)_4]^{2-} < [Pd(CN)_4]^{2-} < [Au(CN)_4]^-$$

It follows that in the halide complexes the transitions are ligand → metal, whereas in the cyanide complexes they are metal → ligand. Since the cyanide ion has relatively stable π^* orbitals, the three transitions are from the three filled metal *d* orbitals to the first available ligand level[459]. The frequencies of the bands for square-planar $[M(CN)_4]^{2-}$ ions are given in Table 39.

TABLE 39. ELECTRONIC SPECTRAL BANDS OF SQUARE-PLANAR CYANIDE COMPLEXES

Complex	λ_{max} (cm^{-1})	ε	Transition
$[Ni(CN)_4]^{2-}$	32,300	700	$xy \rightarrow \pi^*\ {}^1A_{1g} \rightarrow {}^1B_{1u}$
	35,200	4,200	$z^2 \rightarrow \pi^*\ {}^1A_{1g} \rightarrow {}^1A_{2u}$
	37,600	10,600	$xz, yz \rightarrow \pi^*\ {}^1A_{1g} \rightarrow {}^1E_u$
$[Pd(CN)_4]^{2-}$	41,600	1,200	$xy \rightarrow \pi^*\ {}^1A_{1g} \rightarrow {}^1B_{1u}$
	45,400	7,200	$z^2 \rightarrow \pi^*\ {}^1A_{1g} \rightarrow {}^1A_{2u}$
	47,200	9,000	$xz, yz \rightarrow \pi^*\ {}^1A_{1g} \rightarrow {}^1E_u$
$[Pt(CN)_4]^{2-}$	35,700	1,590	$xy \rightarrow \pi^*\ {}^1A_{1g} \rightarrow {}^1B_{2u}$
	38,680 sh	26,000	$xz, yz \rightarrow \pi^*\ {}^1A_{1g} \rightarrow {}^1E_u$
	39,180	29,500	$xy, yz \rightarrow \pi^*\ {}^1A_{1g} \rightarrow {}^1E_u$
	41,320	1,850	$z^2 \rightarrow \pi^*\ {}^1A_{1g} \rightarrow {}^1A_{2u}$
$[Au(CN)_4]^-$ [a]	46,080	2,400	$xy \rightarrow \pi^*\ {}^1A_{1g} \rightarrow {}^1B_{1u}$

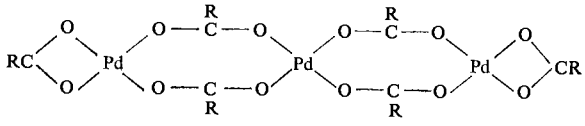
[a] Bands of higher frequency not reported.

Complexes of Oxygen Ligands

Since Pd(II) displays pronounced (b) class behaviour, it is not surprising that relatively few complexes are known with oxygen donors and that most of those which are known are not particularly stable. The oxygen ligand can in most cases be readily displaced by "soft" ligands such as CN^-, AsR_3, PR_3, SR_2, or I^-. If, however, the ligand is bidentate and contains nitrogen, sulphur, or arsenic as the other donor atom—e.g. glycinate $H_2NCH_2CO_2^-$, *o*-methylmercaptobenzoate $MeSC_6H_4CO_2^-$, or *o*-dimethylarsinobenzoate $Me_2AsC_6H_4CO_2^-$—the complexes are more stable.

The tetra-aqua ion $[Pd(H_2O)_4]^{2+}$ has been discussed above.

Carboxylato complexes $Pd(OCOR)_2$ (R = Me, Et, Ph, CF_3, C_2F_5) are known; they are brown. The acetate and propionate were prepared from palladous nitrate and the carboxylic acid; the benzoate, trifluoroacetate and pentafluoropropionate were obtained by exchange reactions. The acetate, propionate and benzoate are trimeric in benzene at 37° but are monomeric at the boiling point of the solvent. The trimers have the carboxylate bridged structure (XI). The fluorocarboxylate complexes are monomeric. The acetate and propionate react with nitrogen, sulphur, phosphorus and arsenic ligands to give *trans*-$[Pd(OCOR)_2L_2]$ (L = py, ½bipy, Me_2SO, PPh_3, $AsPh_3$) [462].



(XI)

A series of heteronuclear acetato-bridged complexes of the type

$$MPd(OAc)_4 \cdot xHOAc \cdot yH_2O$$

(M = Ca, Sr, Ba, Mn, Co, Ni, Cu, Zn, Cd) have been prepared by heating a solution of $Pd(OAc)_2$ with the metal acetate in acetic acid[463].

The golden yellow complex oxalates $K_2[Pd(C_2O_4)_2] \cdot 4H_2O$ and $Na_2[Pd(C_2O_4)_2] \cdot 2H_2O$ can be prepared by the addition of oxalate to a solution containing $[PdCl_4]^{2-}$. The ammonium and silver salts, $(NH_4)_2[Pd(C_2O_4)_2] \cdot 2H_2O$ and $Ag_2[Pd(C_2O_4)] \cdot 3H_2O$ are also known[426]. The crystals darken to greyish black (decomposition to palladium metal) on standing for several weeks even in the absence of light.

The yellow salicylato complex $K_2[Pd(OC_6H_4CO_2)_2] \cdot 3H_2O$ can be obtained by the addition of $K_2[PdCl_4]$ to a hot solution of potassium salicylate. The $Na(3H_2O)$, $NH_4(2H_2O)$ and $Ag(3H_2O)$ salts have also been prepared[426].

The yellow cyanate $Na_2[Pd(CNO)_4] \cdot 5H_2O$ can be prepared from $Pd(NO_3)_2$ and NaCNO. The compound explodes on being struck or when heated[426].

The orange red nitrato complex $K_2[Pd(NO_3)_4]$ can be prepared by the oxidation of the nitro-complex $K_2[Pd(NO_2)_4]$ with concentrated nitric acid. It is stable in air but is immediately hydrolysed in solution[435].

The dialkylnitrosamines R_2N_2O (R = Me, Et, Bu^n) react with $Na_2[PdCl_4]$ to give yellow *trans*-$[(R_2N_2O)_2PdCl_2]$ in which the ligand is coordinated through the oxygen atom. The nitrosamine is readily replaced by other ligands such as pyridine[435].

[462] S. M. Morehouse, A. R. Powell, J. P. Heffer, T. A. Stephenson and G. Wilkinson, *J. Chem. Soc.* 1965, 3632.

[463] R. W. Brandon and D. V. Claridge, *Chem. Communs.* 1968, 677.

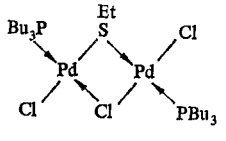
The yellow acetylacetonato-complex $[Pd(acac)_2]$ has a high stability (log β_2, 27.6). The frequency of ν(M–O) for a series of bivalent metal acetylacetonates increases in the order: Zn ≃ Co < Ni < Cu < Pd, which is the order of increasing stability[464]. The reaction of N_2O_4 with $[Pd(acac)_2]$ gives the γ-nitro-substituted complex, while NOCl yields a mixture of the γ-nitroso and γ-chloro complexes, depending on the conditions[438].

Complexes of Sulphur, Selenium and Tellurium Ligands

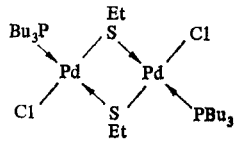
Bivalent palladium forms strong complexes with sulphur ligands and a great many are known. The ligands include mercaptide, sulphite and thiosulphate ions, thioethers, selenoethers, telluroethers, thiourea, triarylphosphine sulphide and selenide, triphenylarsine sulphide and dimethylsulphoxide. Chelate ligands which form strong complexes include dithiocarboxylate, alkyl xanthate, dialkyl dithiocarbamates and diselenocarbamates, dialkyl dithiophosphates and diselenophosphates and α-dithiols. In addition there are a great many chelate ligands which contain a thiol or thioether sulphur and one or more other donor atoms, which may be sulphur, oxygen, nitrogen, phosphorus, or arsenic. Those ligands containing phosphorus or arsenic as the other donor atom(s) are dealt with under Phosphine and Arsine Complexes (p. 1313).

Thiolo complexes. The mercaptide ion RS^-, being highly polarizable, forms strong bonds with (b) class metal ions. Complexes containing RS^- are enthalpy stabilized, whereas those containing the "hard" ligand OH^- are entropy stabilized. Thiols form strong complexes with Ni(II), Pd(II) and Pt(II). The palladium complexes $Pd(SR)_2$ (R = Et, Pr^n, Bu^n, Am^n) are associated in ethylene dibromide and chloroform and are no doubt polymeric in the solid state with two sulphur atoms bridging two adjacent palladium atoms. Thiophenol forms a vermilion coloured complex $Pd(SPh)_2$, yet no similar colour is developed with the other (b) class metal ions Ag(I), Au(III), Rh(III), Ir(III) and Pt(II). The monomeric thiophenol complexes $[Pd(SPh)_2L_2]$ (L = Et_3P, $PhEt_2P$; 2L = $Ph_2PCH_2CH_2PPh_2$) are known[209].

Whereas halogen-bridged dimeric complexes of Pd(II) and Pt(II) are readily split by *p*-toluidine and other unidentate ligands, alkylthio-bridged complexes are not[209]. Ethanethiol reacts with the dichloro-bridged complex $[Bu_3PPdCl_2]_2$ to give the monothiolo-bridged complex (XII) which reacts further with EtSH to give the dithiolo-bridged complex (XIII)[427].



(XII)



(XIII)

Cis-$[Pd(PPr_3)(EtS)Cl]$ has been prepared but the *trans*-isomer has not been obtained[209].

Complexes of chelate ligands containing a thiol group are discussed below (p. 1298).

Sulphito complex. The sulphite ion is unidentate and *S*-bonded in the aqua-complex $[Pd(SO_3)(H_2O)_3]$ which cannot be dehydrated to give a bidentate sulphito complex[209]. The

[464] C. M. Harris and S. E. Livingtone, in *Chelating Agents and Metal Chelates* (F. P. Dwyer and D. P. Mellor, eds.), Academic Press, New York (1964), p. 95.

benzenesulphinato complexes $[Pd(PhSO_2)_2(H_2O)_2]$, $[Pd(PhSO_2)_2L_2]$ and $[PdX_2(PhSO_2)_2]^{2-}$ are *S*-bonded and the sulphinato ligand has a high *trans*-effect[464a].

Thiosulphato complex. In the complex $[Pd(S_2O_3)_2]^{2-}$ the thiosulphite ion is bidentate, being coordinated through one sulphur and one oxygen atom[209].

TABLE 40. PALLADIUM(II) COMPLEXES CONTAINING ORGANIC SULPHIDES, SELENIDES AND TELLURIDES

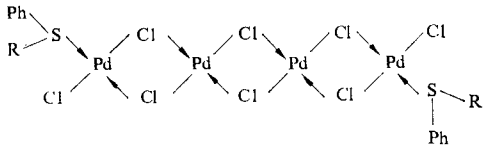
Compound		Colour
$[Pd(SR_2)_2Cl_2]$ [a]	(R = Me, Et, Pr, Bu, Am, heptyl, octyl, vinyl, Ph, $PhCH_2$; R_2 = MeEt, EtBu^t, EtAm^t, Bu^{t}Am^t, BuPh)	Yellow to light brown
$[Pd(SR_2)_2Br_2]$ [a]	(R = Me, Et, Bu^t, Am^t)	Yellowish brown
$[Pd(SR_2)_2I_2]$ [a]	(R = Me, Et, Bu^t, Am^t)	Deep red
$[Pd(SR_2)_2(NO_2)_2]$ [a]	(R = Me, Et, Pr^n, Bu^n, Am^n)	Deep yellow
$[Pd(SR_2)_2(NO_3)_2]$ [a]	(R = Me, Et, Bu^n, Am^n)	Deep yellow
$[Pd(SR_2)_2SO_4]$ [a]	(R = Me, Et, Bu, Am)	Yellow
$[Pd(SEt_2)_2C_2O_4]$ [a]		Yellow
$[Pd(SEt_2)_2(OH)_2]$ [a]		Brownish red
$[Pd(RSCH_2CH_2SR)Cl_2]$ [a]	(R = Me, Et, Ph, *p*-tolyl, $PhCH_2$)	Yellow
$[Pd(RSCH_2CH_2SR)Br_2]$ [a]	(R = Me, Et)	Yellowish orange
$[Pd(RSCH_2CH_2SR)I_2]$ [a]	(R = Me, Et)	Deep red
$[Pd(RSCH_2CH_2SR)(NO_3)_2]$ [a]	(R = Me)	Yellow
$[Pd(RSCH_2CH_2SR)(OH)_2]$ [a]	(R = Me)	Brownish red
$[Pd\{EtSCH_2CH_2SEt\}_2]X_2$ [a]	(X = Cl, picrate)	Yellow
$[Pd\{EtSCH_2CH_2SEt\}_2]Y$ [a]	(Y = $PdCl_4$, $OsCl_6$)	Red, yellow
$[Pd(SR_2)Cl_2]_2$ [b]	(R = Et, Pr^n)	Tan
$[Pd\{S(C_8H_{17})_2\}Cl_2]_2$ [a]		Deep brown
$[Pd(SeR_2)_2Cl_2]$ [a]	(R = Me, Et, Pr^n, Bu^n, Am^n, Ph)	Orange red
$[Pd(SeR_2)_2Br_2]$ [a]	(R = Me, Et, Pr^n, Bu^n, Am^n, Ph)	Orange red
$[Pd(SeR_2)_2I_2]$ [a]	(R = Me, Et, Pr^n, Bu^n, Am^n)	Nearly black
$[Pd(EtSeCH_2CH_2CH_2SeEt)X_2]$ [a]	(X = Cl, Br)	Deep yellow, orange
$[Pd(Pr^iSeCH_2CH_2SePr^i)X_2]$ [c]	(X = Cl, Br)	Yellow, orange
$[Pd(SeEt_2)Cl_2]_2$ [b]		Tan
$[Pd(TeR_2)Cl_2]_2$ [b]	(R = Et, Pr^n)	Dark red brown

[a] *Gmelin's Handbuch der Anorganischen Chemie*, Vol. 65, Verlag Chemie, Berlin (1942).
[b] J. Chatt and L. M. Venanzi, *J. Chem. Soc.* 1957, 2351.
[c] N. N. Greenwood and G. Hunter, *J. Chem. Soc.* A, 1967, 1520.

Complexes of organic sulphides, selenides and tellurides. These compounds are listed in Table 40. The sulphide complexes are readily obtained by the action of the organic sulphide with an aqueous solution of $[PdX_4]^{2-}$. The dimethylsulphide complex $(Me_2S)_2PdCl_2$ has been shown to have a *trans* structure; the other complexes are known in only one form which is presumed to be *trans*. The complexes of the type $(R_2S)_2PdX_2$ are soluble in benzene, chloroform and light petroleum. The chelate complexes are less soluble in organic solvents due to their *cis* configuration. The selenide complexes are similar to the sulphide complexes but the stabilities decrease in the series: $R_2S > R_2Se > R_2Te$. The chloro-bridged complexes $[Pd_2(MR_2)_2Cl_4]$ (M = S, Se, Te) are known.

[464a] B. Chiswell and L. M. Venanzi, *J. Chem. Soc.* A, 1966, 1246.

The Pd(II) complexes of RSPh (R = alkyl) have been used to identify alkyl phenyl sulphides, since, unlike dialkyl sulphides, these alkyl phenyl sulphides do not coordinate with Hg(II). When R = Bu^t or Me_2EtC the red complexes $PhSR \cdot 2PdCl_2$ are formed. These complexes may well possess the tetrameric structure (XIV); if so they are the only known Pd(II) complexes of this type[209].



(XIV)

A study has been made of the lability of thioether ligands coordinated to Pd(II) and Pt(II) and of the kinetics of their displacement by amines[465].

Thiourea complex. Thiourea (thu) acts as a unidentate ligand forming the *S*-bonded complex $[Pd(thu)_4]Cl_2$ [466]. Spectrophotometric studies have been carried out on solutions of Pd(II) containing thiourea[467].

Nitrogen sulphide complex. Nitrogen sulphide N_4S_4 reacts with Pd(II) in methanol to give reddish-brown crystals of $Pd(NS)_4$, soluble in organic solvents[468].

Complexes of triaryl phosphine sulphide and selenide and triphenylarsine sulphide. The donor properties of Ph_3PS and Ph_3PSe appear to be weaker than that of Ph_3PO. The complexes $Pd(Ph_3PS)_2Cl_2$, $Pd(Ph_3PSe)_2Cl_2$ and $Pd\{(m\text{-}MeC_6H_4)_3PSe\}_2Cl_2$ have been isolated[209, 469]. The orange–brown triphenylarsine sulphide complex $Pd(Ph_3AsS)_2Br_2$ is also known. The infrared spectra of these complexes have been discussed with respect to P–S, P–Se and As–S stretching vibrations[469].

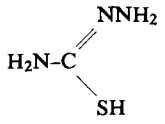
Dimethyl sulphide complexes. Dimethyl sulphoxide forms complexes with many metals by coordinating through oxygen. However, with Ir(III), Pd(II) and Pt(II), which have pronounced (b) class behaviour, the ligand is *S*-bonded[209]. The orange $PdCl_2(Me_2SO)_2$ has the *trans*-configuration, but the yellowish-orange nitrato complex $Pd(NO_3)_2(Me_2SO)_2$ is one of the few examples of a Pd(II) complex with a *cis*-configuration. The nitrato groups are unidentate; the coordinated N–O distance is 1.32 Å compared to 1.22 for the non-coordinated N–O bonds. The Pd–S bonds are non-equivalent with lengths of 2.23 and 2.25 Å, which are significantly shorter than the equivalent Pd–S bond lengths (2.30 Å) in *trans*-$PdCl_2(Me_2SO)_2$. The S–O stretching frequency for *trans*-$PdCl_2(Me_2SO)_2$ is 1116 cm^{-1}, while the two frequencies for *cis*-$Pd(NO_3)_2(Me_2SO)_2$ are 1136 and 1157 cm^{-1}; the crystallographic and infrared data suggest enhanced d_π–d_π bonding in the *cis*-complex[470].

Infrared and n.m.r. data indicate that the tetrakis-ligand complexes $[Pd(Me_2SO)_4]X_2$ (X = ClO_4, BF_4) contain two distinct types of coordinated dimethyl sulphoxide, one *S*- and one *O*-bonded; ν(S–O) occurs at 1150 and 1140 cm^{-1} (*S*-bonded) and 920 and 905 cm^{-1} (*O*-bonded)[471].

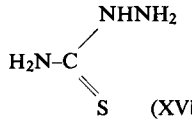
[465] M. Martelli, G. Marangoni and L. Cattalini, *Gazz. chim. ital.* **98** (1968) 1031, 1038.
[466] C. C. Addison and N. N. Greenwood, *Ann. Reports Chem. Soc. London* **55** (1958) 142.
[467] V. I. Shlenskaya, A. A. Biryukov and E. M. Moskovkina, *Zh. Neorg. Khim.* **11** (1966) 600.
[468] E. Fluck, M. Goehring and J. Weiss, *Z. anorg. Chem.* **287** (1956) 51.
[469] P. Nicpon and D. W. Meek, *Chem. Communs.* 1966, 398.
[470] D. A. Langs, C. R. Hare and R. G. Little, *Chem. Communs.* (1967) 1080.
[471] B. B. Wayland and R. F. Schramm, *Chem. Communs.* (1968) 1465; Yu. N. Kukushin, R. A. Vlasova and Yu. L. Pazukhina, *Zh. Priklad. Khim.* **41** (1968) 2381.

Complexes of chelate ligands with thioether or selenoether groups. Complexes containing the bidentate ligands $RSCH_2CH_2SR$ and $RSe(CH_2)_nSeR$ are listed in Table 40.

Thiosemicarbazide (Htsc) exists in the tautomeric forms (XVa, XVb) and can act as a charged or neutral chelate group. The inner complex $[Pd(tsc)_2]$ is known only in the *trans* form. Both *cis*- and *trans*-isomers of the cationic complex $[Pd(Htsc)_2]^{2+}$ have been prepared. The chloride is known only in the *trans* form and the nitrate only in the *cis* form, while both *cis*- and *trans*-isomers of the sulphate have been isolated. In these complexes the ligand coordinates through the sulphur and the terminal nitrogen, making a five-membered chelate ring[472].

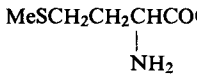


(XVa)

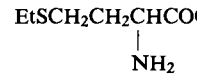


(XVb)

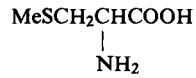
Palladium(II) complexes are known with a number of other S–N chelating agents. With first-row bivalent transition metal ions DL-methionine (XVI; mthH), DL-ethionine (XVII; ethH) and *S*-methyl-L-cysteine (XVIII; SmcH) yield complexes ML_2 (LH = mthH,



(XVI)



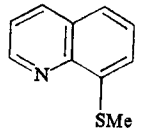
(XVII)



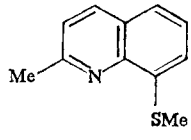
(XVIII)

ethH, SmcH) which are polymeric and 6-coordinate with the ligand bound via nitrogen and one oxygen, while the other oxygen is coordinated to another metal atom. On the other hand, with Pd(II) and Pt(II) these ligands yield the complexes $MX_2(LH)$ (M = Pd, Pt; X = Cl, Br) in which the ligand is coordinated through the nitrogen and sulphur atoms. Infrared evidence indicates that in the palladium and platinum complexes the carboxylic group is not coordinated to the metal atom, since the $\nu_{as}(COO)$ mode occurs in the range 1737–1703 cm^{-1}, i.e. about 120 cm^{-1} higher than in the spectra of the ML_2 complexes. The $\nu(M-S)$ mode occurs at 385–378 cm^{-1}, whereas the complexes of the first-row transition metals do not show a band in this region. An X-ray study on $PdCl_2(mthH)$ shows that the complex is square-planar with the ligand coordinated through sulphur and nitrogen; the molecules pack together as dimers with hydrogen bonding between the carboxylic groups. The interatomic distances are: Pd–Cl, 2.30; Pd–N, 2.07; Pd–S, 2.28 Å[473].

8-Methylthioquinoline (XIX; mtq) forms the mono-ligand complexes PdX_2mtq (X = Cl, Br, SCN) but no bis-ligand complexes could be isolated due to the insolubility of the mono-chelated compounds[474]. 2-Methyl-8-methylthioquinoline (XX; mmtq) forms the complexes



(XIX)



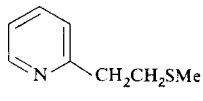
(XX)

[472] R. A. Haines and K. K. W. Sun, *Can. J. Chem.* **46** (1968) 3241.
[473] S. E. Livingstone and J. D. Nolan, *Inorg. Chem.* **7** (1968) 1447.
[474] L. F. Lindoy, S. E. Livingstone and T. N. Lockyer, *Austral. J. Chem.* **19** (1966) 1391; **20** (1967) 471.

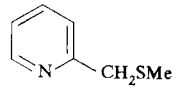
PdX_2mmtq (X = Cl, Br) but attempts to prepare the iodo and thiocyanato complexes were unsuccessful. Molecular models show that one molecule of mmtq and two iodo or *S*-bonded thiocyanato groups cannot fit around a square-plane. The bis-chelated complex $Pd(mmtq)_2(ClO_4)_2 \cdot H_2O$ was isolated. The complex is a bi-univalent electrolyte in nitrobenzene and the infrared spectrum indicates that the perchlorate groups are ionic in the solid complex. Because of steric interaction caused by the methyl groups in the 2-position, two mmtq molecules cannot be accommodated in a square-planar arrangement. Consequently a 5-coordinate trigonal bipyramidal structure, with the water molecule coordinated to palladium, is a likely possibility[475].

2-(2-Methylthioethyl)pyridine (XXI; mep) and 2-methylthiomethylpyridine (XXII; mmp) form the complexes PdX_2L and $[PdL_2](ClO_4)_2$ (L = mep, mmp; X = Cl, Br, I, SCN). Conductimetric titrations of $[Pd(mep)_2](ClO_4)_2$ with halide ion in nitrobenzene indicate that the following reaction occurs (X = Cl, Br, I) [476]:

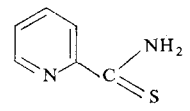
$$[Pd(mep)_2]^{2+} + 2X^- \rightarrow [PdX_2mep] + mep$$



(XXI)



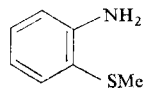
(XXII)



(XXIII)

2-Thiopicolinamide (XXIII; thpic) forms the complexes PdX_2 thpic (X = Cl, Br); infrared data show that the ligand is coordinated through the sulphur and the pyridine nitrogen, whereas with (a) class metals it is bound via both nitrogen atoms[477].

o-Methylthioaniline (XXIV; N-SMe) forms the mono-ligand complexes PdX_2(N–SMe) (X = Cl, Br, I, SCN) which are orange to reddish brown. The bis-ligand complex



(XXIV)

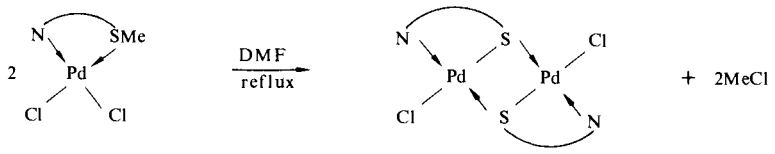
$[Pd(N–SMe)_2](PF_6)_2$ and $PdCl_2(N–SMe)_2$ were also isolated. A conductimetric titration of the former with iodide ion in nitrobenzene shows that the following reaction occurs:

$$[Pd(N–SMe)_2]^{2+} + 2I^- \rightarrow [PdI_2(N–SMe)] + (N–SMe)$$

The mauve colour of the insoluble chloro-complex $PdCl_2(N–SMe)_2$ suggests that it is not $[Pd(N–SMe)_2]Cl_2$, since $[Pd(N–SMe)_2](PF_6)_2$ is buff-coloured; otherwise its structure is unknown[474].

[475] P. S. K. Chia and S. E. Livingtone, *Austral. J. Chem.* **21** (1968) 339.
[476] P. S. K. Chia, S. E. Livingtone and T. N. Lockyer, *Austral. J. Chem.* **19** (1966) 1835; **20** (1967) 239.
[477] G. J. Sutton, *Austral. J. Chem.* **22** (1965) 150.

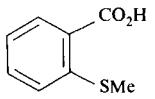
If the orange complex $PdCl_2(N\text{–}SMe)$ is heated in dimethylformamide, *S*-demethylation of the ligand occurs to yield the brown crystalline complex (XXV):



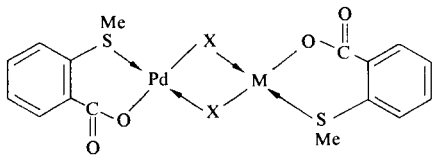
(XXV)

Other similar *S*-demethylation reactions of Pd(II) and Pt(II) chelates of sulphur ligands have been described[478].

o-Methylmercaptobenzoic acid (XXVI) forms inner complexes with Pd(II), Cu(II), Cd(II) and Hg(II) but not with Pt(II), which has a low affinity for oxygen ligands. This and other *o*-alkylmercaptobenzoic acids form halogen-bridged binuclear complexes



(XXVI)

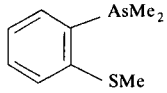


(XXVII)

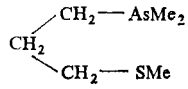
(XXVII; M = Pd, Cu, Hg; X = Cl or Br). The binuclear Pd(II) complexes readily react with unidentate ligands L (L = *p*-toluidine, $MePh_2As$) to yield $Pd(O_2C\cdot C_6H_4\cdot SR)_2$ and $PdBr_2L_2$ [479,480].

Instances of Pd(II) and Pt(II) having a coordination number greater than 4 have been discussed[447]. Further examples are known with the ligands 1,3-di(phenylthio)propane, $PhSCH_2CH_2CH_2SPh$, 1,3-di(phenylseleno)propane and $PhSeCH_2CH_2CH_2SePh$. These ligands yield the mono-ligand complexes PdX_2L, which when treated with another equivalent of ligand together with silver nitrate in methylene dichloride, yield the bis-ligand complexes $PdL_2(NO_3)_2$, which are uni-univalent electrolytes in nitromethane. The perchlorates $[PdL_2](ClO_4)_2$ behave as bi-univalent electrolytes in this solvent[481].

Dimethyl-*o*-methylthiophenylarsine (XXVIII) and dimethyl-3-methylthiopropylarsine (XXIX) yield the mono-ligand complexes $PdX_2(As\text{–}SMe)$ (X = Cl, Br, I; As–SMe



(XXVIII)



(XXIX)

[478] L. F. Lindoy, S. E. Livingstone and T. N. Lockyer, *Inorg. Chem.* **6** (1967) 652.
[479] S. E. Livingstone and R. A. Plowman, *J. Proc. Roy. Soc. NS Wales* **84** (1950) 188; **85** (1951) 116.
[480] S. E. Livingstone, *J. Chem. Soc.* 1956, 1989, 1994.
[481] J. Pluščec and A. D. Westland, *J. Chem. Soc.* 1965, 5371.

= XXVIII, XXIX) [482,483]. Whereas bis-ligand complexes could not be obtained with the aliphatic arsine (XXIX), the aromatic arsine (XXVIII) yields the complexes $[Pd(As–SMe)_2](ClO_4)_2$ and $Pd(As–SMe)_2X_2$. The perchlorate behaves as a bi-univalent electrolyte in nitrobenzene. Evidence from conductivity measurements, molecular weight determinations, and absorption spectra indicates that in acetone and nitrobenzene solutions of the halide complexes there exists an equilibrium[482]:

$$[Pd(As–SMe)_2X]X \rightleftarrows [Pd(As–SMe)X_2]+(As–SMe)$$

An X-ray study on $Pd(As–SMe)_2Br_2$ reveals that the two arsine ligands are chelated in a *cis*-square-planar arrangement, while the bromine atoms are not coordinated but are situated above and below the plane of the square at a distance (3.57 Å) which is too long for any significant degree of covalent bonding. The Pd–As distance is 2.36 Å and the Pd–S distance is 2.35 Å. On the other hand, X-ray analysis of the iodo-complex $Pd(As–SMe)_2I_2$ shows that in the crystalline complex both iodine atoms are coordinated and the ligand is bound via the arsenic atom only. The structure is *trans*-square-planar with the bond distances: Pd–As 2.39 Å and Pd–I 2.58 Å. The Pd–S distance (3.84 Å) is close to the sum of the van der Waals radii (3.92 Å). The As–Pd–I bond angle is 92° but the As–Pd–S angle is only 56° [484].

When the Pd(II) and Pt(II) chelates of dimethyl-*o*-methylthiophenylarsine are heated in dimethylformamide or cyclohexanone *S*-demethylation of the ligand occurs and complexes of dimethyl-*o*-mercaptophenylarsine can be isolated in good yield[478]. The reactions are as follows:

$$M(As\text{-}SMe)_2X_2 \xrightarrow[\text{reflux 8 hr}]{\text{DMF}} \text{[chelate: As, S, M, S, As]} + 2MeX$$

M = Pd; X = Cl, Br and M = Pt; X = Cl, I

$$2M(As\text{-}SMe)X_2 \xrightarrow[\text{reflux 8 hr}]{\text{DMF}} \text{[bridged: As, S, X, M, M, X, S, As]} + 2MeX$$

M = Pd; X = Cl, Br, I and M = Pt; X = I

The complexes $M(As–S)_2$ (M = Pd, Pt) can be *S*-alkylated:

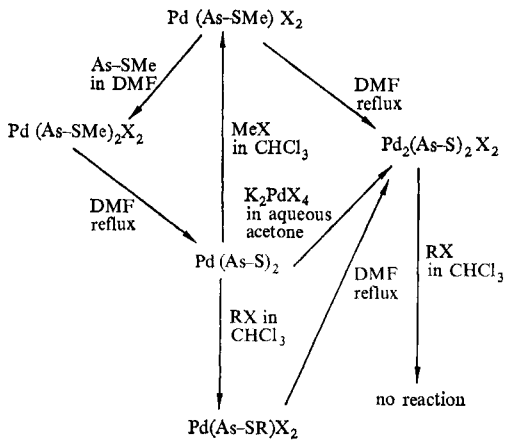
$$M(As–S)_2+2RX \xrightarrow{CHCl_3} M(As–SR)X_2+As–SR$$

---

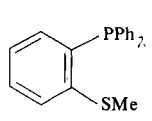
[482] S. E. Livingstone, *J. Chem. Soc.* 1958, 4222.
[483] B. Chiswell and S. E. Livingstone, *J. Inorg. Nucl. Chem.* **23** (1961) 37.
[484] J. P. Beale, S. E. Livingstone and N. C. Stephenson, unpublished results.

However, *S*-alkylation of the thiolo-bridged complexes $M_2(As–S)_2X_2$ could not be effected. These reactions are summarized in Scheme I.

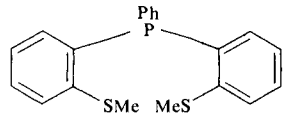
Scheme I



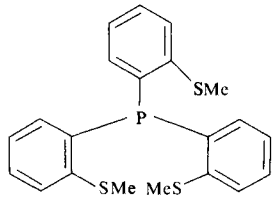
Diphenyl-*o*-methylthiophenylphosphine (XXX; P–SMe) forms the yellow $PdCl_2$(P–SMe) and the pale cream $[Pd(P–SMe)_2](ClO_4)_2$. If a solution of $PdCl_2$(P–SMe) is treated with one equivalent of (P–SMe) in boiling DMF, orange crystals of $Pd(P–S)_2$ can be isolated. If a



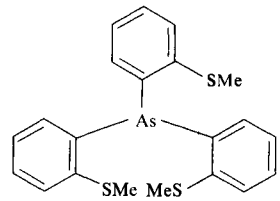
(XXX)



(XXXI)



(XXXII)



(XXXIII)

solution of $PdCl_2$(P–SMe) is heated in DMF, the yellow thiolo-bridged complex $Pd_2(P–S)_2Cl_2$ is formed[485]. The 5-coordinate complex $[Pd(P–SMe)_2I]ClO_4$ has been isolated[486].

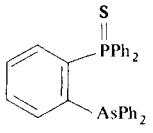
Phenylbis(*o*-methylthiophenyl)phosphine (XXXI; MeS–P–SMe) cannot occupy three coordination positions in a square-plane. The complexes PdX_2(MeS–P–SMe)

[485] S. E. Livingstone and T. N. Lockyer, *Inorg. Nucl. Chem. Letters* **3** (1967) 35.
[486] G. Dyer, M. O. Workman and D. W. Meek, *Inorg. Chem.* **6** (1967) 1404.

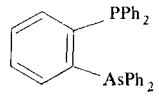
are non-electrolytes and are probably 5-coordinate. The 4-coordinate complex $[Pd(MeS–P–SMe)Cl]ClO_4$ and the bis-ligand complex $[Pd(MeS–P–SMe)_2](ClO_4)_2$, which is probably 6-coordinate, have been reported[485, 486].

The tripod-shaped ligands tris(*o*-methylthiophenyl)phosphine (XXXII; $P(SMe)_3$) and tris(*o*-methylthiophenyl)arsine (XXXIII; $As(SMe)_3$) form the complexes $[PdCl_2L]$, $[PdL_2](ClO_4)_2$ and Pd_2LCl_4 (L = $P(SMe)_3$, $As(SMe)_3$). The coordination number of palladium in these compounds is uncertain but it probably exceeds 4 [486].

Diphenyl(*o*-diphenylarsinophenyl)phosphine sulphide (XXXIV; As–PS) forms the complexes PdX_2(As–PS) (X = Cl, Br, I, SCN, SeCN) and $[Pd(As–PS)_2](NO_3)_2$; the iodo-complex is purple. The lowering of ν(P=S) in these complexes compared to that of the



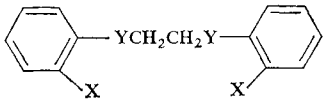
(XXXIV)



(XXXV)

free ligand indicates that the ligand is coordinated through arsenic and sulphur. The electronic spectra of the complexes indicate that the phosphine sulphide (XXXIV) exerts a weaker field than the corresponding phosphine (XXXV) [487].

A study has been made of the complexes formed by Pd(II) with the multidentate ligands of the type (XXXVI). Complexes were obtained of the type PdX_2L (L = ON, SN, OAS, SAS; X = Cl, Br, I, SCN). All the complexes are 4-coordinate with the ligands bidentate.

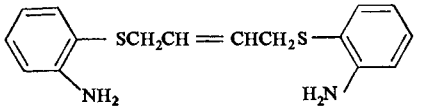


(XXXVI)

ON: X = NH_2; Y = O
SN: X = NH_2; Y = S
OAS: X = Ph_2As; Y = O
SAS: X = Ph_2As; Y = S

The ON and OAS ligands span the *trans* positions about the metal atom and are bonded through the nitrogen and arsenic atoms, respectively. In the SN complexes only the two sulphur atoms are coordinated in a *cis*-square-planar arrangement. The electronic spectrum of PdI_2(SAS) is almost identical with that of PdI_2(As–SMe); therefore it seems certain that the ligand is coordinated via one arsenic and one sulphur atom, each from the same benzene ring[488].

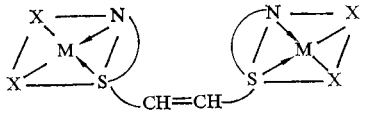
1,4-Di(*o*-aminothiophenoxy)but-*trans*-2-ene (XXXVII; chel) forms insoluble binuclear complexes M_2X_4(chel) (M = Pd, Pt; X = Cl, Br, I, SCN). The complexes react readily



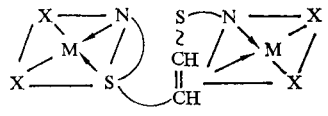
(XXXVII)

[487] P. Nicpon and D. W. Meek, *Inorg. Chem.* **6** (1967) 145.
[488] R. D. Cannon, B. Chiswell and L. M. Venanzi, *J. Chem. Soc.* A, 1967, 1277.

with pyridine and tertiary arsines but not with *p*-toluidine. The palladium complexes are yellow to orange red while the platinum complexes are yellow. The complexes are considered to possess structure (XXXIX) rather than (XXXVIII), since (i) reactions of the



(XXXVIII)



(XXXIX)

complexes indicate that the two metal atoms are in different environments, (ii) reaction with MeI to form a sulphonium ion indicates the non-equivalence of the thioether groups, and (iii) the infrared spectra indicate coordination of the double bond[489].

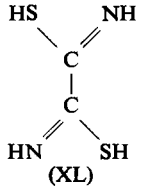
The P–S ligands bis(diphenylphosphinoethyl)sulphide, $Ph_2PCH_2CH_2SCH_2CH_2PPh_2$ (PSP), and 1,2-bis(diphenylphosphinoethylthio)ethane,

$$Ph_2PCH_2CH_2SCH_2CH_2SCH_2CH_2PPh_2 \text{ (PSSP)},$$

form the complexes [Pd(PSP)X]Y (X = Cl, Br, I; Y = X, ClO_4, BPh_4), [Pd(PSSP)][PdX_4] and [Pd(PSSP)X]ClO_4 (X = Br, I) [490].

Complexes of ligands containing one thiol group. There are a number of mercaptocarboxylic acids which can lose protons from the thiol group and from one or two carboxyl groups to yield doubly or triply negatively charged bidentate or tridentate O–S ligands. Among these are the acids thioglycollic $HSCH_2CO_2H$, thiodiglycollic $HO_2CCH_2SCH_2CO_2H$, β-mercaptopropionic $HSCH_2CH_2CO_2H$, mercaptosuccinic $HO_2CCH(SH)CH_2CO_2H$, and thiosalicyclic o-$HS \cdot C_6H_4 \cdot CO_2H$, and cysteine $HSCH_2CH(NH_2)CO_2H$. They form soluble anionic Pd(II) complexes; various species, including bridged species, have been identified in solution[491].

Dithio-oxamide (rubeanic acid) (XL) and its *NN'*-disubstituted derivatives give insoluble



(XL)

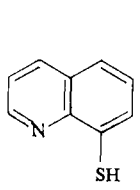
(XLI)

(XLII)

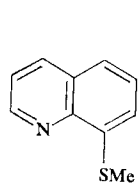
polymeric complexes with Pd(II) [209]. The Pd(II) complexes of *NN'*-bis(2-sulphoethyl)dithiooxamide have been studied spectrophotometrically[492]. Both guanylthiourea (XLI) and dithiobiuret (XLII) can lose a proton and form insoluble inner complexes with Pd(II) [464].

