1 Ruthenium and osmium

1.1 Introduction

Ruthenium and osmium are the first pair of 'platinum metals' [1–13]. They exhibit oxidation states up to +8, the highest observed for any element, as in MO_4 (M = Ru, Os) though this requires the use of the most electronegative elements, fluorine and oxygen, for stability. Generally, the +2 and +3 states are the most important, along with +4 for osmium; however, there is a considerable chemistry of the MO_2^{2+} ('osmyl' and 'ruthenyl') and $M{\equiv}N^{3+}$ groups, as well as the 'classical' hydride complexes $OsH_6(PR_3)_2$, which also involve osmium(VI).

1.2 The elements and uses

Along with iridium, osmium was discovered in 1803 by Smithson Tennant. He took the insoluble residue from the digestion of platinum ores with aqua regia and heated it with sodium carbonate to give soluble yellow $OsO_4(OH)_2^{2-}$. On acidification, distillable OsO_4 formed. Noting the smell of the (very toxic) tetroxide, Tennant gave the element its name from the Greek *osme* ($o\sigma\mu\eta$ = smell); he also noted that it stained the skin, prefiguring a future use.

The last of the metals described in this book to be discovered was ruthenium. As with osmium, it was extracted from the aqua regia-insoluble residue from concentrated platinum ores and was first claimed in 1826 by G.W. Osann but definitely characterized by K.K. Klaus (1844), who oxidized the residue with KOH/KNO_3, acidified and distilled off the OsO_4 then reacted the residue with NH_4Cl. (Aqua regia is a 3 : 1 mixture of concentrated HCl/HNO_3 (containing some chlorine).) Thermal decomposition of the resulting $(NH_4)_2RuCl_6$ in an inert atmosphere gave ruthenium, taking its name from *ruthenia*, the Latin name for Russia.

Both of these elements are silver–white lustrous metals with high melting (ruthenium 2310°C, osmium 3900°C) and boiling (3900 and 5510°C, respectively) points. As usual, the 5d metal is much more dense (ruthenium 12.45, osmium 22.59 g cm^{-3}); both adopt hcp structures; osmium is the densest metal known. The metals are unreactive, insoluble in all acids, even aqua regia. Ruthenium tends to form a protective coating of the dioxide and is not attacked by oxygen below 600°C nor by chlorine or fluorine below

300°C. Powdered osmium is slowly attacked by oxygen at room temperature, yielding OsO_4 (though not below 400°C if in bulk). Osmium reacts with fluorine and chlorine at about 100°C. Both metals are attacked by molten alkalis and oxidizing fluxes.

Ruthenium nowadays finds many uses in the electronics industry, particularly for making resistor tracks. It is used as an ingredient in various catalysts and, importantly, in electrode materials, e.g. RuO_2-coated titanium elements in the chloralkali industry. Osmium tetroxide is a very useful organic oxidant and, classically, is used as a tissue stain. Both elements are employed in making certain platinum alloys.

1.2.1   Extraction

Extraction of ruthenium and osmium is done by solvent extraction [1, 2, 5, 14]. Following the traditional route, however, aqua regia-insoluble residues or anode slimes from nickel refining undergo bisulphate oxidation to remove rhodium, then on alkaline fusion ruthenium and osmium are stabilized as Na_2RuO_4 and $Na_2OsO_2(OH)_4$. The ruthenium(VI) can be reduced (alcohol) to RuO_2, which is then converted into $(NH_4)_3RuCl_6$, giving ruthenium metal in a flow of hydrogen at 100°C. Osmium can be precipitated and stored as $K_2OsO_2(OH)_4$ or first converted into OsO_4 (by distillation of the osmate with HNO_3) which is then reduced with hydrogen or turned into $(NH_4)_2OsCl_6$, reduced in the same manner as the ruthenium analogue.
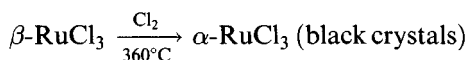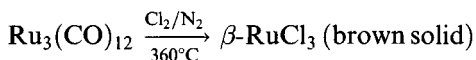
In the solvent-extraction process, the platinum metal concentrate is solubilized in acid using chlorine oxidant. Ruthenium and osmium are separated by turning them into the volatile tetroxides.

1.3   Halides

1.3.1   Ruthenium halides

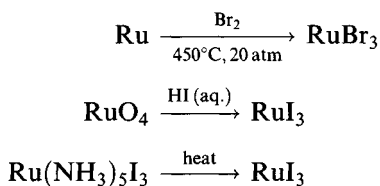Ruthenium forms the whole range of trihalides but only fluorides in higher states.

RuF_3 can be made by iodine reduction of RuF_5. It is obtained as a dark brown powder that contains corner-shared RuF_6 octahedra [15]. $RuCl_3$ exists in α- and β-phases:

$$Ru_3(CO)_{12} \xrightarrow[360°C]{Cl_2/N_2} \beta\text{-}RuCl_3 \text{ (brown solid)}$$

$$\beta\text{-}RuCl_3 \xrightarrow[360°C]{Cl_2} \alpha\text{-}RuCl_3 \text{ (black crystals)}$$

The α-form has the α-$TiCl_3$ structure with 6-coordinate ruthenium and a rather long Ru–Ru distance (3.46 Å) compared with the β-form where

there are one-dimensional chains, again with octahedrally coordinated ruthenium (Ru−Ru 2.83 Å). The β-form transforms irreversibly to the α-form above 450°C. Both these forms are insoluble in water though β-RuCl$_3$ dissolves in ethanol [16].

Commercial 'ruthenium trichloride' purporting to be RuCl$_3$.xH$_2$O is an ill-defined mixture of oxochloro and hydroxychloro species of more than one oxidation state. Obtained by dissolving RuO$_4$ in hydrochloric acid, it can be purified by repeatedly evaporating to dryness with concentrated HCl. RuBr$_3$ is usually made by brominating the metal while several routes to RuI$_3$ are open

$$Ru \xrightarrow[450°C,\, 20\,atm]{Br_2} RuBr_3$$

$$RuO_4 \xrightarrow{HI\,(aq.)} RuI_3$$

$$Ru(NH_3)_5I_3 \xrightarrow{heat} RuI_3$$

Black–brown RuBr$_3$ has roughly octahedral coordination of ruthenium (Ru−Br 2.46–2.54 Å) with short Ru−Ru contacts (2.73 Å) [17]. Black RuI$_3$ has a similar structure. Neither is particularly soluble in water.

RuF$_4$ can be made as a deep pink solid:

$$K_2RuF_6 \xrightarrow{AsF_5/HF} RuF_4$$
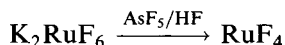
It has a VF$_4$ type puckered sheet structure with 6-coordinated ruthenium; four fluorines bridge, two non-bridging ones are *trans* with the terminal distances shorter as expected (Table 1.1). It is paramagnetic ($\mu_{eff} = 3.04\,\mu_B$ at room temperature).

Green RuF$_5$, sublimeable *in vacuo* (65°C, 10^{-8} torr (1.33×10^{-6} Pa)) can be made by fluorination

$$Ru \xrightarrow{F_2} RuF_5$$

$$Ru \xrightarrow{BrF_3} BrF_2^+RuF_6^- \xrightarrow{120°C} BrF_3 + RuF_5$$
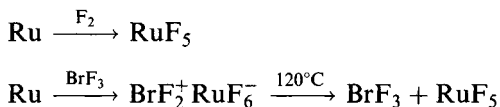
It melts at 86.5°C and boils at 227°C. The tetrameric structure (Figure 1.1) is one adopted by a number of pentafluorides with *cis*-bridges completing the 6-coordination.

Table 1.1 Bond lengths (Å) in ruthenium fluorides

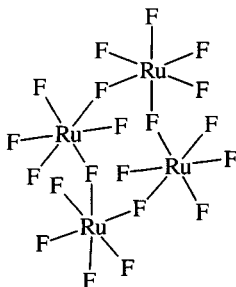|	Ru−F (terminal)	Ru−F (bridge)
RuF$_3$	–	1.982
RuF$_4$	1.82	2.00
RuF$_5$	1.795–1.824	1.995–2.007
RuF$_6$	1.824	–

Figure 1.1 The tetrameric structure of RuF_5.

A second, red form has recently been reported; from mass spectral evidence, it may be a trimer. In the gas phase at 120°C, it consists mainly of a trimer (with octahedrally coordinated Ru) [18].

