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THE CHEMISTRY OF RUTHENIUM, OSMIUM, RHODIUM, IRIDIUM, PALLADIUM AND PLATINUM IN THE HIGHER OXIDATION STATES

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CONTENTS

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ABBREVIATIONS

py	Pyridine
en	Ethylenediamine
phen	1,10-Phenanthroline
bipy	2,2′-Bipyridyl
terpy	2,2′,2″-Terpyridine
H_4EDTA	Ethylenediaminetetraacetic acid
bigH	Biguanidine
acacH	Acetylacetone
R_2dtc	Dithiocarbamate(1 −)
OEP	Octa-ethyl-porphyrin(2 −)
TTP	Tetra-*p*-tolyl-porphyrin(2 −)
INDOR	Inter nuclear double resonance
XPS	X-ray photoelectron spectroscopy
EPR	Electron paramagnetic resonance
NQR	Nuclear quadrupole resonance
MCD	Magnetic circular dichroism
BM	Bohr magneton

A. INTRODUCTION

The chemistry of the six platinum metals has been extensively investigated over the past thirty years, with most of the emphasis on the normal or low oxidation state compounds. The aim of the present review is to summarise the present state of knowledge of the chemistry of these elements in high oxidation states. For this purpose we define (somewhat arbitrarily) "high" as a formal oxidation state of M(IV) or above. The emphasis has been placed

TABLE 1

d^n configuration of metal oxidation states [a]

Oxidation state	Ru	Os	Rh	Ir	Pd	Pt
IV	$\underline{d^4}$	$\underline{d^4}$	d^5	$\underline{d^5}$	$\underline{d^6}$	$\underline{d^6}$
V	d^3	d^3	d^4	d^4	(d^5)	d^5
VI	$\underline{d^2}$	$\underline{d^2}$	d^3	d^3	(d^4)	d^4
VII	d^1	d^1	(d^2)	(d^2)	(d^3)	(d^3)
VIII	d^0	$\underline{d^0}$	(d^1)	(d^1)	(d^2)	(d^2)

[a] Most important states underlined; (d^n) indicates no compounds in this state definitely identified.

upon isolated compounds, and coverage of solution chemistry is restricted to well-defined species.

The d^n configuration of the metal oxidation states is shown in Table 1.

In general corresponding oxidation states are less stable in the 4*d* than the 5*d* series, differences between the pairs Ru–Os, Rh–Ir, Pd–Pt are much more pronounced than in their normal oxidation states. There is hardly any similarity with the 3*d* elements [1], only in a very few compounds such as $[FeO_4]^{2-}/[RuO_4]^{2-}$ or the $[MF_6]^{2-}$ (M = Ni, Pd, Pt) is there more than a formal resemblance. Thermodynamic data for these high oxidation states is not extensive and has been reviewed [2]. The ionisation potentials (IP) and atomisation enthalpies (ΔH^0_{atom}) are shown in Table 2. The lower ΣIP for corresponding oxidation states of a 5*d* element compared to a 4*d* is clearly one factor contributing to the greater stability of the 5*d* state.

The factors which influence the stability of oxidation states for the 4*d* and 5*d* metals have been discussed by several authors, e.g. [3,5], and coupled with the general decreasing stability on moving to the right of the periodic table, account for the often unstable, and highly oxidising nature of the compounds reviewed below. It is also true that states with an even number of *d*-electrons d^6, d^4, d^2, d^0, are more stable than those with an odd number d^5, d^3 or d^1, and that the odd d^n configurations often have a tendency to disproportionate to d^{n+1} and d^{n-1} (always assuming the d^{n+1} state is not prohibitively unstable on thermodynamic grounds, which explains why the d^5 Ir(IV) does not show this behaviour).

The vast majority of the compounds have octahedral or distorted octahedral coordination about the metal. Five-coordination is known in a number of cases, e.g. $[RuNCl_4]^-$, $[OsNCl_4]^-$ and $[OsO(O_2R)_2]$, but tetra-

TABLE 2

Ionisation potentials of the platinum metals [3] (kJ mol^{-1})

IP	Ru	Os	Rh	Ir	Pd	Pt
1	711	840	720	879	804	870
2	1617	1640	1744	1648	1874	1791
3	2746	2410	2996	2602	3177	2745
4	4427	3849	4393	3766	4707	3958
5	6067	5188	6464	5481	6360	5314
6	7824	6569	8201	6945	8661	7238
7	9665	7991	10120	8494	10580	8870
8	?	?	–	–	–	–
H^0_{atom} [4]	669	728	577	690	381	546

hedral (4) coordination is rare being limited to OsO_4, RuO_4 and the $[RuO_4]^{n-}$, $n = 1, 2$ ions. Seven-coordination is only established for Ru and Os, in OsF_7 and a few dithiocarbamate complexes of Ru(IV) and Os(IV).

Although the effort devoted to high oxidation state chemistry has not been as great as that in low oxidation states, the number of compounds falling within the scope of the review is large, and certain limitations have been applied to keep the work to a reasonable size. We have specifically excluded organometallic compounds, kinetic and stability constant studies in solution.

The literature citation is not exhaustive, but aims to include important studies with the emphasis on the most recent work. We have nonetheless been impressed during the data collection by the quantity of work pre 1940, which contains important preparative accounts or which has received little more recent study, and references to this have been included. Whilst many compounds have been reported on only one or two occasions, at the other extreme a few have been intensively examined. In the latter class are OsO_4, the more stable MF_6, and especially the hexachlorometallates(IV). Papers citing $[PtCl_6]^{2-}$ alone run to many hundreds, and in such cases coverage is restricted to representative data. Platinum(IV) compounds are generally very stable and kinetically inert which has resulted in the production of a great many complexes; indeed the total number of such complexes considerably exceeds the number of compounds of the other elements falling within the scope of the present review. Hence coverage of the relevant chemistry of the other five metals is as far as possible comprehensive, but the treatment of Pt(IV) is highly selective, intended only to provide an overview of the chemistry and a comparison with the other metals.

The format used is the conventional arrangement of compounds by formal oxidation state. The sub-divisions within each oxidation state are oxides and oxoanions, halides and haloanions, special classes (e.g. osmyl compounds or nitrides), and finally complexes. The arrangement aims at clarity and the convenience of the reader, rather than following rigorous definitions, and thus haloanions although by definition complexes, are placed in the halide sections.

B. PHYSICAL MEASUREMENTS

Details of the physical and spectroscopic properties of individual compounds are discussed in the main text. In this section we deal with general points about the specific techniques as applied to these oxidation states.

(i) Magnetism

Magnetic properties of the 4*d* and 5*d* elements are not a very useful guide to oxidation state (certainly not in spin-only terms), and rarely indicate stereochemistry. All compounds are low-spin as a result of the large ligand field splittings and the spatial extension of the *d*-orbitals which aids spin-pairing. The spin–orbit coupling constants are very large (they are a function of the fourth power of the effective nuclear charge) and since they are substantially greater than KT (ca. 200 $\mathrm{cm^{-1}}$ at room temperature), the magnetic moments of paramagnetic compounds are often well below the spin-only values. In fact many even-number-d^n ions are diamagnetic, for example the $d^2[\mathrm{OsO_2}]^{2+}$ compounds, which is explained as due to the strong π-donor power of the *trans* oxide ligands producing tetragonal distortion and the configuration d_{xy}^2. Magnetically "non-dilute" compounds further complicate the picture, e.g. the μ_{eff} of $\mathrm{K_2[OsCl_6]}$ is 1.44 BM, but on "dilution" in diamagnetic $\mathrm{K_2[PtCl_6]}$ the moment rises, approaching 2.13 BM at "infinite dilution". A comprehensive summary of the magnetic properties is available [6].

(ii) Electron paramagnetic resonance

The large number of diamagnetic compounds and the unfavourable relaxation times of some d^n configurations, severely limits the usefulness of EPR spectra in this area. Only d^1 which is represented by a few osmium and ruthenium compounds, and d^5 in Rh(IV) and Ir(IV) are easily amenable to EPR spectral studies. Indeed one of the classic EPR experiments, which provided some of the first good evidence of electron delocalisation was performed on $[\mathrm{IrCl_6}]^{2-}$ [7]. The $t_{2g}^5e_g^0$ configuration in Ir(IV) has provided most of the results to date [8].

(iii) Nuclear magnetic resonance

Only $^{103}\mathrm{Rh}$ ($I=\frac{1}{2}$ 100%) and $^{195}\mathrm{Pt}$ ($I=\frac{1}{2}$ 34%) are suitable nuclei for NMR studies, and the low resonance frequency of Rh has limited studies. For compounds relevant to this review only $^{195}\mathrm{Pt}$ in Pt(IV) compounds is of importance. Early studies used the INDOR technique, but recent developments in instrumentation have made direct observation of $^{195}\mathrm{Pt}$ signals possible [9]. There is a considerable amount of data available, although much of it deals with Pt(0) and Pt(II) compounds. The chemical shift is not characteristic of formal oxidation state, $[\mathrm{PtF_6}]^{2-}$ and $[\mathrm{PtI_6}]^{2-}$ lying at opposite ends of the frequency range, although Pt(IV) compounds in general do lie towards the higher frequency end. The very wide range of $^{195}\mathrm{Pt}$

chemical shifts, ca. 1300 ppm, suggests that this technique has great potential for identifying unknown materials; certainly shifts appear to be characteristic of the donor set and rather insensitive to substituents on the donor atoms. The data available have been summarised by Kidd and Goodfellow [9].

The application of ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectroscopy to high oxidation compounds does not require any special comments, although the instability of many of the compounds in solution, or even the lack of a suitable solvent, are complicating factors. It should be noted that for some d^4 Os(IV) phosphines, the ^{1}H and ^{31}P NMR spectra show sharp resonances with spin–spin coupling, despite the paramagnetic nature of the complexes [10].

(iv) Vibrational spectroscopy

The application of IR and Raman spectroscopy to the compounds discussed below does not differ significantly from that in other areas. The deep colours of many compounds restricts Raman studies, although with increasing availability of a choice of laser sources, the problem has been considerably eased. The techniques provide an invaluable guide to the species (groups, ligands, etc.) present, and in suitable cases to the stereochemistry about the metal centre. Particularly notable is their application to the study of compounds containing $Ru=O$ or $Os=O$ bonds, the most important examples being the series of papers by Griffith and co-workers [61,81,171,190].

(v) X-ray and electron diffraction

Electron diffraction data has been reported for a number of volatile species including RuO_4, OsO_4 and OsF_6 [33,35,153]. X-ray diffraction is clearly the pre-eminent method for determining solid state structures, and details of individual structures are reported in the appropriate section. The main problem is the practical difficulty of growing (and keeping) suitable single crystals of unstable or highly reactive materials. The complexity of the chemistry of these elements especially Ru and Os, makes single crystal X-ray studies particularly desirable in the identification of new compounds, and whilst the number of studies in this area is growing, the need for many more becomes obvious when reviewing the descriptive chemistry.

(vi) Electronic spectroscopy

The large ligand field splittings present in high oxidation state metal ions of the 4*d* and 5*d* series means that *d–d* transitions are expected at fairly high energies. Coupled with the movement of charge-transfer bands to lower energies, and the much greater intensity of the CT bands, the *d–d* spectra are observed much less frequently than for the 3*d* analogues. The most extensive *d–d* spectral data is probably that of the $[MX_6]^{n-}$ ions especially $[MF_6]^{n-}$, which has recently been compiled and interpreted in terms of ligand field theory and the strong field model [11]. The study of the charge transfer spectra initiated by Jörgensen [12] for the $[MX_6]^{n-}$ (X = Cl, Br, I) requires a molecular orbital interpretation, which is simplest to apply to high symmetry molecules or ions. Relatively few attempts have been made to interpret CT spectra in detail for the lower symmetry cases, but the prediction of the energy of the lowest energy CT band using the optical electronegativity approach has been widely used, e.g. [13]. There is still considerable scope for detailed studies of the electronic spectra of the less familiar oxidation states of the heavy transition metals.

(vii) Mössbauer spectroscopy

For the platinum metals, Mössbauer spectroscopy is applicable to ^{99}Ru, ^{189}Os, ^{193}Ir and ^{195}Pt. Most data have been reported for ^{99}Ru which has a natural abundance of 12.7%, and for which the transition is the $5/2 \rightarrow 3/2$ and a γ energy of 90 keV. It appears that the ruthenium isomer shift increases monotonically with the metal oxidation state [14]. Greenwood and co-workers [15,16] have used the technique to demonstrate the presence of different oxidation states of Ru in mixed oxides, and to probe the magnetic structure of the oxides. The isomer shift also increases steadily with oxidation state in osmium compounds with σ donor ligands, although in complexes of σ donor/π acceptor ligands the shifts must be interpreted with care [17]. The data on higher oxidation states of iridium are limited but appear to show similar trends [18].

(viii) X-ray photoelectron spectroscopy

Studies of metal electron binding energies have shown that they generally increase in magnitude with increasing formal oxidation state of the metal. The $4f^{7/2}$, $4f^{5/2}$ binding energies are most useful for the 5*d* series, and the $4d^{5/2}$, $4d^{3/2}$ for the 4*d* elements. Potentially then these energies offer a means of "measuring" the formal oxidation state. There are a number of complications, not least surface reduction of unstable high oxidation state compounds, and in polynuclear compounds, or complexes of "non-innocent" ligands the result may be a non-integral oxidation state. For many simple compounds the results are not controversial, for example the $4f^{7/2}$ binding energy varies by ca. 5 eV between Pt(0) and Pt(IV) [19,20]. Whilst other more routine spectroscopic techniques can distinguish Pt(0), (II) and (IV), an important advance using XPS measurements has occurred in osmium chemistry. It has been shown that the $4f^{7/2}$, $4f^{5/2}$ binding energies vary by ca. 6 eV between Os(II) and Os(VIII), with intermediate oxidation state compounds giving values clustering about particular energy values, which are characteristic of the formal oxidation state. Not only does this aid characterisation of new osmium complexes [21], but it has made it possible to examine the nature of the osmium compounds produced in OsO_4 stained biological materials [22], information which is not obtainable in other ways at present.

Previous literature reviews of the area covered by the present article are [23,24], and in the appropriate volumes of the Gmelin Handbook [25].

C. RUTHENIUM AND OSMIUM

(i) M(VIII) d^0

The only well characterised compound of ruthenium in this oxidation state is the tetroxide RuO_4. Osmium is represented by OsO_4, probably the most important single compound of the element, by OsO_3F_2, $[OsO_3N]^-$, $[OsO_4(OH)_2]^{2-}$ and a number of complexes.

Oxides, $[MO_4]$

Osmium tetroxide is usually prepared by direct reaction of the elements above 300°C [26], but can also be obtained from almost any osmium compound and a strong oxidising agent. RuO_4 is not obtainable from the metal and oxygen, but can be prepared from Ru powder and pure ozone [27]. More conventional syntheses for RuO_4 involve oxidation of $RuCl_3$ with $NaClO_3$ or $NaBrO_3$ in aqueous acid solution, or from aqueous $K_2[RuO_4]$ and Cl_2, $[MnO_4]^-$ or $[IO_4]^-$ [26,28,29]. A convenient preparation of RuO_4 in solution is from $RuO_2 \cdot nH_2O$ and $NaIO_4$ in water at 0°C, followed by CCl_4 extraction [30]. Both compounds are yellow crystalline solids (RuO_4, m.p. 25.4°C, b.p. 40°C, OsO_4, m.p. 40.5°C, b.p. 131°C), which vaporise easily, and have pungent characteristic odours. Both are highly toxic, OsO_4 being particularly dangerous due to its ease of formation from most osmium compounds [31].

The most accurate X-ray data [32] shows solid OsO_4 to contain slightly distorted tetrahedra $O\text{–}\widehat{Os}\text{–}O$ 106.7(4)° and 110.7(3)°, with mean $Os\text{–}O = 1.697$ Å, whilst the vapour contains regular tetrahedral molecules with $Os\text{–}O = 1.711$ Å (electron diffraction data) [33]. Only the unit cell dimensions are available for solid RuO_4 [34], but electron diffraction studies of the vapour confirm a T_d structure with $Ru\text{–}O = 1.705$ Å [35]. Vibrational spectra have been reported for both molecules, in the solid, liquid and gas phases

[36–39] and for OsO_4 for the matrix isolated (Ar) molecule [40]. Electronic [41–43], photoelectron [44–46] and MCD [47] spectra have been measured and assigned [48].

RuO_4 is generally less stable and a much stronger oxidising agent than OsO_4. A consequence of this is that whilst a number of other Os(VIII) compounds can be made from OsO_4, the reactions of RuO_4 generally result in compounds in lower oxidation states. Both MO_4 dissolve in water to a small extent and Raman spectra of the solutions suggest that the unchanged T_d monomers are present [49], although there is some evidence that small amounts of weakly acidic "H_2MO_5" may also be formed [50,51]. OsO_4 is also soluble without reaction in CCl_4, C_6H_6, Et_2O and cyclohexane, but for RuO_4 only CCl_4 and freons are suitable; most other organic solvents are violently oxidised. Osmium tetroxide has been extensively used as an oxidant in organic chemistry, especially for the conversion of alkenes to diols. This area has been reviewed several times [52–54], the excellent account by Schröder [55] provides coverage to mid-1979. RuO_4 has been used to a much smaller extent [52,53,56] and differs from OsO_4, in being a much stronger and more destructive oxidant, e.g. it cleaves $>C=C<$ bonds. Use of OsO_4 as a microscopic staining reagent has also been reviewed [57].

Oxoanions

RuO_4 is reduced to $[RuO_4]^-$ by alkali, but OsO_4 and cold aqueous KOH produce the deep red crystalline $K_2[OsO_4(OH)_2]$ [58,59]. Cs [58,59], Ba [58,59] and Na [60] salts are also known. Vibrational spectra suggest the anion is *cis* (C_{2v}) [61]. There are also Cs and Rb salts with a 1:1 M:Os ratio possibly $M[OsO_4(OH)H_2O]$ [59], and a $Ba[OsO_5]$ formed [62] on heating $Ba[OsO_4(OH)_2]$ at 360°C under nitrogen.

Halides and oxohalides

The "OsF_8" of Ruff and Tchirch [63] is now believed to have been impure OsF_6 [64]. There is some possibility that OsF_8 may be formed in addition to OsF_7 by high pressure fluorination of the metal [65], but this has yet to be confirmed. Claims [66,67] for a yellow RuF_8 as a minor product of fluorination of Ru or RuO_2 are similarly unconfirmed. Since other workers [68] have shown that RuO_4 is readily formed by hydrolysis of ruthenium fluorides, it is possible that the "RuF_8" is a mixture of RuO_4 and SiF_4 or HF. The only oxohalide is OsO_3F_2 prepared from Os and F_2/O_2 mixture [69], from OsO_4, KBr and BrF_3 [69] or from OsO_4 and F_2 in a 1:2 ratio at 300°C [70]. OsO_3F_2 is an orange solid which exists in three crystalline modifications, two of which are orthorhombic related to the $MoOF_4$ and RuF_5 structures respectively, and a monoclinic form [71]; all are thought to contain six-coordinate osmium and are fluorine, not oxygen, bridged on the basis of their Raman spectra [71,72]. The compound vaporises as a monomer and the vibrational spectra of the matrix isolated species are consistent with a D_{3h} structure (three equivalent oxygens) [40], although electric deflection measurements suggest a lower symmetry [70]. As required for Os(VIII) the compound is diamagnetic [72]. Several attempts to prepare OsO_2F_4 from OsO_3F_2 and F_2, or $Os + O_2/F_2$ failed [71,73].

The $M[OsO_3F_3]$ salts (M = K, Cs, Ag) are orange crystalline solids prepared from OsO_4, BrF_3 and KBr, CsBr or $Ag[IO_3]$ respectively [69]. The IR and Raman spectra show the anion to have a *fac* structure (C_{3v}) [61,74]. The $M_2[OsO_4F_2]$ (M = Cs, Rb) are made from OsO_4 and MF in aqueous solution [58,59], as unstable yellow solids. The anion probably has a *cis* structure (C_{2v}) [61].

Nitrogen derivatives

Potassium osmiamate $K[OsO_3N]$, is formed as yellow crystals from OsO_4, KOH and aqueous ammonia [75], and can be converted to the less soluble Rb, Cs, [26], Ag [76], $^nBu_4N^+$, Ph_4P^+ or Ph_4As^+ [76,77] by metathesis. Li, Na, NH_4, Ca, Sr, Ba and Mg salts have been made from $Ag[OsO_3N]$ and metal chloride [76,78]. The free acid $HOsO_3N$, is among the products of the reaction of OsO_4 and liquid ammonia [79,80], and on the basis of its IR spectrum is formulated $OsO_2N(OH)$ [81]. The structure of $K[OsO_3N]$ reveals a tetrahedral anion with Os–O, Os–N = 1.75(2) Å [82] or Os–O = 1.78(3) and Os–N = 1.63(3) Å [83]. IR spectra of several salts reveal ν(Os–N) 1020 cm^{-1}, ν(Os–O) 895, 870 cm^{-1} [76,84,85]; the electronic spectrum has also been reported and assigned [77,86].

A series of imido complexes $[OsO(NR)_3]$, $[OsO_2(NR)_2]$ and $[OsO_3(NR)]$ is known [87]. The orange-red $[OsO(N^tBu)_3]$ and yellow $[OsO_2(N^tBu)_2]$ are

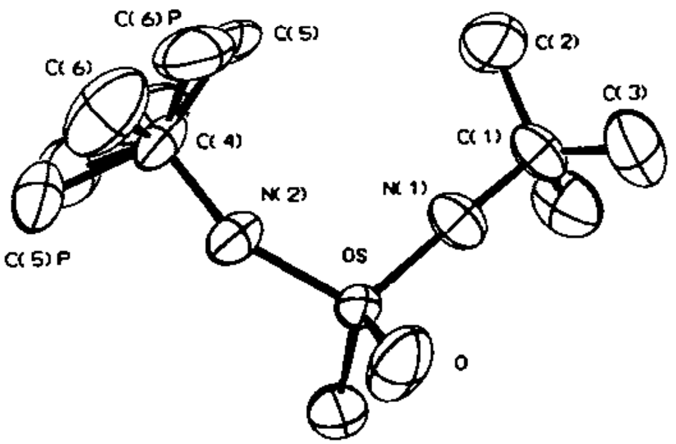


Fig. 1. The structure of bis(*N*-tert-butylimido)dioxoosmium. From ref. 89.

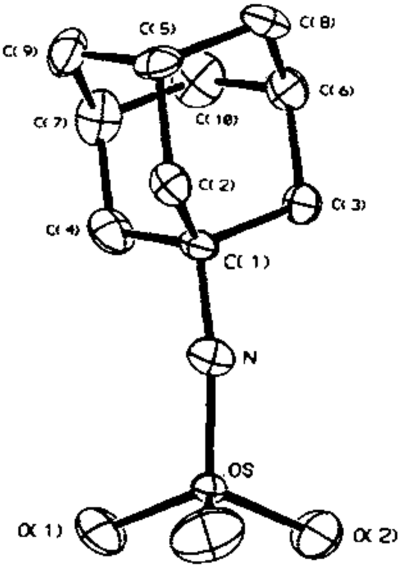


Fig. 2. The structure of *N*-1-adamantylimidotrioxoosmium. From ref. 89.

obtained from OsO_4 and *N*-tert-butyltri-n-butylphosphineimine in the correct ratio in CH_2Cl_2, and the orange-yellow $[OsO_3(N^tBu)]$ from OsO_4 and $^tBuNH_2$ in water or pentane [75,87,88]. The IR [75,88], electronic [77] and ^1H NMR spectra [88] of $[OsO_3(N^tBu)]$ have been published. Other imido species including $[OsO_2(NR)(NR')]$ and $[OsO(NR)(NR')_2]$ are known [87,88]. An X-ray structure of $[OsO_2(N^tBu)_2]$ (Fig. 1) shows approximately tetrahedral coordination about osmium: Os–O = 1.744(6) Å, Os–N = 1.715(8) Å, O–$\widehat{\text{Os}}$–O = 109.9(4)°, N–$\widehat{\text{Os}}$–N = 111.5(4)° [89]. The $[OsO_3NR]$ (Fig. 2) in which R = 1-adamantyl, is similar: Os–N = 1.697(4) Å, Os–O = 1.714(4) Å, O–$\widehat{\text{Os}}$–O = 109.1(2)° [89]. Analogous to the hydroxylation of alkenes by OsO_4, $[OsO_3(NR)]$ and alkenes produce stereospecific *cis* oxyamination, and $[OsO_2(NR)_2]$ and $[OsO(NR)_3]$ *cis* diamination [87,88,90].

Complexes

The yellow-orange $[OsO_4 \cdot 2\ SbCl_5]$ adduct has an IR spectrum consistent with the structure shown in Fig. 3 [91].

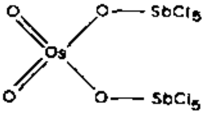


Fig. 3. The proposed structure of $OsO_4 \cdot 2\ SbCl_5$.

The best characterised complexes of OsO_4 with neutral donor ligands are those with amines and nitrogen heterocycles. The simplest is $[OsO_4 \cdot NH_3]$ an orange solid made by reaction of OsO_4 and NH_3 at −25°C [79]. Similar yellow or orange $[OsO_4 \cdot L]$ (L = quinuclidine, isoquinoline, phthalazine, and pyridazine) and $[(OsO_4)_2 \cdot L']$ (L′ = hexamethylenetetramine, pyrazine, 5-Me-pyrimidine, 1,4-diazabicyclo[2.2.2]octane) have been prepared from OsO_4 and the amine in water [92]. The adducts are soluble in most organic solvents and can be used for *cis*-hydroxylations, being more convenient to handle than OsO_4. The vibrational spectra suggest that only terminal Os = O multiple bonds are present [92], and this was confirmed by an X-ray study on $OsO_4 \cdot$ quinuclidine which revealed a structure (Fig. 4) in which the geometry about the osmium is intermediate between T_d and trigonal bipyramidal [93]. The Os–O bonds 1.697–1.722 Å are little changed from OsO_4, and the Os–N bond is very long (2.37 Å) indicating the amine is weakly coordinated. The 2:1 adduct with hexamethylenetetramine is similar with OsO_4 units bound to two of the nitrogens, Os–N = 2.42 Å [93].

The unstable $[OsO_4 \cdot$ pyridine] made from the constituents in an inert solvent [94,95] is monomeric in solution [96], and probably has a similar structure to the amine adducts [96]. The "$OsO_4 \cdot 2$ py" is certainly $[Os_2O_6 \cdot (py)_4]$. A number of other amines appear to form unstable OsO_4 adducts in solution, but these are not sufficiently stable to be isolated [97]. Both RuO_4 and OsO_4 from unstable 1:1 and 2:1 (M:L) compounds with PF_3 of unknown structure [98], but reduction occurs with PCl_3 or PBr_3.

The formation of nitrogen donor adducts by RuO_4 has been reported by

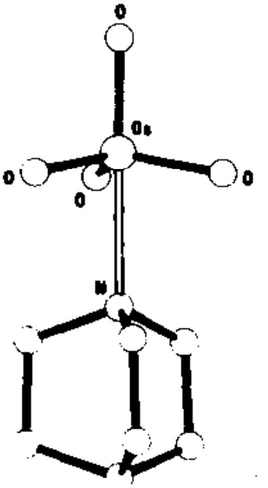


Fig. 4. The structure of the 1:1 adduct of OsO_4 and quinuclidine. From ref. 93.

several workers, but there is considerable doubt about their true nature. At low temperatures RuO_4 and NH_3 may form an explosively unstable $[RuO_4 \cdot NH_3]$ [79] but under different conditions the product is a polymeric Ru(IV) nitride.

Reaction of RuO_4 and pyridine in CCl_4 was reported to give $[RuO_4(py)_2]$ [99], but this diamagnetic dark green solid has only a single band in its IR spectrum assignable to Ru = O groups, and is probably a Ru(VI) compound *trans*-$[RuO_2(OH)_2(py)_2]$ [94,96]. Ishiyama [100] has prepared a complex formulated as $[RuO_4(2,2'\text{-bipyridyl})] \cdot 3H_2O$, which Griffith and Rossetti [96] suggested was $[RuO_2(OH)_2(2,2'\text{-bipyridyl})] \cdot 2H_2O$. Ishiyama [101], however, subsequently described a dark-brown $[RuO_2(OH)_2(2,2'\text{-bipyridyl})] \cdot 3H_2O$ formed by reduction of $[RuO_4(2,2'\text{-bipyridyl})] \cdot 3H_2O$ in methanol. Further work is required to establish the true nature of these products.

Finally there are several substances claimed to be of type $[OsO_2L_2]Cl_4$ (L = 4-benzylamidothiosemicarbazide [102], 1-methoxyphenyl-4-benzamidothiosemicarbazones [103], various ketoanils [104,105], 8-amino-7-hydroxy-4-methylcoumarin [105]) prepared from OsO_4 and the ligand in ethanol, in the presence of HCl. The very limited characterisation reported does not prove the presence of Os(VIII), and they are most likely osmyl species [Os(VI)]. Substituted derivatives of the osmiamate ion $[OsONL_2]X$ and $[OsONL'_2]X_3$ L = *N'*-amidinoisoureas, L' = biguanide or *N*-alkylbiguanide, $X = \frac{1}{2}SO_4$, OH) have been claimed [106].

(ii) M(VII) d^1

This is an unimportant state for both metals, represented by OsF_7, $OsOF_5$, OsO_2F_3, and some oxoanions of which only the perruthenate $[RuO_4]^-$ is well-known.

Oxides and oxoanions

No oxides M_2O_7 are known. Potassium perruthenate $K[RuO_4]$ is formed by fusion of Ru with KOH and KNO_3 (along with $K_2[RuO_4]$), by chlorine oxidation of $K_2[RuO_4]$ in concentrated aqueous alkali, or from RuO_4 and KOH [107–110]. Various other salts including $Na[RuO_4]$ and $Ba[RuO_4]_2$ are known [102,108], but few recent studies of the solid compounds have appeared. $K[RuO_4]$ forms black crystals which contain slightly flattened $[RuO_4]^-$ tetrahedra, Ru–O = 1.79 Å, $O\widehat{Ru}O$ = 106° [111]. Solid $K[RuO_4]$ is stable in air, and decomposes on heating to $K_2[RuO_4]$, RuO_2 and O_2. The green aqueous solution is unstable, decomposing to $[RuO_4]^{2-}$ and oxygen at high pH, and to RuO_4 and either $RuO_2 \cdot nH_2O$ or $Ru_2O_5 \cdot nH_2O$ on acidification [112,113]. In alkaline solution there is some evidence for $[RuO_4(OH)_2]^{3-}$ [112]. The IR and Raman spectra of solid $K[RuO_4]$ have been measured [74,114,115]. There are numerous reports of the electronic spectrum of the perruthenate ion in solution, but agreement between them is poor; clearly many measurements have been made on impure solutions (often containing $[RuO_4]^{2-}$). The best recent data appear to be [112,113,116,117], and for interpretation [48,118]. Oxidation of organic compounds by $M[RuO_4]$ has been briefly examined [e.g. 119].

There is no osmium analogue of $[RuO_4]^-$, but $M_5[OsO_6]$ (M = Li, Na) and $Na_3[OsO_5]$ are formed by heating M_2O with Os in oxygen at 550°C [120]. $K_5[OsO_6]$ and $Ba_5[OsO_6]_2$ form on heating the osmate(VI) with the metal oxide [120]. All are black and decompose to OsO_4 and Os(VI) in water. Mixed metal $M^{II}_2M^I[OsO_6]$ are also known (M^{II} = Ba, Sr, Ca; M^I = Li, Na) [121]. On the basis of their vibrational spectra it has been suggested [61] that the $M^I_3[OsO_5]$ contain $[Os_2O_{10}]^{6-}$ ions with octahedrally coordinated osmium. The IR spectra of the $[OsO_6]^{5-}$ ions are complex, probably due to low site symmetry.

Halides and oxohalides

The only halide is OsF_7 made from Os powder and fluorine under the extreme conditions of 400 atm and 600°C. It is pale yellow, volatile, and decomposes to $OsF_6 + F_2$ at temperatures above -100°C at 1 atm pressure. Mass, EPR and IR spectra were recorded, and it was concluded that the structure is pentagonal bipyramidal [65]. The magnetic moment at 90 K is 1.08 BM. $OsOF_5$ is prepared from OsO_2 and F_2 [73] from $Os/O_2/F_2$ [73,122], OsO_3F_2 and F_2 [73] or from OsF_6/OsO_4 in a 3:1 ratio [72]. The product is emerald green, and has a slightly distorted octahedral structure [123], Os–O = 1.74(3) Å, Os–F = 1.72(3) Å (*trans* O), and 1.78(3) Å(av) (*trans* F). Its magnetic susceptibility is temperature independent $\mu = 1.47$ BM, and approximately obeys the Curie Law ($\theta = +6°$) [73]. Vibrational [73,122] and mass spectra [70] have been measured. The yellow-green very moisture sensitive OsO_2F_3 is formed from 1:1 mixtures of OsF_6 and OsO_4 at 150°C or OsO_3F_2 and $OsOF_4$ at 100°C [72]. The solid is isomorphous with the monoclinic form of OsO_3F_2, and the Raman spectrum indicates F rather than O bridges. The measured $\mu \leqslant 0.25$ BM may be due to impurities, although it is similar to that of ReF_6 ($\mu = 0.26$ BM). The mass spectrum indicates that monomers are present in the vapour, but also shows that substantial disproportionation to OsO_3F_2 and $OsOF_4$ occurs. A further unidentified oxofluoride possibly OsO_3F or $OsO_2F_2(Os^{VI})$ is a minor product of the reaction of OsF_6 with glass [124].

Complexes

The deep green solid obtained from RuO_4 and 1,10-phenanthroline, and formulated as $[Ru_2O_7(phen)_2]$ [125] was suggested to be an oxo-bridged dimeric Ru(VII) species. Its nature is unclear (cf. $[RuO_4 \cdot (2,2'\text{-bipyridyl})] \cdot 3\ H_2O$ but it is improbable that Ru(VII) is present; Ru(VI) is more likely.

(iii) M(VI) d^2

This is an important state for osmium; in addition to OsF_6, there are numerous osmyl $[OsO_2]^{2+}$, nitrido $[OsN]^{3+}$, and diester complexes. Ruthenium forms RuF_6, the ruthenate ion $[RuO_4]^{2-}$, and a small number of unstable ruthenyl $[RuO_2]^{2+}$ complexes.

Oxides and oxoanions

There is no evidence for RuO_3 in the solid state, and claims for $OsO_3 \cdot nH_2O$ as a hydrolysis product of Os(VI) esters [126], or from $K_2[OsO_2(OH)_4]$ and alcohol [127] have not been confirmed. Other workers have suggested that $OsO_2 \cdot nH_2O$ or $Os_2O_5 \cdot nH_2O$ are the products. RuO_3 is thought to be the major gas phase species in the Ru/O_2 system over the temperature range 1100–1800°C [128–130]. There is similar evidence for gaseous OsO_3 between 827–1477°C [131,132].

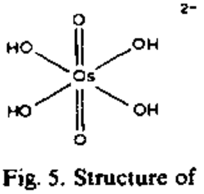
Black crystals of potassium ruthenate $K_2[RuO_4]$, are obtained by treating RuO_4 with excess concentrated aqueous KOH, or by reaction of Ru, KNO_3 and KOH in a melt, and crystallising the product from concentrated alkali [107–115, 133]. The Na [60], Rb, Cs, Mg, Ca, Sr, Ba salts are also known [108,133,134]. Surprisingly no X-ray structure of an alkali metal ruthenate has been reported, but the structure of "$BaRuO_4 \cdot H_2O$" shows that it is $Ba[RuO_3(OH)_2]$ with a trigonal bipyramidal anion with *trans* axial OH groups Ru–OH = 2.04 Å, Ru–O = 1.755 Å [135]. Since hydrated forms of alkali-ruthenates have been reported, X-ray structural confirmation (or otherwise) of the $[RuO_4]^{2-}$ ion in these seems desirable. Vibrational spectra of the ruthenate ion (K, Ba salts) have been measured [49,74,114,115]. In alkaline solution the orange ruthenate ion is stable, but as the pH is lowered, disproportionation to $[RuO_4]^-$ and $RuO_2 \cdot nH_2O$ or $Ru_2O_5 \cdot nH_2O$ occurs [113,117]. The electronic spectrum has been measured in solution many times; differences in the published data are usually ascribable to contamination with $[RuO_4]^-$. The best data appear to be [110,112,116] and recent assignments are in refs. 48 and 118. The EPR spectrum of $Na_2[RuO_4]$ at 20 K gave $g = 2.0$ with an isotropic splitting of 0.02 cm^{-1} [136], and the magnetic susceptibility of $K_2[RuO_4]$ in solution give $\mu_{eff} = 2.75$ BM [137]. The oxidation of organic compounds by ruthenates [138,139] or by $RuCl_3 + K_2S_2O_8$ (which forms K_2RuO_4 in solution) [140] has been briefly studied.

Potassium osmate was originally formulated as $K_2[OsO_4] \cdot 2\ H_2O$, but is in fact an octahedral osmyl species $K_2[OsO_2(OH)_4]$. It is made by reduction of OsO_4 with ethanolic KOH, or by fusion of Os with KNO_3 and KOH

[26,137,141]. Reaction of OsO_4 with MOH in ethanol also produced $M_2[OsO_2(OH)_4]$ (M = Rb, Cs) [141], whilst $M^{II}[OsO_2(OH)_4]$ (M^{II} = Ca, Sr, Ba) are made by metathesis from the potassium salt [61,142]. An X-ray study of the potassium salt shows the anion to have the structure shown in Fig. 5 [143,144] with Os=O = 1.77 Å, Os–OH = 2.03 Å. The violet solid is diamagnetic, which was explained in terms of the tetragonal distortion produced by the strong π-donor oxide ligands resulting in pairing of the two electrons in the d_{xy} orbital (z taken as O = Os = O axis) [137]. The electronic spectrum has been assigned on the basis of this bonding model [137]. The IR spectra of alkali–metal osmates have been recorded by several workers [61,74,141]. Acidification of $K_2[OsO_2(OH)_4]$ solution is said to produce Os(VII) in solution and a precipitate of Os(V) oxide [145], and in alkaline solution $[OsO_3(OH)_3]^{3-}$ may form [146]. It has been suggested that the $BaOsO_4 \cdot H_2O$ is $Ba[OsO_3(OH)_2]$ [142], possibly an oxo-bridged dimer (Fig. 6) on the basis of IR studies. There are similar Sr and Ca salts [142]. Since $Ba[RuO_3(OH)_2]$ has a monomeric TBP anion, an X-ray study of the osmate is clearly desirable. Other osmates have been made by dry methods. Black $Li_6[OsO_6]$ made from Li_2O and $Li_5[OsO_6]$ at 800°C under nitrogen has the β-$Li_6[ReO_6]$ structure with Os–O = 2.06 Å [120,147]. Black $Na_4[OsO_5]$ forms on heating $Na_5[OsO_6]$ in nitrogen at 800°C [120]. Calcium, strontium and barium osmates include $M_3[OsO_6]$ (M = Ca, Sr, Ba) obtained from MO and Os in oxygen at 1000°C; $Ba_2[OsO_5]$ formed from "$BaOsO_4 \cdot H_2O$" and BaO at 800°C [61,120,121,142] and $Sr[OsO_4]$ and $Ba[OsO_4]$ [142,148]. $Sr[OsO_4]$ formed on heating $Sr[OsO_3]$ in air above 920°C has a Scheelite structure [148]. Mixed oxides with ordered perovskite structures $A_2B[OsO_6]$ (A = Sr, Ca, Ba; B = Mg, Zn, Al, etc.) are known; $Ba_2Ca[OsO_6]$ has $\mu_{eff} = 2.2$ BM [121].