[489] D. C. Goodall, *J. Chem. Soc.* A, 1966, 1562.
[490] G. Degischer and G. Schwartzenbach, *Helv. Chim. Acta* **49** (1966) 1927.
[491] A. N. Kumar and H. L. Nigam, *Acta Chim. Acad. Sci. Hung.* **48** (1966) 219; S. C. Sinha and H. L. Nigam, *Indian J. Chem.* **4** (1966) 373.
[492] A. Goeminne, M. Herman and Z. Eeckhaut, *Bull. soc. chim. belges* **77** (1968) 357.

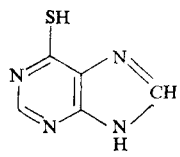
8-Mercaptoquinoline (8-quinolinethiol; XLIII) and its derivatives form strong chelates



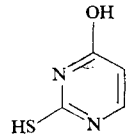
(XLIII)



(XLIV)



(XLV)



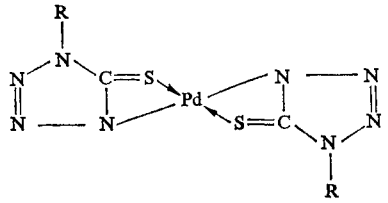
(XLVI)

with (b) class metals. The chelates of the platinum metals with 5-chloro- and 5-bromo-8-mercaptoquinoline are more stable than the corresponding complexes of 8-mercaptoquinoline. The stability of the chelates of 5-chloro-8-mercaptoquinoline is in the order Pd > Pt > Rh > Ir > Ru > Os [209]. The complexes PdX_2(N–SMe) (X = Cl, Br; N–SMe = 8-methylthioquinoline XLIV), when heated in DMF, undergo *S*-demethylation to yield the insoluble thiolo-bridged complexes $[PdX(N–S)]_n$ [478].

6-Mercaptopurine (XLV; 6MPH) is a biologically important anti-carcinogen and the Pd(II) complex $Na_2[Pd(6MP)_2Cl_2]\cdot H_2O$ has been found to be an effective anti-tumour agent[493]. The anti-tumour activity of 6-methylmercaptopurine (6MMP) is about 20% that of 6-mercaptopurine and it is possible that the methyl derivative is converted to 6-mercaptopurine in the host tissue[494]. Since it was thought that the *S*-demethylation *in vivo* might be accomplished by the agency of (b) class metal ions, an attempt was made to *S*-demethylate $PdCl_2$(6MMP), but only products of indefinite composition were isolated[495].

Thiouracil (XLVI; thuH) has been used as a drug for the treatment of hyperthyroidism, since it inhibits the production of thyroxine. The Pd(II) complex $Pd(thu)_2$ is reddish brown. Its insolubility, together with infrared data, suggest that the complex is polymeric with thiolo-bridges and that the ligand is coordinated through sulphur only[495].

1-Alkyltetrazoline-5-thiones form inner complexes with Pd(II); they are believed to possess the structure (XLVII) [496].

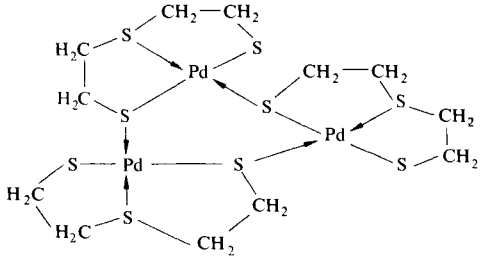


(XLVII)

2,2′-Dimercaptodiethylsulphide forms insoluble 1:1 complexes with Co(II), Ni(II), Pd(II), Pt(II), Hg(II) and Pb(II). The Ni(II) complex is a dimer, while the Pd(II) complex

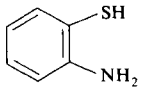
[493] S. Kirschner, Y. Wei, D. Francis and J. C. Bergman, *J. Med. Chem.* **9** (1966) 369.
[494] A. Furst, *The Chemistry of Chelation in Cancer*, Thomas, Springfield, Ill. (1963), p. 52.
[495] L. F. Lindoy, S. E. Livingstone and J. D. Nolan, unpublished results.
[496] U. Agarwala, V. A. Narayan and S. K. Dikshit, *Can. J. Chem.* **45** (1967) 1057.

has the trimeric structure (XLVIII). Each palladium atom has an approximately square-planar arrangement but the molecule is not flat but bent at the bridging sulphur atoms so that the three squares are inclined towards each other[497].

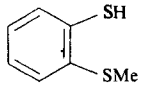


(XLVIII)

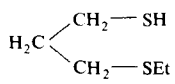
o-Aminobenzenethiol (XLIX), *o*-methylthiobenzenethiol (L), 3-ethylthiopropane-1-thiol (LI), and 3-dimethylarsinopropane-1-thiol (LII) form square-planar inner complexes



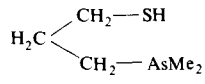
(XLIX)



(L)

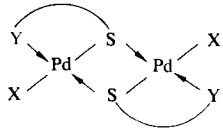


(LI)



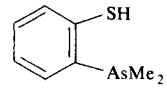
(LII)

with Ni(II), Pd(II), and Pt(II). The Pd(II) complexes react with $K_2[PdX_4]$ in aqueous acetone to give the thiolo-bridged complexes (LIII) which are more stable than halogen-bridged compounds[480].



(LIII)

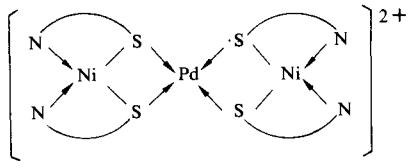
(X = Cl, Br, I, SCN, NO_2)
(Y = N, S, As)



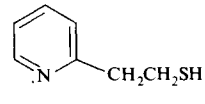
(LIV)

The Pd(II) complex of dimethyl-*o*-mercaptophenylarsine (LIV) was obtained by *S*-demethylation of $PdX_2(As–SMe)_2$ as described on p. 1295[478]. The complex is *trans*-square-planar with Pd–As 2.34 and Pd–S 2.30 Å and the SPdAs angle is 86° [484].

2-Aminoethanethiol gives a monomeric inner complex $[Pd(H_2NCH_2CH_2S)_2]$ and a



(LV)



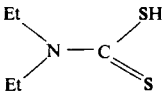
(LVI)

[497] G. A. Barclay, E. M. McPartlin and N. C. Stephenson, *Inorg. Nucl. Chem. Letters* **3** (1967) 397.
[498] D. C. Jicha and D. H. Busch, *Inorg. Chem.* **1** (1962) 872, 878, 884.

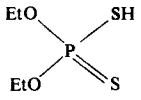
mixed Ni–Pd trinuclear thiolo-bridged cationic complex (LV) [498]. 2-(2-Mercaptoethyl)pyridine (LVI; N–SH) forms the yellow sparingly soluble monomer [Pd(N–S)$_2$] and the orange dimeric complex $Pd_2Cl_2(N–S)_2$ which has the thiolo-bridged structure (LIII; Y = N) [499].

Phosphorus–sulphur ligands of general formula $R_{3-x}P(CH_2CH_2SH)_x$ (R = H, Et, Ph; x = 1, 2, 3) form square-planar complexes with Ni(II), Pd(II), Pt(II) and Au(III) [490].

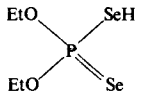
Complexes of diethyldithiocarbamate, diethyldithiophosphate, diethyldiselenophosphate and dithiocarboxylates. Diethyldithiocarbamate (LVII; dtcH), diethyldithiophosphate (LVIII; dtpH), and diethyldiselenophosphate (LIX; dspH) form the orange complexes $Pd(dtc)_2$, $Pd(dtp)_2$, and $Pd(dsp)_2$ [291, 500]. The complex $Pd(dtp)_2$ (LX) exhibits ν(Pd–S) at 317 cm^{-1} [501] and displays carcinostatic activity, being more active than $Ni(dtp)_2$ [502].



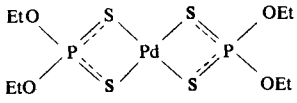
(LVII)



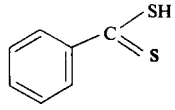
(LVIII)



(LIX)



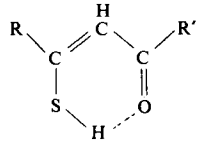
(LX)



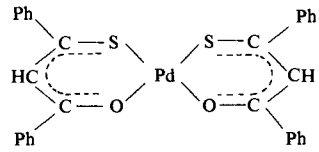
(LXI)

Dithiobenzoic acid (LXI) forms the dark red-violet complex $Pd(PhCS_2)_2$ in which there is virtual planarity of all the atoms; the coordination about the palladium atom is distorted tetragonal. The four sulphur atoms in the plane lie at from 2.32 to 2.34 Å from the palladium atom, while the sulphur atoms from neighbouring molecules are situated at a distance of 3.3–3.5 Å [503].

Complexes of thio-derivatives of β-diketones. Monothio-β-diketones (LXII) form strong complexes with (b) class metals; the Pd(II) complexes are listed in Table 41 [290, 504]. The



(LXII)



(LXIII)

[499] J. W. Wrathall and D. H. Busch, *Inorg. Chem.* **2** (1963) 1182.

[500] C. Furlani, E. Cervone and F. D. Camassei, *Inorg. Chem.* **7** (1968) 265; J. P. Fackler, W. C. Seidel and J. A. Fetchin, *J. Am. Chem. Soc.* **90** (1968) 2707.

[501] S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles and J. S. Shannon, *Austral. J. Chem.* **18** (1965) 673.

[502] S. E. Livingstone and A. E. Mihkelson, *Inorg. Chem.* **9** (1970) 2545.

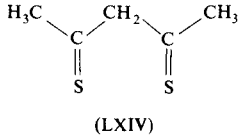
[503] M. Bonamico and G. Dessy, *Chem. Communs.* 1968, 483; C. Furlani and M. L. Luciani, *Inorg. Chem.* **7** (1968) 1586.

[504] R. K. Y. Ho, S. E. Livingstone and T. N. Lockyer, *Austral. J. Chem.* **19** (1966) 1179; **21** (1968) 103.

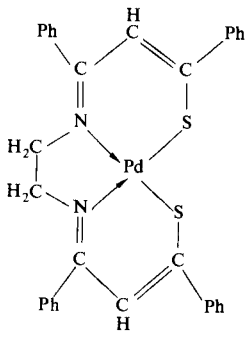
Pd(II) complex of 3-mercapto-1,3-diphenylprop-2-en-1-one (LXII; R = R′ = Ph) has the *cis*-square planar configuration (LXIII) in which the S–Pd–S bonds are close to 90° and the average Pd–S distance is 2.24 Å [505]. Whereas Pd(II) complexes are almost invariably more deeply coloured than their Pt(II) analogues, the Pt(II) complexes of monothio-β-diketones are darker (more red) than the corresponding Pd(II) complexes. The highest frequency band of the Pd(II) complex where R = R′ = Ph occurs at 22,400 cm^{-1}, while that of the Pt(II) complex occurs at 19,600 cm^{-1}. This band is probably the $M \rightarrow L_{\pi}^{*}$ charge-transfer band. The order of increasing frequency of the $M \rightarrow L_{\pi}^{*}$ band is Ni ≃ Pt < Pd for the complexes of maleonitriledithiol and cyanide ion[506]. A similar situation occurs with 2,3-quinoxalinedithiol: the Pd(II) complex is red, while the Pt(II) complex is blue[507].

Adducts of some Pd(II) complexes of monothio-β-diketones have been obtained with 1,10-phenanthroline, 2,2′-bipyridyl and triphenylphosphine (Table 41). The high frequency of ν(C=O)—1670–1620 cm^{-1}—in the spectra of these adducts, compared to ν(C=O) in the spectra of the Ni(II) adducts, indicates that in the Pd(II) adducts the monothio-β-diketone is bound by sulphur only and thus the palladium atom is 4-coordinate[504].

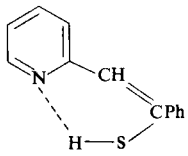
Although dithioacetylacetone (LXIV; SacSacH) cannot be isolated, metal chelates of this ligand have been isolated; $Pd(SacSac)_2$ is bright red and Pt(SacSac) is purple[508].



(LXIV)



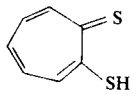
(LXVI)



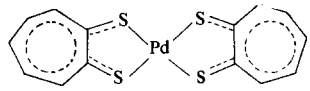
(LXV)

2-Picolylphenylthioketone (LXV) forms a stable Pd(II) complex similar to those formed by monothio-β-diketones[509]. Of similar structure is the yellowish-brown complex (LXVI) [509].

Dithiotropolone (LXVII; SSTH) forms the violet monomeric complex $Pd(SST)_2$ which is considered to possess the delocalized structure (LXVIII) [510].



(LXVII)



(LXVIII)

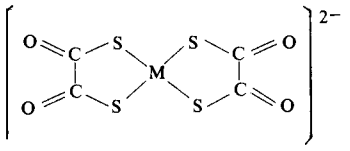
[505] E. A. Shugam, L. M. Shkol'nikova and S. E. Livingstone, *Zh. Strukturnoi Khim.* **8** (1967) 550.
[506] S. H. H. Chaston and S. E. Livingstone, *Austral. J. Chem.* **20** (1967) 1079.
[507] C. K. Jørgensen, *Inorg. Chim. Acta Rev.* **2** (1968) 65.
[508] R. L. Martin and I. M. Stewart, *Nature* **210** (1966) 522.
[509] E. Uhlemann, G. Klose and H. Muller, *Z. Naturforsch.* **19b** (1964) 962; E. Uhlemann, *ibid.* **21b** (1966) 592.
[510] C. E. Forbes and R. H. Holm, *J. Am. Chem. Soc.* **90** (1968) 6884.

TABLE 41. PALLADIUM(II) CHELATES OF MONOTHIO-β-DIKETONES[290, 504]
L, RC(S)=CHCOR′

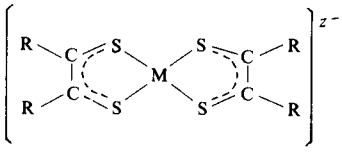
R	R′	Compound	Colour	M.p. (°)
Me	CF_3	PdL_2	Orange	154
2-thienyl	CF_3	PdL_2	Red	246
Ph	Ph	PdL_2	Orange	133
Ph	CF_3	PdL_2	Orange	190
Me	CF_3	PdL_2bipy	Orange	172
Me	CF_3	PdL_2phen	Orange	195
2-thienyl	CF_3	PdL_2phen	Red	181
2-thienyl	CF_3	PdL_2PPh_3	Deep red	166
2-thienyl	CF_3	$PdL_2(PPh_3)_2$	Orange	105
Ph	CF_3	PdL_2bipy	Red	201
Ph	CF_3	PdL_2phen	Orange	212
Ph	CF_3	$PdL_2(PPh_3)_2$	Orange	195

Metal complexes of thiols and thio-derivatives of β-diketones have recently been reviewed[511].

Complexes of α-dithiols. The dithio-oxalate ion forms highly coloured, very stable, square-planar complexes (LXIX; M = Ni, Pd, Pt) [209].



(LXIX)



(LXX)

In 1962 Schrauzer and Mayweg reported the first example of what are now known as 1,2-dithiolene complexes; this was the diamagnetic complex $Ni(Ph_2C_2S_2)_2$. In the same year Gray *et al.* reported the complexes $[NBu]_4[M(MNT)_2]$ (M = Co, Ni, Pd, Pt, Cu, Zn; MNT = maleonitriledithiolate). In 1963 Holm and co-workers pointed out the relationship between the nickel complex of Schrauzer and the MNT complexes and they reported three series of complexes, related by electron transfer reactions, of general formula (LXX; when R = Ph, CF_3, M = Ni, $z = 0, -1, -2$; when R = CN, M = Co, Ni, Pd, Pt, Cu, Au, $z = -1$) [512]. Since then a large number of publications have appeared dealing with these interesting compounds. This work has been discussed in four reviews[209, 459, 513, 514].

[511] R. C. Mehotra, V. D. Gupta and D. Sukhani, *Inorg. Chim. Acta Rev.* **2** (1968) 111.

[512] G. N. Schrauzer and V. Mayweg, *J. Am. Chem. Soc.* **84** (1962) 3221; H. B. Gray, R. Williams, I. Bernal and E. Billig, *ibid.* **84** (1962) 3596; A. Davison, N. Edelstein, R. H. Holm and A. H. Maki, *ibid.* **85** (1963) 2029; *Inorg. Chem.* **2** (1963) 1227.

[513] G. N. Schrauzer, *Transition Metal Chemistry* (R. Carlin, ed.), Edward Arnold, London (1968), Vol. 4, p. 299.

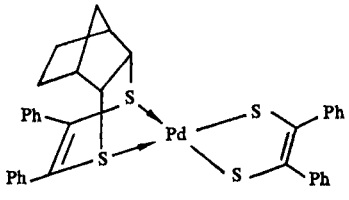
[514] J. A. McCleverty, *Progr. Inorg. Chem.* (F. A. Cotton ed.), Interscience, New York (1968), Vol. 10, p. 49.

TABLE 42. 1,2-DITHIOLATE COMPLEXES OF PALLADIUM[512, 514]

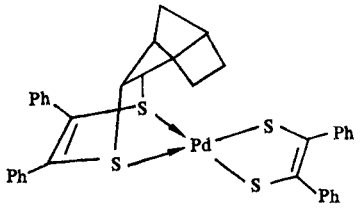
Compound	Colour	M.p. (°)	μ (BM)
$[NBu_4]_2[Pd\{S_2C_2(CN)_2\}_2]$	Green	155–158	diam.
$[NEt_4][Pd\{S_2C_2(CN)_2\}_2]$	Dark red	275 d	diam.
$[Ph_4As]_2[Pd\{S_2C_2(CF_3)_2\}_2]$	Pale green	248–251	diam.
$[Ph_4As][Pd\{S_2C_2(CF_3)_2\}_2]$	Reddish brown	245–247	1.73
$[N_2H_5]_2[Pd(S_2C_2Ph_2)_2]$	Orange	132 d	*
$[Pd(S_2C_2Ph_2)_2]$	Blue	—	diam.
$[Pd\{S_2C_2(p\text{-}MeOC_6H_4)_2\}_2]$		294	diam.
$[NPr_4]_2[Pd(S_2CNCN)_2]$ [a]	Yellow	178	diam.
$[AsPh_4]_2[Pd(CS_3)_2]$ [a]	Brownish red	178	diam.
$[Pd(Ph_3P)_2\{S_2C_2(CF_3)_2\}]$	Pale pink	—	diam.
$[Pd(Ph_3P)_2\{S_2C_2(CN)_2\}]$	Deep pink	—	diam.
$[Pd(S_2C_2Ph_2)(Ph_2CH_2CH_2Ph_2)]$ [b]		—	diam.
$[Pd_2S_4C_4Ph_4(Ph_3P)_2]$ [b]	Green	282 d	diam.

* Not measured.
[a] J. P. Fackler and D. Coucouvanis, *J. Am. Chem. Soc.* **88** (1966) 3913.
[b] V. P. Mayweg and G. N. Schrauzer, *Chem. Communs.* 1966, 640.

The Pd(II) complexes are listed in Table 42. The complexes of trithiocarbonate, CS_3^{2-}, and *N*-cyanodithiocarbimate, $S_2C{=}NCN$, have been included in the table; as yet these complexes have not been reduced to other anionic species. Complexes with one dithiolate and two phosphine ligands can be obtained by substitution of one dithiolate by two phosphines. Of interest is the adduct of $Pd(S_2C_2Ph_2)_2$ with norbornene which could have either of the structures (LXXI) or (LXXII) [513].



(LXXI)



(LXXII)

The polarographic behaviour, infrared, electronic and e.s.r. spectra of some of the Pd(II) dithiolate complexes have been studied[459, 513, 514].

Complexes of Nitrogen Ligands

The Pd–N bond is quite strong and many complexes with nitrogen donors are known. The complexes are of the types $[Pdam_4]^{2+}$, $[Pdam_2X_2]$ and $[PdamX_2]_2$ (am = NH_3, amine, ½ diamine). The palladium complexes are much more labile than those of platinum as can be seen by the fact that the addition of HCl will readily convert $[Pdam_4]Cl_2$ to $[Pdam_2Cl_2]$, whereas the conversion is much more difficult with platinum. Only a few instances of *cis-trans* isomerism are known for palladium, but they are numerous for platinum.

Pd–N stretching frequencies. Metal–nitrogen stretching frequencies are often weak and difficult to assign with certainty. For $[M(NO_2)_4]^{2-}$ and $[M(NH_3)_4]^{2+}$ the order of ν(M–N) is Pt > Pd, whereas the reverse holds for ν(M–X). The values of ν(Pd–N) found in various complexes are listed in Table 43 [106]. The (N–H) frequencies of *trans*-[L, amMCl$_2$] (M = Pd, Pt) give evidence for the interaction between the N–H bonds and the non-bonding *d*-electrons on the metal[466].

TABLE 43. PALLADIUM–NITROGEN STRETCHING FREQUENCIES (cm^{-1})

Compound	ν(Pd–N)	Compound	ν(Pd–N)
$[Pd(NH_3)_4]Cl_2 \cdot H_2O$	498	[PdCldien]Cl	557 ν_{as}
$[Pden_2]Cl_2$	585		486 ν_s
	521		517 ν(Pd–N′)*
$[PdenCl_2]$	561	[PdBrdien]Br	555 ν_{as}
	539		487 ν_s
trans-$[PdCl_2(NH_3)_2]$	496		511 ν(Pd–N′)
trans-$[PdBr_2(NH_3)_2]$	494	[PdIdien]I	554 ν_{as}
trans-$[PdI_2(NH_3)_2]$	486		488 ν_s
cis-$[PdCl_2(NH_3)_2]$	495		499 ν(Pd–N′)
	476	$K_2[Pd(NO_2)_4]$	363
			330

* N′ atom *trans* to X.

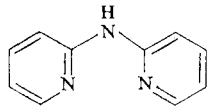
Tetrammine-type complexes. The salts $[Pd(NH_3)_4]X_2$ can be easily prepared; they are known for X = F, Cl, Br, I, NO_3, $AuCl_4$; 2X = SO_3, SO_4, CO_3, $PdCl_4$, $PdCl_6$, $PdBr_4$, $Pd(SCN)_4$, $PtCl_4$, $CuCl_4$, $OsCl_6$ [426]. The $[Pd(NH_3)_4]^{2+}$ ion is colourless. The free base $[Pd(NH_3)_4](OH)_2$ can be obtained as colourless crystals by treating the sulphate with $Ba(OH)_2$. The pink $[Pd(NH_3)_4][PdCl_4]$ is isostructural with Magnus's green salt, $[Pt(NH_3)_4][PtCl_4]$; the Pd–Pd distance (*ca.* 3.3 Å) and the dichroism confirm the existence of some interaction between the palladium atoms[447].

Similar complexes $[Pdam_4]Cl_2$ and $[Pdam_4][PdX_4]$ are formed by amines (X = Cl, Br; am = $MeNH_2$, $EtNH_2$, $PrNH_2$, Bu^tNH_2, py) [426]. The colourless $[Pdam_4]Cl_2$ loses amine and turns yellow with the concomitant formation of *trans*-$[PdCl_2am_2]$. The values of the formation constants (log K_n) for $[Pd(NH_3)_4]^{2+}$ are 9.6, 8.9, 7.5 and 6.8, whereas the values for $[Pdpy_4]^{2+}$ are *ca.* 1.5 log units lower[515].

Ethylenediamine and propylenediamine (pn) form the complexes $[Pden_2]X_2$ (X = Cl, ClO_4; 2X = $PdCl_4$, $PdBr_4$, $PdBr_6$) and $[Pdpn_2]Cl_2$. For $[Pden_2]^{2+}$ log β_2 is 26.9 [460]. The deprotonated en complex [Pden(en–H)]I is known; it can be methylated with methyl iodide under mild conditions[516]. 2,2′-Dipyridylimine (LXXIII) forms a bis-ligand inner

[515] L. Rasmussen and C. K. Jørgensen, private communication.
[516] G. W. Watt and D. H. Carter, *Inorg. Chem.* 7 (1968) 2451.

complex $[Pd(C_{10}H_8N_3)_2]$ in which the four donor nitrogens are exactly coplanar and the ligands are considerably distorted from planarity[517].



(LXXIII)

The deep yellow complexes $[Pdphen_2](ClO_4)_2$ and $[Pdbipy_2](ClO_4)_2$ have been prepared. They can be recrystallized from water but in solution they are readily converted by halide ions into the non-electrolytes $[PdchelX_2]$ (chel = phen, bipy) [518]. Conductimetric titrations of the perchlorates $[Pd(chel)_2](ClO_4)_2$ with X^- ions (X = Cl, Br, I) in nitrobenzene and nitromethane give an end-point after the addition of one equivalent of halide ion, owing to the formation of the ions $[Pd(chel)_2X]^+$. Another end-point is obtained after the addition of a second equivalent of halide ion. Spectral evidence shows that in nitrobenzene $[Pdbipy_2I_2]$ is formed but in the more polar solvent nitromethane the reaction

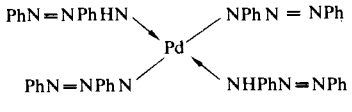
$$[Pd(chel)_2X]^+ + X^- \rightarrow [Pd(chel)X_2] + chel$$

occurs[446]. For two phenanthroline or bipyridyl ligands in planar coordination there is considerable steric interaction between the hydrogen atoms of opposite ligands. In an octahedrally coordinated complex this steric hindrance leads to increased stability of the *cis* over the *trans* isomer of $[M(chel)_2X_2]^{n+}$. It is likely that the ions $[Pd(chel)_2]^{2+}$ exist in solution in either of the solvated forms $[Pd(chel)_2\ (solvent)]^{2+}$ or $[Pd(chel)_2(solvent)_2]^{2+}$ in which the two nitrogen heterocycles are not coordinated in a square plane. Presumably $[Pd(chel)_2X_2]$ has a *cis* configuration[446].

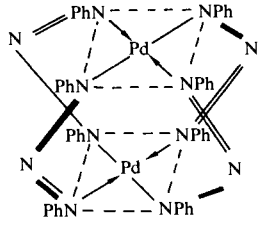
A recent structure determination of $[Pdphen_2](ClO_4)_2$ indicates that the palladium atom does have planar coordination and the ligand molecules appear to be somewhat bowed about their twofold axes by the steric strain[519]. The colourless mixed ligand complexes $[Pd(chel)am_2](ClO_4)_2$ (am = NH_3, py, ½en) have been reported[518]. The colourless $[Pd(den)py](ClO_4)_2$ (den = diethylenetriamine $NH(CH_2CH_2NH_2)_2$ has been prepared[515].

The quadradentate ligand β,β',β''-triaminotriethylamine $N(CH_2CH_2NH_2)_3$ (tren) can coordinate to all four positions in the square plane to yield $[Pdtren]I_2$ which is only slightly soluble in water[427].

1,3-Diphenyltriazen (dptH), also known as diazoaminobenzene, forms a monomeric complex $[Pd(dpt)_2(dptH)_2]$ and a dimeric complex $[Pd_2(dpt)_4]$ with the structures (LXXIV) and (LXXV), respectively[447].



(LXXIV)



(LXXV)

[517] H. C. Freeman, J. F. Geldard, F. Lions and M. R. Snow, *Proc. Chem. Soc.* 1964, 258.
[518] S. E. Livingstone, *J. Proc. Roy. Soc. NS Wales* **85** (1951) 151; **86** (1952) 32.
[519] J. V. Rund, *Inorg. Chem.* **7** (1968) 24.

NN'-bis-(2-aminoethyl)-1,4-diazacycloheptane (baeda) acts as a quadridentate in the complex $[Pd(baeda)](ClO_4)_2$ [520].

A number of complexes have been obtained with quadradentate ligands containing the deprotonated amide group: *NN'*-di-(2-aminoethyl)malondiamide yields

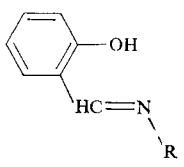
$$Pd\{CH_2(CONCH_2CH_2NH_2)_2\}\cdot 3H_2O;$$

NN'-di-(3-benzylaminopropyl)oxamide gives $Pd\{CH_2(CON[CH_2]_3NHCH_2Ph)_2\}$; and *NN'*-di-(*S*-ethylmercaptoacetyl)-1,3-diaminopropane gives $Pd\{CH_2(CH_2NCOCH_2SEt)_2\}$. Neutral complexes are also formed with the ligands $H_2NCOCH_2S[CH_2]_nSCH_2CONH_2$ (n = 2, 3) [521].

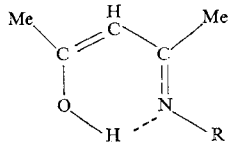
The interesting complexes $[M(L^+)_4](ClO_4)_6$ (M = Cu, Zn, Cd, Pd) have been obtained with the cationic ligand $Me_3N^+CH_2CH_2CH_2NH_2$ (L^+) [522].

The complex stilbenediamine*iso*butylenediaminepalladium(II) chloride was resolved in the same way as the corresponding Pt(II) complex, thus establishing unequivocally the square-planar configuration about Pd(II) [427].

Schiff base complexes. Salicyladoximes (LXXVI; R = cyclohexyl, Pr^i, Bu^s, Bu^t form inner complexes with Pd(II) which are distorted from the square-planar arrangement[523].



(LXXVI)



(LXXVII)

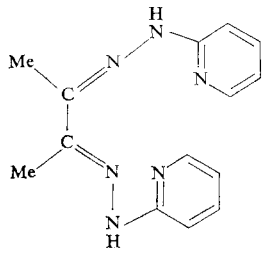
A crystal structure analysis of di-(*N*-ethylsalicylaldimine)palladium(II) shows that the complex is *trans*-square-planar with non-planar chelate rings[624].

In general, complexes of 3*d* metal ions with β-ketoamines (LXXVII) derived from acetylacetone and amines are difficult to isolate. On the other hand, Pd(II) complexes of (LXXVII; R = Me, Et, Pr^n, Bu^n, Ph, benzyl, *o*-, *p*-, *m*-tolyl, *o,o'*-xylidyl) can readily be obtained by either (i) reaction of $Pd(acac)_2$ with amines, or (ii) reaction of the β-ketoamine with $K_2[PdCl_4]$ and KOH [523]. Ethylenediaminebis(acetylacetone) forms a yellow inner complex with Pd(II) [427].

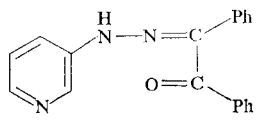
Butane-2,3-dionebis-(2-pyridylhydrazone) (LXXVIII) acts as a quadradentate ligand forming a green complex $[PdL]Cl_2\cdot\frac{1}{2}H_2O$. Benzilmono-(2-pyridyl)hydrazone (LXXIX)

[520] A. T. Phillip, *Austral. J. Chem.* **22** (1969) 259.
[521] H. A. O. Hill and K. A. Raspin, *J. Chem. Soc.* A, 1969, 619.
[522] J. V. Quagliano, J. T. Summers, S. Kida and L. M. Vallarino, *Inorg. Chem.* **3** (1964) 1557.
[523] S. Yamada, H. Nishikawa and E. Yoshida, *Proc. VIIIth Int. Conf. Coord. Chem. Vienna* (V. Gutmann, ed.), Springer-Verlag, Vienna (1964), p. 373; E. Yoshida and S. Yamada, *Bull. Chem. Soc. Japan* **38** (1965) 2179, 2182.
[524] E. Frasson, C. Panattoni and L. Sacconi, *Acta Cryst.* **17** (1964) 85.

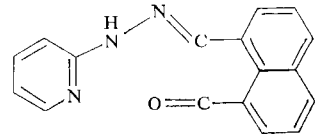
and acenaphthenequinonemono-(2-pyridyl)hydrazone (LXXX) lose a proton from the imino nitrogen and act as tridentates giving the reddish-purple complexes [PdLCl] [525].



(LXXVIII)

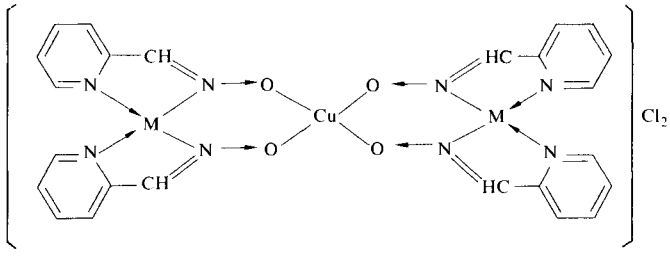


(LXXIX)



(LXXX)

The complexes of *cis*-di(pyridine-2-aldoxime) with Pd(II) and Pt(II) can act as oxygen-donor bidentate ligands to give trinuclear complexes of the type (LXXXI) [526].



(LXXXI; M = Pd, Pt)

The reaction of the Pd(II) complex of bis(acetylacetone)ethylenediimine with nitric oxide has been studied[527].

Diammine-type complexes. A large number of complexes of the type PdB_2X_2 (B = amine, $\frac{1}{2}$ diamine) are known. They can be prepared with virtually any amine and any negatively charged ligand such as Cl^-, NO_2^-, etc. They are usually obtained by adding the amine to a solution of $K_2[PdX_4]$ under either neutral or acid conditions. The complexes are sparingly soluble. *Cis-trans*-isomerism is known in only a few instances.

The ammines $[Pd(NH_3)_2X_2]$ are known where X = F, Cl, Br, I, CN, SCN, NO_2, NO_3, CNO; 2X = SO_3, SO_4, CO_3, C_2O_4 [426]. If a solution of $[PdCl_4]^{2-}$ in alcohol is treated with ammonium acetate at $-15°$, a yellowish-green precipitate of *cis*-$[Pd(NH_3)_2Cl_2]$ is obtained[528]. *Cis*-$[Pd(NH_3)_2Br_2]$ can also be prepared. *Trans*-$[Pd(NH_3)_2Cl_2]$ and *trans*-$[Pd(NH_3)_2Br_2]$ display a single ν(Pd–N) at 493 and 488 cm^{-1} respectively, whereas the *cis*-isomers display two bands in this region: *cis*-$[Pd(NH_3)_2Cl_2]$ at 492 and 473; *cis*-$[Pd(NH_3)_2Br_2]$ at 478 and 459 cm^{-1}. *Trans*-$[Pd(NH_3)_2Cl_2]$ displays ν(Pd–Cl) at 323, whereas *cis*-$[Pd(NH_3)_2Cl_2]$ displays two bands—at 320 and 312 cm^{-1} [529]. *Cis*-$[Pd(NH_3)_2(NO_2)_2]$ has been reported, but it has been shown that this is in error, since the method of preparation yields only $[Pd(NH_3)_3NO_2]Cl$.

[525] B. Chiswell and F. Lions, *Inorg. Chem.* **3** (1964) 490; B. Chiswell, F. Lions and M. L. Tomlinson, *ibid.*, p. 492.

[526] C. F. Liu and C. H. Liu, *Inorg. Chem.* **3** (1964) 678.

[527] I. Masuda, M. Tamaki and K. Shinra, *Bull. Chem. Soc. Japan* **42** (1969) 157.

[528] R. Layton, D. W. Sink and J. R. Durig, *J. Inorg. Nucl. Chem.* **28** (1966) 1965.

[529] J. S. Coe and A. A. Malik, *Inorg. Nucl. Chem. Letters* **3** (1967) 99.

The following complexes have been described: $[Pd(RNH_2)_2X_2]$ and $[Pd(R_2NH)_2X_2]$ (R = Me, Et, Pr^i, Bu^n, Am^i; X = Cl, Br, I); $[Pd(PhNH_2)_2X_2]$ (X = Cl, Br, I); $[Pd(PhNHR)_2X_2]$ (R = Me, Et; X = Cl, Br); $[PdB_2Cl_2]$ (B = *o*-, *m*-, *p*-nitroaniline, *p*-anisidine, *p*-phenetidine, benzalaniline, toluidine, *o*-, *m*-, *p*-xylidine, benzylamine, dibenzylamine, α-phenylethylamine, α- and β-naphthylamine, quinoline, benzonitrile) [426].

Complexes are known with pyridine and its derivatives, viz. $[PdB_2X_2]$ (B = pyridine, α-, β- and γ-picoline, lutidine, collidine, piperidine; X = Cl, Br, I or NO_3). Both *cis*- and *trans*-$[Pdpy_2X_2]$ (X = Cl, Br) are known[426]. *Cis*-$[Pdpy_2Cl_2]$ can be prepared by treating $[Pd(PhSCH_2CH_2SPh)_2Cl_2]$ with pyridine[530]. In the yellow *trans*-$[PdB_2Cl_2]$ (B = 2-, 3- and 4-cyanopyridine) the ligand is bound through the pyridine nitrogen[531].

The chloro-bridged dimeric complexes $L_2Pd_2Cl_4$ (L = amine, R_3P, R_3As, R_3Sb, R_2S, R_2Se, or R_2Te) react with amines:

$$L_2Pd_2Cl_4 + 2am \rightleftarrows 2[LamPdCl_2]$$

However, the monomeric complex can be isolated only when the donor atom in L is P or As. When it is N, S, Se, or Te, the product disproportionates:

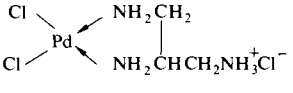
$$2[LamPdCl_2] \rightarrow [L_2PdCl_2] + [am_2PdCl_2]$$

When L = olefin, immediate decomposition occurs[532].

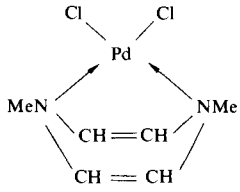
Complexes are known with diamines capable of forming five- or six-membered chelate rings. These are of the type $[PdBX_2]$ (B = ethylenediamine, *N*,*N*′-diphenylethylenediamine, *N*,*N*,*N*′,*N*′-tetraphenylethylenediamine, 1,2-diaminopropane, 2-phenyltrimethylenediamine, isobutylenediamine, *o*-phenylenediamine, *N*,*N*,*N*′,*N*′-tetramethyl-*o*-phenylenediamine, *o*-toluylenediamine; X = Cl, Br and sometimes I) [426, 466].

1,10-Phenanthroline and 2,2-bipyridyl give very stable, sparingly soluble complexes $[Pd(chel)X_2]$ (chel = phen, bipy; X = Cl, Br, I, SCN, NO_2; 2X = C_2O_4) [518].

1,2,3-Triaminopropane acts as a bidentate chelate and the unattached amino group will form a hydrochloride in the complex (LXXXII) [426].



(LXXXII)



(LXXXIII)

A crystal structure determination of the dichloro-complex of dimethylpiperazine shows that the ligand acts as a chelate group as shown in (LXXXIII). The Pd–Cl and Pd–N distances are 2.30 and 2.00 Å respectively. The Cl–Pd–Cl angle is 92°, while the N–Pd–N angle is only 72° [533].

[530] L. Cattalini and M. Martelli, *Gazz. chim. ital.* **98** (1968) 831.
[531] R. A. Walton, *J. Inorg. Nucl. Chem.* **28** (1966) 2229.
[532] J. Chatt and L. M. Venanzi, *J. Chem. Soc.* 1957, 2351, 2445.
[533] *Tables of Interatomic Distances*, Chem. Soc. (London) Special Publications, Nos. 11 (1958) and 18 (1965).

Ethylenediaminetetraacetic acid ($EDTAH_4$) forms the complex $[Pd(EDTAH_4)Cl_2]$ which has a square-planar structure with the $EDTAH_4$ coordinated through the two nitrogen atoms[534].

Palladium forms a more stable chelate complex with glycine than do bivalent 3*d* metal ions[464]. The inner complex of this ligand has been isolated in the pale yellow *cis* and the yellow *trans* isomeric forms[427]. The *cis* form is converted to the *trans* when heated in water. Anthranilic acid and 3-amino-2-naphthoic acid give yellowish inner complexes which are probably *trans*[535].

Monoammine complexes. Monoammine type complexes are few. The compounds which have been reported are $[Pt(NH_3)_4][Pd(NH_3)Cl_3]_2$ and $K[Pd\{CH_3CH(NH_2)CO_2\}Cl_2]$ [426]. Only a few dimeric complexes of the type $[PdLX_2]_2$ are known when L = amine but are numerous when L = R_3P or R_3As [532].

Nitro complexes. The compound $K_2[Pd(NO_2)_4]$ can be obtained as deep yellow crystals from a solution of Pd(II) which has been treated with KNO_2. The Pd–N distance is 2.10 Å [533]. The complex $K_2[Pd(NO)(NO_2)_4(NO_3)]$ has been isolated from a solution of $K_2[Pd(NO_2)_4]$ which has been treated with nitric acid[536].