RuF_6 is made by fluorination of RuF_5 under forcing conditions:

$$RuF_5 \xrightarrow[50\,\text{atm},\,230°C]{F_5} RuF_6$$
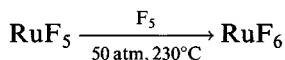
It is an extremely moisture-sensitive dark brown solid (m.p. 54°C); bond lengths have been obtained from an EXAFS study [19].

There is some evidence that $RuCl_3$ reacts with chlorine in the gas phase above 400°C to form $RuCl_4$ but $RuCl_4$ has not been authenticated as a solid, neither has RuF_8, which is claimed to exist at low temperatures.
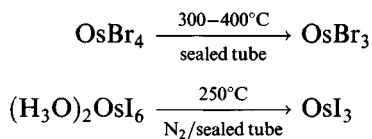
1.3.2   Osmium halides

Unlike ruthenium (and other platinum metals) osmium forms chlorides and bromides in a range of oxidation states [11, 12].

There are no convincing reports of halides in oxidation states below III: early reports of OsI and OsI_2 seem to result from oxide contaminations. Neither is there OsF_3, evidence of the greater stability of the +4 state compared with that of ruthenium.

Dark grey $OsCl_3$ has the 6-coordinate α-$RuCl_3$ structure

$$OsCl_4 \xrightarrow[Cl_2,\,100-500\,\text{torr}]{470°C} OsCl_3$$
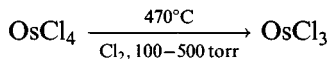
Black $OsBr_3$ and OsI_3 ($\mu = 1.8\,\mu_B$) are also prepared by thermal methods

$$OsBr_4 \xrightarrow[\text{sealed tube}]{300-400°C} OsBr_3$$

$$(H_3O)_2OsI_6 \xrightarrow[N_2/\text{sealed tube}]{250°C} OsI_3$$
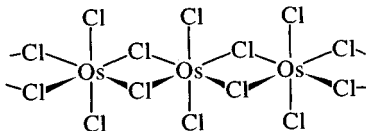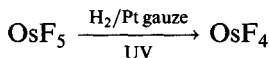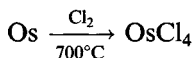
There is evidence for $OsX_{3.5}$ (X = Cl, Br).

Figure 1.2 The structure adopted by $OsCl_4$.

OsF_4, a yellow–brown solid that distills as a viscous liquid, is made by reduction of solutions of OsF_5

$$OsF_5 \xrightarrow[UV]{H_2/Pt\ gauze} OsF_4$$

It is isomorphous with MF_4 (M = Pd, Pt, Ir, Rh).

Black $OsCl_4$ exists in two forms. A high-temperature form is made by reaction of the elements
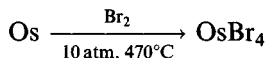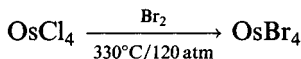
$$Os \xrightarrow[700°C]{Cl_2} OsCl_4$$

It has 6-coordinate osmium in a structure (Figure 1.2) regarded as being made from a hexagonally packed array of chlorides with osmiums occupying half the holes in alternate layers; Os–Cl bond lengths are 2.261 Å (terminal) and 2.378 Å (bridge) [20].

The low-temperature form is made using thionyl chloride as the chlorinating agent.

$$OsO_4 \xrightarrow[reflux]{SOCl_2} OsCl_4$$
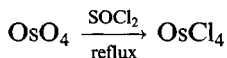
Black $OsBr_4$ (PtX_4 structure) has 6-coordinate osmium [21]

$$OsCl_4 \xrightarrow[330°C/120\ atm]{Br_2} OsBr_4$$

$$Os \xrightarrow[10\ atm,\ 470°C]{Br_2} OsBr_4$$

A second form can be made by refluxing OsO_4 with ethanolic HBr, then drying the product.

The green–blue pentafluoride (m.p. 70°C, b.p. 226°C) is thermochromic, becoming bright blue at its boiling point (the vapour is colourless). It is synthesized by reducing OsF_6: it has the tetrameric structure adopted by RuF_5 (Os–F = 1.84 Å (terminal) 2.03 Å (bridge)) in the solid state [18c].

$$OsF_6 \xrightarrow[55°C]{I_2/IF_5} OsF_5$$
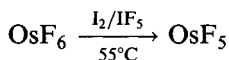
Like RuF_5, it is mainly a trimer $(OsF_5)_3$ in the gas phase.

In contrast to this, very moisture-sensitive black $OsCl_5$, prepared by chlorinating OsF_6 using BCl_3 as the chlorinating agent, has the dimeric

$ReCl_5$ structure (Os−Cl = 2.24 Å (terminal) 2.42 Å (bridge)). Its magnetic moment is 2.54 μ_B

$$OsF_6 \xrightarrow[RT]{BCl_3} OsCl_5$$
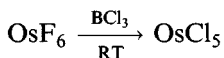
Like several other heavy metals, osmium forms a volatile (bright yellow) hexafluoride (m.p. 33.2°C, b.p. 47°C)

$$Os + 3F_2 \xrightarrow[1\,atm]{250-300°C} OsF_6$$
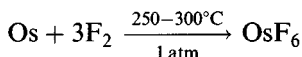
The solid is polymorphic, with a cubic structure above 1.4°C. A bond length of 1.816 Å has been obtained from EXAFS measurements at 10 K, while vapour phase measurements give Os−F of 1.831 Å [22].

There is uncertainty about the heptafluoride, claimed to be formed as a yellow solid from fluorination under very high pressure

$$Os \xrightarrow[600°C/450\,atm]{F_2} OsF_7$$
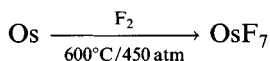
Material with the same IR spectrum has been obtained by fluorination of OsO_3F_2 at 180°C (50 atm). OsF_7 is said to decompose at −100°C (1 atm fluorine pressure) [23].

As osmium forms a tetroxide, OsF_8 might possibly exist, especially in view of the existence of the osmium(VIII) oxyfluorides, but MO calculations indicate the Os−F bond would be weaker in the binary fluoride. It is also likely that non-bonding repulsions between eight fluorines would make an octafluoride unstable [23b].

1.3.3 Oxyhalides

Much less is known about ruthenium oxyhalides than about the osmium compounds. The only compound definitely characterized [24] is $RuOF_4$, synthesized by fluorination of RuO_2, condensing the product at −196°C. It loses oxygen slowly at room temperature, rapidly at 70°C.

$$RuO_2 + 2F_2 \xrightarrow{300-400°C} RuOF_4 + \tfrac{1}{2}O_2$$
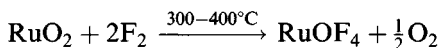
It has also been made by passing RuF_5 vapour down a hot glass tube:

$$RuF_5 + SiO_2 \longrightarrow RuOF_4 + SiF_4$$
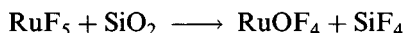
It gives the parent ion in the mass spectrum and has a simple IR spectrum (ν(Ru=O) 1040 cm^{-1} and (ν(Ru−F) 720 cm^{-1}) similar to that of the vapour (1060, 710, 675 cm^{-1}), implying a monomeric structure. Chlorides $RuOCl_2$ and Ru_2OCl_x ($x = 5, 6$) have been claimed; various oxo complexes $Ru_2OX_{10}^{4-}$ are well defined.

Although no OsF_8 has been described, there are oxofluorides in the +8 state.

Table 1.2 Vibrational frequencies[a] for osmium oxyhalides

	State[b]	Vibrational frequencies (cm^{-1})		
		Os=O	Os–F (term)	Os–F (bridge)
cis-OsO_2F_4				
Raman		942, 932	672, 579, 571	
IR		940, 930	675, 588, 570	
OsO_3F_2		954 (947, 942)		
	Matrix	931	646	
$OsOF_5$		960	710, 700, 640	
	Matrix	966.5	713, 638.5	
	Vapour	964	717, 700, 645	
OsO_2F_3		995, 955	720	480–580 (broad)
	Matrix	907	655	
$OsOF_4$		1018	735, 705, 657, 648	529, 423
	Matrix	1079.5	685	
$OsOCl_4$		1028	392 (Os–Cl)	
	Matrix	1032	395	
	Gas	1028	397	

[a] Only IR except for OsO_2F_4; [b] solid unless otherwise stated.

