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TRANSITION METAL OXO COMPLEXES

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CONTENTS

ABBREVIATIONS

acac	acetylacetone	EDTA	ethylenediaminetetraacetic acid
bipy	2,2′-bipyridyl	MNT	maleodithionitrile
Cp	cyclopentadienyl	ox	oxalate
dien	diethylenetriamine	oxine	8-hydroxyquinoline
DMF	dimethylformamide	*o*-phen	1,10-phenanthroline
DMSO	dimethylsulphoxide	py	pyridine
en	ethylenediamine	xan	xanthate

A. INTRODUCTION

This review is concerned with the chemistry of transition metal complexes involving the oxo ligand, O^{2-}. The subject is so large that, in order to keep the review to a reasonable length and not to stretch the reviewer's knowledge to an embarrassing extent, it has been necessary to limit coverage to compounds which contain discrete molecular units $[MO_xX_y]_z^{n-}$, where $z \leqslant 3$. This rather arbitrary limit excludes a very large number of oxo compounds: almost all uncharged metal oxides, most isopoly and heteropoly species, and a substantial number of ternary compounds such as $BaTiO_3$ in which the transition metal atom is part of a long chain, sheet or lattice structure. Wherever possible, general review references to such compounds are quoted where appropriate in Part C, and a list of the principal oxides and oxyhalides is given for each group of metals.

(i) Arrangement of material

This follows a classical pattern. In Part B, which deals with the subject in a general way, a survey of the chemistry of oxo complexes is followed by summaries of the literature on the nature of metal–oxo bonding and of the main physical measurements which have been carried out on the complexes. Finally, in Part C, the oxo complexes will be considered by the periodic group to which their metals belong.

(ii) Nomenclature

In this review we shall use the word oxo to denote the O^{2-} ligand, as recommended by the IUPAC convention[1]; (the older term "oxy" is often still used in the literature). Thus, $K[CrOF_4]$ is potassium oxotetrafluorochromate(V). The ending -yl is commonly used for oxo complexes (uranyl for UO_2^{2+}, osmyl for OsO_2^{2+} *etc.*) though IUPAC deprecates its use; thus, vanadyl sulphate, $VOSO_4$, would be called vanadium oxide sulphate under IUPAC rules.

(iii) Reviews

We list here a number of reviews on general aspects of the chemistry of oxo complexes; reviews which deal with more specific topics — *e g.* oxo chemistry of one particular element — will be mentioned in the relevant section of Part C.

Scholder has reviewed "ortho" (*i e.* tetraoxo) salts, and includes penta- and hexaoxo species[2]; an irritating feature of that review, however, is that it contains an excessive number of references to unpublished work or unobtainable theses. The formation and formulation of polyanions of Groups Va and VIa have been reviewed and an account given of the general methods used in research on this topic[3,4]. Carrington and Symons have reviewed the structures and reactivities of tetraoxo anions with a particular emphasis on bonding theory[5], and bonding theory plays an important part in reviews on the electronic spectroscopy of tetraoxo complexes[6]. Reviews have also been written on oxo cations[7], binuclear complexes having single oxo bridges[8], oxo peroxo and peroxo species[9], oxohalides[10], oxides[11] and metal oxide alkoxides[12].

B GENERAL SURVEY

(i) Occurrence

In Table 1 we summarise those complexes of the type $[MO_xX_y]_z^{n-}$ known for each periodic group From this it will be seen that most oxo species of this type (where $x \geqslant 3$ and $z = 1$) are formed by transition metal atoms in their highest oxidation states, *i e.* with d^0 electron configurations; there are less frequent examples of d^1 and d^2 species, and a very few of d^3 As a consequence, the majority of oxo species are formed by elements in Groups IVa–VIIa since these achieve high oxidation states fairly easily. In Group VIII only ruthenium and osmium have any extensive oxo chemistry, these being the only two elements of that group to form a number of high oxidation state species. The reason for this prevalence of d^0–d^2 configurations is that O^{2-} is a very strong electron donor, both in a σ and a π sense: it will only function efficiently as a ligand if the metal has few outer electrons of its own.