Halides and oxohalides

The hexafluorides are the only binary halides. The bright yellow volatile OsF_6 (m.p. = 31°C, b.p. = 46°C) is the normal product of direct combination of the elements [64,149,150], but the dark red-brown RuF_6 (m.p. = 56°C) is



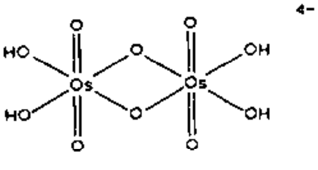


Fig. 5. Structure of the $[OsO_2(OH)_4]^{2-}$ anion.

Fig. 6. Proposed structure of the $[Os_2O_6(OH)_4]^{4-}$ anion in $Ba[OsO_3(OH)_2]$.

thermally unstable, and the vapour from the reaction of Ru and F_2 must be quenched rapidly to $-196°C$ to prevent decomposition. Even then a mixture of RuF_6 and RuF_5 is formed from which RuF_6 is obtained by careful sublimation [151]. Both are dimorphic, cubic at room temperature, and orthorhombic at low temperatures [152]. Electron diffraction shows OsF_6 to be octahedral, $Os-F = 1.831(8)$ Å [153]. The magnetic moment of OsF_6 at 300 K is 1.46 BM [72,149], but that of RuF_6 does not seem to have been measured. Vibrational spectra for both molecules have been measured several times, the preferred values (cm^{-1}) are [154,155]

	$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(F_{1u})$	$\nu_4(F_{1u})$	$\nu_5(F_{2g})$	$\nu_6(F_{2u})$
RuF_6	675	624	735	275	283	186
OsF_6	730.7	668	720	248	276	205

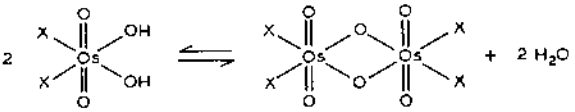
The spectra give evidence for a dynamic Jahn–Teller effect, and it has been proposed that better agreement with experimental data is given by a D_{4h} model. The electronic spectrum of OsF_6 (but not apparently that of RuF_6) has been measured and assigned [11,156]. The ^{19}F NMR spectrum of OsF_6 has been recorded [157]. The oxidising power of OsF_6 compared with other 5*d* MF_6 is $WF_6 < ReF_6 < OsF_6 < IrF_6 < PtF_6$ [158] and RuF_6 is probably comparable with PtF_6 although data are scarce. Neither hexafluoride reacts with alkali-fluorides, but $[NO][OsF_7]$ is formed along with $[NO][OsF_6]$ from NOF and OsF_6 [159].

The oxide halides are $RuOF_4$, $OsOF_4$ and $OsOCl_4$. The data on $RuOF_4$ are rather contradictory. It was first obtained as a minor product of the reaction of Ru and BrF_3, as a stable pale-green solid m.p. 115°C [160]. The room temperature magnetic moment is 2.91 BM [160]. More recently $RuOF_4$ has been obtained by fluorination of RuO_2 [68,161,162], and shown to decompose with evolution of oxygen at room temperature. Mass spectra and low resolution IR spectra suggested it is monomeric in the gas phase, and possibly an oxygen bridged solid [68,162]. Osmium oxide tetrafluoride, $OsOF_4$, is variously reported as yellow or blue-green, but since the X-ray powder patterns are the same, the different colours are presumably due to surface hydrolysis or contamination [70,163–165]. The best preparations are from OsO_4/OsF_6 in a 1:3 ratio at 175°C [70] or from OsF_6 and B_2O_3 [164]; less convenient methods include decomposition of $OsOF_5$ on a tungsten filament [163] or reaction of OsF_6 with glass wool [165]. The mass spectrum [70,163] indicates that only monomers are present in the vapour, and the Raman spectra of the solid shows an $Os=O$ stretch at 1009 cm^{-1} showing the solid is F-bridged [72]. The compound is diamagnetic, and exhibits temperature independent paramagnetism [72].

Red $OsOCl_4$ is made from Os and Cl_2/O_2 (8:1) [69], from OsO_4 and $SOCl_2$ [166] or BCl_3 [167]. The mass [168] and IR spectra of the vapour [167,169] show it is monomeric; high resolution matrix isolation studies confirm a C_{4v} structure for the monomer [167].

Dioxoruthenium(VI) and dioxoosmium(VI)

There are a very limited number of *trans*-dioxoruthenium(VI) (ruthenyl) compounds which contain the *trans*-$[RuO_2]^{2+}$ unit and are very easily reduced. The *trans*-dioxoosmium(VI) (osmyl) compounds are much more stable, and an extensive series is known. The best characterised type are the $[OsO_2L_4]^n$ (e.g. $L = X^-$, $n = 2-$; $L = NH_3$, $\frac{1}{2}H_2NCH_2CH_2NH_2$, $n = 2+$). The so-called 'oxyosmyl' salts formulated by Wintrebert [170] as $[OsO_3X_2]^{2-}$ ($X = Cl$, Br, NO_2, etc.) are less-well characterised. On the basis of IR and Raman spectra they have been reformulated as $[OsO_2X_2(OH)_2]^{2-}$ [74,171]. However, an X-ray study of the oxyosmyl nitrite "$OsO_3(NO_2)_2^{2-}$" established it is the oxo-bridged dimer $[Os_2O_6(NO_2)_4]^{4-}$ [172], which cast doubt upon the identification of the $[OsO_2X_2(OH)_2]^{2-}$ type. The problem will only be resolved by further X-ray studies, but there is a strong possibility for some ligands that both forms may exist under appropriate conditions, since they are related. Certainly both forms have recently been characterised for



$2X = Me_2NCH_2CH_2NMe_2$ [173], and probably *o*-phenanthroline [173]. Depending upon the nature of X, the reaction conditions, solvent, etc., it may be possible to obtain either the monomer or the dimer, which would certainly explain some of the contradictory claims in the literature.

The osmate(VI) ion $[OsO_2(OH)_4]^{2-}$ has already been discussed, and oxoosmium(VI) esters are described below, but the other osmyl complexes are listed in Table 3.

The deep red-purple $M_2[RuO_2Cl_4]$ ($M = Cs$, Rb) are obtained from RuO_4, MCl and HCl [174,175], and the brown $Cs_2[RuO_2Br_4]$ from RuO_4, HBr and CsBr [176]. Other compounds of this type are $[RuO_2(NH_3)_4]Cl_2$, $[RuO_2(2,2'\text{-bipy})Cl_2]$, $[RuO_2(py)_2Cl_2]$ made from RCl ($R = NH_4$, bipyH, pyH) and RuO_4 in alkaline solution; $[RuO_2(C_2O_4)_2]^{2-}$ [176], $[RuO_2(OH)_2(py)_2]$ [96,99], $[RuO_2(bipy)(OH)_2 \cdot nH_2O]$ [101]. All have strong IR bands at ca. 830 cm^{-1} consistent with *trans*-$[RuO_2]^{2+}$, and where measurements have been made, are diamagnetic [69,74,176]. Less certain species which may be ruthenyl derivatives include "$H_2RuO_2Cl_4 \cdot 3H_2O$" [177] and $[RuO_2S_2O_7]$ [178,179]. The black material obtained from $K_2[RuO_4]$ and aqueous ammonia, and variously formulated $(NH_4)_2[RuO_4]$ or

$[RuO_2(NH_3)_2(OH)_2]$ [133] is now believed to be a Ru(IV) nitride [180].

All the osmyl compounds, with the sole exception of the incompletely characterised phthalocyanine derivative (see Table 3) are diamagnetic, as explained for potassium osmate. An X-ray study has been reported for the anionic $K_2[OsO_2Cl_4]$, which is made like most of the other $[OsO_2X_4]^{2-}$ ions from $K_2[OsO(OH)_4]$ and X^-, or OsO_4 and HX. It reveals the expected *trans* octahedral anion with Os–O = 1.750 (22) and Os–Cl = 2.379(5) Å [183]. The cationic $[OsO_2(en)_2]^{2+}$ (Fig. 7) has Os–O = 1.74(1) Å, Os–N = 2.11 Å [192].

The doubts about $[OsO_2X_2(OH)_2]^{2-}$ compounds have been mentioned above; the reported examples include X = Cl [171,198], CN [185], $\frac{1}{2}$ C_2O_4 [170,171]. Behrman and co-workers [173] prepared $[OsO_2(Me_2NCH_2CH_2NMe_2)(OH)_2] \cdot 1.5H_2O$ from $[Os_2O_6(py)_2]$ and the diamine in water, or by reduction of OsO_4 with ethanol in neutral solution containing the diamine. In basic solution the reduction produced the green dimer $[Os_2O_6(Me_2NCH_2CH_2NMe_2)_2 \cdot 2H_2O]$. Monomer and dimer have different IR and ^{1}H NMR spectra, and the conversion of either into a monomer/dimer mixture in aqueous solution can be monitored by ^{1}H NMR spectroscopy [173]. A copper coloured $[OsO_2(phen)(OH)_2]$(phen = *o*-phenanthroline) is obtained from $K_2[OsO_2(OH)_4]$ and the ligand in cold water, and this converts on boiling the solution into a green dimer $[Os_2O_6(phen)_2]$. The $[OsO_2(L)_2(OH)_2]$ complexes show δ(OsOH) at ca. 1000 cm^{-1} and ν(Os–OH) at 570 cm^{-1} [171,173]. It seems generally accepted that for pyridine the dimer $[Os_2O_6(py)_4]$ is the more stable form [94,96] which has $\nu_{asym}(OsO_2) = 833$ cm^{-1}, $\nu_{sym}(OsO_2) = 875$ cm^{-1}, and Os_2O_2 vibrations at 640 cm^{-1}(R) and 448 cm^{-1}(IR). It does appear that $[OsO_2(OH)_2(py)_2]$ is probably present in aqueous solutions [94,199,200]. $[Os_2O_6(bipy)_2]$ appears to be similar [199,201], and there are also $[Os_2O_6L_4]$ compounds of imidazole and 1-methylimidazole [97].

The X-ray of $K_4[Os_2O_6(NO_2)_4]$ (Fig. 8) [172] shows the *trans* OsO_2 units are non-linear $O\hat{-Os-}O$ = 164.1(7)° with an $O-\hat{O}s-O$ bridge 78.2(4)° and Os = O = 1.79(1) Å and Os–O = 1.99(2) Å.

Osmium(VI) esters

This is an important and expanding area of osmium chemistry largely because of interest in the OsO_4 *cis* hydroxylation of unsaturated substances. This proceeds via the formation of an intermediate Os(VI) ester complex. The area has been reviewed by Schröder [55] and Gmelin [25] contains extensive tables of these compounds. The present discussion will be limited to general points about each structural type.

Diesters $[OsO(O_2R)_2]$ can be prepared by several routes including $K_2[OsO_2(OH)_4]$ and the glycol followed by acidification [187] or from OsO_4 and the alkene [202,203]. An X-ray study of $[OsO(O_2C_2H_4)_2]$ derived from

TABLE 3

Dioxoosmium(VI)(osmyl) compounds

Formula	OsO_2		Comments	Refs.
	ν_{asym}	ν_{sym}		
$[OsO_2(OH)_4]^{2-}$	804	852	See text	61, 74, 171
$[OsO_2Cl_4]^{2-}$	837	904	K, Rb, Cs, R_3NH^+, R_4P^+, NH_4^+ salts	61, 69, 74, 137, 181–183
$[OsO_2Br_4]^{2-}$	842	900	K, Cs, NH_4^+ salts	61, 74, 170
$[OsO_2(CN)_4]^{2-}$	830	886	K, Cs, Ag	61, 74, 184, 185, 171
$[OsO_2(CNO)_4]^{2-}$	824		Fulminate Ph_4As^+	186
$[OsO_2(C_2O_4)_2]^{2-}$	824		K, NH_4^+, Cs	61, 74, 81, 120
$K_2[OsO_2(OMe)_4]$	825		Olive-green KOH + OsO_4 in MeOH	96, 126, 177, 187
$K[OsO_2(O_2CMe)_3]$	845		Blue $K_2[OsO_2(OMe)_4]$ + CH_3CO_2H	96, 187
$[OsO_2Cl_2(PPh_3)_2]$	840		OsO_4 + HCl + PPh_3 originally formulated as $[OsOCl_3(PPh_3)_2]$ (ref. 188)	19
$[OsO_2(bigH)_2]Y_2$			bigH = biguanidine Y = Cl, $\frac{1}{2}SO_4$, from $[OsO_2(big)_2]$ + HY	189

$[OsO_2(big)_2]$			$OsO_4 + bigH + OH^-$	189
$[OsO_2(NH_3)_4]Y_2$	867	865	$K_2[OsO_2[OH)_4] + NH_4Cl$, Y = Cl, NO_3, NO_2 etc.	61, 74, 170, 190
$[OsO_2(H_2NCH_2CH_2NH_2)_2]Y_2$			Y = Cl from $K_2[OsO_2(OH)_4]+$ en·2 HCl, metathesis gives $Y = HSO_4^-$, Br, I, ClO_4, etc.	191, 192
$[(H_2O)_5FeOOsO(en)_2]^{4+}$			$[Fe(H_2O)_6]^{2+} + [OsO_2(en)_2]^{2+}$ deep blue	193
$[OsO_2(phthalocyanine) \cdot]C_6H_4(CN)_2$			OsO_4 + phthalocyanine $\mu = 1.41$ deep blue	194
$[OsO_2(TTP)]$	835		TTP = tetra-*p*-tolyl-porphyrin black	195
$[OsO_2(OEP)]$	825		OEP = octa-ethyl-porphyrin olive green	196, 197
$K_2[OsO_2(NO_2)_2(NO_3)_2]$	871		$OsO_4 + KNO_2 + NO$ originally formulated as $K_2[OsO_2(NO_2)_4]$ (ref. 170)	74, 171
$Na_6[OsO_2(SO_3)_4]$			$OsO_4 + SO_2 + NaOH$	170
$[OsO_2(PBT)]$			PBT = *N*-pyridyl-*N′*-benzoylthiourea	243

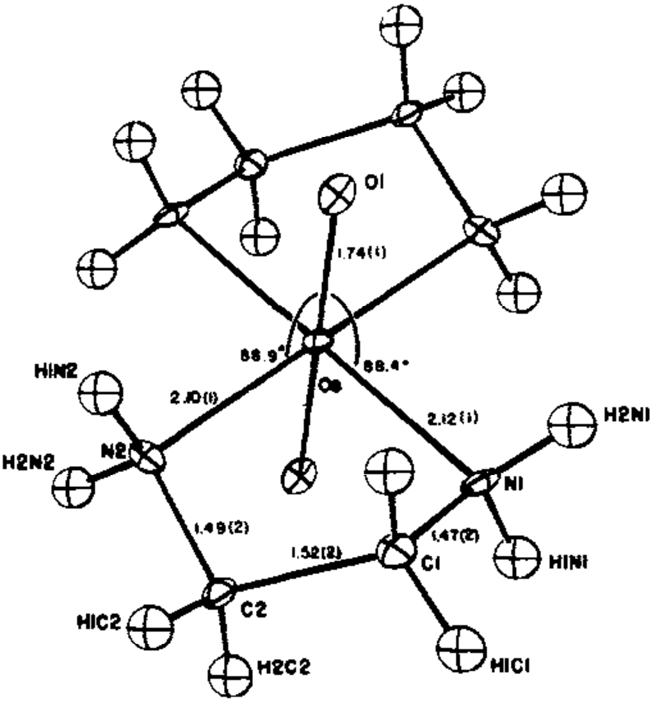


Fig. 7. Structure of the *trans*-$[OsO_2(en)_2]^{2+}$ cation. From ref. 192.

ethylene glycol shows the osmium to have approximately square pyramidal coordination (Fig. 9). $Os{-}O_{axial} = 1.670(12)$ Å, $Os{-}O_{ester} = 1.885(7)$ Å (av) and $O_{ax}{-}\hat{O}s{-}O_{ester} = 110.1°$(mean) [204,205]. The X-ray structure of $[OsO(O_2C_2Me_4)_2]$ shows it to be essentially similar [206]. Complexes of type $K_2[OsO_2(O_2R)_2]$ can be prepared from $K_2[OsO_2(OH)_4]$ and the glycol, $K_2[OsO_2(OH)_4]$ and the alkene, or from $[OsO(O_2R)_2]$ and KOH [187,207]. The anion is thought to be octahedral with a *trans*-$[OsO_2]$ group.

Monoesters of the type $[Os_2O_4(O_2R)_2]$, (originally formulated $[OsO_2(O_2R)]$) are synthesised from OsO_4 and the alkene in a 1:1 ratio [187,207]. An X-ray study of the complex derived from 2,3-dimethylbut-2-ene

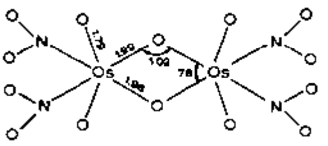


Fig. 8. Structure of the $[Os_2O_6(NO_2)_4]^{4-}$ anion.

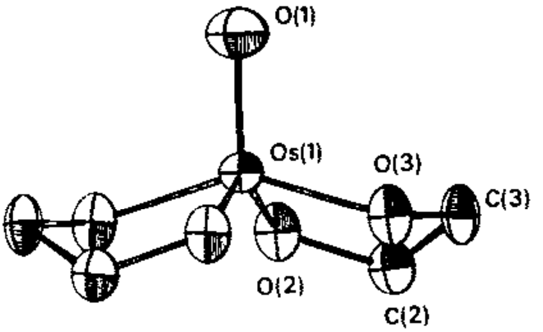


Fig. 9. The structure of $[OsO(O_2C_2H_4)_2]$. From ref. 205.

confirmed the di-μ-oxo dimer structure Os–O_{mean} = 1.922 Å with the two axial oxygens in an *anti*-configuration Os–O = 1.675(7) Å (Fig. 10) [208,209]. Both the *syn* (C_{2v}) and *anti* (C_{2h}) forms are believed to be present in solution on the basis of ^1H and ^{13}C NMR work [210]. Some monoesters $[Os_2O_4(O_2R)_2]$ react with diols to give the diester $[OsO(O_2R)_2]$ [187,207,210].

The direct reaction of OsO_4 with dienes and trienes has received little attention and more work is needed to ascertain the structures of the products [187,211].

Complexes of type $[OsO_2(O_2R)L_2]$(L = N donor) can be prepared from the alkene, OsO_4 and L; from the *cis* diol $R(OH)_2$ and $[Os_2O_6L_4]$; or from the monoesters $[Os_2O_4(O_2R)_2]$ and L [187]. X-ray studies show they all have similar structures (Fig. 11) [212–215]. Recently a series of these compounds has been investigated by NMR spectroscopy using a lanthanide shift reagent [216]. The reaction of ethylene glycol, OsO_4 and pyridine produces the octahedral $[OsO_2(OC_2H_4OH)_2py_2]$ [217].

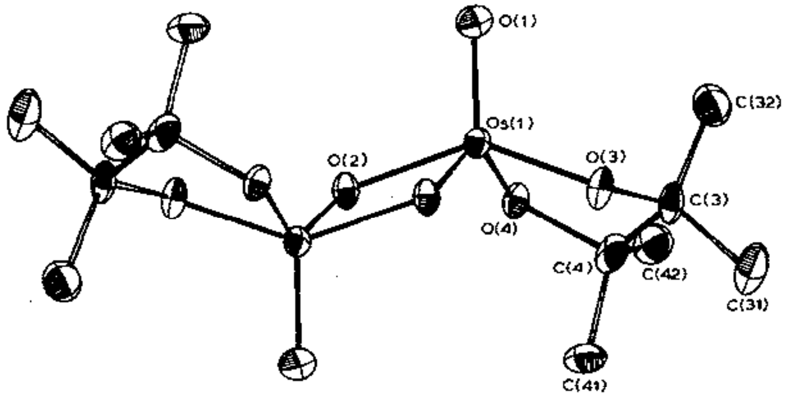


Fig. 10. The binuclear centrosymmetric structure of $[\{OsO_2(O_2C_2Me_4)\}_2]$. From ref. 209.

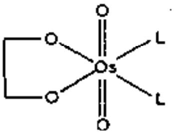


Fig. 11. The structure of complexes of type $[OsO_2(O_2R)L_2]$ (L=N donor).

Dimers of type $[OsO_2(O_2R)L]_2$ are obtained from $[OsO_4 \cdot L]$ (L = quinuclidine) or $[(OsO_4)_2 \cdot L']$ (L′ = hexamethylenetetramine) and the alkene [92,218]. An X-ray of $[OsO_2(O_2C_6H_{10})\text{quinuclidine}]_2$ derived from cyclohexene shows the osmium atoms are linked asymmetrically by the two oxo-bridges (Os–O = 1.78(1) and 2.22(1) Å, $Os–O_{axial}$ = 1.73(1) Å) [219] (Fig. 12). The complexes are believed to be monomeric in solution with a TBP structure on the basis of IR and Raman measurements [218]. Both $[Os_2O_4(O_2R)_2 \cdot \text{TED}]$ (R = parent alkene, TED = 1,4-diazabicyclo[2.2.2] octane) and $[OsO_2(O_2R)]_2$ (R = brucine, strychnine) probably have similar structures [92,218].

The reactions of dienes (R) with OsO_4 in the presence of excess pyridine in a 1:1 and 1:2 molar ratio yields complexes of the type $[OsO_2(O_2R)py_2]$ and $[Os_2O_4(O_4R)py_4]$ [187,220,221]. The complexes are believed to be octahedral with *trans* O = Os = O groups [221] (Fig. 13). For cycloocta-1,5-diene the $[Os_2O_4(O_4R)py_4]$ adduct has recently been X-rayed (Fig. 14): Os = O_{mean} = 1.72 Å, Os–O = 1.95 Å [222]. The compounds $[OsO_2(O_2R)\text{quinuclidine}]_2$ and $[Os_2O_4(O_4R)\text{quinuclidine}]_n$ are formed from OsO_4, the

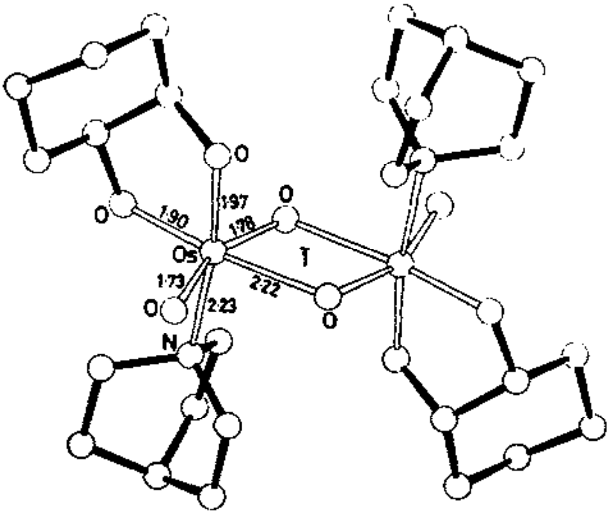


Fig. 12. The dimeric structure of $[OsO_2(O_2C_6H_{10})(C_7H_{13}N)]_2$. From ref. 219.

base and the diene [218]. On the basis of vibrational spectra the [$OsO_2(O_2R)L$] are thought to be dimers (Fig. 15(A)) in the solid state and monomers (Fig. 15(B)) in solution, whilst [$Os_2O_4(O_4R)L_4$] is a polymeric solid and dimeric (Fig. 15(C)) in solution. The corresponding reactions of OsO_4 and trienes in the presence of N-bases has been little studied [97,187].

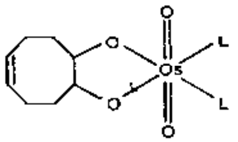


Fig. 13. The proposed structure of [$OsO_2(O_2R)L_2$] (L = N donor).

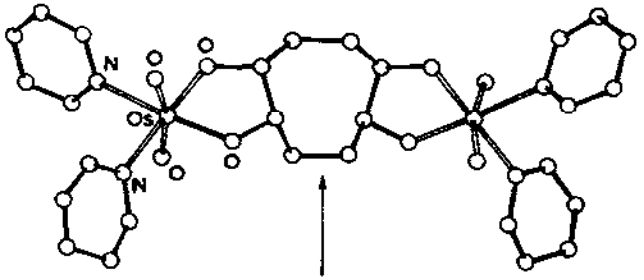


Fig. 14. The molecular structure of [$Os_2O_4(O_4C_8H_{12})py_4$]. The arrow indicates the direction of the twofold axis which passes through the centre of the molecule. From ref. 222.

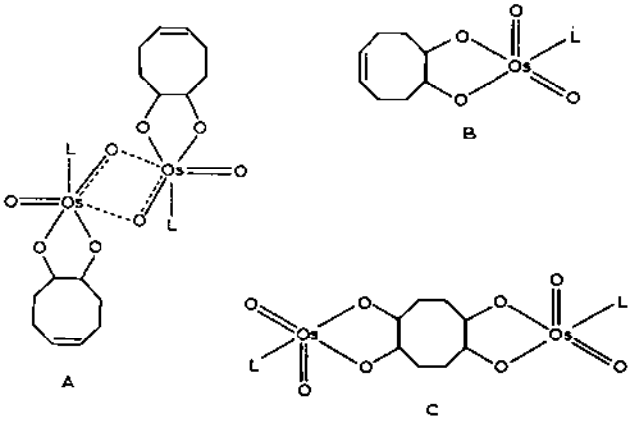


Fig. 15. The proposed structures of [$Os_2O_2(O_2R)L$] in the solid state (A) and in solution (B) and [$Os_2O_4(O_4R)L_4$] in solution (C).

Alkynes react with OsO_4 in the presence of pyridine or quinoline to give $[Os_2O_4(O_4R)L_4]$ which are believed to have the structure shown in Fig. 16 on the basis of IR and Raman data [217,221]. When quinuclidine is the base used the $[Os_2O_4(O_4R)(quinuclidine)_2]_n$ formed is believed to be polymeric as a solid and a dimer in solution [218].

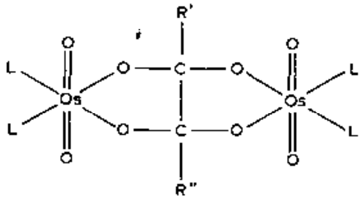


Fig. 16. The proposed structure of $[Os_2O_4(O_4R)L_4]$ (L = N donor).

A number of complexes containing catechol or substituted catechols are known. The simplest type are the dark blue $[Os(O_2R)_3]$ prepared from OsO_4 and $(HO)_2R$ [223]. X-ray structures of $[Os(O_2C_6H_4)_3]$ and $[Os(O_2C_6H_2{}^tBu_2)_3]$ show the osmium to be essentially octahedrally coordinated (Fig. 17) with Os–O lying in the range 1.947–1.985 Å [224].

The reaction of OsO_4 with the catechol in alkaline solution, or between

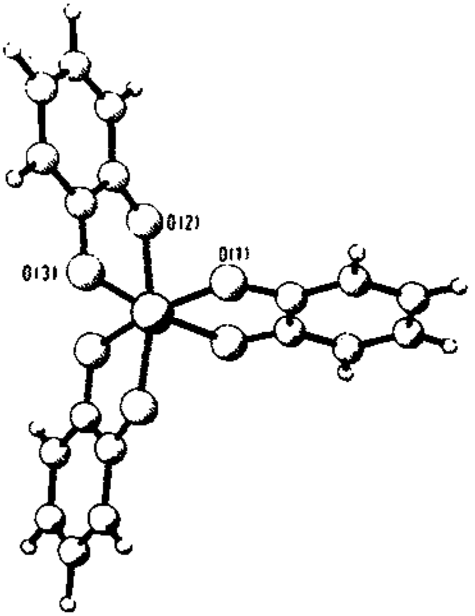


Fig. 17. The structure of $[Os(O_2C_2H_4)_3]$. Bond distances (Å): Os–O(1), 1.954(5); Os–O(2), 1.985(5); Os–O(3), 1.948(5); O(1)–C, 1.32(1); O(2)–C, 1.30(1); O(3)–C, 1.33(1). From ref. 224.

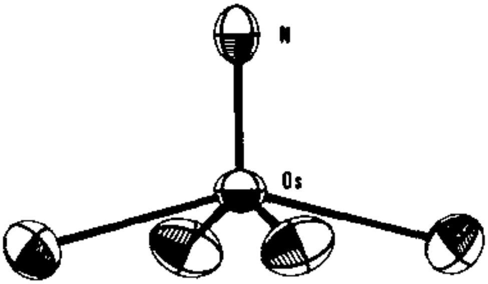


Fig. 18. The structure of the $[OsNCl_4]^-$ anion. From ref. 229.

$K_2[OsO_2(OR)_4]$ (R = H, Me) and $(HO)_2R$, with added Ph_4PCl produces the red $(Ph_4P)_2$ *trans*-$[OsO_2(O_2R)_2]$ [223]. Finally there are the brown *trans*-$[OsO_2(O_2R)py_2]$ obtained from OsO_4, py and catechol [223].

Nitrides

The osmium nitrido anion $[OsNCl_5]^{2-}$ has been known for many years, and more recently $[OsNCl_4(H_2O)]^-$, $[OsNCl_4]^-$, the bromoanalogues, and $[OsNI_4]^-$ have been prepared. The ruthenium analogues $[RuNX_5]^{2-}$ and $[RuNX_4]^-$ (X = Cl, Br) were reported in 1972 [225]. Treatment of ice-cold HX solutions of $[RuO_2X_4]^{2-}$ with sodium azide and CsX gave the brown $Cs_2[RuNX_5]$ (X = Cl, Br) [176]. Use of the large organic cations $^nBu_4N^+$ or Ph_4As^+ produces the pink $[RuNX_4]^-$ salts. The red crystalline $K_2[OsNCl_5]$ is formed by treating $K[OsO_3N]$ with HCl and KCl, and on recrystallisation

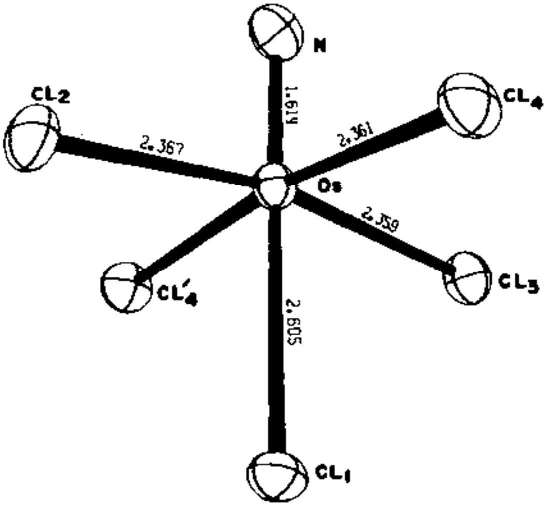


Fig. 19. The structure of the $[OsNCl_5]^{2-}$ anion. From ref. 227.

TABLE 4

X-ray structural data and vibrational spectra of $[MNX_4]^-$, $[MNX_5]^{2-}$, $[MNX_4(H_2O)]^-$ (M=Ru, Os, X=halide)

Ion	M–A (Å)	M–X (Å)	$M–X_{trans N}$ (Å)	$M–OH_2$ (Å)	$N–\hat{M}–X$ (deg)	$X–\hat{M}–X$ (deg)	Ref.
$[RuNCl_4]^-$	1.570 (7)	2.310 (7)			104.6	86.4	228
$[OsNCl_4]^-$	1.604 (10)	2.310 (2)			104.5	86.4	229
$[OsNI_4]^-$	1.626 (17)	2.662 (1)			103.7	86.8	230
$[OsNCl_5]^{2-}$	1.614 (13)	2.363 (4)	2.605 (4)		96 (av.)		227
$[OsNCl_4(H_2O)]^-$	1.74 (7)	2.34 (2)		2.50 (3)			231
$[OsNBr_4(H_2O)]^-$	1.67 (5)	2.485 (3)		2.42 (2)			232

IR and Raman data (cm^{-1}) [85,176]

Ion	ν(M–N) (A_1)	ν(M–X) (A_1)	ν(M–X) (B_1)	ν(M–X) (E)	δ(NMX)	ν(M–X) (A_1) (*trans* N)	Cation
$[RuNCl_4]^-$	1092	346	304	378	267		Ph_4As
$[RuNBr_4]^-$	1088	224	187	304	211		Ph_4As
$[RuNCl_5]^{2-}$	1048	318	307	340	235	284	Cs
$[RuNBr_5]^{2-}$	1045	207	181	257	204	201	Cs
$[OsNCl_4]^-$	1123	358	352	365	271		Ph_4As
$[OsNBr_4]^-$	1119	162	156	220	273		Ph_4As
$[OsNCl_4(H_2O)]^-$	1100						
$[OsNBr_4(H_2O)]^-$	1110		232		261		
$[OsNCl_5]^{2-}$	1084	348	334	336	264	324	K
$[OsNBr_5]^{2-}$	1085	198	172	234	217	192	K

from water is converted into K *trans*$[\mathrm{OsNCl_4(H_2O)}]$. The use of larger cations ($\mathrm{Bu_4N}$, $\mathrm{Ph_4As^+}$) leads to the $[\mathrm{OsNCl_4}]^-$ salts [75,176,226,227]. The $[\mathrm{OsNBr_5}]^{2-}$, $[\mathrm{OsN^+Br_4}]^-$ and $[\mathrm{OsNBr_4(H_2O)}]^-$ ions are prepared in similar ways in HBr solution, the ion produced depending upon the counter-cation [176,226]. X-ray structures have been reported for $[\mathrm{Ph_4As}][\mathrm{RuNCl_4}]$ [228], $[\mathrm{Ph_4As}][\mathrm{OsNCl_4}]$ [229], $[\mathrm{Ph_4As}][\mathrm{OsNI_4}]$ [230], $\mathrm{K_2[OsNCl_5]}$ [227], $\mathrm{K[OsNCl_4(H_2O)]}$ [231], $\mathrm{K[OsNBr_4(H_2O)]}$ [232]. The structures of $[\mathrm{Ph_4As}][\mathrm{OsNCl_4}]$ and $\mathrm{K_2[OsNCl_5]}$ are shown in Figs. 18 and 19, and details are in Table 4.

The original report of the structure of $\mathrm{K_2[OsNCl_5]}$ [232] is in error [227,231] and the data are thought to refer to $\mathrm{K[OsNCl_4(H_2O)]}$ [231]. All these nitrido complexes are diamagnetic as expected [233]. Detailed electronic spectral studies on the $[\mathrm{OsNX_4}]^-$ (X = Cl, Br) ions suggest that the nitride ligand is a very strong π-donor, considerably stronger than oxide [226], and this is supported by the Mössbauer spectra of $[\mathrm{OsNX_4}]^-$ and $[\mathrm{RuNX_4}]^-$ [17,234].

Treatment of $\mathrm{K[OsO_3N]}$ with HCN produces $\mathrm{K[OsN(CN)_4(H_2O)]}$ and with HF, $\mathrm{K[OsNF_2(H_2O)(OH)_2]}$ [81], and with oxalic acid both $[\mathrm{OsN(C_2O_4)_2(H_2O)}]^-$ and $[\mathrm{OsN(C_2O_4)(OH)_2(H_2O)}]^-$ are formed [81]; all contain *trans* $\mathrm{N\equiv Os{-}OH_2}$ linkages. Thermal dehydration of $\mathrm{K[OsNBr_4(H_2O)]}$ produces a green $\mathrm{K[OsNBr_4]}$ in which ν(Os–N) is 1002 $\mathrm{cm^{-1}}$ (1109 $\mathrm{cm^{-1}}$ in the starting material) suggesting a polymeric N-bridged species [176]. The $\mathrm{M\equiv N}$ bonds in the $[\mathrm{MNX_4}]^-$ or $[\mathrm{MNX_5}]^{2-}$ are rather unreactive, although $\mathrm{K_2[OsNCl_5]}$ can be reduced by $\mathrm{SnCl_2/HCl}$ to $\mathrm{K_2[Os(NH_3)Cl_5]}$ [190], and $[\mathrm{MNX_4}]^-$ are converted to phosphine-imidates by $\mathrm{PR_3}$ (see below).

The reaction of $[\mathrm{OsNX_4}]^-$ or $[\mathrm{RuNCl_4}]^-$ with $\mathrm{AsPh_3}$ or $\mathrm{SbPh_3}$(L) in methanol yields $[\mathrm{MNX_3L_2}]$ as orange or brown solids, which are diamagnetic and exhibit ν(M–N) at ca. 1030–1070 $\mathrm{cm^{-1}}$ [235,236]. However, $[\mathrm{OsNCl_4}]^-$ and $\mathrm{PPh_3}$ gave a paramagnetic phosphine-imidate $[\mathrm{Os(NPPh_3)Cl_3(PPh_3)_2}]$ [235], whilst $[\mathrm{RuNCl_4}]^-$ was reduced to Ru(III) $[\mathrm{RuCl_4(PPh_3)_2}]^-$ [236]. More basic $\mathrm{PR_3}$ also reduces the osmium nitrides. Phosphine-imidates containing Ru(IV) or Os(IV) are produced by reaction of $[\mathrm{MNX_3(AsPh_3)_2}]$ with $\mathrm{PR_3}$ ($\mathrm{R_3 = Et_3}$, $\mathrm{Me_2Ph}$, $\mathrm{Et_2Ph}$, $\mathrm{Ph_3}$) in cold acetone [236]. In the case of osmium these can be oxidised by chlorine to $[\mathrm{OsNCl_3(PR_3)_2}]$, but neither $[\mathrm{OsNBr_3(PR_3)_2}]$ nor $[\mathrm{RuNCl_3(PR_3)_2}]$ could be prepared. Nitrogen base (2,2′-bipyridyl, 1,10-phenanthroline, pyridine) substituted derivatives have been prepared from $[\mathrm{OsNX_4}]^-$ and the base in acetone [236] or ethanol (X = Br) [237], or by thermal decomposition of the quaternary salts [Base H]$[\mathrm{OsNX_4}]$ [237]. The $[\mathrm{OsNCl_3(L)_2}]$ react with $\mathrm{S_2Cl_2}$ to give the thionitrosyls $[\mathrm{Os(NS)Cl_3L_2}]$ (L = $\mathrm{PMe_2Ph}$, $\mathrm{AsPh_3}$, $\frac{1}{2}$ bipy) [238].

