

OSMIUM AND ITS COMPOUNDS

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Discovery and Natural Occurrence.—The element was discovered in 1802 by Smithson Tennant (1761—1815) who prepared the volatile tetroxide by the acid distillation of the black residues remaining from digestion of native platinum with aqua regia. He decided to call the new element ptène (from *ptenos*, volatile), but wiser counsels prevailed and he subsequently wrote that “as the smell is one of its most distinguishing characters, I should on that account incline to call the metal *Osmium*.¹”

Like ruthenium, which it in many ways resembles, osmium is a rare and consequently expensive element (the current price for the pure metal is £60 an ounce). Its abundance in the upper part of the earth’s crust is probably no greater than 0.001 part per million, although the abundance in meteorites exceeds the terrestrial figure by a factor of about 1500. In nature it is always found with one or more of the other platinum metals, and occasionally with gold. The most important mineral sources are osmiridium, which is an osmium-iridium alloy containing varying amounts of other heavy metals, found mainly in Alaska and on the Witwatersrand gold reef; and laurite, an osmium-ruthenium disulphide found chiefly in Borneo and the Transvaal. Small quantities of osmium-bearing minerals have also been discovered in the Urals, Ethiopia, and Colombia.

Extraction.—The modern method for extracting osmium in essence duplicates Tennant’s original procedure: the ores are treated with aqua regia and the insoluble residues extracted with an oxidising flux such as sodium peroxide, and the resulting mass is dissolved in water, filtered, and the filtrate distilled with nitric acid to give osmium tetroxide which can then be reduced directly to the metal.

Properties of the Metal.—Osmium has atomic number 76 and atomic weight 190.2. Seven naturally occurring isotopes have been identified with mass numbers (percentage abundances in parentheses): 184 (0.018), 186 (1.59), 187 (1.64), 188 (13.3), 189 (16.1), 190 (26.4) 192 (41.0), and of these only two have nuclear spins (187, $I = \frac{1}{2}$, and 189, $I = 3/2$). The following artificial radioisotopes have been made: 181, 182, 183, 185, 187, 189, 190, 191, 193, 194, and 195, and of these ^{194}Os is the longest-lived with a half-life of about seven hundred days.² The physical properties of the six platinum metals have recently been reviewed:³ annealed osmium metal is the hardest of the six and has the highest melting and boiling points

¹ Smithson Tennant, *Phil. Trans.* 1804, **94**, 411; Nicholson’s *Journal of Natural Philosophy*, 1805, **10**, 24.

² D. Strominger, J. H. Hollander, and G. T. Seaborg, *Rev. Mod. Phys.*, 1958, **30**, 585; K. Rankama, “Progress in Isotope Geology,” Interscience, New York, 1963, 458.

³ *Platinum Metals Review*, 1963, **7**, 147.

(estimated as 3050° and 5500°C). It was once thought to be the densest of all elements but the latest figures³ indicate that it has the same specific gravity as iridium (22.61 for osmium and 22.65 for iridium at 20°C). Like ruthenium but unlike the other platinum metals it has a close-packed hexagonal crystal lattice structure ($a = 2.7341 \text{ \AA}$, $c/a = 1.5800$). Chemically it is the most reactive of the platinum metals. Finely powdered osmium is very slowly oxidised even at room temperatures by the air and so always carries a perceptible odour of the tetroxide, but in more condensed forms the metal is not affected by air or oxygen below 150°C. The product of oxidation is the tetroxide though there is evidence of surface film formation of the dioxide below 400°C.⁴ It is attacked by aqua regia and oxidising acids only over a long period of time and is barely affected by hydrochloric and sulphuric acids. Attack by fluorine and chlorine takes place above 100°C to give a mixture of halides. It is dissolved by molten alkalis and by oxidising fluxes, while the reaction with hydrogen peroxide can be of almost explosive violence.

Catalytic properties. The price of the metal limits its commercial application as a catalyst. Like all the platinum metals it does possess considerable catalytic powers, though there is little evidence that these are superior to those of palladium or platinum. It will catalyse the oxidation of carbon monoxide, carboxylic acids, aldehydes, alcohols, and amines, and the hydrogenation of ketones, olefins, acetylenes, and heterocyclic systems. Little detailed study has been made of such reactions apart from an investigation of the high-temperature synthesis of ammonia at atmospheric pressures over an osmium-silica catalyst⁵ and of the hydrogenation of olefins and acetylenes over osmium-alumina.⁶

Applications of Osmium and its Compounds.—These are few, owing largely to the price of the materials, their nature, and the difficulty of working osmium metal. The latter was once used in alloy for electric light filaments and for fountain pen nibs, and it is still used for the latter purpose and for watch and clock bearings. Osmium tetroxide remains a valuable reagent for organic hydroxylations (see below) and is extensively used in microscopy for staining tissues. Other occasional uses for osmium include passivation of iron, production of artificial diamonds, detection of speeds of explosion in gelignite, and photographic processing.

Compounds of Osmium.—No less than nine oxidation states (VIII to 0) have been established for the compounds (or complexes; in this Review the terms will be used synonymously) of osmium. The tendency of certain ligands to stabilise higher or lower oxidation states is well brought out by the compounds (Table 1). Thus all the "high" oxidation state complexes (VIII to V) contain either fluoride, oxide, or nitride ligands, all of which are

⁴ J. C. Chaston, *Platinum Metals Review*, 1965, **9**, 51.

⁵ M. Temkin and S. L. Kiperman, *Zhur. fiz. Khim.*, 1947, **21**, 927; S. L. Kiperman and V. S. Granovskaya, *ibid.*, 1951, **25**, 557.

⁶ G. Webb, and P. B. Wells, *Trans. Faraday Soc.*, 1965, **61**, 1232.

TABLE 1. *Stabilisation of oxidation states in osmium complexes.*

Oxidation state:	VII	oxyhalides	Donor group	V	IV
VIII		$(\text{OsO}_3\text{F}_2)_n$ $(\text{OsO}_3\text{F}_3)^-$ $(\text{OsO}_4\text{F}_2)^{2-}$	OsO_4 $[\text{OsO}_4(\text{OH})_2]^{2-}$	—	—
VII	—	OsOF_5	$(\text{OsO}_6)^5-$ $(\text{OsO}_5)^3-$	—	—
VI	(OsF_6)	OsOF_4 , OsOCl_4 $(\text{OsO}_2\text{X}_4)^{2-}$ (X = Cl, Br)	OsO_3 ? $[\text{OsO}_2(\text{OH})_4]^{2-}$	—	—
V	$(\text{OsF}_5)_n$ $(\text{OsF}_6)^-$	—	—	—	—
IV	OsF_4 , OsCl_4 , $(\text{Os}_2\text{OCl}_{10})^{4-}$ OsBr_4 , $(\text{OsX}_6)^{2-}$ (X = F, Cl, Br, I)	OsO_2 , OsX_2 (X = S, Se, Te)	—	—	—
III	OsCl_3 , OsI_3 $(\text{OsX}_6)^{3-}$ (X = Cl, Br, I)	—	Os_2O_3 ? (Os acac ₃)	$[\text{Os}(\text{NH}_3)_6]^{3+}$ $(\text{Os phen}_3)^{3+}$ $(\text{Os bipy}_3)^{3+}$	Carbonyl halides $[\text{Os}(\text{CN})_6]^{3+}$
II	OsCl_2 , OsBr_2 , OsI_2	—	OsO $(\text{Os}(\text{SO}_3)_3)^{4-}$	$(\text{Os phen}_3)^{2+}$ $(\text{Os bipy}_3)^{2+}$	Carbonyl halides $[\text{Os}(\text{CN})_6]^{4-}$ $[\text{Os}(\text{CO})_6]^{2+}$?
I	OsI	—	—	—	Carbonyl halides
O	—	—	—	—	$[\text{Os}(\text{CO})_5]$ $[\text{Os}_3(\text{CO})_{12}]$

good π -donors and small in size, while good π -acceptor ligands such as CO, CN⁻, NO⁺, 2,2'-bipyridyl, phosphines, arsines, and stibines stabilise the "low" (II to O) states; the intermediate (IV and III) states are stabilised by ligands which are good σ -donors but poor π -donors or acceptors (NH₃, Cl⁻, Br⁻, I⁻, ethylenediamine,* etc.). Osmium most closely resembles rhenium, particularly in its oxide and fluoride chemistry, and ruthenium, particularly in its halogen and nitrogen chemistry and in its ability to form polynuclear complexes with nitrogen and oxygen donors.

Almost all osmium complexes are octahedrally co-ordinated. The chief exceptions are the tetroxide and the osmiamate (tetrahedral) and the pentacarbonyl (probably trigonal bipyramidal); pentaco-ordination may also occur in the gaseous pentafluoride and in OsO₄.NH₃, while hepta- and octa-co-ordination may be found in (OsOCl₆)²⁻ and [Osen₂(en-H)₂]²⁺ respectively. The general principle that third-row transition elements may often show higher co-ordination numbers than the corresponding second- or first-row elements is exemplified by the oxy-complexes of ruthenium-

*Ethylenediamine = en. Ethylenediamine minus a N-hydrogen is shown as en-H.