Deep red OsO_2F_4 (m.p. 89°C) has recently been made [25]

$$OsO_4 \xrightarrow[-196°C]{HF/KrF_2} cis\text{-}OsO_2F_4$$
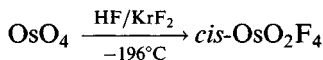
It is thermally stable but instantly hydrolysed in air (like osmium oxyhalides in general); it has a simple vibrational spectrum (ν(Os=O) 940 cm^{-1}; ν(Os–F) 680, 590, 570 cm^{-1}) (Table 1.2) and a cis-octahedral structure has been confirmed by an electron diffraction study (Os=O 1.674 Å, Os–F 1.843–1.883 Å).

Several syntheses have been reported for orange–yellow diamagnetic OsO_3F_2 (m.p. 172–173°C) [26]:

$$OsO_4 \xrightarrow[300°C]{F_2} OsO_3F_2$$

$$OsO_4 \xrightarrow[RT]{ClF_3} OsO_3F_2$$
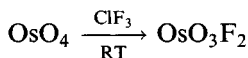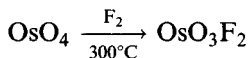
OsO_3F_2 is a monomer in the gas phase, to which a monomeric D_{3h} structure has been assigned. EXAFS and X-ray diffraction measurements show a 6-coordinate solid-state structure with cis-fluorine bridges (Figure 1.3) (Os=O 1.678–1.727 Å, Os–F 1.879 Å (terminal), 2.108–2.126 Å (bridge)).

The other possible osmium(VIII) oxyfluoride $OsOF_6$ has so far eluded synthesis and recent ab initio MO calculations indicate it is unlikely to exist.

Emerald green $OsOF_5$ (m.p. 59.5°C; b.p. 100.6°C) has an octahedral struc-ture like OsF_6 but is rather less volatile (Os=O 1.74 Å, Os–F 1.72 Å (trans) 1.76–1.80 Å (cis)) [27]. It is paramagnetic ($\mu_{eff} = 1.47\,\mu_B$ at 298 K) and ESR
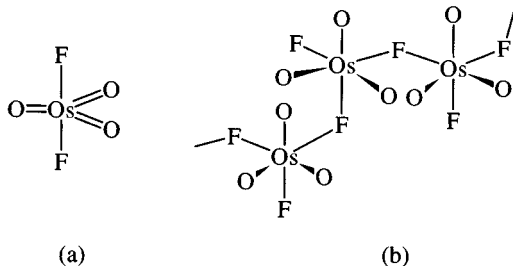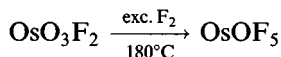
(a)   (b)

Figure 1.3 The structure of OsO_3F_2 in (a) the gas phase and (b) the solid state.

studies in low-temperature matrices indicate delocalization of the unpaired electron 11.5% from the osmium $5d_{xy}$ orbital to each equational fluorine. Syntheses include

$$OsO_3F_2 \xrightarrow[180°C]{\text{exc. } F_2} OsOF_5$$

On heating a $3:1$ OsF_6/OsO_4 mixture at 150–200°C, a mixture of $OsOF_5$ and OsO_4 is obtained that can be separated by using the greater volatility of $OsOF_5$.

OsO_2F_3 is a yellow–green solid, disproportionating at 60°C to OsO_3F_2 and $OsOF_4$, from which it may be made:

$$OsOF_4 + OsO_3F_2 \xrightarrow[12\,h]{100°C} 2OsO_2F_3$$

$$OsO_4 + OsF_6 \xrightarrow[17\,h]{150°C} 2OsO_2F_3$$
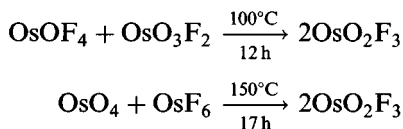
Matrix isolation studies suggest isolated D_{3h} molecules, but the pure solid has a more complicated IR spectrum indicating both bridging and terminal fluorines [28].

Blue–green $OsOF_4$ (m.p. 80°C) is a byproduct in the synthesis of $OsOF_5$ and can also be made in small quantities by reduction of $OsOF_5$ on a hot tungsten wire. In the gas phase it has a C_{4v} pyramidal structure (Os=O 1.624 Å, Os–F 1.835 Å); crystallography suggests a solid-state structure similar to tetrameric OsF_5; the more complex IR spectrum of the solid is in keeping with this [29].

Oxychlorides are less prolific, apart from the red–brown $OsOCl_4$ (m.p. 32°C). This probably has a molecular structure in the solid state as the IR spectra of the solid, matrix-isolated and gas-phase molecules are very similar, and the volatility is consonant with this [30]. Syntheses include heating osmium in a stream of oxygen/chlorine ('oxychlorination') and by:
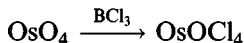
$$OsO_4 \xrightarrow{BCl_3} OsOCl_4$$

Table 1.3 Bond lengths in MX_6^{n-} (Å)

n	RuF_6	$RuCl_6$	$RuBr_6$	OsF_6	$OsCl_6$	$OsBr_6$
0	1.824 (EX)			1.816 (EX)		
				1.831 (ED)		
1	1.845 (EX)			1.882 (EX)	2.284 (X)	
	1.85 (X)				2.303 (X)	
2	1.916 (EX)	2.29 (X)		1.927 (EX)	2.332 (X)	~2.5 (X)
		2.318 (X)			2.336 (X)	
3		2.375 (X)	2.514 (X)			

ED, electron diffraction; X, X-ray; EX = EXAFS.

Electron diffraction measurements on the vapour indicate a C_{4v} square pyramidal structure ($Os=O$ 1.663 Å, $Os-Cl$ 2.258 Å; $O-Os-Cl$ 108.3° $Cl-Os-Cl$ 84.4°) with osmium 0.709 Å above the basal plane.

$OsOCl_2$ can be made as dark olive green needles from heating $OsCl_4$ in oxygen [31]. There are also reports of $OsO_{0.5}Cl_3$ (probably Os_2OCl_6) and a corresponding bromide [32].

1.3.4   Halide complexes

The complexes of ruthenium and osmium in the same oxidation state are generally similar and are, therefore, treated together; the structural (Table 1.3) and vibrational data (Table 1.4) have been set out in some detail to demonstrate halogen-dependent trends.

No complexes have at present been authenticated in oxidation states greater than +6, whereas oxyhalide complexes exist where the +8 state is known; this parallels trends in the halides and oxyhalides.

Oxidation state +6
Reaction of NOF with OsF_6 produces $NO^+OsF_7^-$, along with some $NO^+OsF_6^-$.

Table 1.4 Vibrational frequencies in MX_6^{n-} species (cm^{-1}) (M = Ru, Os; X = halogen)

n	RuF_6	$RuCl_6$	$RuBr_6$	RuI_6	OsF_6	$OsCl_6$	$OsBr_6$	OsI_6
0	675, 735				731, 720			
1	660, 630				688, 616	375, 325		
					(XeF_5^+)	(Et_4N)		
2	609, 581	328, 327	209, 248		608, 547	344, 313	211, 227	152, 170
		(Cs)	(K)		(Cs)	(Cs)	(K)	(Bu_4N)
3		–, 310 (K)	184, 236			313, 294	201, 200	144, 140
			$(PhNH_3^+)$			$(Co(en)_3)$	$(Co(en)_3)$	$(Co(en)_3)$

The first figure given for each species is ν_1 (A_{1g}), the second is ν_3 ($T_{1\mu}$).
Data are for ions in solution except where a counter-ion is indicated.

*Oxidation state +5*
Fluorination of a mixture of alkali metal halide and an appropriate ruthenium or osmium halide affords cream $MRuF_6$ (M = alkali metal, Ag; $\mu_{eff} = 3.5$–$3.8\,\mu_B$) or white $MOsF_6$:

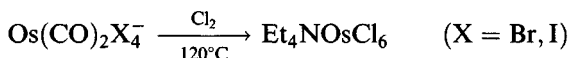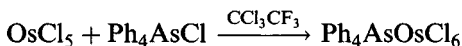$$RuCl_3 \text{ or } OsF_4 \xrightarrow[\text{BrF}_3 \text{ or } F_2]{\text{MCl}} MRuF_6 \text{ or } MOsF_6$$
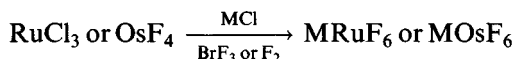
They contain octahedral MF_6^- (Table 1.3) [33]; in $XeF^+RuF_6^-$ the attraction of XeF^+ distorts the octahedron by pulling one fluorine towards it, so that there is one long Ru–F distance of $1.919\,\text{Å}$ compared with the others of 1.778–$1.835\,\text{Å}$ (EXAFS measurements indicate $KRuF_6$ has regular octahedral coordination (Ru–F $1.845\,\text{Å}$)) [19].