Osmium(VI) nitrido porphyrin$[\mathrm{Os(OEP)NClO_4}]$, made from $[\mathrm{Os(OEP)O_2}]$, perchloric acid and hydrazine hydrate, is converted to [Os(OEP)N(OMe)] on recrystallisation from KOH/MeOH [239]. An [Os(OEP)N(F)] has also been characterised (OEP = octaethylporphyrin).

A polymeric osmium(VI) nitride is believed to be formed from OsO_4 and NH_3. Since it is structurally similar to Os(IV) nitrides it is discussed on page 51 and following.

Miscellaneous compounds

A deliquescent brownish-green material obtained from air and $[Os(en\text{-}H)_2en]I_2$(en-H = $HNCH_2CH_2NH_2$) has been formulated $[Os(en\text{-}H)_4]I_2 \cdot 3H_2O$ [240,241]. A brown material obtained by iodine oxidation of $[Ru(en)_3]^{2+}$ has been suggested to be $[Ru(en\text{-}2H)(en\text{-}H)_2]I_2$ [242]. In both cases the deprotonated ethylenediamine ligands are expected to be strong π-donors. Neither complex has been unequivocally characterised.

The red-brown solid formed from $[RuO_4]^{2-}$ (or $[RuO_4]^-$, HClO and sodium periodate has been formulated as a Ru(VI) periodate $Na_6[Ru(IO_6)_2(OH)_2] \cdot 18H_2O$ [244]. It is possible that this is the same species identified by others as complexes of Ru(VII) [245] or Ru(IV) [246].

A hexahydrido complex $[OsH_6(PMe_2Ph)_2]$ is produced by $LiAlH_4$ reduction of $[Os(PMe_2Ph)_2Cl_4]^-$ in tetrahydrofuran [247]. It is a pale yellow oil and has $\nu(Os\text{–}H) = 2028, 1980, 1869\ cm^{-1}$ and $\tau_{Os\text{–}H} = 18.66$ ppm.

(iv) M(V) d^3

This is a rare oxidation state for both metals, best known in the pentafluorides $[MF_5]_4$ and the anions $[MF_6]^-$.

Oxides and oxoanions

There is no evidence for anhydrous M_2O_5 (M = Ru, Os) but hydrated forms are said to be produced by acidification of $[RuO_4]^{2-}$ [110] and $[OsO_2(OH)_4]^{2-}$ [145,248], or by electrolysis of RuO_4 in sulphuric acid [249]. It is possible that these are merely hydrated forms of the dioxides, and examination by Mössbauer (Ru) and XPS (Os) methods would be interesting. Oxoanions are better established. The blue, water soluble $Na_3[RuO_4]$ is made from RuO_2 and Na_2O_2 at 700°C [250]. It has the Na_3NbO_4 structure and its unusual magnetic and Mössbauer spectral properties have been studied in detail [251–253]. Other Ru(V) oxo compounds include $Na_4[Ru_2O_7]$ [253], $Li_3[RuO_4]$, $Li_7[RuO_6]$ [119,254], $Ba_3Mg[Ru_2O_9]$ [255,256], $BaLaM[RuO_6]$ (M = Zn, Mg, Co, Ni) [15], $Ba_2In[RuO_6]$ [257]. Rather surprisingly the $BaLaM[RuO_6]$ compounds obey the Curie–Weiss Law with $\mu_{eff} \sim 3.7$ BM at room temperature. Osmates(V) include cubic

$Li_3[OsO_4]$ [258], $Li_7[OsO_6]$ [119,254] (which has the $Li_7[SbO_6]$ structure, Os–O = 2.07 Å), $Na[OsO_3]$ [259] and $Ca_2[Os_2O_7]$ [259,260].

Halides

These are RuF_5, OsF_5, and the recently obtained $OsCl_5$; there are no oxohalides known. Dark-green crystalline RuF_5 is the normal product of fluorination of the metal, and is also obtained from Ru and BrF_3 [160]. It melts at 86.5°C and boils at 227°C to give a colourless vapour. The solid is composed of tetramers Ru_4F_{20} with *cis* fluorine bridges [261,262], Ru–F = 1.90 Å (av) and F–$\hat{\text{Ru}}$–F (bridge) = 87°. The room temperature magnetic moment is 3.60 BM [261], and the effect of temperature (4.2–300 K) on μ has been studied [263]. Mass spectra show the vapour contains $[RuF_5]_n$, where $n = 1$–4 [264,265]. The electronic spectrum of liquid RuF_5 has been reported [266].

Green-blue OsF_5 has been prepared by reduction of OsF_6 with I_2 in IF_5, H_2/HF, $W(CO)_6$, Si, a heated tungsten filament, or by UV irradiation [267–270]. The solid contains $[OsF_5]_4$ units with a similar structure to $[RuF_5]_4$ [262], with Os–F = 2.03(15) (bridge) and 1.84 Å (terminal) and Os–$\hat{\text{F}}$–Os = 139.3 ± 2°. In the vapour mono, di- and trimers (but not apparently tetramers) are present [264,265]. The room temperature magnetic moment has been reported as 2.06 [261] and 1.60 BM [72]. The reaction of OsF_6 with excess iodine gives a material which may be $OsIF_4$ [261].

Osmium pentachloride $OsCl_5$ has been prepared very recently from OsF_6 and BCl_3 [271] or OsO_4 and SCl_2 [272]. It is black, very moisture sensitive and decomposed to $OsCl_4$ on heating. The structure (Fig. 20) is similar to $ReCl_5$ and is composed of dimers [271]. The magnetic moment is 2.54 BM, and it obeys the Curie–Weiss law. The IR spectrum of the solid is disputed

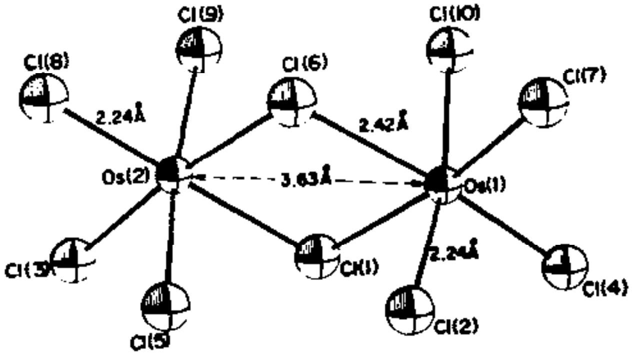


Fig. 20. The structure of $OsCl_5$. Average bond angles: Cl(1)-Os(1)-Cl(6) = 83°; Cl(4)-Os(1)-Cl(7) = 95°. From ref. 271.

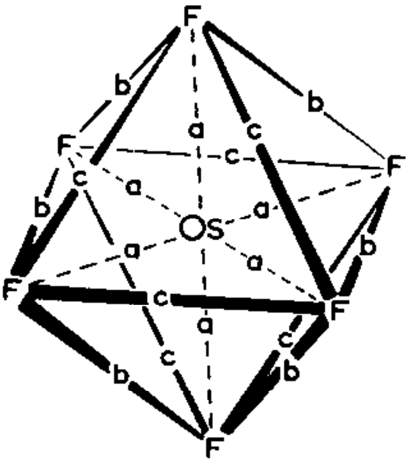


Fig. 21. The $[OsF_6]^-$ octahedron; $a = 1.82$; $b = 2.48$; $c = 2.66$ Å. From ref. 278.

[271,272]. A material of composition $OsCl_{4.3}$ obtained by chlorination of the metal is presumably a mixture of $OsCl_4$ and $OsCl_5$ [273]. The reported Os_2OCl_8 [274] is really $OsOCl_4$ [169].

Haloanions

The cream hexafluororuthenates(V) and white hexafluoroosmates(V) are prepared by fluorination of a mixture of M^ICl and $RuCl_3$ or M^ICl and $OsBr_4$ [275,276] or by treatment of the mixtures with BrF_3 [276–279]. The compounds isolated are $M^I[RuF_6]$ (M = Li, Na, K, Rb, Cs, Tl, Ag),

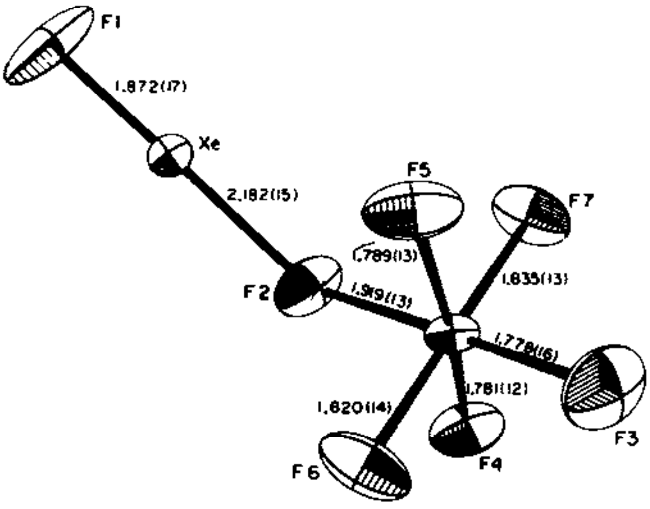


Fig. 22. Structure of $[XeF^+][RuF_6^-]$. From ref. 284.

$M^{II}[RuF_6]_2$ (M^{II} = Ca, Sr, Ba), and $M^I[OsF_6]$ (M^I = Li, Na, K, Rb, Cs, Ag). There are a number of salts with non-metal cations including $[NO]^+$ [158,280], $[N_2H_6]^{2+}$ [281], $[O_2]^+$ [282], $[H_3O]^+$ [283], $[XeF]^+$, $[Xe_2F_3]^+$ and $[XeF_5]^+$ [284,285]. Detailed X-ray structures have been established for $K[OsF_6]$ [278] (Fig. 21), $[XeF][RuF_6]$ [284] (Fig. 22) and $[XeF_5][RuF_6]$ [284]. $K[OsF_6]$ is rhombohedral with a distorted octahedral anion Os–F = 1.82 Å (av). Other $M^I[OsF_6]$ and $M^I[RuF_6]$ (M = K, Rb, Cs) are similar, whilst when M^I = Li, Na, the structure is the $Li[SbF_6]$ type [286]. In $[XeF_5][RuF_6]$ in which the anion is distorted by contacts with the polarising xenon cation $Ru–F_{av}$ = 1.85 Å [284]. The magnetic moments of $M^I[RuF_6]$ lie in the range 3.5–3.8 BM, whilst those of $M^I[OsF_6]$ are slightly lower 3.05–3.3 BM [275,279,287]. In water both anions disproportionate to MO_4 and $[MF_6]^{2-}$. Only incomplete vibrational data of the anions are available.

	$\nu_1(A_{1g})$(R)	$\nu_2(E_g)$(R)	$\nu_3(F_{1u})$(IR)	$\nu_5(F_{2g})$(R)	Ref.
$[RuF_6]^-$	660	572	630	276,266	
$[OsF_6]^-$	688	623 605	616	261,247	285,288,289

The diffuse reflectance spectra of both ions have been recorded, and discussed in detail [11,290,291].

The $[OsCl_6]^-$ ion was first obtained by pulse radiolysis of $[OsCl_6]^{2-}$ in concentrated HCl [292], and more recently $[Ph_4As][OsCl_6]$ has been isolated from $OsCl_5$ and Ph_4AsCl in CF_3CCl_3 [272]. It is easily reduced, even CH_2Cl_2 producing $[OsCl_6]^{2-}$. There are no other reports of Ru(V), but among the unconfirmed claims for Os(V) complexes are $[Os(en\text{-}H)_3(en)]I_2 \cdot 4H_2O$ μ_{eff} = 1.78 BM [240,241] and $[Os(PPh_3)_2Cl_3(NR)]$ (R = Ph, p-$MeOC_6H_4$, p-ClC_6H_4) μ_{eff} = 2.13–2.27 BM [293]. The latter were reported to be produced from "$OsOCl_3(PPh_3)_2$" and $Ph_3P = NCOR$, but since the former is now known to be a mixture of $[OsO_2Cl_2(PPh_3)_2]$ and $[OsCl_4(PPh_3)_2]$ [19], their nature must be in doubt.

(v) M(IV) d^4

Osmium(IV) is the most important oxidation state of the element, and forms a large number of stable complexes. Ruthenium(IV) is a common oxidation state of the element, but is relatively less stable, and most of the compounds are reduced easily, or decompose spontaneously in some cases, to ruthenium(III).

Oxides

Ruthenium dioxide is made by heating the powdered metal in oxygen at 900–1200°C, and is purified by chemical transport techniques [29,129,294,295]. It is the only stable solid oxide of ruthenium at elevated temperatures [128] and on strong heating in vacuum decomposes to the metal and oxygen [294]. Osmium dioxide is reported to exist in two forms: brown obtained from Os and OsO_4 at ca. 600°C and black prepared by heating $K_2[OsCl_6]$ with KOH at 500°C [296]. Both forms have the rutile structure with slightly different lattice parameters [296]. The structures of RuO_2 and brown OsO_2 have been studied by several workers and the agreement between the data from different studies is good [296–300]; the most accurate single-crystal work shows both to contain distorted MO_6 units with $4(M-O) = 1.984 \pm 0.006$ Å (Ru), 2.006 ± 0.008 Å (Os), and $2(M-O) = 1.942 \pm 0.01$ Å (Ru) and 1.962 ± 0.013 Å (Os) [299,300]. The nearest $M \cdots M$ approach is 3.107 Å (Ru) or 3.184 Å (Os) showing that no significant metal–metal interaction is present. OsO_2 is the more reactive of the two; it reacts with O_2 on heating to give OsO_4, and dissolves in aqueous HCl to form $[OsCl_6]^{2-}$; RuO_2 is insoluble in mineral acids. The physical properties of MO_2 have been studied in detail including the magnetism [301–303], electrical conductivity [303,304], and XPS [22,305].

Hydrated forms of the dioxides $MO_2 \cdot nH_2O$ (n is rarely clear, indeed it may be variable) are produced by reduction of RuO_4 with hydrogen under pressure [306], H_2O_2 [302], $NaBH_4$ [307], and reduction of OsO_4 with EtOH [308], $NaBH_4$ [309] and by hydrolysis of Os(VI) esters [248]. On heating the hydrates are converted to the anhydrous MO_2.

The formulation(s) of the Ru(IV) species present in aqueous solution in the absence of complexing acids are unclear; examples proposed under various conditions include $[RuO]^{2+}$ (or $[RuO(H_2O)_n]^{2+}$) [310,311], $[Ru(OH)_3]^+$ or $[RuORu]^{6+}$ [312], $[Ru_4(OH)_{12}]^{4+}$ [313] and $[OsO(OH)_n]^{(n-2)}$ [314]. The best evidence supports the $[Ru_4(OH)_{12}]^{4+}$ formulation in $HClO_4$ or HNO_3 solution [313,320]. Few data have been published on alkali ruthenates(IV) although Gmelin [25] refers to several unpublished studies. Compounds prepared include $Li_2[RuO_3]$, $Na_2[RuO_3]$, $K_2[RuO_3]$ [315–317], $Na[Ru_2O_4]$ [253,318] and the ruthenium bronzes $Na_{3-x}[Ru_4O_9]$ [319], and $K(Rb)[Ru_4O_8]$ [317]. Osmates(IV) include $Li_2[OsO_3]$ and $Na_2[OsO_3]$ [315].

In contrast the mixed oxides of Ru(IV) and Ca, Sr and Ba have been much studied. The blue to violet black $M[RuO_3]$ (M = Ca, Sr, Ba) are made by heating the metal carbonate or oxide with Ru or RuO_2 [15,256,321–325]. The Ca and Sr compounds have perovskite structures [256,321], whilst $Ba[RuO_3]$ has a layer structure with strings of RuO_6 octahedra linked by corner sharing ($Ru-O = 1.96-2.02$ Å) [326]. The magnetic properties are complex [15,315b,321,327–329]. Heating $SrCO_3$ and Ru in the correct ratio in air produces blue $Sr_2[RuO_4]$ with the $K_2[NiF_4]$ structure [320] but $Ba_2[RuO_4]$ is only formed from BaO and $Ba[RuO_3]$ under high pressure [324]. Many other mixed oxides of Ru(IV) are known [315b] including $Ba_3[RuO_5]$ [323], $M_2^{III}[Ru_2O_7]$ (M^{III} = rare earth) [330,331] and $Ba_{1-x}Sr_x[RuO_3]$ [320] but we shall not discuss these further. Black $M^{II}[OsO_3]$ (M^{II} = Ca, Sr, Ba) have been made more recently by heating $M^{II}CO_3$ with OsO_2 in air [332–334]. The Ca and Sr compounds are perovskites, and the barium a hexagonally distorted perovskite like $Ba[RuO_3]$. Thermal decomposition of $M[OsO_3]$ gives various other phases $M_2^{II}[Os_2O_{7-x}]$ [148,332–336]. There are numerous mixed oxides with other metals, e.g. $M_2^{III}[Os_2O_7]$ [331].

Halides and oxide-halides

Both tetrafluorides are known but data on them are few. Sandy-yellow RuF_4 is formed by reduction of RuF_5 with iodine in IF_5 [337]. It has $\mu_{eff} = 3.04$ BM at 290 K, and is decomposed to RuO_2 by water. Yellow OsF_4 is formed in poor yield (along with OsF_5) by reduction of OsF_6 with $W(CO)_6$ [267], or in higher yield by hydrogen reduction of OsF_5 in liquid HF in the presence of Pt gauze under UV irradiation [338]. It is moisture sensitive and dissolves in water to give a clear yellow solution. The mass spectrum shows the presence of oligomers in the vapour [338]. The structure of neither tetrafluoride is known. The reaction of OsF_6 with PF_3/HF gives a yellow solid which may be *trans* $[OsF_4(PF_3)_2]$ [270]. Ruthenium trichloride is volatile in chlorine at temperatures above ca. 700°C and the vapour is believed to contain $RuCl_4$ [339,340]. If the vapour is condensed at −196°C, a solid which may be $RuCl_4$ is obtained, but this decomposes above −30°C [341]. Other workers have suggested the volatile species is an oxochloride [342]. In contrast $OsCl_4$ and $OsBr_4$ are stable solids, although there appears to be no evidence for the existence of OsI_4 [343]. Osmium tetrachloride is dimorphic. The black orthorhombic "high temperature" form is prepared from Os and chlorine either in a flow system, or under pressure in a sealed tube [344–346], from Os and SO_2Cl_2 at 460°C [347] or from OsO_4 and Cl_2/CCl_4 in a sealed tube [348]. The "low temperature" cubic form is made from OsO_4 and $SOCl_2$ [345,348]. The "high temperature" form contains octahedrally coordinated osmium$[OsCl_2Cl_{4/2}]$ ($OsCl_6$ octahedra sharing opposite edges) with $Os{-}Cl_t = 2.261(4)$ Å and $Os{-}Cl_{bridge} = 2.378(2)$ Å, $Cl{-}\hat{O}s{-}Cl = 83°$; the $Os \cdots Os$ separation is 3.560(1) Å suggesting metal–metal interaction is unimportant [346]. The magnetic moment of the high temperature form is reported as 1.6 BM [346] or 1.76 BM [349], and for the low temperature form $\mu = 2.02$ BM [166]. On heating in vacuo $OsCl_4$ is said to give Os_2Cl_7 [350].

Black $OsBr_4$ is made from the elements at 450°C under pressure [351]. It is insoluble in water, acids and organic solvents and decomposed on heating to $OsBr_3$ [351]. The reaction of OsO_4 with HBr/EtOH, followed by thermal dehydration also produces a black $OsBr_4$ [279]; it is not clear if this is a different form. The formation of brown-black $Os_2Br_9 \cdot 6H_2O$ is claimed from "osmic acid" and HBr, and drying gives Os_2Br_9 [352]. The evidence is poor.

Oxide halides of the quadrivalent metals are poorly characterised. There are claims for Ru_2OCl_6 [343,353], $RuOCl_2$ [354a], Ru_2OCl_5 [353], $OsOCl_2$ [350] and Os_2OCl_6 [166,350]. The black Os_2OCl_6 made by heating $OsCl_4$ in oxygen or from OsO_4 and HCl has a strong IR band at 460 cm^{-1} assigned to ν(OsOOs) [166]. There are various reports of $Ru(OH)Cl_3$ or $Os(OH)Cl_3$ [344], but there seems to be no IR evidence for OH ligands, and they may be oxohalides or hydrated halides (see ref. 354b).

Haloanions

Seven of the eight possible $[MX_6]^{2-}$, five oxo-bridged $[X_5M{-}O{-}MX_5]^{4-}$, and a variety of aquo $[MX_{6-n}(H_2O)_n]^{(2-n)-}$ and mixed $[MX_{6-n}Y_n]^{2-}$ halides are known. The $[RuI_6]^{2-}$ ion has not been prepared.

The golden-yellow $M^I_2[RuF_6]$ (M = Na, K, Rb, Cs) are made by hydrolysis of $M[RuF_6]$ in water [277,355]. The sodium salt belongs to the hexagonal $Na_2[SiF_6]$ type, the others have the trigonal $K_2[GeF_6]$ structure [275,277,286,355,358]. Cubic forms of $M_2[RuF_6]$ (M = K, Rb, Cs) are formed from "$Na_2Ru(NO_2)_5$" (actually $Na_2[Ru(NO)(OH)(NO_2)_4]$) and KHF_2 [356]. The magnetic moments reported are K (2.86 BM) [357] and Cs (2.98 BM) [259]. A yellow barium salt $Ba[RuF_6]$ is formed by fluorination of $BaCl_2$ + $RuCl_3$, or from a barium salt, Ru and BrF_3 [275,279,358]. It has $\mu_{eff} = 3.08$ BM [275]. The $M_2[OsF_6]$ are made by hydrolysis of $M[OsF_6]$ (M = Na, K, Rb, Cs) [279,355,359], and $K_2[OsF_6]$ has also been made by fusing $K_2[OsCl_6]$ with KHF_2 [360]. There are also $[N_2H_6]^{2+}$ [281] and alkylammonium [361] salts. The sodium salt occurs in both hexagonal and orthorhombic forms, but only the latter is found for the heavier alkali-metals [286,355,359]. The magnetic moment of $K_2[OsF_6]$ is 1.35 BM [356] or 1.30 BM [357], and of $Cs_2[OsF_6]$ 1.50 BM [357]. The alkali metal hexafluoroosmates(IV) are sparingly soluble in water and the solutions are stable. For IR/Raman data see Table 5 [280,288,362]. The electronic spectra of $[RuF_6]^{2-}$ [290,363] and $[OsF_6]^{2-}$ [363–365] have been reported and detailed assignments proposed [11,365]. Solid state ^{19}F NMR studies suggest that in $M^I_2[MF_6]$ the anions are distorted [366].

Although hexachlororuthenates(IV) were obtained initially by reduction of RuO_4 with concentrated hydrochloric acid in the presence of the appropriate cation, it is difficult to avoid contamination with $[Cl_5RuORuCl_5]^{4-}$ salts, and chlorine oxidation of $[RuCl_5(H_2O)]^{2-}$ in HCl is preferable [107,174,175,177,367–371]. Chlorination of a mixture of powdered Ru and

TABLE 5

Vibrational spectra of $[MX_6]^{2-}$ ions [a]

Ion	$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(F_{1u})$	$\nu_4(F_{1u})$	$\nu_5(F_{2g})$	Refs.
$[RuF_6]^{2-}$	609		581		236	280, 288
$[OsF_6]^{2-}$			548	262, 246		288, 362
$[RhF_6]^{2-}$	592	500	589		242	280, 288
$[IrF_6]^{2-}$	610	528	568		219	280, 288
$[PdF_6]^{2-}$	573	554	602	280	246	280, 288
$[PtF_6]^{2-}$	600	575	583	281	220	280, 288, 402, 837, 841
$[RuCl_6]^{2-}$			346	188		362, 378
$[OsCl_6]^{2-}$	354	269	325	178	171	379, 390, 400–402
$[RhCl_6]^{2-}$			329	184		376, 379
$[IrCl_6]^{2-}$	346	293	333	182	190	362, 379, 402, 414, 668
$[PdCl_6]^{2-}$	317	293	358	175	154	400–402, 849
$[PtCl_6]^{2-}$	343	320	342	183	162	400–402, 668, 686, 849, 852
$[RuBr_6]^{2-}$			267–240			387
$[OsBr_6]^{2-}$	218	162	227	122	107	402, 413
$[IrBr_6]^{2-}$	210	174	230	120	97	379, 402, 414, 668
$[PdBr_6]^{2-}$	198	176	253	130	100	400, 686
$[PtBr_6]^{2-}$	210	191	243	146	115	401, 402, 668, 849–851, 852
$[OsI_6]^{2-}$	128	118				405
$[PtI_6]^{2-}$	150	131	186		69 (?)	402, 850

[a] Data refer to various salts, solution data being used where possible. The stretching vibrations in solid salts vary slightly with cation size.

M^ICl can also be used [372]. The isolated salts include $M^I_2[RuCl_6]$ (M^I = Na, K, Rb, Cs, NH_4, pyH, $R_{4-n}H_nN$). The $M^I_2[RuCl_6]$ are dark reddish-brown or black crystalline solids which decompose on heating to $[RuCl_5]^{2-}$ and Cl_2 [177,373]. The alkali-metal salts have the cubic $K_2[PtCl_6]$ structure [399], and single crystal X-ray work on $K_2[RuCl_6]$ shows the $[RuCl_6]^{2-}$ ion to be a regular octahedron with Ru–Cl = 2.318(2) Å [374,375]. Spectroscopic data on $[RuCl_6]^{2-}$ salts include IR (Table 5), NQR [376] and electronic spectra [12]. Absorption and MCD spectra of Ru^{4+} in a $Cs_2[ZrCl_6]$ host have also been reported [377]. The magnetic moments of $M^I_2[RuCl_6]$ are ca. 2.70–3.0 BM at room temperature and do not increase on dilution into a diamagnetic host, [357,369,380]. The hydrolysis reactions occurring in solutions of $[RuCl_6]^{2-}$ are pH and concentration dependent, and spectrophotometric studies [381–385] have suggested a range of ions including $[Cl_5RuORuCl_5]^{4-}$, $[RuCl_5(H_2O)]^-$, $[RuCl_5(OH)]^{2-}$ and $[Ru(OH)_2Cl_3]^-$ are present.

Hexabromoruthenates(IV) have not been studied in great detail, but are generally similar to the chloroanalogues, although much more easily decomposed to Ru(III) in solution. They are best prepared by treatment of $[RuBr_5]^{2-}$ (or $[RuCl_5]^{2-}$) in HBr with Br_2, when black crystalline $M_2[RuBr_6]$ (M = K, Rb, Cs, NH_4, $R_{4-n}H_nN$) are formed [370,386,387]. The powder X-ray pattern of $K_2[RuBr_6]$ confirms it is cubic [387]. Magnetic data (μ_{eff} = ca. 2.8 BM) [357], absorption and MCD spectra [377] have been reported.

Hexachloroosmates(IV) are among the most important osmium compounds and are widely used as starting materials. The usual method of preparation is by reduction of OsO_4 in concentrated hydrochloric acid with Fe^{2+} or ethanol followed by addition of M^ICl. In contrast to RuO_4, OsO_4 is only very slowly reduced by HCl to $[MCl_6]^{2-}$. A large number of $[OsCl_6]^{2-}$ salts are known including $M_2[OsCl_6]$ (M = Na, K, Rb, Cs, NH_4 [26,388–394], Ag [395], Tl^I [395], R_4N [396,397] R_4P, R_4As [398]). The sodium salt can be prepared by heating Os + NaCl in chlorine, and since it is much more soluble than the other alkali-metal salts, can be converted into them by metathesis [26]. The alkali-metal salts have the $K_2[PtCl_6]$ structure [399]. Extensive spectroscopic data on $[OsCl_6]^{2-}$ salts have been reported; representative data are, IR (Table 5), electronic [12,380,396,403,404], resonance-Raman [405,406], and NQR [407,408,411] spectra. The colour of the $M_2[OsCl_6]$ is cation dependent; thus the K, NH_4 salts are dark red, the Cs orange, and large alkylammonium salts yellow (as is the aqueous solution). This is thought to be due to changes in the cation size causing variations in the lattice parameters, and this in turn broadens and/or shifts the CT bands [395]. Much effort has been devoted to understanding the magnetic properties of the $M^I_2[OsCl_6]$ compounds [357,369,380,409]. The μ_{eff} values are ca.

1.50 BM, and χ_M is virtually invariant with temperature. However, when diluted into a diamagnetic host (K_2PtCl_6) the susceptibilities increase with dilution reaching ca. 2.1 BM at "infinite dilution".

Black hexabromoosmates(IV) $M_2[OsBr_6]$ (M = Na, K, Cs, Rb, NH_4, Ag) are made from OsO_4 and HBr followed by addition of MBr, or by metathesis. Ethanol is often used as a reducing agent, but in contrast to $[OsCl_6]^{2-}$, the reduction proceeds satisfactorily in its absence in the case of the bromide [389,396,398,410,411]. The structures are the $K_2[PtCl_6]$ type [399], and an old X-ray study gave Os–Br ca. 2.5 Å [412]. Spectroscopic data include IR (Table 5), electronic [12,380,396,405,406,415] and resonance Raman [405,406,416]. The magnetic properties are very similar to those of $[OsCl_6]^{2-}$ and show similar effects upon dilution [357,380,409].

Hexaiodoosmates(IV) are made by prolonged action of hydriodic acid on $M_2[OsCl_6]$ or from OsO_4, HI and M^II [12,417,418]. They are green-black solids which give violet aqueous solutions. The magnetic moment of $K_2[OsI_6]$ is 1.65 BM [357], and its electronic spectrum has been recorded [405,419–422].

Extensive studies mainly by Preetz and co-workers [360,361,418,419,423–438] resulted in the synthesis, characterisation and often isolation of mixed haloosmates(IV) $[OsX_{6-n}Y_n]^{2-}$ or $[OsX_nY_mZ_p]^{2-}$ ($n+m+p=6$ X, Y, Z halide), $[OsX_5(H_2O)]^-$, etc. Typical examples are $Cs_2[OsF_3Cl_3]$, *cis*- and *trans*-$Cs_2[OsCl_2F_4]$, *trans*-$Cs_2[OsCl_4F_2]$ and $Cs_2[OsClF_5]$ made from $K_2[OsF_6]$ and BrF_3, followed by treatment with caesium acetate [423], and the treatment of $[OsCl_6]^{2-}$ with concentrated HBr, followed by ionophoresis [425,426] which gives $[OsCl_{6-n}Br_n]^{2-}$ ions. Other separation methods include thin layer and ion exchange chromatography [427,428]. These mixed species have been studied by IR and electronic spectroscopy, and formation constants have been obtained in many cases. More recently other anions have been used to produce new series of haloosmates(IV) e.g. oxalate $[OsI_{4-n}Cl_n(C_2O_4)]^{2-}$ and $[OsX_4(C_2O_4)]^{2-}$ (X = halide) [439,440]. For more detailed discussion of this work the original references should be consulted. The crystal structure of $Cs_2[OsBrClF_4]$ (Fig. 23) has been determined [441]; it has ν(Os–F) at 552 cm^{-1}, ν(Os–Cl) 320 cm^{-1}, and ν(Os–Br) 222 cm^{-1} [423].

Reduction of the tetroxides MO_4, in dilute HX was believed for many years to give monomeric $[M(OH)X_5]^{2-}$ ions [29,394,442]. However, the diamagnetism of $K_2[Ru(OH)Cl_5]$ [443] led to the proposal of a dimeric structure, $[Ru_2OCl_{10}]^{4-}$, and this was confirmed by an X-ray study [444]. Subsequently magnetic [445] and vibrational spectral studies [61,74,446] on other "$[M(OH)X_5]^{2-}$" salts showed that all were of the $[M_2OX_{10}]^{4-}$ type. The diamagnetism has been explained by Dunitz and Orgel [447] in terms of three centre molecular orbital sets involving the linear Ru–O–Ru units. The deep brown-red ruthenium and brown osmium salts are usually obtained by

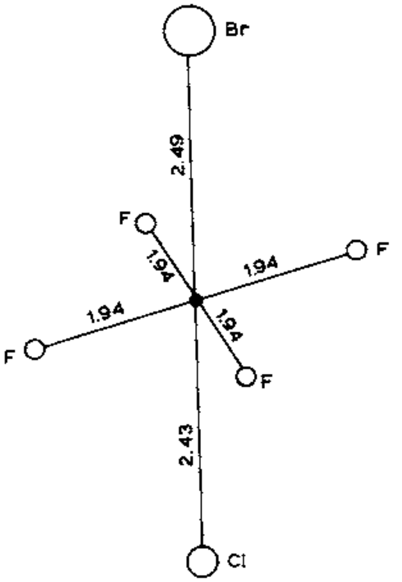


Fig. 23. Structure of the $[OsBrClF_4]^{2-}$ anion. From ref. 441.

the original route from MO_4, although $K_4[Ru_2OCl_{10}]$ has also been made from $RuCl_3 \cdot 3H_2O$ [448], or by fusing Ru with $KClO_3/KOH$ and crystallising the melt from dilute HCl [449]. Salts with the heavier alkali-metals (Rb, Cs) and also NH_4^+ are known [29,394,445,448–450] and mixed halide derivatives $[Os_2OBr_4Cl_6]^{4-}$ [74,466a], $[Ru_2OCl_8Br_2]^{2-}$ [451] have been reported. The evidence for $[Os_2OI_{10}]^{4-}$ is less good [452] although limited spectroscopic data on it has been reported [74]. The most accurate X-ray data on $Cs_4[Os_2OCl_{10}]$ [453] reveals the expected linear Os–O–Os system and $Os\text{–}Cl_{eq} < Os\text{–}Cl_{ax}$ (Fig. 24), and $K_4[Ru_2OCl_{10}]$ (Fig. 25) is similar

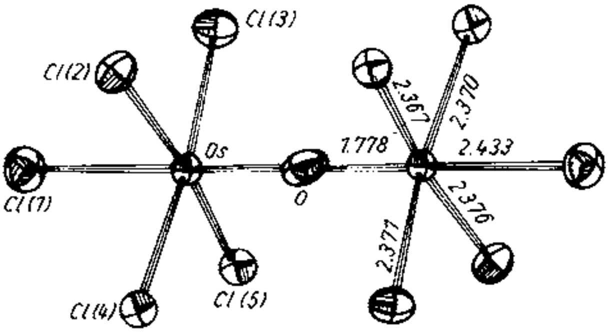


Fig. 24. Structure of the $[Os_2OCl_{10}]^{4-}$ anion. From ref. 453.

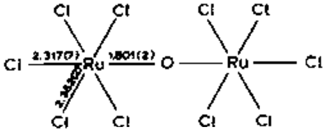


Fig. 25. Structure of the $[Ru_2OCl_{10}]^{4-}$ anion.

[375]. Vibrational spectra show that ν_{asym} OsOOs is ca. 840–850 cm^{-1} and ν_{asym} RuORu ca. 880–890 cm^{-1} with ν_{sym} lying in the range 200–250 cm^{-1} [61,74,446,448,450,454]. Electronic [448,450,454,455] and resonance Raman spectra have also been published. The $[X_5RuORuX_5]^{4-}$ ions appear to be reasonably stable in acid solution, although they can be reduced electrochemically, and aquate in dilute solution [456–460], but the osmium compounds seem to hydrolyse rapidly [445,461]. Species such as $[(H_2O)Cl_4OsOOsCl_4(H_2O)]^{2-}$ and $[(OH)Cl_4OsOOsCl_4(OH)]^{4-}$ have been prepared in solution [438,462].

Complexes

Group VI donors. Few M(IV) complexes with oxygen donor ligands are known and almost all contain anionic ligands. Early reports of $Ru(SO_4)_2$ are

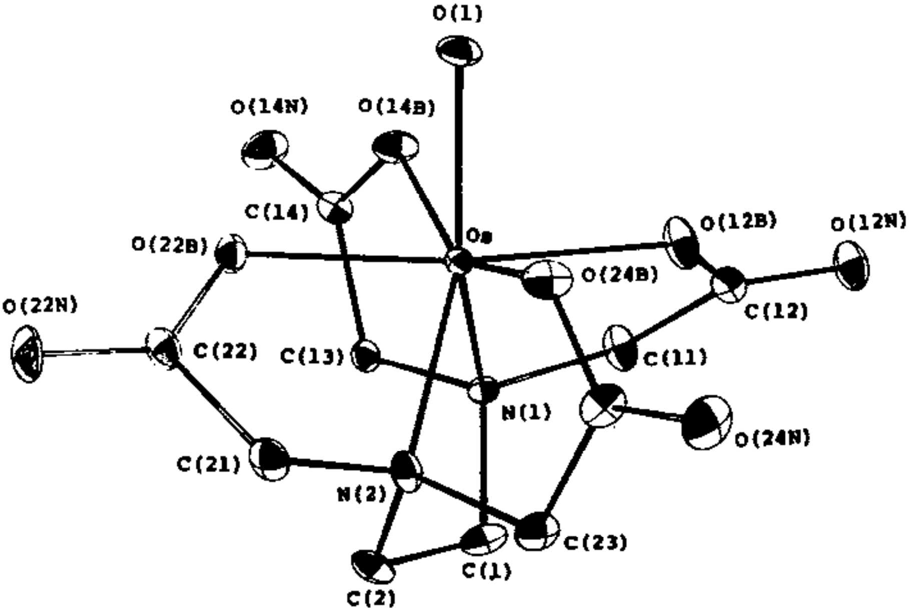


Fig. 26. The structure of $[Os(EDTA)(H_2O)]$. From ref. 453.

thought to be mistaken [179], and the reported [107] oxalate $K_2[Ru(C_2O_4)_3]$ does not appear to have been studied more recently.

The aerial oxidation of $H[Os(H_2EDTA)Cl_2]\frac{1}{2}H_2O$ (H_4EDTA = ethylenediaminetetraacetic acid) in water gives black crystals of $[Os(EDTA)(H_2O)] \cdot H_2O$. An X-ray study shows the osmium has monocapped trigonal prismatic coordination (Fig. 26) with $Os{-}O_{(H_2O)} = 2.040(7)$ Å, $Os{-}O_{EDTA} = 2.06(7)$ Å and $Os{-}N_{(av)} = 2.159(6)$ Å [463]. The $[Ru(H_2EDTA)Cl_2] \cdot 3H_2O$ has been prepared from $K_2[RuCl_6]$ and $Na_2[H_2EDTA]$ at pH 2.5, and can be converted to $K_2[Ru(EDTA)Cl_2] \cdot 3$ H_2O by treatment with potassium acetate [464]. Acetylacetonato complexes *cis*- and *trans*-$[OsX_2(acac)_2]$ (X = Cl, Br, I) are formed by heating $K_2[OsX_6]$ in a 1 : 1 mix of water and acetylacetone (acacH), and the pure isomers are separated by chromatography on silica gel [465]. Treatment of $[Ru(PPh_3)_3Cl_2]$ with tetrachloro-1,2-benzoquinone is reported to give green $[Ru(O_2C_6Cl_4)(PPh_3)_2Cl_2]$ which is presumably the *trans* dichloro isomer since it has a single ν(Ru–Cl) at 342 cm^{-1} in the IR spectrum. Complexes were also obtained with 1,2-naphthaquinone and 9,10-phenanthrenequinone [466a]. An example of an N, O donor ligand complex is $[OsL_2Cl_2]Cl_2$ where L is the *o*-diethylaminoanil of phenyl glyoxal [466b].