(vi), -(vii), and -(viii), all of which are tetrahedral, while for osmium-(vi), -(vii), and -(viii) the only tetrahedral oxy-species is OsO_4 , the others being octahedral.

Wherever possible, mention has been made of work relating to structure and bonding in the complexes. There is little direct structural data (Table 2 summarises the available information), but there is a large body of work

TABLE 2. *Structural data on osmium complexes.*

Oxidation state	Complex	Bond lengths (Å)	Ref.
VIII	$\text{OsO}_4^* \dagger$	Tetrahedral; $\text{Os}-\text{O} = 1.717$	14
"	$\text{K}(\text{OsO}_3\text{N}) \ddagger$	Tetragonal bisphenoid; $\text{Os}-\text{O} =$ $\text{Os}-\text{N} = 1.56$	25
VI	$\text{OsF}_6^* \dagger$	Octahedral; $\text{Os}-\text{F} = 1.831$	33
"	$\text{trans-K}_2[\text{OsO}_2(\text{OH})_4] \ddagger$	D_{4h} ; $\text{Os}-\text{O} = 1.77$; $\text{Os}-(\text{OH}) = 2.03$	39
"	$\text{trans-K}_2(\text{OsO}_2\text{Cl}_4) \ddagger$	D_{4h} ; $\text{Os}-\text{O} = 1.75$; $\text{Os}-\text{Cl} = 2.38$	40
"	$\text{K}_2(\text{OsNCl}_5) \ddagger$	C_{4v} ; $\text{Os}-\text{N} = 1.61$; $\text{Os}-\text{Cl} (\text{trans}) =$ 2.16 ; $\text{Os}-\text{Cl} = 2.40$	42
"	$\text{K}[\text{OsNBr}_4(\text{H}_2\text{O})] \ddagger$	C_{4v} ; $\text{Os}-\text{N} = 1.61$, $\text{Os}-(\text{OH}_2) = 2.07$	42
V	$\text{K}(\text{OsF}_6) \ddagger$	Octahedral; $\text{Os}-\text{F} = 1.82$	48
IV	$\text{K}_2(\text{OsCl}_6) \ddagger$	Octahedral; $\text{Os}-\text{Cl} = 2.36$	53
II	$[\text{OsH}(\text{CO})\text{Br}(\text{PPh}_3)_3]$	$\text{Os}-\text{Br} = 2.60$; $\text{Os}-\text{P} = 2.56$ (1) and 2.34 (2)	102
"	$(\pi\text{-C}_6\text{H}_5)_2\text{Os}$	"Octahedral"; $\text{Os}-\text{ring} = 1.86$; $\text{C}-\text{C} = 1.42$; $\text{Os}-\text{C} = 2.22$	99
O	$[\text{Os}_3(\text{CO})_{12}] \ddagger$	Octahedral; $\text{Os}-\text{C} = 1.95$; $\text{C}-\text{O} =$ 1.14; $\text{Os}-\text{Os} = 2.88$	105

* Electron diffraction determination; all others X-ray.

† Infrared and Raman studies also reported (see text).

‡ Some distortion from full octahedral symmetry.

on electronic spectra of the halogeno-complexes, and in particular there has been much careful and systematic work on magnetic properties (Table 3). There is however room for very much more physicochemical research on the element, particularly on structures and on reaction kinetics.

Osmium (viii).—Osmium octafluoride was long thought to exist and in fact a cubic structure was assigned to it as a result of early electron-diffraction measurements, but recent work has made it clear that the compound is the hexafluoride,⁷ and it seems likely that old reports of an octachloride⁸ may also be discounted. The oxyfluorides (OsO_3F_2)_n and the derived salts (OsO_3F_3)⁻ are however well established⁹ as well as salts of the (OsO_4F_2)²⁻ anion.¹⁰ The greater tendency of fluorine to stabilise high-oxidation states than chlorine is illustrated by the fact that the highest oxychloride is of osmium(vi).

⁷ B. Weinstock and J. G. Malm, *J. Amer. Chem. Soc.*, 1958, **80**, 4466; G. B. Har-greaves and R. D. Peacock, *Proc. Chem. Soc.*, 1959, 85.

⁸ H. Morahrt and C. Wischin, *Z. anorg. Chem.*, 1893, **3**, 153, 166.

⁹ M. A. Hepworth and P. L. Robinson, *J. Inorg. Nuclear Chem.*, 1957, **4**, 24.

¹⁰ F. Krauss and D. Wilken, *Z. anorg. Chem.*, 1925, **145**, 166.

TABLE 3. *Magnetic properties of osmium complexes.*

<i>dⁿ</i>	Complex	Temperature range (°K)	μ eff (R.T.)	μ eff (predicted) ^a	Also studied:	Ref.
1	Ba ₂ Li(OsO ₆)	R.T.	1.44			31
2	OsF ₆	81—297	1.50	1.3		7
3	(OsF ₅) _n	101—295	2.06	3.1		44
3	K(OsF ₆)	80—300	3.34			46
4	K ₂ (OsF ₆)	90—300	1.31	1.4	Cs salt	<i>b</i>
4	K ₂ (OsCl ₆)	90—300	1.51		Cs salt	<i>b</i>
4	K ₂ (OsCl ₆) [*]	90—301	2.13		Cs, NH ₄ , Bu ⁿ ₄ N	52
4	K ₂ (OsBr ₆)	80—300	1.21		Cs salt	<i>b</i>
				1.55 ⁵⁵		
4	K ₂ (OsBr ₆) [*]	90—300	1.96		Cs, NH ₄ , Me ₄ N salts	52
4	K ₂ (OsI ₆)	80—300	1.38		Cs salt	<i>b</i>
5	[OsCl ₃ (AsPh ₂ Me) ₃]	80—295	1.80	1.75		<i>a</i>

* Measured at "infinite dilution" (see text).

R.T. = Room temperature

^a B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 1964, **6**, 162.

^b A. Earnshaw, B. N. Figgis, J. Lewis, and R. D. Peacock, *J.*, 1961, 3132.

Osmium tetroxide, OsO₄, is probably the commonest compound of osmium, although it is one of the most dangerous to handle on account of its high vapour pressure (the solid has a v.p. of 11 mm. at 25°C). It can be made by oxidation of the metal or of any of its compounds with nitric acid (ruthenium tetroxide reacts with nitric acid to give non-volatile products, so nitric acid distillation is a convenient and widely used method of separating the two elements). Osmium tetroxide forms yellow crystals (m.p. 40.6°, b.p. 131.2°) which exist in only one modification, not two as was once claimed. In the vapour phase and in organic solvents it is monomeric, and has no dipole moment. Michael Faraday was the first to demonstrate its diamagnetism. A considerable amount of thermodynamic data has been accumulated on the compound.¹¹ Both X-ray¹² and infrared with Raman¹³ measurements show the molecule to be tetrahedral, and electron-diffraction determinations confirm this¹⁴ (earlier electron-diffraction studies were incorrectly interpreted to indicate a distorted structure). The electronic absorption spectrum of the vapour has been measured¹⁵ and band assignments proposed,¹⁶ and oxygen¹⁷ nuclear resonance measurements made.¹⁷

¹¹ E. Ogawa, *Bull. Chem. Soc. Japan*, 1931, **6**, 314.

¹² A. Zalkin and D. H. Templeton, *Acta Cryst.*, 1953, **6**, 106.

¹³ L. A. Woodward and H. L. Roberts, *Trans. Faraday Soc.*, 1956, **52**, 615; 1960, **56**, 1267.

¹⁴ A. F. Wells, "Structural Inorganic Chemistry", 3rd edn. Oxford, 1962, pp. 456, 920.

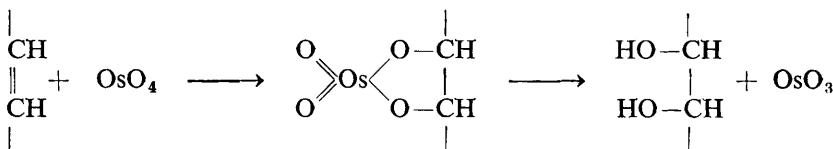
¹⁵ A. Langseth and B. Qviller, *Z. phys. Chem.*, 1934, **27**, B, 79.

¹⁶ A. Carrington and C. K. Jørgensen, *Mol. Phys.*, 1961, **4**, 395; S. P. McGlynn and M. Kasha, *J. Chem. Phys.*, 1956, **24**, 481.

¹⁷ B. N. Figgis, R. G. Kidd, and R. S. Nyholm, *Proc. Roy. Soc.*, 1962, **A**, 269, 469.