Magnetic moments are as expected for d^3 ions. Disproportionation occurs on hydrolysis:

$$MF_6^- \xrightarrow{\text{H}_2\text{O}} MO_4 + MF_6^{2-}$$
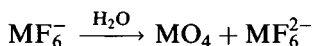
Octahedral $OsCl_6^-$ has been isolated as Ph_4As, Ph_4P and Ph_4N salts (μ_{eff} values of 3.21 and $3.03\,\mu_B$ have been reported) [34]:

$$OsCl_5 + Ph_4AsCl \xrightarrow{\text{CCl}_3\text{CF}_3} Ph_4AsOsCl_6$$

$$Os(CO)_2X_4^- \xrightarrow[120°C]{\text{Cl}_2} Et_4NOsCl_6 \qquad (X = Br, I)$$

$OsCl_6^-$ is reduced to $OsCl_6^{2-}$ in contact with most solvents (e.g. CH_2Cl_2); the redox potential for $OsCl_6^-/OsCl_6^{2-}$ is 0.8 V and for $OsBr_6^-/OsBr_6^{2-}$ it is 1.20 V. PbO_2 can be used to form a transient $OsBr_6^-$ ion by oxidizing $OsBr_6^{2-}$; it will also oxidize $OsCl_6^{2-}$ to $OsCl_6^-$.

Cation size can affect bond lengths in $OsCl_6^-$; Os–Cl is $2.284\,\text{Å}$ and $2.303\,\text{Å}$ in the Ph_4P and Bu_4N salts, respectively. Oxidation, however, has a more significant effect, so that Os–Cl in $(Ph_4P)_2OsCl_6$ is $2.332\,\text{Å}$.
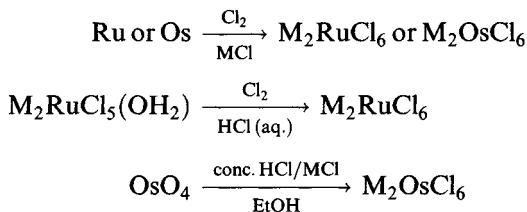
Oxidation state +4
All MX_6^{2-} have been isolated except RuI_6^{2-}. MF_6^{2-} can be made by hydrolysis of MF_6^-, as already mentioned, but other methods are available:

$$RuCl_3 + BaCl_2 \xrightarrow{\text{F}_2} BaRuF_6$$
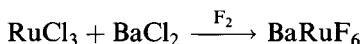
Yellow Na_2RuF_6 has the Na_2SiF_6 structure while M_2RuF_6 adopts the K_2GeF_6 structure (M = K to Cs). EXAFS indicates Ru–F is $1.934\,\text{Å}$ in K_2RuF_6 while in K_2OsF_6 Os–F is $1.927\,\text{Å}$ [35]. Magnetic moments are as expected for a low spin d^4 ion (K_2RuF_6 $2.86\,\mu_B$, Cs_2RuF_6 $2.98\,\mu_B$, K_2OsF_6 $1.30\,\mu_B$, Cs_2OsF_6 $1.50\,\mu_B$); the lower values for the osmium compounds are a consequence of the stronger spin-orbit coupling for the 5d metal.
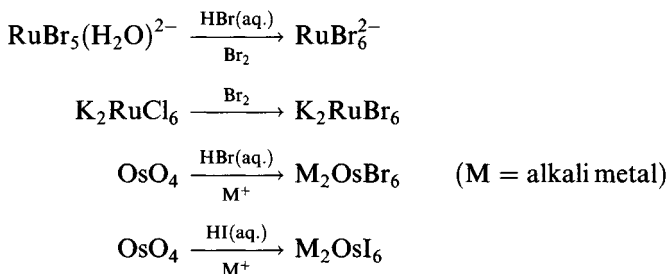
Various routes are available for the chlorides [36]:

$$\text{Ru or Os} \xrightarrow[\text{MCl}]{Cl_2} M_2RuCl_6 \text{ or } M_2OsCl_6$$

$$M_2RuCl_5(OH_2) \xrightarrow[\text{HCl (aq.)}]{Cl_2} M_2RuCl_6$$

$$OsO_4 \xrightarrow[\text{EtOH}]{\text{conc. HCl/MCl}} M_2OsCl_6$$

The last synthesis uses ethanol as the reducing agent. Soluble Na_2OsCl_6 has been used to make the less soluble salts of other alkali metals by metathesis.

Typical colours are red–brown to black (Ru) and orange to dark red (Os). K_2RuCl_6 has the K_2PtCl_6 structure. Magnetic moments for the ruthenium compounds are 2.7–$3.0\,\mu_B$; the osmium compounds have substantially lower moments ($1.51\,\mu_B$ for K_2OsCl_6) but on doping into K_2PtCl_6 the moment of $OsCl_6^{2-}$ rises to $2.1\,\mu_B$, 'superexchange' causing a lowered value in the undiluted salts.

Bromides and iodides can be made (except $X = I$ for Ru).

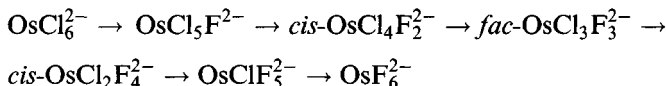$$RuBr_5(H_2O)^{2-} \xrightarrow[\text{Br}_2]{\text{HBr(aq.)}} RuBr_6^{2-}$$

$$K_2RuCl_6 \xrightarrow{Br_2} K_2RuBr_6$$

$$OsO_4 \xrightarrow[\text{M}^+]{\text{HBr(aq.)}} M_2OsBr_6 \qquad (M = \text{alkali metal})$$

$$OsO_4 \xrightarrow[\text{M}^+]{\text{HI(aq.)}} M_2OsI_6$$

These compounds tend to be black in colour. Magnetic moments of 2.84 and $1.65\,\mu_B$ have been reported for K_2RuBr_6 and K_2OsI_6, respectively.

$OsCl_6^{2-}$ is a useful starting material for the synthesis of a range of osmium complexes (Figure 1.4).

The mixed halide species $OsX_{6-n}Y_n^{2-}$ or $OsX_aY_bZ_c^{2-}$ $(a + b + c = 6)$ have been studied in considerable detail [37].

Reaction of $OsCl_6^{2-}$ with BrF_3 affords stepwise substitution

$$OsCl_6^{2-} \rightarrow OsCl_5F^{2-} \rightarrow cis\text{-}OsCl_4F_2^{2-} \rightarrow fac\text{-}OsCl_3F_3^{2-} \rightarrow$$

$$cis\text{-}OsCl_2F_4^{2-} \rightarrow OsClF_5^{2-} \rightarrow OsF_6^{2-}$$

with the stronger *trans*-effect of chloride directing the position of substitution. This can likewise be utilized to synthesize the *trans*- and *mer*-isomers, for example
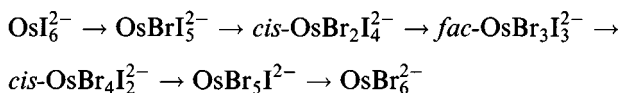
$$cis\text{-}OsCl_2F_4^{2-} \xrightarrow{Cl^-} mer\text{-}OsCl_3F_3^{2-}$$
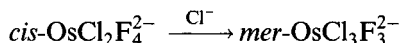
The isomer(s) obtained depend on the reaction time; thus reaction of K_2OsCl_6 with BrF_3 at 20°C affords 90% $cis\text{-}OsF_4Cl_2^{2-}$ after 20 min whereas

Figure 1.4 Reactions of $OsCl_6^{2-}$.
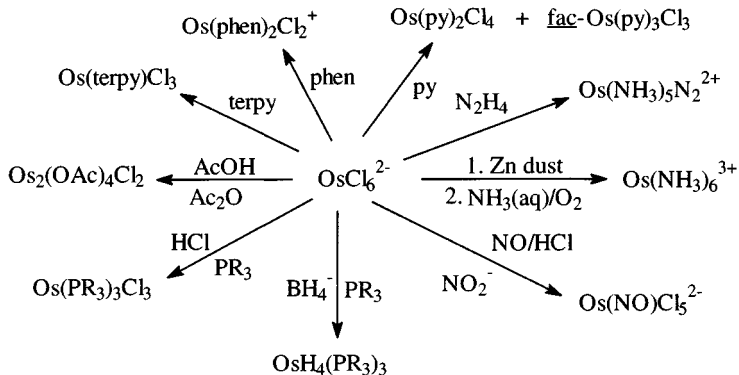
after 10 h the mixture contains 30% cis-$OsF_4Cl_2^{2-}$, 40% OsF_5Cl^{2-} and 30% OsF_6^{2-}. Mixtures can be separated by chromatography or ionophoresis; within this series, the cis-isomers are eluted before the $trans$ (on diethyl-aminoethyl cellulose) whereas in ionophoresis, the $trans$-isomers move 3–5% faster.