The dinitro complexes *trans*-$[PdL_2(NO_2)_2]$ (L = 4-n-pentylpyridine, Bu^n_3P, Ph_3P, Bu^n_3As, Ph_3As, Ph_3Sb, Bu^n_2S, Pr^n_2Se, Pr^n_2Te, py, $\frac{1}{2}$bipy, $\frac{1}{2}$phen) have been prepared and their infrared spectra have been discussed. A correlation exists between the π-bonding ability of L and ν(N–O). In the di-μ-nitro bridged complex $(Bu^n_3P)_2Pd_2(NO_2)_4$ the bridges are Pd–N(O)–O–Pd. In the spectrum of this complex the bridging NO_2 groups give rise to strong bands at 1475 and 1238 cm^{-1} in addition to the nitro stretching frequencies at 1420 and 1330 cm^{-1}, also found in the spectra of the di-μ-chloro-bridged complex $(Bu^n_3As)_2Pd_2Cl_2(NO_2)_2$ and the oxalato bridged complex $(Bu^n_3P)_2Pd_2C_2O_4(NO_2)_2$ [537].

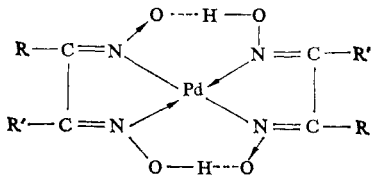
N-Bonded thiocyanate complexes. Thiocyanate ion is usually *S*-bonded to Pd(II), but steric factors may influence the manner of attachment in the complexes $ML_2(SCN)_2$ (M = Pd, Pt; L = amine, $\frac{1}{2}$ diamine, R_3P, R_3Sb) some of which are *S*-bonded and some are *N*-bonded. A crystal structure determination shows that the SCN groups are *N*-bonded in $[Pd(Pr^n_3P)_2(NCS)_2]$. The compounds $[Pd(NH_3)_2(SCN)_2]$, $[Pd(Ph_3Sb)_2(SCN)_2]$, $[Pd(\gamma\text{-pic})_2(SCN)_2]$ and $[PddienSCN]^+$ are *S*-bonded, whereas $[Pd(Et_3P)_2(NCS)_2]$, $[Pd(Ph_3P)_2(NCS)_2]$, $[Pdpy_2(NCS)_2]$ and $[PdEt_4dienNCS]^+$ are *N*-bonded. In the presence of π-bonding ligands there is a tendency for thiocyanate to be *N*-bonded. However, steric effects are also important, e.g. in the case of Et_4dien[209].

Azide complexes. Several azido complexes are known. Azide ion reacts with $[PdCl_4]^{2-}$ in HCl-acetone solution to yield $[Pd(N_3)_2Cl_2]^{2-}$ and $[Pd(N_3)_4]^{2-}$. Several interesting reactions of azide complexes of Pd(II) have been recently reported[538]. The phosphine complex $[(R_3P)_2Pd(N_3)_2]$ reacts with CO to yield $[(R_3P)_2Pd(NCO)_2]$. Organic nitriles react with *trans*-$[(Ph_3P)_2Pd(N_3)_2]$ to yield tetrazolato complexes $[(Ph_3P)_2Pd(N_4CR)_2]$, which are thermally very stable. The dimeric azide-bridged complex $[Ph_3PPd(N_3)_2]_2$ can

[534] D. J. Robinson and C. H. L. Kennard, *Chem. Communs.* 1967, 1236.
[535] S. E. Livingstone, *J. Chem. Soc.* 1956, 437.
[536] W. P. Griffith, J. Lewis and G. Wilkinson, *J. Chem. Soc.* 1961, 775.
[537] J. Chatt, L. A. Duncanson, B. M. Gatehouse, J. Lewis, R. S. Nyholm, M. L. Tobe, P. F. Todd and L. M. Venanzi, *J. Chem. Soc.* 1959, 4073; J. L. Burmeister and R. C. Timmer, *J. Inorg. Nucl. Chem.* **28** (1966) 1973.
[538] W. Beck, W. P. Behlhammer and P. Swoboda, *Proc. XIIth Int. Conf. Coord. Chem. Sydney* (H. C. Freeman, ed.), Science Press (1969), p. 227.

be obtained by heating $[(Ph_3P)_2Pd(N_3)_2]$ in tetralin. The reaction of $[(Ph_3P)_2Pd(N_3)_2]$ with BF_3 in CH_2Cl_2 yields the cationic azide-bridged complex $[(Ph_3P)_4Pd_2(N_3)_2](BF_4)_2$.

Oxime complexes. By loss of a proton glyoximes give bright yellow inner complexes (LXXXIV) which are insoluble in water and dilute acid. Complexes are known with the following glyoximes[426]:



(LXXXIV)

Dimethylglyoxime	R = R′ = Me
Methylethylglyoxime	R = Me; R′ = Et
Methyl-n-propylglyoxime	R = Me; R′ = Pr^n
Methylisobutylglyoxime	R = Me; R′ = Bu^i
Diphenylglyoxime(Benzildioxime)	R = R′ = Ph
Methylbenzylglyoxime	R = Me; R′ = $PhCH_2$
Methyloxyglyoxime	R = Me; R′ = OH

The complex of methylbenzylglyoxime has been obtained in two isomeric forms: α (m.p. 207–208°) and β (m.p. 175°); these were considered to be *cis* and *trans* isomers.

The most studied complex is that of dimethylglyoxime; this compound is used for the estimation of palladium; the precipitated complex, after washing, should be ignited to the metal for the best results. The palladium and platinum complexes are isomorphous with the nickel complex which has a structure such that the square-planar molecules are stacked one above the other so that the nickel atoms lie in chains which extend throughout the crystal. The close approach (*ca.* 3.25 Å) of the metal atoms has led to the postulate of metal–metal bonding; however, the unusual structure may be due to favourable crystal packing rather than metal–metal bonding[539]. The visible spectra of Pd(II) *vic*-dioxime complexes in the solid state show a band which is not present in the solution spectra. The frequencies of the solid state bands fall as the metal–metal distance decreases; the same effect can be obtained by the application of high pressure. The spectra have been discussed by several workers but no general agreement has been reached[449].

The binary metal complexes $NiPd(DMG)_4$ (orange), $NiPt(DMG)_4$ (dark brown) and $PdPt(DMG)_4$ (brown) have been prepared by dissolving stoichiometric amounts of the component complexes in hot dimethylformamide and allowing the solution to cool, whereupon the binary compound crystallizes. The solid state reflectance spectrum of $NiPd(DMG)_4$ is considerably different from that of a ground 1:1 mixture of $Ni(DMG)_2$ and $Pd(DMG)_2$. The binary complexes are isomorphous with the simple complexes $M(DMG)_2$ and have metal–metal distances within the range 3.23–3.25±0.02 Å. The X-ray data show that the binary complexes are not mixed crystals but are homogeneous in that a cell can be chosen

[539] L. F. Lindoy, S. E. Livingstone and N. C. Stephenson, *Inorg. Chim. Acta* **1** (1968) 161 and references therein.

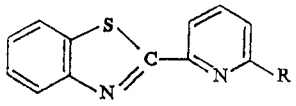
representative of the whole single crystal in which both metal dimethylglyoximate molecules are stacked in a statistically ordered manner[539].

The compounds $M(DMG)_2$ (M = Pd, Pt), when treated with acetyl chloride, yield $M(DMGH)Cl_2$ [540]. Boron is able to substitute the proton of the hydrogen bonds in some dimethylglyoxime complexes. Organoboric acids form the sparingly soluble complexes $[M(DMGBR_2)_2]$ (M = Ni, Pd, Cu, Zn, Pb) [541]. Complexes have been obtained with the composition $Pd(DPG)_2X$ (DPGH = diphenylglyoxime; X = Br, I). The halogens X_2 are clathrated and lie in channels surrounded by the phenyl groups and parallel to the $Pd(DPG)_2$ stacks[542]. The dimethyl- and diethyl-amino derivatives of dimethylglyoxime form inner complexes with Pd(II); the tertiary amine groups show no ligand function and can be protonated to yield quaternary salts[543]).

Bis-chelated complexes of Pd(II) have been obtained with α-oximo-β-substituted hydrazones of acetoacetarylamides, $MeC(=NNHR')C(=NO)CONHR$ (R = *p*-MeC_6H_4, *o*-, *m*-, ClC_6H_4, *o*-, *p*-, $MeOC_6H_4$, *p*-$EtOC_6H_4$, 2,4-$(MeO)_2C_6H_3$; R′ = NH_2CO, NH_2CS, PhCO, *o*-HOC_6H_4CO[543]).

Complexes $[PdL_2X_2]$ (L = mono-oxime such as acetoxime; X = Cl, Br, NO_2) have been prepared; they are moderately stable in the solid state but are unstable in aqueous solution giving a deposit of metallic palladium[544]. The complex of benzoylpyridineoxime $PhC_5H_4NC(NOH)$ is also known[426].

Other nitrogen complexes. The α-diimine, 2-(2-pyridyl)benzothiazole (LXXXV; R = H; pbt) forms the complexes $[PdX_2pbt]$ (X = Cl, Br, SCN, NO_2) [545]. The sulphato-complex



(LXXXV)

$[PdSO_4pbt(H_2O)]$ contains a unidentate sulphato group, whereas the infrared spectrum of the complex $PdSO_4$mpbt (mpbt = LXXXV with R = Me) indicates that the sulphato group is bridging[546].

The reaction of nitrite ion and NH_3 with $Pd(acac)_2$ at pH7 yields the imino derivative. On the other hand, the reaction of $Cu(NO_3)_2 \cdot 3H_2O$ on $Pd(acac)_2$ in acetic anhydride effects nitration of the central carbon atom of the ligand to give mononitro and dinitro derivatives[547].

Palladium(II) phthalocyanine can be prepared from $PdCl_2$ and lithium phthalocyanine. The chloro-substituted derivative is also known[548].

[540] R. A. Krause, D. C. Jicha and D. H. Busch, *J. Am. Chem. Soc.* **83** (1961) 528.

[541] F. Umland, W. Fedder, H. G. von Schnering and D. Thierig, *Proc. XIIth Int. Conf. Coord. Chem. Sydney* (H. Freeman, ed.), Science Press (1969), p. 46.

[542] A. S. Foust and R. H. Soderberg, *J. Am. Chem. Soc.* **89** (1967) 5507.

[543] E. Uhlig and W. Geipel, *Z. anorg. Chem.* **348** (1966) 12; M. R. Patel and B. N. Mankad, *J. Indian Chem. Soc.* **43** (1966) 391.

[544] A. V. Babaeva and M. A. Mosyagina, *Doklady Akad. Nauk SSSR* **89** (1953) 293.

[545] L. F. Lindoy and S. E. Livingstone, *Inorg. Chim. Acta* **2** (1968) 119.

[546] P. S. K. Chia, L. F. Lindoy and S. E. Livingstone, *Inorg. Chim. Acta* **2** (1968) 459.

[547] C. Djordjevic, J. Lewis and R. S. Nyholm, *J. Chem. Soc.* 1962, 4778; A. Kasahara, K. Uji-Ie and K. Tanaka, *Bull. Chem. Soc. Japan* **39** (1966) 2227.

[548] A. B. P. Lever, *Adv. Inorg. Radiochem.* **7** (1965) 28.

Phosphine, Arsine and Stibine Complexes

Complexes of unidentate ligands. Tertiary phosphines, arsines and stibines form stable complexes $[Pd(R_3M)_2X_2]$, but the stibine complexes are somewhat less stable than those of phosphines and arsines. They are soluble in non-polar solvents, have sharp melting points, and are easily recrystallized. Dipole moment measurements indicate that the phosphine and arsine complexes have the *trans* configuration, but solutions of the stibine complexes may contain 40% of the *cis* isomer, which, owing to its lower solubility, can be isolated. The complexes of unidentate phosphines, arsines and stibines are listed in Table 44 [426,549–51]. The thiocyanato complexes with phosphines are *N*-bonded, while $[Pd(Ph_3Sb)_2(SCN)_2]$ is *S*-bonded[209].

TABLE 44. PALLADIUM(II) COMPLEXES OF UNIDENTATE PHOSPHINES, ARSINES AND STIBINES

Complex		Colour
$[Pd(Ph_2P)_2(Ph_2PH)_2]$		Salmon pink
$[Pd(PCl_3)_2Cl_2]$		Yellow
$[Pd\{P(OR)_3\}_2Cl_2]$	(R = Me, Et)	White
$[Pd(R_3P)_2Cl_2]$	(R = Me, Et, Pr^n, Bu^n, Am^n, Ph, C_6F_5; R_3 = Et_2Ph, Bu^n_2Ph)	Yellow
$[Pd(R_2PH)_2Cl_2]$	(R = Et, Ph; R = EtPh)	Pale yellow
$[Pd(R_3P)_2Br_2]$	(R = Et, Pr^n, Bu^n, Ph, C_6F_5; R_3 = Et_2Ph)	Orange
$[Pd(R_2PH)_2Br_2]$	(R = Et, Ph; R_2 = EtPh)	Yellow
$[Pd(R_3P)_2I_2]$	(R = Et, Pr^i, Bu^n)	Orange
$[Pd(R_2PH)_2I_2]$	(R = Et, Ph; R_2 = EtPh)	Yellow to reddish orange
$[Pd(R_3P)_2(NCS)_2]$	(R = Et, Pr^n, Ph)	Yellow
$[Pd(R_3P)_2(NO_2)_2]$	(R = Et, Bu^n; R_3 = Et_2Ph)	Yellow
$[Pd(Et_3P)_2(NO_3)_2]$		Yellow
$[Pd(R_3As)_2Cl_2]$	(R = Me, Et, Pr^n, Bu^n, Am^n; R_3 = Me_2Ph)	Yellow to orange
$[Pd(R_3As)_2Br_2]$	(R = Me, Pr^n; R_3 = $MePh_2$)	Orange
$[Pd(MePh_2As)_3Br]Br$		Orange
$[Pd(MePh_2As)_2I_2]$		Orange–brown
$[Pd(R_3As)_2(NO_2)_2]$	(R = Me, Et, Bu^n)	Yellow
$[Pd(Me_3As)_2(NCS)_2]$		Yellow
$[Pd(R_3Sb)_2Cl_2]$	(R = Me, Et, Pr^n, Bu^n, Ph)	Yellow
$[Pd(Ph_3Sb)_2(SCN)_2]$		Yellow
$[Pd(R_3P)amCl_2]$	(R = Et, Pr^n, Ph, OMe, OPh; am = *p*-toluidine, piperidine)	Orange–yellow
$[Pd(P^n_3P)amI_2]$	(am = *p*-toluidine)	Red
$[Pd(Et_3As)amCl_2]$	(am = piperidine)	Orange–yellow

Binuclear complexes with unidentate ligands. If the complexes $[Pd(R_3M)_2Cl_2]$ (M = P, As) are boiled in alcohol, one ligand is lost to give dimeric chloro-bridged complexes:

$$2[Pd(R_3M)_2Cl_2] \rightarrow [Pd_2(R_3M)_2Cl_4] + 2R_3M$$

Bridged complexes can also be obtained by the reaction:

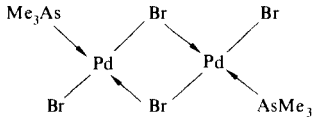
$$[Pd(R_3M)_2X_2] + (NH_4)_2[PdX_4] \rightarrow [Pd_2(R_3M)_2X_4] + 2NH_4X \quad (M = P, As; X = Cl, Br, SCN, NO_2)$$

549 J. Chatt and R. G. Wilkins, *J. Chem. Soc.* 1953, 70; P. L. Goggin and R. J. Goodfellow, *J. Chem. Soc.* A, 1966, 1462.

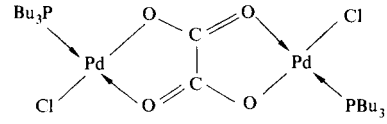
550 G. Booth, *Adv. Inorg. Chem. and Radiochem.* **6** (1964) 1.

551 R. G. Hayter, *Preparative Inorganic Reactions* (W. L. Jolly, ed.), Wiley Interscience, New York (1965), Vol. 2, p. 211.

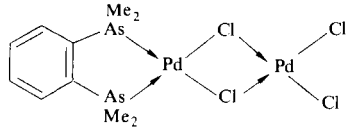
X-ray analysis of $[Pd_2(Me_3As)_2Br_4]$ shows that the complex has the symmetrical *trans* structure (LXXXVI) in which all the Pd–Br distances are equivalent (2.45 Å) and the Br–Pd–Br angle is 86°. The oxalato complex $[Pd_2(Bu_3P)_2(C_2O_4)_2Cl_2]$ has the structure (LXXXVII); the Pd–Pd distance is 5.48 Å compared to 3.4 Å in chloro-bridged complexes. Attempts to prepare unsymmetrical bridged complexes of the type (LXXXVIII) were unsuccessful.



(LXXXVI)



(LXXXVII)



(LXXXVIII)

A list of binuclear Pd(II) complexes containing phosphines, arsines and stibines is given in Table 45 [426, 532]. Binuclear complexes containing palladium and another metal atom are known: viz. $[Pd(Pr_3As)_2Br_4Hg]$ and $[Pd(Pr_3P)_2Cl_2SnCl_4]$ [552].

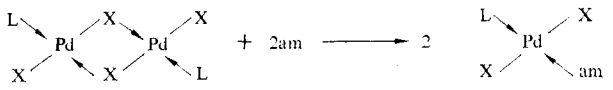
TABLE 45. BINUCLEAR PALLADIUM(II) COMPLEXES OF UNIDENTATE PHOSPHINES, ARSINES AND STIBINES

Complex		Colour
$[Pd_2Cl_2^*(PCl_3)_2Cl_2]$		Brown
$[Pd_2Br_2^*(PBr_3)_2Br_2]$		Reddish brown
$[Pd_2Cl_2^*(P(OR)_3)_2Cl_2]$	(R = Me, Et, Ph)	Orange
$[Pd_2Cl_2^*(R_3P)_2Cl_2]$	(R = Me, Et, Pr^n, Bu^n, Am^n, Ph)	Orange–red
$[Pd_2I_2^*(R_3P)_2I_2]$	(R = Pr^n, Bu^n)	Deep reddish purple
$[Pd_2(NO_2)_2^*(Bu_3P)_2(NO_2)_2]$		Yellow
$[Pd_2(SCN)_2^*(Bu_3P)_2X_2]$	(X = Cl, SCN)	Orange
$[Pd_2(C_2O_4)^*(R_3P)_2X_2]$	(R = Pr^n, Bu^n; X = Cl, NO_2)	Yellow
$[Pd_2(EtS)_2^*(R_3P)_2Cl_2]$	(R = Pr^n, Bu^n)	Deep yellow
$[Pd_2Cl^*(EtS)^*(Bu_3P)_2Cl_2]$		Yellow
$[Pd_2(ClC_6H_3S_2)_2^*(Bu_3P)_2]$		Red
$[Pd_2Cl_2^*(R_3As)_2Cl_2]$	(R = Me, Et, Pr^n, Bu^n, Am^n; R_3 = Bu_2Ph)	Deep red
$[Pd_2Br_2^*(Me_3As)_2X_2]$	(X = Cl, Br)	Reddish brown
$[Pd_2(NO_2)_2^*(R_3As)_2X_2]$	(R = Me, Bu^n; X = Cl, NO_2)	Yellow
$[Pd_2(SCN)_2^*(R_3As)_2X_2]$	(R = Pr^n, Bu^n; X = Cl, Br, SCN)	Orange–red
$[Pd_2Cl_2^*(Et_3Sb)_2Cl_2]$		Tan

* Bridging groups.

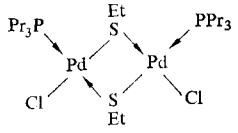
[552] J. A. C. Allison and F. G. Mann, *J. Chem. Soc.* 1949, 2915.

The halogen-bridge in complexes of the type (LXXXVI) can be split by neutral ligands (am) such as *p*-toluidine and piperidine; however, the product (LXXXIX) can only be isolated when L = R_3P or R_3As [532].

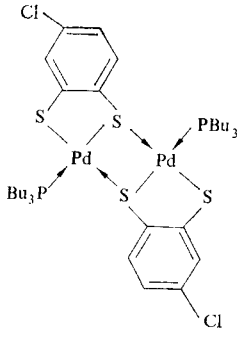


(LXXXIX)

Ethanethiol reacts with μ-halogeno-bridged complexes to form more stable thiolo-bridged complexes. The reaction proceeds by the successive replacement of the two bridging halogen atoms by SEt; consequently by the use of one equivalent of thiol, mixed chloro-thiolo-bridged complexes have been obtained. The thiolo-bridge is not split by other ligands even in boiling solution. The complex $[Pd_2(Pr_3P)_2(SEt)_2Cl_2]$ has the unsymmetrical *cis* configuration (XC) [553].



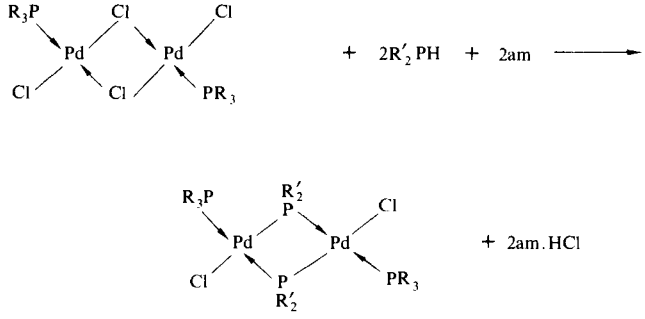
(XC)



(XCI)

The thiolo-bridged complex (XCI) has been prepared by the reaction of 4-chloro-phenylenedithiol on $[Pd_2(Bu_3P)_2Cl_4]$ [426].

Complexes containing bridging phosphines. Secondary phosphines usually react with Pd(II) halides to give the mononuclear complexes $[Pd(R_2PH)_2X_2]$ (R = Et, Ph; R_2 = EtPh; X = Cl, Br, I), which lose HX in the presence of a base, usually an amine, to give phosphorus-bridged binuclear complexes $[Pd_2(R_2P)_2X_2(R_2PH)_2]$. The phosphorus-bridged complexes may be prepared from chloro-bridged complexes by the following reaction:



[553] J. Chatt, *Nature* **169** (1952) 673.

The reaction is carried out in refluxing benzene. The amine hydrochloride is precipitated quantitatively, leaving the phosphorus-bridged complex in solution. The complexes $[Pd_2(R_2P)_2(R_2PH)_2X_2]$ (R = Et, Ph; R_2 = EtPh; X = Cl, Br, I) and also some mixed phosphine complexes of the type $[Pd_2(R_2'P)_2(R_3P)_2X_2]$ have been prepared[551].

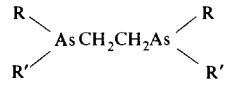
If the phosphorus-bridged complex $[Pd_2(Ph_2P)_2(Ph_2PH)_2Cl_2]$ is treated with the diphosphine $C_2H_4(PPh_2)_2$ in benzene at ambient temperature, the two secondary phosphine ligands are replaced by two chelate ligands to give the phosphorus-bridged cationic complex $[Pd_2(Ph_2P)_2\{C_2H_4(PPh_2)_2\}_2]Cl_2$. Analogous complexes $[Pd_2(R_2P)_2(chel)_2]X_2$ (R = Et, Ph; chel = en, phen; X = Cl, I, NO_3, ClO_4, BPh_4) have been prepared similarly[551].

The primary phosphines Ph_2PH_2 and $C_6H_{11}PH_2$ react with $PdCl_2$ in refluxing benzene to yield bridged complexes[551].

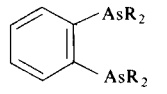
The four-membered rings in all these bridged complexes may have their stability enhanced by some electron delocalization due to π-bonding between the filled d_{xz} and d_{yz} orbitals and empty orbitals on the phosphorus atom. The extent of this delocalization would be expected to decrease in the order P > S > Cl.

Complexes of bidentate chelate ligands. The complexes of several bidentate chelating agents containing phosphorus or arsenic and sulphur as donor atoms have already been discussed under Complexes of Sulphur, Selenium and Tellurium Ligands (pp. 1295–1300). Complexes of ligands containing arsenic and an olefinic group will be discussed under Olefin Complexes (p. 1322).

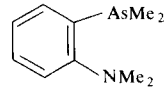
Stable complexes are formed by Pd(II) with the ligands (XCII)–(CII) [447,464]. All yield



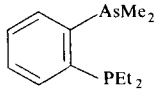
(XCII; R = Bu^n, Ph; R'=Bu^n, Ph)



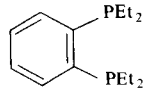
(XCIII; R = Me, Bu^n)



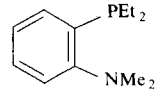
(XCIV)



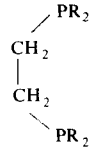
(XCV)



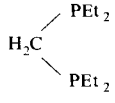
(XCVI)



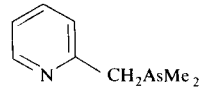
(XCVII)



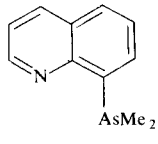
(XCVIII; R = Et, Ph)



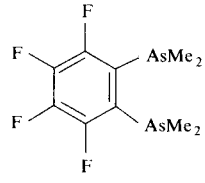
(XCIX)



(C)



(CI)



(CII)

mono-ligand complexes of the type $[Pd(chel)X_2]$. The most studied complexes are those of *o*-phenylenebisdimethylarsine (XCIII; R = Me). The bis-ligand perchlorate $[Pd(As–As)_2](ClO_4)_2$ is colourless, whereas the colours of the complexes $Pd(As–As)_2X_2$ range from yellow (X = Cl and SCN) through orange (X = Br and NO_2) to deep red (X = I). These coloured complexes behave as uni-univalent electrolytes in nitrobenzene due to the presence of the species $[Pd(As–As)_2X]X$. The perchlorates $[Pd(As–As)_2X]ClO_4$ were also isolated. X-ray crystal analysis of the iodo-complex $Pd(As–As)_2I_2$ shows that the metal atom is surrounded by four coplanar arsenic atoms with the two iodine atoms completing a distorted octahedron. The short Pd–As bond lengths (2.4 Å) suggest some double bond character, while the Pd–I distances (3.40 Å) are much longer than the sum of the covalent radii (2.65 Å). The deep red complex $Pd(As–As)_2I_2$ forms a yellow solution in water from which the addition of NaI precipitates orange crystals of the monohydrate. The monohydrate dissolves in acetone and the solution deposits deep red crystals of the anhydrous complex. The marked differences in colour and solubility of the anhydrous and hydrated compound suggest that the latter is $[Pd(As–As)_2I(H_2O)]I$ [447, 464].

o-Dimethylaminophenyldimethylarsine (XCIV) forms complexes $Pd(As–N)_2X_2$ (X = Cl, Br, I, NO_2) whose colours range from pale greenish yellow (X = NO_2) to deep reddish orange (X = I), indicating some covalent bonding between palladium and X. This does not necessarily mean that the metal atom has a coordination number greater than 4, since the nitrogen atom may not be coordinated. An analogous situation has been found to occur in the complex $Pd(Me_2AsC_6H_4SMe)_2I_2$ where the sulphur atoms are not coordinated[484].

o-Dimethylaminophenyldiethylphosphine (XCVII) forms the colourless $Pd(P–N)_2X_2 \cdot 2H_2O$ (X = Cl, Br) and $Pd(P–N)_2(NO_2)_2 \cdot 3H_2O$. However, the colours of the compounds $Pd(P–N)_2X_2$ (X = NO_3, SCN, I) range from yellow to red, like those of the diarsine complexes. The complex $Pd(As–P)_2Br_2 \cdot H_2O$, formed by *o*-diethylphosphinodimethylarsine, is yellow[447].

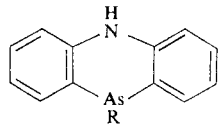
The diphosphines (XCVIII; R = Et, Ph) and (XCIX) form the mono-ligand complexes $[Pd(P–P)Cl_2]$ and the bis-ligand complexes $[Pd(P–P)_2]Br_2$ [439].

α-Picolyldimethylarsine (C) forms the pale yellow bis-ligand complex $[Pd(As–N)_2](ClO_4)_2$ [554].

8-Dimethylarsinoquinoline (CI) forms 4-, 5- and 6-coordinate complexes with Pd(II) and Pt(II). The complexes $[Pd(As–N)X_2]$ (X = Cl, Br, I, SCN) are coloured cream to dark brown, depending on X, while $[Pd(As–N)_2](ClO_4)_2$ is white. The 5-coordinate complexes $[Pd(As–N)_2X]ClO_4$ (X = Cl, Br, I) are cream to brown. The complexes $Pd(As–N)_2X_2$ are presumably 6-coordinate in the solid state but behave as uni-univalent electrolytes in nitromethane and nitrobenzene[555].

The reaction of Pd(II) and Pt(II) halides with 10-substituted 5,10-dihydrophenarsazines (CIII; R = Me, OH) yield the complexes $[MX_2L_2]$ (L = CI; M = Pd, Pt) in which the phenarsazine is unidentate. No bidentate or bridging complexes could be isolated. The Pd(II) complexes are red or maroon. The infrared spectra indicate that the complexes have a *cis* configuration, since two ν(M–Cl) are observed; ν(M–As) occurs in the range 300–240 cm^{-1} [556].

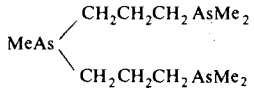
[554] H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.* **81** (1959) 311.
[555] G. A. Barclay, M. A. Collard, C. M. Harris and J. V. Kingston, *J. Chem. Soc.* A, 1969, 830.
[556] E. A. Allen and L. A. Nixon, *J. Inorg. Nucl. Chem.* **31** (1969) 1467.



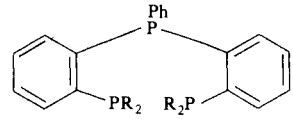
(CIII)

Complexes of multidentate chelate ligands. The complexes of several multidentate ligands containing sulphur and phosphorus or arsenic have been discussed under Complexes of Sulphur, Selenium and Tellurium Ligands (p.1296).

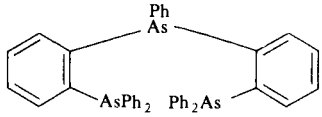
Complexes of Pd(II) are known with the tridentate ligands (CIV–CVI).



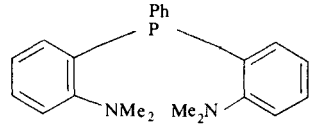
(CIV)



(CV; R = Et, Ph)



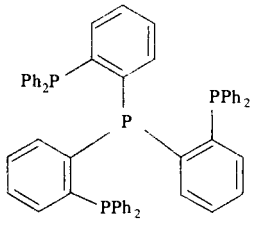
(CVI)



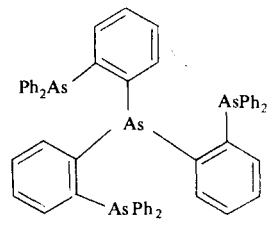
(CVII)

Bis(bis-3-dimethylarsinopropyl)arsine (CIV; As–As–As) gives the complex [Pd(As–As–As)Br]Br; the square-planar configuration was confirmed by X-ray structural analysis[447]. Bis(*o*-diethylphosphinophenyl)phenylphosphine (CV; R = Et) also gives a 4-coordinate cream-coloured complex [Pd(P–P–P)Cl]Cl [439]. Bis(*o*-diphenylphosphinophenyl)phenylphosphine (CV; R = Ph) and bis(*o*-diphenylarsinophenyl)phenylarsine (CVI) form the orange square-planar complexes [Pd(P–P–P)I]ClO_4 and [Pd(As–As–As)I]ClO_4. A 5-coordinate complex of the tridentate phosphine (CV; R = Ph), viz. [Pd(P–P–P)I_2], has been isolated[450]. On the other hand, bis(*o*-dimethylaminophenyl)phenylphosphine (CVII) forms the complexes [Pd(N–P–N)X_2] (X = Cl, Br, I) in which only the phosphorus and one nitrogen atom are coordinated[557].

Complexes of several quadradentate ligands have been investigated.

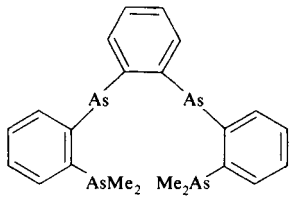


(CVIII)

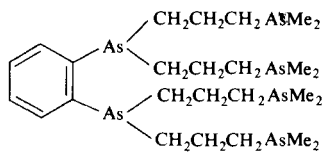


(CIX)

[557] H. P. Fritz, J. R. Gordon, K. E. Schwarzhaus and L. M. Venanzi, *J. Chem. Soc.* 1965, 5210.



(CX)



(CXI)

Tris-(*o*-diphenylphosphinophenyl)phosphine (CVIII; QP) forms the reddish-purple 5-coordinate complex $[Pd(QP)I]BPh_4$. The analogous arsenic ligand tris-(*o*-diphenylarsinophenyl)arsine (CIX; QAS) forms the 5-coordinate complexes [Pd(QAS)X]X (X = Cl, Br, I, SCN) and [Pd(QAS)X]Y (X = Cl, I, SCN; Y = ClO_4 or BPh_4). The complexes are dark reddish purple to purplish brown. The conformation of these two tripod-like ligands is such that a trigonal-bipyramidal configuration is forced on the central metal atom. An X-ray structural determination on the Pt(II) complex $[Pt(QAS)I]BPh_4$ confirmed the trigonal-bipyrimidal arrangement[450].

o-Phenylenebis[(*o*-dimethylarsinophenyl)methylarsine] (CX; TPAS) also gives rise to 5-coordinate complexes of Pd(II) and Pt(II). The Pd(II) complexes reported are $[Pd(TPAS)Cl]ClO_4$ (red) and [Pd(TPAS)I]I (orange). The 4-coordinate complex $[Pd(TPAS)](ClO_4)_2$ (white) was also isolated. The electronic spectra of the 5-coordinate complexes differ from those of the trigonal-bipyramidal complexes formed by QAS and other "tripod-like" ligands. This suggests a square-pyramidal configuration, which was confirmed by X-ray structure analysis of $[Pd(TPAS)Cl]ClO_4$. The palladium atom is surrounded by one chlorine and three arsenic atoms at the corners of a square, while the fourth arsenic atom is at the apex of the square pyramid. The Pd–As distances for the three arsenic atoms in the plane are 2.33–2.41 Å; for the apical arsenic atom the Pd–As distance is much longer (2.86 Å) [558].

The hexa-arsine, tetrakis-(3-dimethylarsinopropyl)*o*-phenylenediarsine (CXI; SAS) has the conformation such that the six arsenic atoms can occupy the corners of an octahedron. It forms the orange complex $[Pd(SAS)_2](ClO_4)_2 \cdot 3H_2O$; evidence has been obtained which is consistent with the palladium atom's having an octahedral configuration in this complex[559].

Carbonyl Complexes

No carbonyl of palladium is known analogous to $Ni(CO)_4$ but, whereas halogeno carbonyls are unknown with nickel, several are known with palladium and platinum. The yellow compound $[PdCl_2(CO)]_n$ can be obtained by the action of CO on a suspension of $PdCl_2$ in alcohol at 0°; it is probably dimeric. The action of CO on $PdCl_2(PhCN)_2$ yields the diamagnetic yellow compound $[Pd_2Cl(CO)_2]_n$. An anionic complex has been obtained for which the formulae $[Pd_2Cl_4(CO)_2]^{2-}$ and $[PdCl_3(CO)]^-$ have been reported[162].

The palladium-catalysed carbonylation of unsaturated compounds has been discussed[560].

[558] R. S. Nyholm, M. L. Tobe and A. T. Phillip, *Proc. XIIth Int. Conf. Coord. Chem. Sydney* (H. C. Freeman, ed.), Science Press (1969), p. 164.

[559] G. A. Barclay, C. M. Harris and J. V. Kingston, *Chem. Communs.* 1968, 965.

[560] D. Medema, R. van Helden and C. F. Kohll, *Proc. Ist Int. Symposium Metal Carbonyls and Derivatives, Inorg. chim. Acta* (1968), p. E3.

When $[(C_2H_4)PdCl_2]_2$ is treated with CO (1 atm, 20°) in benzene and other solvents, β-chloropropionyl chloride is formed along with $[PdCl_2(CO)]_2$ and $[Pd_2Cl(CO)_2]_n$. When π-allyl palladium chloro-complexes are used as catalysts for the carbonylation of allylic compounds, the yellowish-green polymeric complexes [π-allyl $Pd_2Cl_2(CO)]_n$ are produced[560].

Acyl Derivatives

Acyl derivatives of the type *trans*-$[Pd(COR)(PEt_3)_2X]$ (X = Cl, Br, NCS, NO_2, or NO_3; R = Me, Et, Ph) have been obtained by the reaction of CO in benzene at atmospheric temperature and pressure on the appropriate alkyl or aryl complex *trans*-$[PdR(PEt_3)_2X]$. The platinum complexes require increased pressure and a temperature of 90° for reaction[561].

Isocyanide Complexes

Aryl isocyanides react with Pd(II) halides to give stable orange complexes $[PdX_2(CNR)_2]$ (X = Cl, Br, I; R = aryl) which are monomeric and soluble in solvents such as benzene and chloroform. Dipole moment measurements indicate that an appreciable concentration of the *cis* form is present in benzene solution. No tetrakis complexes of the type $[Pd(CNR)_4]^{2+}$ could be prepared[434].

Alkyl and Aryl Complexes

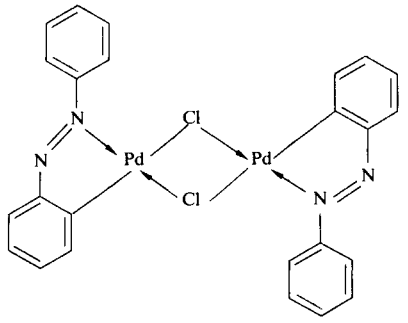
σ-Bonds between palladium and alkyl or aryl groups can be stabilized if strongly π-bonding ligands, such as tertiary phosphines, are present. Grignard reagents or organolithium compounds react with *trans*-$[(Et_3P)_2PdX_2]$ to yield $[(Et_3P)_2RPdX]$ and $[(Et_3P)_2PdR_2]$ (R = Me, Ph, *p*-$C_6H_4CF_3$, C≡CPh, or *p*-$NO_2C_6H_4C{\equiv}C$; X = Br, SCN or CN). All the compounds are *trans*; most are colourless and unstable, turning grey and finally black, due to decomposition to metallic palladium. The complex $[(Et_3As)_2PdMe_2]$ is *cis* but the phosphorus analogue exists in benzene solution as a mixture of *cis* and *trans* isomers. Complexes with chelate ligands do not yield *cis*-diaryl derivatives but the *cis*-dimethyl complexes [(chel)$PdMe_2$] (chel = bipy, $MeSCH_2CH_2SMe$, $EtSCH_2CH_2SEt$, $Ph_2PCH_2CH_2PPh_2$, *o*-$C_6H_4(AsMe_2)_2$, cycloocta-1,5-diene) have been reported. The ethanethiolo-bridged complex $[(Bu_3P)Pd(SEt)Me]_2$ can be obtained but not the chloro-bridged analogue[562].

One or both of the methyl groups in [bipy$PdMe_2$] may be replaced by heptafluoro-n-propyl by the use of C_3F_7I [435]. The reaction of $[(C_6F_5)_2TlBr]_2$ with $Pd(Ph_3P)_2$ causes oxidation of palladium to give $Pd(Ph_3P)_2(C_6F_5)_2$ [563].

Azobenzene (azb) forms the chloro-bridged dimer (CXII) which contains a metal–carbon σ-bond. The bridge can be split by triethylphosphine to give $[(Et_3P)_2Pd(azb)Cl]$ in which the azobenzene moiety is σ-bonded through the α-carbon atom; the rather long Pd–Cl bond (2.38 Å; calc., 2.30 Å) is due to the *trans* effect of the Pd–C bond[564]. The dimer also reacts with neutral ligands to give [PdCl(azb)L] (L = py, R_3P) which can be obtained in two isomeric forms, depending on whether L or Cl is *trans* to the σ-bonded

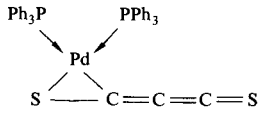
[561] G. Booth and J. Chatt, *J. Chem. Soc.* A, 1966, 634.
[562] G. Calvin and G. E. Coates, *J. Chem. Soc.* 1960, 2008.
[563] R. S. Nyholm and P. Royo, *Proc. XIIth Int. Conf. Coord. Chem. Sydney* (H. C. Freeman, ed.), Science Press (1969), p. 57.
[564] R. W. Siekman and D. L. Weaver, *Chem. Communs.* 1968, 1021.

carbon atom. When Cl is *trans* to carbon, ν(Pd–Cl) is significantly lower than when Cl is *trans* to nitrogen[565].