(ii) Stereochemistry

Most oxo complexes $[MO_xX_y]_z^{n-}$ are either basically tetrahedral where $x > 2$ and $z = 1$; or octahedral when $x = 2$ or 1 and $z = 1$. Although heptacoordination occurs in $K_3[NbOF_6]$ and $(NH_4)_3[NbO\ ox_3]$ there are few other authenticated examples (both $[OsOCl_6]^{2-}$ and $[ReOCl_6]^{2-}$ have been claimed but there is little evidence for their existence). Five coordination undoubtedly occurs for

TABLE 1

GENERAL TYPES OF OXO COMPLEXES (GROUPS IVa, Va, VIa, VIIa AND VIII)

Complex type	d^n	*IVa* *M = Ti, Zr, Hf* *M′ = Zr, Hf*	*Va* *M = V, Nb, Ta* *M′ = Nb, Ta*	*VIa* *M = Cr, Mo, W* *M′ = Mo, W*	*VIIa* *M = Mn, Tc, Re* *M′ = Tc, Re*	*VIII* *M′ = Ru, Os*
$[MO_4]^{n-}$	d^0	$[MO_4]^{4-}$	$[MO_4]^{3-}$	$[MO_4]^{2-}$	$[MO_4]^-$	$M'O_4$
	d^1		$[VO_4]^{4-}$ $[NbO_4]^{4-}$	$[CrO_4]^{3-}$	$[MnO_4]^{2-}$	$[RuO_4]^-$
	d^2			$[CrO_4]^{4-}$ $[MoO_4]^{4-}$	$[MnO_4]^{3-}$	$[RuO_4]^{2-}$ $[FeO_4]^{2-}$
$[MO_4X_2]^{n-}$	d^0				$[ReO_4(OH)_2]^{3-}$	$[OsO_4X_2]^{2-}$ [a]
$[MO_3X]^{n-}$	d^0			$[CrO_3X]^-$	ReO_3X	
				$[MoO_3N]^-$	$[ReO_3N]^{2-}$	$[OsO_3N]^-$
				$[MoO_3S]^{2-}$	$[ReO_3S]^-$	
$[MO_3X_3]^{n-}$	d^0			$[M'O_3F_3]^{3-}$	$[ReO_3Cl_3]^{2-}$	$[OsO_3F_3]^-$
MO_2X_2	d^0			MO_2X_2	$[ReO_2Br_2]^-$	
cis- $[MO_2X_4]^{n-}$	d^0		$[VO_2X_4]^{3-}$	$[M'O_2X_4]^{2-}$	$[ReO_2F_4]^-$	
trans- $[MO_2X_4]^{n-}$	d^2			$[M'O_2(CN)_4]^{2-}$	$[ReO_2X_4]^{2-}$	$[M'O_2X_4]^{2-}$
$[MOX_4]^{n-}$	d^0	$[TiOX_4]^{2-}$	$[MOX_4]^-$			$M'OF_4$
	d^1, d^2		$[VOX_4]^-$	$[MOX_4]^-$	$[ReOX_4]^-$	
$[MOX_5]^{n-}$	d^0		$[MOX_5]^{2-}$			
	d^1, d^2		$[VOX_5]^{3-}$	$[MOX_5]^{2-}$	$[M'OX_5]^{2-}$	
$[M_2OX_{10}]^{n-}$	d^0	$[Ti_2OCl_{10}]^{4-}$		$[W_2OCl_{10}]^{4-}$	$[Re_2OCl_{10}]^{4-}$	$[M'_2OX_{10}]^{4-}$
	d^3, d^4			$[Cr_2O(NH_3)_{10}]^{4+}$		
$[M_3OX_9]^{n-}$	d^3, d^5			$[Cr_3O(OAc)_6(H_2O)_3]^+$		$[Ru_3O(OAc)_6(H_2O)_3]^+$ $[Fe_3O(OAc)_6(H_2O)_3]^+$

[a] X = halogen.

some MOX_4 species in the vapour state, but in the solid they are usually polymeric; however a few solid pentacoordinate species such as $VO(acac)_2$ and salts of $[ReOBr_4]^-$ are known.

Unsubstituted oxo complexes are usually tetrahedral; some hexa- and penta-oxo species have been reported but it is unlikely that they contain discrete $[MO_6]^{n-}$ or $[MO_5]^{n-}$ units, rather they have layer lattice structures with metal atoms in octahedral holes There are no established examples of transition metal $[MO_6]^{n-}$ species existing as such in aqueous solution, although $[TeO_6]^{6-}$ and $[IO_6]^{5-}$ exist in very alkaline aqueous media. Many tetraoxo anions, however, are stable in aqueous solution. The reason for the prevalence of four- rather than six-coordination in unsubstituted oxo complexes is probably a consequence of the extensive oxide-to-metal electron delocalisation; high coordination numbers would place an excessive burden of negative charge on the central metal atom. It is noteworthy that some second and third row elements tend to give substituted oxo complexes of higher coordination numbers than their first row analogues, in line with the general tendency of heavier transition elements to expand their coordination spheres. Thus $[ReO_4]^-$ and OsO_4 react with alkali to give $[ReO_4(OH)_2]^{3-}$ and $[OsO_4(OH)_2]^{2-}$ while $[MnO_4]^-$ and $[RuO_4]^-$ do not; osmium forms hexacoordinate oxo species in its (VII) and (VI) oxidation states, whereas ruthenium forms only the tetrahedral $[RuO_4]^-$ and $[RuO_4]^{2-}$.