Such octahedral anions are, of course, amenable to study by vibrational spectroscopy; as the anion symmetry descends from $O_h(MX_6^{2-})$, the number of bands increases as the degeneracy of vibrations is removed. Pairs of isomers can be distinguished; thus for $OsF_2Cl_4^{2-}$, the more symmetric $trans$-isomer (D_{4h}) gives rise to fewer stretching vibrations (5) than the cis-isomer (C_{2v}), which has 6. Moreover the centre of symmetry in the $trans$-isomer means there are no IR/Raman coincidences. The $Os-F$ vibrations can be associated with bands in the 490–560 cm^{-1} region and $Os-Cl$ stretching vibrations in the 300–360 cm^{-1} region (Figure 1.5).

Other series of mixed hexahalide complexes have been made. Thus from K_2OsI_6 and concentrated HBr:

$$OsI_6^{2-} \rightarrow OsBrI_5^{2-} \rightarrow cis\text{-}OsBr_2I_4^{2-} \rightarrow fac\text{-}OsBr_3I_3^{2-} \rightarrow$$

$$cis\text{-}OsBr_4I_2^{2-} \rightarrow OsBr_5I^{2-} \rightarrow OsBr_6^{2-}$$

As before the $trans$-isomers can be obtained using $OsBr_6^{2-}$ and concentrated HI; similarly, starting from $OsCl_6^{2-}$ and concentrated HI, the sequence $OsCl_5I^{2-}$, $trans$-$OsCl_4I_2^{2-}$, mer-$OsCl_3I_3^{2-}$, $trans$-$OsCl_2I_4^{2-}$, $OsClI_5^{2-}$ and OsI_6^{2-} is obtained. A more drastic synthesis of this type has been achieved by taking mixed crystals K_2OsBr_6/K_2SnCl_6 and using the nuclear process $^{190}Os(n, \gamma)^{191}Os$, when all the mixed species $^{191}OsCl_nBr_{6-n}^{2-}$ were obtained.

Mixed species with three different halogens have been made

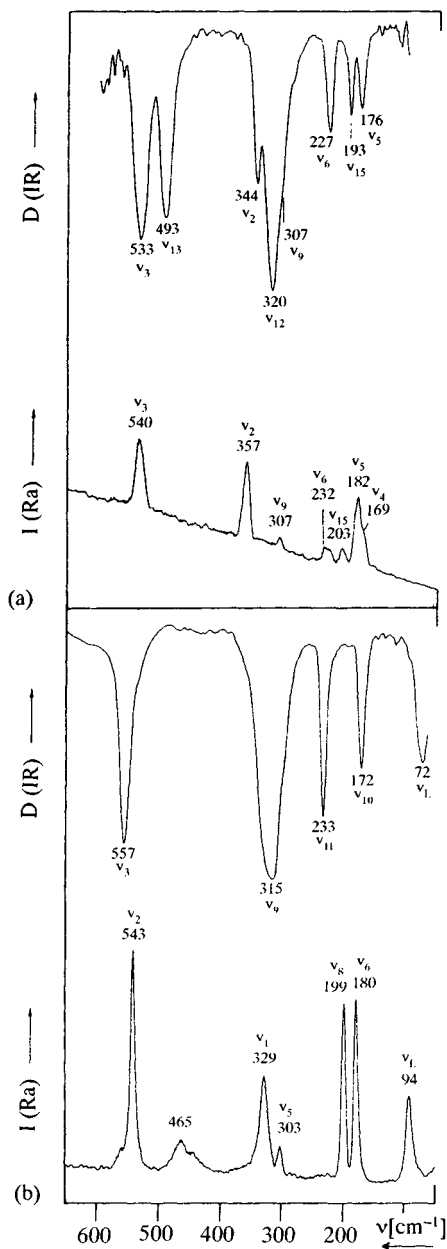$$OsF_5Cl^{2-} \xrightarrow[50°C, 30\,min]{conc.\ HBr} trans\text{-}OsF_4ClBr^{2-}$$
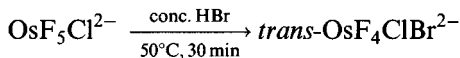
Figure 1.5 The vibrational spectra of the *cis* (a) and *trans* (b) isomers of $[OsCl_2F_4]^{2-}$ in their caesium salts. (Reproduced with permission from *Z. Naturforsch.*, Teil B, 1984, **39**, 1100.)

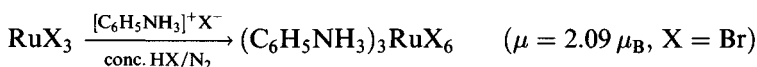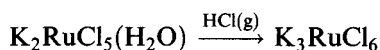**Table 1.5** Bond lengths (Å) in dipyridinio methane salts

	OsF_5Cl^{2-}	$fac\text{-}OsF_3Cl_3^{2-}$	$mer\text{-}OsF_3Cl_3^{2-}$	$cis\text{-}OsF_2Cl_4^{2-}$	$trans\text{-}OsF_2Cl_4^{2-}$
Os–F					
trans to F	1.918		1.944		1.926
trans to Cl	1.959	1.948	1.976	1.948	
Os–Cl					
trans to F	2.329	2.320	2.278	2.316	
trans to Cl			2.307	2.338	2.337

The crystal structure of the caesium salt shows Os–F, Os–Cl and Os–Br bonds of 1.94, 2.43 and 2.49 Å, respectively. The complex exhibits strong IR bands at 552, 320 and 222 cm^{-1}, assigned to Os–F, Os–Cl and Os–Br stretching, respectively (compare ν_3 of OsX_6^{2-} at 547 cm^{-1} (F), 313 cm^{-1} (Cl) and 227 cm^{-1} (Br)) [38].

Bond lengths in the dipyridinio methane salts [$(C_5H_5N)_2CH_2$][OsF_5Cl], *fac*- and *mer*-[$(C_5H_5N)_2CH_2$][OsF_3Cl_3] and *cis*- and *trans*-[$(C_5H_5)_2CH_2$][OsF_2Cl_4] show the mutual *trans*-influence of chlorine and fluorine; thus Os–Cl bonds *trans* to fluorine are shorter than those *trans* to chlorine, while Os–F bonds *trans* to chlorine are longer than those *trans* to fluorine (Table 1.5) [38c].

Oxidation state +3
Halide complex ions of ruthenium and osmium in the +3 state are known for all except OsF_6^{3-} [39]. Syntheses include:
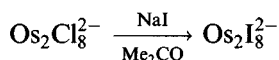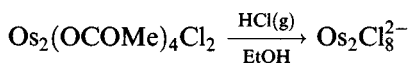
$$RuCl_3 \xrightarrow[\text{fuse}]{KHF_2} K_3RuF_6 \quad (\mu = 1.25\,\mu_B)$$

$$K_2RuCl_5(H_2O) \xrightarrow{HCl(g)} K_3RuCl_6$$

$$RuX_3 \xrightarrow[\text{conc. HX/N}_2]{[C_6H_5NH_3]^+X^-} (C_6H_5NH_3)_3RuX_6 \quad (\mu = 2.09\,\mu_B, X = Br)$$

A general synthesis for the osmium compounds is

$$OsX_6^{2-} \xrightarrow{\text{conc. HX/N}_2} (Coen_3)^{3+}OsX_6 \quad (X = Cl, Br, I)$$
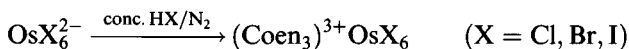
Magnetic moments reported for the OsX_6^{3-} salts are 1.70, 1.67 and 1.61 μ_B for X = Cl, Br and I, respectively, consonant with the low-spin d^5 configuration.