Chemically the compound is reactive and a powerful oxidising agent, though less so than ruthenium tetroxide. With alkalis it gives rather unstable octahedral osmium(viii) complexes of the form *trans*-[OsO₄(OH)₂]²⁻ and [OsO₄(OH)H₂O]⁻,^{10,18} while with such donor groups as ammonia and phosphorus trihalides, 1:1 and 2:1 adducts of unknown structures are obtained.¹⁹ Polarographic studies on solutions of the compound in various media and at various pH are reported,²⁰ and there is polarographic evidence for the existence of a peroxyosmate(viii).²¹

Osmium tetroxide is extensively used in organic chemistry as an oxidising agent and as a catalyst for oxidation. When dissolved in an inert organic solvent, it will react smoothly at room temperatures with olefinic double bonds to give *cis* diols, and in the presence of bases such as pyridine the reagent is sufficiently reactive to attack the π -system of aromatic hydrocarbons. Criegee showed in a classic piece of work that the reaction involved an osmium(vi) intermediate which can in many cases be isolated:²²



Olefinic hydroxylations can be carried out catalytically with a mixture of osmium tetroxide with barium or silver chromate (the mechanism is obscure; intermediates such as OsO₄ClO₃ and cyclic osmium esters have been proposed²³), or with Milas's reagent, which consists of an organic solution of hydrogen peroxide activated with a little osmium tetroxide. A recent review on alkene hydroxylations has been published.²⁴

There is some rather unconvincing evidence for the existence of an osmium(viii) tetrasulphide.

The osmiamates. Addition of aqueous ammonia to an alkaline solution of osmium tetroxide yields the very stable yellow ammonium osmiamate, (NH₄)(OsO₃N). X-Ray studies on the potassium salt show that the anion has a slightly distorted tetrahedral configuration (tetragonal bisphenoidal, a structure also shown by potassium per-ruthenate, KRuO₄), in which the osmium-oxygen and osmium-nitrogen distances are both given as

¹⁸ W. P. Griffith, *J.*, 1964, 245.

¹⁹ M. L. Hair and P. L. Robinson, *J.*, 1960, 2775; 1958, 106.

²⁰ L. Meites, *J. Amer. Chem. Soc.*, 1957, **79**, 4631; R. E. Cover and L. Meites, *ibid.*, 1961, **83**, 4706; J. Perichon, S. Palous, and R. Buvet, *Bull. Soc. chim. France*, 1963, 982.

²¹ K. Fulop and L. J. Csanyi, *Acta Chem. Acad. Sci. Hung.*, 1963, **38**, 193.

²² R. Criegee, *Annalen*, 1936, **522**, 75; R. Criegee, B. Marchand, and H. Wannowius, *ibid.*, 1942, **550**, 99.

²³ L. J. Csanyi, *Acta Chem. Acad. Sci. Hung.*, 1959, **21**, 35.

²⁴ F. D. Gunstone, "Advances in Organic Chemistry", Interscience, New York, 1960, vol. 1, 110.

1.56 Å;²⁵ and a similar conclusion was reached from studies on the infrared and Raman spectra of the compound.²⁶ The elucidation of the structure by purely chemical methods was one of the later triumphs of Werner, who showed in 1901 that the previously accepted formulation as a nitrosyl derivative, $[\text{Os}(\text{NO})\text{O}_2]^-$, was unlikely since thermal decomposition of the compound gave nitrogen rather than oxides of nitrogen, and treatment with hydrochloric acid gave the oxygen-free species $\text{K}_2(\text{OsNCl}_5)$, indicating the presence of a direct metal–nitrogen bond.²⁷ Free osmiamic acid is one of the products of the rather complicated reaction between liquid ammonia and osmium tetroxide;¹⁹ infrared studies on this and its deuterated form show that the proton in the anhydrous acid is attached to the oxygen rather than to the nitrogen to give $[\text{OsN}(\text{OH})\text{O}_2]^{28}$.

Osmium(vii).—This is a rare oxidation state both for osmium and ruthenium. An oxyfluoride (OsOF_5) has been made by the fluorination of osmium dioxide. It is paramagnetic and shows an unresolved fluorine magnetic resonance spectrum.²⁹ Recently some heptavalent osmates have been prepared: these include alkali metal salts of $(\text{OsO}_6)^{5-}$ and $(\text{OsO}_5)^{3-}$, made by heating potassium osmate and potassium superoxide with alkali-metal oxides.³⁰ The magnetic moment of $\text{Ba}_2\text{Li}(\text{OsO}_6)$ is consistent with the presence of osmium(vii).³¹ It is possible that the $(\text{OsO}_5)^{3-}$ ion should in fact be formulated as $[\text{OsO}_4(\text{OH})_2]^{3-}$, the osmium(vii) analogue of the “perosmate” ion $[\text{OsO}_4(\text{OH})_2]^{2-}$.

Osmium(vi).—The hexafluoride can be made by direct union of the elements. It forms yellow crystals (m.p. 32.1, b.p. 45.9 °C).⁷ A considerable amount of thermodynamic information is available on the compound.³² X-Ray studies show that the molecule is octahedral⁷ and the osmium–fluorine bond length of 1.831 Å is found from electron-diffraction.³³ The magnetic susceptibility has been measured over a temperature range⁷ and has been interpreted on the basis of the orbital reduction factor being about 0.5 [implying that the two magnetic 5d electrons of osmium (vi) spend about an equal amount of time on the metal and on the ligands].³⁴ The electronic absorption spectrum has been measured and assignments suggested.³⁴ The compound is of particular interest because its

²⁵ F. M. Jaeger and J. E. Zanstra, *Proc. Acad. Amsterdam*, 1932, **35**, 610.

²⁶ L. A. Woodward, J. A. Creighton, and K. A. Taylor, *Trans. Faraday Soc.*, 1960, **56**, 1267; J. Lewis and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **6**, 12.

²⁷ A. Werner and K. Dinklage, *Ber.*, 1901, **34**, 2698; 1906, **39**, 500.

²⁸ W. P. Griffith, *J.*, 1965, 3694.

²⁹ N. Bartlett, S. Beaton, L. W. Reeves, and E. J. Wells, *Canad. J. Chem.*, 1964, **42**, 2531; N. Bartlett, N. K. Jha, and J. Trotter, *Proc. Chem. Soc.*, 1962, 277.

³⁰ R. Scholder and G. Schatz, *Angew. Chem.*, 1963, **2**, 264; R. Scholder, *ibid.*, 1958, **70**, 591.

³¹ A. W. Sleight, J. Longo, and R. Ward, *Inorg. Chem.*, 1962, **1**, 245.

³² G. H. Cady and G. B. Hargreaves, *J.*, 1961, 1563.

³³ B. Weinstock and J. G. Malm, *Proc. U.N. Conf. on Peaceful Uses of Atomic Energy, Geneva*, 1958, **28**, 125.

³⁴ J. C. Eisenstein, *J. Chem. Phys.*, 1961, **34**, 310.

t_{2g}^2 ground state suggests that Jahn-Teller effects may be observed: although the electrons are in the "non-bonding" t_{2g} level, distortion effects are likely to be small but may become apparent as a form of vibronic coupling to give a "dynamic" Jahn-Teller effect,³⁵ in which case this should perhaps be observed in the vibrational spectra of the compound. Studies on the infrared and Raman spectra of the gaseous hexafluoride do reveal the expected anomalies: the ν_2 symmetric stretching mode is not observed in the Raman spectrum in conditions in which it should normally be easily apparent, and all combination bands involving ν_2 are abnormally broad [somewhat similar effects are found for $(\text{OsCl}_6)^{2-}$]. The vibrational spectra confirm the octahedral symmetry of the molecule.³⁶ An oxyfluoride OsOF_4 is formed in small amounts during the preparation of the hexafluoride, and OsOCl_4 can be made by treating osmium metal with an oxygen-chlorine mixture (no hexahalides other than the fluoride are known for osmium). Both the complexes are diamagnetic, owing no doubt to the low molecular symmetries. An apparently heptaco-ordinated complex, $\text{Cs}_2(\text{OsOCl}_6)$, can be made from caesium chloride and osmium oxychloride.⁹

There is some doubt about the existence of osmium(VI) oxides: the trioxide has not been obtained pure, but the product of decomposition of the cyclic osmium(VI) esters mentioned above may be a hydrated trioxide. It is curious that the parent acid of the osmates, $\text{H}_2[\text{OsO}_2(\text{OH})_4]\text{aq}$, has not been made.

Osmium shares with rhenium, ruthenium, and the actinide elements the property of forming very stable *trans* dioxo-complexes. The "osmyl" complexes, *trans*- $(\text{OsO}_2\text{X}_4)^{2-}$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \frac{1}{2}\text{ox}^{2-}$) can be made by the action of the appropriate acid on the tetroxide, and other complexes of the same type ($\text{X} = \text{CN}^-, \text{OH}^-, \text{OCH}_3^-, \text{SO}_3^{2-}$) can be made from potassium osmate and the appropriate alkali-metal salt.³⁷ The "oxy-osmyl" series originally formulated as $(\text{OsO}_3\text{X}_2)^{2-}$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{NO}_2^-$ and $\frac{1}{2}\text{ox}^{2-}$) are made by similar methods,³⁷ and have recently been shown to be of the form *trans*- $[\text{OsO}_2(\text{OH})_2\text{X}_2]^{2-}$.^{18,38} The *trans* arrangement of the oxy-groups in $\text{K}_2[\text{OsO}_2(\text{OH})_4]$ ³⁹ and in $\text{K}_2(\text{OsO}_2\text{Cl}_4)$ ⁴⁰ has been confirmed by *X*-ray studies. All the osmyl complexes are diamagnetic, and it has been suggested that this arises from the axial compression of the octahedron (O_h to D_{4h}) brought about by the two short *trans* $\text{Os} = \text{O}$ bonds, the compression being sufficient to split the t_{2g} lower triplet into a lower singlet [into which the two $5d$ electrons of osmium(VI) are paired] and an upper

³⁵ H. A. Jahn and E. Teller, *Proc. Roy. Soc.*, 1937, **A**, **161**, 220; J. H. van Vleck, *J. Chem. Phys.*, 1939, **7**, 61, 72.