(iii) Oxidation states

The tetra- and tri-oxo species, $[MO_4]^{n-}$, $[MO_4X_2]^{n-}$, $[MO_3X]^-$ and $[MO_3X_3]^{n-}$ are usually associated with the highest oxidation state of the metal, *viz.* a d^0 electron configuration There are a few examples tetraoxo species of d^1 ($[CrO_4]^{3-}$, $[MnO_4]^{2-}$ and $[RuO_4]^-$) and d^2 ($[CrO_4]^{4-}$, $[FeO_4]^{2-}$ and $[RuO_4]^{2-}$); $[FeO_4]^{3-}$, if it really exists (*cf.* p. 504) is the only example of a d^3 tetraoxo complex. The general tendency of second and third row elements to exhibit higher oxidation states than their first row conterparts is shown by the fact that ruthenium is the only such element to form tetraoxo complexes with one or more outer *d* electron. The d^0 dioxo species are $[MO_2X_2]^{n-}$ (Cr^{VI}, Mo^{VI}, W^{VI}, Re^{VII}) and *cis*-$[MO_2X_4]^{n-}$ (Mo^{VI}, W^{VI}, V^{V}), while the d^2 dioxo species take the form *trans*-$[MO_2X_4]^{n-}$ (Os^{VI}, Ru^{VI}, Re^{V}, Mo^{IV}, W^{IV}). The few d^1 dioxo species reported of the form $[MO_2X_3]^{n-}$ (Mo^{V}, W^{V}) are probably binuclear with one bridging oxygen atom, $[M_2O_3X_8]^{2n-}$ (see below, p. 496). Monooxo species $[MOX_5]^{n-}$ and $[MOX_4]^{n-}$ are d^0 (V^{V}, Nb^{V}, Ta^{V} and a few Ti^{IV}), d^1 (Cr^{V}, Mo^{V}, W^{V}, and a very large number of V^{IV}, the so-called "vanadyl" compounds), and occasionally d^2 (Re^{V}, Tc^{V}). Species containing terminal oxo ligands coordinated to a metal atom with more than two *d* electrons are rare, though as a bridge ligand it is often found with d^0 (Ti^{IV}, Mo^{VI}), d^1 (Mo^{V}, W^{V}), d^2 (W^{IV}), d^3 (Re^{IV}, Cr^{III}, Fe^{III}, Ru^{III}) and d^4 (Os^{IV}, Ru^{IV}) configurations

(iv) Similarities between O^{2-} and other ligands

Other ligands which are comparable with O^{2-} in various respects are the isoelectronic nitride, N^{3-} and fluoride, F^-, and also the "pseudoisoelectronic" peroxide, $O_2{}^{2-}$ and sulphide, S^{2-}ions.

The nitride ion is such an efficient electron donor that, up to now, only mononitrido species are known, though the field is at present little investigated. The following pairs of isoelectronic complexes indicates the formal similarity with O^{2-}:

$[MoO_3N]^{3-}$	$[ReO_3N]^{2-}$	$ReNCl_2(PPh_3)_3$	$[OsO_3N]^-$	$[Ru_2NCl_{10}]^{5-}$
$[MoO_4]^{2-}$	$[ReO_4]^-$	$ReOCl_3(PPh_3)_2$	OsO_4	$[Ru_2OCl_{10}]^{4-}$

In general, nitrido complexes seem to be more common for second and third row elements than for the first row, consistent with the role of N^{3-} as a very effective π-donor.

The peroxide ligand, $O_2{}^{2-}$ may often replace O^{2-} in complexes; in those complexes which have been subjected to X-ray analysis it appears that it functions as a sideways-bonded ligand.

The following pairs of species are isoelectronic, and indeed the peroxo species listed here can be made from the oxo compounds by simple reaction with hydrogen peroxide:

$[TiO_2(SO_4)_2]^{2-}$ $[V(O_2)_4]^{3-}$ $[MoO(O_2)_2F_2]^{2-}$ $[WO(O_2)F_4]^{2-}$
$[TiO(SO_4)_2]^{2-}$ $[VO_4]^{3-}$ $[MoO_3F_2]^{2-}$ $[WO_2F_4]^{2-}$

Peroxy complexes are most frequently found with elements from Groups IVa, Va and VIa; mixed oxo peroxo species are quite common[9].