(CXII)

The Pd(0) phosphine complex $Pd(Ph_2MeP)_4$ reacts with $F_2C{=}CFX$ (X = Cl, Br) to yield *trans*-$[(Ph_2MeP)_2Pd(FC{=}FC_2)X]$ [565]. Oxidative addition also occurs when $Pd(Ph_3P)_4$ reacts with carbon subsulphide, which has the linear structure $S{=}C{=}C{=}C{=}S$, in alcohol at $-70°$ to give the yellow complex $[Pd(Ph_3P)_2C_3S_2]$ which probably has the structure (CXIII) [566].



(CXIII)

Other compounds containing Pd–C σ-bonds are discussed under Allyl Complexes (p. 1326) and Acetylene Complexes (p. 1325).

Cyclopentadienyl Complexes

Several cyclopentadienyl complexes are known; they are orange or red. They include $[(C_5H_5)PdCl]_2$, $(C_5H_5)Pd(all)$ (all = allyl, methylallyl, cyclohexenyl, cycloheptatrienyl), $(C_5H_5)PdR(C_3H_5)$ (C_3H_5 = allyl; R = Me, Et, Pr^n, C_3H_5) and $(C_5H_5)PdMe(C_6H_9)$ (C_6H_9 = cyclohexenyl). They are obtained from the reaction of sodium cyclopentadienyl on a Pd(II) allyl complex, usually the chloro-bridged compound: e.g. sodium cyclopentadienyl splits the bridge in $[PdCl(C_6H_9)]_2$ to give $(C_5H_5)Pd(C_6H_9)$ and in the μ-dichloro-complex of 1-methoxy-1,1,4,4-tetramethylbutane to give $(C_5H_5)Pd(C_9H_{17}O)$ [567].

The cationic complex $[(Ph_4C_4)Pd(C_5H_5)]^+$ contains the palladium atom sandwiched between a tetraphenylcyclobutadiene ring and a cyclopentadienyl ion. Similar "sandwich"

[565] B. Crociani, T. Boschi, U. Belluco, C. Panattoni and U. Croatto, *Proc. XIIth Int. Conf. Coord. Chem. Sydney* (H. C. Freeman, ed.), Science Press (1969), p. 179; F. G. A. Stone, *ibid.*, p. 159.

[566] A. P. Ginsberg and W. E. Silverthorn, *Proc. XIIth Int. Conf. Coord. Chem. Sydney* (H. C. Freeman, ed.), Science Press (1969), p. 16.

[567] J. M. Birmingham, *Adv. Organomet. Chem.* **2** (1964) 365.

compounds have been prepared containing a tetraphenylcyclobutadiene ring and a dicarbollide ion "cage" symmetrically sandwich-bonded to Pd(II). The compounds which have been isolated are $(Ph_4C_4)Pd(B_9C_2H_{11})$ and $(Ph_4C_4)Pd(B_9C_2H_9Me_2)$. The former was prepared by the reaction of sodium 2,3-dicarbollide, $Na_2B_9C_2H_{11}$, on $[(Ph_4C_4)PdCl_2]_2$ in tetrahydrofuran[568].

Olefin Complexes

The ethylene complex of empirical formula $PtCl_2(C_2H_4)$ was prepared by Zeise in 1830; it is now known to be a chloro-bridged dimer. The analogous Pd(II) complexes $[PdCl_2(ol)]_2$ (ol = ethylene, isobutylene, styrene, cyclohexene) were prepared by Kharasch *et al.* in 1938 by the reaction of the olefin with $[Pd(PhCN)_2Cl_2]$ in benzene or chloroform solution. The olefin complexes are soluble in benzene, chloroform, alcohol and acetone but insoluble in ligroin. They are less stable than their platinum analogues. Their colours range from deep yellow to brown or reddish brown[426]. The complex $[PdCl_2(C_2H_4)]_2$ can be obtained from the action of $PdCl_2$ with ethylene under pressure. Many olefins react with $PdCl_2$ in 50% acetic acid at ambient temperature to give $[PdCl_2(ol)]_2$; however, at higher temperatures π-allylic complexes are formed.

The bonding in olefin complexes is considered to involve (i) a σ-component arising from overlap of the π-electron density of the C=C bond with a σ-type acceptor orbital on the metal atom, and (ii) a π-component resulting from back donation from the filled *d* orbital on the metal atom to the anti-bonding orbitals on the carbon atoms[121].

In olefin complexes the C–C distance lies in the range 1.40–1.47 Å (cf. 1.34 Å in the uncoordinated olefin), indicating some reduction in the bond order on coordination. There is a concomitant decrease in ν(C=C) of about 150 cm^{-1}. In $[PdCl_2(C_2H_4)]_2$ the double bond is normal to the plane containing the palladium and chlorine atoms, but in $[PdCl_2(PhC{=}CPh)]_2$ it is not.

With fluoroolefins the σ-donor linkage is likely to be weak due to the inductive effect of the fluorine atoms but the π-bond would be expected to be stronger because the fluorine atoms would lower the energy of the π^*-orbitals, making them more accessible for bonding. Fluoroolefins do not seem to form π-bonded complexes with Pd(II).

Oxidation and isomerization of olefins catalysed by bivalent palladium. The oxidation of olefins to carbonyl compounds is catalysed by Pd(II) compounds via the formation of a palladium–olefin complex as intermediate. Ethylene can be oxidized almost quantitatively by air to acetaldehyde in the presence of $PdCl_2$ and $CuCl_2$ in aqueous solution containing hydrochloric acid. The reactions may be summarized as follows:

$$H_2C{=}CH_2 + PdCl_2 + H_2O \rightarrow CH_3CHO + Pd + 2HCl$$

$$Pd + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl$$

$$2CuCl + 2HCl + \tfrac{1}{2}O_2 \rightarrow 2CuCl_2 + H_2O$$

The cupric chloride serves to oxidize Pd(0) and the resulting cuprous chloride is oxidized by air. This reaction is used on an industrial scale. The process has also been used for the production of acetone from propylene and of methyl ethyl ketone from butenes[569, 570].

[568] P. A. Wegner and M. F. Hawthorne, *Chem. Communs.* 1966, 861.

[569] A. Aguiló, *Adv. Organomet. Chem.* **5** (1967) 321.

[570] J. Smidt, W. Hafner, R. Jira, R. Sieber, J. Sedlmeier and A. Sabel, *Angew. Chem.*, Int. Edn., **1** (1962) 80.

Mono-olefins containing at least one hydrogen atom on each carbon atom of the double bond are oxidized to ketones; the ketonic oxygen is attached according to the Markownikoff rule. The mechanism and kinetics of the olefin oxidation reaction have been discussed: it is clear that π-olefin complexes of Pd(II) are involved as reactive intermediates[569].

Similar reactions have been investigated in non-aqueous solvents. In alcohol vinyl ethers and acetals can be made: e.g. $[PdCl_2(C_2H_4)]_2$ reacts with alcohols to produce diacetals and small amounts of vinyl ethers according to the reactions:

$$[PdCl_2(C_2H_4)]_2 + 4ROH \rightarrow CH_3CH(OR)_2 + 2Pd + 4HCl$$
$$[PdCl_2(C_2H_4)]_2 + 2ROH \rightarrow 2CH_2{=}CHOR + 2Pd + 4HCl$$

In acetic acid solutions vinyl esters can be obtained:

$$H_2C{=}CH_2 + PdCl_2 + 2CH_3CO_2^- \rightarrow CH_3COOCH{=}CH_2 + Pd + CH_3CO_2H + 2Cl^-$$

The ethylene oxidation in acetic acid has been developed into a process for the commercial production of vinyl acetate[569].

A group of reactions, which are catalysed by Pd(II) compounds but do not involve reduction of Pd(II), include the vinylation of carboxylic acids with vinyl esters of other carboxylic acids:

$$RCO_2CH{=}CH_2 + R'CO_2H \overset{PdX_2}{\rightleftharpoons} RCO_2H + R'CO_2CH{=}CH_2$$

It is assumed that nucleophilic attack by a carboxylate or hydroxyl ion occurs at the complexed vinyl ester. The saponification of vinyl esters is also catalysed by Pd(II) [570].

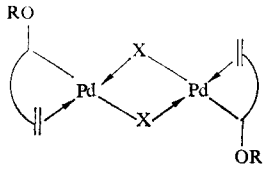
Isomerization of olefins has been found to occur in the presence of Pd(II): e.g. octene-1 isomerizes in the presence of $PdCl_2$ in acetic acid to give a mixture of octenes-2, -3 and -4. It has been suggested that an intramolecular hydrogen transfer takes place in the olefin complex; however, it is possible that the isomerization may involve a hydrido-π-olefin Pd(II) complex as intermediate[571]. The reaction of cyclohexene with sodium acetate in acetic acid in the presence of $PdCl_2$ and benzoquinone yields cyclohex-2-enyl acetate and the 3-enyl derivative rather than the 1-enyl compound[572]. 4-Phenylbut-1-ene isomerizes to a mixture of *cis*- and *trans*-1-phenylbut-2-ene and *trans*-1-phenylbut-1-ene in the presence of $Pd(PhCN)_2Cl_2$ [573].

Diolefin complexes. Diolefins having favourable steric arrangements of their double bonds can form two π-bonds and thus act as chelating ligands. The greater stability of diolefin complexes, compared to mono-olefin compounds, leads to a further lowering of ν(C=C). In general the palladium complexes are more deeply coloured, more readily prepared, more reactive and somewhat less stable than the corresponding platinum compounds. The monomeric complexes $[PdX_2(diene)]$ (X = Cl, Br; diene = hexa-1,5-diene, bicyclo-[2,2,1]-hepta-2,5-diene, tricyclo-[4,2,2,0]-decatriene, dicyclopentadiene, cycloocta-1,5-diene, cyclooctatraene, norbornadiene) are readily formed and have significant dipole moments. Replacement of the halide with alkyl lowers the stability: e.g. $[PdCl_2(C_8H_{12})]$ is very stable, whereas $[PdMe_2(C_8H_{12})]$ is unstable (C_8H_{12} = cycloocta-1,5-diene).

The monomeric compounds $[PdX_2(diene)]$ react with sodium carbonate in alcohol to give halogen-bridged complexes of the type (CXIV) in which each organic moiety is bound to palladium by one σ-bond and one π-bond from the olefin; the R group comes from the

[571] N. R. Davies, *Rev. Pure Appl. Chem.* **17** (1967) 83.
[572] M. Green, R. N. Haszeldine and J. Lindley, *J. Organomet. Chem.* **6** (1966) 107.
[573] N. R. Davies, A. D. Di Michiel and V. A. Pickles, *Austral. J. Chem.* **21** (1968) 385.

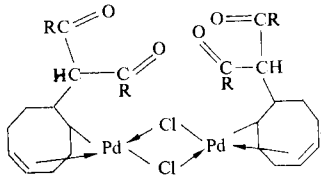
alcohol. The halogen bridge in these complexes can be split by amines to yield [PdX(dieneOR)(amine)]. Butadiene forms an unstable complex $PdCl_2(C_4H_6)$ which has been formulated as a dimer with two butadiene bridges[121, 566, 574].



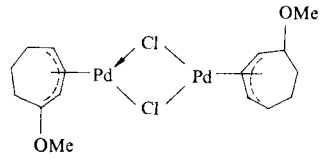
(CXIV)

The far infrared spectra of $[PdCl(C_8H_{12}OMe)L]$ (L = py, Ph_3P) suggest that L is *cis* to the double bond in the pyridine complex but is *trans* in the phosphine complex[575]. Silver acetate reacts with $[PdCl_2(C_8H_{12})]$ to give the acetato-bridged complex $[Pd(OAc)(C_8H_{12}OAc)]_2$ with the structure (CXIV; X = OAc; R = OAc); the chloro-bridged complex $[PdCl(C_8H_{12}OAc)]_2$ was also isolated[576].

The complexes $[PdCl_2(diene)]$ react with amines to give chloro-bridged dimers $[PdCl(dieneNHR)]_2$ with structures similar to (CXIV); the dimeric complexes react with Ph_3P to give $[PdCl(dieneNHR)(Ph_3P)]$. The β-diketone derivatives [Pd(diene-diketone)(diketone)] (diene = cyclooctadiene, norbornadiene, dicyclopentadiene) react with HX to yield bridged dimers $[Pd(diene\text{–}diketone)X]_2$ such as (CXV), which react with Ph_3P to yield $[Pd(diene\text{–}diketone)X(Ph_3P)]$ [577].



(CXV)



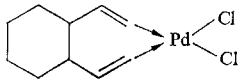
(CXVI)

Cyclohexa-1,3-diene(C_6H_8) and cyclohepta-1,3-diene (C_7H_9) react with $[Pd(CO)Cl_2]_2$ to give the chloro-bridged π-allylic complexes $[PdCl(C_6H_9)]_2$ and $[PdCl(C_7H_{11})]_2$. A similar compound $[PdCl(C_7H_{10}OMe)]_2$ (CXVI) can be obtained from Na_2PdCl_4 and C_7H_9 in methanol. The analogous methoxy-substituted π-allyl complex of cycloocta-1,3-diene can be obtained in the same way. The halogen bridges in these complexes can be split by pyridine[578].

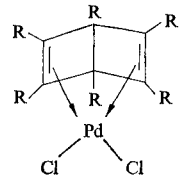
The reaction of $PdCl_2(PhCN)_2$ with cyclodeca-1,5-diene brings about the isomerization of the diolefin to give the Pd(II) complex (CXVII) of 1,2-vinylcyclohexane[579]. Palladium(II)

[574] E. O. Fischer and H. Werner, *Angew. Chem.*, Int. Edn., **2** (1963) 80.
[575] B. Crociani, P. Uguagliati, T. Boschi and U. Belluco, *J. Chem. Soc.* A, 1968, 2869.
[576] C. B. Anderson and B. J. Burreson, *J. Organomet. Chem.* **7** (1967) 181.
[577] G. Paiaro, A. de Renzi and R. Palumbo, *Chem. Communs.* 1967, 1150; B. F. G. Johnson, J. Lewis and M. S. Subramanian, *ibid.*, p. 117.
[578] M. A. Bennett, *Adv. Organomet. Chem.* **4** (1966) 354.
[579] J. C. Trebellas, J. R. Olechowski and H. B. Jonassen, *J. Organomet. Chem.* **6** (1966) 412.

also catalyses the isomerization of 4-vinylcyclohexene and cycloocta-1,3-diene to cycloocta-1,5-diene[580].



(CXVII)



(CXVIII)

The reaction of $[PdCl_2(PhCN)_2]$ on Dewar benzene and its hexamethyl derivative yield the yellow complexes (CXVIII; R = H, Me). The complex (CXVIII; R = Me) reacts with Ph_3P to give $[PdCl_2(Ph_3P)_2]$ with the liberation of hexamethyl-Dewar-benzene; however, pyrolysis of (CXVIII; R = Me) yields hexamethylbenzene and not its Dewar analogue[581].

Complexes of tetra-substituted cyclobutadiene of the type $[PdX_2(R_4C_4)]_2$ (X = Cl, Br or I; R = Ph, *p*-ClC_6H_4, *p*-$MeOC_6H_4$) can be obtained from the reaction of diphenylacetylenes with $PdCl_2$. If the cyclobutadiene ring is regarded as a four-electron donor, then in these complexes the palladium atom is formally 5-coordinate. Since the angle (45°) which the ligand subtends at the metal atom is considerably less than that subtended by other dienes ($\sim 70°$), the substituted cyclobutadiene could be considered as a unidentate ligand. The dimers $[PdCl_2(R_4C_4)]_2$ react with R_3P to give $PdCl_2(R_3P)_2$ and octa-substituted cyclooctatetraene. The complexes $[PdX_2(R_4C_4)]_2$ (X = Cl, Br, or I) react with alkoxide ions (OR′−) to give π-allyl halogen-bridged complexes $[PdX(R_4C_4OR')]_2$ [582].

Mass spectral studies show that $[PdCl_2(Ph_4C_4)]_2$ gives diphenylindenoindene and 1,4-dichlorotetraphenylbutadiene in the mass spectrometer[583].

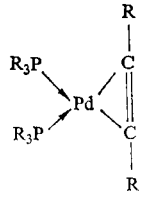
Chelate complexes containing an olefinic group and another donor atom. *o*-Allylphenyldimethylarsine (AA) and *o*-allylphenyldiphenylphosphine (AP) form the complexes $[PdX_2(AA)]$ (X = Cl, Br) and $[PdX_2(AP)]$ (X = Cl, Br, I) in which AA and AP act as bidentate ligands, since ν(C=C) occurs at 1527–1535 cm^{-1}, indicating that the olefinic bond is coordinated. On the other hand, in the complexes $[PdI_2(AA)]_2$, $[Pd(NCS)_2(AA)_2]$ and $Pd(NCS)_2(AP)_2$ ν(C=C) occurs at 1640 cm^{-1}, denoting that the olefinic group is not coordinated. Similarly in the dimeric complex $[PdCl_2\{CH_2{=}CH(CH_2)_3PPh_2\}]_2$ the olefinic bond is not coordinated[584].

Acetylene Complexes

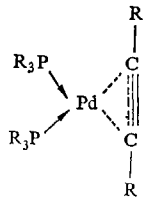
The acetylide complexes $K_2[Pd(CN)_2(C{\equiv}CR)_2]$ have been obtained from the reaction of $K_2[Pd(CN)_4]$ with KC≡CR in liquid ammonia[435]. However, the first acetylenic complexes of Pd(II) were reported in 1966. Although Pt(II) π-bonded complexes of the type $[Pt(RC{\equiv}CR')Cl_2L]$ are known, their Pd(II) analogues have not been prepared, probably because acetylenes are rapidly polymerized in the presence of palladium compounds.

[580] D. Chinn and H. Frye, *Inorg. Nucl. Chem. Letters* **5** (1969) 135.
[581] R. B. King, *Organomet. Chem. Rev.* **4** (1968) 137.
[582] P. M. Maitlis, *Adv. Organomet. Chem.* **4** (1966) 95.
[583] M. I. Bruce, *Adv. Organomet. Chem.* **6** (1968) 273.
[584] M. A. Bennett, H. W. Kouwenhoven, J. Lewis and R. S. Nyholm, *J. Chem. Soc.* 1964, 4570; M. A. Bennett, W. R. Kneen and R. S. Nyholm, *Inorg. Chem.* **7** (1968) 556.

Complexes of the type $[Pd(R_2C_2)(R'_3P)_2]$ (R = CF_3, CO_2Me; R′ = Ph, Bu^n; R'_3 = Me_2Ph) have been obtained by the reaction of $Pd(R'_3P)_4$ with acetylenes, containing electron-withdrawing substituents, in methylene chloride under nitrogen. The infrared spectra display two $\nu(C\equiv C)$ bands at 1795–1830 and 1837–1845 cm^{-1}, whereas $\nu(C\equiv C)$ occurs at *ca.* 2000 cm^{-1} in uncoordinated acetylenes. This suggests that the acetylene is σ-bonded as in (CXIX); however, the intermediate structure (CXX) has been proposed. The n.m.r. spectra suggest that the complexes are planar[585].



(CXIX)



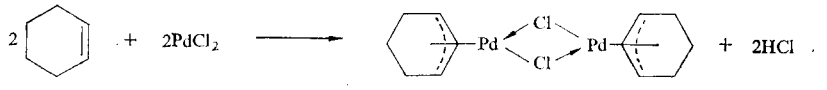
(CXX)

The compounds $[PdX\{HC\equiv CC(OH)MePh\}_4]$ and $PdX\{Me_2C(OH)C\equiv C(OH)Me_2\}$ (X = Cl, Br, I) have been reported; nothing is known of their structure except that the former are monomeric[586].

Allyl Complexes

More π-allylic complexes are known with palladium than with any other metal. In these π-complexes the delocalized allylic system RCH⋯CH⋯CHR′ acts as a three-electron donor, giving rise to a stronger bond between the metal and the allylic ligand than obtains in σ-allyl complexes. The Pd(II) complexes are very stable, often to temperatures above 200°. π-Allylic complexes include the yellow to red halogen-bridged dimers $[(C_3H_5)PdX]_2$ (C_3H_5 = allyl; X = Cl, Br, I) and $[(all)PdCl]_2$ (all = 1- and 2-chloroallyl, 2-bromoallyl, 1- and 2-methylallyl, 1-chloromethylallyl, 1-methoxy-1-methallyl, 1-methoxy-2-methylallyl, cyclohexenyl, 1-methylcyclohexenyl, diisobutenyl, α- and β-methylsteryl, α-dimethylsteryl, methylstilbenyl and triisobutenyl), the yellow $[(C_3H_5)PdCl(p\text{-}NH_2C_6H_4Me)]$, and the red cyclopentadienyl derivatives $[(all)Pd(C_5H_4R)]$ (all = allyl, R = H, Me, Et, Pr^n; all = cyclohexenyl; R = H, Me) [587].

The complexes can be prepared by various methods. One method involves the reaction between an allyl halide or alcohol with $PdCl_2$ or Na_2PdCl_4: e.g. the reaction of $CH_2{=}CHCH_2OH$ with Na_2PdCl_4 in 50% acetic acid at 50° yields $[(C_3H_5)PdCl]_2$, palladium metal, propylene and other products. Palladium metal will react with allyl bromide to give $[(C_3H_5)PdBr]_2$. Another method uses an olefin as the starting material:

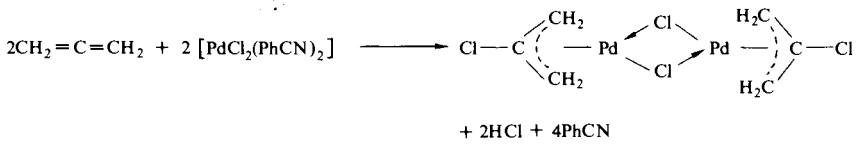


[585] E. O. Greaves and P. M. Maitlis, *J. Organomet. Chem.* **6** (1966) 104; E. O. Greaves, C. J. L. Lock and P. M. Maitlis, *Can. J. Chem.* **46** (1968) 3879.

[586] A. V. Babaeva and T. I. Beresneva, *Zh. Neorg. Khim.* **11** (1966) 1966, 2520, 2671.

[587] M. L. H. Green and P. L. I. Nagy, *Adv. Organomet. Chem.* **2** (1964) 325.

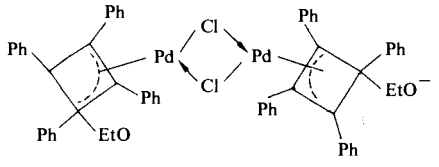
Allylic complexes have also been obtained from allenes, e.g.:



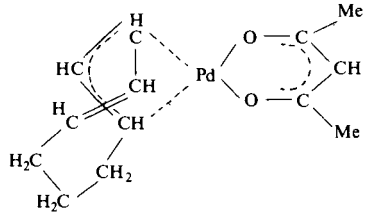
Donor ligands split the chloro-bridge in the dimeric π-allylic complexes. The cyclopentadienyl–cyclohexenyl complex $[(C_5H_5)Pd(C_6H_9)]$ reacts with Ph_3P to yield the Pd(0) complex $[Pd(Ph_3P)_4]$ [587].

It is believed that π- → σ-allyl conversion occurs in solvents such as dimethylformamide and the role of DMF in the interaction of olefins with $PdCl_2$ to yield π-allyl complexes has been discussed[588].

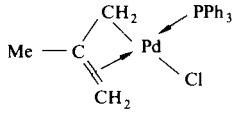
Some structural investigations on π-allylic complexes of Pd(II) have been carried out. In $[(C_3H_5)PdCl]_2$ the three carbon and five hydrogen atoms form a plane oriented at 111.5° to the plane of the $PdCl_2Pd$ bridge system and the C–C distances are 1.376 Å. Reaction of this complex with silver acetate gives a π-allyl acetato-bridged dimer which has a structure similar to copper acetate monohydrate. The complex $[(Ph_4C_4EtO)_2Pd_2Cl_2]^{2-}$ has the structure (CXXI). In cyclooctadienylacetylacetonatopalladium (CXXII) only three carbon atoms of the dienyl ligand are involved in bonding to the metal; for these atoms the average Pd–C distance is 2.11 Å, whereas the remaining carbon atoms are at 2.93 and 3.93 Å. X-ray analysis shows that $[(CH_2{=}CHCMeCH_2)PdCl(Ph_3P)]$ is a σ–π-allyl complex with the structure (CXXIII); the methylallyl ligand is non-planar and the Me group is 0.5 Å out of the plane[589].



(CXXI)



(CXXII)



(CXXIII)

In the orange complex monothiodibenzoylmethanato-π-methylallylpalladium(II) the bond lengths and angles are as follows: Pd–O 2.067, Pd–S 2.291, Pd–C 2.08, 2.15 and

[588] R. Ugo, F. Conti and M. Donati, *Chem. Communs.* 1967, 801.
[589] M. R. Churchill and R. Mason, *Adv. Organomet. Chem.* **5** (1967) 93.

2.21 Å; S–Pd–O 95.8, C_1–Pd–C_3 67.8, C_1–Pd–S 99.4, C_3–Pd–O 96.7°. The long Pd–C bond length of 2.21 Å is opposite the sulphur atom and is ascribed to a *trans* effect[590]. The Pd–S distance is considerably shorter than the sum of the covalent radii (2.49 Å) but not as short (2.24 Å) as found in *cis*-bis-(monothiobenzoylmethanato)palladium(II) [505].

Hexamethyl-Dewar-benzene ($C_{12}H_{18}$) by loss of a proton forms the dimeric complexes $[PdX(C_{12}H_{17})]_2$ (X = Cl, Br, I) which undergo bridge-splitting reactions to yield $[PdX(C_{12}H_{17})L]$ (L = R_3P, Ph_3As) and $[Pd(C_{12}H_{17})L']$ (L' = acac, C_5H_5). Spectral evidence suggests that in these complexes $C_{12}H_{17}$ is a π-allylic ligand and the X-ray structure determination of $[Pd(C_{12}H_{17})(acac)]$ confirms this[591].

The transfer of a π-allyl group from palladium to iron and mercury can be effected[592]. A variety of reactions involving π-allylic complexes of palladium has been reported[560, 581, 593].

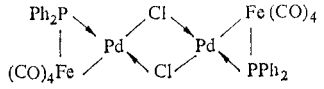
Hydride Complexes

The hydride complexes $[HPdCl(R_3P)_2]$ (R = Et, Ph) can be obtained by the reduction of $[PdCl_2(R_3P)_2]$ with $HGeMe_3$. The complexes are stable in the absence of oxygen but only in neutral media[594]. The hydridocarbonyl anion $[HPd(CO)Cl_2]^-$ is formed by the reaction of CO on $PdCl_2$ in 2-methoxymethanol. It can be isolated as the $[AsPh_4]^+$, $[pyH]^+$ or quinolinium salts; ν(Pd–H) occurs at 1960–2010 cm^{-1} [595].

Complexes Containing Metal–Metal Bonds

The complex $[(Et_3P)_2Pd(GePh_3)_2]$ decomposes at 97° but is unstable in solution at −20°. Hydrogenation of this complex at 100 atm yields $[HPd(Et_3P)_2(GePh_3)_2]$. Treatment of $[(Et_3P)_2Pd(GePh_3)_2]$ with KCN gives the anionic complex $K_2[(CN)_2Pd(GePh_3)_2]$ [594]. The reaction of $[PdCl_4]^{2-}$ with $SnCl_2$ in HCl/methanol solution yields $[AsPh_4][PdCl(SnCl_3)_3]$ [596].

The complex (CXXIV) can be obtained as deep red needles in quantitative yield by the reaction of $(CO)_4Fe(Ph_2PH)$ with $[(C_3H_5)PdCl]_2$ in toluene[597].



(CXXIV)

[590] S. J. Lippard and S. M. Morehouse, *J. Am. Chem. Soc.* **91** (1969) 2504.

[591] J. F. Malone, W. S. McDonald, B. L. Shaw and G. Shaw, *Chem. Communs.* 1968, 869; B. L. Shaw and G. Shaw, *J. Chem. Soc.* 1969, 602.

[592] A. N. Nesmeyanov, S. P. Gubin and A. Z. Rubezhov, *Izvest. Akad. Nauk SSSR, Ser. Khim.* 1966, 194, 1680; *J. Organomet. Chem.* **16** (1969) 163.

[593] K. Vrieze, A. P. Praat and P. Cossee, *J. Organomet. Chem.* **12** (1968) 533; S. Wolfe and P. Campbell, *Proc. XIIth Int. Conf. Coord. Chem. Sydney* (H. C. Freeman, ed.), Science Press (1969), p. 54.

[594] E. H. Brooks and F. Glocking, *J. Chem. Soc.* A, 1966, 1241; 1967, 1030.

[595] J. V. Kingston and G. R. Scollary, *Chem. Communs.* 1969, 455.

[596] M. A. Khattak and R. J. Magee, *Chem. Communs.* 1965, 400.

[597] B. C. Benson, R. Jackson, K. K. Joshi and D. T. Thompson, *Chem. Communs.* 1968, 1506.

6.6. COMPLEXES OF PALLADIUM(IV)

Complexes of Pd(IV) are not numerous.

Halogen Complexes

The halogen complexes $[PdX_6]^{2-}$ are known for X = F, Cl and Br but not for X = I. The fluoro-complexes $M_2[PdF_6]$ (M = K, Rb, Cs), which are bright yellow to orange, can be prepared by fluorination of the corresponding chloro-complexes; they are readily hydrolysed by water. The caesium salt $Cs_2[PdF_6]$ has the $K_2[PtCl_6]$ structure[598]. The compound $Pd[PdF_6]$ has been discussed (see p. 1278). The bright red chloro-complexes $M_2[PdCl_6]$ (M = K, Rb, Cs, NH_4) can be prepared by saturating a solution of $[PdCl_4]^{2-}$ with chlorine. The caesium and rubidium salts are almost insoluble in water. These salts evolve Cl_2 when boiled with water; $K_2[PdCl_6]$ loses Cl_2 when heated to 175°. The bromo-complexes $M_2[PdBr_6]$ (M = K, Rb, Cs, NH_4) can be obtained by the action of Br_2 on a concentrated solution of $M_2[PdBr_4]$; they are black. Like the chloro-complexes, they decompose in hot water with the liberation of Br_2. The rubidium salt $Rb_2[PdBr_6]$ was one of the first metal complexes to be investigated by X-ray analysis; it was found to be octahedral as predicted by Werner[427].

Complexes of Nitrogen Ligands

The reddish-orange diammine-type complexes $[Pd(NH_3)_2Cl_4]$, $[Pdpy_2Cl_4]$, $[Pd(chel)Cl_4]$ (chel = en, phen, bipy) can be prepared by treating a suspension of the dichlorodiammine complex in chloroform with Cl_2 [426, 518]. The bipyridyl complex is stable to 160° and is not decomposed by boiling water[518], but the other compounds rapidly lose Cl_2 in moist air. The complex $[Pd(NH_3)_2(NO_2)_2Cl_2]$ is also stable.

Several tetrammine-type complexes have been reported, viz. $[Pd(NH_3)_4X_2]X_2$ and $[Pden_2X_2]X_2$ (X = Cl, Br, I). The reduction potentials for $[Pden_2Cl_2]^{2+}$, $[Pden_2Br_2]^{2+}$ and $[Pden_2I_2]^{2+}$ have been reported as 1.13, 0.692 and 0.625 V respectively. The ion $[Pden_2Cl_2]^{2+}$ has been obtained in *cis* and *trans* isomeric forms; the structures were assigned from the infrared spectra. The reaction of KX (X = Br, I) on *trans*-$[Pden_2Cl_2](NO_3)_2$ yields *trans*-$[Pden_2X_2]X_2$, while concentrated HCl gives *cis*-$[Pden_2Cl_2]Cl_2$. *Cis* and *trans* isomers of $[Pden_2Cl_2][PdCl_4]$ have been isolated[599].

The black compound $Pd(NH_3)_2Cl_3$ does not contain Pd(III) but exists as infinite chains of - - - Cl–Pd^{IV}–Cl - - - Pd^{II} - - - Cl–Pd^{IV}–Cl - - - in the crystalline state[447].

Complexes of Phosphorus and Arsenic Ligands

The chelating ligands *o*-phenylenebisdimethylarsine (XCIII; R = Me) and 8-dimethylarsinoquinoline (CI) form the complexes $[PdL_2Cl_2](ClO_4)_2$ (L = XCIII, CI); the Pd(IV) complexes were obtained by oxidation of PdL_2Cl_2 [464, 555].

The Pd(IV) complex $[PdCl_2(Ph_3P)_2(C_6F_5)_2]$ has been prepared by the reaction of $[PdCl_2(Ph_3P)_2]$ with $[(C_6F_5)_2TlBr]_2$ [563].

[598] R. Hoppe and W. Klemm, *Z. anorg. Chem.* **268** (1952) 364; A. G. Sharpe, *J. Chem. Soc.* 1953, 197.
[599] A. V. Babaeva and E. Ya. Khananova, *Zh. Neorg. Khim.* **10** (1965) 2579, 2653; **12** (1967) 393.

7. PLATINUM

7.1. GENERAL CHEMISTRY

Platinum is a silver–white ductile metal. Like palladium it dissolves in aqua regia—although rather slowly in massive form—but unlike palladium it does not form a film of oxide when heated in air. Platinum can be obtained in various forms: platinum sponge is made by heating $(NH_4)_2[PtCl_6]$; platinum black can be obtained by warming an aqueous solution containing $PtCl_2$, KOH and alcohol; colloidal platinum is made by arcing platinum electrodes under water. All these forms have catalytic power, particularly for hydrogenation reactions. The finely divided metal can absorb hydrogen strongly but to a much lesser degree than palladium.

Although the yellow salt $K_2[PtCl_6]$ is the most readily available compound of platinum, because of its low solubility it is generally less suitable for the preparation of complexes than the red Pt(II) salt $K_2[PtCl_4]$. There are many published methods for the preparation of $K_2[PtCl_4]$ but the author has found the following the most satisfactory. Platinum sponge (30 g) was dissolved in aqua regia and the mixture was taken twice to dryness with HCl. A solution of KCl (22.9 g) in water (200 ml) was added. The precipitate of $K_2[PtCl_6]$ was made granular by heating the mixture on the steam bath. The mixture was cooled in ice and the $K_2[PtCl_6]$ was filtered off and washed with acetone. The yield of $K_2[PtCl_6]$ (78.5 g) was added to a solution of hydrazine sulphate (10.95 g) in water (250 ml). The mixture was heated to boiling then kept on a steam bath for 40 min, whereupon it was filtered to remove a small amount of platinum and $K_2[PtCl_6]$. The filtrate was cooled in ice and the red crystals of $K_2[PtCl_4]$ were filtered off and washed with acetone; yield, 54.7 g (86%). The ammonium salt can be prepared similarly.

Some electrode potentials for platinum are given in Table 46. The oxidation states are listed in Table 47. In the bivalent state platinum closely resembles palladium, exhibiting pronounced (b) class behaviour, although Pt(II) is much more inert than Pd(II) and numerous examples of *cis–trans* isomerism are known. Olefin complexes are readily formed and hydride complexes are relatively numerous.

TABLE 46. ELECTRODE POTENTIALS FOR PLATINUM [a, b]

Reaction	Potential (V)
$PtCl_4^{2-} + 2e = Pt + 4Cl^-$	0.73
$PtBr_4^{2-} + 2e = Pt + 4Br^-$	0.58
$Pt(OH)_2 + 2H^+ + 2e = Pt + 2H_2O$	0.98
$PtCl_6^{2-} + 2e = PtCl_4^{2-} + 2Cl^-$	0.68
$PtO_2 + 4H^+ + 2e = Pt(II) + 2H_2O$	0.84
$PtO_3 + 2H^+ + 2e = PtO_2 + H_2O$	2.00

[a] W. M. Latimer, *Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd edn., Prentice-Hall, Englewood Cliffs, New Jersey (1952), p. 204.

[b] T. J. Walsh and E. A. Hausman, The Platinum Metals, in *Treatise on Analytical Chemistry*, Part II, Vol. 8 (I. M. Kolthoff and P. J. Elving, eds.), Wiley Interscience, New York (1963), p. 397.

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[a] W. M. Latimer, *Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd edn., Prentice-Hall, Englewood Cliffs, New Jersey (1952), p. 204.

[b] T. J. Walsh and E. A. Hausman, The Platinum Metals, in *Treatise on Analytical Chemistry*, Part II, Vol. 8 (I. M. Kolthoff and P. J. Elving, eds.), Wiley Interscience, New York (1963), p. 397.

TABLE 47. OXIDATION STATES OF PLATINUM

Oxidation state	Coordination number	Stereochemistry	Examples
Pt(0)	3	?	$Pt(Ph_3P)_3$
	4	Tetrahedral	$Pt(Ph_3P)_4$, $Pt(PF_3)_4$
Pt(I)	4	Square-planar ?	$[(C_5H_5)Pt(CO)_2]$
Pt(II)	4	Square-planar	$[PtCl_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$, $[PtenCl_2]$
	5	Trigonal bipyramidal	$[Pt(QAS)I]BPh_4$ [a], $[Pt(SnCl_3)_5]^{3-}$
	5	Square-pyramidal	$[Pt(TPAS)I]I$ [b]
	6	Tetragonal	$Pt(As\text{–}As)_2I_2$ [c]
Pt(IV)	6	Octahedral	$[PtCl_6]^{2-}$, $[Pt(NH_3)_6]^{4+}$, $[Pten_2Cl_2]^{2+}$, $[Pt(As\text{–}As)_2Cl_2]^{2+}$
Pt(V)	6 (?)	Octahedral (?)	$[PtF_5]_n$
	6	Octahedral	$[PtF_6]^-$
Pt(VI)	?	?	PtO_3, $PtOF_4$
	6	Octahedral	PtF_6

[a] QAS = tris-(*o*-diphenylarsinophenyl)arsine (CIX).
[b] TPAS = *o*-phenylenebis-{(*o*-dimethylarsinophenyl)methylarsine} (CX).
[c] As–As = *o*-phenylenebisdimethylarsine (XCIII; R = Me).

The quadrivalent state is second in importance to the bivalent state and Pt(IV) forms a large number of very stable and kinetically inert complexes; the coordination number is invariably 6. There is a marked tendency for Pt(IV) to form σ-bonds to carbon. The affinity for "soft" ligands is much less than that of Pt(II) and Pt(IV) approaches (a) class behaviour: most but not all phosphine, arsine and thiol ligands reduce Pt(IV) to Pt(II) and form complexes with the metal in the lower oxidation state.

Although no carbonyl analogous to $Ni(CO)_4$ has been reported, a few tetrahedral Pt(0) species are known; these are of great importance in synthesis and catalysis. The oxidation state +1 is not definitely established, although the complex $[(C_5H_5)PtCO]_2$ apparently contains Pt(I).

The oxidation states +6 and +5 are confined to PtF_6, $PtOF_4$ and to the ion $[PtF_6]^-$, derived from the reduction of PtF_6. The trivalent state does not seem to occur.

Thermodynamic data for platinum and some platinum compounds are listed in Table 48.

7.2. BINARY COMPOUNDS

The halides and chalcogenides are listed in Table 49.

Halides

Platinum hexafluoride, PtF_6, can be prepared by the reaction of fluorine on a heated platinum filament; the red vapours are condensed on to a cold finger to give dark red crystals. Like other hexafluorides, PtF_6 has an extremely short liquid range (7.8°) and undergoes a solid phase transition from a low temperature orthorhombic form to a high temperature cubic form, the transition temperature being 0° (ΔH_{trans} 2.14 kcal mole^{-1}). Platinum(VI)

TABLE 48. THERMODYNAMIC DATA ON PLATINUM AND ITS COMPOUNDS [a]

Substance	State	$\Delta H°$	$\Delta F°$	$S°$
Pt	g	121.6	110.9	45.96
Pt	c	0	0	10.0
$PtCl_2$	c	−35.5	−26.3 [b]	
$PtCl_4$	c	−62.9	−42.3 [b]	
$PtCl_4^{2-}$	aq	−123.4	−91.9	42
$PtCl_6^{2-}$	aq	−167.4	−123.1	52.6
H_2PtCl_6	aq	−167.3		
$PtBr_4$	c	−41.3		
$PtBr_4^{2-}$	aq	−91.1	−71.5 [b]	
$PtBr_6^{2-}$	aq	−117.1		
PtI_4	c	−21.6	−22.0 [b]	
PtI_6^{2-}	aq	−55.7		
$Pt(OH)_2$	c	−87.2	−68.2	26.5
PtS	c	−20.8	−21.6	
PtS_2	c	−27.8	−25.6	

[a] Unless otherwise indicated, values are from the US National Bureau of Standards Circular 500, *Selected Values of Thermodynamic Properties* (1952).