³⁶ B. Weinstock, H. H. Claassen, and J. G. Malm, *J. Chem. Phys.*, 1960, **32**, 181; H. H. Claassen, *ibid.*, 1959, **30**, 968.

³⁷ L. Wintrebert, *Ann. Chim. phys.*, 1903, **28**, 54, 102, 134.

³⁸ W. P. Griffith, *J.*, 1962, 3248.

³⁹ M. A. Porai-Koshits, L. O. Atovyan, and V. G. Adrianov, *J. Struct. Chem. U.S.S.R.*, 1960, **2**, 686.

⁴⁰ F. Kruse, *Acta Cryst.*, 1961, **14**, 1035.

doublet, an explanation which receives support from the electronic spectra of the complexes.⁴¹ Infrared spectra have been measured on a wide range of these complexes.¹⁸ It is worth noting that potassium osmate was long formulated as $K_2(OsO_4)$ by analogy with the tetrahedral potassium ruthenate, $K_2(RuO_4)$, but is of course octahedral, $K_2[OsO_2(OH)_4]$.

A series of nitrido-osmium(vi) complexes of the form $(OsNX_5)^{2-}$ ($X = Cl^-$, Br^-),²⁷ *trans*- $[OsN(H_2O)X_4]^-$ ($X = Br^-$, CN^- , $\frac{1}{2}ox^{2-}$)^{27,28} and *trans*- $[OsN(H_2O)(OH)_2X_2]^-$ ($X = F^-$, $\frac{1}{2}ox^{2-}$)²⁸ can be made by reaction of the appropriate acid with potassium osmiamate; it is noteworthy that in this reaction it is the three osmium–oxygen bonds which are attacked while the osmium–nitrogen triple bond remains intact. *X*-Ray studies on $K_2(OsNCl_5)$ show that the chlorine atom *trans* to the nitrogen is 0.3 Å closer to the metal than the four equatorial groups,⁴² a situation very difficult to understand since it might be expected that the strongly π -donating nitrido-group should labilise the ligand opposite to it. Infrared studies have been carried out on these nitride complexes.²⁸

Osmium(v).—This somewhat rare oxidation state for the element is represented only by the fluoride and its derived anionic complexes. Reduction of osmium hexafluoride with tungsten carbonyl yields a mixture of the tetrafluoride and the blue pentafluoride; the latter melts at 70°C to a green liquid and boils at 225.9° to a colourless vapour. These colour changes on heating suggest that the compound in the solid and liquid forms has a polymeric form (probably like RuF_5 which has recently been shown to be tetrameric with fluorine bridges⁴³) and monomeric in the gas phase; this is supported by the unexpectedly low magnetic moment.⁴⁴ The mixed compound $OsIF_4$ has also been reported.⁴⁴ A series of salts containing the $(OsF_6)^-$ ion can be made from osmium tetrabromide, bromine tetrafluoride, and an alkali-metal bromide.⁴⁵ The susceptibilities of these (Table 3) give values much closer to those expected for octahedral osmium(v) than does the pentafluoride.⁴⁶ The fluorine magnetic resonance of the solid potassium salt has been measured,⁴⁷ and *X*-ray studies made on a wide range of the salts.⁴⁸

Osmium(iv).—The tetrafluoride can be made in the same way as the pentafluoride; it is a yellow solid (m.p. 230°C), probably polymeric.⁴⁴ A tetrachloride⁴⁹ and a tetrabromide are both known,⁵⁰ being made

⁴¹ K. Lott and M. C. R. Symons, *J.*, 1960, 973.

⁴² E. A. Atovyan and G. B. Bokii, *J. Struct. Chem. U.S.S.R.*, 1960, **1**, 501.

⁴³ J. H. Holloway, R. D. Peacock, and R. W. H. Small, *J.*, 1964, 644.

⁴⁴ G. B. Hargreaves and R. D. Peacock, *J.*, 1960, 2618.

⁴⁵ M. D. Hepworth, P. L. Robinson, and G. J. Westland, *J.*, 1954, 4269.

⁴⁶ B. N. Figgis, J. Lewis, and F. E. Mabbs, *J.*, 1961, 3138.

⁴⁷ D. Elwell, *Proc. Phys. Soc.*, 1964, **48**, 409.

⁴⁸ M. A. Hepworth, K. H. Jack, and K. J. Westland, *J. Inorg. Nuclear Chem.*, 1956, **2**, 79; R. D. W. Kemmitt, D. R. Russell, and D. W. A. Sharp, *J.*, 1963, 4408.

⁴⁹ Vauquelin, *Ann. Chim. phys.*, 1841 (1), **89**, 248.

⁵⁰ I. N. Semenov and N. I. Kolbin, *Russ. J. Inorg. Chem.*, 1962, **7**, 111; S. A. Schukarev, N. I. Kolbin, and I. N. Semenov, *ibid.*, 1961, **6**, 638.

directly from their elements, but the long-claimed tetraiodide has been shown not to exist.⁵¹ The complexes $(\text{OsX}_6)^{2-}$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{F}^-$) are all known and are very stable. The fluorides are made by reduction of $(\text{OsF}_6)^-$ and the others by prolonged action of the appropriate halogen acid on osmium tetroxide. An extensive study has been made of the magnetic properties of these complexes (Table 3), but interpretation of the results is not a simple matter. It has been demonstrated that there is magnetic exchange in salts of $(\text{OsCl}_6)^{2-}$ and of $(\text{OsBr}_6)^{2-}$, since the moments of these ions when dispersed in a suitable diamagnetic host lattice are much higher than the bulk values, and it is only at "infinite dilution" that the Kotani theory predictions for t_{2g}^4 configurations are obeyed. It has been suggested that this exchange operated through $d\pi-p\pi$ (metal-ligand) and $p\pi-p\pi$ (ligand-ligand) bonding orbitals.⁵² Finally, to add to the complexities of the problem, recent observations on the solid-state fluorine magnetic resonance of $\text{K}_2(\text{OsF}_6)$ have been interpreted as indicating that there is a considerable departure from simple occupancy of the t_{2g}^4 ground state by the four osmium(IV) 5d electrons, although confirmation of these results must await single-crystal experiments.⁴⁷

The X-ray crystal structure of $\text{K}_2(\text{OsCl}_6)$ has been determined and the octahedral symmetry confirmed.⁵³ Infrared and Raman studies of $(\text{OsCl}_6)^{2-}$ indicate that, as with the hexafluoride, dynamic Jahn-Teller effects may be operative.⁵⁴ Mixed chloro-bromo-⁵⁵ and chloro-iodo-osmium(IV)^{55a} species have been detected in solution and, in the former case, separated by high-voltage paper electrophoresis. In this way all five complexes⁵⁵ of the $(\text{OsCl}_n\text{Br}_{6-n})^{2-}$ series were isolated, and it was found that variations in absorption spectra maxima and migration velocities formed a consistent pattern.⁵⁵ Jørgensen has made an extensive survey of the electronic absorption spectra of platinum metal hexahalogeno-complexes including $(\text{OsX}_6)^{2-}$ and $(\text{OsX}_6)^{3-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) over the range 180 to 1000 m μ , and he has assigned the ligand field bands and also the many electron-transfer transitions,⁵⁶ a subject also dealt with in a recent paper by Englman.⁵⁷ The colours of some of these osmium(IV) hexahalides vary remarkably with the nature of the cation; thus, while $(\text{OsCl}_6)^{2-}$ ion in aqueous solution is yellow, the potassium salt is deep red, the caesium salt orange, and the silver and thallous salts are respectively deep brown

⁵¹ J. E. Fergusson, B. H. Robinson, and W. R. Roper, *J.*, 1962, 2113.

⁵² A. D. Westland and N. C. Bhiwandker, *Canad. J. Chem.*, 1961, **39**, 1284, 2353; A. D. Westland, *ibid.*, 1963, **41**, 2692; R. B. Johannessen and G. A. Candela, *Inorg. Chem.*, 1963, **2**, 67.

⁵³ J. D. McCullough, *Z. Krist.*, 1936, **A**, **94**, 143.

⁵⁴ L. A. Woodward and M. J. Ware, *Spectrochim. Acta*, 1964, **20**, 711.

⁵⁵ E. Blasius and W. Preetz, *Z. anorg. Chem.*, 1965, **335**, 16.

^{55a} E. Fenn, R. S. Nyholm, P. G. Buxton, and A. Turco, *J. Inorg. Nuclear Chem.*, 1961, **17**, 387; C. K. Jørgensen, *Acta Chem. Scand.*, 1963, **17**, 1043; F. Rallo, *J. Chromatog.*, 1962, **8**, 132.