Fluoride and oxide have a number of similarities as ligands, but oxide is somewhat more efficient than fluoride in stabilising high oxidation states (compare OsO_4 and RuO_4 with the very unstable OsF_8 and unknown RuF_8) The fluoride ion tends to form complexes with higher coordination numbers than oxide (it prefers octahedral coordination).

The sulphide ion S^{2-} has certain formal similarities with O^{2-}. Thus a number of unsubstituted and substituted thio species analogous to oxo complexes are known:

$[MoO_2S_2]^{2-}$ $[MoS_4]^{2-}$ $[ReO_3S]^{-}$
$[MoO_4]^{2-}$ $[MoO_4]^{2-}$ $[ReO_4]^{-}$

The considerable tendency of sulphide to catenate is not of course shared by the oxo ligand.

(v) Preparation and properties

Most unsubstituted oxo complexes involving the metal in its highest oxidation state are made by treatment of a lower valency salt with an alkaline oxidising flux (for preparation of oxo anions) or oxidation in acid media (for uncharged species like Mn_2O_7, RuO_4, OsO_4). Salts involving oxo anions in lower states can be made by controlled reduction of the corresponding d^0 species (*e.g.* $[MnO_4]^{2-}$ and $[MnO_4]^{3-}$ from $[MnO_4]^{-}$). Oxohalides are normally prepared either by hydrolysis of the binary halides, from oxygen and the halides, or from the metal, oxygen and halogen. Substituted trioxo, dioxo and monooxo species are often obtained from the unsubstituted oxo anions or oxides with the appropriate ligands.

Most oxo complexes are oxidising agents. For a series of complexes in a periodic group the oxidising power normally falls in the sequence

1st row $\gg$ 2nd row $>$ 3rd row

as do the acid strengths of the unsubstituted oxo anions. The tendency of oxo anions to polymerise in solution increases with increasing acidity of the solution (since H^+ is usually involved in the process) and normally falls in the sequence

3^{rd} row > 2^{nd} row ≫ 1^{st} row

This may be associated with the increase of acid strength of the oxo anions in this series together with the higher preferred coordination numbers of second and third row elements, the latter factor giving more possibilities of polymerisation. For first row elements this polymerisation decreases in the sequence

$Ti^{IV} > V^{V} > Cr^{VI} > Mn^{VII}$

Protonation of the oxo ligands in oxo complexes is usually difficult except for tetraoxo anions. In the dioxo species, *trans*-$[MO_2X_4]^{n-}$, protonation to $[MO(OH)X_4]^{(n-1)-}$ by strong acids does not occur for Os^{VI} or Ru^{VI} but does for Re^{V}, Mo^{IV} and W^{IV}, the lower oxidation state presumably giving more *p*-character to the sp_σ-orbital containing the oxygen lone pair. Protonation of monooxo species is very rare indeed.

(vi) Structure and bonding

In this section we shall briefly summarise the various approaches which have been made to the difficult subject of metal–oxygen bonding in oxo species. It is both convenient and logical to include in this section a summary of structural data which have been obtained on such species, but a comprehensive catalogue has not been given because some of the earlier measurements are of low accuracy.

Tetra- and tri-oxo species —Bond length data for a number of tetra- and tri-oxo species are listed in Table 2; all the M–O distances are short, indicating the presence of a considerable degree of M–O double bonding

There has been a number of attempts to describe the bonding in $[MO_4]^{n-}$ complexes on the basis of molecular orbital theory. The test of success for these

TABLE 2

BOND LENGTHS IN TETRAOXO COMPLEXES, $[MO_4]^{n-}$

Complex	d_{M-O} *(Å)*	*Space group*	[z]	*Ref*
$Ba_2[TiO_4]$	2 at 1 63 (0 02) 2 at 1.78 (0 02)	$P2_1/n$	4	13
$Bi[VO_4]$ (pucherite)	1 86 (0 07) av.	*Pnca*	4	14
Y, $Yb[NbO_4]$	1 89	$I4_1/a$	4	15
$K_2[MoO_4]$	1 76 (0 01)	$C2/m$	4	16
$Pb[MoO_4]$	1.772 (0 006)	$I4_1/a$	4	17
$Li_2[WO_4]$	1.79 (0 02)	$R\bar{3}$	6	18
$K[MnO_4]$	1 629 (0 008)	*Pnma*	4	19
$K_2[MnO_4]$	1 659 (0 008)	*Pnma*	4	20
$K[RuO_4]$	1 79	$I4_1/a$	4	21
OsO_4(gas)[a]	1 711 (0 003)			22
OsO_4	1 74 (0 03)	$C2/c$	4	23

[a] All X-ray data on solids except OsO_4(gas) electron diffraction on vapour

schemes is that they should be able to explain the observed electronic spectra of the complexes, and also the ESR spectra of those ions which are paramagnetic. The high oxidation states of the metal atoms in all $[MO_4]^{n-}$ complexes infers that the M–O bond is likely to have a high degree of covalency with attendant extensive σ and π delocalisation of charge (both the t_2 and e orbitals on the metal are involved in π-bonding in tetrahedral species), and there is likely to be considerable mixing of d and p metal orbitals. All these factors lead to considerable difficulties in formulating a consistent theory for tetraoxo complexes.