Ru(IV) and Os(IV) complexes of dithiocarbamate ligands are the most numerous sulphur donor compounds [467,468]. Recently, however, Os(IV) complexes with thioethers have been prepared from $Na_2[OsCl_6]$ and L ($L = RS(CH_2)_2SR$, *cis*-RSCH = CHSR, and *o*-$C_6H_4(SR)_2$ (R = Me, Ph)) in 2-ethoxyethanol which gave $[OsLCl_4]$ [469]. The complexes $[OsL'Br_4]$($L' = MeS(CH_2)_2SMe$ or *cis*-MeSCH = CHSMe) were similarly prepared from $K_2[OsBr_6]$. They are green or grey-green powders with μ_{eff} 1.3–1.4 BM [469]. Ruthenium(III) complexes of bidentate thioethers were not oxidised to Ru(IV) either chemically or electrochemically [469]. Irreversible electrochemical oxidation of $[Ru(Me_2S)_3Cl_3]$ (at 1.65 V versus Ag/AgI) in CH_2Cl_2 has been reported [470].

The chemical and electrochemical oxidation of $[Ru(Et_2dtc)_3]$ has been the subject of a number of studies, and some of the earlier work is now thought to be erroneous. The electrochemical oxidation of $[Ru(RR'dtc)_3]$ is generally not reversible and the $[Ru(RR'dtc)_3]^+$ produced exhibit varying degrees of instability depending upon the nature of R, R′ [471]. It was reported that the reaction of $[Ru(R_2dtc)_3]$ with BF_3 under aerobic conditions gave diamagnetic Ru(IV) compounds [472]. However, later work including an X-ray structure determination showed the products to be dimeric Ru(III) species $[Ru_2(R_2dtc)_5]BF_4$ [473,474]. The photolysis of $[Ru(R_2dtc)_3]$ (R = Me, Et) in $CHCl_3$ or CH_2Cl_2, or reaction with gaseous HCl in benzene produced green $[Ru(R_2dtc)_3Cl]$ complexes. A single crystal X-ray structure determination (R = Et) shows a distorted pentagonal-bipyramidal configuration about the

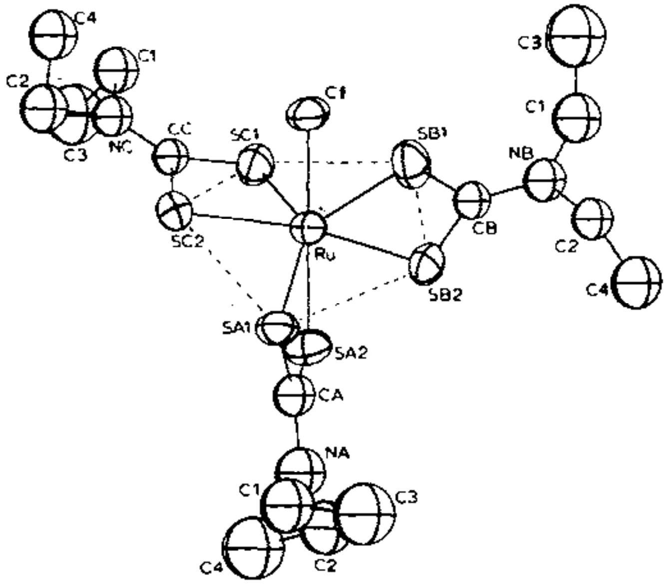


Fig. 27. The structure of $[Ru(Et_2dtc)_3Cl]$. From ref. 475.

Ru(IV) (Fig. 27) where $Ru{-}S_{av} = 2.40$ Å and $Ru{-}Cl = 2.448(7)$ Å [475]. The $[Ru(R_2dtc)_3Cl]$ react with $AgBF_4$ in acetone to give $[Ru_2(R_2dtc)_5]BF_4$ and the thiuram disulphide [475]. Treatment of $[Ru(Me_2dtc)_3]$ with I_2 in $CHCl_3$

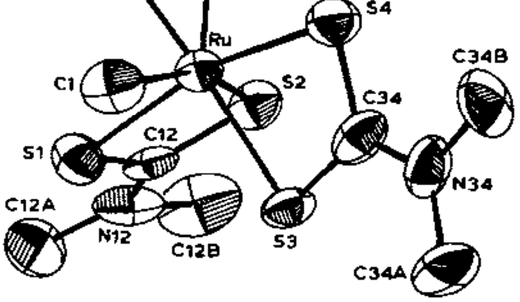


Fig. 28. The structure of $[RuCl(S_2CNMe_2)_2(\eta^2\text{-}SCNMe_2)]$. From ref. 478.

gave golden crystals of $[Ru(Me_2dtc)_3I_3]$, which have a similar pentagonal-bipyramidal structure to the chloride, with the iodine atoms forming infinite chains ($Ru-S_{av} = 2.39$ Å, $Ru-I = 2.752(4)$ Å) [476]. A more detailed investigation of the photolysis of $[Ru(R_2dtc)_3]$ in $CHCl_3$ shows $[Ru(R_2dtc)_3Cl]$ to be the major product with $[Ru_2(R_2dtc)_5Cl]$ as the minor product [477]. However, when benzophenone is used as a triplet sensitizer photolysis at 366 nm unexpectedly produced the $[Ru(Me_2dtc)_2(\eta^2\text{-}SCNMe_2)Cl]$. The X-ray structure of the latter (see Fig. 28) shows a distorted pentagonal bipyramid $Ru-S_{av} = 2.395$ Å, $Ru-Cl = 2.425(3)$ Å [478]. Recently the electrochemical oxidation of $[Ru(R_2dtc)_3]$ in CH_3CN has been reported to give $[Ru(R_2dtc)_3(CH_3CN)]^+$, and this can be synthesised by controlled potential electrolysis and isolated as the BF_4^- salt. The complexes $[Ru(R_2dtc)_3(PPh_3)]X$ ($X = Cl$, BF_4; $R = Me$, Et) were prepared in solution from $[Ru(R_2dtc)_3Cl]$ and PPh_3 in CH_3CN, using $NaBF_4$ in the case of the fluoroborate [479]. Only $[Ru(Me_2dtc)_3(PPh_3)]BF_4$ was isolated as a solid; all these seven coordinate complexes are stereochemically non-rigid in solution [479].

The complex $[Os(Et_2dtc)_3]$ reacts with a variety of oxidants to produce $[Os(Et_2dtc)_3X]$ ($X = Cl$, I, BF_4) [480]. The $[Os(Et_2dtc)_3X]$ are obtained from $[Os(Et_2dtc)_3]$ and dry HCl ($X = Cl$) or I_2 ($X = I$) in toluene and are diamagnetic red-brown materials. $[Os(Et_2dtc)_3Cl]$ is also produced by UV photolysis of $[Os(Et_2dtc)_3]$ in $CHCl_3$, and on treatment with PPh_3 gives $[Os(Et_2dtc)_3(PPh_3)]Cl$ [480]. If BF_3 is bubbled into $[Os(Et_2dtc)_3]$ in CH_2Cl_2 impure brown paramagnetic $[Os(Et_2dtc)_3]BF_4$ is formed. The electrochemistry and ^1H NMR spectra of the complexes were also studied [480]. Pure $[Os(Et_2dtc)_3]PF_6$ is formed from $[Os(Et_2dtc)_3]$, BF_3 and $[Et_4N][PF_6]$ in CH_2Cl_2 and has been shown to exhibit a monomer ⇌ dimer equilibrium in CH_2Cl_2 solution [481].

$$2[Os(Et_2dtc)_3]^+ \rightleftharpoons [Os_2(Et_2dtc)_6]^{2+}$$

The monomer rapidly reacts with donor ligands such as CH_3CN and Cl^- to form the diamagnetic seven-coordinate complexes. The structure of $[Os_2(Et_2dtc)_6](PF_6)_2 \cdot CH_2Cl_2$ has been determined ($Os-S_{av} = 2.415(3)$ Å) [481] (Fig. 29).

Dark-green $[Os(Et_2dtc)_4]$ is formed from $(NH_4)_2[OsCl_6]$ and $Na[Et_2dtc] \cdot 3H_2O$ in aqueous methanol in a 1:5 ratio, but decomposes in organic solvents [482]. The $[Os_2N(Me_2dtc)_5]$ is discussed below.

Mixed S, O donor ligand complexes include Os(IV) derivatives of α-mercaptopropionic acid [483] and 3-mercapto-1,2-propanediol [484,485]. With S, N donors there are Ru(IV) and Os(IV) complexes of 2-mercaptobenzimidazole, 2-mercaptobenzoxazole [486,487], and Os(IV) complexes of dimethylaminoethanethiol $Na[Os(C_4H_{10}NS)(OH)_4]$ [488,489], di-isopropylaminoethanethiol, $[Os(C_8H_{18}NS)_2(OH)_2]$ [490], glutathione $[Os(C_{10}H_{15}$

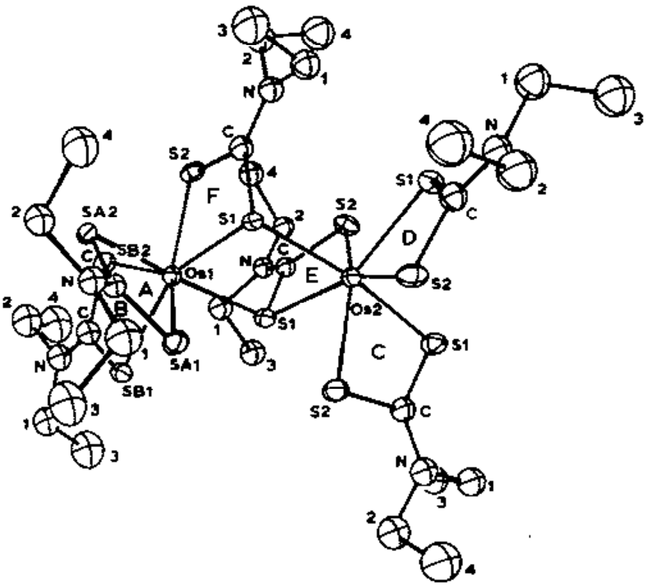


Fig. 29. The structure of $[Os_2(Et_2dtc)_6](PF_6)_2 \cdot CH_2Cl_2$. From ref. 481.

$O_6SN_3)_2]$ [97] and 6-methyl-8-mercaptoquinoline [491]. There is also a claim [492] for selenourea complexes of Ru(IV).

Group V donors. The *cis* and *trans* isomers of $[Os(NH_3)_4X_2]^{2+}$, *mer*-$[Os(NH_3)_3X_3]^+$ (X = Cl, Br, I) and $[Os(NH_3)Cl_5]^-$ were prepared by oxidising the Os(III) analogues with Fe^{3+}. The isomers were separated by column chromatography and reactions, IR and electronic spectra, and electrochemical data reported [493,494]. A number of complexes of deprotonated ethylenediamine have been claimed, although none have been unequivocally characterised. The reaction of ethylenediamine and $(NH_4)_2[OsBr_6]$ gives a pink material formulated as $[Os(en{-}H)_2en]Br_2$ (en-H = $HNCH_2CH_2NH_2$). The compounds $[Os(en{-}H)_3]I$, $[Os(en{-}H)_2en_2]I_2$ and $[Os(en{-}H)en_2]X_3$ (X = Br, I) were also prepared [240,495]. Red $[Os(en)Cl_4]$, deep green $[Os(en)Br_4]$ and $[Os(en)(C_2O_4)_2]$ are prepared from $[Os(en{-}H)_2en]Br_2$ and HX (X = Cl, Br, $\frac{1}{2}C_2O_4$), whilst deep blue $[Os(en)I_4]$ is produced from the corresponding chloride and hydriodic acid [496]. Reduction of $[OsO_2(en)_2]Cl_2$ with Zn/Hg and HCl produces yellow $[Os(en)_2H_2]ZnCl_4$ ($\mu_{eff} = 0.22$ BM) which was converted to the dichloride $[Os(en)_2H_2]Cl_2 \cdot H_2O$ by an ion exchange resin [192].

The synthesis of yellow $[Rupy_2Cl_4]$ from pyH^+Cl^-, $RuCl_3$ and H_2O_2 in hydrochloric acid [107] has been reinvestigated [497], and it is suggested that the product is a red-brown material of empirical formula $[pyH][RuCl_3]$. An

$[Ru(HSO_4)_2py_4]Cl_2 \cdot 3H_2O$ has also been claimed [498]. The photolysis of $[Bu_4N]_2[OsX_6]$ ($X = Cl$, Br, I) in the presence of pyridine, or direct reaction in non-polar solvents gives $[Bu_4N][OsX_5py]$, and mixed halide analogues such as $[Bu_4N][OsCl_4Ipy]$ are known [499–501]. Dark purple $[Ru(phen)Cl_4]$ was prepared by oxidation (HNO_3/Ce^{4+}) of $[phenH][Ru(phen)Cl_4]$, and dark brown $[Ru(phen)Br_4]$ from $[phenH][Ru(phen)Br_4]$ and Br_2/HBr [502]. Chlorine oxidation of $[bipyH][Ru(bipy)Cl_4]$ produces black $[Ru(bipy)Cl_4]$ $\mu = 2.87$ BM [502], which is also claimed as the product of the reaction of $RuCl_3 \cdot 3H_2O$ and 2,2′-bipyridyl in hydrochloric acid [503]. The osmium analogues $[Os(phen)Cl_4]$ and $[Os(bipy)Cl_4]$ are produced by heating the corresponding $[LH]_2[OsCl_6]$ ($L = $ phen, bipy) [504]. An alternative preparation of $[Os(bipy)Cl_4]$ and its electronic spectrum have been published [505,506].

It is claimed that reduction of "$[RuO_4(bipy)]$" or "$[RuO_3phen]_2O$" in methanol with the appropriate ligand yields $[RuO_2(bipy)_2] \cdot 3H_2O$, $[RuO_2(phen)_2]$ and $[RuO_2(bipy)(phen)] \cdot 3H_2O$. All three are diamagnetic and were assumed to contain *trans* $O=Ru=O$ units, although IR spectral support for this grouping was not provided [101]. Chemical ($Ce^{4+}/HClO_4$) or electrochemical oxidation of $[Ru(bipy)_2py(OH)_2](ClO_4)_2$ gives bright green $[Ru(bipy)_2(py)O](ClO_4)_2$ which has $\nu(Ru=O)$ at 792 cm^{-1} (752 for the ^{18}O labelled compound) [507,508]. A study of the oxidation of PPh_3 by $[Ru(bipy)_2pyO]^{2+}$ in CH_3CN has recently appeared [509], and it has been shown that chemically catalysed net electrochemical oxidation of ROH,

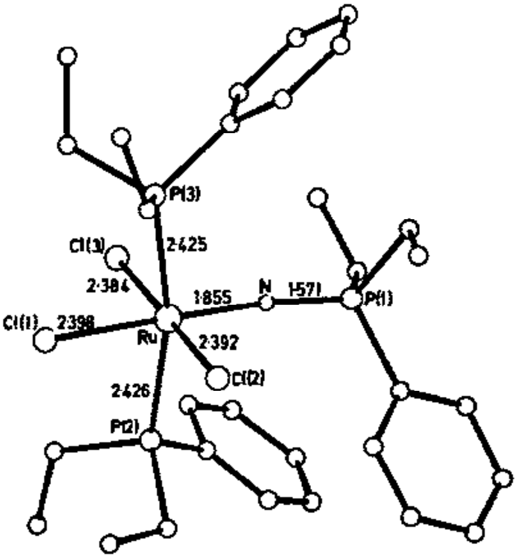


Fig. 30. The structure of $[Ru(NPEt_2Ph)Cl_3(PEt_2Ph)_2]$. From ref. 512.

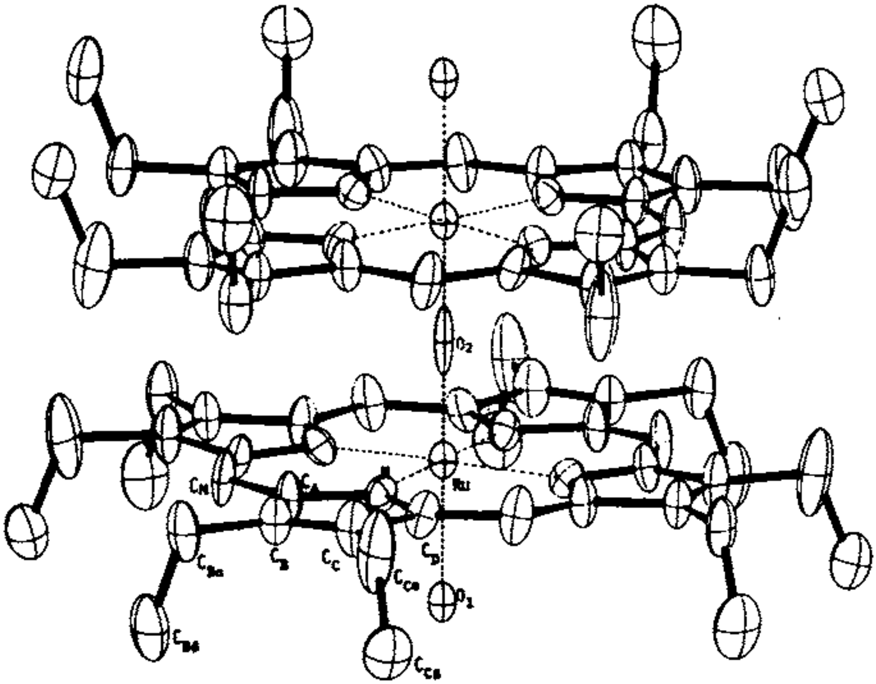


Fig. 31. The structure of [(OEP)Ru(OH)]$_2$O. From ref. 513.

RCHO, and unsaturated hydrocarbons can be achieved using the system $[Ru(terpy)(bipy)(OH)_2]^{2+}$/$[Ru(terpy)(bipy)O]^{2+}$ (terpy = 2,2′,2″-terpyridine) [510].

Nitrile substituted anions of ruthenium(IV) $[NEt_4][RuCl_5(RCN)]$ (R = Me, Ph) have recently been obtained from $RuCl_3 \cdot 3H_2O$, $[Et_4N]Cl$ and RCN [511], and $[OsCl_5MeCN]^-$ is produced by photolysis of $OsCl_6^{2-}$ in MeCN [499].

Phosphine imidato complexes $[M(NPR_3)Cl_3(PR_3)_2]$ (PR_3 = PPh_3, PPh_2Et, $PPhEt_2$, PEt_3, PPh_2Me) are produced by reaction of PR_3 with $[MNCl_3(AsPh_3)_2]$ (M = Ru, Os), and for $PPhMe_2$, the intermediate $[M(NPPhMe_2)Cl_3(AsPh_3)_2]$ can be isolated [236]. Osmium bromoanalogues $[Os(NPR_3)Br_3(PR_3)_2]$ and an $[Os(NHPPh_3)(PPh_3)Cl_4]$ can be obtained. A single crystal X-ray structure determination of $[Ru(NPEt_2Ph)Cl_3(PEt_2Ph)_2]$ shows the ruthenium has a distorted octahedral coordination (Fig. 30) ($Ru{-}Cl_{mean}$ = 2.39 Å, $Ru{-}P_{mean}$ = 2.425 Å, Ru–N = 1.841 Å) [512].

Dark violet crystals of $[Ru(OEP)(OH)]_2O$ are formed by oxidation of [Ru(OEP)(CO)] with ^tBuOOH in benzene [513]. An X-ray study confirms the binuclear oxo-bridged structure (Fig. 31) [513] with $Ru{-}O_{bridge}$ = 1.847(13) Å, Ru–OH = 2.195(20) Å, Ru–N = 2.067(14) Å. The dark blue

$[Os(OEP)(OMe)_2]$ has been prepared from $[Os(OEP)O_2]$ by reduction with $SnCl_2$ in methanol [196] or with hydrazine hydrate in methanol/tetrahydrofuran [514]. The optical absorption and emission spectra of $[Os(OEP)(OMe)_2]$ and their rationalisation in terms of iterative extended Hückel calculations have been reported [197,514]. The reduction of $[Os(TTP)O_2]$ in methanol produces the analogous $[Os(TTP)(OMe)_2]$ [176]. Orange-red $[Os(OEP)Br_2]$ can be made from $[Os(OEP)(N_2)(THF)]$ and CBr_4 [515]. Complexes of Ru(IV) [516] and Os(IV) [517,518] with phthalocyanine have been reported.

Surprisingly all attempts to isolate simple Ru(IV) halide complexes with phosphine or arsine ligands have failed [519–521], although both iron(IV) [1] and osmium(IV) (see below) analogues are known. Electrochemical studies have shown that $[RuL_2Cl_4]^-$ ($L = PPh_3$, $AsPh_3$) [470] and $[Ru(L\text{–}L)_2Cl_2]^+$ ($L\text{–}L = o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6H_4(AsMe_2)_2$) [519], undergo irreversible one electron oxidations, but the products decompose rapidly in the electrolyte medium.

There are a few formally Ru(IV) hydrides of which $[RuH_4(PPh_3)_3]$ is the best known. The preferred synthetic route is the reaction between $NaBH_4$ and $[Ru(PPh_3)_3Cl_2]$ in ethanol [522,523]. Other examples are $[RuH_4(PR_3)_3]$ ($PR_3 = (p\text{-tolyl})_3P$, 5-phenyl-5H-dibenzophosphole) [524,525], whilst cationic $[RuH_3L_4]PF_6$ ($L = PMe_2Ph$, $\frac{1}{2}Ph_2P(CH_2)_nPPh_2$, $n = 2\text{–}4$) are formed from $[RuHL_4(MeOH)]^+$ and hydrogen [526].

Osmium(IV) complexes *trans*-$[Os(ER_3)_2X_4]$ ($X = Cl$, Br; $ER_3 = PPh_3$, PMe_2Ph, P^nBu_2Ph, P^nPr_2Ph, $PMePh_2$, P^iBu_2Ph, $PEtPh_2$, [21,236,247,527–531], $AsPh_3$, As^nPr_3, $AsMe_2Ph$, $AsEt_2Ph$, [247,521,527,529]) are readily obtained from OsO_4, HX and ER_3, from $[OsX_6]^{2-}$ and ER_3, or for the chlorides by oxidation of *mer*$[Os(ER_3)_3Cl_3]$ with Cl_2 or CCl_4 under reflux. The chlorides are usually yellow or brown solids, and the bromides red-purple, with $\mu_{eff} = 1.5\text{–}1.6$ BM. A black $[Os(SbPh_3)_2Cl_4]$ is produced by prolonged reflux of $[Os(SbPh_3)_3Cl_3]$ in CCl_4 [527], and yellow $[Os(P(OMe)_3)_2Cl_4]$ forms on reaction of $[OsCl_6]^{2-}$ with $P(OMe)_3$ and Zn/Hg in THF [531]. The X-ray of $[Os(PMe_2Ph)_2Cl_4]$ confirms the *trans* octahedral structure Os–P = 2.448(3) Å, Os–Cl = 2.319(3) Å [532]. There are several spectroscopic studies of these complexes, viz. IR [247,527,529,533], charge transfer spectra [13], ^1H NMR [10,529,533,534] and XPS [19,21,235,236]. The red $[Ph_4As][Os(PPh_3)Cl_5]$ can be obtained from $[Os(NHPPh_3)(PPh_3)Cl_4]$ and $[Ph_4As]^+[HCl_2]^-$ in acetone [236].

Bis(diphenylarsino)methane bonds as a monodentate in brown *trans*-$[Os(Ph_2AsCH_2AsPh_2)_2Cl_4] \cdot EtOH$ [527], but chelating phosphines are present in $[Os(L\text{–}L)Cl_4]$ ($L\text{–}L = Ph_2PCH_2CH_2PPh_2$, *cis*-$Ph_2PCH=CHPPh_2$) [529]. Treatment of $[Os(L\text{–}L)_2X_2]X$ ($L\text{–}L = o\text{-}C_6H_4(AsMe_2)_2$; $X = Cl$, Br) and $[Os(L\text{–}L)_2I_2]ClO_4$ with concentrated nitric acid followed by $HClO_4$ produces blue-black $[Os(L\text{–}L)_2Cl_2](ClO_4)_2$, black $[Os(L\text{–}L)_2Br_2](ClO_4)_2$ and brown $[Os(L-L)_2I_2](ClO_4)_2$ respectively, with $\mu_{eff} = 1.16-1.25$ BM [535]. The $[Os(L-L)_2Cl_2]^+/[Os(L-L)_2Cl_2]^{2+}$ couple is reversible in MeCN at room temperature [519]. Most surprisingly in view of the results with the diarsine, all attempts to isolate $[Os(o\text{-}C_6H_4(PMe_2)_2)_2X_2]^{2+}$ have failed; only transient blue solutions which rapidly decolourise are formed by $HNO_3/HClO_4$ treatment of the Os(III) complexes. The Os(III)/Os(IV) couple for the diphosphine complexes is only reversible in MeCN solution at temperatures $< -30°C$ [519]. Yellow $[OsCl_4L]$ ($L = PhP(CH_2CH_2PPh_2)_2$) presumably with a P_2Cl_4 donor set is formed from the ligand and OsO_4 in a mixture of concentrated HCl and ethanol [536].

Like W, Re and Ir, osmium forms a series of stable multihydride complexes. White $[OsH_4(PR_3)_3]$ are obtained as air-stable crystalline solids by $NaBH_4$ or $LiAlH_4$ reduction of $[Os(PR_3)_3Cl_3]$ in THF [247,537–540]. The best characterised is $[OsH_4(PMe_2Ph)_3]$ which has been structurally studied by both X-ray and neutron diffraction. The structure (Fig. 32) is distorted pentagonal bipyramidal with two axial phosphines, and an essentially planar OsH_4P unit in the equatorial plane $Os-H_{av} = 1.663(3)$ Å, $Os-P_{eq} = 2.347(3)$

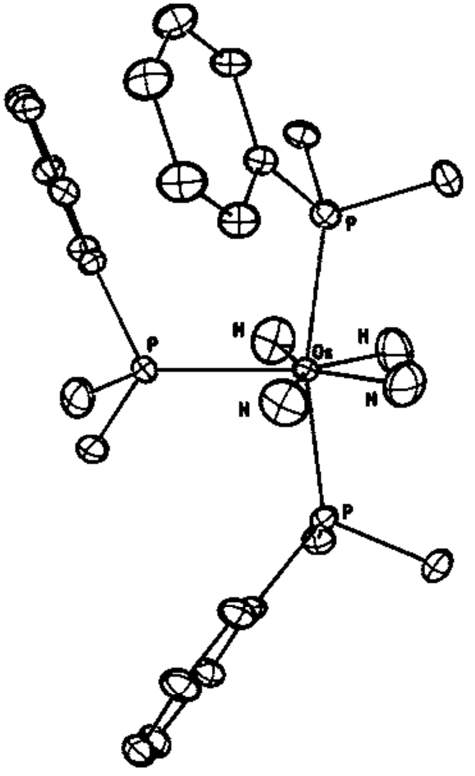


Fig. 32. The structure of $[OsH_4(PMe_2Ph)_3]$. From ref. 541.

Å, Os–P_{ax} = 2.311(3) Å [541–543]. Arsine hydrides $[OsH_4(AsR_3)_3]$ are made by similar methods, and there is a mixed complex $[OsH_4(AsMe_2Ph)(PMe_2Ph)_2]$ [247,538–540]. White $[OsH_3(PEt_2Ph)_4]BPh_4$ is obtained from $[OsH_2(PEt_2Ph)_4]$ and HCl in methanol, followed by addition of $Na[BPh_4]$ [537], and $[OsH_3(PEt_2Ph)_2(Ph_2PCH_2CH_2PPh_2)]^+$ is probably produced from $[Os(PEt_2Ph)_2(Ph_2PCH_2CH_2PPh_2)H_2]$ and HBF_4. Complexes of type $[Os(PR_3)_3H_2Cl_2]$ are prepared from *mer*$[Os(PR_3)_3Cl_3]$ and amalgamated zinc in THF under a hydrogen atmosphere and are converted to $[Os(PR_3)_3HCl_3]$ by HCl [544].

Groups IV and III. Organometallic compounds are not included in this review. The silyl compounds $[RuH_3(SiR_3)L_n]$ ($R_3 = F_3$, MeF_2, Cl_2Me, $(OEt)_3$, $ClMe_2$, HPh_2, $MePh_2$, Ph_3; L = PPh_3, $AsPh_3$, p-$(C_6H_4Me)_3P$; n = 2, 3) were formed by reaction of excess $HSiR_3$ with $[RuH_2L_4]$, $[RuHClL_3]$, $[RuCl_2L_3]$ or $[RuCl_3(AsPh_3)_3]$. The $[RuH_2X(SiR_3)L_3]$ (X = Cl, I) are obtained by reaction of the chlororuthenium(II) complexes with $HSiCl_3$ or of $[RuH_3[Si(OEt)_3](PPh_3)_3]$ with $CDCl_3$ or I_2 [545]. These workers disagree with some of the earlier formulations [546,547] of the products of these reactions.

Oxidative addition of the trimethylammonium salts of the carboranes 7,9- and $[7,8\text{-}C_2B_9H_{12}]^-$ to $[RuHCl(PPh_3)_3]$ in ethanol gave $[2,2\text{-}(PPh_3)_2\text{-}2,2\text{-}H_2\text{-}$

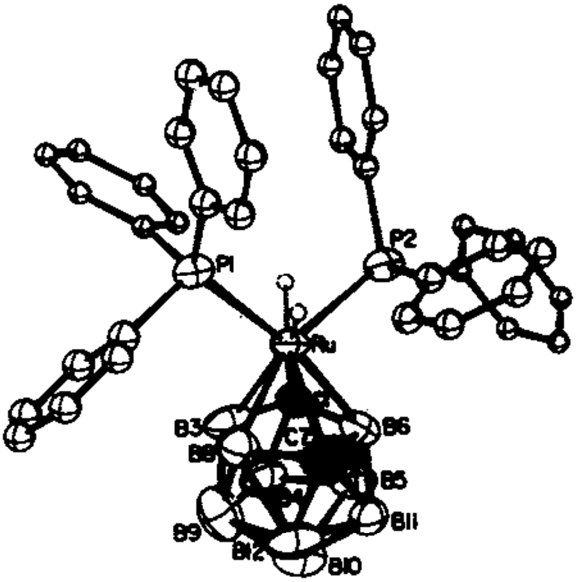


Fig. 33. The structure of $[2,2\text{-}(PPh_3)_2\text{-}2,2\text{-}H_2\text{-}2,1,7\text{-}RuC_2B_9H_{11}]$. Hydride atoms, which were not located, are shown as dotted circles in calculated positions. From ref. 548.

2,1,7-$RuC_2B_9H_{11}$] and [3,3-$(PPh_3)_2$-3,3-H_2-3,1,2-$RuC_2B_9H_{11}$] in high yield. Preliminary X-ray results show the structure of the former to be that shown in Fig. 33 [548].

Polynuclear compounds. There are a number of bi and polynuclear compounds with bridging oxo or nitrido ligands.

Nitrido bridged. A brown solid of composition $[Os_2NCl_x]$ ($x = 5$–7) is formed on heating $(NH_4)_2[OsCl_6]$ in chlorine [344], and is probably the substance described as "$OsCl_3$" by Ruff and Bornemann [549]. It has ν(OsNOs) at 1020 cm^{-1} suggesting a linear nitrido-bridge [550]. A brown gelatinous $Ru_2N(OH)_5 \cdot nH_2O$ is produced from formaldehyde and $K_2[Ru(NO)Cl_5]$ in alkaline solution, or from aqueous ammonia and $K_2[RuO_4]$ [180,550]. It dissolves in hydrochloric acid to yield the $[Ru_2NCl_8(H_2O)_2]^{3-}$ ion [180,550], which is also produced by $SnCl_2$ reduction of $[Ru(NO)Cl_5]^{2-}$ [551], or by hydrolysis of the sulphamate $[Ru(NH_2SO_3)Cl_5]^{3-}$ [552]. There are independent single crystal X-ray studies of $K_3[Ru_2NCl_8(H_2O)_2]$ [553] and $(NH_4)_3[Ru_2NCl_8(H_2O)_2]$ [554] which show the anion has the structure shown in Fig. 34 with very short Ru–N bonds of 1.720 Å and the water coordinated *trans* to the N. There are related ions $[Ru_2NBr_8(H_2O)_2]^{3-}$, $[Ru_2N(NCS)_8(H_2O)_2]^{3-}$ and $[Ru_2N(NO_2)_6(OH)_2(H_2O)_2]^{3-}$, which have similar structures on the basis of their vibrational spectra [180,550,555a]. The resonance Raman spectrum of $K_3[Ru_2NCl_8(H_2O)_2]$ has been recorded [555b]. In freshly prepared solutions $K_3[Ru_2NCl_8(H_2O)_2]$ is a 3:1 electrolyte but the conductance increases rapidly with time, and it has been suggested that $[Ru_2NCl_5(H_2O)_5]$ is the final product [556]. Most unusually for a high oxidation state complex $[Ru_2NCl_8(H_2O)_2]^{3-}$ in concentrated HX (X = Cl, Br) takes up carbon monoxide to form $[Ru_2NX_8(CO)_2]^{3-}$ [176], whilst with KCN the very stable $K_5[Ru_2N(CN)_{10}]$ is produced. The latter is particularly interesting since $[Ru_2NCl_{10}]^{5-}$ is not stable.

Red crystals of $M^I_3[Os_2NCl_8(H_2O)_2]$ (M^I = K, Cs) are formed by dissolving "Os_2NCl_5" in hydrochloric acid containing M^ICl [550] and

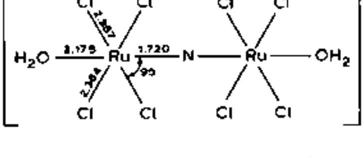


Fig. 34. Structure of the $[Ru_2NCl_8(H_2O)_2]^{3-}$ anion.

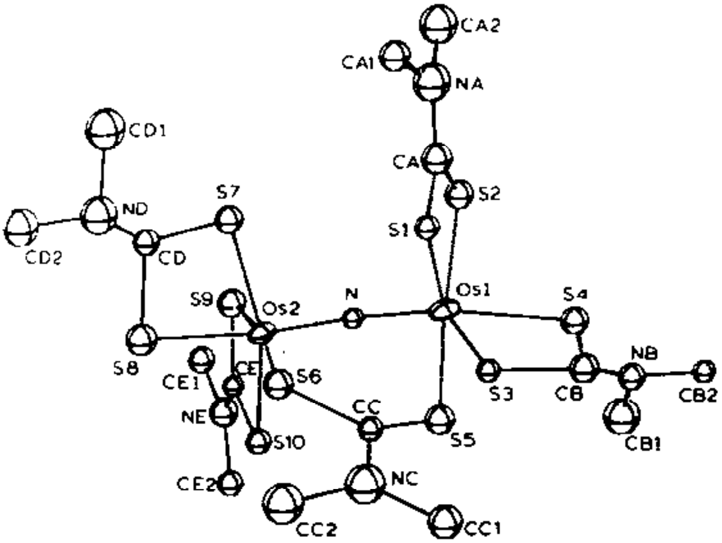


Fig. 35. The structure of $[Os_2N[S_2CN(CH_3)_2]_5]$. From ref. 559.

$Cs_3[Os_2NBr_8(H_2O)_2]$ is produced in low yield from $(NH_4)_2[OsBr_6]$ and Br_2 at 450°C, followed by treatment with HBr/CsBr [550]. Hydrolysis of $K_3[Os(NH_2SO_3)Cl_5]$ gives a poor yield of $K_3[Os_2NCl_8(H_2O)_2]$ and a second product which may be $K_5[Os_2NCl_{10}]$ [552].

Cationic $[Os_2N(NH_3)_8Cl_2]Cl_3$ are formed by heating $Na_2[OsCl_6]$ with aqueous ammonia under pressure [550,552,557] or from $K_3[Os_2NCl_8(H_2O)_2]$ and ammonia [550]. The corresponding bromide can be obtained from the chloride by metathesis or directly from $K_2[OsBr_6]$ and liquid ammonia at +25°C [558]. Metathesis in cold aqueous solution converts $[Os_2N(NH_3)_8Cl_2]Cl_3$ into $[Os_2N(NH_3)_8Cl_2]Y_3$ ($Y = Br$, I, NO_3, N_3, NCS, etc.), and on heating $[Os_2N(NH_3)_8Y_2]Y_3$ are produced [550]. Vibrational spectra suggest all contain linear Os–N–Os units [446,550]. Ruthenium gives similar octammines $[Ru_2N(NH_3)_8X_2]^{3+}$ made from $[Ru_2NX_8(H_2O)_2]^{3-}$ and ammonia, but unlike osmium, hexammines $[Ru_2N(NH_3)_6(H_2O)Y_3]^{2+}$ form on boiling the aqueous solutions ($Y = Cl$, N_3, NO_3, NCS) [180,550].

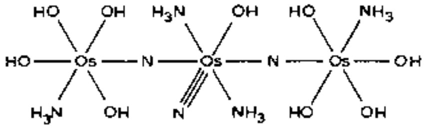


Fig. 36. The proposed structure of $Os_3N_7O_9H_{21}$.

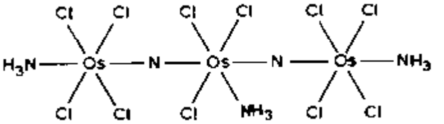


Fig. 37. The proposed structure of the $[Os_3N_2(NH_3)_3X_{11}]^{3-}$ anion.

Treatment of $[Ru_2NCl_8(H_2O)_2]^{3-}$ with $H_2NCH_2CH_2NH_2$ and 2,2′-bipyridyl (L) give $[Ru_2NL_4Cl_2]^{3+}$, whilst $NaEt_2dtc$ produces $[Ru_2N(Et_2dtc)_4Cl]$ [176]. Osmium forms an orange $[Os_2N(Me_2dtc)_5]$ from reaction of $[OsNCl_5]^{2-}$, $Na[Me_2dtc]$, and $[Os(Me_2dtc)_3]$, which has the structure shown in Fig. 35. The unusual non-linear Os–N–Os arrangement is a result of the short "bite" of the bridging dithiocarbamate group [480,559].