⁵⁶ C. K. Jørgensen and J. S. Brinen, *Mol. Phys.*, 1962, **5**, 535; C. K. Jørgensen, *Acta Chem. Scand.*, 1962, **16**, 793; 1963, **17**, 1043; *Mol. Phys.*, 1959, **2**, 309.

⁵⁷ R. Englman, *Mol. Phys.*, 1963, **6**, 345.

and orange-green. Studies of the reflectance spectra of these and other hexahalide salts suggests that these effects arise from shifting and broadening in electron-transfer bands, brought about by varying lattice parameters caused by the change in cation.⁵⁸ Shifts and broadening effects in these bands are also produced when high pressures are applied to solid solutions of osmium(IV) hexahalides,⁵⁹ and the dielectric constant of the solvent also affects the position of the bands in liquid solutions.⁵⁸

A recent study of the rate of exchange of labelled bromide ion with $(\text{OsBr}_6)^{2-}$ is one of the very few kinetic investigations on osmium complexes; another is the study of aquation of $(\text{OsCl}_6)^{2-}$.⁶⁰

Group VI donors. The dioxide is normally made by heating the metal in a stream of nitric oxide or in the vapour of the tetroxide. It is said to exist in a black and also in a brown form, the latter (which is rather less reactive) having the rutile structure. Osmium disulphide, diselenide, and ditelluride can all be made from their elements at red heat. No aquo-complex is reported although there is some polarographic evidence for the existence of aquo- or hydroxy-complexes formed by reduction of buffered solutions of the tetroxide [by comparison with the chemistry of ruthenium, one might expect the existence of such complexes of both osmium-(III) and -(IV)]. Infrared evidence suggests that the complex originally formulated as $(\text{NH}_4)_2(\text{OsCl}_5\text{OH})^{61}$ is in fact binuclear, $(\text{NH}_4)_4(\text{Os}_2\text{OCl}_{10})$, with a linear $\text{O}=\text{Os}=\text{O}$ skeleton similar to the analogous ruthenium compound.

Nitrogen and carbon donor complexes are somewhat rare for this oxidation state of the element. The reaction between ethylenediamine (en) and osmium(IV) hexahalides is a complicated one, yielding $[\text{Os}^{\text{IV}}(\text{en}-\text{H})\text{en}_2]\text{Br}_3$, $[\text{Os}^{\text{IV}}(\text{en}-\text{H})_2\text{en}]\text{Br}_2$, $[\text{Os}^{\text{IV}}(\text{en}-\text{H})_2\text{en}_2]\text{I}_2$, together with some rather obscure products believed to contain quinque- and sexi-valent osmium.⁶² [en-H is an ethylenediamine molecule with one proton removed, *i.e.*, $\text{H}_2\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}^-$; it will have a lone pair on the deprotonated end of the molecule suitably placed for π -donation to the metal and might therefore be expected to stabilise osmium(IV); it is noteworthy that $(\text{Os en}_3)^{4+}$ is unknown]. The diamagnetism of these quadrivalent osmium complexes may well arise from the asymmetry of the ligand field brought about by the non-equivalent ligands. It was suggested that $[\text{Os}^{\text{IV}}(\text{en}-\text{H})_2\text{en}_2]\text{I}_2$ contained eight co-ordinate osmium(IV),⁶² but a more reasonable explanation of the unusual formula would be that two of the ligands, probably (en-H), were unidentate, leading to the conventional octahedral co-ordination for the metal atom. A few osmium(IV) complexes

⁵⁸ C. K. Jørgensen, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1587; *Acta Chem. Scand.*, 1963, **17**, 1034.

⁵⁹ A. S. Balchan and H. G. Drickamer, *J. Chem. Phys.*, 1961, **35**, 356.

⁶⁰ G. Schmidt, *Z. Naturforsch.*, 1961, **16a**, 748; G. A. Rechnitz and H. A. Catherino, *Inorg. Chem.*, 1965, **4**, 112.

⁶¹ F. P. Dwyer and J. W. Hogarth, *J. Proc. Roy. Soc. New South Wales*, 1950, **84**, 194.

⁶² F. P. Dwyer and J. W. Hogarth, *J. Amer. Chem. Soc.*, 1955, **77**, 6152.

of *o*-phenanthroline (phen) and 2,2'-bipyridyl (bipy) are known,⁶³ these being ligands which, by virtue of their conjugated ring systems, are capable of stabilising a fairly wide range of oxidation states,⁶⁴ and in fact osmium-(III) and -(II) complexes with phen and bipy are also known. A single arsine complex $[\text{OsBr}_4(\text{AsPh}_3)_2]$ is reported, with a magnetic moment of 1.5 B.M. at room temperatures.⁶⁵ Although no unsubstituted ammines of quadrivalent osmium are known, the binuclear species $[\text{Os}_2\text{N}(\text{NH}_3)_8\text{X}_2]\text{X}_3$ ($\text{X} = \text{Cl}^-$, Br^-) can be made by treating the hexahalogeno-complexes with ammonia under pressure.⁶⁶ Infrared spectra indicate that the bromide contains a linear N-Os-N skeleton, analogous to $(\text{Os}_2\text{OCl}_{10})^{4-}$ and $(\text{Ru}_2\text{OCl}_{10})^{4-}$ mentioned above; the π -donor abilities of the bridging nitrido-group no doubt help to stabilise the high oxidation state.²⁸

Carbon donor complexes. The only one reported for this oxidation state is a cyclopentadiene complex, probably $[\pi\text{-C}_5\text{H}_5]_2\text{Os}(\text{OH})_2$, made by the oxidation of osmocene in solution (chronopotentiometric studies show that ruthenocene but not ferrocene can also be oxidised to their respective quadrivalent oxidation states).⁶⁷ Recently, amine salts of the form $(\text{amine-H})_2[\text{Os}^{\text{IV}}(\text{CN})_6]$ and $(\text{amine H})_2[\text{Ru}^{\text{IV}}(\text{CN})_6]$ (amine = aniline, 1,2,3-benzotriazole, etc.) have been claimed, made by addition of the amine to $\text{K}_2[\text{Os}(\text{CN})_6]$ and $\text{K}_2[\text{Ru}(\text{CN})_6]$.⁶⁸ Since osmium(IV) and ruthenium(IV) cyano-complexes are not elsewhere reported in the literature and as it seems unlikely that the cyanide group would stabilise quadrivalent states alone, the Reviewer wrote to the firm who supplied the cyano-complexes to the original workers, and they confirm that their products were the normal $\text{K}_4[\text{Os}(\text{CN})_6]$ and $\text{K}_4[\text{Ru}(\text{CN})_6]$ but had been incorrectly labelled. It is clear therefore that the amine salts should be reformulated as $(\text{amineH})_2\text{H}_2[\text{Os}^{\text{II}}(\text{CN})_6]$ and $(\text{amineH})_2\text{H}_2[\text{Ru}^{\text{II}}(\text{CN})_6]$, similar to the salts $(\text{amineH})_2\text{H}_2[\text{Fe}^{\text{II}}(\text{CN})_6]$ which have long been known⁶⁹ for ferro-cyanides.

Osmium(III).—While both ruthenium trifluoride and $(\text{RuF}_6)^{3-}$ salts are well known, the osmium analogues do not exist, exemplifying once again the tendency to stabilise higher oxidation states in the third row of the Periodic Table; thus, for osmium, the quadrivalent is the commonest oxidation state, the tervalent for ruthenium and the bivalent for iron. Osmium trichloride, tribromide, and tri-iodide are known, the chloride made from the elements or by heating ammonium hexachloro-osmate(IV)

⁶³ D. A. Buckingham, F. P. Dwyer, H. A. Goodwin, and A. M. Sargeson, *Austral. J. Chem.*, 1964, **17**, 315, 325.

⁶⁴ J. Chatt, *J. Inorg. Nuclear Chem.*, 1958, **8**, 515.

⁶⁵ L. Vaska, *Chem. and Ind.*, 1961, 1402.

⁶⁶ F. P. Dwyer and J. W. Hogarth, *J. Proc. Roy. Soc. New South Wales*, 1950, **84**, 117; V. I. Belova and Y. K. Syrkin, *Russ. J. Inorg. Chem.*, 1958, **3**, 2016; G. Watt and L. Vaska, *ibid.*, 1958, **6**, 246.

⁶⁷ T. Kuwana, D. E. Bublitz, and G. Hoh, *J. Amer. Chem. Soc.*, 1960, **82**, 5811.

⁶⁸ R. F. Wilson and P. Marchant, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1057; R. F. Wilson and J. James, *Z. Anorg. Chem.*, 1963, **321**, 180; 1962, **315**, 235.