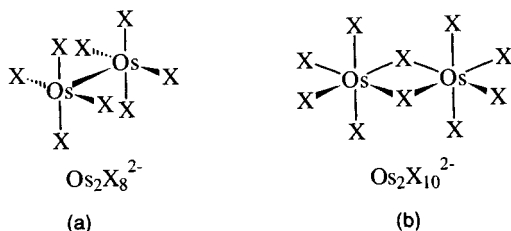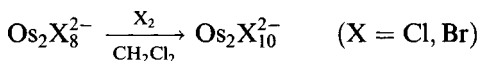A number of dinuclear complexes have been synthesized [40]

$$Os_2(OCOMe)_4Cl_2 \xrightarrow[\text{EtOH}]{HCl(g)} Os_2Cl_8^{2-}$$

$$Os_2Cl_8^{2-} \xrightarrow[\text{Me}_2CO]{NaI} Os_2I_8^{2-}$$

Figure 1.6 The structures of the diosmate ions $Os_2X_8^{2-}$ (a) and $Os_2X_{10}^{2-}$ (b).

Oxidation with halogens gives the decahalogenodiosmate (IV) (2−) ions (Figure 1.6):

$$Os_2X_8^{2-} \xrightarrow[CH_2Cl_2]{X_2} Os_2X_{10}^{2-} \qquad (X = Cl, Br)$$

The short Os−Os bonds in $Os_2X_8^{2-}$ correspond to triple bonds and give rise to stretching vibrations associated with bands around $280\,cm^{-1}$ in the Raman spectrum (Table 1.6).

The $Os_2X_8^{2-}$ ions participate in various redox processes: at 235 K $Os_2Cl_8^{2-}$ undergoes reversible oxidation to $Os_2Cl_8^{n-}$ ($n = 1, 0$), the bromide behaves similarly. At high temperatures, the Os−Os bond is broken and $OsCl_6^-$ is formed. $Os_2Cl_8^{2-}$ can also be cleaved with Bu^tNC to form *trans*-$OsCl_4(CNBu^t)_2^-$ [41].

In addition to the doubly bridged $Os_2X_{10}^{2-}$, triply bridged $Os_2Br_9^-$ can be made (Figure 1.7):

$$OsBr_6^{2-} \xrightarrow[40°C]{CF_3CO_2H} Os_2Br_{10}^{2-} \xrightarrow[110°C]{CF_3CO_2H} Os_2Br_9^-$$
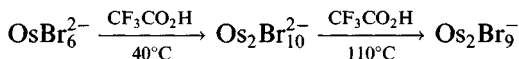
It can be reduced electrochemically to $Os_2Br_9^{n-}$ ($n = 2, 3$), with $Os_2Br_{10}^{n-}$ ($n = 3, 4$) similarly accessible. $Rb_3Os_2Br_9$ has Os−Os 2.799 Å [42].

Table 1.6 Characteristics of $Os_2X_8^{2-}$

	Counter-ion	Os−Os (Å)	ν_{sym} (Os−Os) (cm^{-1})
$Os_2Cl_8^{2-}$	Bu_4N	2.182	285
$Os_2Br_8^{2-}$	Bu_4N	2.196	287
$Os_2I_8^{2-}$	$(Ph_3P)_2N$	2.212	270

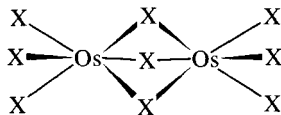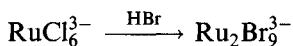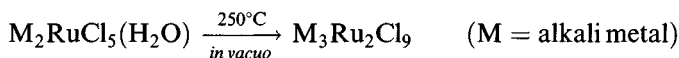**Figure 1.7** The structures of the diosmate ions $Os_2X_9^{3-}$.

In the case of ruthenium, the Ru_2X_9 system with confacial octahedra is important

$$M_2RuCl_5(H_2O) \xrightarrow[\text{in vacuo}]{250°C} M_3Ru_2Cl_9 \qquad (M = \text{alkali metal})$$

$$RuCl_6^{3-} \xrightarrow{HBr} Ru_2Br_9^{3-}$$

These evidently have some Ru–Ru bonding with Ru–Ru distances of 2.73 and 2.87 Å in $Cs_3Ru_2Cl_9$ and (1-methyl-3-ethylimidazolinium)$_3Ru_2Br_9$, respectively; the magnetic moments of $(Bu_4N)_3Ru_2X_9$ of $0.86\,\mu_B$ (Cl) and $1.18\,\mu_B$ (Br) are lower than expected for low spin d^5 and indicate some metal–metal interaction. $Ru_2X_9^{3-}$ again forms part of a redox-related series $Ru_2X_9^{n-}$ ($n = 1$–4) obtainable in solution by low-temperature electrochemistry [42].

1.3.5 'Ruthenium blues' [43]

It has long been known (Claus, 1846) that reduction (e.g. Zn, H_2 with Pt catalyst) of some ruthenium salts gives a blue solution, which on treatment with HCl or oxidation turns green. Various claims have been made for the species present: $RuCl_4^{2-}$, $Ru_2Cl_3^{2+}$, $Ru_2Cl_4^+$ and $Ru_5Cl_{12}^{2-}$. A cluster $(Cl_3Ru(\mu\text{-}Cl)_3Ru(\mu\text{-}Cl)_3RuCl_3)^{4-}$ has been isolated and characterized from such a solution [44]. At present it seems likely that the compound in solution is a cluster, that the ruthenium valency is between 2 and 2.5 and that more than one species is present.

The blue solutions have been found to catalyse alkene isomerization and hydrogenation and have very considerable synthetic utility (Figure 1.8).
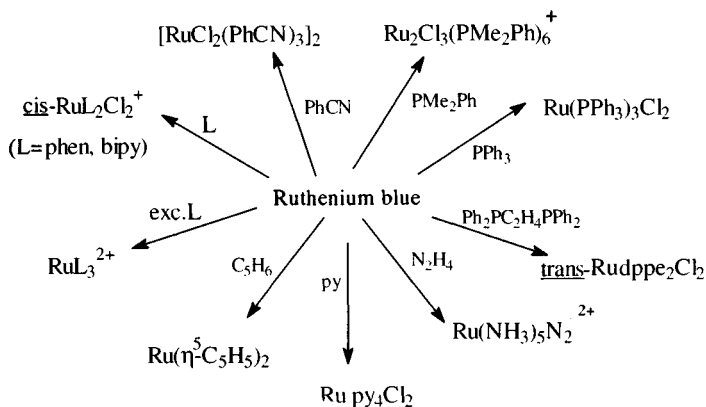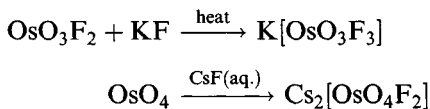

Figure 1.8 Syntheses using 'Ruthenium blue'.
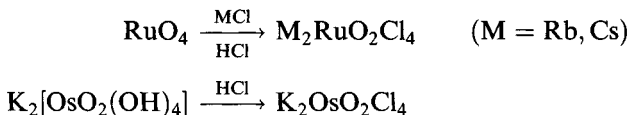
1.3.6 Oxyhalide complexes

Various anionic complexes have been made [26a]:

$$OsO_3F_2 + KF \xrightarrow{heat} K[OsO_3F_3]$$

$$OsO_4 \xrightarrow{CsF(aq.)} Cs_2[OsO_4F_2]$$

EXAFS measurements on $KOsO_3F_3$ indicate the presence of $fac\text{-}OsO_3F_3^-$ with Os=O 1.70 Å, Os–F 1.92 Å; in $Cs_2OsO_4F_2$, $cis\text{-}OsO_4F_2^{2-}$ has Os=O 1.70 Å and Os–F 2.05 Å.

Reaction of Ph_4PCl with OsO_4 gives $Ph_4P^+OsO_4Cl^-$, the anion having a tbp structure with a very long equatorial Os–Cl bond (2.76 Å) [45].

Both ruthenium and osmium form $trans\text{-}MO_2X_4^{2-}$ species (X = Cl, Br), for example

$$RuO_4 \xrightarrow[HCl]{MCl} M_2RuO_2Cl_4 \qquad (M = Rb, Cs)$$

$$K_2[OsO_2(OH)_4] \xrightarrow{HCl} K_2OsO_2Cl_4$$

Typical bond lengths are M=O 1.709 Å (Ru) 1.750 Å (Os) and M–Cl 2.388–2.394 Å (Ru) 2.379 Å (Os) in $[(Ph_3P)_2N]RuO_2Cl_4$ and $K_2OsO_2Cl_4$, respectively. Characteristic $\nu(M{=}O)$ bands can be seen in the vibrational spectra owing to both the symmetric and asymmetric stretches: for $OsO_2X_4^{2-}$ the symmetric stretch is at 904 (X = Cl) and 900 (X = Br) cm^{-1}, with corresponding values for the asymmetric stretch of 837 and 842 cm^{-1} (in the potassium salts).