[b] W. M. Latimer, *Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd edn., Prentice-Hall, Englewood Cliffs, New Jersey (1952), p. 203.

has the configuration $t_{2g}^3 e_g^1$ and PtF_6 exhibits Jahn–Teller distortion, whereas IrF_6 (t_{2g}^3) does not. PtF_6 is the least stable of the hexafluorides MF_6 (M = W, Re, Os, Ir, Pt) and is one of the most powerful oxidizing agents known. This property led to the discovery of the remarkable compounds $O_2^+[PtF_6]^-$ and $Xe^+[PtF_6]^-$, which were obtained by the reaction of PtF_6 with O_2 and Xe respectively. PtF_6 is reduced by NO and ClF_3 to give $NO^+[PtF_6]^-$ and $ClF_2^+[PtF_6]^-$. The electron affinity of PtF_6 has been estimated at −156 kcal $mole^{-1}$. The infrared spectrum has been obtained in the vapour phase and, like the spectra of other hexafluorides, shows six bands: 655 (ν_1), 601 (ν_2), 705 (ν_3), 273 (ν_4), 242 (ν_5) and 211 (ν_6) [600, 601].

Fluorination of platinum or $PtCl_2$ at 350° yields the dark red PtF_5 which has a tetrameric structure like that of $[RhF_5]_4$ with the four PtF_4 units linked by bridging fluorine atoms. The magnetic moment is 2.05 BM [600, 602].

The reaction of BrF_3 on Pt metal yields $PtF_4 \cdot BrF_3$. Heating of this adduct *in vacuo* for 12 hr at 180° removes most of the BrF_3; the remainder is removed as BrF_5 by diluted F_2 at 250°. PtF_4, when prepared in this way, is yellowish brown, quite pure and diamagnetic. The structure is similar to that of UCl_4 and PdF_4 with the metal atom 8-coordinate and at the centre of two flattened tetrahedra. The compound is violently hydrolysed by water.

Platinum tetrachloride can be prepared by heating platinum with chlorine at 250–300° or with $AsCl_3$ or $SeCl_4$ in a sealed tube. It is more easily obtained by heating chloroplatinic acid $H_2PtCl_6 \cdot 6H_2O$ to 300°. It forms reddish-brown crystals which are soluble in water

[600] J. H. Canterford, R. Colton and T. A. O'Donnell, *Rev. Pure Appl. Chem.* **17** (1967) 123.

[601] N. Bartlett in *Preparative Inorganic Reactions* (W. L. Jolly ed.), Interscience, New York (1965), Vol. 2, p. 301.

[602] N. Bartlett, F. Einstein, D. F. Stewart and J. Trotter, *Chem. Communs.* 1966, 550.

TABLE 49. HALIDES AND CHALCOGENIDES OF PLATINUM

Compound	Colour	Remarks
PtF_6	Dark red	Melting point 61.3°; boiling point 69.1°; Jahn–Teller distorted octahedral
$[PtF_5]_4$	Deep red	Melting point 80°; tetrameric with F bridges; μ, 2.05 BM
PtF_4	Yellowish brown	d. *ca.* 600°; diamagnetic
$PtCl_4$	Reddish brown	d. 370° (in Cl_2)
$PtBr_4$	Brownish black	d. slowly at 180°
PtI_4	Brownish black	d. 130°
$PtCl_2$	α, Olive green β, Reddish black	d. 581° (in Cl_2) Octahedral with Pt_6Cl_{12} clusters
$PtBr_2$	Brown	d. 250°
PtI_2	Black	d. 360°
PtO_3	Reddish brown	Impure, unstable
PtO_2	Brown	d. 380–400°
PtS_2	Greyish black	d. 225–250°; CdI_2 structure
$PtSe_2$	Greyish black	d. 140° in air; CdI_2 structure
$PtTe_2$	Black	Melting point 1300–1400°; CdI_2 structure
PtO	Black	d. 560° into $Pt + O_2$
PtS	Greyish black	Zincblende structure

and acetone and crystallizes from water with 1, 4, 5 or $7H_2O$. These hydrates are certainly complex and some or possibly all contain the species $[PtCl_4(OH)_2]^{2-}$ [604].

The tetrahalides $PtBr_4$ and PtI_4 can be obtained as brownish-black powders by reaction of the elements at 150°. The tetrabromide can also be obtained by dissolving platinum in a mixture of hydrobromic and nitric acids, followed by evaporation and heating of the residue to 180°. The tetraiodide is precipitated when KI is added to a hot concentrated solution of H_2PtCl_6. Both $PtBr_4$ and PtI_4 are only slightly soluble in water but are moderately soluble in alcohol and ether. They decompose on being heated into PtX_2 and free halogen[604].

The addition of KI to a cold $[PtCl_6]^{2-}$ solution yields a black precipitate of stoichiometry PtI_3. Since the substance is diamagnetic, it probably contains Pt(II) and Pt(IV), but it is apparently not a mixture of PtI_2 and PtI_4. It yields PtI_2 at 270° [605]. Although $PtCl_3$ and $PtBr_3$ have been reported, it is extremely doubtful if these products contain Pt(III).

Attempts to confirm the existence of PtF_2 were unsuccessful, and it is unlikely that the compound can be obtained[603]. The other dihalides are known but $PtBr_2$ and PtI_2 have

[603] N. Bartlett and D. H. Lohmann, *J. Chem. Soc.* 1964, 619.

[604] N. V. Sidgwick, *The Chemical Elements and their Compounds*, Clarendon Press, Oxford (1950), p. 1578.

[605] G. R. Argue and J. J. Banewicz, *J. Inorg. Nucl. Chem.* **25** (1963) 923.

narrow thermal stability ranges and are difficult to obtain pure. Platinum dichloride $PtCl_2$ can be obtained by heating platinum in chlorine at 500° or by heating $PtCl_4$. It is known in two forms: the normal or α-form is olive green, insoluble in water, but soluble with difficulty in hydrochloric acid. A reddish-black β-form has been obtained; X-ray analysis shows that the crystals contain discrete $[Pt_6Cl_{12}]$ groups; the twelve chlorine atoms are situated above the edges of an octahedron of six platinum atoms; the coordination about the platinum atom is square-planar. Vaporization in the mass spectrometer shows that the heaviest particles are Pt_6Cl_{12}, but Pt_5Cl_{10} and Pt_4Cl_8 occur with lower intensity, whereas $PdCl_2$ gives only Pd_6Cl_{12}[606].

The other dihalides $PtBr_2$ and PtI_2 can be obtained with difficulty by thermal decomposition of the tetrahalides. The action of heat on $H_2PtBr_6 \cdot aq$ gives $PtBr_2$, but the decomposition is slow. Treatment of $K_2[PtCl_4]$ with KI and I_2 gives a black precipitate of PtI_2. Both $PtBr_2$ and PtI_2 are insoluble in water and in the appropriate halogen acid[604].

The monochloride PtCl and the trihalides PtX_3 (X = Cl, Br, I) have been reported but they have not been sufficiently characterized and it is questionable whether these compounds, which were prepared at elevated temperatures, contain Pt(I) or Pt(III) [607].

The oxofluoride $PtOF_4$ is formed along with PtF_6 and PtF_5 by the action of F_2 on Pt at 350° in silica apparatus; it forms dark red crystals, m.p. 75°. The brown $PtOF_3$ has been obtained by the action of F_2 on PtO_2 at 200° [603].

Chalcogenides

An impure brownish-red product with a composition approximating to PtO_3 has been obtained by anodic oxidation. It is unstable and slowly evolves O_2 in water and oxidizes HCl to Cl_2. It is not reduced by H_2O_2; this suggests that the compound is not a peroxide and that it probably contains Pt(VI) [604].

The dioxide PtO_2 can be obtained as a brownish-black powder by heating $PtO_2 \cdot H_2O$, although the last traces of water cannot be removed without some loss of O_2. It liberates O_2 at 380–400°. The hydrated forms $PtO_2 \cdot nH_2O$ (n = 1, 2, 3, 4) have been reported. When $PtCl_4$ is boiled with excess NaOH and the solution is acidified with acetic acid, a white precipitate is formed which turns yellow on digestion. This yellow product is the trihydrate $PtO_2 \cdot 3H_2O$ which dissolves in KOH to give $K_2[Pt(OH)_6]$. The trihydrate loses one molecule of water over H_2SO_4 to give the brown dihydrate, which loses a second molecule at 100° to form $PtO_2 \cdot H_2O$; the monohydrate is nearly black. The tri- and di-hydrates dissolve readily in HCl but the monohydrate is insoluble in HCl and aqua regia[604].

A mixed oxide Pt_3O_4 has been obtained by the prolonged oxidation of platinum wire. Structural investigations show that all the platinum atoms are crystallographically equivalent; there are eight oxygen atoms at the corners of a cube and the coordination number of the oxygen atoms is six[608]. The hydrated sesqui-oxide $Pt_2O_3 \cdot aq$ has been reported as a dark brown precipitate obtained by treating a solution of $PtCl_2$ with KOH. It cannot be dehydrated without loss of oxygen, and anhydrous Pt_2O_3 has not been prepared[604, 607].

The disulphide PtS_2, diselenide $PtSe_2$ and ditelluride $PtTe_2$ can be prepared by heating the elements together. The compounds are greyish black with a CdI_2 lattice[607]. The action of H_2S on $[PtCl_6]^{2-}$ produces a black precipitate of PtS_2 which is readily oxidized by air.

606 H. Schafer, U. Wiese, K. Rinke and K. Brendel, *Angew. Chem.*, Int. Edn., **6** (1967) 253.
607 *Gmelin's Handbuch der Anorganischen Chemie*, Verlag Chemie, Berlin (1940), Vol. 68C.
608 A. F Wells, *Structural Inorganic Chemistry*, 3rd edn., Clarendon Press, Oxford (1962).

Platinum(II) oxide has been obtained as an impure greyish-black powder by heating $Pt(OH)_2$. The hydroxide is precipitated by the action of hot KOH solution on $[PtCl_4]^{2-}$; it is black and is readily oxidized by air. The greyish-black sulphide PtS can be obtained by heating together $PtCl_2$, Na_2CO_3 and S. The platinum atom has approximately square-planar coordination, while the sulphur atom is tetrahedral. The platinum atom has two bond angles of 82.5° and two of 97.5°, while the sulphur atom has two of 97.5° and four of 115° [608]. Platinum(II) telluride has been obtained by the reduction of $PtTe_2$; it has the NiAs structure.

Other Binary Compounds

Platinum forms stoichiometric compounds with a number of non-metals and B subgroup metals; they are obtained by heating the elements together. The oxidation state of the platinum in these alloy-type compounds is open to question. Platinum boride, PtB, has been obtained from the elements at 600° and 40,000 atm [609]. Silicon forms two compounds, Pt_2Si and PtSi[604]. PtP_2 and $PtAs_2$ are resistant to acid; $PtAs_2$ has the pyrite structure. PtSn, PtPb, PtSb and PtBi have the NiAs structure[608].

Two yellow cyanides $Pt(CN)_2$ and $Pt(CN)_3$ have been described but their structures are unknown[604].

7.3. COMPLEXES OF PLATINUM(0)

The existence of a number of Pt(0) complexes has been definitely established and some of these compounds, e.g. $Pt(Ph_3P)_4$, have been of great importance in the synthesis of new compounds. In addition there have been reports of several complexes, e.g. $Pt(NH_3)_4$, for which confirmatory evidence is meagre, and it is possible that some of these compounds are actually hydrides of Pt(II). A discussion on the zerovalent state of nickel, palladium and platinum has been given (p. 1281).

Complexes of Nitrogen Ligands

Reduction of $[Pt(NH_3)_4]Br_2$ with potassium in liquid ammonia yields a product said to be $[Pt(NH_3)_4]$; it is decomposed by heat into metallic platinum and NH_3. The analogous compound $[Pten_2]$ is obtained by reduction of $[Pten_2]I_2$ in liquid NH_3 [336, 610].

Phosphine and Arsine Complexes

In 1958 the complexes $Pt(R_3P)_4$ and $Pt(R_3P)_3$ (R = aryl) were reported as being obtained by the reaction of hydrazine with $PtX_2(R_3P)_2$ in the presence of excess R_3P; the compounds are stable in air for several hours but slowly decompose in benzene. The triarylphosphite complexes $Pt\{P(OR)_3\}_n$ (n = 3, 4) and the less stable arsine complexes $Pt(R_3As)_4$ were prepared in a similar way. It was subsequently suggested that these compounds were actually hydrides such as $H_2Pt(R_3P)_4$ but the complexes $Pt(R_3P)_4$ and $Pt(R_3P)_3$ (R = Ph, C_6H_4F) have been established as genuine Pt(0) complexes and not hydrides[611]. In $Pt(Ph_3P)_4$ ν(Pt–P) occurs at 424 cm^{-1} [106].

[609] E. D. Whitney and R. F. Giese, *Nature* **197** (1963) 1293.
[610] G. W. Watt, R. E. McCarley and J. W. Dawes, *J. Am. Chem. Soc.* **79** (1957) 5163.
[611] L. Malatesta and R. Ugo, *J. Chem. Soc.* 1963, 2080.

The tetraphosphine derivative $Pt(Ph_3P)_4$ dissociates in solution to give $Pt(Ph_3P)_3$ which may exist in solution as $Pt(Ph_3P)_3$(solvent) but is nevertheless quite reactive. The golden yellow diphosphine complex $Pt(P–P)_2$ (P–P = $Ph_2PCH_2CH_2PPh_2$) can be obtained by reduction of $[Pt(P–P)_2]Cl_2$ with $NaBH_4$ and the colourless $Pt(Me_2PCH_2CH_2PMe_2)_2$ can be prepared by reduction with sodium naphthalenide in THF [612].

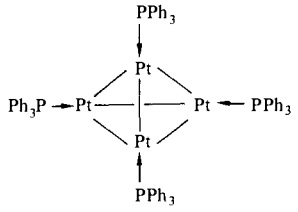
The yellow bis-phosphine complex $Pt(Ph_3P)_2$ can be obtained by the reaction

$$2[HPt(Ph_3P)_3]HSO_4 + 2KOH + O_2 \xrightarrow{EtOH} 2[Pt(Ph_3P)_2] + 2Ph_3PO + 2KHSO_4 + 2H_2O$$

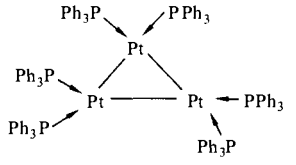
It can also be obtained in lower yield by the reaction

$$trans\text{-}[HPtCl(Ph_3P)_2] + LiC_4H_9 \rightarrow [Pt(PPh_3)_2] + LiCl + C_4H_{10}$$

The compound reacts to form $Pt(Ph_3P)_2L$ (L = Ph_3P, CO, PhCH=CHPh, PhC≡CPh). It does not catalyse hydrogenation or isomerization of olefins. The mono-phosphine complex $Pt(Ph_3P)$ has been obtained by the action of air on $Pt(Ph_3P)_4$ in cycloocta-1,5-diene; it is tetrameric in benzene. A red trimeric form of $Pt(Ph_3P)_2$ has been obtained. Both $[Pt(Ph_3P)]_4$ and $[Pt(Ph_3P)_2]_3$ are considered to be metal-cluster compounds with the structures (CXXV) and (CXXVI). The tetramer is very stable and unreactive, but the trimeric cluster dissociates very readily unless additional stabilization is present as in the carbonyl bridges of $[Pt_3(Ph_3P)_4(CO)_3]$. Additional cluster compounds such as $Pt_3(Ph_3P)_5 \cdot C_6H_6$ and $Pt_3(Ph_3P)_4 \cdot C_6H_6$ have been reported[613].



(CXXV)



(CXXVI)

The reaction of $PtCl_2$ with PF_3 under pressure at 100° in the presence of copper powder yields $Pt(PF_3)_4$ [614].

The coordinative reactivity of phosphine complexes of Ni(0), Pd(0) and Pt(0) has been recently reviewed[433]. Oxygen reacts with $Pt(Ph_3P)_4$ in solution to give $Pt(O_2)(Ph_3P)_2$ which will react with C_2H_4 to give the isoelectronic $Pt(C_2H_4)(Ph_3P)_2$. The reaction of SO_2 yields $Pt(SO_2)(Ph_3P)_3$ which can be oxidized to $Pt(SO_4)(Ph_3P)_3$; the infrared spectrum shows that the sulphato complex contains a chelated or bridging SO_4 group. The monomeric complexes $[Pt(Ph_3P)_2L]$ (L = CS_2, COS) (CXXVII) have been obtained from the reaction of $Pt(Ph_3P)_3$ with CS_2 and COS.

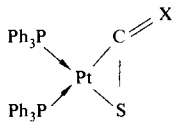
The complexes $Pt(Ph_3P)_n$ (n = 3, 4) react with HCl to give $[HPt(Ph_3P)_3]Cl$, $[HPtCl(Ph_3P)_2]$ and $[H_2PtCl_2(Ph_3P)_2]$, with HCN to give $[HPt(CN)(Ph_3P)_2]$, and with

[612] J. Chatt and G. A. Rowe, *Nature* **191** (1961) 1191.

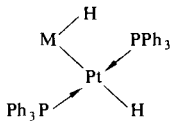
[613] R. Ugo, F. Cariati and G. La Monica, *Chem. Communs.* 1966, 868; R. D. Gillard, R. Ugo, F. Cariati, S. Cenini, and F. Bonati, *ibid.*, p. 869; R. Ugo and S. Cenini, *New Aspects of the Chemistry of Metal Carbonyls, Inorg. Chim. Acta* (1968), p. D9.

[614] T. Kruck and K. Baur, *Angew. Chem.* 77 (1965) 505.

acids to give $[HPt(Ph_3P)_3]X$ (X = HSO_4, ClO_4, BF_4, $MeOSO_3$). The chalcogen hydrides H_2S and H_2Se react with $Pt(Ph_3P)_3$ and $Pt(Ph_3P)_2$ to yield the monomeric complexes $Pt(Ph_3P)_2MH_2$ (CXXVIII; M = S, Se), which are air-stable and display ν(Pt–H) at 2116–2140 cm^{-1}. Thiophenol yields the analogous compound $[HPt(Ph_3P)_2(PhS)]$.



(CXXVII; X = O, S)



(CXXVIII)

Sulphonyl and acyl halides react with Pt(0) phosphine complexes to give *S*-sulphinate and acyl derivatives which, when heated, lose SO_2 and CO to give alkyl and aryl Pt(II) complexes[615].

Carbonyl Complexes

The platinum analogue of $Ni(CO)_4$ is unknown, but an ill-defined polymeric dicarbonyl $[Pt(CO)_2]_n$ has been reported. The complexes $Pt(CO)(R_3P)_3$ and $Pt(CO)_2(R_3P)_2$ (R = aryl) can be obtained by the reaction of $Pt(R_3P)_4$ with CO under pressure. The dimeric carbonyl $[Pt(CO)(Ph_3P)_2]_2$ can be obtained by the prolonged passage of CO through a solution of $Pt(Ph_3P)_4$ in hexane. The stable trinuclear carbonyls $Pt_3(CO)_3(R_3P)_4$, $Pt_3(CO)_4(R_3P)_3$ and $Pt_3(CO)_3(R_3P)_3$ (R_3 = Ph_3, Ph_2Me or Ph_2Bz) have been prepared by the reaction of CO on a solution of R_3P, Na_2PtCl_4, N_2H_4 and KOH in hot 90% ethanol. They are, no doubt, cluster compounds[162].

In $Pt(CO)(Ph_3P)_3$ the metal atom has a distorted tetrahedral coordination; the mean Pt–P distance is 2.35 Å, cf. 2.26 Å in $Pt(Ph_3P)_3$ [616].

Acetylide Complexes

The complexes $K_2[Pt(CN)_2(C{\equiv}CR)_2]$ can be reduced by potassium in liquid ammonia to give the pyrophoric Pt(0) complexes $K_2[Pt(C{\equiv}CR)_2]$ [435].

Olefin Complexes

The cycloocta-1,5-diene complex $Pt(C_8H_8)Cl_2$ reacts with Pr^iMgBr to yield $PtPr^i_2(C_8H_8)$ which upon irradiation with ultraviolet light yields the Pt(0) complex $Pt(C_8H_8)_2$ [617].

The complexes Pt(ol)$(Ph_3P)_2$ (ol = stilbene, *trans*-4,4-dinitrostilbene, acenaphthylene, tetracyanoethylene) can be obtained by reduction of *cis*-$[PtCl_2(Ph_3P)_2]$ with hydrazine in the presence of the olefin in ethanol at 60° [618].

615 C. D. Cook and G. S. Jauhal, *Can. J. Chem.* **45** (1967) 301.

616 V. Albano, P. L. Bellon and V. Scatturin, *New Aspects of the Chemistry of Metal Carbonyls, Inorg. Chim. Acta* (1968), p. B6.

617 J. Muller and P. Göser, *Angew. Chem.*, Int. Edn., **6** (1967) 364.

618 J. Chatt, B. L. Shaw and A. A. Williams, *J. Chem. Soc.* 1962, 3269; S. Cenini, R. Ugo, F. Bonati and G. La Monica, *Inorg. Nucl. Chem. Letters* **3** (1967) 191.

7.4. COMPLEX OF PLATINUM(I)

It is doubtful if Pt(I) exists in simple or complex compounds. However, the red dimeric cyclopentadienyl complex $[(C_5H_5)Pt(CO)]_2$ has been reported[619]. Its diamagnetism suggests that the compound does not contain Pt(I).

7.5. COMPLEXES OF PLATINUM(II)

Bivalent platinum has the d^8 configuration and all the complexes are diamagnetic. In this oxidation state there is a close resemblance to palladium and the great majority of Pt(II) complexes are square-planar, but there are a few examples of tetragonal (6-coordinate) complexes, and, where the conformation of the ligand requires it, of square-pyramidal and trigonal bipyramidal coordination. Complexes of Pt(II) are more kinetically inert than those of Pd(II), and, as a consequence, many more examples of *cis–trans* isomerism are known. Pt(II) complexes, like those of other d^8 metals Rh(I), Ir(I) and Pd(II), undergo oxidative addition reactions and molecules such as Cl_2, HCl or MeI can add across the plane; furthermore, Pt(II) complexes can be oxidized to Pt(IV) complexes with retention of configuration (*cis* or *trans*).

The aqua ion $[Pt(H_2O)_4]^{2+}$ does not appear to be formed.

Halide, Thiocyanate and Cyanide Complexes

The complexes $[PtX_4]^{2-}$ (X = Cl, Br, I, SCN, SeCN, CN) are known but not the corresponding fluoro-complex. The colours are: chloro, pinkish red; bromo, reddish brown; iodo, yellowish brown; thiocyanato and the selenocyanato, carmine; cyano, colourless. The potassium salts are well known and readily prepared, but salts of NH_4, Na, Rb, Cs, Ca, Sr and Ba can also be prepared. The halogen-bridged anionic complexes $[Pt_2X_6]^{2-}$ (X = Br, I) have been obtained as $[NR_4]^+$ salts, and an X-ray crystal analysis of $[NEt_4]_2[Pt_2Br_6]$ shows that the $[Pt_2Br_6]^{2-}$ ion is planar; both bridging and terminal Pt–Br bond-lengths are within the range 2.41–2.45 Å [458]. The halogen bridges are split by unidentate ligands in acetone solution to yield $[NEt_4][PtX_3L]$ (L = NH_3, amine, $AsMePh_2$, Et_2S) [461]. The absorption spectrum of $[PtCl_4]^{2-}$, in contrast to that of $[PdCl_4]^{2-}$, is the same in 1 M $HClO_4$ and in 10 M HCl, indicating that no higher chloro-species are formed in solution[445].

The electronic spectra of $[PtX_4]^{2-}$ and other square-planar $[MX_4]^{n-}$ ions have been discussed[277, 459]; a summary of the essential features has been given (see p. 1285). The $[PtCl_4]^{2-}$ ion displays three spin-allowed transitions: 20,600 ($^1A_{1g} \rightarrow {}^1A_{2g}$), 25,600 ($^1A_{1g} \rightarrow {}^1B_{1g}$) and 29,800 cm^{-1} ($^1A_{1g} \rightarrow {}^1E_g$). Only the band at 25,600 cm^{-1}, which is z polarized, exhibits any detectable circular dichroism; this suggests that the dissymmetrical influences of the solvent are concentrated and directed at the tetragonal positions ($+z$, $-z$) and that solvent coordination must be extremely small[620]. Two charge-transfer bands are observed at 37,900 and 46,000 cm^{-1}; these move to higher energy in the sequence Br < Cl and are L → M transitions, involving excitation of a π lone pair from the halogen to the $d_{x^2-y^2}$ orbital on the metal[277].

[619] E. O. Fischer, H. Schuster-Woldan and K. Bittler, *Z. Naturforsch.* **18b** (1963) 429.
[620] B. Bosnich, *J. Am. Chem. Soc.* **88** (1966) 2606.

The Pt–Pt distance in K_2PtCl_4 is 4.13 Å and in $[NEt_4]_2[Pd_2Br_6]$ it is ~6 Å. The admixture of solutions of colourless $[Pt(NH_3)_4]Cl_2$ and red K_2PtCl_4 results in the precipitation of the sparingly soluble Magnus's green salt $[Pt(NH_3)_4][PtCl_4]$ which has a tetragonal structure consisting of alternate square-planar $[Pt(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$ ions stacked above each other with a Pt–Pt distance of 3.25 Å. Other salts of the type $[ML_4][M'X_4]$ (M = Cu, Pd, Pt; M' = Pd, Pt; X = Cl, Br, SCN; L = NH_3, $MeNH_2$) are isostructural with Magnus's green salt with M–M distances of 3.23–3.35 Å. Only when both M and M' are platinum are the compounds green. Marked dichroism along the direction of the metal chains suggests some metal–metal interaction[447, 449, 621].

A regular square-planar $[MX_4]^{n-}$ ion has seven fundamental vibrations of which only ν_2, ν_6 and ν_7 are infrared active. For K_2PtCl_4 the following bands have been assigned: ν_1 335, ν_2 164, ν_3 160, ν_4 304, ν_6 316, ν_7 185 cm^{-1}. For K_2PdBr_4 only the infrared-active bands have been measured; these are: ν_2 80, ν_6 233, ν_7 135 cm^{-1} [106, 622].

The stability constant (log β_4) for $[PtCl_4]^{2-}$ is 16 and for $[PtBr_4]^{2-}$ is ~20 [460].

The $[Pt(CN)_4]^{2-}$ ion is colourless in solution and in the sodium, potassium and rubidium salts but many of the hydrated salts are coloured: Li,$4H_2O$ green; Ba,$4H_2O$, Sr,$5H_2O$, Ca,$5H_2O$, yellow; Mg,$7H_2O$, red; Sc,$21H_2O$ red. The barium, strontium, calcium and magnesium complexes have short Pt–Pt distances of 3.13–3.23 Å, whereas the Pt–Pt distance in the colourless $Na_2[Pt(CN)_4]\cdot 3H_2O$ is 3.7 Å [447]. The $[Pt(CN)_4]^{2-}$ salts of alkali and alkaline earth metals are quite soluble in water, whereas the salts of transition metals are insoluble due to N → M bonds[623].

The free acid can be obtained by extraction of a concentrated aqueous solution with ether followed by concentration of the ethereal solution; it is obtained as red crystals of the pentahydrate $H_2Pt(CN)_4\cdot 5H_2O$. An infrared study of the anhydrous acids reveals that symmetrical N–H–N bonds are present in $H_2Pd(CN)_4$ and $H_2Pt(CN)_4$ [117]. The stability constant for $[Pt(CN)_4]^{2-}$ (log β_4) is 41. The electronic spectral bands for $[Pt(CN)_4]^{2-}$ are given in Table 39 (p. 1287).

Platinum(II) cyanide $Pt(CN)_2$ can be prepared by heating $(NH_4)_2[Pt(CN)_4]\cdot 2H_2O$; ν(C–N) occurs at 2153 and 2210 cm^{-1}, showing that some bridging CN groups are present. The compound reacts with neutral ligands to give *cis*-$[Pt(CN)_2L_2]$ (L = NH_3, py, $CS(NH_2)_2$; 2L = en).

Complexes of Oxygen Ligands

Bivalent platinum has an even lower affinity for oxygen ligands than has Pd(II), but chelate complexes with oxalate ion and acetylacetone are quite stable.

Cis- and *trans*-$[Pt(NH_3)_2(NO_3)_2]$ have been prepared by the action of $AgNO_3$ on solutions of *cis*- and *trans*-$[Pt(NH_3)_2I_2]$ [5]. The passage of NO_2, SO_2 or CO_2 into a solution of $Pt(Ph_3P)_2O_2$ results in the formation of the nitrato, sulphato and carbonato complexes, *cis*-$[Pt(Ph_3P)_2(NO_3)_2]$, $[Pt(Ph_3P)_2(SO_4)]$ and $[Pt(Ph_3P)_2(CO_3)]$. The nitrato-complex liberates NO_3^- ion in boiling water. The sulphato-complex can also be obtained by oxidation of $Pt(Ph_3P)_3(SO_2)$. The infrared spectra indicate that the sulphato and carbonato

[621] J. R. Miller, *J. Chem. Soc.* (1965) 713.

[622] R. J. H. Clark, *Halogen Chemistry* (V. Gutmann, ed.), Academic Press, New York (1967), Vol. 3, p. 85.

[623] I. B. Baranovskii and Yu. Ya. Kharitonov, *Doklady Akad. Nauk SSSR* **169** (1966) 1335; *Zh. Neorg. Khim.* **11** (1966) 1732; Yu. Ya. Kharitonov, O. N. Evstaf'eva, I. B. Baranovskii, G. Ya. Mazo and A. V. Babaeva, *ibid.*, p. 1733.

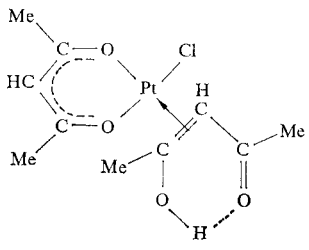
groups are chelated. The carbonato-complex reacts with HNO_3 to form *cis*-$[Pt(Ph_3P)_2(NO_3)_2]$. X-ray data on the carbonato-complex are: Pt–P 2.24, Pt–O 2.07, C–O 1.28 Å; P–Pt–P 98.2, O–Pt–P 98.8, O–Pt–O 64° [433].

Oxalic acid reacts with $K_2[Pt(NO_2)_4]$ to give the yellow $K_2[Pt(NO_2)_2(C_2O_4)]\cdot H_2O$; the Na,H_2O and $Ba,5H_2O$ salts are also known. With $[PtCl_4]^{2-}$ oxalate ion gives $[Pt(C_2O_4)_2]^{2-}$; several salts are known: $K,2H_2O$, red; $Na,4H_2O$, yellow and red forms; $Ca,8H_2O$, yellow, $5H_2O$, red[604].

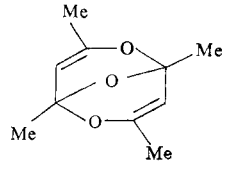
Metal complexes of acetylacetone were first reported in 1901 by Werner who prepared the Pt(II) complexes: $Pt(acac)_2$, yellow and soluble in benzene, $K[PtCl_2acac]$ (orange yellow), $K[PtCl(acac)_2]$ (pale yellow) and $Na_2[PtCl_2(acac)_2]\cdot 5H_2O$ (deep yellow). Recent infrared and n.m.r. studies on these and other β-diketone complexes have established that in all these complexes the platinum atom is 4-coordinate. The ligand can be bound in several ways: (i) chelated through both oxygen atoms as in $Pt(acac)_2$ and $K[PtCl_2acac]$; (ii) σ-bonded through the α-carbon atom as in $Na_2[PtCl_2(acac)_2]$; (iii) π-bonded through the protonated enol form; (iv) π-bonded as a bicyclic dienyl ring[624].

In the green tris-ligand complex $K[Pt(acac)_3]$ and in $K[Pt(diketone)_2X]$ (diketone = acac, trifluoroacetylacetone, benzoylacetone; X = Cl, Br) both *O*- and *C*-bonded β-diketone groups are present. In the complexes $M[Pt(acac)_2X]_2$ (M = bivalent transition metal) M is octahedrally coordinated via the oxygen atoms of the *C*-bonded ligand, which behaves as a terdentate, and an X atom. The action of strong acids on $K[Pt(acac)_2Cl]$ gives the yellow complex $Pt(acac)(acacH)Cl$ (CXXIX), which is slowly converted in benzene to the chloro-bridged dimer $[Pt(acac)Cl]_2$. The action of HCl on $K[Pt(acac)_3]$ yields the complex $Pt(C_{10}H_{14}O_3)Cl_2$ which contains the bicyclic dienyl ring (CXXX). The pyridine adduct $Pt(acac)_2py_2$ contains two *C*-bonded ligands.

Cacodyl oxide, $Me_2AsOAsMe_2$, forms the complexes $PtX_2(Me_2AsOAsMe_2)(H_2O)$ (X = Cl, Br, I) which can be dehydrated at 150°. The anhydrous iodo-complex is dimeric



(CXXIX)



(CXXX)

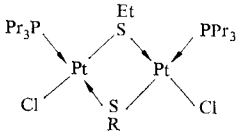
and probably iodo-bridged[604]. A large number of Pt(II) complexes of pyridine *N*-oxide of the type $PtCl_2(pyO)L$ (pyO = 4-substituted pyridine *N*-oxide; L = olefin, alkyne or CO) [625].

Complexes of Sulphur, Selenium and Tellurium Ligands

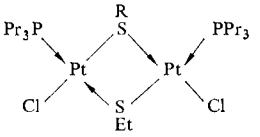
Complexes are formed by Pt(II) with a wide range of sulphur ligands. They closely resemble those of Pd(II) and many are extremely stable.

[624] D. Gibson, J. Lewis and C. Oldham, *J. Chem. Soc.* A, 1967, 72.
[625] M. Orchin and P. J. Schmidt, *Coord. Chem. Rev.* 3 (1968) 345.

Thiolo complexes. Whereas halogen-bridged Pt(II) complexes are readily split by unidentate ligands, alkylthio-bridged complexes are not. *Cis-* and *trans*-isomers of $[Pt(Pr^n_3P)(EtS)X]_2$ (X = Cl, EtS) have been prepared. Another type of isomerism occurs in alkylthio Pt(II) complexes containing two different thiols; the isomers have structures (CXXXI) and (CXXXII) [209]. Pentafluorophenyl mercaptan forms the yellow polymeric complex $Pt(SC_6F_5)_2$ and the orange anionic species $[Pt(SC_6F_5)_4]^{2-}$ [507].



(CXXXI)



(CXXXII)

Sulphito complex. Complexes of the type $M_6[Pt(SO_3)_4]$ have been prepared; the SO_3 group is unidentate and *S*-bonded[209].

Thiosulphato complexes. In the complexes $[Pt(S_2O_3)_2]^{2-}$, $[Pt(S_2O_3)Cl_2]^{2-}$ and $[Pt(NH_3)_2(S_2O_3)]$ the thiosulphato group is almost certainly chelated with the ligand bound through one sulphur and one oxygen atom. The complexes $[Pt(S_2O_3)_3]^{4-}$ and $[Pt(S_2O_3)_4]^{6-}$ are also known. The group *trans* to $S_2Os_3^{2-}$ is labilized in the same way as in thiourea complexes of Pt(II), indicating that the ligand is bound through sulphur[209].

Complexes of organic sulphides, selenides and tellurides. These compounds are listed in Table 50. Sulphide and selenide complexes are known with 4, 2 and 1 molecules of a unidentate ligand and with 2 and 1 molecules of a bidentate. Halogen-bridged complexes $[Pt(MR_2)Cl_2]_2$ (M = S, Se, Te) are also known. Dimethyl sulphide forms three isomeric compounds of general formula $Pt(SMe_2)_2Cl_2$. The γ-isomer is $[Pt(SMe)_4][PtCl_4]$. The complexes $Pt(SR_2)_2Cl_2$ (R = Et, Pr^n, Bu^n) were among the first metal complexes to be investigated by dipole moment measurements. The α-isomers (*trans*) have moments of approximately 2.4*D*, while the β-isomers (*cis*) have moments in the range 9.0–9.5*D*. The *trans* structure was confirmed by an X-ray investigation. *Cis–trans* isomerism has been observed with the selenoether complexes. The telluroether complexes are much less stable and the few complexes which have been prepared are known in only one isomeric form. The dipole moment of $[Pt(TeEt_2)_2Cl_2]$ is 6*D*, hence the complex has a *cis* configuration; the complexes $[Pt(TeR_2)_2Cl_2]$ (R = Ph, Bz) are possibly *cis* also.

All the *trans* complexes are readily soluble in organic solvents; the *cis* compounds, including those with chelate ligands, are less soluble. A study of ν(N–H) of the series $[amPtLCl_2]$ (am = RNH_2 or R_2NH) shows the increasing inductive effect transmitted across the platinum atom from the ligand donor atom to the N–H bond when the ligands are arranged in the order: γ-picoline < piperidine < R_2S < R_2Se < R_2Te < R_3As < R_3P < R_3Sb < $P(OR)_3$ < C_2H_4[209].

Thiourea complexes. Thiourea and its mono-, di- and tri-*N*-alkylated derivatives form tetrakis-ligand complexes $[Ptthu_4]X_2$ (X = Cl, Br, I, NO_3, etc.) which are yellow to orange and bis-ligand complexes $[Ptthu_2Cl_2]$ which are orange or pink; infrared data show that the ligands are *S*-bonded. Thiourea has a marked *trans* effect [209, 626].

[626] *Gmelin's Handbuch der Anorganischen Chemie*, Verlag Chemie, Weinheim (1957), Vol. 68D.

TABLE 50. PLATINUM(II) COMPLEXES CONTAINING ORGANIC SULPHIDES, SELENIDES AND TELLURIDES

Compound		Colour
$[Pt(SR_2)_4]X_2$ [a]	(R = Me, Et, Pr^n, Bu^n; X = Cl, I, NO_3, picrate; 2X = SO_4, $PtCl_4$, $PtBr_4$, $PtCl_6$)	
$[Pt(RSCH_2CH_2SR)_2]X_2$ [a]	(R = Me, Et, Pr^n, Bu^n; X = Cl, NO_2; 2X = $PtCl_4$, $Pt(NO_2)_4$)	
$[Pt(RSCH_2CH_2CH_2SR)_2]X_2$ [a]	(R = Et, Pr^n, Am^i; X = Cl; 2X = $PtCl_4$)	
$[Pt(SeR_2)_4]X_2$ [a]	(R = Me, Et; X = Cl, NO_3; 2X = $PtCl_4$, SO_4)	
$[Pt(EtSeCH_2CH_2CH_2SeEt)_2]X_2$ [a]	(X = Cl, picrate; 2X = $PtCl_4$)	
cis-$[Pt(SR_2)_2Cl_2]$ [a]	(R = Me, Et, Pr^n, Bu^n, Bu^i, Ph, Bz)	Yellow or greenish yellow
trans-$[Pt(SR_2)_2Cl_2]$ [a]	(R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Am^n)	Deep yellow
cis-$[Pt(SR_2)_2Br_2]$ [a]	(R = Et, Bz)	Pale yellow
trans-$[Pt(SR_2)_2Br_2]$ [a]	(R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s)	Orange yellow to brownish yellow
$[Pt(SR_2)_2I_2]$ [a]	(R = Me, Et, Pr^n, Pr^i, Bu^i, Bu^s, Am^n, Bz)	Red to reddish brown
cis-$[Pt(SR_2)_2(NO_2)_2]$ [a]	(R = Et, Pr^n, Bu^i)	Colourless
trans-$[Pt(SR_2)_2(NO_2)_2]$ [a]	(R = Pr^n, Bu^n, Bu^i, Bz)	Colourless
cis-$[Pt(SR_2)_2(NO_3)_2]$ [a]	(R = Et, Pr^n, Bu^i)	Pale green
trans-$[Pt(SR_2)_2(NO_3)_2]$ [a]	(R = Pr^n, Bu^n, Bu^i)	Yellow
$[Pt(SR_2)_2SO_4]$ [a]	(R = Me, Et, Pr^n)	Yellow
$[Pt(SEt_2)_2(C_2O_4)]$ [a]		Colourless
cis-$[Pt(SR_2)_2(OH)_2]$ [a]	(R = Me, Et, Pr^n, Bu^i)	Pale yellow
$[Pt(SR_2)Cl_2]_2$ [b]	(R = Me, Et, Pr^n, Bu^n, n-octyl)	Bright yellow
$[Pt(SEt)I_2]_2$ [a]		Dark red
$[Pt(1,4\text{-dithian})X_2]_2$ [a]	(X = Cl, Br, I)	Yellow
$[Pt(EtSCH_2SEt)Cl_2]$ [a]		Deep yellow
$[Pt(RSCH_2CH_2SR)Cl_2]$ [a]	(R = Me, Et, Pr^n, Pr^i, Bu^n, Bz)	Yellow
$[Pt(RSCH_2CH_2CH_2SR)Cl_2]$ [a]	(R = Et, Pr^n)	Yellow
$[Pt(EtSCH_2CH_2SEt)Br_2]$ [a]		Yellow
$[Pt(RSCH_2CH_2SR)(NO_2)_2]$ [a]	(R = Me, Et, Pr^n, Bu^n)	Colourless
cis-$[Pt(SeR_2)_2Cl_2]$ [a]	(R = Me, Et, Am^i, Ph)	Deep yellow
trans-$[Pt(SeR_2)_2Cl_2]$ [a]	(R = Me, Et, Pr^n, Bu^i, Am^i)	Orange red
trans-$[Pt(SeR_2)_2Br_2]$ [a]	(R = Me, Et)	Red
trans-$[Pt(SeEt_2)_2I_2]$ [a]		Deep red
cis-$[Pt(SeEt_2)_2(NO_2)_2]$ [a]		Colourless
cis-$[Pt(SeEt_2)_2(NO_3)_2]$ [a]		Yellow
$[Pt(SeEt_2)_2(SCN)_2]$ [a]		Orange
$[Pt(SeEt_2)_2SO_4]$ [a]		Yellow brown
$[Pt(SeR_2)Cl_2]_2$ [b]	(R = Et, Pr^n)	Brownish orange
$[Pt(SeEt_2)Br_2]_2$ [b]		Dark red
$[Pt(Pr^iSeCH_2CH_2SePr^i)Cl_2]$ [c]		Yellow
$[Pt(EtSeCH_2CH_2CH_2SeEt)Cl_2]$ [a]		Deep yellow
$[Pt(Pr^iSeCH_2CH_2SePr^i)Br_2]$ [c]		Yellow
cis-$[Pt(TeR_2)_2Cl_2]$ [a]	(R = Et, Ph, Bz)	Yellow to orange
$[Pt(TeR_2)Cl_2]_2$ [b]	(R = Et, Pr^n)	Brownish orange
trans-$[Pt(am)(SR_2)Cl_2]$ [b]	(R = Et, Pr^n, Bu^n; am = piperidine, *p*-toluidine)	Orange
$[NEt_4][Pt(SEt_2)Br_3]$ [d]		Orange
$[NEt_4][Pt(SEt_2)I_3]$ [d]		Reddish brown
trans-[Pt(piperidine)$(SeEt_2)Cl_2$] [b]		Orange

[a] *Gmelin's Handbuch der Anorganischen Chemie*, Vol. 68D, Verlag Chemie, Weinheim (1957).
[b] J. Chatt, L. A. Duncanson and L. M. Venanzi, *J. Chem. Soc.* 1955, 2787, 3858.
[c] N. N. Greenwood and G. Hunter, *J. Chem. Soc.* A, 1967, 1520.
[d] S. E. Livingstone and A. Whitley, *Austral. J. Chem.* **15** (1962) 175.