The prolonged reaction of OsO_4 with liquid ammonia yields a black diamagnetic material $Os_3N_7O_9H_{21}$ [80,560] which was suggested to have the structure shown in Fig. 36 by Cleare and Griffith, who used vibrational spectroscopy and isotopically labelled material (^2H and ^{15}N) [550]. Formally this material contains Os(VI). OsO_4 and aqueous ammonia give the black "Claus salt" [561], which is believed to contain an $[Os_3N_2]^{8+}$ core and is formulated as $[Os_3N_2(NH_3)_4(OH)_8(H_2O)_2]$ [550]. It dissolves in HX (X = Cl, Br) to give $[Os_3N_2(NH_3)_3X_{11}]^{3-}$ ions [176] (Fig. 37). Hall and Griffith [562] have characterised materials with $[Os_3N_2]^{6+}$ and $[Os_3N_2]^{7+}$ cores made by aeration of aqueous ammoniacal solutions of OsO_4, $[OsCl_6]^{2-}$ or $[Os(NH_3)_5Cl]Cl_2$. The major product is the diamagnetic "osmium violet" $[Os_3N_2(NH_3)_8(H_2O)_6]Cl_6$ (Fig. 38), and the minor product is "osmium brown" $[Os_3N_2(NH_3)_8(H_2O)_6]Cl_7$ ($\mu = 0.87$ BM). Osmium violet is converted to $K_4[Os_3N_2(H_2O)_4(CN)_{10}] \cdot 4H_2O$ by concentrated aqueous KCN, and this probably has a central $Os(H_2O)_4$ unit and terminal $Os(CN)_5$ groups linked by nitrido bridges. XPS data on osmium violet support the presence of Os(IV), and suggest a higher oxidation state overall (non-integral) for $[Os_3N_2]^{7+}$ and $[Os_3N_2]^{8+}$ species [562]. A blue-black ruthenium violet $[Ru_3N_2(NH_3)_8(OH)(H_2O)_5]Cl_5$ ($\mu = 0.8$ BM) is formed from aqueous ammoniacal solutions of $RuCl_3$. The "$Ru_4O_{12}N_{11}H_{33}$" produced from RuO_4 and liquid ammonia [80] presumably has a related structure. There is a

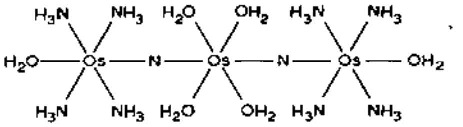


Fig. 38. The proposed structure of the $[Os_3N_2(NH_3)_8(H_2O)_6]^{6+}$ cation.

unique nitrido anion $Ba_9[Os_3N_{10}]$ ($\mu = 1.76$ BM) formed on heating metallic osmium with Ba_3N_2 [563].

Amido-complexes are not well characterised but Preetz and Pfeifer [564] have isolated materials formulated as $Cs_2[Os_5(NH_2)_8Br_{14}]$ and $Cs_2[Os_2(NH_2)_2Br_8]$ from among the large number of products produced on boiling $[Os(NH_3)_6][OsBr_6]$ with conc. HBr.

Oxo-bridged. The most important oxo-bridged dimers are the haloanions $[M_2OX_{10}]^{4-}$ discussed on p. 36. Cationic dimers have been obtained only recently. Brown $[(bipy)_2ClRuORuCl(bipy)_2]^{3+}$, formally an Ru(III)–Ru(IV) species is produced by chlorination of the corresponding Ru(III) dimer [565]. Electrochemical oxidation of $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$ gives the corresponding 3+ ion, and at much higher potential the 4+ ion, corresponding to a Ru(IV)–Ru(IV) dimer, although the latter has not been isolated. The XPS data on $[(bipy)_2ClRuORuCl(bipy)_2]^{3+}$ show the ruthenium atoms are equivalent, which can be rationalised in terms of a strongly coupled RuORu unit and a similar MO scheme to that of Dunitz and Orgel for the halide dimers [565]. The ruthenium atoms are also equivalent in $[(NH_3)_5RuORu(NH_3)_5]^{5+}$ produced by electrochemical or bromine oxidation of the Ru(III) analogue [566]. Other oxo-dimers containing Ru(IV) are the violet $[Ru_2OCl_6(RCN)_4]$ (R = Me, Ph, *o*-tolyl) produced by reaction of commercial $RuCl_3 \cdot 3H_2O$ with warm solutions of the nitriles [567]; $[Ru(phen)(OH)_3]_2O$ [101], and the $[Ru(porphyrin)]_2O$.

The intensely red species produced on air oxidation of a solution of $RuCl_3 \cdot 3H_2O$ in aqueous ammonia has long been known, but its correct formulation was only proposed as recently as 1961 by Fletcher et al. [568]. "Ruthenium red" as it is known, is an oxo-bridged trimer $[Ru_3O_2(NH_3)_{14}]Cl_6$, and a recent X-ray of the thiosulphate salt* [569] showed a linear $[RuORuORu]^{6+}$ system (Fig. 39) with octahedral coordination about the Ru. Curiously whilst the central and one terminal Ru group are almost eclipsed, the other terminal Ru unit is twisted 31°. Oxidation of ruthenium red with H_2O_2, HNO_3 or Ce^{4+} gives "ruthenium brown" $[Ru_3O_2(NH_3)_{14}]^{7+}$ [568,571]. In alkali the reduction of "ruthenium brown" to "red" occurs [568,572]. The magnetic properties of ruthenium red are $\mu_{eff} = 0.77$ BM/Ru and brown 1.13 BM/Ru [568].

Vibrational and resonance Raman spectra [511,573] and electronic spectra [574] suggest that linear Ru–O–Ru–O–Ru units are present in ruthenium brown also. The Mössbauer spectra indicate that discrete oxidation states are

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[*] An independent X-ray [570] of "ruthenium red" deduced a $Ru_3Cl_8(OH)_3(NH_3)_{12}(H_2O)_3$ molecular structure, which is incorrect [569]. Presumably this material is a new trinuclear complex.

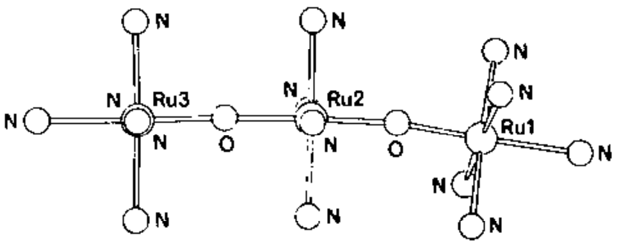

Fig. 39. Structure of the Ruthenium Red cation. From ref. 569.

present in both types: red Ru^{III}–ORu^{IV}–ORu^{III} and brown Ru^{IV}–ORu^{III}–ORu^{IV} [575]. Whilst studying the reactions of $[Ru(NH_3)_5(N_2)]^{2+}$ supported on zeolites, Good and co-workers [576] observed that air oxidation gave supported ruthenium red. Prolonged reaction of ruthenium red with ethylenediamine in aqueous solution gives $[Ru_3O_2(en)_2(NH_3)_{10}]Cl_6$, which was shown by X-ray analysis to be $[(NH_3)_5RuORu(en)_2ORu(NH_3)_5]Cl_6$ [577] (Fig. 40). This can be oxidised to the 7+ cation, the en analogue of ruthenium brown [571].

Oxo-centred acetates $[Ru_3O(O_2CCH_3)_6L_3]^{n+}$ (L = pyridine and related ligands) are known for $n = -2, -1, 0, +1, +2, +3$ [578,579]. The 2+ cation which can be isolated as $[Ru_3O(O_2CCH_3)_6py_3](PF_6)_2$ is obtained by electrolytic oxidation of the "all Ru^{III}" monopositive cation. The 3+ cation cannot be isolated, but has been detected by cyclic voltammetry. The 2+ and 3+ cations are formally $Ru^{III}Ru^{III}Ru^{IV}$ and $Ru^{III}Ru^{IV}Ru^{IV}$ compounds but there is only a single $3d^{5/2}$ signal in the XPS spectrum of the former, and it is little shifted in energy from other members of the series. It was concluded that the metal ions were strongly coupled through the oxo-ligand.

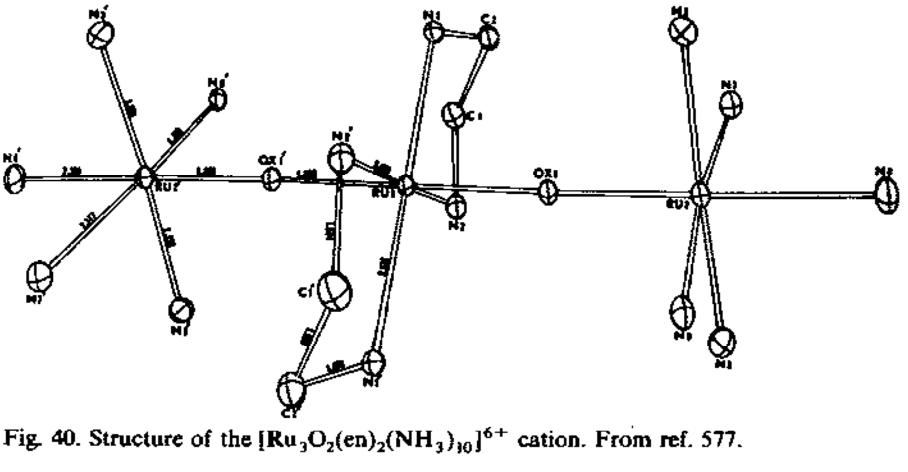

Fig. 40. Structure of the $[Ru_3O_2(en)_2(NH_3)_{10}]^{6+}$ cation. From ref. 577.

Brown and green polymeric Ru(IV) sulphates of uncertain formulae have been claimed to be formed on heating a variety of ruthenium compounds with conc. H_2SO_4 [580,581]. Suggested formulae include $[Ru_4O_6(SO_4)_6]^{10-}$ and $[Ru_3O(SO_4)_9]^{8-}$.

D. RHODIUM AND IRIDIUM

(i) M(VIII) d^1 and M(VII) d^2

There are no established examples of either oxidation state. An IrO_4 was claimed many years ago as an oxidation product of the metal [582], and more recently has been suggested as a product of the hydrolysis of $[Xe_2F_3][IrF_6]$ [583]. The former claim is erroneous and the latter lacks confirmation.

(ii) M(VI) d^3

This is a rare oxidation state for both metals represented by the hexafluorides, and possibly by some ill-defined oxo species.

There is only an unpublished claim (see ref. 132) for gaseous RhO_3, but the formation of gaseous IrO_3 on heating Ir or IrO_2 in oxygen > 1100°C has been demonstrated [584–587]. Solid IrO_3 has not been prepared [588].

Deep-blue violet solutions are formed by oxidation of Rh(III) in concentrated alkali with Cl_2, OCl^- or OBr^- [589–593], or by electrochemical oxidation of rhodium(III) perchlorate [594–596]. The oxidation appears to be very sensitive to the reaction conditions and the literature results and interpretation are contradictory, but it does seem that under carefully controlled conditions, the majority of the rhodium is present as Rh(VI) probably as the tetrahedral $[RhO_4]^{2-}$ ion. These solutions decompose on concentration, but an impure barium salt can be precipitated by addition of Ba^{2+}. This has a magnetic moment of ca. 1.4 BM consistent with one unpaired electron, which would make the $[RhO_4]^{3-}$ ion a low-spin tetrahedral complex [593,597].

The information on iridates(VI) is even less certain. There are old reports [588,589,598] of black materials of uncertain formulae produced by oxidation of iridium with KOH/KNO_3 in a melt. The presence of iridium(VI) is far from certain. Crystal data, but no preparative details have been given for a material said to be $Ca_3[IrO_6]$ [599]. Electrochemical oxidation of Ir(IV) to Ir(V) and (VI) in solution has been reported, but no materials have been isolated [600–602].

The yellow volatile IrF_6 is the normal product of fluorination of iridium powder either in a flow system or in a bomb [603,604], but black RhF_6 can only be made under carefully controlled conditions [605]. Both solids are cubic at room temperature but undergo a phase change to orthorhombic on cooling [152]. Rhodium hexafluoride is the least stable of the known MF_6, and decomposes at room temperature. It gives a red-brown vapour, but its b.p. is unknown due to the extensive decomposition which occurs on heating [605]. IrF_6 is a regular octahedron with Ir–F = 1.830(8) Å on the basis of an electron diffraction study of the vapour [153]. Electric deflection measurements are consistent with the absence of any dipole moment [604]. The vibrational spectra of both hexafluorides have been studied, and considerable effort has been devoted to the search (unsuccessful) for evidence for a Jahn–Teller effect in IrF_6 [154,155].

	$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(F_{1u})$	$\nu_4(F_{1u})$	$\nu_5(F_{2g})$	$\nu_6(F_{2u})$
RhF_6	634	595	724	283	269	192
IrF_6	701.7	645	719	276	267	206

The electronic spectrum of RhF_6 does not seem to have been measured but detailed studies on IrF_6 have been described [156,606,607]. The ^{19}F NMR spectrum of IrF_6 is a single broad line [157], and the magnetic moment is variously reported as 2.9 BM [287] or 3.3 BM [603] at room temperature. IrF_6 is less reactive and oxidising than PtF_6, but on the basis of the very limited data available RhF_6 is a very strong oxidant [158].

Surprisingly no oxide fluorides are known. The reported [608] $IrOF_4$ has not been confirmed [603], and reactions which lead to oxofluorides for osmium($OsOF_4$) such as hydrolysis of MF_6 with H_2O/HF [283] or reaction of MF_6 with B_2O_3 [164], give $[H_3O][IrF_6]$ and IrF_5 respectively with IrF_6.

(iii) M(V) d^4

The only well characterised compounds are the pentafluorides MF_5 and the anions $[MF_6]^-$. Ir(V) is formally present in the pentahydrides $[IrH_5(PR_3)_2]$.

No oxides M_2O_5 have been reported. Rhodium(V), variously formulated $[RhO]^{3+}$, $[RhO_2]^+$ or $[RhO_3]^-$, is claimed to be produced by oxidation of Rh(III) solutions with OCl^-, OBr^- or $NaBiO_3$ [590–593,609a]. Some of these "products" may be incompletely oxidised mixtures containing Rh(III) and Rh(VI), but there is spectrochemical evidence for an $[RhO_4]^{3-}$ ion, and a material which forms mixed crystals with K_3PO_4 is present in the solutions produced by OCl^- oxidation [593].

Sleight [259] has prepared $M_{0.5}[IrO_3]$ (M = Sr, Ba) by heating together IrO_2 and MO, and $Ca_2[Ir_2O_7]$ by fusing CaO, IrO_2 and $KClO_3$. There are also cubic perovskites $Ba_2M^{III}[IrO_6]$ (M^{III} = lanthanide) [609b]. The first alkali metal iridate(V) is $K[IrO_3]$ obtained as black crystals by heating KO_2 and iridium at 700°C for 7 days [610]. The presence of Ir(V) was confirmed by the Mössbauer spectrum. Its magnetic moment is 1.04 BM at room temperature and the X-ray data show the iridium is six-coordinate. The $[Ir(OH)_6]^-$ ion is formed in solution by $[S_2O_8]^{2-}$ oxidation of $[Ir(OH)_6]^{2-}$ [601].

Dark red RhF_5 is prepared by heating RhF_3 with fluorine at 6 atm/400°C [611]. Iridium pentafluoride was correctly identified in 1965 [612] having been previously thought to be the tetrafluoride [603,608]. It is a yellow solid obtained by reaction of the stoichiometric amounts of the elements, or by reduction of IrF_6 with heated glass, hydrogen at 60°C, or hydrogen or silicon in anhydrous HF [268,270,603,612]. Both have tetrameric $[MF_5]_4$ structures [611,612], and the structure of RhF_5 has been determined by a single crystal X-ray study [613] (Fig. 41) which showed that $Rh{-}F_{bridge} = 2.01(1)$ Å, $Rh{-}F_{term} = 1.808(8)$ Å, $Rh{-}\hat{F}{-}Rh = 135°$. The magnetic moments of RhF_5 = 2.39 BM [611] and of IrF_5 = 1.32 BM [612]. Limited IR [338] ^{19}F NMR [614] and electronic spectral data [338] are available. Mass spectra [264,265] show the presence of oligomers $[MF_5]_n$ (n = 1–4) in the vapour.

No other halides or oxohalides have been isolated, but there is some

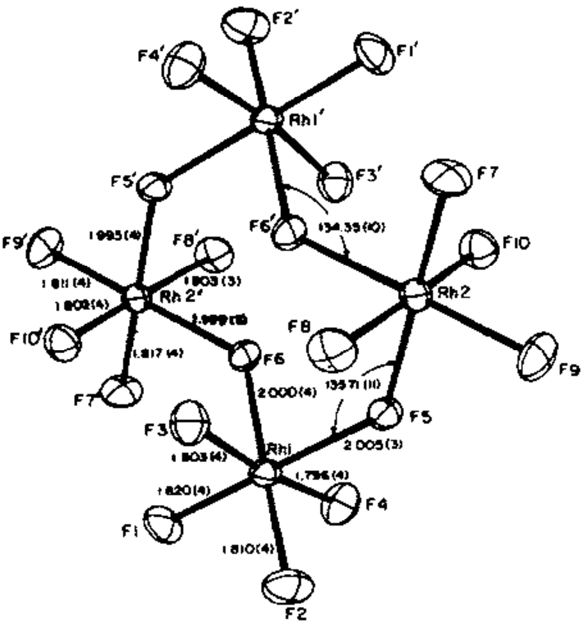

Fig. 41. Structure of the RhF_5 tetramer. From ref. 613.

evidence that IrO_2Cl is formed in the gas phase when iridium is heated in a chlorine-oxygen mixture [587].

Combination of CsF and RhF_5 in IF_5 solution produced a red-brown $Cs[RhF_6]$ [611]. Using high pressure fluorination of mixtures of MCl and $RhCl_3$ (M = Na, K, Rb, Cs) Wilhelm and Hoppe [615] prepared $M^I[RhF_6]$ as bright yellow powders which were very moisture sensitive. The structures belong to the $Li[SbF_6]$ (Na) or $Ba[GeF_6]$ (K, Rb, Cs) type.

The sodium salt appears to be the most stable. The magnetic behaviour of $Na[RhF_6]$ ($\mu_{eff} = 2.8$ BM at room temperature) deviates considerably from the Curie Law. Attempts to prepare $Li[RhF_6]$ have failed [611].

Hexafluororhodates(V) have been prepared with non-metal cations including $[O_2]^+$ [282], $[NO]^+$ [280], $[KrF]^+$, $[XeF]^+$ [616]. The deep colour and unstable nature of these salts have hindered spectroscopic studies, but some vibrational data have been obtained for $NO[RhF_6]$: $\nu_1 = 632$ cm^{-1}, $\nu_2 = 584$ cm^{-1}, $\nu_5 = 262$, 248 cm^{-1} [280].

Hexafluoroiridates(V) are usually prepared by fluorination of a mixture of MBr and $IrBr_3$ with BrF_3 [279]. In this way the thermally stable white $M^I[IrF_6]$ (M^I = Li, Na, K, Rb, Cs, Ag) and $Ba[IrF_6]_2$ have been prepared. They turn brown in moist air, and in water decompose to $[IrF_6]^{2-}$, O_2 and some $IrO_2 \cdot n\ H_2O$. The magnetic moments are: $Na[IrF_6]$, 1.23 BM; $K[IrF_6]$, 1.27 or 1.18 BM; $Cs[IrF_6]$, 1.29 BM; and the susceptibilities are essentially temperature independent [279,356,357]. The structures show the usual cation dependence, viz. Li, Na, ($Li[SbF_6]$); K, Rb, Cs, ($K[OsF_6]$); Ag, ($K[NbF_6]$) [276,278,617]. Non-metal cations which form $[IrF_6]^-$ salts are $[NO]^+$, $[NO_2]^+$, $[XeF]^+$, $[Xe_2F_3]^+$ [158,159,280,285,618]. The vibration frequencies of the anion in $[XeF][IrF_6]$ are $\nu_1 = 679$ cm^{-1}, $\nu_2 = 564$ cm^{-1}, $\nu_3 = 633$ cm^{-1}, $\nu_4 = 274$ cm^{-1}, $\nu_5 = 256$, 230 cm^{-1}, $\nu_6 = 204$ cm^{-1} [285]. The electronic spectrum of $Cs[IrF_6]$ has been recorded and assigned [290,363]. There is a single report of the $[Ir_2F_{11}]^-$ ion as the $[XeF]^+$ salt [280].

The reduction of *mer*-$[Ir(PR_3)_3Cl_3]$ or $[PR_3H][Ir(PR_3)_2Cl_4]$ with $LiAlH_4$ in tetrahydrofuran produces white, crystalline pentahydrides $[IrH_5(PR_3)_2]$ ($PR_3 = PEt_2Ph$, PEt_3, PMe_3, PPh_3, P^iPr_3) [619–623]. Several of these were originally formulated as trihydrides, and the correct formulation was established by Shaw and co-workers [619] on the basis of the ^1H NMR spectra, and their reaction with ligands (Q) to give $[IrH_3(PR_3)_2Q]$. Treatment of $[IrHCl_2(P^nPr^tBu_2)_2]$ or $[IrH_2Cl(PR_3)_2]$ ($PR_3 = P^tBu_3$, P^tBu_2Ph) with NaO^iPr under a hydrogen atmosphere gives the corresponding $[IrH_5(PR_3)_2]$ [624,625]. The low dipole moments suggest *trans* phosphines, and the ^1H and ^{31}P NMR spectra show the hydrides are all equivalent.

(iv) M(IV) d^5

The chemistry of rhodium(IV) is restricted to RhF_4, RhO_2, $[RhF_6]^{2-}$, $Cs[RhCl_6]$ and some mixed oxides. Iridium(IV) has a more extensive chemistry, simple compounds are few (IrO_2, IrF_4), but there is a reasonable (and growing) number of complexes of N, P, As and S donor ligands in addition to the well known anions $[IrX_6]^{2-}$ ($X = F, Cl, Br$).

Oxides

Hydrated forms of rhodium dioxide are produced by electrochemical or chlorine oxidation of rhodium(III) solutions followed by addition of alkali [626]. Attempts to dehydrate these at atmospheric pressure result in loss of oxygen [626]. The black anhydrous oxide can, however, be obtained by heating $Rh_2O_3 \cdot 5H_2O$ under pressure in oxygen [627,628], or by thermal decomposition of "$Rh(OH)_3$" or $Rh(NO_3)_3 \cdot 6\ H_2O$ in air at 1 atm pressure and 450°C [629]. On strong heating it loses oxygen to give α-Rh_2O_3, but is chemically inert, and is not dissolved even by aqua regia [627]. It has the rutile structure [627–629]. Black IrO_2 is readily formed by dehydration of the hydrated form $IrO_2 \cdot n\ H_2O$ ($n = 2$?) [630] or by heating the powdered metal in oxygen [584,631,633]. It can be obtained in a crystalline form by chemical transport techniques [584]. It has a rutile structure with $Ir{-}O(av) = 1.99$ Å and an $Ir \cdots Ir$ separation of 3.15 Å [297]. Physical properties measured include magnetism [301], XPS [305] and electrical properties [632]. On heating it decomposes to the metal and oxygen [584,633].

Very little is known about metal rhodates(IV). Although there are references to various ill-defined materials, the $M^I_2[RhO_3]$ ($M = Li, Na$) [634] prepared from the metal carbonate and rhodium in air, which belong to the sodium stannite structural type, and $Sr_4[RhO_6]$ [635] appear to be the only characterised examples.

Iridates(IV) are better characterised. The $M^I_2[IrO_3]$ ($M^I = Li, Na, K$) are produced by heating the metal carbonate or oxide with IrO_2 or metallic Ir, [315a,315b,634,636]. The Li and Na compounds have the Na_2SnO_3 structure, are paramagnetic ($\mu \approx 1.6$ BM), hydrolyse in water, and slowly deteriorate in air [315b,636]. A black $Li_8[IrO_6]$ [254] and a cubic $Na_4[Ir_3O_8]$ [636] have also been reported. Treatment of $K_2[IrCl_6]$ with KOH forms red crystalline $K_2[Ir(OH)_6]$ which has a structure related to brucite [639]. Water is lost from $K_2[Ir(OH)_6]$ on heating to give $K_2[IrO_3]$ [637]. The $[Ir(OH)_6]^{2-}$ ion appears to form in solution on reducing $[IrCl_6]^{2-}$ with alkaline $NaBH_4$ solution, and on heating $IrO_2 \cdot n\ H_2O$ is precipitated [640]. Alkaline earth iridates(IV) have been reported with formulae $M^{II}[IrO_3]$ ($M^{II} = Ca, Sr, Ba$), $M^{II}_2[IrO_4]$ ($M^{II} = Ca, Sr$), $Sr_4[IrO_6]$, $Sr_2[Ir_3O_8]$, $Sr_3[Ir_2O_7]$, $Sr_4[Ir_3O_{10}]$ [255, 315b,321,324,637,638,641–643]. These are made by heating together $MO +$

IrO_2, MCO_3 + Ir or IrO_2, under various conditions of temperature and pressure. Mostly the structures have been deduced from the X-ray powder patterns, although crystals of $Ca[IrO_3]$ and $Ca_2[IrO_4]$ have been grown from $CaCl_2$ and Na_2CO_3 melts [641,642]. Both contain IrO_6 octahedra. The magnetic properties have been examined, μ_{eff} ranging from ca. 1–1.6 BM at room temperature. $Sr_2[IrO_4]$ is ferromagnetic as is $Ba[IrO_3]$, but most of the others do not seem to have shown strong evidence for magnetic interactions between the metal ions. Mixed oxides are formed with the lanthanide and certain other transition metals.

Tan coloured $M[Ir(OH)_6]$ (M = Ca, Sr, Ba) have been prepared [644] and shown to decompose to $M[IrO_3]$ on heating.

Halides

A purple-red RhF_4 was reported to be formed by treatment of $RhBr_3$ with BrF_3 [645], although a bromine-free product was not obtained. This material has $\mu_{eff} = 1.1$ BM [646]. Bartlett and co-workers [647] obtained a brown solid RhF_4 by fluorination of Rh sponge at 250°C/2–3 atm, and showed it was isomorphous with IrF_4 and PtF_4. The material is paramagnetic and hydrolyses rapidly in air. In the light of Bartlett's results, the nature of the purple-red "RhF_4" is in need of clarification. Old reports (pre 1965) of "IrF_4" refer to the pentafluoride. The brown IrF_4 has been made by reaction of Ir with the calculated amount of fluorine under pressure [647], by reduction of IrF_5 with H_2/HF on platinum gauze [338], or by reducing IrF_6 on a heated iridium filament [648]. It has $\mu_{eff} = 1.69$ BM and disproportionates to IrF_3 and IrF_5 on heating [647].

There is no evidence for other rhodium or iridium tetrahalides, although by comparison with osmium and platinum, $IrCl_4$ and $IrBr_4$ might have been expected. Poorly characterised black materials produced by evaporating $[IrCl_6]^{2-}$ with HBr or by reaction of $IrO_2 \cdot 2H_2O$ with HBr, followed by treatment with Br_2 under pressure have been formulated $IrBr_{3.5}$ and $[Ir_2OBr_6]$ respectively [279,649].

Yellow hexafluororhodates(IV) $M^I_2[RhF_6]$ were prepared by fluorination of $M^I_2[RhCl_5]$ (M = K, Rb, Cs) [650] and $Na_2[RhF_6]$ from BrF_3 and 2 NaCl + $RhCl_3$ [645]. The room temperature magnetic moments are ca. 2.0 BM at room temperature. Structurally the K and Rb salts belong to the trigonal $K_2[GeF_6]$ type, whilst $Cs_2[RhF_6]$ appears to exist in both trigonal and hexagonal forms [286,450]. A very moisture sensitive and thermally unstable $Li_2[RhF_6]$ has been obtained by high pressure fluorination of a mixture of Li_2CO_3 and $RhCl_3$ [651]. Wilhelm and Hoppe [652] have prepared $M^{II}[RhF_6]$ (M^{II} = Ca, Sr, Ba, Cu, Zn, Mg, Ni, Hg) which are yellow or brown, and Mueller and Hoppe the black $Ag^{II}[RhF_6]$ [653]. The strontium and barium compounds which have the $BaSiF_6$ structure are surprisingly resistant to hydrolysis. Chlorine trifluoride has been used as a vapour phase fluorinating agent to prepare alkali and alkaline earth hexafluororhodates [654]. The reaction of a large excess of NOF with RhF_6 or $[O_2][RhF_6]$ produces $(NO)_2[RhF_6]$ [280]. The electronic spectrum of $Cs_2[RhF_6]$ has been measured by the diffuse reflectance technique [290,363].

White hexafluoroiridates(IV) are normally produced by hydrolysis of the corresponding hexafluoroiridate(V) in water, or by neutralisation of the "acid" H_2IrF_6 with the appropriate base [279,359,655]. The acid cannot be isolated, but is made in aqueous solution by passing $Na_2[IrF_6]$ solution down a column of ion-exchange resin in the acid form or by hydrolysis of $(NO)_2[IrF_6]$ [359,655]. On concentration this solution deposits the hydrated dioxide [655]. The alkali-metal salts are white (red colours mentioned in early work are due to impurities); $Na_2[IrF_6]$ belongs to the hexagonal $Na_2[SiF_6]$ type, the heavier alkali salts have the $K_2[GeF_6]$ lattice [59,656]. $K_2[IrF_6]$ is conveniently made by fusing $K_2[IrCl_6]$ with KHF_2 [360], and is also formed using an iridium(III) starting material $K_3[Ir(NO_2)_6]$ [657]. The $Ba[IrF_6]$ is almost insoluble in water, the K, Rb, Cs salts slightly soluble, and Na, $[NH_4]$, $[NMe_4]^+$ salts readily soluble. In basic solution decomposition occurs, but in neutral or acid solutions the $[IrF_6]^{2-}$ ion is stable to hydrolysis [279,359,658]. The magnetic moments are 1.42 BM (Cs) and 1.18 BM (K) [356,359] and IR (Table 5) and electronic spectral measurements have been reported [363,364]. Absorption and MCD spectra of Ir^{4+} in $Cs_2[GeF_6]$ have been studied [365]. Non-metal cations forming $[IrF_6]^{2-}$ salts include $[NO]^+$ and $[NO_2]^+$ made from IrF_6 and NO or NO_2 respectively [158,280,655].

Only one example of the hexachlororhodate(IV) ion, the green $Cs_2[RhCl_6]$ is known. This is prepared by oxidation of $Cs_3[RhCl_6]$ suspended in ice-cold water with chlorine and cerium(IV) nitrate [659–662]. The material must be isolated rapidly to prevent hydrolysis to $Cs_2[RhCl_5(H_2O)]$ and Cl_2 [661]. The product is isomorphous with $Cs_2[IrCl_6]$ [376]. The magnetic moment is 1.7 BM at room temperature, and the effect of dilution into $Cs_2[PtCl_6]$ on χ_M has been studied [661,662]. The diffuse reflectance electronic spectrum of $Cs_2[RhCl_6]$ exhibits a charge transfer band at lower energy than any other platinum metal $[MX_6]^{2-}$ ion [663]. Attempts to prepare salts with other cations have failed, and the insolubility of the Cs salt appears to be a major contributing factor in its isolation [663].

The hexachloroiridate(IV) ion is well known, and chloroiridic acid and $Na_2[IrCl_6]$ are common starting materials for the preparation of iridium(III) complexes. Chloroiridic acid, usually formulated $H_2[IrCl_6]\cdot 6H_2O$ (presumably $(H_3O)_2[IrCl_6]\cdot 4H_2O$ is the actual constitution) is a purple-black deliquescent solid sometimes described as iridium tetrachloride in older literature. It is made by treatment of $[NH_4]_2[IrCl_6]$ with chlorine or aqua regia, by dissolving the product of fusing KNO_3 with iridium in aqua regia or conc. HCl [664], or by ion-exchange from $M^I_2[IrCl_6]$ [665,666]. The corresponding "H_2IrBr_6" is obtained in solution by dissolving $IrO_2 \cdot nH_2O$ in conc. aqueous HBr, or prolonged boiling of $H_2[IrCl_6]$ with HBr [667,668].

Anhydrous sodium hexachloroiridate(IV) is made by heating a mixture of $2NaCl + Ir$ in chlorine, and on crystallisation of the product from aqueous HCl the hexahydrate $Na_2[IrCl_6] \cdot 6H_2O$ is obtained as blue-black crystals [669–671]. Since the heavier alkali-metal and ammonium salts are much less soluble than the sodium salt, they can be prepared by metathesis in dilute HCl, although direct synthesis from $2M^ICl$ and Ir ($M \neq NH_4$) is also possible [26,376,414,666,669–673,676,677]. As expected they have the $K_2[PtCl_6]$ structure [672,674]. Thermal decomposition of the alkali-metal salts produces M^ICl, chlorine and metallic iridium [672].

The blue-black $M^I_2[IrBr_6]$ (M^I = Na, K, Rb, Cs, NH_4, etc.) can be made by dissolving $IrO_2 \cdot nH_2O$ in HBr and adding M^IBr, or by prolonged treatment of $M^I_2[IrCl_6]$ with HBr or M^IBr [675–677]. $K_2[IrI_6]$ was reported in 1857 [678] and has not apparently been described since, although the vibrational spectrum of a "commercially obtained" sample was reported in 1972 [414]. Its existence must be regarded as highly doubtful. The physical and spectroscopic properties of the alkali-metal hexachloro- and hexabromo-iridates(IV) have been studied in great detail. The magnetic properties of the pure salts lie in the range 1.6–1.8 BM, although there is some disagreement about the values for individual salts. On dilution in a diamagnetic host the susceptibility increases, suggesting that a super-exchange mechanism operates in the pure salts. Variable temperature studies show that the Curie–Weiss Law is obeyed by the chlorides over a limited temperature range, but that at very low temperatures (< 5 K) the salts become antiferromagnetic [409,679–682]. The EPR spectra of $K_2[IrCl_6]$ and $K_2[IrBr_6]$ have been much studied both in attempts to estimate the extent of delocalisation of the odd electron and the degree of covalency in the Ir–X bond, and to clarify the nature of the exchange interactions [7,683,684]. Low temperature ^{193}Ir Mössbauer spectra of $K_2[IrF_6]$ and $M^I_2[IrCl_6]$ have been reported [685]. Vibrational spectral data are in Table 5. Studies of the electronic spectra of the pure salts [12,673,687] and of dilute solutions in $[SnX_6]^{2-}$, $[PtX_6]^{2-}$, $[ZrCl_6]^{2-}$ or $[HfCl_6]^{2-}$ [396,687–689] have been described and Jörgensen has reported the effect of solvents and of cation size [395,690] upon the energies of the CT bands. Assignments of the spectra have also been based upon MCD [689,691–693] and resonance-Raman [402,694] studies.

Aquo-haloiridates(IV) $[Ir(H_2O)_xCl_{6-x}]^{n-}$ ($x = 1, 2, 3$; $n = 1, 0, -1$) and mixed haloiridates(IV) $[IrCl_xBr_{6-x}]^{2-}$, $[IrF_xCl_{6-x}]^{2-}$ have been detected in solution and in some cases isolated [422,425,429,665,695–699]. The results are similar to those obtained for Os(IV) but the studies are as yet considerably less extensive.

Group VIB. There are numerous reports that rhodium(IV) species can be produced in solution by chemical or electrochemical oxidation of $Rh_2O_3 \cdot n\ H_2O$ or $[Rh(H_2O)_6]^{3+}$. Electrochemical oxidation in aqueous HNO_3, HF, H_2SO_4 or $HClO_4$ produces green solutions which seem to contain unidentified Rh(IV) ions [593–596]. Chemical oxidation (O_3, $NaBiO_3$, NaOCl, etc.) of rhodium(III) salts with weakly coordinating anions is also claimed to produce Rh(IV) under certain conditions, and some at least of these oxidants can further increase the oxidation state to either (V) or (VI) (q.v.) [591–593]. A red solution said to contain Rh(IV) perchlorate is known [700]. Iridium(IV) solution species, in the absence of coordinating halide ions are similarly ill-defined. Violet coloured solutions formed by oxidation of Ir(III) with Ce^{4+} or $[MnO_4]^-$ are said to contain $[IrO(OH)]^+$ and $[IrO]^{2+}$ has been proposed for the red-violet solution generated electrochemically [701–703]. The presence of oxo-centred trimers or other polymeric species related to $[Ir_3O(SO_4)_9]^{10-}$ (see page 67) is also likely.

Deep red very moisture sensitive $M^I_2[Ir(NO_3)_6]$ (M = K, Rb, Cs) are prepared by the reaction of N_2O_5 with $M^I_2[IrBr_6]$. The magnetic moments are $\mu_{eff} = 1.83$ BM (K), 1.88 BM (Rb) and 1.52 BM (Cs). The IR spectra, powder X-ray diffraction and EPR patterns are consistent with the presence of bidentate nitrate ligands, and the EPR spectrum of $K_2[Ir(NO_3)_6]$ in $K_2[Pt(NO_3)_6]$ has been interpreted as showing considerable $M–O_2NO$ π-bonding [704,705].

A few iridium(IV) sulphate complexes have been claimed in solution [706], but no mononuclear species seems to have been clearly identified. The claimed formate $K_2[Ir(O_2CH)Cl_5]$ [707] appears to be an Ir(III) carbonyl [708]. A red solution containing $K_2[Ir(C_2O_4)_3]$ is produced by Ce(IV) oxidation of $K_3[Ir(C_2O_4)_3]$ in water, but no solid complex could be isolated [709]. Deep-red $Cs_2[Ir(C_2O_4)Cl_4]$ is formed by oxidation of the iridium(III) analogue with chlorine water [710]. Unstable violet $K[Ir(C_2O_4)(py)Cl_3]$ is produced from $K_2[Ir(C_2O_4)(py)Cl_3]$ and chlorine, and there appear to be Rb, Cs, Ag analogues [710,711].

Paramagnetic brown or black Ir(IV) complexes $[Ir(AsPh_3)(p\text{-}MeC_6H_4CN)L_2]$ are produced in the curious reaction between $[IrH_3(AsPh_3)_2(p\text{-}MeC_6H_4CN)]$ and *o*-amino- or *o*-hydroxyphenols or *o*-amino- or *o*-hydroxyacids (L = $o\text{-}O_2C_6H_4$, $o\text{-}NHC_6H_4O$, $o\text{-}OC_6H_4CO_2$, $o\text{-}NHC_6H_4CO_2$, $O_2CCH(O)Me$, $O_2CCH(NH)CH_2Ph$) [712].

Evaporation of "$H[Ir(SEt_2)_2Cl_4]$" solution (produced from $Ag[Ir(Et_2S)_2Cl_4]$ and H_2S in water) followed by extraction with $CHCl_3$ produced the violet $[Ir(SEt_2)_2Cl_4]$ $\mu_{eff} = 1.77$ BM [713]. The MCD and electronic spectra of *trans*-$[Ir(SEt_2)_2Cl_4]$ have been recorded and the assignments, discussed in detail [714], provide a rare example of a lower symmetry case (D_{4h}) treatment of CT band assignments. Neutral thioether complexes of Ir(III) do not oxidise, but the anions $[NMe_4][IrLCl_4]$ (L = $RS(CH_2)_nSR$, RSCH= CHSR, o-$C_6H_4(SR)_2$, in which n = 1, 2; R = Me, Ph) are oxidised by chlorine in CCl_4 suspension to dark red-brown or purple *cis* $[IrLCl_4]$ [469]. *Cis*- and *trans*-$[Ir(SMe_2)_2Cl_4]$ were similarly obtained from the corresponding anions, but although $[Ir(SPh_2)_2Cl_4]^-$ and $[Ir(SPh_2)Cl_5]^{2-}$ oxidise in solution, the products decompose on attempted isolation [469]. The complexes have $\mu_{eff} = 1.69-1.78$ BM, and are stable in the solid state, but decompose rapidly in solution. Attempts to prepare $[IrLBr_4]$ were unsuccessful, and there was no evidence that chemical or electrochemical oxidation of $[Rh(MeSCH_2CH_2SMe)Cl_4]^-$ to Rh(IV) is possible [469]. A thiobenzamide complex $[Ir(S(NH_2)CPh)_2Cl_4]$ is claimed to be the product of the reaction of "$IrCl_4$" and the ligand in water [715].