In solution $[(Ph_3P)_2N]_2$ RuO_2Cl_4 loses chloride to form $[(Ph_3P)_2N]$ RuO_2Cl_3, which has a tbp structure with two axial chlorines (Ru–Cl 2.37–2.39 Å); the equatorial bond lengths are 1.66–1.69 Å (Ru–O) and 2.13 Å (Ru–Cl) [46].

The dimeric $M_2OCl_{10}^{4-}$ ions contain linear M–O–M units (Figure 1.9); in $Cs_4Os_2OCl_{10}$ the Os–O–Os stretching vibration is at 852 cm^{-1} in the IR spectrum [47] while its crystal structure reveals Os=O 1.778 Å, Os–Cl 2.367–2.377 Å (cis to O) and 2.433 Å (trans to O). In $K_4Ru_2OCl_{10}$, Ru=O is 1.801 Å, Ru–Cl is 2.363 (cis) and 2.317 Å (trans). The shortness of the M–O bridge bonds is explained by the formation of two M–O–M three-centre MOs. Figure 1.10 shows the formation of one of these by overlap of

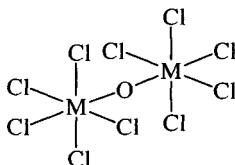**Figure 1.9** The dimeric $[M_2OCl_{10}]^{4-}$ ions (M = Ru, Os).

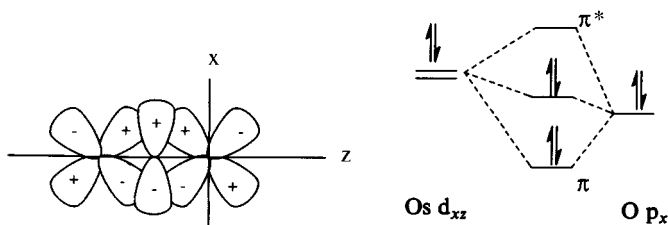**Figure 1.10** The three-centre molecular orbitals in $[Os_2OCl_{10}]^{4-}$.

osmium 5d and oxygen 2p orbitals; each MO contains two osmium electrons and two from the oxygen occupying the bonding and non-bonding MOs. These two MOs account for two of the four electrons belonging to each Os^{4+} ion (d^4); the remaining two occupy the d_{xy} orbital (unused in the MO scheme) explaining the diamagnetism of these M^{IV} compounds.

## 1.4   Oxides and related anions

The oxides are dominated by the very volatile and toxic tetroxides. Yellow RuO_4 (m.p. 25.4°C, b.p. 40°C) is isomorphous with OsO_4; electron diffraction measurements indicate that it is tetrahedral in the gas phase (Ru—O 1.706 Å) [48a]. It is light sensitive and thermodynamically unstable with respect to RuO_2 (from which, however, it can be made) and can be explosive. Because of the lesser stability of ruthenium(VIII) compared with osmium (VIII), RuO_4 is a stronger oxidizing agent than OsO_4 (and therefore less selective); solutions in CCl_4 are stable [48b]. A convenient synthesis involves periodate oxidation of $RuCl_3$ or RuO_2:

$$RuCl_3 \text{ or } RuO_2 \xrightarrow{\ NaIO_4\ } RuO_4$$
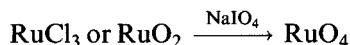
RuO_4 reacts with pyridine to form $RuO_3(py)$, probably a dimer $Py_2(O)_2Ru(\mu\text{-}O)_2Ru(O)_2Py_2$, an aerobically assisted oxidant [48c].

RuO_2 can be made by high-temperature oxidation of ruthenium. It has the rutile structure (Ru—O 1.942 Å and 1.984 Å) and forms blue–black crystals [49b].

Recently RuO_3 has been made as a brown solid by photolysis:

$$RuO_4 \xrightarrow[370\text{–}440\,nm]{h\nu} RuO_3$$
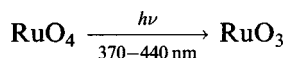
In matrices, RuO_2 is bent (149°) while RuO_3 is trigonal planar.

Copper-coloured OsO_2 also has the rutile structure: it can be made from the metal and NO at 650°C.

OsO_4 is obtained on oxidation of any osmium compound or by direct synthesis at 300–800°C from the elements [50]. Its solubility in CCl_4 and volatility make it easy to purify; it forms pale yellow crystals (m.p. 40.46°C, b.p. 131°C). Like RuO_4 it forms tetrahedral molecules with Os–O 1.684–1.710 Å, O–Os–O 106.7–110.7° in the solid state; Os–O 1.711 Å in the gas phase [51]. It is soluble in water as well as in CCl_4 and is very toxic (TLV 2.5 ppm), affecting the eyes. (Its use as a biological stain involves its reaction with tissue.)

Gas-phase vibrational data for OsO_4 are $\nu_1 = 965.2$, $\nu_2 = 333.1$, $\nu_3 = 960.1$ and $\nu_4 = 322.7\,cm^{-1}$.

Photoelectron spectra have been interpreted with a MO scheme, shown in Figure 1.11 [52].

OsO_4 will add to C=C bonds but will only attack the most reactive aromatic bonds; thus benzene is inert, but it will attack the 9,10 bond in phenanthrene and will convert anthracene to 1,2,3,4-tetrahydroxytetra-hydroanthracene. It can be used catalytically in the presence of oxidizing agents such as $NaClO_3$ or H_2O_2 [53].
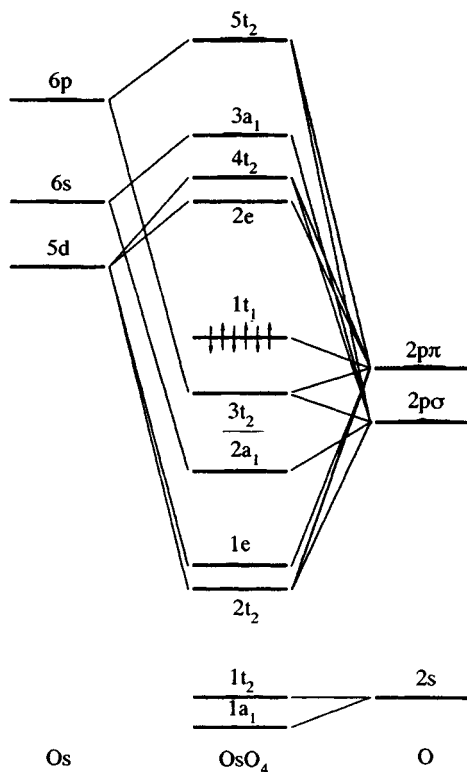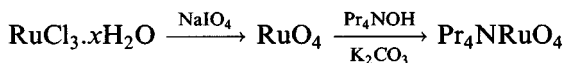

Figure 1.11 A molecular orbital diagram for OsO_4. (Reprinted with permission from *Inorg. Chem.*, 1992, **31**, 1588. Copyright American Chemical Society.)

1.4.1 Anions

Alkalis reduce RuO_4 to RuO_4^-; various salts have been prepared

$$RuCl_3.xH_2O \xrightarrow{NaIO_4} RuO_4 \xrightarrow[K_2CO_3]{Pr_4NOH} Pr_4NRuO_4$$

On heating it decomposes in a similar manner to $KMnO_4$:

$$2KRuO_4 \rightarrow K_2RuO_4 + RuO_2 + O_2$$

The anion in $KRuO_4$ has a slightly flattened tetrahedral structure (Ru–O 1.73 Å). Organic-soluble salts like Pr_4NRuO_4 are selective mild oxidants that will oxidize alcohols to carbonyl compounds but will not affect double bonds [54a]. ESR indicates that RuO_4^- ($g_x = 1.93$; $g_y = 1.98$; $g_z = 2.06$) has a compressed tetrahedral geometry with the electron in d_{z^2} [54b].

RuO_4^{2-}, which is believed to be tetrahedral in solution, is formed from RuO_4 and excess concentrated aqueous KOH, isolable as black crystals of $K_2RuO_4.H_2O$, which is actually $K_2[RuO_3(OH)_2]$. The anion has a tbp structure with axial OH groups (Ru=O 1.741–1.763 Å, Ru–OH 2.028–2.040 Å) [55].