Thioacetamide complexes. Thioacetamide ($MeCSNH_2$; thac) forms the yellow complexes $[Pt(thac)_2Cl_2]$ and $[Pt(thac)_4]Cl_2$ and $[Pt(thac)_4]SO_4$ in which the ligand is *S*-bonded[626].

Triphenylphosphine selenide complex. The light tan compound $[PtCl_2(Ph_3PSe)_2]$ is known; ν(P=Se) occurs at 540 cm^{-1} [469].

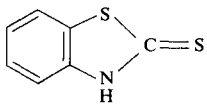
Complexes of chelate ligands with thioether or selenoether groups. Complexes containing two thioether or selenoether groups are listed in Table 50.

Thiosemicarbazide (XV; tscH) forms an inner complex *trans*-$[Pt(tsc)_2]$, the mono-ligand complex $[Pt(tscH)Cl_2]$ and the bis-ligand compounds *cis*-$[Pt(tscH)_2]Cl_2$, *trans*-$[Pt(tscH)_2]Cl_2$ and *cis*-$[Pt(tscH)_2]SO_4$ [472].

DL-Methionine (XVI), DL-ethionine (XVII) and *S*-methyl-L-cysteine (XVIII) form the complexes $PtX_2(LH)$ (X = Cl, Br) in which the amino-acid is coordinated through the nitrogen and sulphur atoms[473] (see p. 1292).

With 8-methylthioquinoline (XIX; mtq) the mono-ligand complexes $[PtX_2mtq]$ (X = Br, I, SCN) have been obtained. With 2-methyl-8-methylthioquinoline (XX; mmtq) the compounds $[PtX_2mmtq]$ (X = Cl, Br) were obtained but attempts to prepare the iodo and thiocyanato analogues were unsuccessful, presumably because molecular models show that one mmtq moiety and two I or SCN groups cannot coordinate in a square plane due to steric interaction[474, 475].

2-(2-Methylthioethyl)pyridine (XXI; mep) forms the mono-ligand compounds $[PtX_2mep]$ (X = Cl, Br, I, SCN) and the bis-ligand compound $[Pt(mep)_2](ClO_4)_2$. With the similar 2-methylthiomethylpyridine (XXII; mmp) $[Pt(SCN)_2mmp]$, $[Pt(mmp)_2](ClO_4)_2$ and $[Pt(mmp)_2]PtCl_4$ have been reported[476]. 2-Thiopicolinamide (XXII; thpic) forms the complexes $[PtX_2thpic]$ (X = Cl, Br, I, SCN, NO_2) and $[Pt(thpic)_2](ClO_4)_2$, in which coordination occurs through the sulphur and pyridine nitrogen atom[477]. 2-Thiobenzothiazole (tbt) exists entirely in the thioketo form (CXXXIII) and forms the complexes $[PtX_2(tbt)_2]$ (X = Cl, Br) and the Pt(IV) compound $[PtCl_4(tbt)_2]$; in these compounds the ligand is unidentate.



(CXXXIII)

o-Methylthioaniline (XXIV; N–SMe) yields the complexes $[PtX_2(N–SMe)]$ (X = Br, I, SCN) and $[Pt(N–SMe)_2]PtCl_4$. If the latter complex is heated in dimethylformamide, *S*-demethylation of the ligand occurs to yield the thiolo-bridged complex $[Pt(N–S)Cl]_2$ [474].

1,3-Di(phenylthio)propane and its selenium analogue form the complexes $[Pt(chel)X_2]$ and $Pt(chel)_2Y_2$ (chel = $PhSC_3H_6SPh$, $PhSeC_3H_6SePh$; X = Cl, Br; Y = NO_3, ClO_4). The complexes $Pt(chel)_2Y_2$ exhibit ion association in non-aqueous solvents and the conductance reaches a limiting value in the presence of excess ligand; this behaviour has been interpreted in terms of a coordination number greater than 4 for platinum and palladium. ν(Pt–S) occurs as two bands at 350 and 329 cm^{-1}, while ν(Pt–Se) occurs at 295 and 285 cm^{-1}. The larger difference between ν(M–S) and ν(M–Se) for platinum compared to palladium is considered to arise because platinum forms a weaker π-bond to selenium than to sulphur, while the reverse is true for palladium[481].

Dimethyl-*o*-methylthiophenylarsine (XXVIII; As–S) yields the complexes $[Pt(As–S)I_2]$, $[Pt(As–S)_2]Y$ ($Y = 2ClO_4$, $PtCl_4$, $PtBr_4$, $PtCl_6$, $PtBr_6$), $[Pt(As–S)_2X]X \cdot 2H_2O$ and $[Pt(As–S)_2X]ClO_4$ (X = Cl, Br, I) [628]. In the cations $[Pt(As–S)_2X]^+$ either the platinum atom has a coordination number greater than 4 or one (As–S) ligand is bound via the arsenic atom only. The first possibility seems the more likely, since with the aliphatic ligand dimethyl-3-methylthiopropylarsine (XIX) only the complexes $[Pt(As–S)I_2]$ and $[Pt(As–S)_2]Y$ ($Y = PtCl_4$, $PtBr_4$, $PtCl_6$, $PtBr_6$) were obtained[483]. The structures of some Pd(II) complexes of (XXVIII) have been determined by X-ray analysis (see p. 1295). *S*-Demethylation reactions of the Pt(II) chelates of (XXVIII) have been discussed (see p. 1295).

1,4-Di-(*o*-aminothiophenoxy)but-*trans*-2-ene (XXXVII; chel) forms the yellow insoluble binuclear complexes Pt_2X_4(chel) (X = Cl, Br, I, SCN); the structure of these complexes has been discussed (p. 1297).

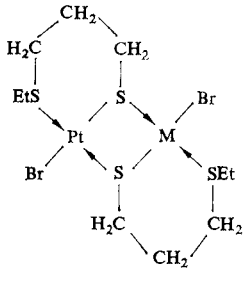
β-Aminodiethyl sulphide forms the yellow complex $[PtCl_2(EtSCH_2CH_2NH_2)]$. *β,β'*-Diaminodiethyl sulphide acts as a tridentate in the deep yellow complex $[PtCl\{S(CH_2CH_2NH_2)_2\}]Cl$ and as a bidentate in the buff complex

$$[PtCl_2\{S(CH_2CH_2NH_2)CH_2CH_2NH_3Cl\}]$$ [626].

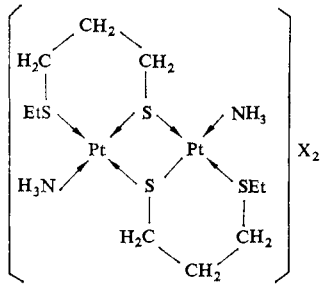
Thiodiglycolic acid, by loss of a proton from one of the carboxyl groups, acts as a chelate in the anionic complex $[Pt\{S(CH_2CO_2H)CH_2CO_2\}_2]^{2-}$ which has been isolated as the sodium, potassium, calcium, barium and silver salts. It also acts as a unidentate ligand in the complexes $[PtX_2\{S(CH_2CO_2H)_2\}]$ (X = Cl, Br, I). Similar complexes are known with *S*-ethylthioglycolic acid and *S*-ethylthiolactic acid[626].

Complexes of chelate ligands containing one thiol group. 8-Mercaptoquinoline (XLIII; N–SH) and its 5-chloro- and 5-bromo- derivatives form inner complexes with Pt(II); the complexes of the 5-chloro and 5-bromo- derivatives are more stable than $[Pt(S–N)_2]$. Surprisingly, the Pd(II) complex of 5-chloro-8-mercaptoquinoline is more stable than the Pt(II) complex[209]. The complexes PtX_2(N–SMe) (X = Cl, Br; N–SMe = 8-methylthioquinoline, XLIV), when heated in DMF, undergo *S*-demethylation to yield the insoluble thiolo-bridged complexes $[PdX(N–S)]_n$ [478]. 2,2'-Dimercaptodiethylsulphide forms a 1:1 complex with Pt(II); it is probably trimeric like the Pd(II) complex (XLVIII) [497].

o-Aminobenzenethiol (XLIX), *o*-methylthiobenzenethiol (L), 3-ethylthiopropane-1-thiol (LI) and 3-dimethylarsinopropane-1-thiol (LII) form stable inner complexes with



(CXXXIV)



(CXXXV)

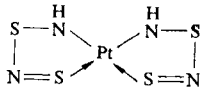
[627] R. F. Wilson and P. Merchant, *J. Inorg. Nucl. Chem.* **29** (1967) 1993.
[628] B. Chiswell and S. E. Livingstone, *J. Chem. Soc.* 1960, 1071.

Pt(II). Thiolo-bridged Pt(II) complexes have been obtained with (LI) and (LII). The former gives binuclear complexes (CXXIV; M = Pd, Hg; X = Cl, Br or I) containing another metal atom in addition to Pt, and the cationic binuclear complex (CXXXV; X = Cl, ClO_4) [480].

2-(2-Mercaptoethyl)pyridine (LVI; N–SH) forms the inner complex $[Pt(N–S)_2]$ and the thiolo-bridged species $[Pt(N–S)Cl]_2$ [499]. Although no complex of the type $[Pt(N–S)_2]$ could be isolated with 2-aminoethanethiol, the trinuclear cationic species $[PtNi_2(N–S)_2]^{2+}$, similar to (LV), was obtained[498].

Square-planar Pt(II) complexes have been obtained with P–S ligands of general formula $R_{3-x}P(CH_2CH_2SH)_x$ (R = H, Et, Ph; x = 1, 2, 3) [490].

The thionitrosyl complex $Pt(S_2N_2H)_2$ has the *cis*-planar configuration (CXXXVI), whereas the Ni(II) complex of the *N*-methyl derivative, viz. $Ni(S_2N_2Me)_2$, is *trans*-planar[209].



(CXXXVI)

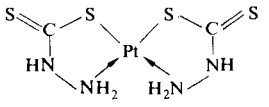
Complexes of xanthates, diethyldithiophosphate, dithiocarbonate and trithiocarbonate. Ethyl xanthate forms an orange–yellow complex $[Pt(EtOCS_2)_2]$ which is sparingly soluble in organic solvents[626]. This complex forms a 1:1 adduct with $MePh_2P$; with excess of phosphine in $CHCl_3$ solution the colourless bisphosphine-dithiocarbonato complex $[(MePh_2P)_2Pt(S_2CO)]$ is produced. A similar Pd(II) complex has been isolated; it is yellow[500, 629].

The square-planar trithiocarbonato complexes $[Pt(CS_3)_2]^{2-}$ (yellowish orange) and $[Pd(CS_3)_2]^{2-}$ (brownish red) have been obtained as their $[Ph_4As]^+$ and $[Ph_3BzP]^+$ salts; they react with Ph_3P in DMF to give the yellow $[M(Ph_3P)_2CS_3]$ (M = Pt, Pd) [500, 629].

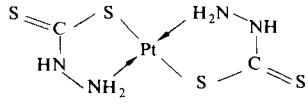
The yellow diethyldithiophosphato complex $[Pt\{S_2P(OEt)_2\}_2]$ can be obtained by reacting K_2PtCl_4 with P_4S_{10} in ethanol; it is moderately soluble in organic solvents[502].

Dithiobenzoic acid and dithiophenylacetic acid give the dark green $[Pt(PhCS_2)_2]$ and the greenish-blue $[Pt(PhCH_2CS_2)_2]$ [503].

The Pt(II) complex of hydrazinedithiocarbamate, $H_2NNHC(S)SH$, has been reported as an orange–yellow *cis* and a bright yellow *trans* form with structures (CXXXVII) and (CXXXVIII) [626]. The existence of two isomers is doubtful, since it is more likley that the complex has the structure (CXXXIX).

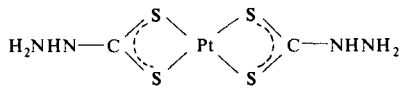


(CXXXVII)



(CXXXVIII)

[629] J. P. Fackler and W. C. Seidel, *Inorg. Chem.* **8** (1969) 1631; J. P. Fackler and D. Coucouvanis, *J. Am. Chem. Soc.* **88** (1966) 3913.



(CXXXIX)

Complexes of thio-derivatives of β-diketones. The Pt(II) complexes of monothio-β-diketones are listed in Table 51 [290, 504]. The electronic spectra of the complexes PtL_2 have been discussed (see p. 1302). The complex $[Pt(PhCS{=}CHCOPh)_2]$ is isomorphous with the corresponding Pd(II) complex which has a *cis*-configuration[505].

TABLE 51. PLATINUM(II) CHELATES OF MONOTHIO-β-DIKETONES [290, 504]

L, RC(S)=CHCOR′

R	R′	Compound	Colour	M.p. (°)
Me	CF_3	PtL_2	Red	144
2-thienyl	CF_3	PtL_2	Brown	218
Ph	CF_3	PtL_2	Red	208
Ph	Ph	PtL_2	Dark red	235
2-thienyl	CF_3	PtL_2phen	Red	> 300
Ph	CF_3	PtL_2phen	Yellow	216 d
Ph	CF_3	PtL_2bipy	Orange	218 d
Ph	CF_3	$PtL_2(Ph_3P)_2$	Yellow	240 d

d, with decomposition.

Adducts have been obtained with 1,10-phenanthroline, 2,2′-bipyridyl and triphenylphosphine (see Table 51). The high frequency of ν(C=O)—1670–1620 cm^{-1}—indicates that the monothio-β-diketone is bound by the sulphur atom only and accordingly it would appear that the platinum atom is 4-coordinate in these adducts[504].

The purple complex of dithioacetylacetone, viz. $[Pt(MeCS{=}CHCSMe)_2]$, like the Pt(II) complexes of monothio-β-diketones, is more deeply coloured than its Pd(II) analogue[508] (see p. 1302).

Dithiotropolone (LXVII) forms a black complex $[Pt(C_7H_5S_2)_2]$ which is considered to possess a delocalized electronic structure similar to that shown for the Pd(II) complex (LXVIII) [510].

Complexes of α-dithiols. The dithio-oxalato complex $K_2[Pt(C_2O_2S_2)_2]$ is known[209]. 2,3-Quinoxalinedithiol forms the blue neutral complex $[Pt(C_6H_4N_2C_2S_2H)_2]$ and the red anionic species $[Pt(C_6H_4N_2C_2S_2)_2]^{2-}$ [507].

1,2-Dithiolene complexes of Pt(II) are listed in Table 52. The compounds $[Pt(S_2C_2R_2)_2]^{z-}$ are square-planar with the structure (LXX). Although the complexes $[Pt(S_2C_2R_2)_2]^{-}$ have magnetic moments corresponding to a value of $S = \frac{1}{2}$, the unpaired electron is considered to be delocalized on the ligands and the oxidation state of the platinum atom in all the complexes $[Pt(S_2C_2R_2)_2]^{z-}$ ($z = 0, 1, 2$) can be regarded as 2. The Pt–S stretching frequencies for some dithiolate complexes are given in Table 53. The perturbed ν(C=C) mode occurs

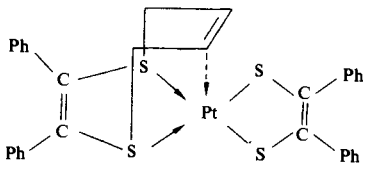
TABLE 52. 1,2-DITHIOLATE COMPLEXES OF PLATINUM

Compound	Colour	M.p. (°)	μ (BM)
$[NBu_4]_2[Pt\{S_2C_2(CN)_2\}_2]$	Red	164–167	diam.
$[NEt_4][Pt\{S_2C_2(CN)_2\}_2]$	Black	288 d	1.05
$[Ph_4As]_2[Pt\{S_2C_2(CF_3)_2\}_2]$	Golden yellow	240–242	diam.
$[Ph_4As][Pt\{S_2C_2(CF_3)_2\}_2]$	Red	169	1.73
$[Ph_4P][Pt\{S_2C_2(CF_3)_2\}_2]$	Red	174–175	1.79
$[Pt\{S_2C_2(CF_3)_2\}_2]$	Purple	174–175	diam.
$[Ph_4As]_2[Pt(S_2C_6H_3Me)_2]$	Orange		diam.
$[NBu_4][Pt(S_2C_6H_3Me)_2]$	Greenish brown	160–161	1.77
$[Pt(S_2C_2Ph_2)_2]$	Red	310	diam.
$[Pt\{S_2C_2(p\text{-}ClC_6H_4)_2\}_2]$	Red	340	diam.
$[Pt\{S_2C_2(p\text{-}MeOC_6H_4)_2\}_2]$	Red	341	diam.
$[Pt(S_2C_2MePh)_2]$	Red	350	diam.
$[Pt(S_2C_2Me_2)_2]$		360 d	diam.
$[Pt\{S_2C_2(CN)_2\}_2(Ph_3P)_2]$	Yellow		diam.
$[Pt\{S_2C_2(CF_3)_2\}_2(Ph_3P)_2]$	Lemon yellow		diam.
$[Pt(S_2C_2Ph_2)_2(Ph_3P)_2]$	Yellow		diam.
$[Pt(S_2C_2Ph_2)_2(Ph_2PCH_2CH_2PPh_2]$	Blue		diam.

in the range 1324–1515 cm^{-1}. The electronic spectra of some of the complexes have been measured and assignments have been made: e.g. the observed bands and assignments for $[Pt\{S_2C_2(CN)_2\}_2]^{2-}$ are:

14,410 cm^{-1}	(ε, 49)	$d \rightarrow d$
15,650	(56)	$d \rightarrow d$
18,500	(1220)	$d \rightarrow d$
21,100	(3470)	$Pt \rightarrow L_\pi$
29,700	(15,600)	$L_\pi \rightarrow L_\pi^*$

Several phosphine adducts of the type $[Pt(S_2C_2R_2)_2(R_3P)_2]$ have been reported (see Table 52). They can be obtained by treating $[PtCl_2(R_3P)_2]$ with the dithiol or by direct reaction of R_3P with $[Pt(S_2C_2R_2)_2]$. The infrared and electronic spectra indicate that the adducts contain "dithiolate" ligands. 2,3-Dimethyl-1,3-butadiene forms an adduct with $[Pt(S_2C_2Ph_2)_2]$; it is considered to possess the structure (CXL).



(CXL)

The e.s.r. spectra and polarographic behaviour of 1,2-dithiolene complexes have been studied and the extensive work on these compounds has been recently reviewed[513, 514].

TABLE 53. M–S, M–Se AND M–Te STRETCHING FREQUENCIES IN Pt(II) AND Pd(II) COMPLEXES

Compound	Bands (cm^{-1})	Assignment	Reference
$K_2[Pt(SCN)_4]$	293, 283	ν(Pt–S)	106
$K_2[Pd(SCN)_4]$	300, 286	ν(Pd–S)	106
$[PtCl_2(PhSCH_2CH_2CH_2SPh)]$	350, 329	ν(Pt–S)	481
$[PtBr_2(PhSCH_2CH_2CH_2SPh)]$	349, 324	ν(Pt–S)	481
$[PdCl_2(PhSCH_2CH_2SPh)]$	331, 312	ν(Pd–S)	481
$[PdCl_2(PhSCH_2CH_2CH_2SPh)]$	323, 308	ν(Pd–S)	481
$[PdBr_2(PhSCH_2CH_2CH_2SPh)]$	316	ν(Pd–S)	481
$K_2[Pt(S_2C_2O_2)_2]$	322	ν(Pt–S)	106
$[Pt(S_2CNH_2)_2]$	375	ν(Pt–S)	106
$[Pt(S_2COMe)_2]$	362, 330	ν(Pt–S)	106
$[Pt(S_2COEt)_2]$	338, 312	ν(Pt–S)	106
$[Pd(S_2COMe)_2]$	347, 335	ν(Pd–S)	106
$[Pd(S_2COEt)_2]$	340, 323	ν(Pd–S)	106
$[Pd\{S_2P(OEt)_2\}_2]$	317	ν(Pd–S)	501
$[Pt(PhCS{=}CHCOPh)_2]$	399	ν(Pt–S)	290
$[Pd(PhCS{=}CHCOPh)_2]$	393	ν(Pd–S)	290
$[PtCl_2(ethH)]$	381	ν(Pt–S)	473
$[PtBr_2(ethH)]$	378	ν(Pt–S)	473
$[PdCl_2(ethH)]$	380	ν(Pd–S)	473
$[PdBr_2(ethH)]$	378	ν(Pd–S)	473
$[PtCl_2(SmcH)]$	388	ν(Pt–S)	473
$[PdCl_2(SmcH)]$	385	ν(Pd–S)	473
$[Pt(S_2C_2Me_2)_2]$	405	ν(Pt–S)	106
$[Pt(S_2C_2Ph_2)_2]$	403, 373	ν(Pt–S)	106
$[Pd(S_2C_2Ph_2)_2]$	401, 352	ν(Pd–S)	106
trans-$[PtCl_2(SMe_2)_2]$*	346	ν(Pt–S)	630
trans-$[PtBr_2(SMe_2)_2]$*	344	ν(Pt–S)	630
cis-$[PtCl_2(SMe_2)_2]$*	320, 310	ν(Pt–S)	630
cis-$[PtBr_2(SMe_2)_2]$*	317, 305	ν(Pt–S)	630
trans-$[PdCl_2(SMe_2)_2]$*	322	ν(Pd–S)	630
trans-$[PdBr_2(SMe_2)_2]$*	313	ν(Pd–S)	630
$[NMe_4]_2[Pd(SeCN)_4]$	240	ν(Pt–Se)	106
$[PtCl_2(PhSeCH_2CH_2CH_2SePh)]$	294, 285	ν(Pt–Se)	481
$[PtBr_2(PhSeCH_2CH_2CH_2SePh)]$	296, 283	ν(Pt–Se)	481
$[PdCl_2(PhSeCH_2CH_2CH_2SePh)]$	314, 296	ν(Pd–Se)	481
$[PdBr_2(PhSeCH_2CH_2CH_2SePh)]$	315, 297	ν(Pd–Se)	481
trans-$[PtCl_2(SeMe_2)_2]$*	176	ν(Pt–Se)	630
trans-$[PtBr_2(SeMe_2)_2]$*	173	ν(Pt–Se)	630
trans-$[PtI_2(SeMe_2)_2]$*	172	ν(Pt–Se)	630
cis-$[PtCl_2(SeMe_2)_2]$*	193, 152 (?)	ν(Pt–Se)	630
$[PdCl_2(SeMe_2)]_2$ *	187, 156	ν(Pt–Se)	630
trans-$[PtCl_2(TeMe_2)_2]$*	169	ν(Pt–Te)	630
cis-$[PtCl_2(TeMe_2)_2]$*	187, 156	ν(Pt–Te)	630
$[PdCl_2(TeMe_2)]_2$ *	183	ν(Pd–Te)	630

* Raman spectra; ethH = DL-ethionine; SmcH = *S*-methyl-L-cysteine.

M–S, M–Se *and* M–Te *stretching frequencies.* Some stretching frequencies for M–S, M–Se and M–Te are listed in Table 53. The stretching frequencies ν(Pt–S) and ν(Pd–S) lie in the range 440–280 cm^{-1}; except for some α-dithiol complexes, ν(M–S) for Pd(II) and Pt(II)

lies below 400 cm^{-1}. In most cases two bands are observed; one of medium to strong intensity and a weaker band at a frequency 10–40 cm^{-1} lower than the stronger band. In chelate complexes coupling can occur with ring deformation modes and bands occur which can be attributed to ν(M–S)+ring deformation. In the spectrum of the dithiocarbamate complex $[Pt(S_2CNH_2)_2]$ the band at 375 cm^{-1} is due largely to ν(Pt–S), but two other bands—at 560 and 288 cm^{-1}—involve both Pt–S bond stretching and ring deformation.

Fewer data are available for ν(M–Se) and ν(M–Te). For chelate complexes ν(M–Se) lies in the range 315–283 cm^{-1}, but it lies below 200 cm^{-1} for $[MX_2(SeEt_2)_2]$. As would be expected, the frequencies fall in the order S > Se > Te.

Complexes of Nitrogen Ligands

The Pt–N bond is even stronger than the Pd–N bond; exchange studies show that there is rapid exchange between platinum and Br^- ions, but there is virtually no exchange with NH_3 groups. Ammine complexes are very numerous; they are known for all four types: $[Ptam_4]^{2+}$, $[Ptam_3X]^+$, $[Ptam_2X_2]$ and $[PtamX_3]^-$ (am = NH_3, amine). In addition there are a few binuclear complexes of the type $[PtamX_2]_2$.

Pt–N stretching frequencies. Bands arising from ν(Pt–N) are usually weak and there is uncertainty about some assignments. In $[PtenCl_2]$ ν(Pt–N) occurs at 570 cm^{-1} but in pyridine complexes it occurs below 300 cm^{-1}. Some Pt–N stretching frequencies are listed in Table 54.

TABLE 54. PLATINUM–NITROGEN STRETCHING FREQUENCIES (cm^{-1})

Compound	ν(Pt–N)	Compound	ν(Pt–N)
$K_2[Pt(NO_2)_4]$	377, 357	$[Pt(NH_3)_4]Cl_2$	510
$K_2[PtCl(NO_2)_3]$	370, 341	*cis*-$[Pt(NH_3)_2Cl_2]$	510
cis-$K_2[PtCl_2(NO_2)_2]$	369	*trans*-$[Pt(NH_3)_2Cl_2]$	510
$K_2[PtCl_3NO_2]$	375	$[PtenCl_2]$	570

Tetrammine-type complexes. The colourless tetrammine $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ was the first ammine complex to be prepared (by Magnus in 1828) and was one of the earliest compounds to be investigated by X-ray crystal analysis. The water is lost *in vacuo* at 100°. Salts of $[Pt(NH_3)_4]^{2+}$ can be obtained with virtually any anion and a large number have been characterized[5, 626]. The hydroxide $[Pt(NH_3)_4](OH)_2$ can be obtained by treating the sulphate with $Ba(OH)_2$ or the chloride with Ag_2O; it is a strong soluble base and readily takes up CO_2 to form the carbonate $[Pt(NH_3)_4]CO_3 \cdot H_2O$. The stability constant (log β_4) for $[Pt(NH_3)_4]^{2+}$ is 35.3 [460]. Magnus's green salt $[Pt(NH_3)_4][PtCl_4]$ is precipitated by the addition of $K_2[PtCl_4]$ to a solution of $[Pt(NH_3)_4]Cl_2$. The structure of this compound has been discussed (see p. 1339). It is also known in a pink form in which the Pt–Pt distance is not less than 5 Å, compared to 3.25 Å in the green salt[447].

Tetrammine-type complexes are known with methylamine, ethylamine, propylamine, hydrazine, hydroxylamine, pyridine and other amines. Chelate complexes $[Pt(chel)_2]X_2$

are known where chel = ethylenediamine, propylenediamine, 1,3-diaminopropane, isobutylenediamine, stilbenediamine, 2,3-toluenediamine, 1,2-diaminocyclohexane and 1,2-diaminocyclopentane. Of particular interest is the complex isobutylenediaminestilbenediamineplatinum(II) chloride which was resolved through its diacetyltartrate to give the optically active iodide. This optical resolution, carried out in 1935, gave final proof of the square-planar coordination of Pt(II), since in this complex if the coordination is planar, the structure is asymmetric and the compound should be optically active, but if the coordination is tetrahedral the structure has a plane of symmetry and the complex will be optically inactive[631].

Conductimetric titrations of the bipyridyl complex $[Pt(bipy)_2](ClO_4)_2$ with halide ions in nitrobenzene and nitromethane give one end-point, indicating the formation of $[Pt(bipy)_2X]^+$ which is stable in the presence of excess X^- ion (X = Cl, Br, I). Since there would be considerable steric interaction if two bipy ligands were arranged in planar coordination, the configuration must be appreciably distorted from square-planar. Some 6-coordinate complexes have been isolated. If the yellow $[Pt(bipy)_2](ClO_4)_2$ is treated with excess KI, the red $[Pt(bipy)_2I(H_2O)]I \cdot H_2O$ is obtained. This compound on exposure to air loses water and is converted to the black $[Pt(bipy)_2I_2]$ which is a non-electrolyte. *In vacuo* the black iodo complex loses bipyridyl and is converted to yellow $[Pt(bipy)I_2]$. The reddish-brown perchlorate $[Pt(bipy)_2I(H_2O)]ClO_4 \cdot H_2O$ was also isolated[446].

The phthalocyanine complex $[Pt(C_{32}H_{16}N_8)]$ has been prepared[604].

The deprotonated complexes [Pt(en–H)en]I, $[Pt(en–H)_2]$ and K[Pt(en–H)(en–2H)] have been obtained by the action of KNH_2 on $[Pten_2]I_2$ in liquid NH_3. The deprotonated ligand in [Pt(en–H)en]I is methylated with MeI under mild conditions. The acidity of coordinated ethylenediamine is markedly enhanced by the presence of bipyridyl, since $[Pt(bipy)en]^{2+}$ is deprotonated much more readily than $[Pten_2]I_2$ [516, 610]. The complex $[Pt(bipy)sdmen)]I_2$ (sdmen = *N*,*N*-dimethylethylenediamine) is deprotonated by KNH_2 in liquid ammonia to give [Pt(bipy)(sdmen–2H)] which reacts with MeCl to give $[Pt(bipy)(tetmen)]Cl_2$ (tetmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine[632].

The acetonitrile complex $[Pt(NH_3)_4(MeCN)_2]Cl_2 \cdot H_2O$, which had been reported earlier and considered to contain 6-coordinate Pt(II), has been shown to be a 4-coordinate derivative of acetamidine, viz. *trans*-$[Pt(NH_3)_2\{MeC(NH_2)=NH\}_2]Cl_2 \cdot H_2O$ [447].

Complexes are known with derivatives of biguanide, $H_2NC(=NH)NHC(=NH)NH_2$; these are $[PtL_2]X_2$ (L = morpholinebiguanide, *β*-phenylethylbiguanide and 1-(*p*-chlorophenyl)-5-isopropylbiguanide; X = Cl, Br or SCN) [633].

Schiff base complexes. Yellow *trans*-bis-ligand complexes of *N*-substituted salicylaldimines, $HOC_6H_4C=NR$, are known. The complex *trans*-$[Pt(OC_6H_4C=NH)_2]$ exists in two crystalline forms, neither isomorphous with the corresponding nickel and palladium compounds[634]. A trinuclear complex of *cis*-di(pyridine-2-aldoxime) containing one copper and two platinum atoms has been reported; it has the structure (LXXXI) [526].

Triammine-type complexes. A considerable number of triammine-type complexes is known. These include $[Pt(NH_3)_3X]^+$ (X = Cl, Br, NO_2, NO_3), $[Pt(NH_2OH)_3NO_2]_2PtCl_4$

[630] J. R. Allkins and P. J. Hendra, *J. Chem. Soc.* A, 1967, 1325; P. J. Hendra and P. M. Stratton, *Chem. Rev.* **69** (1969) 325.

[631] W. H. Mills and T. H. H. Quibell, *J. Chem. Soc.* 1935, 839.

[632] G. W. Watt and D. G. Upchurch, *J. Am. Chem. Soc.* **89** (1967) 177.

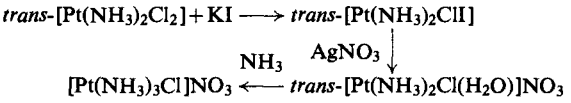
[633] P. Spacu, G. Gheorghiu and N. Vladescu, *Z. Chem.* **6** (1966) 188; *Rev. Roumaine Chem.* **12** (1967) 269.

[634] R. H. Holm, G. W. Everett and A. Chakravorty, *Prog. Inorg. Chem.* **7** (1966) 83.

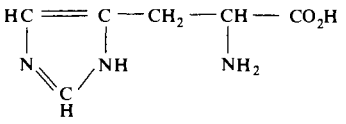
and [Pt(trident)X]$^+$ (trident = 1,2,3-triaminopropane, 2,2′-diaminodiethylamine, 2,2′,2″-terpyridyl; X = Cl, Br or I). There are also the mixed amine complexes [Pt$(NH_3)_2$amX]$^+$ (am = NH_2OH, $PhNH_2$, py, MeCN, EtCN) and [$PtNH_3$(bident)X]$^+$ (bident = en, bipy, 1,3-diaminopropane)[626].

Square-planar complexes [MABCX]$^+$ can exist in three isomeric forms: all three forms have been obtained for the species [Pt(NH_3)py$(NH_2OH)(NO_2)$]X (X = Cl or $\frac{1}{2}PtCl_4$) [626].

The triammine complexes [Pt$(NH_3)_3$X]$^+$ are known as Cleve's salts; they are usually prepared by the addition of NH_3 to the diammine or by the removal of NH_3 from the tetrammine, but in both cases the yields are low. Recently yields of 40% have been reported[635] from the method:

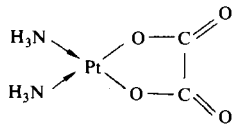


Histidine (CXLI; hist) forms [Pt$(hist)_2$]Cl_2 and a binuclear complex $Pt_2(hist)_3Cl_2 \cdot 2H_2O$, in which one histidine moiety acts as a bridge using an amine nitrogen and a nitrogen of the imidazole ring, while the other two histidine moieties act as bidentate ligands, being coordinated through the same two nitrogen atoms[636].

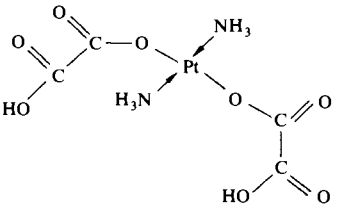


(CXLI)

Diammine-type complexes. These are very numerous. *Cis* and *trans* forms of the ammine complexes [Pt$(NH_3)_2X_2$] occur for X = OH, Cl, Br, I, SCN, CN, NO_2, NO_3 and picrate. *Cis* and *trans* forms of [Pt$(NH_3)_2$ClX] (X = OH, NO_2) are also known. The *cis* complexes [Pt$(NH_3)_2$Y] (Y = C_2O_4, SO_4) can be obtained. If *cis*-[Pt$(NH_3)_2Cl_2$] is treated with $AgNO_3$ followed by oxalic acid, the *cis*-oxalato complex (CXLII) is produced, but *trans*-[Pt$(NH_3)_2Cl_2$] under the same conditions yields the complex acid (CXLIII).



(CXLII)



(CXLIII)

[635] M. I. Gel'fman, *Doklady Akad. Nauk SSSR* **167** (1966) 819; Kh. I. Gil'dengershel, *Zh. Priklad. Khim.* **39** (1966) 223.

[636] L. M. Volshtein and I. G. Luk-yanova, *Zh. Neorg. Khim.* **11** (1966) 1327; D. D. Nelson and H. Frye, *Z. Naturforsch.* **21b** (1966) 630.

The nitrato- and sulphato-complexes react with water to give the colourless complexes $[Pt(NH_3)_2(H_2O)_2]^{2+}$ which are weak dibasic acids yielding $[Pt(NH_3)_2(OH)H_2O]^+$ and $[Pt(NH_3)_2(OH)_2]$; the *trans*-diaqua complex is a stronger acid than the *cis*.

Diammine-type complexes $[Ptam_2X_2]$ are known for a large number of amines and can be prepared with almost any amine and charged ligand X^-. The complexes are only sparingly soluble in water but will dissolve in an aqueous solution containing excess amine to give the tetrammine complexes $[Ptam_4]^{2+}$. Diamines, such as en, bipy, phen, etc., form the similar complexes $[Pt(diamine)X_2]$, which have the *cis*-configuration, since the chelate group must occupy two adjacent positions in the square-plane.

Monoammine-type complexes. Although by no means as numerous as the diammine-type complexes, more monoammine complexes are known for Pt(II) than for Pd(II). The anionic species $[PtamCl_3]^-$ are known where am = NH_3, NH_2OH, $EtNH_2$, py, MeCN and EtCN; they have usually been isolated as NH_4, K, Rb, Cs or pyH salts[626].

Dimeric bridged complexes $[PtNH_3X_2]_2$ are known where X = Cl, NO_2, SCN and CN. The di-μ-amido complex $[Pt(NH_2)(NH_3)Cl]_2$ can be prepared by treating *trans*-$[Pt(NH_3)_2Cl_2]$ with concentrated NaOH solution[626].

The N–H stretching frequencies of *trans*-$[LamPtCl_2]$ provide evidence for the interaction between the N–H bonds and the non-bonding *d*-electrons of platinum and for intermolecular hydrogen bonds[637].

Ligand displacement and the trans effect. A detailed discussion of ligand displacement reactions is outside the scope of this review, but since most of the studies of reactions of square-planar complexes have been concerned with Pt(II), a very brief summary will be given. The overall process is that a group X is replaced by a group Y. The group X is probably first displaced by H_2O which is the rate-determining step, followed by rapid displacement of H_2O by Y. Complexes of Pt(II) undergo ligand displacement reactions by an S_N2 mechanism and it is considered most likely that a 5-coordinate complex is formed in the transition state. The nucleophilic strength of the entering ligands (i.e. the ease with which Y replaces H_2O) is in the order:

$$F^- \sim H_2O \sim OH^- < Cl^- < Br^- \sim NH_3 \sim C_2H_4 < py < NO_2^- < N_3^- < I^- \sim SCN^- \sim R_3P$$

In the ligand displacement reactions:

$$[PtLX_3]^- + Y^- \rightarrow [PtLX_2Y]^- + X^-$$

and

$$[PtLL'X_2] + Y^- \rightarrow [PtLL'XY] + X^-$$

the entering group Y can occupy a position either *cis* or *trans* to L. Many of these reactions have been studied and ligands can be arranged in order of their increasing ability to cause displacement in the *trans* position. This is known as the *trans effect* and the (incomplete) order of ligands is:

$$H_2O < OH^- < NH_3 < Cl^- < Br^- < I^- \sim SCN^- < NO_2^- \sim R_3P < CO \sim C_2H_4 \sim CN^-.$$

The *trans* effect depends upon a number of factors including the permanent and induced dipole moment, the polarizability, the charge and the size of the ligand, and on the degree of π-bonding. The tendency of a ligand to accept d_π electrons from the non-bonding (d_{xz}, d_{yz}) orbitals of the metal atom lowers the electron density in the *trans* position and

[637] J. Chatt, L. A. Duncanson and L. M. Venanzi, *J. Chem. Soc.* 1958, 3203; L. A. Duncanson and L. M Venanzi, *ibid.* 1960, 3841.

also facilitates the approach of the incoming nucleophilic ligand. π-Bonding between M and L also stabilizes the 5-coordinate activated complex. Thus ligands capable of forming strong π-bonds exert a strong *trans* effect. However, strong σ-donor ligands, such as Me, Ph and H^-, produce a marked *trans* effect by polarization of the metal atom. The factors determining the magnitude of the *trans* effect are complex and the mechanistic role of the ligands *cis* to the leaving group in nucleophilic substitution has recently been examined[638].