⁶⁹ W. M. Cumming, *J.*, 1922, 1287.

in a current of chlorine⁷⁰ (data on the dissociation of both the tetra- and tri-chlorides of osmium have recently been presented⁷¹) and the iodide also from its elements.⁵¹ In addition to the tribromide,⁸⁰ Os₂Br₉ (made by the prolonged action of hydrobromic acid on the tetroxide)⁸ and Os₂Br₇ (formed as a by-product during preparation of the tetrabromide⁵⁰) have been claimed. Salts of (OsX₆)³⁻ (X = Cl⁻, Br⁻, I⁻) are known but are unstable with respect to oxidation to the quinquevalent hexahalogeno-species, from which they are usually prepared by electrolytic or chemical reduction processes. The electronic absorption spectra of all three ions in solution have been measured and the electron-transfer and ligand-field bands assigned.⁵⁶ It is likely that complexes of the form [Os^{IV}X_n(H₂O)_{6-n}]⁽³⁻ⁿ⁾⁺ should exist, since such systems are known for osmium(IV) chloro-species⁶⁰ and have been extensively investigated for both ruthenium(III) and rhodium(III).

Although the sesquioxide, Os₂O₃, is reported in the early literature its existence is highly questionable, and neither is there convincing evidence for the existence of the sesqui-sulphide, -selenide, or -telluride. There are few Group VI donor complexes of osmium(III); none with oxy-, hydroxy-, or aquo-ligands has been isolated, although as with the quadrivalent state there is some polarographic evidence for their existence in reduced solutions of osmium tetroxide.²⁰ Neither are there any sulphato-, sulphito-, nitroato-, nitrito-, nor (surprisingly) oxalato-complexes. The species normally used for the colorimetric analysis of the element was long believed to be [Os^{IV}(thiourea)₆]Cl₃(OH) [made from (OsCl₆)²⁻ and thiourea], but it is in fact [Os(thiourea)₆]Cl₃ and its instability constant has been measured.⁷² It can be reduced electrolytically to [Os(thiourea)₆]²⁺. An analogous osmium(III) selenourea complex, allegedly with a 1:8 metal: ligand ratio has been made.⁷³ With acetylacetone (acac), osmium(IV) hexahalogeno-complexes give (Os acac₃) together with a number of unidentified halogen-containing species of higher oxidation states.⁷⁴ A number of mixed acac-phen and acac-bipy complexes have also been prepared.⁶³

The most important donors for this oxidation state are of Group V. The hexammines [Os(NH₃)₆]X₃ (X = Cl⁻, Br⁻, I⁻) are difficult to prepare, the method normally used being the high-pressure reaction between ammonia and the hexahalogeno-osmates(IV) at 280°C,⁷⁵ a method which also gives [Os^{IV}(NH₃)₆](Os^{IV}Br₆). The latter complex has recently been

⁷⁰ O. Ruff and E. Bornemann, *Z. anorg. Chem.*, 1910, **65**, 450, 501.

⁷¹ N. I. Kolbin and I. N. Semenov, *Russ. J. Inorg. Chem.*, 1964, **9**, 108; N. I. Kolbin, I. N. Semenov, and Y. M. Shutov, *ibid.*, 1964, **9**, 563.

⁷² R. D. Sauerbrann and E. B. Sandell, *J. Amer. Chem. Soc.*, 1953, **75**, 3554; *Analyt. Chim. Acta*, 1953, **9**, 86.

⁷³ A. T. Pilipenko and I. P. Sereda, *Russ. J. Inorg. Chem.*, 1961, **6**, 209.

⁷⁴ F. P. Dwyer and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1955, **77**, 1285.

⁷⁵ F. P. Dwyer and J. W. Hogarth, *J. Proc. Roy. Soc. New South Wales*, 1951, **84**, 117; 1952, **85**, 113; G. W. Watt and L. Vaska, *J. Inorg. Nuclear Chem.*, 1958, **6**, 246; 1958, **5**, 308.

examined by infrared spectroscopy with normal, deuterated, and nitrogen-15-substituted ammine groups, and the metal-nitrogen fundamental stretching vibration found near 450 cm^{-1} .⁷⁶ The room-temperature magnetic moments of the hexammines are close to 1.8 B.M.⁷⁵ With a solution of potassium in liquid ammonia, products which analyse as $[\text{Os}(\text{NH}_3)_6]\text{Br}$ and $[\text{Os}(\text{NH}_3)_6]$ are obtained; it is possible that these may be hydrido-complexes of osmium(II).⁷⁷ Measurements of the rates of exchange of hydrogen with a number of metal ammines $[\text{M}^{\text{III}}(\text{NH}_3)_6]^{3+}$ and ammines $(\text{M}^{\text{III}}\text{en}_3)^{3+}$ ($\text{M} = \text{Co, Rh, Ir, Cr, Ru, Os}$) have been made and conclusions drawn as to the relative strengths of metal-nitrogen bonding between the compounds.⁷⁸ The halogenopentammines are somewhat more stable than the hexammines and are prepared by similar methods;⁷⁵ it is likely that a wide range of substituted osmium(III) ammines could be made.

The reaction between $(\text{OsBr}_4)^{2-}$ and ethylenediamine in the presence of a reducing agent yields $(\text{Os en}_3)^{3+}$ [curiously, no tris-ethylenediamine ruthenium(III) complexes are reported].⁶² With the aromatic bases *o*-phenanthroline (phen) and 2,2'-bipyridyl (bipy) the complexes $(\text{Os phen}_3)^{3+}$ and $(\text{Os bipy}_3)^{3+}$ are formed, and some salts of these have been resolved,⁷⁹ while mixed phen and bipy complexes with other ligands have also been made.⁶³ A considerable amount of work has been done on the electron-transfer reactions between these and the corresponding bivalent tris-phenanthroline and -bipyridyl complexes (in acid solution, oxidation potentials are +0.86 and +0.73 v respectively), and in fact these systems have been used as redox indicators.⁷⁹ The rates of electron exchange between the bi- and ter-valent tris-phenanthroline and -bipyridyl complexes are extremely high, suggesting that little energy is needed to reorganise the co-ordination shells of reactants and products in the reaction, and the observed rates are in excellent agreement with the predictions of the Marcus theory of electron exchange.⁸⁰ Such agreement is also found for the reaction of $(\text{Os bipy}_3)^{3+}$ with ferrocyanide ions.^{80,81} Although pyridine is a stronger base (*i.e.*, a better σ -donor) than either phenanthroline or bipyridyl it is a less effective π -acceptor owing to its lower degree of conjugation, and the only known pyridine-osmium complexes are $(\text{Os}^{\text{IV}}\text{Cl}_2\text{py}_4)$, $(\text{Os}^{\text{IV}}\text{Br}_2\text{py}_4)$, and $(\text{Os}^{\text{III}}\text{Cl}_3\text{py}_3)$.⁶³ A number of phosphine and arsine complexes of osmium-(IV), -(III), and -(II) are reported. Tertiary phosphines, arsines, and stibines react^{65,82} with hexahalogeno-osmates(IV) to give

⁷⁶ W. P. Griffith, unpublished work.

⁷⁷ G. W. Watt, E. M. Potrafke, and D. S. Klett, *Inorg. Chem.*, 1962, **2**, 868.

⁷⁸ J. W. Palmer and F. Basolo, *J. Inorg. Nuclear Chem.*, 1960, **15**, 279.

⁷⁹ F. P. Dwyer and E. C. Gyarfas, *J. Amer. Chem. Soc.*, 1952, **74**, 4699; F. P. Dwyer, E. C. Gyarfas, and N. A. Gibson, *J. Proc. Roy. Soc. New South Wales*, 1950, **54**, 80, 83.
⁸⁰ E. Eichler and A. C. Wahl, *J. Amer. Chem. Soc.*, 1958, **80**, 4145; A. Wahl, *Z. Elektrochem.*, 1960, **64**, 90; R. Campion, N. Purdie, and N. Sutin, *J. Amer. Chem. Soc.*, 1963, **85**, 3528.

⁸¹ D. H. Irvine, *J.*, 1959, 2977; 1957, 1841.

⁸² F. P. Dwyer, R. S. Nyholm, and B. T. Tyson, *J. Proc. Roy. Soc. New South Wales*, 1947, **81**, 272.

[OsX₃(MR₃)₃] (X = Cl⁻, Br⁻; M = P, As, Sb), while the versatile ligand *o*-phenylenebisdimethylarsine (diars) gives complexes of the form (Os diars₂X₂)⁺;⁸² these can be reduced to (Os diars₂X₂)⁰ and the far infrared spectra of both series have been measured.⁸³

Carbon donor complexes of osmium(III) are rare. There is polarographic evidence for the existence of [Os(CN)₆]³⁻ in solution,²⁰ and the oxidation potential of the [Os(CN)₆]³⁻/[Os(CN)₆]⁴⁻ couple is -0.99V (for the corresponding ruthenium system the potential is +0.86V).⁸⁴

Osmium(II).—The dichloride is said to exist in both a green and brown form, but the latter is probably the only pure form of the compound, and it is made by thermal decomposition of the trichloride in a stream of chlorine.⁷⁰ It is insoluble in water but soluble in alkalis, possibly to give hydroxy-complexes, and surprisingly it is claimed to be paramagnetic.⁸⁶ There seem to be no reports of a dibromide, but the di-iodide can be made from the elements.⁵¹ The reduction products of acid solutions of (OsCl₆)³⁻ are violet-blue,⁸⁷ possibly owing to the presence of (OsCl₆)⁴⁻ or an aquated form of this.