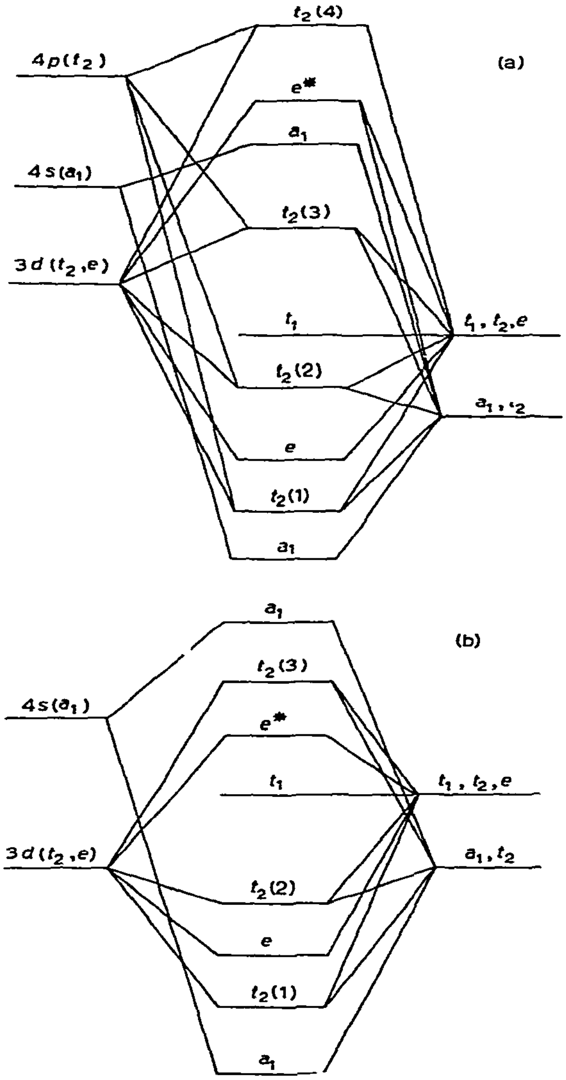


Fig. 1. Molecular orbital schemes for $[MO_4]^{n-}$ species: (a) Wolfsberg and Helmholz[24], (b) Ballhausen and Liehr[25].

The earliest attempt at a semi-empirical MO approach was that of Wolfsberg and Helmholz on the permanganate and chromate ions[24] (Fig. 1a). Their scheme was criticised by Ballhausen and Liehr who proposed a somewhat different order of energy levels[25] (Fig. 1b), which was found by Carrington and Schonland to be more consistent with the electronic spectra of d^0 tetraoxo anions and the ESR and electronic spectra of d^1 and d^2 species[26]. A recent critical reassessment of the two theories as applied to the ions $[MnO_4]^-$, $[MnO_4]^{2-}$, and $[MnO_4]^{3-}$, suggests that either method is capable of explaining the spectral data depending on the degree of *s* and *p* participation in the hybrid ligand orbitals[27].

The most comprehensive molecular orbital scheme for tetraoxo anions has been proposed by Viste and Gray; their treatment is basically similar to that of Ballhausen and Gray, but, unlike the former, it takes account of oxygen 2*s* orbital participation as well as oxygen 2*p*, metal 3*d*, 4*s* and 4*p* orbitals (as applied to $[MnO_4]^-$)[28]. The resulting scheme was applied to d^0 species ($[VO_4]^{3-}$, $[CrO_4]^{2-}$, $[MnO_4]^-$, $[MoO_4]^{2-}$, $[TcO_4]^-$, RuO_4, $[WO_4]^{2-}$, $[ReO_4]^-$, OsO_4); d^1 systems ($[CrO_4]^{3-}$, $[MnO_4]^{2-}$, $[RuO_4]^-$); and d^2 systems ($[MnO_4]^{3-}$, $[FeO_4]^{2-}$, $[RuO_4]^{2-}$) For some of these ions it was possible to establish Δ-values[28]:

Value of orbital parameter Δ in tetraoxo anions ($cm^{-1} \times 10^{-3}$)