From a study of ν(Pt–H) in the complexes $[HPtL(Et_3P)_2]$, the relative *trans* effect of L in these complexes is

$$NCO^- < Cl^- < N_3^- < SCN^- < CNO^- < CN^-$$ [639]

Evidence from n.m.r. spectra indicates that $SnCl_3^-$ is a weak σ-donor but a strong π-acceptor and that it has a strong *trans* effect[640]. Data on sulphur ligands are meagre but it is apparent that most sulphur ligands are strongly *trans* directing.

The *trans* effect explains the synthesis of *cis* and *trans* isomers, as can be seen from the following. Treatment of $[PtCl_4]^{2-}$ with NH_3 yields *cis*-$[Pt(NH_3)_2Cl_2]$, since Cl^- has a greater *trans* effect than NH_3; thus substitution by NH_3 in $[PtNH_3Cl_3]^-$ takes place in the position *trans* to Cl, i.e. *cis* to NH_3. On the other hand, the addition of HCl to $[Pt(NH_3)_4]^{2+}$ yields *trans*-$[Pt(NH_3)_2Cl_2]$, since the second Cl^- ligand will attack the position *trans* to Cl in $[Pt(NH_3)_2Cl_2]$.

Nitro complexes. The infrared spectra of *trans*-$[PtL_2(NO_2)_2]$ (L = Bu_3^nP, Bu_3^nAs, SBu_2^n, $SePr_2^n$, $TePr_2^n$) and of *cis*-$[PtL_2(NO_2)_2]$ (L = Bu_3^nP, Ph_3P, Ph_3As, Ph_3Sb, Bu_2S, py, $\frac{1}{2}$bipy, $\frac{1}{2}$phen) have been rationalized in terms of a correlation between ν(N–O) and the π-bonding ability of L. The N–O stretching frequency increases with increase in the π-bonding capacity of L [537].

The *cis*-isomer of $[Pt(NO_2)_2(SPr_2)_2]$ has a dipole moment of 13.1*D*, while the moment of the *trans*-isomer is 2.5*D*. The small moment of the *trans*-isomer arises from the resultant moment of the S–C bonds not being directed along the Pt–S bond, since the three sulphur bonds are pyramidal[608].

Azide complex. The orange–red azido complex $[Ph_4As]_2[Pt(N_3)_4]\cdot H_2O$ has been reported; $\nu_{as}(N_3)$ and $\nu_s(N_3)$ occur at 2030 and 1270 cm^{-1} respectively[641].

Amino-acid complexes. The bis-ligand complexes $[PtL_2]$ (LH = glycine, $H_2NCH_2CO_2H$, alanine, $H_2NCH(Me)CO_2H$) are known in *cis*- and *trans*-isomeric forms. The compounds $[PtL_2]$ (LH = *N*,*N*-diethylglycine, *o*-aminobenzoic acid) are known in one form only. The mono-ligand compounds $K[PtCl_2gly]$, $[Pt(NH_3)_2gly]$ and $[Pt(NH_3)_2alan]$ (glyH = glycine; alanH = alanine) have also been described[626]. Complexes of methionine, ethionine and *S*-methyl-L-cysteine have been discussed (see p.1292).

Amino-acid complexes of Pt(II) have been studied by n.m.r. spectroscopy[642].

Oxime complexes. Glyoximes form brown complexes PtL_2 (LH = dimethylglyoxime, methylethylglyoxime, methyl-n-propylglyoxime, methyl-iso-butylglyoxime, α-benzildioxime);

[638] L. Cattalini, U. Croatto and G. Marangoni, *Proc. XIIth Int. Conf. Coord. Chem. Sydney* (H. C. Freeman, ed.), Science Press (1969), p. 33.

[639] W. Beck and K. Feldl, *Z. Naturforsch.* **21b** (1966) 588.

[640] J. Powell and B. L. Shaw, *J. Chem. Soc.* 1965, 3879.

[641] W. Beck, E. Schuierer and K. Feldl, *Angew. Chem.*, Int. Edn., **5** (1966) 249.

[642] L. E. Erickson, J. W. McDonald, J. K. Howie and R. P. Clow, *J. Am. Chem. Soc.* **90** (1968) 6371.

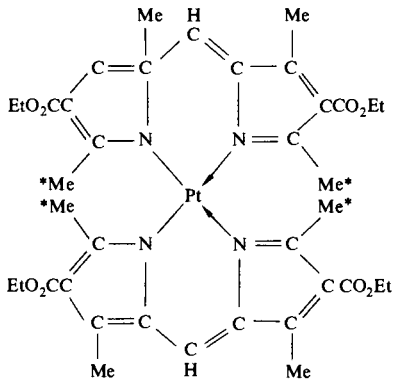
the structures are similar to that shown for the palladium complexes (LXXXIV). The dimethylglyoxime complex is isomorphous with the nickel and palladium compounds and forms the binary metal complexes $NiPd(DMG)_4$ and $PdPt(DMG)_4$ [539] (see p. 1311). It can be oxidized by Br_2 to $[PtBr_2(DMG)_2]$. The reaction of acetyl chloride with $Pt(DMG)_2$ yields $Pt(DMGH)Cl_2$ [540].

A yellow complex of salicylaldoxime and a brown complex of α-furfuraldoxime have also been reported[626].

TABLE 55. PLATINUM(II) COMPLEXES OF UNIDENTATE PHOSPHINES, ARSINES AND STIBINES

Complex		Colour
$[Pt(PX_3)_2Cl_2]$	(X = F, Cl, Br)	White
cis-$[Pt(R_3P)_2Cl_2]$	(R = Me, Et, Pr^n, Bu^n, Am^n, Ph, OEt; R_3 = Me_2CF_3, $MePh_2$, Et_2Ph)	White
trans-$[Pt(R_3P)_2Cl_2]$	(R = Et, Pr, Bu^n, OEt, C_6F_5; R_3 = $Me(CF_3)_2$, Ph_2CF_3, $Ph(CF_3)_2$, Et_2Ph)	Yellow
cis-$[Pt(R_3P)_2Br_2]$	(R = Me, Et, Pr^n, Ph, OEt)	White, orange
trans-$[Pt(R_3P)_2Br_2]$	(R = Et, Pr^n, OEt, C_6F_5)	Yellow
cis-$[Pt(R_3P)_2I_2]$	(R = Et, Bu^n, Ph, OEt)	Yellow
trans-$[Pt(R_3P)_2I_2]$	(R = Me, Et, Pr^n, Bu^n, OEt, C_6F_5; R_3 = Et_2Ph)	Deep yellow
cis-$[Pt(R_3P)_2(NO_2)_2]$	(R = Et, Bu^n)	White
trans-$[Pt(R_3P)_2(NO_2)_2]$	(R = Et, Bu^n)	White
cis-$[Pt(Et_3P)_2(NO_3)_2]$		White
trans-$[Pt(Et_3P)_2(NO_3)_2]$		Yellow
cis-$[Pt(Et_3P)_2(SCN)_2]$		White
trans-$[Pt(Et_3P)_2(SCN)_2]$		White
cis-$[Pt(Et_3P)_2R'_2]$	(R′ = Ph, C_6F_5)	White
trans-$[Pt(Et_3P)_2R'_2]$	(R′ = Ph, C_6F_5)	White
cis-$[Pt(R_3As)_2Cl_2]$	(R = Et, Pr^n, Ph; R_3 = Me_2Et, Bu^n_2Ph, $MePh_2$, $CH{=}CH_2$)	Pale yellow
trans-$[Pt(R_3As)_2Cl_2]$	(R = Et, Pr^n, Bu^n, Ph; R_3 = Me_2Et, Bu^n_2Ph, Me_2Ph)	Yellow
cis-$[Pt(Et_3As)_2Br_2]$		White
trans-$[Pt(R_3As)_2Br_2]$	(R_3 = Et_3, $MePh_2$, Me_2Ph)	Yellow
cis-$[Pt(Et_3As)_2I_2]$		Yellow
trans-$[Pt(R_3As)_2I_2]$	(R_3 = Et_3, $MePh_2$, Ph_3)	Orange
cis-$[Pt(Et_3As)_2(NO_2)_2]$		White
trans-$[Pt(R_3As)_2(NO_2)_2]$	(R = Et, Bu^n)	White
cis-$[Pt(R_3Sb)_2Cl_2]$	(R = Me, Et, Pr^n, Bu^n, Ph)	Greenish yellow
cis-$[Pt(R_3Sb)_2Br_2]$	(R = Et, Pr^n)	Greenish yellow
trans-$[Pt(Et_3Sb)_2I_2]$		Yellow
trans-$[Pt(Et_3Sb)_2(NO_2)_2]$		Greenish yellow

The compound bis-(3,3′,5,5′-tetramethyl-4,4′-dicarbethoxypyrromethanatoplatinum (CXLIV) is of interest, since there must be considerable distortion of the planar bonds about the platinum atom to avoid steric interference between the Me* groups[626].



(CXLIV)

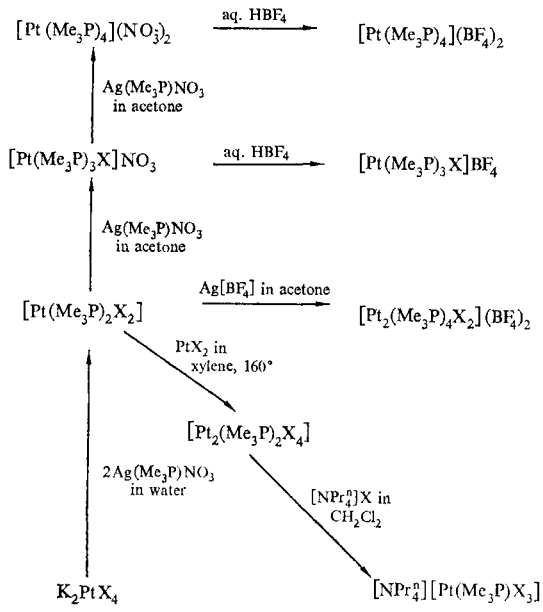
Phosphine, Arsine and Stibine Complexes

Complexes of unidentate ligands. The mononuclear complexes of unidentate phosphines, arsines and stibines are listed in Table 55. Both *cis*- and *trans*-isomers are known for most of the complexes; however, some of the stibine complexes have been isolated in the *cis* form only, although the more soluble *trans*-isomers have been found to be present in solution in equilibrium with the *cis*-isomers. The *cis*-isomers are much less soluble in organic solvents and usually have higher melting points. The dipole moments of the *trans*-isomers are close to zero, while the *cis*-isomers have moments of 9–13*D*. The complex $Pt(MePh_2As)_3Br_2$ dissociates in solution to the ionic species $[Pt(MePh_2As)_3Br]Br$ [550].

For *trans*-$[Pt(Et_3P)_2Cl_2]$ the infrared active ν(Pt–P) mode occurs at 415 cm^{-1}, while the symmetrical stretching frequency occurs at 443 cm^{-1}. In *cis*-$[Pt(Et_3P)_2Cl_2]$ two infrared active ν(Pt–P) modes occur at 442 and 427 cm^{-1}. This distinction has been used to identify the isomers of $[Pt(Et_3P)_2X_2]$ (X = Br, I, SCN, CN, Ph, C_6F_5) [643]. Little is known about ν(M–As) modes. The strong band at 276 cm^{-1} in the spectrum of *cis*-$[Pt(Me_3As)_2Cl_2]$ has been assigned as ν(Pt–As); in the *trans*-isomer a very weak band appears at 265 cm^{-1} which has also been assigned as ν(Pt–As) [106]. The *trans*-complexes $[Pt(R_3M)_2Cl_2]$ (M = P, As, Sb) exhibit ν(Pt–Cl) as one band at $\sim$330 cm^{-1}, whereas the *cis*-isomers display two ν(Pt–Cl) bands at $\sim$310 and $\sim$280 cm^{-1}. For *trans*-$[Pt(R_3M)_2Br_2]$ ν(Pt–Br) occurs at $\sim$250 cm^{-1} [106].

A complete assignment of the skeletal stretching modes—ν(Pt–P) and ν(Pt–X)—has been made for the trimethylphosphine-Pt(II) halide system; the complexes investigated were $[PtL_4]^{2+}$, $[PtL_3X]^+$, $[Pt_2L_4X_2]^{2+}$, $[PtL_2X_2]$, $[Pt_2L_2X_4]$ and $[PtLX_3]^-$ (L = Me_3P; X = Cl, Br) [644]. The complexes were prepared according to the following scheme:

[643] P. L. Goggin and R. J. Goodfellow, *J. Chem. Soc.* A, 1966, 1462.
[644] D. A. Duddell, P. L. Goggin, R. J. Goodfellow and M. G. Norton, *Chem. Communs.* 1968, 879.



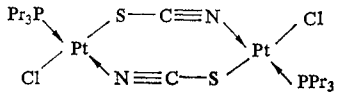
The low temperature ^{19}F n.m.r. spectra of *trans*-[Pt{$(C_6F_5)_3P$}$_2X_2$] (X = Cl, Br, I) indicate hindrance to rotation of the C_6F_5 rings due to steric interaction of the *ortho*-fluorine atom with the halogen atom: this hindrance is in the order: I > Br > Cl [645].

The Pt–P distances are 2.30 Å in *trans*-[$Pt(Et_3P)_2Cl_2$], whereas in the *cis*-isomer they are 2.26 and 2.24 Å. This shorter bond-length in the *cis*-complex together with the larger ^{195}Pt–^{31}P coupling constants has been interpreted as indicative of enhanced π-bonding[470]. It has been assumed that the "soft" character of phosphorus and arsenic ligands and their preference for (b) class metals are due to π-bonding between the metal and the heavy donor atom. Furthermore, since the ^{195}Pt–^{31}P coupling constants are appreciably greater in the *cis*- than in the corresponding *trans*-isomers, it has also been assumed that d_π–d_π bonding is stronger in the *cis*-complexes. This view has been recently challenged and the following alternative explanation has been proposed[646]. All the above phenomena can be rationalized without invoking π-bonding with the concept that with (b) class metals like platinum, phosphines form strong σ-bonds having a large amount of *s*-character.

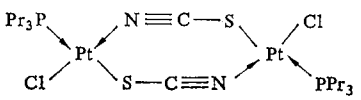
The complexes [$Pt(R_3P)_2Cl_2$] react with phosphine and other neutral ligands to yield complexes such as [$Pt(Et_3P)_4]Cl_2$, [$Pt(Et_3P)_2(NH_3)_2]Cl_2$, [$Pt(Ph_3P)_2en]^{2+}$ and [$Pt(Et_3P)_2$(thiourea)$_2]^{2+}$ [550]. Although $[PtCl_6]^{2-}$ is reduced by phosphines to yield the Pt(II) complexes, the diphosphine complexes can be oxidized by X_2 to the Pt(IV) compounds [$Pt(R_3P)_2X_4$]. Redox potentials for the system [$Pt(Pr_3P)_2Cl_4$]/[$Pt(Pr_3P)_2Cl_2$] have been measured and the *cis*-isomer system has a higher potential than the *trans*-analogue[647]. The methyl complex *trans*-[$PtClMe(Ph_3P)_2$] reacts with HCl to give the labile Pt(IV) intermediate [$HPtMe(Ph_3P)_2Cl_2$] which yields *trans*-[$Pt(Ph_3P)_2Cl_2$] with concomitant slow elimination of CH_4 [648]. The complexes [$Pt(Ph_3P)_2L$] (L = CO_3, SO_4) have already been mentioned (p. 1339).

[645] R. D. W. Kemmitt, D. I. Nichols and R. D. Peacock, *Chem. Communs.* 1967, 599.
[646] L. M. Venanzi, *Chemistry in Britain* **4** (1968) 162.
[647] S. Ahrland and J. Chatt, *J. Chem. Soc.* 1957, 1379.
[648] U. Belluco, M. Giustiniani and M. Graziani, *J. Am. Chem. Soc.* **89** (1967) 6494.

Binuclear complexes. Many halogen-bridged binuclear complexes are known; they are crystalline and readily soluble in organic solvents. If platinum sponge is heated with PCl_5 the dimeric complex $[Pt(PCl_3)Cl_2]_2$ is produced; $[Pt(PF_3)F_2]_2$ can be made similarly. $[Pt(PCl_3)Cl_2]_2$ reacts with water to yield $[Pt\{P(OH)_3\}Cl_2]_2$ and with alcohol to give $[Pt\{P(OEt)_3\}Cl_2]_2$. The chloro-bridge in the latter compound is split by pyridine to give $[Pt\{P(OEt)_3\}Cl_2py]$ and by NH_3 to give $[Pt\{P(OEt)_3\}(NH_3)_2Cl]Cl$ [604]. The halogen-bridged complexes $[Pt(R_3M)X_2]_2$ (M = P, As, Sb; X = Cl, Br) have the *trans*-planar symmetrical structure; they are prepared by heating $[Pt(MR_3)_2X_2]$ and PtX_2 together. When X = Cl and M = P the compounds are pale orange; when M = As or Sb, the compounds are reddish orange. These bridged complexes react with amines to give *trans*-$[Pt(R_3M)X_2am]$ [550]. However, reaction of $[Pt(R_3P)X_2]_2$ with CO or C_2H_4 yields *cis*-$[Pt(R_3P)LX]$ (L = CO, C_2H_4) due to the high *trans* effect of CO and C_2H_4 [400]. The thiocyanato-bridged complex $[Pt(Pr_3P)(SCN)Cl]_2$ has been obtained in two isomeric forms. Treatment of $[Pt(Pr_3P)Cl_2]_2$ with two equivalents of KSCN in cold acetone yields the yellow α-form (μ, 1.57*D*), whereas if the reaction is carried out in the boiling solvent, the pale greenish-yellow β-form (μ, 1.36*D*) is obtained. X-ray structural determinations show that the α- and β-forms have the structures (CXLV) and (CXLVI), respectively[649].

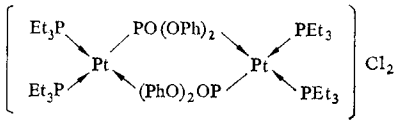


(CXLV)



(CXLVI)

The action of NaOEt on the complexes $[Pt(PHR_2)LCl_2]$ yields the phosphorus-bridged complexes $[Pt(PR_2)LCl]_2$; arsenic-bridged complexes $[Pt(AsR_2)LCl]_2$ can be prepared similarly[308, 551]. A phosphonato-bridged complex (CXLVII) has been reported[650].



(CXLVII)

Complexes of bidentate chelate ligands. A few complexes of diphosphines are known; these include $[Pt(R_2PCH_2CH_2PR_2)_2]Cl_2$ (R = Ph, Me) [550] and the diethylphosphonato complex $[Pt(Ph_2PCH_2CH_2PPh_2)\{PO(OEt)_2\}_2]$ [650].

o-Phenylenebisdimethylarsine (XCIII; R = Me; As–As) forms the colourless $[Pt(As\text{–}As)_2](ClO_4)_2$ and the yellow complexes $Pt(As\text{–}As)_2X_2$ and $[Pt(As\text{–}As)_2X]ClO_4$ (X = Cl, Br, I) which are uni-univalent electrolytes in nitrobenzene. A crystal structure analysis of $Pt(As\text{–}As)_2I_2$ shows that the four arsenic atoms are in a plane at a distance of 2.38 Å while the two iodine atoms complete a distorted octahedral configuration. The Pt–I distances (3.50 Å) are much longer than the sum of the covalent radii (2.64 Å). The shortening of the Pt–As distance by ~0.1 Å compared to the observed bond length in

[649] J. Chatt and F. A. Hart, *J. Chem. Soc.* 1961, 1416.
[650] A. Pidcock and C. R. Waterhouse, *Inorg. Nucl. Chem. Letters* 3 (1967) 487.

$PtAs_2$ is consistent with the postulate of some d_π–d_π bonding existing in the Pt–As bonds[447].

α-Picolyldimethylarsine (C; As–N) forms a pale cream bis-ligand complex $[Pt(As–N)_2](ClO_4)_2$ [554]. 8-Dimethylarsinoquinoline (CI; As–N) forms 4- and 5-coordinate complexes with Pt(II). The 4-coordinate complexes are represented by $[Pt(As–N)X_2]$ (X = Cl, Br, I, SCN), which are cream to yellow, and the colourless $[Pt(As–N)_2](ClO_4)_2$. The 5-coordinate complexes $[Pt(As–N)_2X]ClO_4$ are cream when X = Cl or Br while the iodo-complex is brown[555].

The potential tridentate bis-(*o*-dimethylaminophenyl)phenylphosphine (CVII) forms the complexes $[Pt(N–P–N)X_2]$ (X = Cl, Br, I) in which only the phosphorus and one nitrogen atom are coordinated[557].

Complexes of multidentate chelate ligands. Bis-(bis-3-dimethylarsinopropyl)arsine (CIV; As–As–As) forms the 4-coordinate complex [Pt(As–As–As)Br]Br [447]. Bis-(*o*-diphenylarsinophenyl)phenylarsine (CVI; As–As–As) forms the square-planar complex $[Pt(As–As–As)I]ClO_4$ [450].

Five-coordinate Pt(II) complexes have been obtained with several quadradentate ligands. Tris-(*o*-diphenylphosphinophenyl)phosphine (CVIII; QP) forms the orange–yellow [Pt(QP)X]X and $[Pt(QP)X][BPh_4]$ (X = Cl, I). The similar tris-(*o*-diphenylarsinophenyl)-arsine (CIX; QAS) forms [Pt(QAS)X]X and $[Pt(QAS)X][BPh_4]$ (X = Cl, Br, I, SCN), which are yellowish orange to red depending on X. An X-ray structural investigation on $[Pt(QAS)I][BPh_4]$ showed that the coordination around the platinum atom is trigonal bipyramidal with three arsenic atoms in the equatorial plane. Spectral studies have shown that this geometry prevails in all the complexes of the type $[M^{n+}(Q)X]^{(n-1)+}$ (Q = quadradentate tripod-like ligand)[450].

On the other hand, *o*-phenylenebis-[(*o*-dimethylarsinophenyl)methylarsine] (CX; TPAS) forms the white 4-coordinate $[Pt(TPAS)](ClO_4)_2$ and the 5-coordinate yellow [Pt(TPAS)I]I, which has a square-pyramidal configuration[558].

The sexadentate arsine, tetrakis-(3-dimethylarsinopropyl)-*o*-phenylenediarsine (CXI; SAS), forms the yellow octahedral complex $[Pt(SAS)](ClO_4)_2 \cdot 3H_2O$ [559].

Carbonyl Complexes

A number of carbonyl halides have been characterized. The monomeric complexes $[Pt(CO)_2X_2]$ (X = Cl, Br, I) can be prepared by the action of CO on H_2PtX_4 or PtX_2 under *ca.* 200 atm. The colourless chloro- and bromo-derivatives are stable but the red iodo-compound slowly converts to $[PtCOI_2]_2$ with loss of CO. The dipole moment of $[Pt(CO)_2Cl_2]$ is 4.65*D*, indicating a *cis*-planar configuration; furthermore two $\nu(C\equiv O)$ bands are observed. The compounds are volatile and soluble in organic solvents. The phosphine complexes *cis*-$[Pt(CO)X_2(R_3P)]$ (X = Cl, Br, I; R = Et, Pr^n, Bu^n) can be obtained by the reaction of CO on $[PtX_2(R_3P)]_2$ [162].

The brick-red binuclear chloro-bridged compound $[PtCOCl_2]_2$ is one of the products obtained from the reaction of CO_2 and Cl_2 on platinum sponge at 250°. The bromo- and iodo-complexes have been obtained from the chloro-compound by treatment with HX. The spectra display only one $\nu(C\equiv O)$ frequency, so they probably possess a symmetric *trans*-configuration. These bridged complexes react with amines to give $[Pt(CO)X_2am]$ (am = NH_3, py, *p*-toluidine) and [Pt(CO)Xbipy][Pt(CO)X_3]. The yellow anionic complex $[Pt(CO)Cl_3]^-$ is formed by the reaction of HCl with $[Pt(CO)Cl_2]_2$; it was isolated as the pyH^+ salt. The chloro- and bromo-analogues have also been prepared. The complexes

$Pt_2(CO)_3X_4$ (X = Cl, Br) have been obtained from the controlled decomposition of $[Pt(CO)_2X_2]$ in benzene. Their structures are unknown but the infrared spectra indicate the absence of CO bridges[162].

It was reported that the reaction of PtF_4 with CO under pressure yielded $Pt(CO)_2F_8$. A reinvestigation has shown that PtF_4, because of its method of preparation, usually contains appreciable amounts of $PtF_4 \cdot 2BrF_3$, and the latter reacts with CO to give high yields of *cis*-$[Pt(CO)_2Br_2]$. The material reported as $Pt(CO)_2F_8$ is actually the bromo-complex *cis*-$[Pt(CO)_2Br_2]$ [651].

The reaction of $Li_2[PtCl_4]$ with oct-1-ene in DMF containing formic acid yields $[(C_8H_{17})Pt(CO)Cl]_2$ which reacts with acetylacetone to give $[(C_8H_{17})Pt(CO)acac]$. The compounds $[RPt(CO)Cl]_2$ (R = Et, Pr^n, C_7H_{15}) have also been prepared[652].

Acyl Derivatives

Acyl derivatives *trans*-$[Pt(COR)X(PEt_3)_2]$ (X = Cl, Br, I; R = Me, Et, Ph) have been obtained by the reaction of *trans*-$[PtR(PEt_3)_2X]$ in benzene solution at 90° with CO under pressure[561].

Isocyanide Complexes

Isocyanides react readily with $[PtX_4]^{2-}$ to give stable complexes $[PtX_2(CNR)_2]$ and $[Pt(CNR)_4][PtX_4]$ (X = Cl, Br, I, CN; R = Me, Et, Ph); the nitro-complexes are known only in the monomeric form $[Pt(NO_2)_2(CNR)_2]$. The cyano-complexes are colourless but the other complexes are mostly yellow to red. The monomeric complexes are soluble in most organic solvents[434].

Treatment of an aqueous solution of $[PtCl_4]^{2-}$ with MeCN, followed by hydrazine, yields a bright red crystalline product $[Pt_2(N_2H_3)_2(CNMe)_8]Cl_2$; the corresponding iodide and perchlorate have also been prepared. The compounds have been formulated as di-μ-hydrazido complexes of 6-coordinate Pt(II). However, the structures of this complex and of the yellow $[Pt_2(N_2H_3)_2(CNMe)_4]Cl_2$ have not been established[434].

Alkyl and Aryl Complexes

Alkyl complexes can be prepared by the reaction of Grignard reagents or lithium or mercury alkyls on $[PtX_2(R_3P)_2]$. Similarly, aryl, alkenyl and alkynyl groups may be introduced by using the appropriate Grignard reagent, e.g.:

$$[PtI_2(diolefin)] + 2PhMgI \rightarrow [PtPh_2(diolefin)] + 2MgI_2$$

Alkyl groups can be introduced by oxidative addition reactions, e.g.:

$$Pt(Ph_3P)_3 + MeI \rightarrow PtMe(Ph_3P)_2I + Ph_3P$$

and

$$Pt(Ph_3P)_3 + PhCH{=}CHBr \rightarrow [PtBr(CH{=}CHPh)(Ph_3P)_2]$$

Transition M–C σ-bonds can be formed by the insertion of a carbon-containing species into an M–H bond. Olefins yield alkyls, while acetylenes yield alkenyl complexes, e.g.:

$$[HPtCl(Et_3P)_2] + CH_2{=}CH_2 \rightarrow [CH_3CH_2PtCl(Et_3P)_2]$$

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[651] R. D. W. Kemmitt, R. D. Peacock and I. L. Wilson, *Chem. Communs.* 1968, 772.
[652] D. Wright, *Chem. Communs.* 1966, 197.

Elimination reactions have also been used, e.g.[653]:

$$[PhN_2PtCl(Et_3P)_2] \xrightarrow{Al_2O_3} [PhPtCl(Et_3P)_2] + N_2$$

The Pt–C bond is quite strong: in *trans*-$[PtPh_2(Et_3P)_2]$ it is 60 kcal mole^{-1}. Stabilization of M–C bonds in transition metal complexes is achieved by the use of strong σ-donor ligands or π-acceptor ligands. The explanation is that the initial step in decomposition of metal alkyls is the promotion of an electron from the highest energy orbital to a vacant anti-bonding orbital. σ-Donors lower the energy of the bonding orbitals and destabilize anti-bonding orbitals, while π-acceptors stabilize the non-bonding *d*-orbitals on the metal by forming π-bonds. Hence both strong σ-donors and π-acceptors increase the energy difference between the filled orbitals and the vacant anti-bonding orbitals. Tertiary phosphines stabilize Pt(II) alkyls[653].

The perfluorophenyl complex $[Pt(Ph_3P)_2(C_6F_5)_2]$ can be obtained by the reaction of $[(C_6F_5)_2TlBr]_2$ on $Pt(Ph_3P)_3$ [563].

Fluoro-olefins react to give not π-bonded olefin complexes but σ-bonded vinyl derivatives, e.g. $F_2C{=}CF_2$ reacts with $[HPtCl(Et_3P)_2]$ to give the trifluorovinyl complex $[(Et_3P)_2PtCl(CF{=}CF_2)]$ and hexafluorocyclobutadiene reacts to give the pentafluorocyclobutenyl derivative. A lowering of ν(C–F) has been observed in the spectra of the fluorovinyl derivatives due to partial double bonding between Pt and the fluorovinyl group[581]. Fluoro-olefins can also react to yield compounds such as $[(Ph_2MeP)_2Pt(C_2F_3Br)]$ in which the fluorocarbon forms a metallo-cyclopropane ring[565].

Carbon subsulphide, S=C=C=C=S, reacts with $Pt(Ph_3P)_4$ in alcohol at $-70°$ to give the reddish-brown Pt(II) complex $[Pt(Ph_3P)_2(C_3S_2)]$ which is similar to the Pd(II) complex for which the structure (CXIII) has been proposed[566].

Cyclopentadienyl Complexes

The known cyclopentadienyl complexes of Pt(II) differ from those of Pd(II). They include the colourless $[(C_5H_5)PtMe_3]$, the red $[(C_5H_5)PtCO]_2$ and the black iodo-compound $[(C_5H_5)Pt(CO)I]$ [567]. The dark green binuclear compound $[Pt_2(C_5H_5)_4]$ has been obtained from a suspension of NaC_5H_5 and $PtCl_2$ in hexane; it is believed to have a Pt–Pt bond[581].

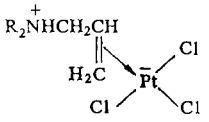
Olefin Complexes

The first metal–olefin compound, Zeise's salt $K[PtCl_3(C_2H_4)]$, was prepared in 1827. Similar yellow salts have been obtained with other mono-olefins. The stabilities decrease in the order: ethylene > styrene > amylene > indene > cyclohexene. An X-ray structural determination on Zeise's salt shows that the C–C axis of the ethylene ligand is normal to the plane containing the platinum and chlorine atoms. The C–C bond length in ethylene complexes is $\sim$0.1 Å longer than in ethylene itself, indicating the reduction in bond order[604, 608]. A normal coordinate analysis of the infrared spectrum of Zeise's salt has been made over the range 4000–33 cm^{-1}: ν(Pt–olefin) occurs at 407 cm^{-1} [654]. The far infrared spectra of $K[PtCl_3(RHC{=}CH_2)]$ (R = H, Me, CH_2OH, Ph) and *trans*-[Pt(olefin)Cl_2am] have been measured and assignments have been made[655].

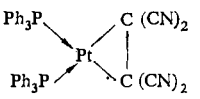
[653] G. W. Parshall and J. J. Mrowca, *Adv. Organomet. Chem.* **7** (1968) 157.
[654] M. J. Grogan and K. Nakamoto, *J. Am. Chem. Soc.* **88** (1966) 5454.
[655] H. P. Fritz and D. Sellmann, *J. Organomet. Chem.* **6** (1966) 558.

The orange complex $PtCl_2(C_2H_4)$ was made by Zeise in 1830; it is dimeric with chloro bridges, which are split by amines to give $[PtCl_2(C_2H_4)am]$. Dimeric chloro-bridged complexes are known for other olefins; $\nu(C{=}C)$ occurs in the range 1490–1515 cm^{-1} [106]. Yellow *trans*-$[PtCl_2(C_2H_4)_2]$ was obtained by passing C_2H_4 through a saturated solution of $[PtCl_2(C_2H_4)]_2$ in acetone at $-70°$; the complex decomposes at $\sim 0°$ to yield the bridged dimer and a small amount of white *cis*-$[PtCl_2(C_2H_4)_2]$ [626]. The preparation and infrared and n.m.r. spectra of a series of 4-substituted pyridine complexes of the type *trans*-$[(C_2H_4)PtCl_2(pyR)]$ (pyR = 4-substituted pyridine) have been reviewed[656].

A series of allylamine complexes, which are zwitterion analogues of Zeise's salt, has been reported; they have the structure (CXLVIII). Tetracyanoethylene forms the complex $Pt(Ph_3P)_2C_2(CN)_4$ which is considered to be a Pt(II) complex with the structure (CXLIX). A similar σ-bonded Pt(II) complex $Pt(Ph_3P)_2(PhHCCHPh)$ has been obtained with stilbene. Other Pt(II) complexes of substituted olefins have been described[657].



(CXLVIII)



(CXLIX)

Diolefin complexes. Diolefin complexes of the type $[Pt(diolefin)X_2]$ are known where the diolefin is norbornadiene, cycloheptatriene, cyclooctatetraene, cycloocta-1,5-diene, dipentene, dicyclopentadiene, butadiene and hexadiene and X = Cl, Br or I. The compounds have significant dipole moments[574]. They react with alcohol in the presence of a weak base to give halogen-bridged complexes $[PtX(dieneOR)]_2$, analogous to the palladium complexes (CXIV). The reaction can be regarded as a nucleophilic attack of the alkoxide ion on one of the unsaturated carbon atoms[657]. Similar reactions occur between $[PtX_2(diene)]$ and amines, alkoxides and β-diketones to yield chloro-bridged dimers $[PtCl(dieneY)]_2$ (Y = NHR, OR') or C-bonded β-diketone[577].

The reaction of $Na_2[PtCl_4]$ with cyclodeca-1,5-diene effects the isomerization of the diolefin to give the Pt(II) complex of 1,2-vinylcyclohexane[579].

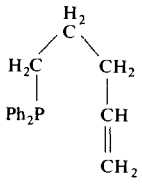
The cyclooctatetraene complex $[(\pi\text{-}C_8H_8)PtI_2]$ reacts with alkyl and aryl Grignard reagents to give mononuclear complexes, such as $[(\pi\text{-}C_8H_8)PtMe_2]$, $[(\pi\text{-}C_8H_8)PtEtI]$ and $[(\pi\text{-}C_8H_8)Pt(p\text{-tolyl})_2]$, and also binuclear complexes $[(\pi\text{-}C_8H_8)Pt_2Me_4]$ and $[(\pi\text{-}C_8H_8)Pt_2Ph_4]$. In the mononuclear complexes $\nu(C{=}C)$ occurs at 1635 cm^{-1} but, since this band is absent from the spectra of the binuclear complexes, the latter probably contain the tub form of cyclooctatetraene bridging the two platinum atoms[578].

The orange tetraphenylcyclobutadiene complex $[Pt(Ph_4C_4)Cl_2]_n$ was obtained from the reaction of $[Pt(CO)_2Cl_2]$ with diphenylacetylene in boiling benzene. It reacts with NaI to yield the dimeric iodo-bridged complex $[Pt(Ph_4C_4)I_2]_2$ [658].

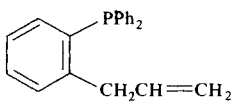
[656] M. Orchin and P. J. Schmidt, *Inorg. Chim. Acta Rev.* **2** (1968) 123.
[657] R. Jones, *Chem. Rev.* **68** (1968) 785.
[658] P. Chini, F. Canziani and A. Quarta, *Proc. Ist. Int. Symposium on Metal Carbonyls and Derivatives, Inorg. Chim. Acta*, Padova (1968), p. D8.

Dewar hexamethylbenzene reacts with $[(C_2H_4)PtCl]_2$ to yield $[(C_6Me_6)PtCl_2]$ with a structure similar to the analogous palladium compound (CXVIII). In the presence of $SnCl_2$, HCl and MeOH, Dewar hexamethylbenzene reacts with $K_2[PtCl_4]$ to give [(pentamethylcyclopentadiene)$PtCl_2$] [659].

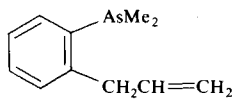
Chelate complexes containing an olefinic group and another donor atom. Complexes have been obtained with the potential olefin chelating agents, penten-4-yldiphenylphosphine (CL; PP), *o*-allylphenyldiphenylphosphine (CLI; AP), *o*-allylphenyldimethylarsine (CLII; AA) and *o*-styryldimethylarsine (CLIII; SA) [584, 660]. The phosphine (PP) forms complexes



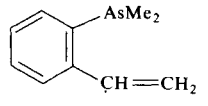
(CL)



(CLI)



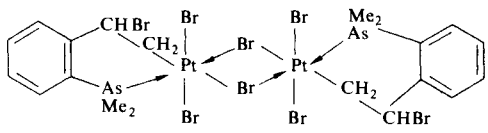
(CLII)



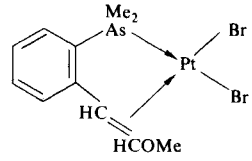
(CLIII)

$[Pt(PP)X_2]_2$ (X = Cl, Br, I) in which the olefinic group is not coordinated. On the other hand, the aromatic ligands (AP) and (AA) form complexes $[Pt(AP)X_2]$ and $[Pt(AA)X_2]$ (X = Cl, Br, I) in which the olefinic group is coordinated, since ν(C=C) occurs at 1493–1508 cm^{-1}.

The arsine (SA) forms $Pt(SA)Br_2$; this complex reacts with Br_2 to give the orange Pt(IV) complex (CLIV) which contains a Pt–C σ-bond. Heating of the bromo-bridged complex with methanol causes loss of HBr to give the monomeric methoxy Pt(II) complex (CLV). The arsine (AA) gives similar complexes, but in the methoxy compound $[Pt(Me_2AsC_6H_4CH{=}CHCH_2OMe)Br_2]$ the C=C bond has shifted.



(CLIV)



(CLV)

Acetylene Complexes

The acetylide compounds $K_2[Pt(C{\equiv}CR)_4]$ have been prepared[435].

The dihydroxo-acetylene $Me_2C(OH)C{\equiv}CC(OH)Me_2$(ac) forms the complexes K[$PtCl_3$(ac)] and *cis*- and *trans*-[$PtCl_2$am(ac)] by reactions similar to those used for the preparation of olefin complexes. The alkynes $Bu^tC{\equiv}CR$ (R = Me, Et, Pr^i, Bu^t, CMe_2Ph; ac′) give complexes K[$PtCl_3$(ac′)], [$PtCl_2$(ac′)]$_2$ and *trans*-[$PtCl_2$am(ac′)]. In all these complexes the alkyne is bonded through the triple bond, since ν(C≡C) is lowered by

[659] P. V. Balakrishnan and P. M. Maitlis, *Chem. Communs.* 1968, 1303.

$\sim 200\ cm^{-1}$ [121]. A structural determination on $[Pt(Bu^tC{\equiv}CBu^t)(p\text{-toluidine})Cl_2]$ shows that the two carbon atoms are equidistant from the platinum atom on a line perpendicular to the coordination plane; the C–C distance is 1.27 Å, indicating a bond order between 2 and 3 [661].