Oxygen donor complexes. The oxide OsO is said to be formed when K₆[Os(H₂O)(SO₃)₅] is heated,⁸⁷ but the evidence for the products being the monoxide is inconclusive. The monosulphide may exist⁸⁸ but neither the selenide or telluride are known. Osmium(II) complexes with Group VI donors are rare: mixed acetylacetone complexes with 2,2'-bipyridyl and with *o*-phenanthroline have recently been reported⁶³ and [Os(thiourea)₆]²⁺ has been made in solution.⁷² Stable sulphito-complexes are however known, although the nature of the bonding (whether *via* oxygen, sulphur, or both) is not clear. Treatment of hexahalogeno-osmates(IV) with sulphites⁸⁹ gives compounds claimed to be [Os^{IV}(SO₃)₄(HSO₃)₂]⁶⁻ and [Os^{IV}(H₂O)(SO₃)₅]⁶⁻ but the fact that they are colourless suggests that they may in fact be derivatives of bivalent osmium. Treatment of the species formed by the tetroxide with glycols and sodium sulphite yields Na₄[Os(SO₃)₃]₆H₂O,²² which may contain bridging or bidentate sulphito-groups or could alternatively be formulated as [Os(SO₃)₃(H₂O)₃]⁴⁻ with unidentate ligands. Claus reported in 1863 a blue sulphite, OsSO₃, as a volatile product of the complicated reaction between osmium tetroxide and sulphur dioxide.⁸⁷

Group V donors are important for bivalent osmium. Although [Os(NH₃)₆]²⁺ has not been isolated, there is evidence for its intermediate formation in the reaction between potassium in liquid ammonia and the

⁸³ J. Lewis, R. S. Nyholm, and G. A. Rodley, *J.*, 1965, 1483.

⁸⁴ W. P. Griffith, *Quart. Rev.*, 1962, **16**, 188.

⁸⁵ W. Hieber and H. Stallmann, *Z. Elektrochem.*, 1943, **49**, 288; *Ber.*, 1942, **75**, B, 1472; W. Manchot and J. Konig, *Ber.*, 1925, **58**, 229.

⁸⁶ B. Cabrera and A. Duperier, *Compt. rend.*, 1927, **185**, 415.

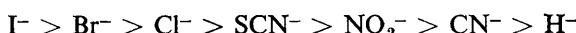
⁸⁷ C. Claus, *J. prakt. Chem.*, 1863, **90**, 80.

⁸⁸ J. E. McDonald and J. W. Cobble, *J. Phys. Chem.*, 1962, **66**, 791.

⁸⁹ A. Rosenheim and E. A. Sasserath, *Z. anorg. Chem.*, 1889, **21**, 143; A. Rosenheim, *ibid.*, 1900, **24**, 422; A. Sachs, *Z. Krist.*, 1901, **34**, 166.

tervalent hexammines,⁷⁷ and it is possible that the products of this reaction may be hydrido-ammines of osmium(II). Complexes with aromatic bases are very stable; these include $(\text{Os phen}_3)_2^{2+}$, $(\text{Os bipy}_3)_2^{2+}$,⁷⁸ $(\text{Os tripy}_2)_2^{2+}$ (terpyridyl, a tridentate ligand),⁹⁰ and $(\text{OsBr}_2\text{py}_4)_2^{2+}$,⁶³ while mixed bipy and phen complexes have also been prepared.⁶³ Electron-exchange reactions between the tris-bipy and -phen complexes with their tervalent analogues have already been mentioned,⁸⁰ and to this may be added the extensive work carried out on the kinetics of the fast electron exchange between $(\text{Os bipy}_3)_2^{2+}$ with a large number of other spin-paired oxidants⁸⁰ and on the kinetics of reaction of the same complex with thallous and persulphate ions.⁸¹

A wide range of phosphine and arsine complexes with bivalent osmium have recently been prepared. These ligands are good π -acceptors and behave like phenanthroline and bipyridyl in stabilising low oxidation states. A review on such complexes has recently been published⁹¹ so only a very brief summary is given here. With hexahalogeno-osmates(IV), tertiary phosphines and arsines give $[\text{OsX}_2(\text{MR}_3)_4]$ and^{65,82} $[\text{Os}_2\text{Cl}_3(\text{PR}_3)_6]\text{Cl}$ (the latter are dimeric with halogen bridges),⁹² while with diphosphines *cis*- and *trans*- $[\text{OsX}_2(\text{diphosphine})_2]$ ($\text{X} = \text{Cl}^-$, I^-) are formed.⁹² The latter complexes can be reduced with lithium aluminium hydride to *trans*- $[\text{Os}^{\text{II}}\text{HX}(\text{diphosphine})_2]$, in which there is a direct metal-hydrogen bond.⁹³ Infrared studies on these hydrides show that there is a relationship between the metal-hydrogen stretching frequency and the *trans*-effect of the group X; the frequency decreases along the series⁹³



With *o*-phenylenebisdimethylarsine (diars) the complexes $(\text{Os diars}_2\text{X}_2)$ ($\text{X} = \text{Cl}^-$, Br^-) are formed.⁸² Carbonyl and alkyl phosphines are discussed below.

A number of osmium(II) nitrosyl complexes are known, although their range is not comparable with that found for ruthenium(II). The complex originally formulated by Wintrebert³⁷ as $\text{K}_2[\text{Os}(\text{NO}_2)_5]$ [prepared by the prolonged action of potassium nitrite on $\text{K}_2[\text{OsCl}_6]$] is diamagnetic and is in all probability a nitrosyl derivative, $\text{K}_2[\text{Os}^{\text{II}}(\text{NO})(\text{OH})(\text{NO}_2)_4]$.⁷⁶ Action of halogen acids on this gives $[\text{Os}(\text{NO})\text{X}_5]^{2-}$ ($\text{X} = \text{Cl}^-$, Br^- , I^-).³⁷ In all these compounds the nitric oxide is likely to be functioning as a three-electron donor as in most of its complexes.⁹⁴ Although no pentacyanonitrosyl is reported, it is probable that the "nitrocyanide"⁹⁵ obtained by the reaction between nitric acid and $\text{K}_4[\text{Os}(\text{CN})_6]$ is or contains

⁷⁰ G. Morgan and F. H. Burstall, *J.*, 1937, 1649.

⁷¹ G. Booth, *Adv. in Inorg. Chem. and Radiochem.*, 1964, **6**, 1.

⁷² J. Chatt and R. G. Hayter, *J.*, 1961, 896.

⁷³ J. Chatt and R. G. Hayter, *J.*, 1961, 2605.

⁷⁴ J. Lewis, *Science Progress*, 1959, **47**, 506; C. C. Addison and J. Lewis, *Quart. Rev.*, 1955, **9**, 115.

⁷⁵ C. A. Martius, *Annalen*, 1861, **117**, 362.

$K_2[Os(NO)(CN)_5]$, since this is precisely the method normally used to make the pentacyanonitrosyls of ruthenium(II) and iron(II).

Carbon donor complexes are also of importance for bivalent osmium, chiefly, as might be expected, with good π -acceptor ligands such as CO , CN^- , and $-C_5H_5^-$. The cyanide complex is prepared by fusion of osmium compounds with potassium cyanide and has long been known;⁹⁵ its electronic and vibrational spectra have been reported.⁹⁶ The free acid $H_4[Os(CN)_6]$ can easily be made and it has recently been shown by infrared and far infrared spectroscopy that the anhydrous solid acid contains unsymmetrical $N-H \cdots N$ hydrogen bonds.⁹⁷ The "sandwich" compound osmocene, $[(\pi-C_5H_5)_2Os]$ is made from the tetrachloride and sodium cyclopentadienide,⁹⁸ and an X -ray crystal-structure determination on the compound shows that the two rings are in the eclipsed position as in ruthenocene.⁹⁹ The only olefin complex so far reported is the cyclo-octa-1,5-diene (C_8H_{12}) species $[OsCl_2(C_8H_{12})(PEtPh_2)_3]$, prepared from the olefin and $[Os_2Cl_3(PEtPh_2)_6]$;⁹² since this is a very stable substance it seems likely that an extensive range of osmium olefin complexes could be made. Alkyl and aryl phosphines in which the alkyl and aryl groups are attached to the osmium by a metal–carbon σ -bond have been made from the appropriate lithium salts together with $[OsCl_2(diphosphine)_2]$ {diphosphine = $[C_2H_4(PPh_2)_2]$ }; these are *cis*- and *trans*- $[OsR_2(diphosphine)_2]$ ($R = Me, Et, Ph$). Reduction of either the *cis* or *trans* isomer yields the hydride $[OsRH(diphosphine)_2]$ ($R = Me, Et$), and similar products are obtained from the ruthenium analogues. Infrared, nuclear magnetic resonance, and dipole moment studies on these are reported.^{99a}

The carbonyl complex $[Os(CO)_6]Cl_2$ has been very briefly reported;¹⁰⁴ its existence is somewhat surprising since this is a very high oxidation state for carbon monoxide ligands alone to stabilise. There are three types of carbonyl halides of osmium(II), all made by the action of carbon monoxide under pressure on osmium dihalides.⁸⁵ The monomeric $[Os(CO)_4X_2]$ and dimeric $[Os(CO)_3X_2]_2$ ($X = Cl^-, Br^-, I^-$) species are all quite stable, while the action of heat on $[Os(CO)_4I_2]$ yields the inert and highly polymeric $[Os(CO)_2I_2]_n$.⁸⁵ The reaction of hexahalogeno-osmates(IV) with tertiary phosphines and arsines in the presence of alcohols or ethanolic potassium hydroxide gives the remarkable series of carbonyl complexes of the general form $[Os^{II}HX(CO)(MR_3)_3]$ ($X = Cl^-, Br^-$; $M = P, As$).¹⁰⁰ These were earlier wrongly formulated as square planar derivatives of

⁹⁶ K. Masumo and S. Waku, *Nippon Kagaku Zasshi*, 1962, **83**, 116; I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, 1962, **18**, 89; J.-P. Mathieu and H. Poulet, *Compt. rend.*, 1959, **248**, 2325.