The Rh(IV) dithiocarbamate complexes "$[Rh(R_2dtc)_3BF_4]$" produced by BF_3 oxidation of $[Rh(R_2dtc)_3]$ [472] are now known to be dimeric Rh(III) compounds $[Rh_2(dtc)_5]BF_4$ [716]. Cyclic voltammetry also shows that $[Rh(Me_2dtc)_3]$ is irreversibly oxidised in acetone/0.1 M Et_4NClO_4 at a potential of 1.24 V vs. Ag/AgCl [716]. No iridium(IV) dithiocarbamates are known, although they should be obtainable.

Group VB. The very old reports of $[Ir(NH_3)_4Cl_2]Cl_2$, $[Ir(NH_3)_4Cl_2]SO_4$ and $[Ir(NH_3)_2py_2Cl_2]Cl_2$ have not been confirmed [717,718]. A violet-black $[Ir(en)Cl_4]$, $\mu_{eff} = 1.65$ BM, was obtained by oxidation of $K[Ir(en)Cl_4]$ in conc. HCl with chlorine. It is reduced to Ir(III) by water [719]. Iridium(IV) complexes of heterocyclic N-donors are the best known examples with neutral ligands. Oxidation of *cis*- or *trans*-$[Ir(py)_2Cl_4]^-$ with aqua regia gives the violet $[Ir(py)_2Cl_4]$ [720,721]. The *cis* isomer is the stronger oxidant converting Br^- to Br_2 and being reduced by alcohol; neither reaction occurs with the *trans* isomer. Aqueous ammonia reduces both isomers to $[NH_4][Ir(py)_2Cl_4]$. The MCD and electronic spectrum of the *trans* isomer has been recorded [714], and ^{193}Ir Mössbauer spectra of both forms have been observed [722]. Brown *trans*-$[Ir(py)_2Br_4]$ is made by HNO_3 oxidation of $[NH_4]$*trans*$[Ir(py)_2Br_4]$ [723]. *Cis*- and *trans*-[Ir(β-picoline)$_2$Cl$_4$] are also known [724]. Very dark red pentachloro(pyridine)iridates(IV) $M^I[Ir(py)Cl_5]$ (M = Na, K, Rb, Cs, NH_4) are produced by chlorine oxidation of $M^I_2[Ir(py)Cl_5]$, and the heavier alkali-metal salts and some heavy-metal salts can be produced by precipitation from the $Na[Ir(py)Cl_5]$ and M^ICl [725]. M[Ir(β-picoline)Cl$_5$] [726] and the binuclear $K_2[(pyrazine)(IrCl_5)_2]$ [727] have been obtained by HNO_3 oxidation of the iridium(III) analogues. A purple-black $[Ir(phen)Cl_4]$ ($\mu_{eff} = 2.06$ BM) is formed by chlorine oxidation of aqueous $H_3O[Ir(phen)Cl_4]$ or nitric acid oxidation of $[phenH][Ir(phen)Cl_4]$ in the presence of sulphamic acid [667].

Biguanide complexes have been reported for both rhodium(IV) and iridium(IV), and the former appear to be the best characterised examples of Rh(IV) complexes of neutral ligands. The iridium complexes of N^1-parachlorophenyl-N^5-isopropylbiguanide (L^B) are the red-brown $[Ir(L^B)_3]Cl_4 \cdot 3H_2O$ ($\mu_{eff} = 1.68$ BM) and $[Ir(L^B)_2Cl_2]Cl_2 \cdot 4H_2O$ ($\mu_{eff} = 1.56$ BM) produced by oxidation of a mixture of $IrCl_3 \cdot 3H_2O$ and L^B with $NaClO_2$ in ethanol [728]. The violet $[Ir(L^B)_2L_2]Cl_4$ ($L = NH_3$, py) are produced similarly in the presence of L. The rhodium(IV) analogues are prepared in a similar manner: (μ_{eff} (BM) in parentheses) $[Rh(L^B)_3]Cl_4$ (1.68); $[Rh(L^B)_2(NH_3)_2]Cl_4$ (1.65); $[Rh(L^B)_2py_2]Cl_4$ (1.82); $[Rh(L^B)_2Cl_2]Cl_2$ (1.79); and $[Rh(L^B)_2(NO_2)_2](NO_2)_2$ (1.80). The $[Rh(L^P)_2Cl_2]Cl_2$ type have been made with N^1-phenyl or N^1-*o*-tolyl-N^5-isopropylbiguanide (L^P) [729,730].

Cyclic voltammetry shows that [RhR(salen)py] ($R = {}^nPr$, ${}^iPr$; salenH_2 = bis(salicylaldehydeethylenediimine) undergo reversible $1e^-$ oxidations to Rh(IV) cations at fast scans in CH_3CN [731].

Halogen oxidation of $[RhL_4]^+$ and $[IrL_4]^+$ ($L = PPh_2OMe$, $PMePh_2$) in CH_2Cl_2 or Me_2CO produced materials of stoichiometry RhL_2X_4 (X = Br, I) and IrL_2I_4. However, an X-ray study of "$Ir(PPh_2Me)_2I_4$" showed it to be the halide-bridged dimer $[Ir_2(PMePh_2)_4I_5]^+I_3^-$ [732], and presumably the rhodium compounds are similar. Chlorine oxidation of $[Ir(EPh_3)_3Cl]$ (E = P, As) in benzene produces the deep purple iridium(IV) complexes $[Ir(EPh_3)_3Cl_4]$, [733,734]. Similar treatment of $[Ir(SbPh_3)_3Cl]$ gave an impure purple stibine complex [733]. Chlorine oxidation of $[IrH_2(PPh_3)_3Cl]$ or $[Ir(N_2)(PPh_3)_2Cl]$ [521,734], also produces $[Ir(PPh_3)_2Cl_4]$. The IR spectrum shows $[Ir(PPh_3)_2Cl_4]$ to be the *trans* isomer [533,735], and this is confirmed by the EPR spectrum [533]. The magnetic moment is said to be 1.9 BM [521], but a variable temperature study showed the moment to be temperature independent with $\mu_{eff} = 1.52$ BM [735]. A more general method for preparing *trans*-$[Ir(ER_3)_2Cl_4]$ is chlorine oxidation of the iridium(III) anions $[ER_3H][Ir(ER_3)_2Cl_4]$ ($ER_3 = PMe_3$, PEt_3, P^nPr_3, PMe_2Ph, PEt_2Ph, As^nPr_3) [19,529,533,714,733]. Various spectroscopic properties have been recorded including IR [533,736], electronic [13,714,735], ^1H NMR [533], EPR [533,737] and XPS [19]. A single crystal X-ray structure determination of $[Ir(PMe_2Ph)_2Cl_4]$ confirmed the *trans* structure with Ir–Cl = 2.324(5) Å, Ir–P = 2.392(5) Å [532]. The redox properties of $[Ir(PMe_2Ph)_2Cl_4]$ towards organometallic compounds have been described [738].

The attempted electrochemical or chemical oxidation of $[M(L\text{–}L)_2Cl_2]^+$ (L–L = *o*-$C_6H_4(PMe_2)_2$, *o*-$C_6H_4(AsMe_2)_2$; M = Rh, Ir) gave no indication of M(IV) species [519].

Polynuclear complexes. These are restricted to iridium, the best established types being the oxo- and nitrido-centred trimers. The reaction of $IrBr_3$ with

N_2O_5 produces the purple very deliquescent $[Ir_3O(NO_3)_9]NO_3$ [739]. The magnetic moment is 1.24 BM and the IR spectrum is consistent with the presence of both bidentate and monodentate nitrate groups. A structure based upon an Ir_3O unit with six-bidentate NO_3 bridges and three terminal monodentate NO_3 is likely. It is hydrolysed by water and insoluble in non-coordinating organic solvents, but gives blue or green solutions in donor solvents or HNO_3 or H_2SO_4 [739]. In contrast to the nitrate which is formally Ir^{IV}, there are oxo-centred acetates which formally contain $Ir^{III}Ir^{III}Ir^{IV}$ [740]. Blue $[Ir_3O(O_2CCH_3)_6(H_2O)_2HO_2CCH_3](O_2CCH_3)_2$ is produced by ozonisation of the green $[Ir_3O(O_2CCH_3)_6(H_2O)_3]^+$ in acetic acid. Reaction of the blue complex with PPh_3 in methanol in the cold gives $[Ir_3O(O_2CCH_3)_6(PPh_3)_3]^{2+}$, whilst in boiling alcohol $[Ir_3O(O_2CCH_3)_6L_3]^+$ (all Ir^{III}) are formed with pyridine bases, and these can be electrochemically oxidised to the dipositive cation $[Ir^{III}, Ir^{III}, Ir^{IV}]$. The magnetic moment of the blue aquo complex is 0.96 BM [740].

The best known oxo-trimer is the blue-green "Lecoq de Boisbaudran's" salt, prepared by boiling $K_2[IrCl_6]$ with conc. H_2SO_4 [741,742]. It is formulated $K_{10}[Ir_3O(SO_4)_9] \cdot 3H_2O$ and is believed to have the structure shown in Fig. 42. A green complex of identical formula, but with a different X-ray powder pattern can be made by a modified route [742]. The differences are not understood. The magnetic moment is 1.87 BM [742], and the IR vibrations of the Ir_3O unit have been identified at 615, 233 cm^{-1} [573]; the ^{193}Ir Mössbauer spectrum is consistent with two "types" of iridium and hence supports an $Ir^{III}Ir^{III}Ir^{IV}$ rather than a delocalised $Ir(3\frac{1}{3})$ formulation [742]. The blue-green salt can be shown by cyclic voltammetry to undergo reversible one-electron reduction (to $Ir^{III}Ir^{III}Ir^{III}$) and two one-electron oxidations to $Ir^{III}Ir^{IV}Ir^{IV}$ and $Ir^{IV}Ir^{IV}Ir^{IV}$ forms, and the electronic spectra of these has been recorded [742]. The $[Ir_3O(SO_4)_9]^{9-}$ ion ($Ir^{III}Ir^{IV}Ir^{IV}$) has

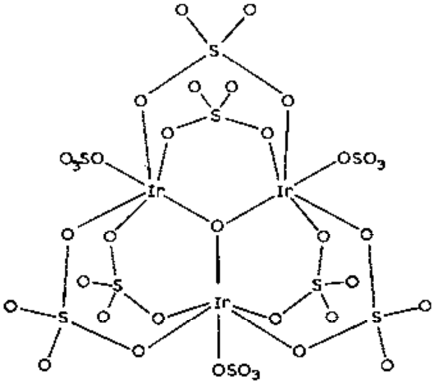

Fig. 42. Proposed structure of the $[Ir_3O(SO_4)_9]^{10-}$ anion.

been isolated as $K_6[Co(NH_3)_6]_7[Ir_3O(SO_4)_9]_3$ and $[Co(NH_3)_6]_3[Ir_3O(SO_4)_9]$ salts [742,743]. Other less certainly identified products are $K_9H[Ir_3(OH)_2(SO_4)_9] \cdot 2H_2O$, a green solid formed from $K_2[IrCl_6]$ and conc. H_2SO_4 [744]; $K_7(H_3O)[Ir_3O(SO_4)_{8.5}] \cdot H_2O$ made from $IrCl_3 \cdot 3H_2O$, M_2SO_4 and K_2SO_4 which is suggested to be dimeric with a sulphato-bridged anion. It is $Ir^{III}Ir^{IV}Ir^{IV}$ as formulated [743]. The nature of the blue completely oxidised forms, i.e. $Ir^{IV}Ir^{IV}Ir^{IV}$, are less clear. Cerium(IV) oxidation of $K_9H[Ir_3(OH)_2(SO_4)_9]$ in H_2SO_4 produces a blue powder formulated [744] as $K_7H_3[Ir_3O_2(SO_4)_9] \cdot 2H_2O$, but other workers [742] found that the chemically and electrochemically (above) oxidised forms had different properties, and doubted if the former was a genuine trinuclear form. The preparation of related complexes in which the terminal $[SO_4]^{2-}$ groups are replaced by water or amines has been reported more recently and materials such as $Cs_4[Ir_3O(SO_4)_6(H_2O)_3]$ and $[RNH_3]_4[Ir_3O(SO_4)_6(RNH_2)_3]$ have been identified [745–747]. Although there seems little doubt that most of these sulphato-complexes contain an "$Ir_3O(SO_4)_6$" group, an X-ray structure of one or more examples would be valuable.

Attempts to prepare selenate analogues failed [742]. Ill-defined blue or blue-green phosphate complexes prepared by evaporation of $H_2[IrCl_6]$ with H_3PO_4 in the presence of various cations [706,748] may well be oxo-centred species. A blue iodate of unknown (presumably polymeric) structure is formed on treating the red "Ir^{IV} perchlorate" solution with $NaIO_3$ [749]. The solid precipitated is analytically "$IrIO_8H_7$" and this can be dehydrated to "$IrIO_6H_3$".

Reaction of $(NH_4)_3[IrCl_6]$ with conc. H_2SO_4, followed by addition of K_2SO_4 gives the green "Delépines Salt". This was originally formulated as an Ir^{III} material, but careful analytical work revealed it to be a nitrido-centred

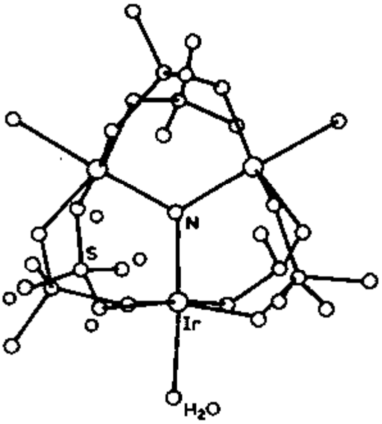

Fig. 43. Structure of the $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ anion. From ref. 752.

trimer $K_4[Ir_3N(SO_4)_6(H_2O)_3]$, formally an $Ir^{III}Ir^{IV}Ir^{IV}$ material [741,742,750,751]. The corresponding NH_4^+ and Cs^+ salts are known [550,750]. The structure of the ammonium salt has been determined [752], and shown to contain an Ir_3N unit with bridging bidentate sulphate groups, and the water coordinated *trans* to N (Ir–N = 1.918(2) Å, Ir–O = 2.005–2.056 Å, Ir–OH_2 = 2.059 Å) (Fig. 43). The IR [550] and ^{193}Ir Mössbauer spectrum [742] have been reported, and the latter suggests discrete $Ir^{III}Ir^{IV}Ir^{IV}$ ions are present. Electrochemical oxidation to the $Ir^{IV}Ir^{IV}Ir^{IV}$ form is possible [742], but only one reduction wave was seen, although the yellow $Ir^{III}Ir^{III}Ir^{III}$ form can be produced by V^{II} reduction [753]. Delépine [754,755] has prepared the $[Ir_3N(SO_4)_6L_3]^{4-}$ ions (L = py, NH_3, β-picoline).

The $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ ion is converted to red-brown $K_7[Ir_3N(SO_4)_6(OH)_3]$ by cold aqueous KOH [550,750], whilst on boiling a precipitate of approximate composition $[Ir_3N(OH)_{11}] \cdot nH_2O$ forms [180]. This precipitate dissolves in dilute HCl and on addition of M^ICl [M^I = K, Cs) dark brown $M_4[Ir_3NCl_{12}(H_2O)_3]$ are produced [550,750]. It has been claimed [756] that reaction of $(NH_4)_3[IrCl_6]$ with sodium benzeneselenates ($Na[O_2SeR]$ R = *m*, *p*-ClC_6H_4, *m*-BrC_6H_4, etc.) gives olive-green paramagnetic $[Ir(O_2SeR)_3]$ complexes. The paramagnetism (μ_{eff} = 0.72–1.6 BM) is inconsistent with t_{2g}^6 Ir(III), and these may well be nitrido-centred mixed valence complexes.

E. PALLADIUM AND PLATINUM

(i) M(VI) d^4 and M(V) d^5

The only certainly established compound of platinum(VI) is the hexafluoride PtF_6. Platinum(V) is present in the hexafluoroplatinate(V) ion and in PtF_5. Palladium is the only platinum metal which does not form either a hexafluoride or pentafluoride, and the only palladium compounds known in an oxidation state greater than (IV) are the recently reported $[PdF_6]^-$ salts.

The existence of a gaseous PtO_3 has been suggested [757] and there is mass spectral evidence for $[PtO_3]^+$ [758], but the evidence is much less complete than for other gaseous platinum metal oxides. Electrochemical oxidation of hydrated platinum(IV) oxide in 2 M KOH solution is said [759] to produce a grey-green material of composition $K_2O \cdot 3PtO_3$, which on washing with dilute acetic acid is converted into an orange-red PtO_3. This material is apparently always oxygen deficient, and loses oxygen rapidly on standing. It is reduced by HCl with liberation of Cl_2, but does not react with H_2O_2 or ROH [759]. Materials of a similar composition have been reported to form on platinum black electrodes under highly oxidising conditions [760–762].

There does not seem to be any recent chemical study of this material and its nature is unclear.

Dark red PtF_6 is formed by igniting a platinum wire electrically in fluorine, and rapidly cooling the vapour in liquid nitrogen. Vacuum sublimation produces the pure material m.p. 61.3°C, b.p. 69.14°C [763,764]. It has recently been reported [765] that good yields of PtF_6 can be obtained by heating platinum with a large excess of fluorine under pressure at 200°C. Solid PtF_6 is cubic at room temperature and orthorhombic below 3°C [152,764]. Electric deflection measurements show there is no permanent dipole moment [604]. The magnetic susceptibility is essentially temperature independent with $\mu_{eff} = 1.4$ BM at 300 K [766]. The vibrational spectrum has been studied several times and the best values are $\nu_1 = 656$ cm^{-1}, $\nu_2 = 601$ cm^{-1}, $\nu_3 = 705$ cm^{-1}, $\nu_4 = 273$ cm^{-1}, $\nu_5 = 242$ cm^{-1}, $\nu_6 = 211$ cm^{-1} [155,767]. The electronic [156], and ^{19}F NMR spectra [157] have been reported. Platinum hexafluoride is the most strongly oxidising of the 5*d* hexafluorides [158], attacking dry glass and quartz. It is violently decomposed by water to $[PtF_6]^{2-}$ and O_2 [764], and decomposes to PtF_5, PtF_4 and F_2 on heating. Its oxidising behaviour towards non-metal halides and oxides has been much investigated since Bartlett's now classic experiments with O_2 and Xe [158,768,769]. The products are usually hexafluoroplatinate(V) salts.

$$NO + PtF_6 \rightarrow [NO]^+[PtF_6]^-$$

$$ClOF_3 + PtF_6 \rightarrow [ClOF_2]^+[PtF_6]^- + \tfrac{1}{2}F_2$$

$$ClF_3 + PtF_6 \rightarrow [ClF_2]^+[PtF_6]^- + \tfrac{1}{2}F_2$$

There are no known oxofluorides of Pt(VI), the "$PtOF_4$" reported in 1960 [770] is in fact $[O_2][PtF_6]$ [768], and the ease with which the latter compound is formed from F_2/O_2 mixtures and platinum, or even by fluorination of platinum in glass apparatus would seem to rule out "direct" synthesis. Attempts to convert PtF_6 to an oxofluoride with H_2O/HF (which gives $[H_3O]^+[PtF_6]^-$) or B_2O_3 ($PtF_5 + O_2$) have failed [164,283].

Red PtF_5 is formed by fluorination of $PtCl_2$ at 350°C [770]. It melts at 80°C to a viscous liquid but on further heating decomposes to PtF_6 and PtF_4. The structure is unknown, but presumably consists of tetramers like RhF_5 (see p. 58). The magnetic moment is 2.05 BM [771]. The mass spectrum is difficult to obtain due to the disproportionation, but contains monomer, dimer and trimer species supporting the suggested polymeric structure of the solid [264,265]. Fluorination of PtO_2 at 200°C gave a brown solid which analysed as $PtOF_3$ [770]. It is involatile and hydrolyses in moist air. Fluorination of a mixture of platinum and powdered glass also gives $PtOF_3$ and a black material PtO_xF_{3-x} [770]. Nothing more seems to be known about either material, and re-examination is desirable, especially since they are the only platinum metal oxide fluorides outside the Ru, Os group.

The hexafluoropalladate(V) ion $[PdF_6]^-$ has been reported in two salts $[O_2][PdF_6]$ and $Na[PdF_6]$ [616,772], formed by oxidation of PdF_4 in HF with KrF_2 in the presence of O_2 and NaF respectively. The dioxygenyl salt is also produced by reaction of powdered palladium with a F_2/O_2 mixture at 320°C and at 60,000 psi [772]. The product is a gold-brown powder which evolves $O_2 + F_2$ on gentle heating. The Raman spectrum of the $[PdF_6]^-$ ion is comparable with those of other $[MF_6]^-$ ions, $\nu_1 = 643$ cm^{-1}, $\nu_2 = 570$ cm^{-1}, $\nu_5 = 268$ cm^{-1}.

A considerable number of non-metal hexafluoroplatinates(V) are known, but only very few data on alkali-metal salts have been published. Direct fluorination of a mixture of KCl and $PtCl_2$ gives impure $K[PtF_6]$ [773], and pure materials $M^I[PtF_6]$ (M = K, Rb, Cs) are best obtained from $[O_2][PtF_6]$ and MF in IF_5 solution [770,774]. The orange-yellow solids are rhombohedral ($K[OsF_6]$ structure), and react with water to give $[PtF_6]^{2-}$, some $PtO_2 \cdot n\ H_2O$ and ozonised oxygen [770]. The magnetic moment of $KPtF_6$ is 0.87 BM compatible with a $t_{2g}^5 eg_g^0$ configuration [770]. The most studied salt is $[O_2]^+[PtF_6]^-$ [282,618,768,770] a volatile red paramagnetic solid ($\mu = 2.57$ BM). The X-ray and neutron diffraction studies [775] show Pt–F = 1.82(3) Å. The known [non-metal]$^+$-$[PtF_6]^-$ compounds include those with the following cations $[XeF]^+$, $[Xe_2F_3]^+$, $[XeF_5]^+$ [285,768,776,777], $[KrF]^+$ [616,778], $[NO]^+$, $[NO_2]^+$ [280,618,779], $[ClF_2]^+$, $[ClF_6]^+$ [780,781] and $[ClOF_2]^+$, $[ClO_2F_2]^+$ [782,783], $[H_3O]^+$ [283]. Varying degrees of interaction between cation and anion are present in these compounds which is evident in the extent of splitting of the vibrational fundamentals of the anion. The best data is probably that for the $[NO]^+$ salt: $\nu_1 = 647$ cm^{-1}, $\nu_2 = 590$, 572 cm^{-1}, $\nu_3 = 630$ cm^{-1}, $\nu_5 = 249$, 236 cm^{-1} [280,285]. The interaction is also evident from the X-ray of $[XeF_5]^+[PtF_6]^-$ [776] (Fig. 44). The electronic

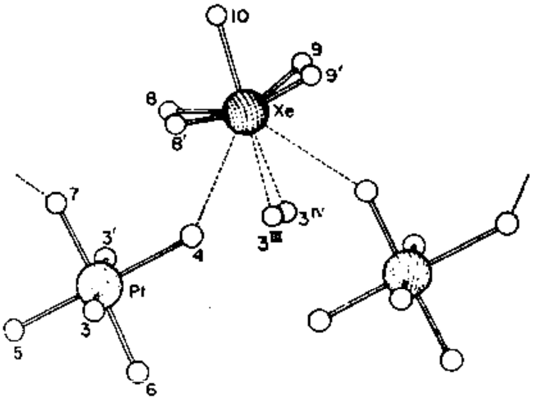

Fig. 44. The structure of $[XeF_5]^+[PtF_6]^-$. From ref. 776.

spectrum of the $[PtF_6]^-$ ion has been little studied [11], and is in need of detailed re-examination. It appears that the $[Pt_2F_{11}]^-$ ion can be formed with $[XeF]^+$ [285] and $[KrF]^+$ [616] cations.

There are no complexes of Pt(V) with neutral ligands, and cyclic voltammetry showed no evidence of oxidation of $[PtLCl_5]^-$ (L = e.g. P^nPr_3) in MeCN or CH_2Cl_2 solution [784].

(ii) M(IV) d^6

The chemistry of palladium(IV) is limited; the best characterised examples are PdF_4 and $[PdX_6]^{2-}$ (X = F, Cl, Br). Complexes with neutral ligands can be prepared but most decompose very easily. Platinum(IV) in contrast is a major oxidation state of the element, and a great many complexes are known. Simple compounds include PtO_2, all four halides PtX_4 and the anions $[PtX_6]^{2-}$ (X = F, Cl, Br, I).

Oxides and oxoanions

Precipitation of $K_2[PdCl_6]$ solution with alkali produces a dark red solid formulated as $PdO_2 \cdot nH_2O$ (n is variously given as 1 or 2), which slowly loses oxygen at room temperature and rapidly on heating, and thus cannot be dehydrated without loss of O_2 [785,786]. It is very easily reduced by H_2, H_2O_2 or organic material, and dissolves in mineral acids to give Pd(II) compounds, but it is slightly soluble in concentrated alkali to give hydroxopalladates(IV), e.g. $Na_2[Pd(OH)_6]$ [787,788]. Black anhydrous PdO_2 is formed by heating PdO with $KClO_3$ at 950°C under pressure (65 kbar), followed by washing with water. It has the expected rutile structure, and is insoluble in acids or alkalis. Oxygen is lost very easily on gently warming to give a PdO_{2-x} phase, and on heating more strongly PdO is produced [789].

Platinum dioxide is known as a gas phase species [758,790], in two solid forms α and β-PtO_2, and as various hydrates. The α-PtO_2 is obtained by heating various platinum compounds (PtI_2, $PtO_2 \cdot nH_2O$, Pt-black, etc.) under pressure in oxygen, or by fusing $H_2[PtCl_6]$ with $NaNO_3$ [627,628,791,792]. It appears that hydrated forms cannot be converted to PtO_2 under 1 atm without some concomitant oxygen loss [793]. This form is an active hydrogenation catalyst for many organic materials, known as "Adams catalyst" [792]. The structure of α-PtO_2 is disputed although it is generally agreed that the lattice is hexagonal; much of the trouble is a result of the poorly crystalline nature of many preparations [627,791]. At higher oxygen pressures β-PtO_2 is produced, a black chemically inert material with a distorted rutile structure [627,628,794]. The distortion is slight Pt–O = 2.02 Å ($2x$) and 1.98 Å ($4x$) [794]. The cream $PtO_2 \cdot 4H_2O$ is better formulated $H_2[Pt(OH)_6]$ (see below), and there are reports of 3, 2, 1 hydrates [793,795].

An oxide Pt_3O_4 and phases $M^I_x[Pt_3O_4]$ (M^I usually Na; $1 > x > 0$) are known, and much confusion has arisen over the distinction of these forms, and the alkali content [628,634,636,796]. It appears that alkali free material can be prepared from PtI_2/O_2, and the alkali containing material from Pt and M_2CO_3. Palladium forms related $M^I_x[Pd_3O_4]$ but alkali free forms are not known [627,634,797,798].

Red-brown $Na_2[PdO_3]$ [799] and $A^{III}_2[Pd_2O_7]$ (A^{III} = rare earth) [800] are the best established palladates(IV). Attempts to prepare $M^I_2[PdO_3]$ (M^I = K, Rb) gave black paramagnetic materials of the approximately correct composition, the paramagnetism being tentatively ascribed to the presence of some Pd(II) [799,801]. Sodium platinates(IV) include α-$Na_2[PtO_3]$ (yellow, $Na_2CO_3 + Pt$ in O_2) [315a,634,636,802], β-$Na_2[PtO_3]$ ($Na_2O_2 + Pt$ under argon) [802], and the metastable $Na_4[Pt_3O_8]$ [636]. Again materials of composition approximating to "K_2PtO_3" and "Rb_2PtO_3" can be prepared but have not been obtained in the pure state [802]. The alkaline earth compounds are $Sr_4[PtO_6]$, $Sr_3[Pt_2O_7]$ [321,635], $Ba[PtO_3]$ and $Ba_3[Pt_2O_7]$ [803,804], obtained by heating together appropriate amounts of the alkaline earth oxide or carbonate with PtO_2.

Hexahydroxoplatinatic acid $H_2[Pt(OH)_6]$ is the correct formula for the yellow material often described as $PtO_2 \cdot 4H_2O$. It is prepared from $Na_2[PtCl_6]$ and NaOH in aqueous solution, followed by treatment with acetic acid [795,805]. It dissolves in acids to give Pt(IV) salts and in aqueous alkali forms $M^I_2[Pt(OH)_6]$. On heating it loses water to give orange "$PtO_2 \cdot 3H_2O$". X-ray studies [806,807] show that $H_2[Pt(OH)_6]$ contains $[Pt(OH)_6]^{2-}$ octahedra Pt–O = 2.08 Å, linked by hydrogen bonds. Alkali hexahydroxoplatinates(IV) are made by reaction of $H_2[PtCl_6]$ with M^IOH (M^I = Li, Na, K) or by dissolving $H_2[Pt(OH)_6]$ in aqueous alkali [795,805,808–810]. Metathesis between $Na_2[Pt(OH)_6]$ and $M^{II}Cl_2$ produces the corresponding $M^{II}[Pt(OH)_6]$ (M = Ca, Sr, Ba, Mg, Ni, Co, Fe, Mn, Cd) [644,811,812]. The presence of $[Pt(OH)_6]^{2-}$ ions has been confirmed by X-ray studies on $Li_2[Pt(OH)_6]$, $Ca[Pt(OH)_6]$, $Ba[Pt(OH)_6] \cdot H_2O$ and $Na_2[Pt(OD)_6]$ [813–815]. On heating all these salts lose water to give platinates(IV), $M^I_2[PtO_3]$ or $M^{II}[PtO_3]$ respectively.

Halides

The only simple halide of Pd(IV) is the brick-red PdF_4 formed by fluorination of PdF_3 preferably under pressure (ca. 7 atm) [647,816]. Prepared in this way the material often contains some PdF_3, and fluorination of $PdSnF_6$ or $PdGeF_6$ gives a purer product [647,777]. PdF_4 is diamagnetic, isostructural with RhF_4, IrF_4 and PtF_4, and X-ray and neutron diffraction measurements on the powder are consistent with PdF_6 octahedra composed of two terminal (1.94 Å) and four bridging fluorines (1.91, 2.05 Å) [647,817].

It is easily reduced to PdF_3 and is violently hydrolysed by water. The yellow-brown PtF_4 can be prepared from $PtBr_2$ or $PtCl_4$ and BrF_3 [645,770], or by thermal decomposition of PtF_6 [765]. The compound is diamagnetic and only slowly decomposed by water.

The other platinum(IV) halides have been known for many years, but their structures have been established only recently. Platinum(IV) chloride is a red-brown, very hygroscopic solid prepared by heating $H_2[PtCl_6] \cdot 6H_2O$ in chlorine at 250°C [818,819], from Pt and SO_2Cl_2 in a sealed tube [347], or less conveniently by chlorination of Pt or $PtCl_2$ [820]. The dark red $PtBr_4$ is best made by thermal decomposition of $H_2[PtBr_6]$ in a stream of bromine [821]; the direct preparation from $Pt + Br_2$ is also possible, but the product is often contaminated with lower bromides. Platinum(IV) iodide is polymorphic, the form obtained depending upon the reaction conditions, which coupled with the ease with which iodine deficient samples are produced makes older descriptions of its properties suspect. The α-PtI_4 is made from platinum sponge, KI, I_2 and water in a sealed ampoule at 140°C/6 days [822] or from α-PtI_2 and I_2. The γ-PtI_4 is produced from H_2PtCl_6 and NaI in water (4 days), whilst the unstable β-form is produced from $H_2[PtCl_6]$ and HI using short reaction times [822]. The structures of $PtCl_4$, $PtBr_4$ and α-PtI_4 are orthorhombic, based upon 6-coordinate platinum with two terminal and four bridging halides [822–825] in the $\overset{1}{\infty}[PtX_2PtX_{4/2}]$ chains as shown in Fig. 45. An alternative description is hexagonal close packed halide ions with 1/4 of the octahedral holes filled by Pt, such that the chains run parallel to [001]. In γ-PtI_4 the iodide ions are cubic close packed, giving two orientations of the chains [822]. The structure of the unstable β-PtI_4 is less clear, but may be based upon a $[PtI_{6/2}]I$ unit [822]. Thermal decomposition

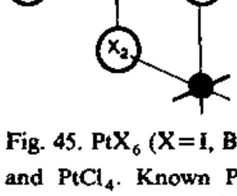

Fig. 45. PtX_6 (X = I, Br, Cl) octahedra in the $\overset{1}{\infty}[PtX_2X_{4/2}]$ chains of α-PtI_4, γ-PtI_4, $PtBr_4$ and $PtCl_4$. Known Pt–X distances (pm) in the order X_1, X_2, X_3, X_4, $X_{1'}$, $X_{2'}$, are: α-PtI_4 = 263, 270, 262, 266, 272, 278; γ-PtI_4 = 265, 265, 265, 265, 272, 272; $PtBr_4$ = 246, 244, 241, 244, 250, 254. From ref. 822.

of $PtCl_4$ or $PtBr_4$ gives the platinum(II) halides, but PtI_4 gives PtI_3 in an open system and a Pt_3I_8 phase in a closed ampoule [822]. Hydrolysis of $K_2[PtI_6]$ gives $PtI_4 \cdot 2H_2O$ which has an octahedral structure Pt–I = 2.651 Å, Pt–O = 2.1 Å [826]. There have been reports from time to time of mixed halides, usually of the PtX_2Y_2 type ($X \neq Y$ = halide) prepared from $PtX_2 + Y_2$, and said to exist in isomeric forms (e.g. [827,828]), but the evidence is generally unconvincing. Seven of the eight possible $[MX_6]^{2-}$ ions as well as a number of mixed halides $[PtX_{6-x}Y_x]^{2-}$ are known. There is no evidence for $[PdI_6]^{2-}$ *. The literature, particularly on $[PtCl_6]^{2-}$, is extensive and only the essentials are outlined here.

The yellow hexafluoropalladates(IV) are prepared by fluorination (F_2, ClF_3 or BrF_3) of $M_2[PdCl_4]$, $M_2[PdCl_6]$ (M = alkali-metal) or of $M^{II}CO_3 + [NH_4]_2[PdCl_4]$ mixture (M^{II} = Hg, Ca, Zn, Cd, etc.) [645,654,829–833]. The Pd(II) salt, $Pd^{II}[Pd^{IV}F_6]$ is the "PdF_3" of Ruff, readily obtained from $PdBr_2$ and BrF_3, $\mu_{eff} = 2.08$ BM, Pd^{II}–F = 2.17 Å, Pd^{IV}–F = 1.90 Å [645,816,834,835]. The structures of the other salts are cation dependent, viz: $Li_2[PdF_6]$ ($Na_2[SnF_6]$ type); $Na_2[PdF_6]$ ($Na_2[SiF_6]$); $K_2[PdF_6]$ ($K_2[GeF_6]$ and $K_2[MnF_6]$); $Rb_2[PdF_6]$ ($K_2[GeF_6]$ and $K_2[MnF_6]$); $Cs_2[PdF_6]$ ($K_2[PtCl_6]$); $M^{II}[PdF_6]$ in which M^{II} = Sr, Ba ($K[OsF_6]$ type) but where M^{II} = Hg, Ca, Zn, Cd ($Li[SbF_6]$ type) [286,355,829–831,834]. The compounds turn brown in air and are immediately decomposed by water to $PdO_2 \cdot n\ H_2O$ [829,830]. There are also $[(NO)_2][PdF_6]$ [280], and $[XeF_5]_2[PdF_6]$ (Pd–F = 1.89 Å) [836].

Pale yellow hexafluoroplatinates(IV) can be made by fluorination of $M_2[PtCl_6]$ but since they are not decomposed by water, can also be obtained by wet methods [653,829,831,837–841]. $K_2[PtF_6]$ is conveniently obtained by melting $K_2[PtCl_6]$ with KHF_2 [360]. The structures are generally similar to the $[PdF_6]^{2-}$ analogues; the main differences are that two forms of $K_2[PtF_6]$ ($K_2[GeF_6] + K_2[PtCl_6]$) are known, and that the Rb and Cs salts are of the hexagonal $K_2[GeF_6]$ type [286]. The platinum analogue of "PdF_3" $Pt^{II}[Pt^{IV}F_6]$ has recently been made [842], and there are NO^+ and NO_2^+ salts [280,618]. Spectroscopic data on $M_2[PdF_6]$ and $M_2[PtF_6]$ include IR (Table 5), electronic spectra [290,363,843,844] and ^{19}F NMR [845–848].

The compounds XeM_2F_{10} (M = Pd, Pt) may be $[XeF]^+$ salts of $[M_2F_9]_n^{n-}$ ions [777].

Platinum dissolves in aqua regia or hydrochloric acid saturated with chlorine to give hexachloroplatinic acid $H_2[PtCl_6]$, isolated as the red hexahydrate on evaporation [853]. There are also 4- and 2-hydrates, and a recent IR study [854] showed these to contain $[PtCl_6]^{2-}$ ions and $[H_7O_3]^+$,

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* *Note added in proof.* Cs_2PdI_6 has been recently reported, D. Sinram, C. Brendel and B. Krebs, Inorg. Chim. Acta, 64 (1982) L131.

$[H_5O_2]^+$, $[H_3O]^+$ cations. The corresponding $H_2[PtBr_6] \cdot 6\,H_2O$ is produced from Pt, HBr and Br_2 [821] as dark red crystals. Solutions of $H_2[PtCl_6]$ containing excess HI, probably contain $H_2[PtI_6]$, although there is no recent claim for its isolation, and whilst $H_2[PdCl_6]$ and $H_2[PdBr_6]$ can be prepared in solution, they too have not been isolated. There are also various "hydrates" of the platinum(IV) halides, which are probably better formulated as hydroxohaloplatinates(IV) such as $[PtCl_4(OH)_2]^{2-}$.

Hexahalopalladates(IV) and -platinates(IV) are readily made by treating the free acids with appropriate alkali-metal halides, or by halogen oxidation of solutions of the Pd(II) or Pt(II) analogues [855–860]. Chlorination of a mixture of Pt and M^ICl also yields $M_2[PtCl_6]$ [861]. The salts of the lighter alkali metals are very soluble; those of NH_4, Rb, K, Cs are generally slightly soluble in water. The orange-red $M_2[PdCl_6]$ salts are readily reduced, and lose chlorine on gentle heating (ca. 200°C) to form $M_2[PdCl_4]$ [859,862], whilst the almost black $M_2[PdBr_6]$ decompose with liberation of bromine on boiling the aqueous solutions. The haloplatinates(IV) are much more stable thermally. The sodium salt $Na_2[PtCl_6]$ is hygroscopic, rapidly changing into $Na_2[PtCl_6] \cdot 6\,H_2O$ in air, a reaction reversed by heating above ca. 120°C [855]. A large number of alkylammonium, phosphonium, etc. salts especially of $[PtCl_6]^{2-}$ have been described [25].