$[CrO_4]^{2-}$	16.0	$[FeO_4]^{2-}$	12.72
$[MnO_4]^-$	26.0	$[RuO_4]^-$	28.5
$[MnO_4]^{2-}$	19.0	$[RuO_4]^{2-}$	21.6
$[MnO_4]^{3-}$	11.0		

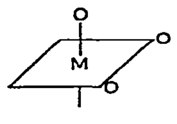
It is significant that the Δ-values decrease in the expected sequences,

e g. $Mn^{VII} > Mn^{VI} > Mn^{V}$
and $Ru^{VII} > Ru^{VI} > Fe^{VI}$ [28]

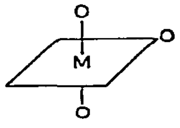
A SCF–LCAO treatment has been applied to $[CrO_4]^{3-}$ using D_{2d} rather than T_d symmetry for the anion[29].

For tetraoxo complexes of the form $[MO_4X_2]^{n-}$ there have been no theoretical treatments; it has been proposed that, for d^0 complexes of this type, a *cis* rather than a *trans* stereochemistry is likely on the basis of the distribution of metal–oxo π-bonding, and this is found to be the case from studies of the vibrational spectra of known species of this type[41].

Trioxo and dioxo complexes. — (See Table 3). No bonding theory has been proposed for $[MO_3X]^{n-}$ or $[MO_3X_3]^{n-}$ complexes. For the latter a *cis* (1, 2, 3) (1) rather than a "*trans*" (1, 2, 6) (2) stereochemistry is expected on the basis of the competition of oxygen p_π orbitals for metal t_{2g} electrons[41,42].



(1)



(2)

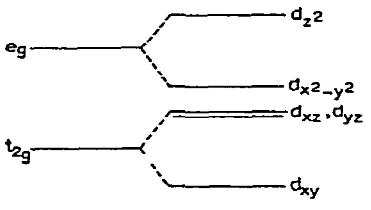
TABLE 3

STRUCTURAL DATA ON TRIOXO AND DIOXO COMPLEXES

Complex	d_{M-O} *(Å)*	*Other data*	*Space group*	[z]	*Point group*	*Ref*
$VOCl_3$ (gas)[a]	1 56 (0 04)	V–Cl 2.12 (0 03)			C_{2v}	30
$K[CrO_3Cl]$	1.53	Cr–Cl 2 16	$P2_1/c$	4	C_{3v}	31
MoO_3(dien)	1 736 (0 008)	Mo–N 2 330 (0 009) $\widehat{OMoO}$ 106° (0 3)	*Pbcm*	4	C_{3v}	32
MnO_3F (gas)[b]	1 586 (0 005)	Mn–F 1.724 (0 005) $\widehat{OMnF}$ 108 3°			C_{3v}	33
ReO_3F[b]	1 692 (0 003)	Re–F 1 859 (0 008)			C_{3v}	34
ReO_3Cl[b]	1 761 (0 003)	Re–Cl 2 230 (0 004)			C_{3v}	35
$K[OsO_3N]$	1 75 (0 02)		$I4_1/a$	4	C_{3v}	35*a*
CrO_2Cl_2 (gas)[a]	1 57	Cr–Cl 2 12 $\widehat{OCrO}$ 105°			C_{2v}	30
MoO_2Cl_2 (gas)[a]	1.75 (0 1)	Mo–Cl 2 28 (0 03)			C_{2v}	36
$K_2[MoO_2F_4] \cdot H_2O$	1 71 (0 02)	Mo–F 1 94 (0 02) $\widehat{OMoO}$ 95 1 (1)°	$P2_1/c$	4	C_{2v}	36*a*
$MoO_2Cl_2(Me_2NCHO)_2$	1 68 (0.01)	Mo–O 2 20 (0 01) Mo–Cl 2 341 (0 007)	$C2/c$	4	C_{2v}	36*b*
$NaK_3[MoO_2(CN)_4]$ $6H_2O$	1 834 (0 009)	Mo–C 2 204 (0 013)	*Pmna*	2	D_{4h}	37
$K_3[ReO_2(CN)_4]$	1 87	Re–C 1 91			D_{4h}	38
$K_2[OsO_2Cl_4]$	1 750 (0 02)	Os–Cl 2 379 (0 005)	$I4/mmm$		D_{4h}	39
$K_2[OsO_2(OH)_4]$	1 77	Os–(OH) 2 03	$I4/m$	2	D_{4h}	40

[a] Electron diffraction [b] Microwave spectroscopy

For dioxo complexes of the type $[Os^{VI}O_2X_4]^{n-}$ there has been some discussion of possible molecular orbitals[43]. Lott and Symons first explained the diamagnetism of d^2 *trans*-$[Os^{VI}O_2X_4]^{n-}$, $[Ru^{VI}O_2X_4]^{n-}$ and $[Re^{V}O_2X_4]^{n-}$ species by suggesting that the D_{4h} symmetry of the complex anion split the ligand field to give a low lying d_{xy} orbital in which the two d electrons pair up (3)[44]:



(3)

The strong π-donor effect of the oxo ligand in octahedral complexes makes it likely that d^0 species of the type $[MO_2X_4]^{n-}$ will take a *cis* configuration while d^2 species will be *trans*[42].