In contrast to ruthenium, osmium exists in alkaline solution as $OsO_4(OH)_2^{2-}$, believed to be *cis* and isolable as crystalline salts:

$$OsO_4 + 2KOH \rightarrow K_2OsO_4(OH)_2$$
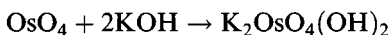
Similarly, instead of forming OsO_4^{2-}, reduction of OsO_4 with ethanolic KOH yields $K_2[OsO_2(OH)_4]$.

The osmiamate ion, OsO_3N^-, is isoelectronic with OsO_4. The yellow potassium salt is the most convenient one to prepare; other, less soluble, salts, can be made by metathesis:

$$OsO_4 + NH_3 \xrightarrow{KOH} KOsO_3N$$
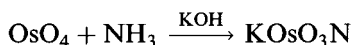
The crystallographic study of the potassium salt is complicated by disorder but in $CsOsO_3N$ Os≡N is 1.676 Å and Os=O 1.739–1.741 Å. Assignments of the vibrational spectrum of OsO_3N^- is assisted by isotopic substitution: the higher frequency absorption is shifted significantly on ^{15}N substitution whereas the band just below $900 \, cm^{-1}$ is scarcely affected (Table 1.7); conversely the latter band is shifted by some $50 \, cm^{-1}$ on replacing ^{16}O by ^{18}O [56].

Nitrido salts are discussed later (section 1.12.2).

Table 1.7 Vibrational data for osmiamate ions (in cm^{-1})

|	ν_1 (Os≡N)	ν_2 (Os=O)
OsO_3N^-	1029	898
$OsO_3{}^{15}N^-$	998	896
$K[Os^{18}O_3N]^-$	1024	844

1.5   Other binary compounds

Ruthenium and osmium form no stable binary hydrides, but very recently heating mixtures of the metals with alkaline earth metal hydrides under pressure in a hydrogen atmosphere have been shown to give oxygen- and moisture-sensitive hydrides M_2RuH_6 (M = Mg, Ba), M_2OsH_6 (M = Mg to Ba) and Li_4OsH_6. These contain MH_6^{4-} (K_2PtCl_6 structure) with Ru–D 1.673 and Os–D 1.682 Å in the corresponding deuterides [57]. $LiMg_2RuH_7$ has RuH_6^{2-} with Ru–D 1.704 Å in the deuteride.

The mineral laurite is the mixed sulphide $(Ru,Os)S_2$; this and RuS_2 and OsS_2 have the pyrite structure as does RuQ_2 (Q = Se, Te). These can be made from the reaction of the chalcogen with the metals, while $RuCl_3$ will also react with Se and Te.

MP_2, MAs_2 and MSb_2 all have a compressed form of the marcasite structure, while the carbides MC have trigonal prismatic coordination in the WC structure. Several borides are known: MB_2 has nets of boron atoms. $Ru_{11}B_8$ has branched chains while Ru_7B_3 has isolated borons.

1.6   Aqua ions [58]

Diamagnetic, low-spin d^6 $Ru(H_2O)_6^{2+}$ has been made by reduction of RuO_4 with activated Pb (or Sn) followed by ion-exchange purification. The pink tosylate salt contains octahedral $Ru(H_2O)_6^{2+}$ (Ru–O 2.122 Å); though the solid is air stable, it is readily oxidized in solution by oxygen and ClO_4^-. The hexaqua ions also occur in the red diamagnetic Tutton salts $M_2Ru(H_2O)_6(SO_4)_2$ (M = NH_4, Rb)

$$RuO_4 \xrightarrow[H^+]{Pb/Hg} Ru(H_2O)_6^{2+} \xrightarrow{(NH_4)_2SO_4} (NH_4)_2Ru(H_2O)_6(SO_4)_2$$
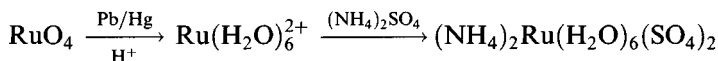
Ru $(H_2O)_6(BF_4)_2$ has been isolated but decomposes on standing.

Aerial oxidation of $Ru(H_2O)_6^{2+}$ produces lemon-yellow $Ru(H_2O)_6^{3+}$ (Ru–O 2.029 Å in the tosylate salt)

$$Ru(H_2O)_6^{2+} \rightarrow Ru(H_2O)_6^{3+} + e^- \qquad E^\ominus = -0.205 \, V$$
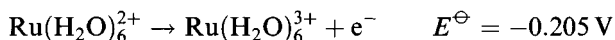
The yellow alum $CsRu(H_2O)_6(SO_4)_2.6H_2O$ has also been synthesized with $\mu_{eff} = 2.20 \, \mu_B$ at 300 K; the Ru–O distance is 2.010 Å.

Vibrational spectra of octahedral $Ru(H_2O)_6^{n+}$ ($n = 2$, $\nu_1 = 424 \, cm^{-1}$, $\nu_3 = 426 \, cm^{-1}$; $n = 3$, $\nu_1 = 532 \, cm^{-1}$, $\nu_3 = 529 \, cm^{-1}$) have been interpreted in terms of the force constants 1.91 mdyn $Å^{-1}$ ($n = 2$) and 2.98 mdyn $Å^{-1}$ ($n = 3$), showing a stronger bond for the ruthenium(III) species.

The ruthenium(II) aqua ion reacts with nitrogen at room temperature under high pressure (200 bar) forming yellow–brown $[Ru(H_2O)_5N_2]^{2+}$, isolated as a tosylate salt, showing $\nu(N\equiv N)$ at 2141 cm^{-1} in its IR spectrum [59].

The ruthenium(IV) aqua ion, best made by electrochemical oxidation of $Ru(H_2O)_6^{2+}$, but also made by the reaction of RuO_4 with $H_2O_2/HClO_4$, is tetranuclear, formulated as $[Ru_4O_6(H_2O)_{12}]^{4+}$, though this may be protonated [60]. FAB mass spectra of a pyrazolylborate complex show Ru_4O_6-containing fragments.

No simple osmium aqua ion has been definitely isolated and characterized, though in alkaline solution (and the solid state) the osmium(VIII) species $OsO_4(OH)_2^{2-}$ is well characterized (sections 1.4.1 and 1.12.1).

Osmium(II) is probably too reducing to exist as $Os(H_2O)_6^{2+}$, but $Os(H_2O)_6^{3+}$ and a polynuclear Os_4^+(aq.) species are likely.

1.7   Compounds of ruthenium(0)

Apart from $Ru(CO)_5$ and other carbonyls, there are mixed carbonyl–phosphine species and a few simple phosphine complexes like $Ru(PF_3)_5$ and $Ru[P(OMe)_3]_5$ [61a].

Photochemistry of $Ru(CO)_3(PMe_3)_2$ and the ruthenium(II) compound $Ru(CO)_2(PMe_3)_2H_2$ in low-temperature matrices affords $[Ru(CO)_2(PMe_3)_2 \cdots S]$ ($S = Ar$, Xe, CH_4) [61b]. These monomers all have 18-electron tbp structures.

The phosphine complex $Ru(dmpe)_2$ has been studied in matrices [62]. $Ru(diphos)_2$ (diphos = depe, dppe, $(C_2F_5)_2P(CH_2)_2P(C_2F_5)_2$) has similarly been formed by photolysis of $Ru(diphos)_2H_2$ in low-temperature matrices. They probably have square planar structures and undergo oxidative addition with cobalt, C_2H_4 and hydrogen [63].

Additionally a number of nitrosyls such as $Ru(NO)_2(PPh_3)_2$ (section 1.8.5) exist.

1.8   Complexes of ruthenium(II and III)

Because of the relationship between compounds in the adjacent oxidation states $+2$ and $+3$, they are grouped together here; the section is subdivided by ligand, concentrating on some classes of complex important in their diversity and in current research interest.

1.8.1   Ammine complexes

Orange $Ru(NH_3)_6^{2+}$ can be obtained by various routes (see Figure 1.12).

As expected for the $+2$ state of a heavy metal, it is reducing:

$$Ru(NH_3)_6^{2+} \rightarrow Ru(NH_3)_6^{3+} + e^- \qquad E^{\ominus} = +0.214 \, V$$
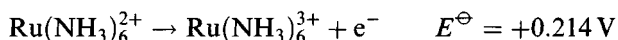
Historically, the most important ruthenium(II) ammine species is $[Ru(NH_3)_5N_2]^{2+}$, the first stable dinitrogen complex to be isolated (1965). It was initially obtained by refluxing $RuCl_3$ in hydrazine solution (but many