The structures of $M^I_2[MX_6]$ ($M = Pd$, Pt; $X = Cl$, Br) are the $K_2[PtCl_6]$ type [863–869], dimensions of particular ions being Pd–Cl $(NH_4)_2[PdCl_6]$ 2.300(7) Å [867], Pt–Cl $K_2[PtCl_6]$ 2.323 Å [868], Pt–Br, $K_2[PtBr_6]$ 2.463(30) Å [869]. Spectroscopic data: IR (Table 5), electronic [12,402,870,876a], NQR [871] and ^{195}Pt NMR [9].

The brown-black $M_2[PtI_6]$ ($M = K$, Rb, Cs) are best made by treating aqueous $H_2[PtCl_6]$ with excess MI [872]; the K salt is orthorhombic, the others tetragonal. A considerable number of mixed haloplatinates(IV) have been prepared in solution, and in some cases isolated. Examples include the orange $[PtF_3Cl_3]^{2-}$ produced from $[PtCl_6]^{2-}$ and BrF_3 at room temperature [872], $[PtF_nCl_{6-n}]^{2-}$, $n = 1$–5, [698,848], $[PtBr_2F_4]^{2-}$, $[PtBrF_5]^-$ [873], $[PtCl_{6-x}Br_x]^{2-}$ [874]. Hydroxohaloplatinates(IV) are also known, the best characterised examples being the $[PtF_{6-x}(OH)_x]^{2-}$, $x = 1$, 2 [848,875], and $K_2[PtCl_4(OH)_2]$ [876b].

Complexes

Group VIB. Palladium(IV) nitrate $[Pd(NO_3)_4]$ is prepared from commercial "$Pd(NO_3)_2$" and excess N_2O_5 at −78°C. On warming to room temperature brown plate-like crystals of $[Pd(NO_3)_4]$ form [877]. When palladium metal is dissolved in nitric acid, followed by evaporation, the product is $[Pd(NO_3)_2(OH)_2]$ rather than $[Pd(NO_3)_2]$ as previously reported [877].

Platinum(IV) nitrate is unknown, but reaction of $K_2[PtBr_6]$ with N_2O_5 produces $K_2[Pt(NO_3)_6]$, in which the nitrate groups are nominally bidentate on the basis of IR evidence [704]. In $K_2[Pt(NO_2)_6]$ the NO_2 groups are N-bonded (nitro), and this and related complexes are discussed under N-donors. Boiling $K_2[Pt(NO_2)_6]$ with excess conc. HNO_3 gives white $K_2[Pt(NO_2)_3(NO_3)_3]$ [878–880], believed to be the facial isomer [881]. On more prolonged heating of $K_2[Pt(NO_2)_3(NO_3)_3]$ with nitric acid, brick-red $K_2[Pt(NO_3)_3(OH)_3]$ is produced, also obtained from $K_2[PtBr_6]$, $K_2[PtI_6]$ or $K_2[Pt(OH)_6]$ and HNO_3 [882]. Orange $K_2[Pt(NO_3)_4(OH)_2]$ is said to form on addition of a stoichiometric amount of KNO_3 to a freshly prepared solution of hydrated platinum(IV) oxide in conc. HNO_3 [880].

Attempts to prepare $[Pd(SO_3F)_4]$ have failed, but oxidation of Pd metal with $HSO_3F/S_2O_6F_2$, followed by removal of all volatile materials gives pure $Pd[Pd(SO_3F)_6]$ (cf. $Pd[PdF_6]$) [883,884]. If the reaction is conducted with added CsCl the product is dark-red $Cs_2[Pd(SO_3F)_6]$, and Ba^{2+}, NO^+ and ClO_2^+ salts are also known [884]. Dark brown $[Pt(SO_3F)_4]$ was originally formed from Pt and $BrOSO_2F$ [885], but a later paper [884] suggests that $Pt + HSO_3F/S_2O_6F_2$ provides a better route. Green $Pd^{II}[Pt^{IV}(SO_3F)_6]$ can be formed by heating together $[Pd(SO_3F)_2]$, $[Pt(SO_3F)_4]$ and HSO_3F [884]. Vibrational and electronic spectra and magnetic data have been reported for this series of complexes [884].

The diamagnetic iodato-complex $K_2[Pt(IO_3)_6]$ is produced by reaction of PtO_2 or $H_2[PtCl_6]$, KNO_3 and HIO_3 [886]; NH_4^+, Rb^+ and Cs^+ salts are also known, but attempts to prepare chlorate or bromate analogues have been unsuccessful [886]. $K_2[Pt(IO_3)_6]$ is reported [886] to be isostructural with $K_2[Ge(IO_3)_6]$ which has an octahedral anion with bidentate iodate ligands [887]. Periodate complexes formulated $K_6[Pt(IO_6)_2] \cdot 12H_2O$, $K_6[Pt(IO_6)_2]KOH \cdot 14H_2O$, $K_3H_3[Pt(IO_6)_2] \cdot 22H_2O$, $Na_6[Pt(IO_6)_2] \cdot 20H_2O$ and $K_6[Pd(IO_6)_2]KOH \cdot 12H_2O$ are prepared from $[M(OH)_6]^{2-}$, $[H_2IO_6]^{3-}$ and M^IOH [888]. It is thought that the IO_6 groups behave as tridentate ligands.

Palladium(IV) tellurato complexes are formed by boiling $PdCl_2$, telluric acid, NaOH and NaOCl together in water. The orange-yellow product is formulated $Na_5H_3[Pd(TeO_6)_2] \cdot 4H_2O$ [889]. The yellow $Na_5H_3[Pt(TeO_6)_2] \cdot 2H_2O$ is produced from $PtCl_4$, H_6TeO_6 and NaOH [889].

Platinum(IV) β-diketone complexes cannot be prepared from $[PtX_6]^{2-}$ and the ligand, which causes reduction [890]. However, $[Pt(acac)_2]$ (acacH = acetylacetone) oxidatively adds iodine both in the solid state and in solution to yield *trans*-$[Pt(acac)_2I_2]$ [891,892]. Both solution spectrophotometric measurements and gas phase (mass spec.) data indicate the reaction is reversible [892]. An X-ray study [892] shows the metal ion is octahedrally coordinated by two oxygen-chelated acac ligands and two *trans* iodides (Fig. 46), $Pt-O_{av}$

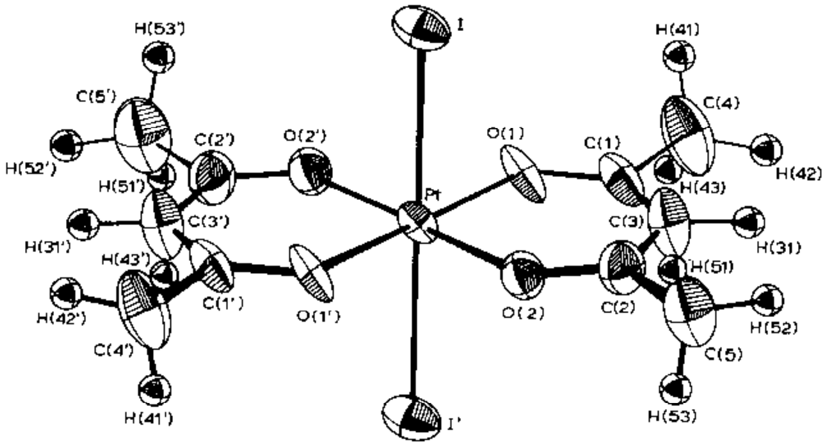

Fig. 46. The structure of *trans*-[Pt(acac)$_2$I$_2$]. From ref. 892.

$= 1.995$ Å, Pt–I $= 2.667(1)$ Å. The iodide ligands are weakly linked into infinite chains ($I \cdots I = 3.559(2)$ Å).

A Pd(IV) selenoxide complex [Pd(Me$_2$SeO)$_2$Cl$_4$] was suggested to be formed by reaction of PdCl$_2$ and Me$_2$SeO in aqueous ethanolic HCl [893], and to contain O-bonded Me$_2$SeO. Since no oxidising agent was used this is implausible and the product may be the [PdCl$_4$]$^{2-}$ salt of the protonated selenoxide.

Platinum(IV) complexes of other ligands containing oxygen donor sites include those of quinazoline-2-thione-4-one [894], *N*-ethoxycarbonylpyrrole-2-thiocarboxamide [895], keto-anils [896], Schiff bases [466b,897,898], 1-salicyl-4-benzylamidothiosemicarbazone [899], and 3,3′-diamino-4,4′-dihydroxydiphenylsulphone [900]. Palladium(IV) Schiff base complexes have been claimed [901].

A range of monodentate thioether complexes has been prepared including *trans*-[Pt(Me$_2$S)$_2$X$_4$] (X = Cl, Br, I), *cis*-[Pt(Me$_2$S)$_2$Cl$_4$], *cis*- and *trans*-[Pt(Et$_2$S)$_2$Cl$_4$] and [Pr$_4$N][Pt(Me$_2$S)X$_5$] (X = Cl, Br) [902–905]. The preparation of *cis*-[Pt(Me$_2$S)$_2$Cl$_4$] by chlorine oxidation of *cis*-[Pt(Me$_2$S)$_2$Cl$_2$] in cold benzene solution (to minimise isomerisation) is typical, the bright yellow *cis* isomer being formed in high yield [904]. Pale lemon-yellow *trans*-[Pt(Me$_2$S)$_2$Cl$_4$] is similarly produced from *trans*-[Pt(Me$_2$S)$_2$Cl$_2$]. The mixed isomers can be completely separated by TLC [906]. The IR, Raman and ^{1}H NMR spectra of the Me$_2$S complexes have been studied in detail [902,903]. The redox potential of the system *trans*-[Pt(^{n}Pr$_2$S)$_2$Cl$_2$]–*trans*-[Pt(^{n}Pr$_2$S)$_2$Cl$_4$] has been measured [907]. On heating *cis*-[Pt(Et$_2$S)$_2$Cl$_4$] isomerises to the *trans* form [906,908]. Other thioether complexes include [Pt(dithiane)$_2$Cl$_4$], obtained from H$_2$[PtCl$_6$] and C$_4$H$_8$S$_2$ in alcohol, and [Pt(dithiane)(dioxan)Cl$_4$] similarly formed in dioxan [909]. Thioxane (C$_4$H$_8$SO) [910], thiopyrine [911] complexes and [Pt(SCl$_2$)$_2$Cl$_4$] [912] are also known.

Chlorination of *trans*-[Pd(Me_2S)$_2$$Cl_2$] produces an orange-red material which could not be isolated or characterised before it decomposed [913]. Deep red-orange [Pr_4N][Pd(Me_2S)Cl_5], apparently the only known Pd(IV) thioether complex, is produced by chlorine oxidation of [Pr_4N][Pd(Me_2S)Cl_3]; it too is unstable, decomposing in a few days [913]. Attempts to oxidise [Pd(dithioether)Cl_2] with Cl_2, Ce(IV) or HNO_3 have failed [469]. In contrast oxidation of [Pt(dithioether)X_2] (dithioether = RS(CH_2)$_n$SR, *cis*-RSCH=CHSR, *o*-C_6H_4(SR)$_2$; $n = 2, 3$; R = Me, Ph; X = Cl, Br) with the appropriate halogen in CCl_4/CH_2Cl_2 gives high yields of the yellow [Pt(dithioether)Cl_4] and orange [Pt(dithioether)Br_4] [469]. Only two iodides [Pt(MeS(CH_2)$_n$SMe)I_4] ($n = 2, 3$) were isolated, iodine oxidation of complexes of the other ligands gave materials of variable composition which lost iodine very easily [469]. Infrared, electronic and ^{1}H NMR spectra were reported and discussed, and it was shown by variable temperature NMR studies that inversion at sulphur coordinated to Pt(IV) is more difficult than in the Pt(II) analogues [469,914]. Thermal decomposition of [Pt(*o*-C_6H_4(SPh)$_2$)X_4] to the platinum(II) analogues is straightforward, but for the dithioethers with alkylsubstituents, thermal decomposition involves both loss of halogen and dealkylation [469].

Platinum(IV) selenoether complexes are few, and some of the reports are very old [915]. Complexes formulated [Pt($SeBz_2$)$_4$$Cl_2$]$Cl_2$ [916] and [Pt(MeSe(CH_2)$_n$SeMe)Cl_4] [917] have been mentioned but no preparative data or spectroscopic details were given. The values of $^1J(^{195}Pt-^{77}Se)$ have been obtained for [Pt(Me_2Se)X_5]$^-$ (X = Cl, Br, I) by the INDOR technique [918]. The only detailed study of Pt(IV)-selenoethers is the work of Abel et al. [919,920] on [$PtMe_3$X(diselenoether)] complexes, in which it was shown that the activation energies for the inversion process in the coordinated

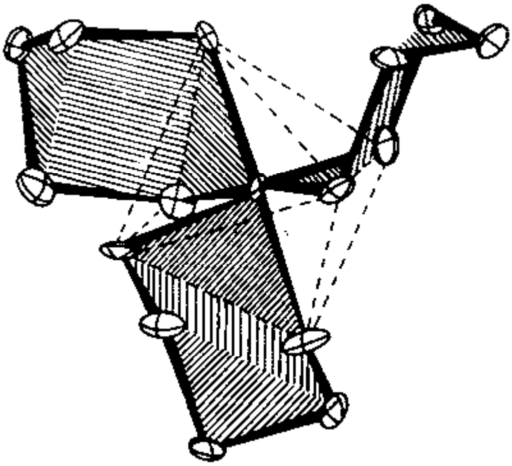

Fig. 47. Structure of $(NH_4)_2[Pt(S_5)_3]$. From ref. 925.

selenoethers, were greater than in the thioether analogues.

Oxidative-addition of H_2Se to *trans*-$[PtH(X)(PEt_3)_2]$ (X = Cl, Br, I, SH, SeH, CN) gives six-coordinate platinum(IV) dihydrides which were characterised by NMR spectroscopy. Addition of HY (Y = Cl, I) to *trans*-$[PtH(SH)(PEt_3)_2]$ was also investigated [921].

The brick-red $(NH_4)_2[Pt(S_5)_3]$ was prepared as long ago as 1903 [922] although an improved preparation from aqueous $H_2[PtCl_6]$ and $(NH_4)_2S_5$ with careful control of the pH has been published very recently [923]. The enantiomers of $[Pt(S_5)_3]^{2-}$ were separated by classical resolution using $(+)[Ru(phen)_3]^{2+}$ [924]. An X-ray study of $(NH_4)_2[Pt(S_5)_3] \cdot 2H_2O$ shows the anion consists of three bidentate pentasulphide groups octahedrally coordinated to Pt(IV), to form three six-membered rings in the chair conformation [Pt–S = 2.365(7)–2.428(8) Å) [925]. The synthesis and X-ray structure of $K_2[Pt(S_5)_3]$ has also been reported [926] (Pt–S = 2.332(5)–2.479(5) Å) (Fig. 47).

Cationic dithiocarbamate complexes $[M(R_2dtc)_3]^+$ (M = Pd, Pt) can be prepared from $[M(R_2dtc)_2]$, the counter-anion depending upon the oxidant used. For example $[Pd(R_2dtc)_2]$ and $[R_4bitt][Cu_2X_6]$ (R_4bitt = 3,5-bis(*N*,*N*-diethyliminium)-1,2,4-trithiolane) gave $[Pd(R_2dtc)_3]_2[Cu_2X_6]$. As expected the ease of oxidation and the stability is Pt > Pd [927,928]. Cyclic voltammetry has been used to examine the oxidation of $[M(R_2dtc)_2]$ and $[M(R_2dsc)_2]$ (R_2dsc = diselenocarbamate), and the reduction of $[M(R_2dtc)_3]^+$ and $[M(R_2dsc)_3]^+$. The Pt(IV)diselenocarbamate complexes are the most stable [929]. The other main type of dithiocarbamate complexes are exemplified by $[M(Bu_2dtc)_2X_2]$ (M = Pd, Pt; X = Br, I) prepared by halogen oxidation of $[M(Bu_2dtc)_2]$ in solution [928]. For M = Pt two complexes were obtained

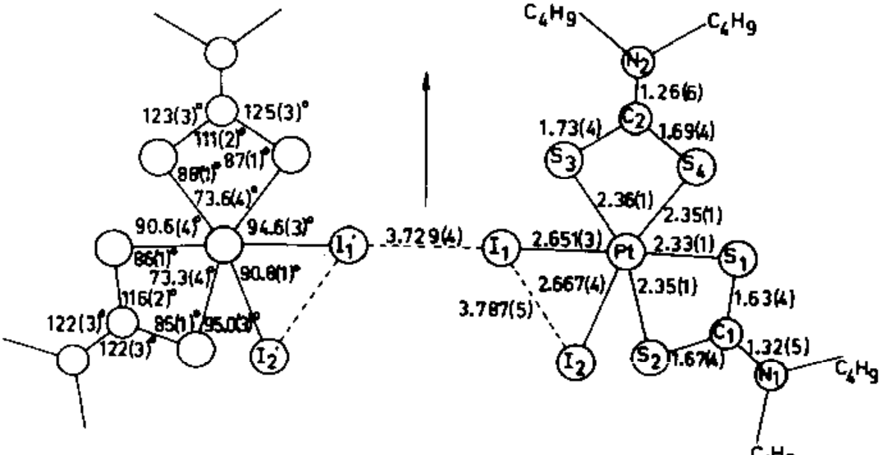

Fig. 48. The structure of *cis*-$[Pt(Bu_2dtc)_2I_2]$. From ref. 928.

from these reactions, believed to be the *cis* and *trans* isomers on the basis of their ^{1}H NMR spectra. The structure of *cis*-$[Pt(Bu_2dtc)_2I_2]$ has been established by an X-ray study [928]. The platinum is in a distorted octahedral environment Pt–I = 2.66 Å, Pt–S = 2.35 Å, and the intra- and one intermolecular I–I distances are short compared with the value expected for I · · · I van der Waals contact [928] (Fig. 48). Variable temperature ^{1}H NMR spectra of this complex have been reported, and the *trans* → *cis* isomerism of $[Pt(Bu_2dtc)_2I_2]$ followed by ^{1}H NMR [930]. The production of *cis*-$[Pt[Se_2CN(^iBu_2)]_2X_2]$ (X = Br, I) by halogen oxidation of the Pt(II) analogues has been reported [931].

Sulphoxide complexes of Pt(IV) include *cis*-$[Pt(R_2SO)_2Cl_4]$ ($R_2 = Et_2$ or $(CH_2)_4$) [911], *cis*- and *trans*-$[Pt(Me_2SO)_2Cl_4]$ [908], $[Et_3NH][PtLCl_5]$ (L = Me_2SO, Et_2SO) [932,933], and all are S-bonded on the basis of the S–O stretching frequencies in their IR spectra [933]. Sulphur bonding is also present in the $[PtL_2Cl_4]$ L = thiourea [934], *NNN′N′*-tetramethylthiourea and *NN′*-ethylenethiourea [935].

Phosphine sulphide and selenide complexes have been little studied. Platinum(IV) forms complexes with tri(*o*, *m*, *p*-tolyl)phosphine sulphides [936], R_3PS (R = 2-methylaziridine) [937], and there is a report of a material analysing as $PtCl_4 \cdot 3.3Ph_3PS$ [938]. Diphosphine disulphide, $Ph_2P(S)(CH_2)_nP(S)Ph_2$ complexes [Pt(L–L)Cl_4] have been claimed but no preparative or characterisation data were given [939].

$[^nBu_4N]_2[Pt(SCN)_6]$ can be precipitated by adding $^nBu_4NCl$ to a neutral aqueous solution containing $[PtCl_6]^{2-}$ and excess NaNCS, and $[^nBu_4N]_2[Pt(SeCN)_6]$ is similarly produced using KSeCN [870]. The best syntheses for the potassium salts are in [940,941]. Spectroscopic investigations include electronic [942,970] and IR [943–945] for both ions and ^{195}Pt NMR [946] and ^{14}N NQR [947] for $[Pt(SCN)_6]^{2-}$. The crystal structure of $[VO(Me_2SO)_5][Pt(SCN)_6]$ confirms the Pt–SCN linkage inferred from IR studies; Pt–S = 2.355(4)–2.387(3) Å [948]. It was reported that $M_2[Pt(XCN)_6]$ (M = K, Rb, NH_4; X = S, Se) are isostructural and in $K_2[Pt(SeCN)_6]$ Pt–Se is 2.8 Å [949].

A few Pd(IV), and many Pt(IV) complexes of N, S donor ligands have been reported. In many of these studies the donor atoms actually bound to the metal and the stereochemistries of the complexes are not clearly established. Typical examples are for Pd(IV); -N-aminorhodamine [950], thiosemicarbazones [951], quinazoline-2-thione-4-one [894], and quinazoline-2,4-dithione [952], and for Pt(IV) 3-14-pyridyltriazoline-5-thione [953], 3,8-diphenyl-4,5,6,9-tetrahydro-1,4,7-thiadiazonenes [954], quinazoline-2,4-dithione [952], dimethylaminoethanethiol [955], substituted thiosemicarbazones [899,956], and di(2-aminoethyl)sulphide [957]. The ligand 1,3,4-thiadiazole-2,5-dithiol is claimed to form Pd(IV) and Pt(IV) complexes bound via sulphur [958].

Group VB

N-Donors. Pale yellow cubic crystals of $K_2[Pt(NO_2)_6]$ are prepared by heating $K_2[Pt(NO_2)_4]$ with excess HNO_3 and NH_4NO_3 [878,879], or with HNO_3 and NO_2 [959,960]. Vibrational spectroscopy shows it to contain nitro ($Pt-NO_2$) groups [959,960]. It has the $K_2[PtCl_6]$ structure; similar Na, Ag, Rb, Cs and N^nBu_4 salts are known [870,959,960]. The complexes $[Pt(NO_2)_{6-x}Cl_x]^{2-}$ ($x = 0$–5) together with some bromo and iodo analogues are known, and their vibrational spectra have been recorded and assigned [960–963]. For example $K_2[Pt(NO_2)_4Br_2]$ is produced as a yellow precipitate by oxidation of $K_2[Pt(NO_2)_4]$ in water with Br_2 in methanol. It is stable as a solid, but slowly reduced in aqueous solutions [961]. Other mixed anions include $K_2[Pt(NO_2)_2Cl_2(OH)_2]$, $K_2[Pt(NO_2)_3Cl(OH)_2]$ and $K_2[Pt(NO_2)_4(OH)_2]$ [964].

Orange-yellow $Na_2[Pt(N_3)_6]$ is prepared by heating aqueous solutions of $H_2[PtCl_6]$ with NaN_3 [965]. The K, $[NH_4]$, $[Et_4N]$, $[Ph_4As]$ and n-cetyltrimethylammonium salts can be prepared by cation exchange, and IR and electronic spectra have been recorded [965–968,970]. Although the $[Pd(N_3)_6]^{2-}$ ion is mentioned in ref. 966 the citation is to a paper which contains only Pd(II) complexes, and is presumably a misprint.

If $[Pd(NH_3)_2Cl_2]$ is treated with excess Cl_2 in water, dark red $[Pd(NH_3)_2Cl_4]$ is produced, which on standing in aqueous solution decomposes to black $[Pd(NH_3)_2Cl_2][PdCl_4(NH_3)_2]$ [969–972], and on heating in the solid state to $[Pd(NH_3)_2Cl_2]$ and Cl_2 [969,973]. Chlorine oxidation of $[Pd(NH_3)_2Cl_2]$ in $CHCl_3$ or CCl_4 is more satisfactory [969]. $[PdL_2Cl_4]$ ($L = MeNH_2$, piperidine) can be prepared by the latter route, and have similar properties [970,973]. The electronic and circular dichroism spectra of *trans*-$[PdL'_2Cl_4]$ ($L' =$ 1-phenylethylamine) have been recorded [974]. Chlorine oxidation of $[Pd(NH_3)_4Cl_2]$ in CCl_4 gives yellow $[Pd(NH_3)_4Cl_2]Cl_2$, which decomposes in aqueous solution and gives $[Pd(NH_3)_2Cl_2]$ on heating [975,976].

In contrast to the paucity of Pd(IV) complexes a large number of Pt(IV) ammines are known. They include complexes containing other ligands such as NO_2 [977], NO_3 [977], N_3 [978] and CN [979] for example, and virtually every combination of substituents has been claimed, even in the extreme, e.g. $[Pt(NH_3)pyClBrINO_2]$ [980]. The full range of ammine complexes $[PtCl_{6-n}(NH_3)_n]^{(n-2)}$ ($n = 1$–6) are known. *Cis*-$[Pt(NH_3)_2Cl_4]$ is produced by chlorine oxidation of an aqueous solution of *cis*-$[Pt(NH_3)_2Cl_2]$ at 75–80°C, and *trans*-$[Pt(NH_3)_2Cl_4]$ similarly from *trans*-$[Pt(NH_3)_2Cl_2]$ at 100°C; both are lemon yellow [981]. $[Pt(NH_3)_6]Cl_4$ is best made indirectly from $[Pt(MeNH_2)_4Cl_2]Cl_2$, itself made from aqueous $K_2[PtCl_4]$ and $MeNH_2$, followed by chlorine oxidation. This is converted to $[Pt(NH_3)_6](SO_4)_2$ by heating with aqueous $(NH_4)_2SO_4$ and ammonia, followed by addition of

$BaCl_2$ and filtration. Precipitation with conc. HCl gives the snow-white $[Pt(NH_3)_6]Cl_4$ [982]. Other salts are known including $[Pt(NH_3)_6](OH)_4$ [983] and $[Pt(NH_3)_6]I_4$ [984]. IR and Raman spectra have been reported for $K[Pt(NH_3)Cl_5]$ [985], *cis*- and *trans*-$[Pt(NH_3)_2X_4]$ (X = Cl, Br, I) [903,963,986], *mer*-$[Pt(NH_3)_3Cl_3]Cl$ [985], *cis*- and *trans*-$[Pt(NH_3)_4X_2]X_2$ [963,986,987], $[Pt(NH_3)_5X]X_3$ (X = Cl, Br) [985] and $[Pt(NH_3)_6]Cl_4$ [985,988,989]. Electronic spectra have been recorded for *trans*-$[Pt(NH_3)_4X_2]^{2+}$ [962,990], $[Pt(NH_3)_5X]^{3+}$ [962,991] and $[Pt(NH_3)_6]^{4+}$ [870,991]. There are several old reports of X-ray work on platinum ammines, viz., $[Pt(NH_3)_4Cl_2]Cl_2$, Pt–Cl = 2.25 or 2.32 Å, Pt–N = 2.03 Å [992,993]; $[Pt(NH_3)_5Cl]Cl_3 \cdot H_2O$, Pt–Cl = 2.30 Å, Pt–N = 2.00 Å [994]; *cis*-$[Pt(NH_3)_2Cl_4]$ [995]; *trans*-$[Pt(NH_3)_2Cl_4]$, Pt–Cl = 2.30 Å, Pt–N = 2.00 Å [996].

The acid dissociation constant of $[Pt(NH_3)_6]^{4+}$ has been determined spectrophotometrically and further deprotonation occurs in strongly alkaline solutions [997]. Compounds containing 1,2,3-amido groups/Pt ion were isolated from aqueous solution, and using KNH_2 in liquid ammonia, $[Pt(NH_3)_2(NH_2)_4]$ and $K_2[Pt(NH_2)_6]$ can be prepared [997]. $[Pt(NH_3)_6]^{4+}$ and acetylacetone or trifluoroacetylacetone condense rapidly at pH 9 to give stable ring systems [998] (Fig. 49). By varying the reaction conditions a mixture of products is obtained including *cis*- and *trans*-$[Pt(NH_3)_2(2{,}4\text{-pentanediiminate})_2](ClO_4)_2$ [999]. An X-ray of the *trans* isomer shows almost regular octahedral coordination about the metal, and the presence of planar π-delocalised β-diiminate rings (Fig. 50) in which $Pt{-}NH_3 = 2.053(5)$ Å, Pt–N = 2.011(4), 2.002(5) Å [999]. Condensation reactions also occur between acacH and $[Pt(en)_3]Cl_4$ [999].

Chlorination of a very dilute aqueous solution of $[Pt(NH_3)_5Cl]Cl_3$ forms $[Pt(NH_3)_3(NCl_2)_2Cl]Cl$, whose structure has been determined [1000] (Fig. 51).

Complexes of primary and secondary amines are also numerous, but those of tertiary amines are rare. Solid $[Pr_4N][Pt(NMe_3)Cl_5]$ was isolated from the chlorine oxidation of $[Pr_4N][Pt(NMe_3)Cl_3]$ in CH_2Cl_2, but *trans*-$[Pt(NMe_3)_2X_4]$ (X = Cl, Br) had to be studied in solutions prepared in situ [902].

The treatment of $[Pd(en)Cl_2]$ with Cl_2 in aqueous solution results in

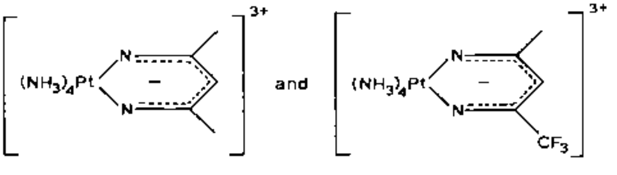

Fig. 49. The condensation products of $[Pt(NH_3)_6]^{4+}$ and β-diketones.

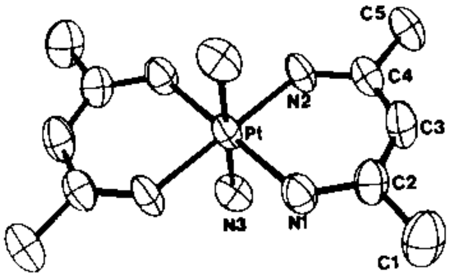

Fig. 50. The cation of *trans*-[Pt(NH_3)$_2$(2,4-pentanediiminate)$_2$](ClO_4)$_2$. From ref. 999.

$[PdCl_6]^{2-}$, but in CCl_4 the product is brown [Pd(en)Cl_4] [969,970]. The bis(ethylenediamine) Pd(IV) complexes are disputed. Concentrated nitric acid oxidation of [Pd(en)$_2$]Cl_2 gives a green solid claimed to be [Pd(en)$_2$$Cl_2$]($NO_3$)$_2$ [1001,1002]. The complexes [Pd(en)$_2$$Br_2$]($NO_3$)$_2$ and [Pd(en)$_2$$X_2$]$X_2$ (X = Cl, Br, I) were also claimed. However, other workers [1003] characterised the green material as *trans*-[Pd(en)$_2$$Cl_2$Pd(en)$_2$]($NO_3$)$_4$, and converted this to yellow-green *trans*-[Pd(en)$_2$$Cl_2$]($ClO_4$)$_2$ by Cl_2 oxidation in aqueous HCl. Bromine oxidation of *trans*-[Pd(en)$_2$]Cl_2 in aqueous HBr gives orange [Pd(en)$_2$$Br_2$]$Br_2$ · 2HBr [1003]. Bright yellow *trans*-[Pd(L-propylenediamine)$_2$$Cl_2$]($NO_3$)$_2$ was, however, obtained without difficulty by nitric acid oxidation of the Pd(II) complex and its electronic and CD spectra recorded [1004].

[Pt(en)Cl_4] can be prepared by chlorination of a hot aqueous solution of [Pt(en)Cl_2] [1005], and *trans*-[Pt(en)$_2$$Cl_2$]$Cl_2$ by cautious chlorination of

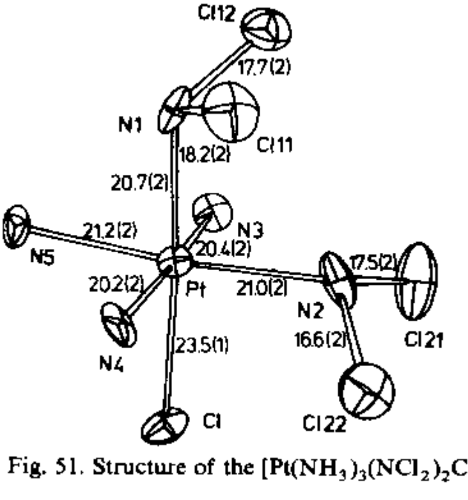

Fig. 51. Structure of the [Pt(NH_3)$_3$(NCl_2)$_2$Cl]$^+$ cation. From ref. 1000.

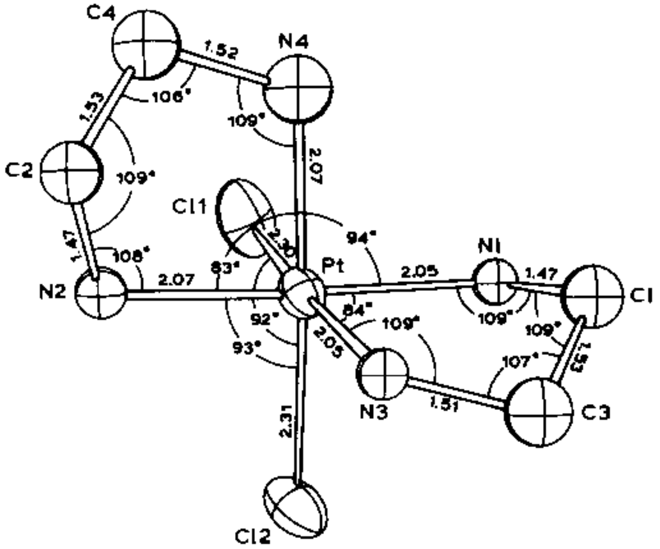

Fig. 52. Structure of the *cis*-$[Pt(en)_2Cl_2]^{2+}$ cation. From ref. 1009.

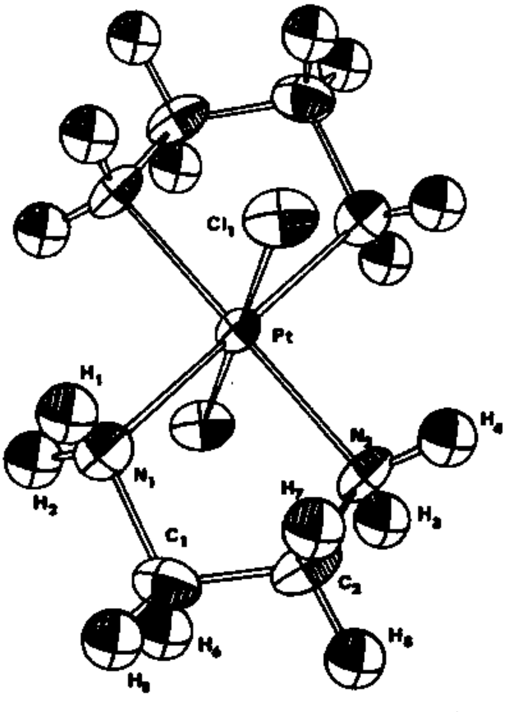

Fig. 53. The structure of *trans*-$[Pt(en)_2Cl_2]^{2+}$ in *trans*-$[Pt(en)_2Cl_2][CuCl_4]\cdot H_2O$. From ref. 1010.

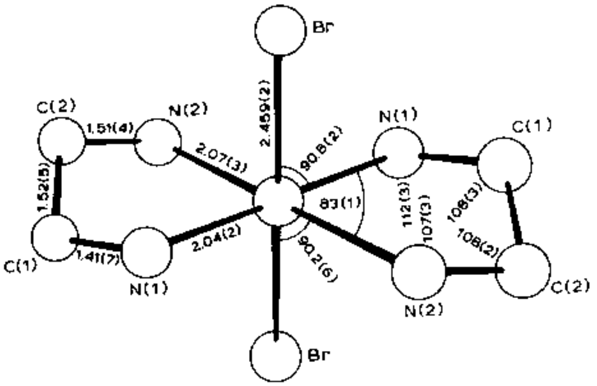

Fig. 54. The structure of *trans*-$[Pt(en)_2Br_2]^{2+}$ in *trans*-$[Pt(en)_2Br_2][C_4O_4]\cdot 2H_2O$. From ref. 1011.

$[Pt(en)_2]Cl_2$, but prolonged chlorination gives the 1:1 complex [1005]. The $[Pt(en)Br_4]$ and *trans*-$[Pt(en)_2Br_2]Br_2$ are prepared similarly [1006], and $[Pt(en)X_4]$ (X = Br, I) can be made from $K_2[PtX_6]$ and en [1006]. Electronic spectra of both 1:1 and 2:1 en complexes have been obtained and interpreted [962,1007,1008]. The structure and absolute configuration of $(+)_{450}$-*cis*-

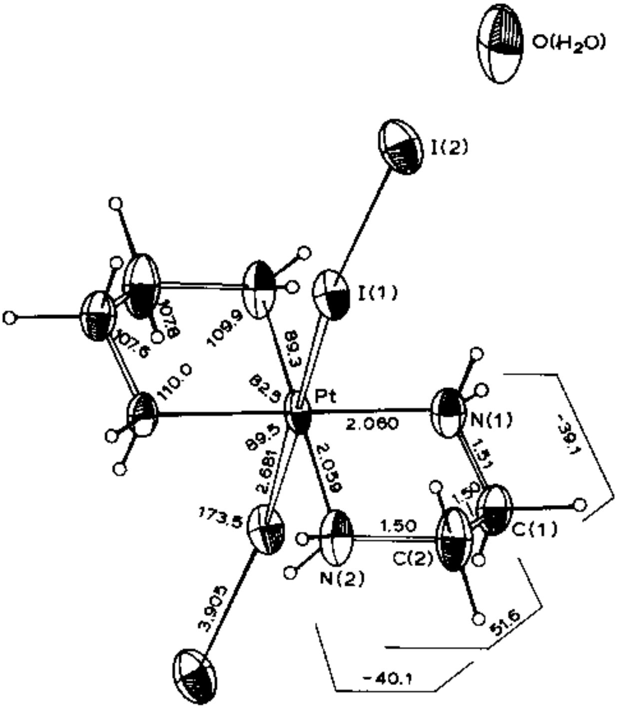

Fig. 55. The structure of *trans*-$[Pt(en)_2I_2]I_2\cdot 2\,H_2O$. From ref. 1012.

$[Pt(en)_2Cl_2]Cl_2$ have been determined: Pt–Cl = 2.306(4) Å and Pt–N = 2.057(6) Å (av) [1009] (Fig. 52). The structure (Fig. 53) of the *trans* isomer (as $[Pt(en)_2Cl_2][CuCl_4] \cdot H_2O$) shows Pt–Cl = 2.313(4) Å and $Pt–N_{av}$ = 2.081(8) Å. The grass-green prismatic material is prepared by reaction between $[Pt(en)_3]Cl_4$, LiCl and $CuCl_2$ in acidic solution, followed by recrystallisation from hot conc. HCl [1010]. *Trans*-$[Pt(en)_2Br_2][C_4O_4] \cdot 2H_2O$ has also been X-rayed: Pt–Br = 2.459(2) Å [1011] (Fig. 54). The *trans*-$[Pt(en)_2I_2]I_2 \cdot 2H_2O$ contains tetragonal bipyramidal cations (Fig. 55) with rather short contacts to the I^- ions from the coordinated iodide (3.905 Å) forming almost linear I · · · I–Pt–I · · · I units [1012].