⁹⁷ D. F. Evans, D. Jones, and G. Wilkinson, *J.*, 1964, 3164; W. Beck and H. S. Smedal, *Z. Naturforsch.*, 1965, **20b**, 109.

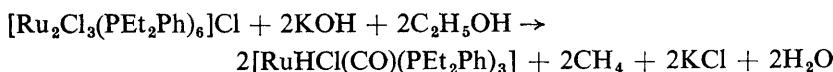
⁹⁸ E. O. Fischer and H. Grubert, *Ber.*, 1959, **92**, 2301.

⁹⁹ F. Jellinek, *Z. Naturforsch.*, 1959, **14b**, 737.

^{99a} J. Chatt and G. Hayter, *J.*, 1963, 6017.

¹⁰⁰ L. Vaska and J. W. diLuzio, *J. Amer. Chem. Soc.*, 1961, **83**, 1262; L. Vaska, *ibid.*, 1964, **86**, 1943; J. Chatt and B. L. Shaw, *Chem. and Ind.*, 1960, 931.

univalent osmium, $[\text{OsX}(\text{MR}_3)_3]$. The mechanism of their formation is not clear, but a suggestion recently put forward to explain the corresponding reaction with ruthenium complexes (and presumably the osmium reaction takes the same path) is that first an ethoxide complex is formed, followed by the transfer of a hydride ion (H^-) from the α -carbon atom of the ethoxide group to the metal giving an acetaldehyde complex which finally breaks down to methane and the carbonyl halide;¹⁰¹ the overall reaction is then



Methane has been detected amongst the reaction products,¹⁰¹ and tracer experiments with carbon-14 show that the carbonyl group comes from the alcohol.¹⁰⁰ The X-ray crystal structure of $[\text{OsBrH}(\text{CO})(\text{PPh}_3)_3]$ shows that the phosphine group *trans* to the supposed position of the hydrogen atom is 0.2 Å further from the metal than the other two (equatorial) phosphines, which may perhaps be taken as an illustration of the *trans* effect of the hydride group.¹⁰²

Osmium(I).—This is the rarest oxidation state for the element. The iodide, OsI , can be made from the elements and has a room-temperature magnetic moment of 0.5 B.M.⁵¹ No other halides or oxides are known. The carbonyl halides $[\text{Os}(\text{CO})_4\text{X}]_2$ ($\text{X} = \text{Br}^-, \text{I}^-$) are extremely stable and probably have halogen bridges and metal–metal interaction; they are made by the action of carbon monoxide and the halides at high temperatures in a high-pressure apparatus.⁸⁵ As mentioned earlier, $[\text{Os}(\text{NH}_3)_6]^+$ may be a hydride of bivalent osmium, while the “univalent” phosphines $[\text{OsX}(\text{PPh}_3)_3]$ are in fact the carbonyl hydrides $[\text{OsXH}(\text{CO})(\text{PPh}_3)_3]$.¹⁰⁰

Osmium(0).—The only established examples of this oxidation state are the carbonyls $[\text{Os}(\text{CO})_5]$ and $[\text{Os}_3(\text{CO})_{12}]$, although it is to be expected that the element should form zero-valent phosphine complexes of the type recently reported for ruthenium.¹⁰³

The pentacarbonyl is a colourless, monomeric liquid (m.p. -15°C) which can be made by the action of carbon monoxide under pressure on the trihalides together with silver or copper powder to take up the halogen. Although its structure has not yet been determined its monomeric nature suggests that it may have the trigonal bipyramidal structure of iron pentacarbonyl.^{85,104} During its preparation, yellow crystals (m.p. 224°C) of another carbonyl, originally formulated as the ennea-compound $\text{Os}_2(\text{CO})_9$, are formed (the same product results from the high pressure

¹⁰¹ J. Chatt, B. L. Shaw, and A. E. Field, *J.*, 1964, 3466.

¹⁰² P. L. Orioli and L. Vaska, *Proc. Chem. Soc.*, 1962, 333.

¹⁰³ J. Chatt and J. M. Davidson, *J.*, 1965, 843.

¹⁰⁴ H. Hieber and H. Fuchs, *Z. anorg. Chem.*, 1941, 248, 256; W. Hieber and T. Krück, *Angew. Chem.*, 1961, 73, 580.

reaction of osmium tetroxide with carbon monoxide).^{85,104} A recent *X*-ray determination, however, shows that the correct formulation is as a dodecacarbonyl, $\text{Os}_3(\text{CO})_{12}$. The molecule has approximately D_{3h} symmetry, the three metal atoms forming an equilateral triangle with four terminal carbonyl groups each, two approximately perpendicular to, and two parallel to, the triangular plane. The three tetracarbonyl osmium units are joined by metal-metal bonds (2.88 Å), and it was suggested that the bonding could best be understood in terms of octahedrally disposed metal orbitals which, instead of pointing directly at each other, form "bent" metal-metal bonds.¹⁰⁵ The infrared spectrum of $[\text{Os}_3(\text{CO})_{12}]$ has been recorded and is consistent with the above structure.¹⁰⁶

Hieber and Stallmann report that small quantities of a highly volatile substance, probably the carbonyl hydride $[\text{Os}(\text{CO})_4\text{H}_2]$ [strictly an osmium(II) derivative], were formed during preparations of the carbonyls.⁸⁵

Analysis of Osmium.—Almost all analytical methods for osmium are colorimetric.¹⁰⁷ The commonest, and probably the best, provided great accuracy is not demanded, makes use of the complex $(\text{Os thiourea}_6)^{3+}$; ruthenium interferes and should not be present to an extent greater than 10% of the osmium concentration.¹⁰⁷ For determination of small quantities of the element (down to 0.01γ) the accelerating effect of the tetroxide on the reaction between arsenic(III) and cerium(IV) in acid solution has been used.¹⁰⁸ In the presence of large amounts of ruthenium, osmium can be estimated colorimetrically as $(\text{Ph}_4\text{As})_2(\text{OsCl}_6)$,¹⁰⁹ but in general it is preferable to separate the metals first by acid distillation.

Toxicology of Osmium.—Osmium tetroxide is a violent poison, but fortunately has a characteristic and powerful odour. There is only one fatality (in 1874) recorded in the literature from tetroxide poisoning, death having been caused by capillary bronchitis and confluent pneumonia. The vapour attacks the eyes and may cause temporary blindness, lasting in some cases for a number of days, conjunctivitis and corneal ulceration, and it also attacks the nose, throat, and bronchial passages. The best treatment for chest symptoms is to administer penicillin or sulphapyridine drugs, and a propamidine lotion for any conjunctivitis which may develop.¹¹⁰ The traditional treatment with hydrogen sulphide gas dates from 1847 and is not recommended. A method for the quantitative estimation of tetroxide in the atmosphere has been developed and

¹⁰⁵ E. R. Corey and L. F. Dahl, *Inorg. Chem.*, 1962, **1**, 521.

¹⁰⁶ E. R. Corey and L. F. Dahl, *J. Amer. Chem. Soc.*, 1961, **83**, 2203; W. Beck and K. Lottes, *Chem. Ber.*, 1961, **94**, 2578; D. K. Huggins, N. Flitcroft, and H. D. Kaesz, *Inorg. Chem.*, 1965, **4**, 166.

¹⁰⁷ E. B. Sandell, "Colorimetric Methods for Traces of Metals", Interscience, New York, 1959, 702.

¹⁰⁸ R. D. Sauerbrann and E. B. Sandell, *Microchim. Acta*, 1953, 22.

¹⁰⁹ R. Neeb, *Z. analyt. Chim.*, 1957, **54**, 23.

¹¹⁰ A. I. G. McLaughlin, R. Milton, and K. M. A. Parry, *Brit. J. Ind. Medicine*, 1946, **3**, 183.

there are reviews on the toxicology of the element.^{110,111} Almost all osmium compounds are very easily oxidised to the tetroxide, particularly in acid solution, and consequently all work involving the element should be carried out in a well-ventilated laboratory.

The author is indebted to Dr. D. F. Evans and Dr. L. Pratt for their helpful and constructive criticism of the manuscript.

¹¹¹ F. R. Brunot, *J. Industr. Hygiene*, 1933, **15**, 136; D. Hunter, *J. Pharm. Pharmacol.*, 1953, **5**, 149; *Brit. Med. Bull.*, 1950, **7**, 11.