Of a different type are the planar compounds $[(Ph_3P)_2M(RC_2R)]$ (M = Ni, Pd, Pt; R = CF_3, Ph, CO_2Me) in which the alkyne behaves as a bidentate ligand and is probably σ-bonded through both carbon atoms which lie in the coordination plane, as in (CXIX), although the intermediate structure (CXX) has been proposed[585].

Allyl Complexes

Platinum, unlike palladium, shows little tendency to form π-allyl complexes. However, the n.m.r. spectrum of the lemon yellow allyl-cyclopentadienyl complex $[(C_3H_5)Pt(C_5H_5)]$ confirms that the allyl group is π-bonded[121, 587].

Hydride Complexes

The Pt(II) hydride complexes are listed in Table 56; those containing M–M bonds are discussed below under Complexes Containing Metal–Metal Bonds. The complexes of the type *trans*-$[HPtX(R_3M)_2]$ (M = P, As) are best prepared by reduction of *cis*-$[PtX_2(R_3M)_2]$

TABLE 56. HYDRIDE COMPLEXES OF PLATINUM(II)

trans-$[HPtCl(R_3P)_2]$ [a]	(R = Me, Pr^n)
trans-$[HPtX(Et_3P)_2]$ [a]	(X = Cl, Br, I, NO_3, CNO, NO_2, SCN, CN)
trans-$[HPtX(R_3P)_2]$ [a]	(R_3 = Ph_2Et, $PhEt_2$; X = Cl, I)
trans-$[HPtX(Ph_3P)_2]$ [a, b]	(X = Cl, I, SCN, CN)
$[HPt(Ph_3P)_3]X$ [b]	(X = Cl, NO_3, ClO_4, BF_4, $MeOSO_3$, HSO_4, BPh_4)
trans-$[HPtX(Et_3As)_2]$ [a, b]	(X = Cl, Br, I, SCN)
$[HPt(NH_3)(Et_3M)_2]Cl$ [a]	(M = P, As)
trans-$[HPt(CO)(Et_3P)_2]ClO_4$ [c]	
trans-$[HPt(CNCMe_3)(Et_3P)_2]ClO_4$ [c]	
trans-$[H_2Pt(Et_3P)_2]$ [a]	
trans-$[H_2Pt_2(Ph_2P)_2(Et_3P)_2]$ [d]	

[a] A. P. Ginsberg, *Transition Metal Chem.* **1** (1965) 111.
[b] F. Cariati, R. Ugo and F. Bonati, *Inorg. Chem.* **5** (1966) 1128.
[c] M. J. Church and M. J. Mays, *Chem. Communs.* 1968, 435.
[d] J. Chatt and J. M. Davidson, *J. Chem. Soc.* 1964, 2433.

with hydrazine hydrate in dilute aqueous or alcoholic solution. The corresponding *trans* compounds are not reduced under these conditions: the strong *trans* effect of R_3M causes the Cl group in the *cis* compounds to be very labile and hence it can be replaced by other ligands. Other methods of preparation have been used: e.g. *cis*-$[PtCl_2(Et_3P)_2]$, on hydrogenation at 95° and 50 atm in alcohol, gives *trans*-$[HPtCl(Et_3P)_2]$ in good yield. The only dihydride known is $[H_2Pt(Et_3P)_2]$ which was prepared by high-pressure hydrogenation of $Pt(Ph_3P)_4$ in benzene[662].

[660] M. A. Bennett, J. Chatt, G. J. Erskine, J. Lewis, R. F. Long and R. S. Nyholm, *J. Chem. Soc.* A, 1967, 501; M. A. Bennett, G. J. Erskine and R. S. Nyholm, *ibid.*, p. 1260.
[661] G. R. Davies, W. Hewerston, R. H. B. Mais and P. G. Owston, *Chem. Communs.* 1967, 423.
[662] A. P. Ginsberg, *Transition Metal Chemistry* **1** (1965) 111.

The reaction of $Pt(Ph_3P)_3$ with HCl yields $[HPt(Ph_3P)_3]Cl$; other salts of the cationic complex $[HPt(Ph_3P)_3]^+$ can be obtained (see Table 56). The complex $[HPtCl(Ph_3P)_2]$ reacts with HCl to give the Pt(IV) hydride $[H_2PtCl_2(Ph_3P)_2]$ [663]. In the presence of $NaClO_4$ *trans*-$[HPtCl(Et_3P)_2]$ reacts with CO in acetone solution under ambient conditions to give *trans*-$[HPt(CO)(Et_3P)_2]ClO_4$. t-Butyl isocyanide reacts similarly to give *trans*-$[HPt(CNCMe_3)(Et_3P)_2]ClO_4$ [347].

In general, the tertiary phosphine hydrides are remarkably stable, being resistant to thermal decomposition, oxidation and hydrolysis. They have relatively large dipole moments, ranging from 4.2*D* for *trans*-$[HPtCl(Et_3P)_2]$ to 7.4*D* for *trans*-$[HPt(SCN)(Et_3P)_2]$. The proton-resonance chemical shifts τ(Pt–H) are unusually high, varying from 17.8 ppm for *trans*-$[HPt(CN)(Et_3P)_2]$ to 33.8 ppm for *trans*-$[HPt(NO_3)(Et_3P)_2]$. The infrared spectra display ν(Pt–H) at 2229–2041 cm^{-1} and δ(Pt–H) at 840–803 cm^{-1}. For the series *trans*-$[HPtX(Et_3P)_2]$ ν(Pt–H) falls in the order: $NO_3 > CNO > Cl > Br > I > NO_2 > SCN > CN$. This is in the order of increasing *trans* effect: $NO_3 < CN$. The dihydrido complex $[H_2Pt(Et_3P)_2]$ displays ν(Pt–H) at 1640 cm^{-1}; this low frequency is apparently due to the presence of two hydrogens in *trans* positions. In the dimeric $[H_2Pt_2(Ph_2P)_2(Et_3P)_2]$ ν(Pt–H) occurs at 2041 cm^{-1}; this suggests that the bridging phosphido group has a *trans* effect comparable with CN.

Hydrogen-transfer occurs when *trans*-$[HPtCl(Et_3P)_2]$ is treated with ethylene in cyclohexane at 95° and 40 atm to give the ethyl derivative *trans*-$[PtClEt(Et_3P)_2]$ [662].

Complexes Containing Metal–Metal Bonds

In compounds such as $Pt(DMG)_2$ and Magnus' green salt the platinum atoms are stacked directly above each other so that the Pt–Pt distances are *ca.* 3.3 Å, indicating some metal–metal interaction, which in some cases is characterized by marked dichroism[447]. In addition to these "columnar packed" compounds, there are numerous complexes in which platinum forms a bond with boron, silicon, germanium, tin, lead, nickel, platinum, copper, gold or mercury.

The hydride $[HPtCl(Et_3P)_2]$ reacts with Ph_2BCl to yield the yellow compound $[Ph_2BPtCl(Et_3P)_2]$. Silyllithium and silylmercury reagents react with $[PtCl_2(R_3P)_2]$ to give complexes of the types $[HPt(SiPh_3)(Et_3P)_2]$, $[(MePh_2Si)_2Pt(PhMe_2P)_2]$ and *trans*-$[(Me_3Si)PtCl(Et_3P)_2]$. Similar germanium complexes have been reported; however, they are more stable than their silyl analogues. The complexes $[Me_3SnPtCl(Ph_3P)_2]$ and *trans*-$[Ph_3MPtCl(Ph_3P)_2]$ (M = Sn, Pb) have been prepared from *trans*-$[HPtCl(Ph_3P)_2]$ [664].

A general method for the preparation of silyl-platinum complexes is the reaction[665]

$$cis\text{-}[PtCl_2(Me_2PhP)_2] + R_3SiH + NEt_3 \rightarrow trans\text{-}[R_3SiPtCl(Me_2PhP)_2] + Et_3NHCl$$

The yellow compound $[(Ph_3Ge)_2Pt(Et_3P)_2]$ can be prepared by the reaction of Ph_3GeLi with $[PtCl_2(Et_3P)_2]$; it is cleaved by H_2 under ambient conditions to yield $[HPt(GePh_3)(Et_3P)_2]$ and $HGePh_3$. In the spectra of $[Me_3GePtX(Et_3P)_2]$ (X = Cl, Br, I, SCN, CN, Ph) and $[Me_3SiPtCl(Et_3P)_2]$ ν(Pt–Ge) occurs at 292–322 cm^{-1} and ν(Pt–Si) occurs at 352 cm^{-1} [666].

Platinum forms complexes with $SnCl_3^-$ in the same way as ruthenium, rhodium and

[663] F. Cariati, R. Ugo and F. Bonati, *Inorg. Chem.* **5** (1966) 1128.
[664] M. C. Baird, *Progr. Inorg. Chem.* **9** (1968) 1.
[665] J. Chatt, C. Eaborn, S. Ibekwe and P. M. Kapoor, *Chem. Communs.* 1967, 869.
[666] R. J. Cross and F. Glocking, *Proc. Chem. Soc.* 1964, 143; F. Glocking and K. A. Hooton, *J. Chem. Soc.* 1967, 1066.

iridium. In ethanol $SnCl_2$ reacts with $[PtCl_4]^{2-}$ to give *cis*-$[Pt(SnCl_3)_2Cl_2]^{2-}$. Treatment of $[PtCl_4]^{2-}$ with a large excess of $SnCl_2$ in dilute HCl yields $[Pt(SnCl_3)_5]^{3-}$. The compound $[Ph_3PMe]_3[Pt(SnCl_3)_5]$ has a trigonal bipyramidal configuration with Pt–Sn distances of 2.54 Å. If acetone is used as a solvent, the species $[Pt_3Sn_8Cl_{20}]^{4-}$ is formed. Treatment of this anionic complex with cycloocta-1,5-diene yields red crystals of $(C_8H_{12})_3Pt_3(SnCl_3)_2$. Both complexes contain the Pt_3Sn_2 cluster. A structural determination of $(C_8H_{12})_3Pt_3(SnCl_3)_2$ shows that the molecule consists of a triangle of platinum atoms each coordinated to a diene ring and capped above and below by $SnCl_3$ groups. The bond lengths are: Pt–Pt, 2.80 Å; Pt–Sn, 2.39 Å [667].

The complexes $[HPt(SnCl_3)(R_3P)_2]$ (R = Et, Ph) and *cis*- and *trans*-$[Pt(SnCl_3)Cl(Ph_3P)_2]$ have been prepared by treating the chloro-complexes with $SnCl_2$ [664].

The complexes $L_2XPtAuL$ (L = Ph_3P; X = Cl, Br), $L_2XPtHgX$ (X = Cl, I), $L_2IPtMIL_2$ (M = Ni, Pt), $L_2ClPtCuL_3$ and $L_2ClPtSnPh_3$ have been prepared from $Pt(Ph_3P)_3$ and L_nMX_n or MX_n [668].

7.6. COMPLEXES OF PLATINUM(IV)

Quadrivalent platinum has the d^6 configuration and all the complexes are diamagnetic. This oxidation state is much more stable for platinum than for palladium. Complexes are formed with halide ions, nitrogen ligands and alkyl groups; all are octahedral. As with Pt(II), numerous examples of *cis–trans* isomerism are known.

Halide, Thiocyanate and Cyanide Complexes

The complexes $[PtX_6]^{2-}$ (X = F, Cl, Br, I, SCN, SeCN) are known but the corresponding cyano-complexes do not appear to have been isolated. The colours are: fluoro, pale yellow; chloro, deep yellow; bromo, dark red; iodo, brownish black; thiocyanato, orange; selenocyanato, deep orange. The spectra of $[PtCl_6]^{2-}$ and $[PtBr_6]^{2-}$ display weak shoulders at 22,000 and 19,000 cm^{-1}, respectively; these have been assigned as the transition $^1A_{1g}(t_{2g})^6 \rightarrow {}^3T_{1g}(t_{2g})^5(e_g)$. Stronger bands occurring at 28,400 and 23,000 cm^{-1} respectively have been identified with the transition $^1A_{1g} \rightarrow {}^1T_{1g}(t_{2g})^5(e_g)$ [669].

The acids $H_2[PtX_6]\cdot aq$ and the lithium and sodium salts are hydrated and very soluble, whereas the NH_4, potassium, rubidium and caesium salts are anhydrous and sparingly soluble in cold water. The salts $M_2[PtF_6]$ (M = K, Rb, Cs) are isomorphous with $K_2[GeF_6]$. Radiochemical and other studies have established that the Pt–Cl bond is *ca.* 12 kcal stronger than the Pt–I bond; the replacement of chlorine by iodine occurs in solution because of entropy and solvation factors[670]. Treatment of $M_2[PtCl_6]$ with BrF_3 yields $M_2[PtCl_3F_3]$ (M = K, Rb, Cs) [671]. The pentachloro complex $[PtCl_5OH]^{2-}$ has been isolated as the barium, silver and thallium salts, while tetrahalides of the type $M_2[PtX_4(OH)_2]$ (X = Cl, Br, I) and $M_2[PtCl_2(OH)_4]$ have also been obtained[604].

Several cyano-complexes have been reported. Oxidation of *trans*-$[Pt(NH_3)_2(CN)_2]$ with X_2 or HNO_3 yields *trans*-$[Pt(NH_3)_2(CN)_2X_2]$ (X = Cl, Br, I, NO_3). The complexes

[667] L. J. Guggenberger, *Chem. Communs.* 1968, 512.
[668] A. J. Layton, R. S. Nyholm, G. Pneumaticakis and M. L. Tobe, *Chem. Ind.* 1967, 465.
[669] C. J. Ballhausen, *Introduction to Ligand Field Theory*, McGraw-Hill, London (1962), p. 283.
[670] A. J. Poë and M. S. Vaidya, *Nature* **184** (1959) 1139.
[671] D. H. Brown, K. R. Dixon and D. W. A. Sharp, *J. Chem. Soc.* A, 1966, 1244.

$K_2[Pt(CN)_5X]$ (X = Cl, Br), $[Pt(NH_3)_2(CN)_3I]$, $[Pt(NH_3)_2(CN)_2(NO)(NO_3)]$ and $[Pt(MeNH_2)_2(CN)X_3]$ (X = Cl, Br, I; $X_3 = ClBr_2$, $Cl(NO_2)_2$) have been reported[623, 672].

Complexes of Oxygen Ligands

The hydrated oxide $PtO_2 \cdot 4H_2O$ can be made by heating a solution of $H_2[PtCl_6] \cdot aq$ to boiling with NaOH, then adding acetic acid which precipitates the compound as a pale yellow insoluble powder. It has been formulated as $H_2[Pt(OH)_6]$ but this cannot be correct as there is nothing to solvate the protons. The compound undoubtedly has a polymeric structure. However, when freshly precipitated, it dissolves in alkali to give a pale yellow solution from which $M_2[Pt(OH)_6]$ (M = Na, K, Ag, Tl) have been obtained. The potassium salt is isomorphous with $K_2[Sn(OH)_6]$ [604].

The action of Cl_2 on $Na_2[Pt(C_2O_4)_2]$ yields the yellow Pt(IV) oxalato-complex $Na_2[Pt(C_2O_4)_2Cl_2]$; the potassium and caesium salts have also been prepared[604].

Complexes of Sulphur and Selenium Ligands

Fewer complexes of sulphur ligands are known for Pt(IV) than for Pt(II). Most thiols reduce Pt(IV) to Pt(II). The organic sulphide complexes $[Pt(SR_2)_2X_4]$ (R = Me, Et, Pr^n, Pr^i, Bu^t, Bu^s, Bz; X = Cl, Br or I) have been prepared by oxidation of the Pt(II) complexes $[Pt(SR_2)_2X_2]$ with X_2. Some have been obtained in two forms, which may be *cis*- and *trans*-isomers. The selenide complexes $[Pt(SeR_2)_2X_4]$ (R = Me, Et, Bz; X = Cl, Br, I or NO_3) and the mixed compounds $[Pt(SEt_2)(SeEt_2)X_4]$ (X = Cl, Br, I) have been reported[626].

The compounds $[Pt(dth)_2Cl_4]$ (dth = 1,4-dithian or 1,3,5-trithian) are similar to the dialkyl sulphide complexes. The compound $[PtCl_4(H_2NCH_2CH_2SCH_2CH_2)\overset{+}{N}H_3]Cl^-$ was optically resolved, the assymmetry of the complex being due to the trigonal pyramidal arrangement of the sulphur atom.

Complexes of Nitrogen Ligands

Ammine complexes are known of every type from $[Ptam_6]X_4$ to $M[PtamX_5]$ (am = NH_3 or amine).

Hexammine-type complexes. The hexammine chloride $[Pt(NH_3)_6]Cl_4 \cdot 2H_2O$ has been obtained by the action of liquid NH_3 on $(NH_4)_2[PtCl_6]$; the hydroxide, carbonate, nitrate and fluoride are also known. The chelate complexes $[Pt(chel)_3]X_4$ (chel = en, pn) are known with halide and oxy-anions and have been resolved into *d*- and *l*-optical antimers. The mixed complex $[Pt(NH_3)_4en]^{4+}$ can also be prepared[626].

Pentammine-type complexes. The chloropentammine can be prepared by the action of concentrated NH_3 solution on $(NH_4)_2[PtCl_6]$ in the presence of $(NH_4)_2CO_3$ which precipitates $[Pt(NH_3)_5Cl]_2(CO_3)_3$. When once isolated, the pentammines are very stable. All attempts to replace chlorine by any other radical except bromine and OH have failed. The bromo- and hydroxo-pentammine series $[Pt(NH_3)_5X]^{3+}$ (X = Br, OH) can be prepared. The sulphates, oxalates and chromates of the pentammine salts are insoluble[626].

Tetrammine-type complexes. These salts can usually be made by oxidation of $[Pt(NH_3)_4]^{2+}$ with X_2. The dichlorotetrammine is known in *cis* and *trans* forms. The species $[Pt(NH_3)_4X_2]^{2+}$ (X = OH, Br, SCN, NO_2; 2X = SO_3), $[Pt(NH_3)_2am_2Cl_2]^{2+}$ (am = $MeNH_2$, $EtNH_2$, py) and $[Ptpy_4X_2]^{2+}$ (X = Cl, Br, OH) have been prepared[626].

[672] I. I. Chernyaev and T. N. Leonova, *Zh. Neorg. Khim.* **10** (1965) 1935.

The very slow exchange of Cl^- ions with $[Pten_2Cl_2]^{2+}$ is catalysed by the presence of $[Pten_2]^{2+}$; use has been made of this phenomenon in the synthesis of a series of $[Pten_2X_2]^{2+}$ salts by adding a catalytic amount of $[Pten_2]Cl_2$ to a solution of $[Pten_2Cl_2]^{2+}$, together with the anion required for substitution[673]. Optical resolution has been achieved for *cis*-$[Pten_2Cl_2]Cl_2$; the dextro-isomer was reacted with ethylenediamine to give optically pure D-$[Pten_3]Cl_4$ [674]. Two geometrical isomers of $[PtenNH_3pyClBr]Cl_2$ have been characterized; the D- and L-forms of $[PtenNH_3pyCl_2]Cl_2 \cdot 4H_2O$ have been obtained and both display positive and negative Cotton effects[675]. The chelates $[Pten_2X_2]^{2+}$ (X = Br, SCN, OH; 2X = CO_3), $[Pten_2XY]^{2+}$ (X = OH; Y = F, Cl), $[Ptpn_2X_2]^{2+}$ and $[Pt\{N(CH_2CH_2NH_2)_3\}Cl_2]^{2+}$ have been obtained[626].

Triammine-type complexes. These are not very numerous; they can be made by oxidation of Pt(II) triammine complexes. The following types are known: $[Pt(NH_3)_3X_3]^+$ (X = Cl, Br, I), $[Pt(NH_3)_3X_2Y]^+$ (X = Cl, I, NO_2; Y = Cl, Br, NO_2); many of these are known in two geometric isomeric forms[626, 676]. The salts $[Pt(en)amCl_2NO_2]^+$ and $[Pt(en)amCl(NO_2)_2]^+$ (am = NH_3, $EtNH_2$ or py) have been optically resolved[604]. Complexes containing tridentate amines are known: $[Pt(trid)Cl_3]Cl$ (trid = 2,2′-diaminodiethylamine, 1,2,3-triaminopropane, 2,2′,2″-terpyridyl)[626].

Diammine-type complexes. The neutral diammine-type complexes are very numerous. They can be made by oxidation of Pt(II) diammines, whereby the *cis* or *trans* configuration is preserved, or by heating a solution of $[PtCl_6]^{2-}$ with the amine. The compounds $[Ptam_2X_4]$ are insoluble. Chelate complexes $[Pt(chel)X_4]$ (chel = en, phen, bipy) are also known.

Improved synthetic routes have been described for the preparation of neutral Pt(IV) complexes containing five or six different ligands: e.g. $[PtNH_3pyClBrI(NO_2)]$ has been prepared into two isomeric forms[677].

Monoammine-type complexes. These are not very numerous; they can be prepared by oxidation of Pt(II) monoammines or by reaction of $[PtCl_6]^{2-}$ with the amine. The known complexes include $[PtamCl_5]^-$ (am = NH_3, py, β-picoline, MeCN) and $[Pt(NH_2OH)Br_5]^-$ [626].

Azide complex. The orange–yellow $[AsPh_4]_2[Pt(N_3)_6]$ is known[641].

Nitrosyl complexes. Several nitrosyl complexes have been prepared by the reaction of concentrated HNO_3 on Pt(II) compounds. They apparently contain the negatively charged ligand NO^-, which is known in only a few other instances, e.g. $[Co(NO)(CN)_5]^{3-}$. The compounds which have been reported include $K_2[Pt(NO_2)_4(NO)(NO_3)]$, $[Pt(NH_3)_2(NO_2)_2(NO)(NO_3)]$ and $[Pten_2(NO)X](NO_3)_2$ (X = Cl, NO_3) [678].

Other nitrogen complexes. Ethylenediamine-*N*,-*N*′diacetic acid forms $[PtCl_2(O_2CCH_2NHCH_2CH_2NHCH_2CO_2)] \cdot 2H_2O$, which is known in *cis* and *trans* forms. Oxidation of the Pt(II) complex is of interest, since the incoming chloro groups are *cis*, which is unusual[679].

[673] R. C. Johnson and F. Basolo, *J. Inorg. Nucl. Chem.* **13** (1960) 36.
[674] Chui Fan Liu and J. Doyle, *Chem. Communs.* 1967, 412.
[675] I. I. Chernyaev, T. N. Fedotova and A. N. Adrianova, *Zh. Neorg. Khim.* **11** (1966) 1349, 1729.
[676] I. I. Chernyaev and V. S. Orlova, *Zh. Neorg. Khim.* **12** (1967) 2415.
[677] L N. Essen and A. D. Gel'man, *Zh. Neorg. Khim.* **1** (1956) 2475.
[678] L. A. Nazarova, I. I. Chernyaev and A. N. Kolesnikova, *Zh. Neorg. Khim.* **10** (1965) 2828.
[679] C. F. Liu, *Inorg. Chem.* **3** (1964) 680.

Compounds containing Pt(II) *and* Pt(IV). There are several deeply coloured compounds whose stoichiometry suggests that they contain Pt(III); however, they are lattice compounds containing equimolar quantities of Pt(II) and Pt(IV). If Cl_2 is passed into a solution of Cs_2PtCl_4 at 0°, a dark green complex having the stoichiometry Cs_2PtCl_5 is precipitated[604]. X-ray analysis of $Pt(NH_3)_2Br_3$ shows that the structure consists of alternate layers of octahedral $Pt(NH_3)_2Br_4$ and square-planar $Pt(NH_3)_2Br_2$ molecules with the *trans*-bromo groups of the Pt(IV) complex acting as bridges: Pt(IV)–Br (chain) 2.5 Å; Pt(II)–Br (chain) 3.1 Å [447]. The structure of $PtenBr_3$ is similar[680]; in the crystalline state no isotopic exchange occurs but in DMF solution exchange is catalysed by Br^- ions[681]. Wolffram's red salt $Pt(EtNH_2)_4Cl_3 \cdot 2H_2O$ consists of octahedral $[Pt(EtNH_2)_4Cl_2]^+$ and $[Pt(EtNH_2)_4]^{2+}$ ions linked by chloro-bridges with the other four Cl^- ions in the lattice; it is strongly dichroic[447].

Phosphine and Arsine Complexes

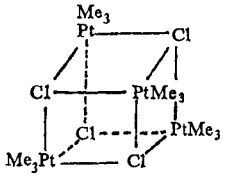
Phosphines and arsines reduce Pt(IV) to yield Pt(II) complexes. Nevertheless, some Pt(IV) complexes can be obtained by oxidation of Pt(II) complexes: *cis*- and *trans*-$[Pt(Pr_3P)_2Cl_4]$ and the chloro-bridged dimer $[Pt(Pr_3P)Cl_4]_2$ have been reported[550].

The bidentate arsine ligands *o*-phenylenebisdimethylarsine (As–As) and 8-dimethylarsinoquinoline (N–As) form the complexes $[Pt(As–As)_2X_2](ClO_4)_2$ (X = Cl, Br, I) [464] and $[Pt(N–As)_2Cl_2](ClO_4)_2$ [555] and the triarsine bis(bis-3-dimethylarsinopropyl)arsine forms $[Pt(As–As–As)X_3]ClO_4$ (X = Br, I) [550].

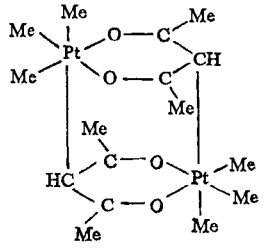
Alkyl Complexes

Quadrivalent platinum forms a number of σ-bonded carbon complexes which are remarkably stable. There are compounds like $[(PR_3)_2PtMe_2I_2]$ which can be obtained by the reaction of MeI with *trans*-$[(PR_3)_2Pt(Me)I]$ [550]. The reaction of MeMgI with $PtCl_4$ yields mainly Me_3PtI but Me_2PtI_2, $MePtI_3$ and $MePtI_5$ have been isolated; apart from Me_3PtI, the structures are not known. The trimethyls Me_3PtX (X = Cl, I, OH) are tetrameric in benzene and are not attacked by acids or alkalis in the cold.

The chloro-complex $[Me_3PtCl]_4$ has three-way chloro-bridges as shown in (CLVI); the Pt–Pt distance is 3.73 Å [449]. The tetramethyl $[Me_4Pt]_4$ was reported to have a similar structure with methyl bridges but the existence of this compound has recently been questioned and the structure determination was apparently carried out on $[Me_3PtOH]_4$ [682].



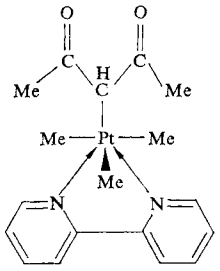
(CLVI)



(CLVII)

[680] T. D. Ryan and R. E. Rundle, *J. Am. Chem. Soc.* **83** (1961) 2814.
[681] R. E. McCarley, D. S. Martin and L. T. Cox, *J. Inorg. Nucl. Chem.* **7** (1958) 113.
[682] G. R. Hoff and C. H. Brubaker, *Inorg. Chem.* **7** (1968) 1655; M. N. Hoechstetter and C. H. Brubaker, *ibid.* **8** (1969) 400.

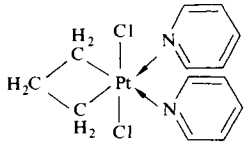
The acetylacetonato complex $[Me_3Ptacac]_2$ has the structure (CLVII); this was the first reported instance of acetylacetone being bound through the γ-carbon atom; the bipyridyl complex $[Me_3Pt(acacH)(bipy)]$ has the structure (CLVIII) in which the β-diketone is coordinated via the γ-carbon atom only[464].



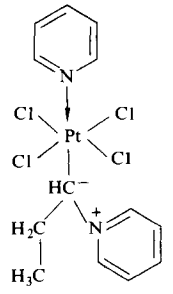
(CLVIII)

A structure determination of $Me_6Pt_2en_3I_2$ shows that the complex contains the centrosymmetric cation $[enMe_3Pt\text{–}en\text{–}PtMe_3en]^{2+}$ which has one ethylenediamine bridge[449]. In $Me_6Pt_2(acac)_2en$ the acetylacetonato groups are chelated through the oxygen atoms and the two $Me_3Pt(acac)$ moieties are also linked by an en bridge[683]. In $[Me_3Pt(chel)]_2$ (chelH = salicylaldehyde, 8-quinolinol) the platinum atoms are 6-coordinate, being bridged by two phenolic oxygen atoms[684]. In view of these rather unexpected structures which Pt(IV) complexes assume in order to attain octahedral coordination, it is extremely doubtful if any other configuration is adopted by Pt(IV).

Whereas the compounds $[Me_3PtX]_4$ (X = Cl, I, OH) are soluble in benzene and insoluble in water, $[Me_3Pt]NO_3$ and $[Me_3Pt]_2SO_4$ are insoluble in benzene and strong electrolytes in water[682]. In benzene solution $[Me_3PtI]_4$ takes up NH_3 to form $[Me_3Pt(NH_3)_2I]$. The complexes $[Me_xPt_{4-x}L_2]$ (L = R_3P, R_3As; x = 1–3) and $[Me_3PtL_3]X$ (L = amine, pyridine, thiourea; X = Cl, Br, I) have been prepared[685, 686]. The ethyl complex $[Et_3PtCl]_4$ and the cyclopentadienyl complex $[(\pi\text{-}C_5H_5)PtMe_3]$ have also been reported[687, 688].



(CLIX)



(CLX)

683 A. Robson and M. R. Truter, *J. Chem. Soc.* 1965, 630.

684 K. Kite and M. R. Truter, *J. Chem. Soc.* A, 1966, 207; M. R. Truter and R. C. Watling, *ibid.* 1967, 1955.

685 O. M. Ivanova and A. D. Gel'man, *Zh. Neorg. Khim.* 3 (1958) 1334.

686 J. D. Ruddick and B. L. Shaw, *Chem. Communs.* 1967, 1135.

Cyclopropane reacts with a solution of $PtCl_2$ in acetic anhydride to yield $[(C_3H_6)PtCl_2]_n$ which is converted by pyridine into the monomeric complex $[(C_3H_6)PtCl_2py_2]$. The latter has the structure (CLIX). In warm benzene this complex changes to a yellow "isomer" which, on recrystallization from $CHCl_3$–CCl_4 solution, yields a complex with the "ylide" structure (CLX) [589].

o-Allylphenyldimethylarsine forms the Pt(IV) complex (CLIV) which contains a σ-carbon bond (see p. 200).

Hydride Complexes

Oxidative addition of HCl to *trans*-$[HPtCl(R_3P)_2]$ yields the Pt(IV) hydrides $[H_2PtCl_2(R_3P)_2]$ (R = Et, Ph) [662, 663].

7.7. COMPLEXES OF PLATINUM(V)

This oxidation state is confined to salts of the $[PtF_6]^-$ ion. The complexes $M[PtF_6]$ ($M = O_2$, Xe, K, NO, NO_2, ClF_2, IF_4, XeF_5) have been reported; their colours range from yellow to reddish orange. The powerful oxidizing agent PtF_6 is able to oxidize O_2 and Xe to O_2^+, Xe^+ and Xe^{2+}, giving the complexes $O_2[PtF_6]$, $Xe[PtF_6]$ and $Xe[PtF_6]_2$. The oxygenyl compound can also be obtained by the action of a mixture of F_2 and O_2 on platinum sponge at 450°. Upon hydrolysis it gives $K[PtF_6]$ [601, 603].

Xenon reacts with $[PtF_5]_4$ at 180–220° and 5 atm to give $[XeF_5][PtF_6]$. A structure determination shows that the xenon atom has five close fluorine atoms in a square-pyramidal arrangement[602].

In the spectra of $M[PtF_6]$ ν(Pt–F) (ν_3) occurs at 583–650 cm^{-1}. The magnetic moment of $[PtF_6]^-$ is 1.74 BM at 300° and the complexes $M[PtF_6]$ obey the Curie–Weiss law with values of θ in the range 30–50° [689].

[687] S. F. A. Kettle, *J. Chem. Soc.* 1965, 5737, 6664.
[688] S. D. Robinson and B. L. Shaw, *Z. Naturforsch.* **18b** (1963) 507.
[689] N. Bartlett and S. P. Beaton, *Chem. Communs.* 1966, 167.

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INDEPENDENT OPINION

"These books are attractively bound and have clear print. Since the length and cost are not prohibitive, this set of books should be well within the budget of most libraries. Not only will the professional chemist find these books useful, but students and other readers will find them a valuable reference source. (Comprehensive Inorganic Chemistry) should be found in every undergraduate and graduate library, as well as industrial libraries. Many professional chemists may even consider them for personal libraries. Highly recommended."

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INDEPENDENT OPINION

Volume 1 1467 pp + index

"This covers the chemistry of hydrogen, the noble gases, and of the elements of Groups IA, IIA, IIIB, carbon and silicon. The first three chapters deal with hydrogen, hydrides, deuterium and tritium and the fourth is an interesting discussion of the proton, protonic acids and the hydrogen bond. Two chapters follow on the inert gases, including interesting and extensive recent knowledge about their compounds set out by N. Bartlett and F. O. Sladky. Four chapters on the alkalis and alkaline earths contain a wealth of detail, although perhaps along traditional lines. N. N. Greenwood has written an excellent account on boron chemistry of book length in itself, and another chapter deals at length with much new informationabout aluminium, gallium, indium and thallium. Chapters 13 and 15 deal with carbon and silicon. Here it might have been expected that more would have been included on the high pressure chemistry of carbon and silicates, and mineral chemistry. Chapter 14 by M. L. H. Green and P. Powell is a useful introduction to the organic chemistry of the metallic elements, along modern lines of ligand field theory and ideas about metal complexes.

Throughout this volume, with its different authors, it is perhaps inevitable that there is some lack of uniformity in the extent of detail given. There are also a few lapses in symbolism, notation, and uniformity of units. Yet the whole must be regarded as a highly commendable collection of material which will be valuable to chemists of all kinds."

Professor Sir Harold Thompson FRS
Oxford

Volume 2 1594 pp + index

"Volume 2 is concerned with the chemistry of the elements of Groups IV, V, VI, VII. The general impression on reading the various chapters of this volume is the great effectiveness in reporting a considerable amount of chemistry in a very digestible form. The systematic presentation applied to each chapter allows a rapid assessment of the appropriate chemical information, and the text is well documented with reference to the original literature plus good review articles for a more detailed coverage. Perhaps a minor criticism of this work lies in the indexing; the subject index is relatively sparse for a text of such magnitude and it would have been of considerable utility to have a formulae index to the text.

The area of chemistry covered by this work is obviously very great, but it does appear to have dealt with it in a very succinct manner for the majority of the text, which extends to approximately 1500 pages. The two major chapters in the book are associated with the chemistry of nitrogen, approximately 240 pages, and the chemistry of the halogens (excepting fluorine), approximately 500 pages. The book thus encompasses in one volume what would normally be a series of books. Both of the above mentioned chapters are admirable and the authors, K. Jones on nitrogen with A. J. Downs and C. J. Adams on the halogens, are to be commended on both the presentation and coverage. The chapter on the halogens illustrates the real strength of the series, in that detailed chemical information is not only presented but discussed in physico-chemical theoretical terms. A scientific compendium of this size often suffers from the "catalogue" approach, but the present text presents the chemistry in critical mode with a realistic assessment of the various physical methods used in property determination. Thus the properties of the halogens are discussed in terms of bond energies, bond lengths, vibrational properties, e.s.r., n.m.r., n.q.r. and Mossbauer spectroscopy, electronic and magnetic properties and dipole moments allowing a detailed appraisal of the use of various modern methods in studying the chemical properties reviewed.

Considering the magnitude of the task undertaken, it is extremely pleasing to note the number of chapters referring to papers in the 1971 period—a truly great commendation on the overall editorship of these volumes. Perhaps a general note in each volume stating the period covered by the references would have been of help. In general this work provides a welcome and unique addition to the inorganic literature."

Professor J. Lewis FRS
Cambridge

Volume 3 1370 pp + index

"This volume covers the chemistry of the elements of the d-block of the Periodic Table (the transition elements), with the exception of the Lanthanide elements (Vol. 4), the Actinide elements (Vol. 5) and some special aspects which are common to many of the transition elements (Vol. 4). The volume is therefore concerned specifically with the three elements which characterize each of the ten transition groups, and the chapters are mostly grouped in this way. However, the six platinum metals are treated in one chapter which is the best way to fit these similar elements into the overall scheme which is standard for all five volumes. There are altogether 17 chapters, written by 14 authors who are internationally

recognized 1370 pages of text and a useful 17 page index.

The five volumes are quite remarkable, in that they can justifiably claim to be comprehensive, yet at the same time remain interesting and readable; they are probably unique in this respect. Volume 3 serves as an excellent source-book for the essential physical constants of all important compounds (simple and complex) of the transition metals. These are arranged so that significant comparisons are made wherever possible, and there are extensive references. It says much for the ingenuity of the editors, authors, and particularly the printers that the presentation of such an amount of information has been possible, while still maintaining the readability of the text. Throughout the volume chemical properties and reactions are discussed and interpreted rather than listed. The need for skilled correlation of data is particularly important in Volume 3, since it is in the area of the transition elements that a major part of the research work in inorganic chemistry has been published in recent years, and in this area also there has been a major interaction of inorganic with theoretical chemistry.

This volume must surely become the first point of reference for research workers and teachers alike. The transition elements play an important role in Pure and Applied Chemistry, Physics, Materials Science and Biology, and the authors clearly intend their chapters to be of value to this wide audience. Teachers at any level will also appreciate the very high quality of the general presentation, discussion, formulae and diagrams. Apart from reference to the original literature, few scientists will find it necessary to look outside this volume for their material."

Professor C. C. Addison FRS
Nottingham

Volume 4 994 pp + index

"Volume 4 is concerned with the general chemistry of the lanthanides and some special topics in transition metal chemistry.

Therald Moeller has packed a great amount of the fundamental chemistry of the lanthanides into his 101 pages in an interesting and scholarly manner with tables of essential data. Important recent developments in their organometallic chemistry have come too late to be included, but the chapter provides a useful fairly detailed first reference to their inorganic chemistry.

The subjects of the surveys are topical and obviously bear the mark of the late Sir Ronald Nyholm. They vary considerably in detail of treatment, interest and authority. Generally they emphasize recent work until about 1969–70 but rarely show a sense of history. They vary in length from 60 to 200 pages, mostly around 100 pages. They are authoritative and useful surveys all giving numerous references to recent reviews and original work. The authors are well known chemists whose style and subject matter are familiar to most inorganic chemists. There are eight surveys as follows:—

Carbonyls, cyanides, isocyanides and nitrosyls by W. Griffith. Compounds of the transition elements involving metal-metal bonds by D. L. Kepert and K. Vrieze. Transition metal hydrogen compounds by J. C. Green and M. L. H. Green. Non-stoichiometric compounds: an introductory essay by D. J. M. Bevan. Tungsten bronzes, vanadium bronzes and related compounds by P. Hagenmuller. Isopolyanions and heteropolyanions by D. L. Kepert. Transition metal chemistry by B. F. G. Johnson. Organo-transition metal compounds and related aspects of homogeneous catalysis by B. L. Shaw and N. I. Tucker.

This volume has its own subject index of sixteen and a half pages, and is well produced with numerous tables of data and references provided at the foot of each page."

Professor J. Chatt FRS
Sussex

Volume 5 635 pp + Master index

"Volume 5 is devoted to the Actinides (635 pp) and the Master Index (78 pp). The latter serves little purpose since it merely indicates the subsections of CIC, and thus repeats the indexes in each individual volume. Indeed, as the treatment of each element or series of elements follows a standard pattern, the volumes are essentially self-indexing anyway. A one-page table of contents at the beginning of Volume 5 would have been more helpful and is a curious omission. The running headings at the top of each double page are also singularly uninformative, only three being used: 'The Elements' for 102 pages, 'Compounds' for 361 pages and 'Solution Chemistry' for the remaining 171 pages.

The treatment of actinium and the actinides (elements 89–103) is both readable and authoritative. Nine of the contributors are from AERE, Harwell, and the other five (with one exception) are from nuclear chemistry institutes in Sweden and Germany. In reviewing these 5f elements it is salutary to recall that the majority have been synthesized for the first time within the last 30 years—yet the number of compounds known and the amount of information on them has already outstripped the more limited chemistry of their 4f congeners, the lanthanides. The authors have done a magnificent job in assembling, collating, assessing, and systematizing a vast amount of data on the physical and chemical properties of these elements and their numerous compounds. The work, which is extensively referenced, will undoubtedly remain the standard first source of information in this area for many years to come."

Professor N. N. Greenwood FRIC
Leeds