The preparations and electronic spectra of *cis*- and *trans*-$[Pt(pn)_2Cl_2]Cl_2$, have been described [1013] as have those of *trans*-$[Pt(L\text{-}pn)_2X_2](ClO_4)_2$ ($pn = H_2NCH_2CH_2CH_2NH_2$) (X = Cl, Br) together with the associated circular dichroism spectra [1004]. Complexes of type $[Pt(L–L)Cl_4]$ where L–L is a substituted ethylenediamine have been prepared by boiling aqueous solutions of the Pt(II) complexes with conc. HCl until chlorine is evolved [1014]. Tertiary amine complexes are rare, and $[Pt(Me_2NCH_2CH_2NMe_2)X_4]$ (X = Cl, Br) have only recently been obtained [1015]. Mixed ligand complexes $[Pt(en)(Me_2NCH_2CH_2NMe_2)X_2]X_2$ (X = Cl, Br) are also known [1016].

$[Pt(en)_3]Cl_4$ is prepared by reaction between $H_2[PtCl_6]$ and en, although several recrystallisations are necessary to obtain a pure product [1017]. Vibrational [1018] and electronic [870] spectra have been recorded. The complexes of type $[Pt(L'–L')(L''–L'')(L'''–L''')]^{4+}$ (L–L = bidentate N-donor) have been extensively investigated because of interest in their absolute configuration and in the conformational properties of the ligands [1019–1024]. The ^1H NMR spectrum of $[Pt(en)_3]^{4+}$ suggests incomplete conformational averaging so that a conformational preference exists in the cation [1019]. The ^{195}Pt NMR of the ion has also been reported [946]. Similar studies on $[Pt(L'–L')(L''–L'')X_2]^{2+}$ have been published [1009,1025–1028,1031].

Boiling an aqueous solution of *cis*-$[Pt(^iPr_2NCH_2CH_2NH_2)(H_2O)_2]^{2+}$ in hydrochloric acid gives the unusual zwitterionic Pt(IV) amine complex [1029] (Fig. 56).

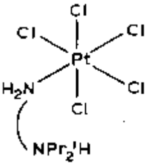

Fig. 56. The proposed structure of $[H^iPr_2N–NH_2PtCl_5]$.

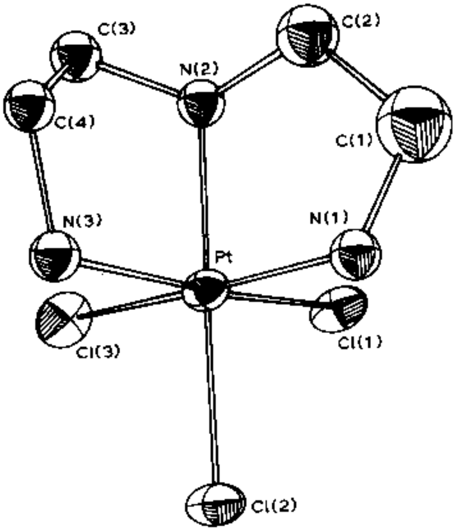

Fig. 57. Structure of the *fac*-[Pt(diethylenetriamine)Cl_3]$^+$ cation. From ref. 1032.

The preparation and the X-ray structure of *fac*-[Pt(L–L–L)Cl_3]Cl · H_2O has been described [1030]. The structure comprises discrete *fac* octahedral cations, Cl^- ions and water molecules, with Pt–Cl = 2.315(3)–2.332(4) Å, Pt–N = 2.05(1)–2.08(1) Å (Fig. 57).

Red-orange [Pd$(py)_2Cl_4$] can be prepared by chlorine oxidation of [Pd$(py)_2Cl_2$] in $CHCl_3$, CCl_4 or H_2O [969,973,1033] or from NOCl and [Pd$(py)_2Cl_2$] [1034]. It decomposes to [Pd$(py)_2Cl_2$] on heating [973]. [Pd(γ-picoline)$_2Cl_4$] has similar properties [973]. There is an old report of the formation of [Pd$(py)_2Cl_2I_2$] by iodine oxidation of aqueous [Pd$(py)_2Cl_2$] [1033]. *Cis*-[Pt$(py)_2Cl_4$] can be prepared by oxidising *cis*-[Pt$(py)_2Cl_2$] with H_2O_2 in *N*,*N*-dimethylformamide containing HCl [1035]. A number of complexes of substituted pyridines have been prepared by this route [1035]. Ruby-red [Pt$(py)_2I_4$] is prepared from Pt black, iodine and pyridine in toluene solution [1036], and [Pt$(py)_3Br_3$]Br and [Pt$(py)_4I_2$]I_2 have been claimed [1037]. The IR spectra of *cis*-[Pt$(py)_2X_4$] (X = Cl, Br) and [Pt$(py)_4X_2$]X_2 have been recorded [903,1038], and the redox potential of the system *trans*-[Pt$(L)_2Cl_2$]-[Pt$(L)_2Cl_4$] (L = 4-pentylpyridine) determined [1039].

Reddish-orange [Pd(bipy)Cl_4] [1040] and red [Pd(phen)Cl_4] [1041] were prepared by chlorine oxidation of the palladium(II) analogues in $CHCl_3$. [Pd(phen)Cl_4] decomposes in moist air and loses chlorine readily on heating [1041], but the bipyridyl complex is air-stable and does not decompose in boiling water [1040]. However, the 2,9-dimethyl-1,10-phenanthroline complex [Pd(dmphen)Cl_4] · $4H_2O$ is reported to be more stable, losing only the water on gentle heating [1042]. TGA on [Pd(bipy)Cl_4] shows conversion to [Pd(bipy)Cl_2] on heating [973].

[Pt(bipy)Cl_4] and [Pt(phen)Cl_4] can be prepared by the method described above for *cis*-[Pt$(py)_2Cl_4$] and form yellow microcrystalline solids [1043]. Several complexes of substituted phenanthrolines were obtained by this route [1043]. [Pt(bipy)Cl_4] can also be prepared by boiling aqueous K_2[PtCl_6] with 2,2′-bipyridyl and conc. HCl [1044]. Complexes of 2,9-dimethyl-1,10-phenanthroline including [Pt$(dmphen)_2X_2$]X_2 (X = Cl, Br) have been reported [1042]. Oxidative-addition of halogens and pseudo-halogens to Pt(II) bipy or phen complexes have been the subjects of some more recent studies. Oxidation of [Pt(phen)X_2] (X = Cl, Br, I) with Cl_2, Br_2, I_2, ICl, ICN and $(SCN)_2$ (AB) was reported to give complexes of the type [Pt(phen)X_2AB]. The complexes containing mixed anions were characterised by analysis and IR spectral data [1045]. However, X-ray work will be necessary to confirm all these conclusions and some X-ray work contradicts the claims for AB = I_2 [1046]. Addition of iodine to [Pt(bipy)X_2] (X = Cl, Br) gives materials of stoichiometry [Pt(bipy)X_2I_2]; however, with [Pt(phen)X_2] the products are [Pt(phen)X_2I_4], [Pt(phen)I_5] and [Pt(phen)Cl_2I_5S] (S = $CHCl_3$ or CCl_4). An X-ray study of [Pt(phen)I_6] shows it consists of [Pt(phen)I_4] and I_2 molecules, the latter connected to coordinated iodide ligands (Fig. 58): Pt–I = 2.548(3)–2.677(2) Å, Pt–N = 2.09(2), 2.10(2) Å [1046]. The structure of [Pt(phen)I_5] is more complicated, in that it is built up from two different types of [Pt(phen)I_4] octahedra, one type of which are associated with an I_2 molecule as in [Pt(phen)I_6]. The second type of [Pt(phen)I_4] molecules are not associated with free I_2, but there are some short contacts to iodine ligands in other [Pt(phen)I_4] groups [1046] (Fig. 59) (Pt–I = 2.604(2)–2.669(2) Å, Pt–N = 2.06(2)–2.12(2) Å).

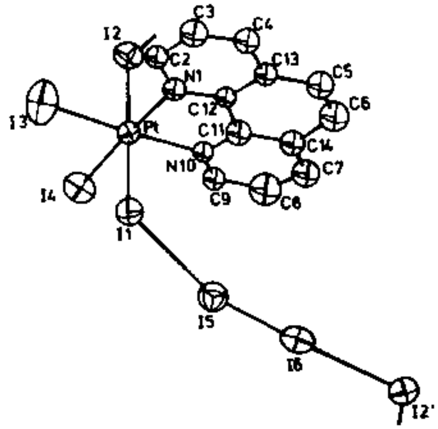

Fig. 58. The structure of [Pt(phen)I_6]. From ref. 1046.

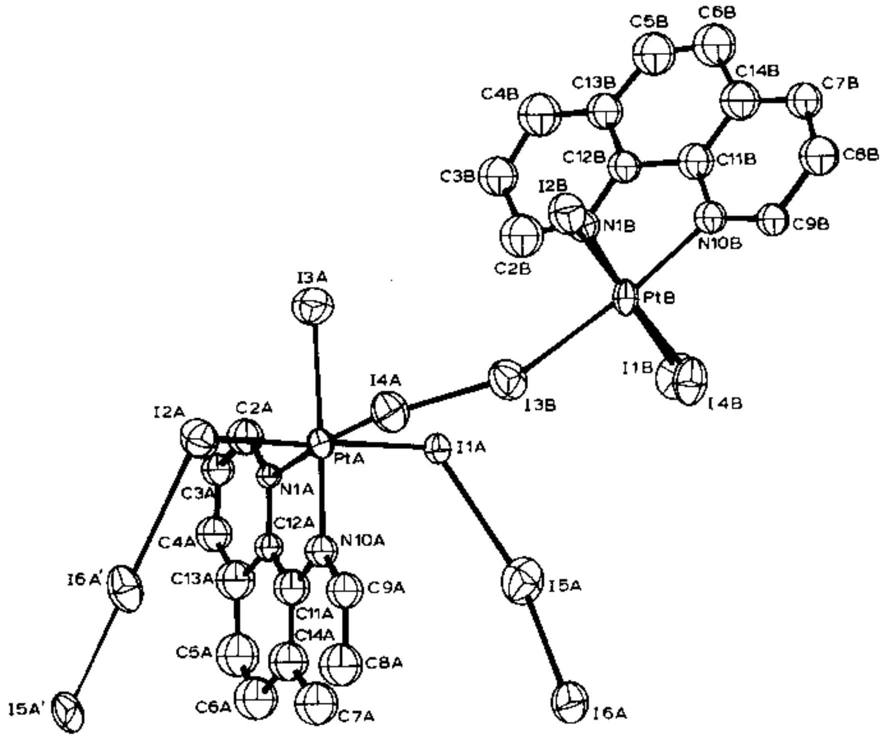

Fig. 59. The structure of $[Pt(phen)I_5]$. From ref. 1046.

Biguanidine and some of its derivatives form complexes with both Pd(IV) [1047,1048] and Pt(IV) [1047–1050]. The first Pt(IV) porphyrin $[Pt(TPP)Cl_2]$ (TPP = tetra-*p*-tolylporphinate(2 −)] has been prepared by oxidation of the Pt(II) complex [Pt(TPP)] with H_2O_2 in acetic acid, followed by treatment with HCl [1051]. It forms violet needle crystals.

Finally in nitrogen donors, we mention the Pt(IV) nitrile complexes $[Pt(RCN)_2X_4]$ (X = Cl, Br; R = Et, Pr, Bu, Ph) [1052–1056]. $Cs[Pt(MeCN)Cl_5]$ has also been claimed [1057].

P, As, Sb donors. There are no published reports of Pd(IV) complexes with monodentate P or As ligands. However, careful chlorine oxidation of the corresponding Pd(II) complex in CH_2Cl_2/CCl_4 produces $[PdL_2Cl_4]$ and $[Et_4N][PdLCl_5]$ (e.g. $L = P^nPr_3$) [913]. All are very unstable, decomposing in a few days.

Monodentate phosphine and arsine complexes of Pt(IV) have been the subject of many investigations (Table 6). Their stability follows the trends $P \sim As \gg Sb$ and $Cl \sim Br \gg I$. The *cis* and *trans* isomers of the invariably octahedrally coordinated Pt(IV) are usually separated by solubility dif-

TABLE 6

Pt(IV) complexes with monodentate P, As donor ligands

Complex type	Ligand	Stereochemistry [a]	Halide	Ref.
$[PtL_2X_4]$	PMe_3	*cis/trans*	Cl, Br, I [b]	902
	PEt_3	*cis*	Cl, Br	903
	PEt_3	*trans*	Cl, Br, I	903
	P^nPr_3	*cis/trans*	Cl	1058
	P^nBu_3	*cis/trans*	Cl	906
	PMe_2Ph	*trans*	Cl	532
	$AsMe_3$	*cis/trans*	Cl, Br	902
	$AsEt_3$	*cis*	Cl	903, 1059
	$AsEt_3$	*trans*	Cl, Br, I	903, 1059
	$AsMePh_2$		Cl, Br, I	1059
	$AsEtPh_2$	*trans*	Cl, Br	1060
	As^nPrPh_2	*trans*	Cl, Br	1060
	$SbMe_3$	*cis*	Cl, Br	1015
$[PtLCl_4]_2$	P^nPr_3		Cl	1058
$[PtL_3X_3]BF_4$	PMe_3	*mer*	Cl	902
$[PtL_3X_3]NO_3$	PMe_3	*mer*	Cl [c]	1061
$[PtL_3X_3]ClO_4$	PEt_3	*mer*	Cl	1062
$[Pr_4N][PtLX_5]$	PMe_3		Cl, Br, I	902
	PEt_3		Cl	1062
	P^nBu_3		Cl	1062
	$AsMe_3$		Cl, Br	902

[a] Where reported. [b] Iodides reported to be of low stability. [c] Identified in solution.

ferences (*trans* generally the more soluble isomer), although TLC has been used [906]. Isomerisation can occur on oxidation, for example *cis*-$[Pt(P^nPr_3)_2Cl_2]$ gives 30% *trans*-$[Pt(P^nPr_3)_2Cl_4]$ as well as the *cis* isomer [1058]. Both isomers are difficult to reduce, the *trans* particularly so [1058]. The standard redox potential of the system *trans*-$Pt(P^nPr_3)_2Cl_2/Pt(P^nPr_3)_2Cl_4$ was investigated [1039]. In a preliminary report [1063] $[Pt(PPh_3)_2F_2Cl_2]$ is said to be the decomposition product of $[Pt(PPh_3)_2Cl(SF_5)]$ and Pt(IV) fluoro complexes have been reported as unstable reaction intermediates [1064].

In bromination of Pt(II) complexes of olefin phosphine and arsine ligands e.g. $[Pt(p\text{-}CH_2{=}CHCH_2C_6H_4AsMe_2)_2Br_2]$, the halogen adds to the metal first to give Pt(IV), then to the double bond. However, in some cases rearrangement with the formation of Pt(IV)–σ-carbon bonds can occur [1065,1066].

Cis- and *trans*-$[Pt(PEt_3)_2Cl_4]$ have been X-rayed. For the *trans* isomer the

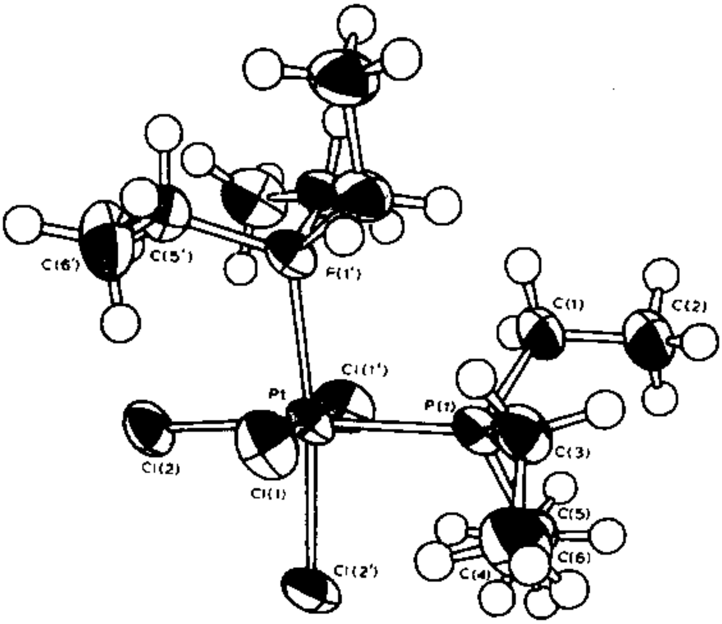

Fig. 60. The structure of *cis*-$[PtCl_4(PEt_3)_2]$. From ref. 1069.

bond lengths are given as Pt–P = 2.393(5) Å, Pt–Cl = 2.332(5) Å [532] and the nature of the bonding has been discussed [1067]. The *cis* isomer is distorted by steric interactions between the phosphines (P–$\widehat{\mathrm{Pt}}$–P = 98.1°, Pt–P = 2.335(3) Å, $\mathrm{Pt{-}Cl}_{trans\,P}$ = 2.394(3) Å, $\mathrm{Pt{-}Cl}_{trans\,Cl}$ = 2.321(3) Å [1068] (Fig. 60).

Vibrational spectra of Pt(IV) complexes of types $[PtLX_5]^-$, $[PtL_2X_4]$, $[PtL_3X_3]^+$ (L = PR_3, AsR_3) have been comprehensively studied [533,902,903,1069]. NMR (^1H, ^{13}C, ^{31}P, ^{195}Pt) studies have been reported, the proton NMR being characterised by smaller $^3J_{\mathrm{Pt-H}}$ coupling constants in Pt(IV) than in Pt(II), although the chemical shifts vary little between corresponding complexes in the two oxidation states [902,1061,1070,1071]. Proton NMR studies showed that in solution *trans*-$[Pt(PMe_3)_2I_4]$ is partially dissociated into $[Pt(PMe_3)_2I_2] + I_2$ even in the presence of excess iodine [902]. ^{13}C NMR data has been reported for a series of $[Pt(PR_3)_2Cl_4]$ complexes and $^2J_{\mathrm{Pt-C}}$ listed [1072]. The chemical shift of ^{31}P is not indicative of metal oxidation state in $Pt(PR_3)_2X_n$ ($n = 2$ or 4), and most phosphorus NMR studies have concentrated on the measurement of $^1J_{\mathrm{Pt-P}}$ and the relationship to the Pt–P bond [1062,1073,1074]. Although direct measurement of ^{195}Pt resonances is possible, parameters are often obtained via the INDOR technique [9]. The charge transfer spectra of *trans*-$[PtL_2X_4]$ (L =

PEt_3, $AsEt_3$) [13,533] and XPS data on $[Pt(PEt_3)_2Cl_4]$ [19] have been recorded.

Complexes of the type $[NBu_4][Pt(PY_3)X_5]$ (X = Cl, Br; Y = F, Cl, Br, OMe) have been prepared in solution, and in some cases isolated as stable solids in the absence of moisture [1075]. NMR studies show that *cis*-$[Pt(PF(OPh)_2)_2X_4]$ (X = Cl, Br) form in solution but cannot be isolated, but *cis*-$[Pt(P(OMe)_3)_2X_4]$ can be isolated easily, and $P(OEt)_3$, $P(O^iPr)_3$ analogues are known [1076–1079].

^1H NMR spectroscopy and double resonance techniques have been used to show that HX adds to *trans*-$[Pt(PEt_3)_2HY]$ (X, Y = Cl, Br, I) to give *trans*, *cis*-$[Pt(PEt_3)_2H_2XY]$ and if $X \neq Y$ halogen scrambling occurs. Hydrogen halides also add to *trans*-$[Pt(PEt_3)_2Y_2]$ to give $[Pt(PEt_3)_2HXY_2]$, but addition of X_2 to *trans*-$[Pt(PEt_3)_2HX]$ (X = Cl, Br) does not give the expected $[Pt(PEt_3)_2HX_3]$, but a mixture of $[Pt(PEt_3)_2H_2X_2]$ and $[Pt(PEt_3)_2X_4]$ [1061,1080]. Addition of HCl to $[Pt(PEt_3)_3H]^+$ yields $[Pt(PEt_3)_3H_2Cl]^+$ and of HX to *trans*-$[Pt(PEt_3)_2H(CN)]$ gives $[Pt(PEt_3)_2H_2X(CN)]$ at −80°C [1084]. The complexes *trans*, *cis*, *cis*-$[Pt(PEt_3)_2H_2X_2]$ were also characterised by IR and Raman spectroscopy [1080,1081]. A claim [1082] for $[Pt(PPh_3)_2H_2Cl_2]$ is mistaken; the material isolated was *trans*-$[Pt(PPh_3)_2HCl]$ [1083].

Complexes of type $[Pd(L{-}L)Cl_4]$ (L–L = $Ph_2PCH_2CH_2PPh_2$, *o*-$C_6H_4(AsMe_2)_2$ and $Me_2As(CH_2)_3AsMe_2$] can be produced by cautious chlorine oxidation of the $[Pd(L{-}L)Cl_2]$ analogue [913]. The chemistry of Pt(IV) with bidentate group VB ligands has been surprisingly neglected until recently. The far IR spectra of $[Pt(L{-}L)X_4]$ (X = Cl, Br; L–L = $Ph_2PCH_2CH_2PPh_2$, $Ph_2AsCH_2CH_2AsPh_2$) were reported [1085] but without preparative data, and it was claimed [1086] that $PtCl_4$ and $Ph_2AsCH_2CH_2AsPh_2$ gave a polymeric $[Pt(L{-}L)Cl_4]$ complex, polymerisation being inferred on the extremely tenuous grounds of poor solubility. The synthesis of a series of octahedral platinum(IV) complexes $[Pt(L{-}L)X_4]$ (X = Cl, Br; L–L = $Ph_2PCH_2CH_2PPh_2$, *cis*-$Ph_2PCH{=}CHPPh_2$, $Me_2AsCH_2CH_2CH_2AsMe_2$, *o*-$C_6H_4(AsPh_2)_2$, *cis*-$Ph_2AsCH{=}CHAsPh_2$, *o*-$C_6H_4(SbPh_2)_2$ and $Me_2Sb(CH_2)_3SbMe_2$), prepared by oxidation of $[Pt(L{-}L)X_2]$ with X_2 in CCl_4 solution has been described. The phosphine and arsine complexes are very stable thermally, but the stibines decompose slowly at ambient temperature and immediately in solution [1015]. Unstable $[Pt(L{-}L)I_4]$ were prepared which lose I_2 easily and are partially dissociated in solution. The complexes were characterised by IR, electronic and ^1H NMR spectroscopy [1015].

Bis(bidentate) complexes $[Pt(o\text{-}C_6H_4(AsMe_2)_2)_2X_2](ClO_4)_2$ (X = Cl, Br, I) [1087], and $[Pt(o\text{-}C_6H_4(PMe_2)_2)_2X_2](ClO_4)_2$ (X = Cl, Br) [519] were prepared by nitric acid oxidation of $Pt(L{-}L)_2X_2$ followed by addition of

$HClO_4$. The *trans* stereochemistry of $[Pt(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2]^{2+}$ has been confirmed by ^1H NMR spectroscopy and an unstable $[Pt(Ph_2PCH_2CH_2PPh_2)_2Cl_2](ClO_4)_2$ has been prepared [1015]. Oxidation of $Pt(L\text{–}L)_2Cl_2$ (L–L = $o\text{-}C_6H_4(AsMe_2)_2$, $o\text{-}C_6H_4(AsMe_2)(PMe_2)$, $Me_2PCH_2CH_2PMe_2$) produced bright yellow *trans*-$[Pt(L\text{–}L)_2Cl_2]Cl_2$, but when L–L = $o\text{-}C_6H_4(AsPh_2)_2$, *cis*-$Ph_2AsCH{=}CHAsPh_2$ or $Ph_2PCH_2CH_2PPh_2$ the products were $[Pt(L\text{–}L)Cl_4]$ and oxidised ligand [1015]. Palladium(IV) complexes are less stable, but $[Pd(o\text{-}C_6H_4(AsMe_2)_2)_2X_2](ClO_4)_2$ (X = Cl, Br only, cf. Pt) [1087] and $[Pd(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2](ClO_4)_2$ [519], were prepared by analogous routes to the platinum complexes. Preliminary X-ray data show that $[Pd(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2](ClO_4)_2$ has identical cell dimensions to the platinum analogue and hence is the *trans* isomer [1088].

Complexes of the N, As donor bidentate 8-dimethylarsinoquinoline (8-dmaq) are the $[Pt(8\text{-dmaq})_2Cl_2](ClO_4)_2 \cdot H_2O$ and $[Pd(8\text{-dmaq})_2Cl_2](ClO_4)_2$ prepared by nitric acid oxidation of the M(II) complexes followed by addition of $HClO_4$ [1089]. The unstable Pd(IV) complex was not obtained in an analytically pure condition.

The complexes of multidentate phosphines and arsines are limited. Orange $[Pt(MeAs(CH_2CH_2CH_2AsMe_2)_2)Br_3](ClO_4)$, red $[Pt(MeAs(CH_2CH_2CH_2AsMe_2)_2)I_3]I$ [1090], and pale yellow $[Pt(QAS)Cl_2]Cl_2$ (QAS = tris-(*o*-diphenylarsinophenyl)arsine) [1091,1092] have been prepared by halogen oxidation of the Pt(II) analogues. A comparatively unstable $[Pd(QAS)Cl_2]Cl_2$ was prepared only by using a large excess of chlorine [1091]. A recent study of $[Pt(PhP(CH_2CH_2PPh_2)_2)X_3]X$ and $[Pt(MeAs(CH_2CH_2CH_2AsMe_2)_2)X_3]X$ showed them to be the *mer* isomers [1015], whilst the complexes of the tripod tetradentates$[Pt(P(CH_2CH_2PPh_2)_3Cl_2]Y_2$ and $[Pt(As(CH_2CH_2CH_2AsMe_2)_3)Cl_2]Cl_2$ (Y = Cl, ClO_4) have the halides in a *cis* stereochemistry [1015]. Complexes of two linear tetradentates $[Pt(CH_2P(Ph)CH_2CH_2\text{-}PPh_2)_2Cl_2]Y_2$ and $[Pt o\text{-}C_6H_4(As(Me)CH_2CH_2CH_2AsMe_2)_2Cl_2]Cl_2$ are octahedral, but the detailed stereochemistry is unknown [1015]. Spectroscopic data on all these complexes were reported, and conductivity measurements suggest that whilst the tridentate ligand complexes are stable in solution, those of the tetradentates appear to rearrange with Cl^- displacing some of the coordinated group VB donors.

Group IVB. Potassium hexacyanoplatinate(IV) is readily prepared from $K_2[PtI_6]$ and KCN [1093,1094]; its IR and Raman spectra have been assigned [1095,1096] and the UV/visible spectrum of $[Bu_4N]_2[Pt(CN)_6]$ published [870]. Colourless $K_2[Pd(CN)_6]$ is obtained in poor yield (19%) by fractional crystallisation of the solution produced by reaction of $K_2[PdCl_6]$, KCN and $K_2S_2O_8$; the latter is necessary to prevent reduction [1097]. The preparation of salts with other cations including $H_2[Pt(CN)_6]$ [1098] and $[H_3O]_2[Pd(CN)_6]$ [1099] have been described [870,1094,1095,1098–1101,1111]. The X-ray study [1102] of $K_2[Pt(CN)_6]$ shows the anion is a regular octahedron with Pt–C = 2.005(6) Å and C–N = 1.1148 Å. Heavy metal cyanopalladates(IV) such as $Cd[Pd(CN)_6]$ have an uninterrupted cubic Cd–N–C–Pd framework with both metals in a perfectly regular octahedral environment Pd–C = 2.07(2) Å and C–N = 1.11(4) Å [1103].

The addition of halogens to aqueous $K_2[Pt(CN)_4]$ yields nearly colourless $K_2[Pt(CN)_4Cl_2]$, yellow $K_2[Pt(CN)_4Br_2]$ and dark brown $K_2[Pt(CN)_4I_2]$ respectively [961,1104–1108]. The chloride and bromide are indefinitely stable but the iodide loses iodine on standing [1104]. Vibrational and electronic spectra have been reported [962,1104,1107]. The addition of KCN to $K_2[Pt(CN)_4X_2]$ produces $K_2[Pt(CN)_5X]$ (X = Cl, Br, I) [1108,1109]. Assignment of the IR and Raman fundamentals in $M_2[Pt(CN)_5X]$ (M = Na, K, Cs; X = Cl, Br, I, CN) have been discussed [1096], and the solution electronic spectra interpreted [962]. Azido-complexes are produced from $K_2[Pt(CN)_4Br_2]$ and aqueous KN_3, a small excess of the latter giving $K_2[Pt(CN)_4N_3Br]$, and a large excess $K_2[Pt(CN)_4(N_3)_2]$ [1110].

Platinum(IV) carbonyls $[Pt(CO)X_5]^-$ (X = Cl, Br) have been prepared in solution by halogen oxidation of $[Pt(CO)X_3]^-$. IR spectroscopy showed the ν(CO) to be at 2184 cm^{-1} (for X = Cl), the highest value reported for a metal carbonyl in solution. Oxidation is incomplete even with excess halogen and the complexes decompose slowly in solution to $[Pt(CO)X_3]^-$ [1075].

Isocyanides are better ligands to Pt(IV) than CO, but less good than CN^-, paralleling the σ donor power of the three ligands. Neutral and cationic isocyanide complexes of types $[Pt(CNR)_2Cl_4]$, $[Pt(CNR)(PMe_2Ph)Cl_4]$, $[Pt(CNR)(PMe_2Ph)_2Cl_3]^+$ and $[Pt(CNR)_2(Me_2PhP)_2Cl_2]^{2+}$ (R = Me, ${}^tBu$, C_6H_{11}, *p*-tolyl) are prepared by chlorine oxidation of the platinum(II) analogues, and characterised by IR and ^1H NMR spectra. The cationic CN^tBu complexes readily lose the ${}^tBu$ moiety to form the corresponding cyanide complex. Isocyanide–cyanide compounds $[Pt(CNR)_2(CN)_2Cl_2]$ and $[Pt(CNR)(CN)(PMe_2Ph)_2Cl_2]^+$ are also known (R = ${}^tBu$) [1112]. *Cis*-$[Pt(CNMe)_2X_4]$ and $[Bu_4N][Pt(CNMe)X_5]$ (X = Cl, Br) have been characterised by IR, Raman, ^1H NMR and INDOR measurements [1113]. The electrochemical oxidation of $[Pt(CNR)L_2Cl]^+$ (L = PR_3) has also been investigated [1114].

Platinum(IV) silyl, germyl and stannyl complexes are usually unstable, and readily eliminate two ligands to give Pt(II). They are thought to be intermediates in many addition–elimination reactions, e.g. [1115,1116]. However, a number of complexes have been identified and some isolated. *Trans*-$[Pt(PEt_3)_2(SiH_2I)I]$ adds HI to give $[Pt(PEt_3)_2(SiH_2I)(H)I_2]$ isolated, and characterised by IR and NMR spectroscopy [1117]. The same complex is formed from *trans*-[Pt(PEt$_3$)$_2$I$_2$] and SiH$_3$I in benzene [1117]. The silylacetylenes YC≡CSiH$_3$ (Y = H, CF$_3$) react with *trans*-[Pt(PEt$_3$)$_2$I$_2$] at 243 K to give [Pt(PEt$_3$)$_2$(SiH$_2$C≡CY)(H)I$_2$], which were characterised by NMR, but were too unstable to isolate [1071,1116]. Oxidative addition of EXH$_3$ to *trans*-[Pt(PEt$_3$)$_2$I$_2$] yields [Pt(PEt$_3$)$_2$(EH$_2$X)(H)I$_2$] (E = Si, Ge; X = Cl, Br, I), identified by NMR, which slowly lose H$_2$ at room temperature [1071,1118]. Treatment of [Pt(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(PEt$_3$)GeMe$_3$]Cl with HCl in benzene precipitates white [Pt(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(PEt$_3$)(GeMe$_3$)HCl]Cl, identified by IR spectroscopy [1119]. The reaction between *trans*-[Pt(PEt$_3$)$_2$HCl] or *trans*-[Pt(PEt$_3$)$_2$(GeH$_2$Cl)Cl] and an excess of GeH$_3$Cl in benzene gives a mixture of four products of the type [Pt(PEt$_3$)$_2$(GeH$_2$Cl)$_n$(GeHCl$_2$)$_{3-n}$H] ($n = 1$–3) [1120,1121].

[Pt(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(SnMe$_3$)$_2$HCl] is formed reversibly in benzene solution from [Pt(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(SnMe$_3$)Cl] and Me$_3$SnH, whilst [Pt(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(SnMe$_3$)$_2$] and Me$_3$SnH gives [Pt(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(SnMe$_3$)$_3$H] [1122]. Pale orange-yellow [Pt(PPh$_3$)$_2$(SnCl$_3$)$_2$Cl$_2$] rapidly precipitates from a solution of *trans*-[Pt(PPh$_3$)$_2$HCl] and SnCl$_4$ in benzene [1123]. Its ^{119}Sn Mössbauer spectrum has been reported [1124]. R$_3$SnH (R = Ph, PhCH$_2$, *o*-, *m*-, *p*-MeC$_6$H$_4$) react with [Pt(PMe$_2$Ph)$_2$CO$_3$] in methanol to give *cis*, *trans*, *cis*-[PtH$_2$(SnR$_3$)$_2$(PMe$_2$Ph)$_2$], which reversibly lose H$_2$ in benzene, and which were identified by ^{1}H and ^{31}P(^{1}H) NMR [1115]. *Cis*, *trans*-[PtH$_2$(SnR$_3$)$_2$(bipy)] is formed from R$_3$SnH and [Pt(bipy)CO$_3$] [1125].

Mixed valence compounds

Palladium and especially platinum form a number of compounds of empirical formulae ML$_2$X$_3$ or ML$_4$X$_3$ (L = monodentate, L$_2$ = bidentate, usually N-donor, X = halide) which contain M^{II} and M^{IV} units linked in chains X$\cdots$M$^{II}\cdots$X$\cdots$M$^{IV}\cdots$X, which are mixed valence Class II compounds on the Robin and Day [1126] classification. The metal oxidation states are "trapped" and the two metal atom sites are structurally distinguishable. The complexes are strongly dichroic, display intense broad absorption bands in the visible or near IR region, and have high electrical conductivity along the chains. Such complexes show intense resonance Raman spectra [971,1127,1128]. It is notable that Pd(IV) entities seem to be greatly stabilised in these mixed valence compounds [971,1129]. The area was reviewed some years ago [1126] and a recent review [1130] discusses a theoretical approach to such compounds. X-ray data on various examples have appeared [1126,1131 and refs. therein].

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ADDENDUM

This brings the coverage up to the end of 1981 literature.

Section C(i)

The ^{99}Ru and ^{101}Ru NMR spectra of RuO_4 have been recorded [A1], and the reaction of OsO_4 with cytosine in the presence of amines studied [A2].

Section C(iii)

X-ray powder patterns of $M_2[OsO_2(OH)_4]$ ($M = K$, Rb, Cs) have been recorded and indexed [A3]. A simplified apparatus for preparing RuF_6 has been described, and some reactions of the product studied, e.g. its reduction to RuF_5 and RuF_4, and the formation of Lewis acid–base adducts with non-metal fluorides [A4].

The structure of $OsOF_4$ in the vapour phase has been determined by electron diffraction [A5]. The reaction of OsO_4 with glycine produces *trans*-$OsO_2(NH_2CH_2CO_2)_2$ which has been characterised by a single crystal X-ray study [A6]. Raman and IR data have been reported for $[OsO_2(SO_3)_4]^{6-}$ [A7]. The X-ray crystal structures of $[Ph_4As][OsNBr_4]$ [A8] and $[Ph_4As][RuNBr_4]$ [A9] have been determined; the anions are square pyramidal as expected (cf. Table 4), $Os{-}N = 1.583(15)$ Å, $Os{-}Br = 2.457(1)$ Å, $Ru{-}N = 1.580(11)$ Å, $Ru{-}Br = 2.453(1)$ Å. Polarised single crystal electronic spectra of $[OsNX_4]^-$ ($X = Cl$, Br, I) and $[RuNX_4]^-$ ($X = Cl$, Br) as $AsPh_4^+$ salts have been studied and assigned [A8,A9].

Section C(v)

A number of sodium ruthenates(IV) have been characterised including $Na_4[RuO_4]$, $Na[Ru_4O_8]$, $Na_2[RuO_3]$ and $Na_4[Ru_3O_8]$ [A10]. The reversible electrochemical reduction of the $Ru_4(OH)_{12}^{4+}$ ion has been demonstrated [A11]. The preparation of a material of composition $OsCl_4(SCl_4)_2$ has been described [A12]; it may be $[SCl_3]_2[OsCl_6]$. Two papers dealing with ligand exchange reactions in chlorobromoosmates(IV)$[OsCl_{6-n}Br_n]^{2-}$ have been published [A13,A14].

Blue crystals of $[OsCl(O_2CMe)(O_2CCF_3)_2(py)_2]$ are formed from $[OsCl(O_2CMe)_2]_n$ and AgO_2CCF_3 in the presence of pyridine [A15]. The $[(PPh_3)_4RuH_3]^+$ cation has been identified in solution by ^{31}P and ^1H NMR spectroscopy [A16].

A further study has been made [A17] of the reduction of "ruthenium brown" by OH^- ions.

Dinuclear osmium(IV) compounds studied include $[(OEP)Os(OMe)]_2O$ [A18], $[Os(PR_3)X_2]_2O(O_2CR)_2$ [A19] and $[Os_2N(SO_3)(NH_3)_8(H_2O)]^{3+}$ [A7].

Section D

A short account of the effect of pH upon the $[RhO_4]^{3-}$ ion solution has been published [A20], and the luminescence spectra of $[IrCl_6]^{2-}$ and $[IrBr_6]^{2-}$ in various hosts have been recorded [A21].

Section E

Hexahydroxopalladates(IV) $M_2[Pd(OH)_6]$ (M = K, Rb) [A22] and $M^{II}[Pd(OH)_6]$ (M = Ca, Sr, Ba) [A23] have been prepared. On heating they decompose to M_xPdO_3, ($x = 2$(K, Rb), $x = 1$(Ca, Sr, Ba)). The bromine oxidation of *trans*-$[Pt(PEt_3)_2Cl_2]$ in the dark gives the all *trans*-$[Pt(PEt_3)_2Br_2Cl_2]$, which has Pt–Cl = 2.358(2) Å, Pt–Br = 2.469(1) Å, Pt–P = 2.410(3) Å [A24]. In solution in the presence of light, halogen scrambling occurs to give a mixture of $[Pt(PEt_3)_2Cl_{4-n}Br_n]$ ($n = 1$–4). Substances of formulae $[PtCl_4(ECl_2)_2]$ (E = S, Se) $[PtCl_4(QCl_4)_2]$ (Q = Se, Te) are known [A12].

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