Monooxo complexes, $[MOX_5]^{n-}$ *and* $[MOX_4]^{n-}$. —(See Table 4). A molecular orbital treatment has been given for the bonding in vanadyl(IV) species,

TABLE 4

STRUCTURAL DATA ON MONOOXO COMPLEXES

Complex	d_{M-O} (Å)	*Other data*	*Space group*	[z]	*Point group*	*Ref*
$(Et_4N)_2[TiOCl_4]$	1.79	Ti–Cl 2.34		2	C_{4v}	45
$(NH_4)_2[VO(NCS)_4(H_2O)]$	1.62 (0.06)	V–OH_2 2.22 (0.05) V–N 2.04 (0.03)	$P2_1/n$	4	C_{4v}	46
$VO(acac)_2$	1.56 (0.01)	V–O(acac) 1.97 (0.01)	$P\bar{1}$	2	C_{2v}	47
$K_2[NbOF_5]$[a]	1.68	Nb–F(4) 1.84 Nb–F(*tr*) 2.06	$P4/mmm$	2	C_{4v}	48
$K_3[NbOF_6]$	2.0	Nb–F 2.0	$Fm3m$	4	C_{3v}	49
$(NH_4)_3[NbOox_3]H_2O$	1.71 (0.01)	Nb–O(ox) 2.14 (0.01)	$P2/c$	4	C_s	50
$CrO(O_2)_2py$	1.576 (0.002)	Cr–O(per.) 1.796, 1.844 Cr–N 2.047 (0.002)	$Pnma$	4	C_s	51
$K_2[MoO(O_2)F_4] \cdot H_2O$	1.64 (0.02)	Mo–O 1.93 (0.02), $\widehat{OMoO}$ 43°	$P2_1/c$	4	C_s	51*a*
$(Ph_4As)\,[MoOBr_4(H_2O)]$	1.78 (0.07)	Mo–OH_2 2.39 (0.03) Mo–Br 2.516 (0.004)	$P4/n$	2	C_{4v}	52
$(Et_4N)\,[ReOBr_4(H_2O)]$	1.71 (0.04)	Re–OH_2 2.32 (0.01) Re–Br 2.51 (0.01)	$Pnam$	4	C_{4v}	53
$(Ph_4As)\,[ReOBr_4(MeCN)]$	1.73 (0.06)	Re–N 2.31 (0.06) Re–Br 2.48 (0.03)	$P\bar{1}$	2	C_{4v}	54
$ReOCl_3(PEt_2Ph)_2$	1.60 (0.02)	Re–P 2.45 (0.02) Re–Cl 2.41 (0.02)	$P2_1/c$	4		55

[a] Electron diffraction

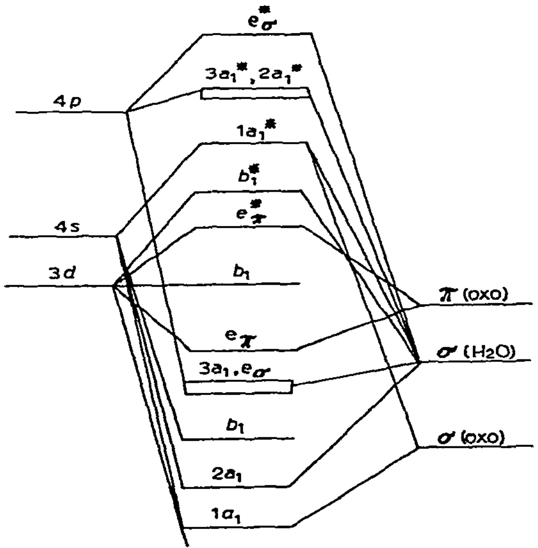


Fig. 2. Molecular orbital scheme for $[VO(H_2O)_5]^{2+}$ [56].

$[VO(H_2O)_5]^{2+}$, $[CrOCl_5]^{2-}$ and $[MoOCl_5]^{2-}$[56,57], and satisfactorily accounts for the observed electronic absorption and electron spin resonance spectra of these d^1 species. The MO scheme for the vanadyl ion together with the appropriate axes is given in Fig. 2 below[56]. For $[MOX_5]^{n-}$ species the bonding may be summarised as follows[56,57]:

O–M σ-bond: sp_σ to $nd_{z^2}+(n+1)s$ (a_1)
O–M π-bonds: (two, degenerate) $2p_x$ and $2p_y$ to nd_{xz} and nd_{yz} (e)
X_4–M (cis) bonds. $sp_\sigma(H_2O)$ to $(n+1)s-nd_{z^2}$ (a) $(n+1)p_x$
and $(n+1)p_y$ (e); $nd_{x^2-y^2}$ (b_1)
X–M bond (trans): $sp_\sigma(H_2O)$ to $(n+1)p_z$ (a_1)

This leaves the d_{xy} orbital non-bonding (b_2).

The resistance of monooxo complexes to protonation is then ascribed to the fact that the remaining lone pair on oxygen is in a sp_σ hybrid orbital (since two $2p_\pi$ orbitals are used from the oxygen to bond to the metal atom); its considerable s character renders it less suitable for bonding purposes[56].

This scheme of Ballhausen and Gray works well for vanadyl and chromyl complexes, but the observed electronic spectra of $[MoOBr_5]^{2-}$ and $[WOX_5]^{2-}$ (X = Cl, Br) are not in such good agreement with theoretical predictions. It has been suggested that the reason for this may be that the properties of the halogen ligands become more important for these second and third row complexes[58] (this factor is of course neglected in the simple theory).

Recent studies on the electronic spectra of the $[VOCl_4]^{2-}$ ion have been interpreted on the basis of a slightly different MO scheme. The order of levels is the same as that proposed by Ballhausen and Gray but the π-interaction of the d_{xy} orbital with the equatorial ligands was considered, and it was suggested that the treatment could be extended to cover other $[MOX_5]^{n-}$ species (M = Cr, Mo, W)[59]. As with Ballhausen and Gray's scheme, metal–oxygen $4p_\pi$–$2p_\pi$ bonding was neglected. Selbin *et al* have considered the bonding in vanadyl(IV) complexes[60].

Polynuclear complexes — (See Table 5). No full calculations on the bonding in oxo-bridged polynuclear species have been made. However, Dunitz and Orgel have given an account of the bonding in the $[Ru_2OCl_{10}]^{4-}$ ion which accounts well for the observed electronic and magnetic properties of the ion. In $[Ru_2OCl_{10}]^{4-}$ the structure is centrosymmetric D_{4h}[70] (Fig 3).
Neglecting σ-bonding there are six t_{2g} orbitals ($2\ d_{xy}$, $2\ d_{xz}$, $2\ d_{yz}$) from the two

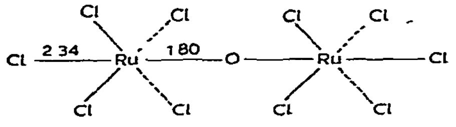


Fig 3 Structure of anion in $K_4[Ru_2OCl_{10}]$.

TABLE 5

STRUCTURAL DATA ON POLYNUCLEAR COMPLEXES

Complex	d_{M-O} *(Å) (bridge)*	*Other data*	*Space group*	[*z*]	*Point group*	*Ref*
$[CpTiCl_2]_2O$	1.74	Ti–C 2 38 Ti–Cl 2 28	$P2_1/c$	2	C_s	61
$K_2Cr_2O_7$	1 79 (0 01)	Cr=O 1 61 (0 03), $\widehat{CrOCr}$ 106°	$P\bar{1}$	4	C_{2v}	61*a*
$Cd_2[V_2O_7]$	1.76 (0 04)	V–O(ter) 1 70 $\widehat{VOV}$ 180°	$C2/m$	2	C_{2h}	62
$[Cr_3O(OAc)_6(H_2O)_3]Cl \cdot 5H_2O$	2 0	Cr–O(OAc) 2 0	$P2_12_12$	4	D_{3h}	63
$Na_2[Mo_2O_4(cysteine)_2] \cdot 5H_2O$	2 at 1 93	Mo–O(ter) 1.71 Mo–O(cyst.) 2 29 $\widehat{MoOMo}$ 83°	$P2_12_12$	4	C_s	63*a*
$K_2[Mo_2O_5ox_2(H_2O)_2]$	1 876 (0 002)	Mo–O(ter) 1.690 (0 02) Mo–O(ox) 2 10 (0 02) $\widehat{MoOMo}$ 180°	$P2_1/c$	2	C_s	64
$Ba[Mo_2O_4ox_2(H_2O)_2]$	2 at 1 93 (0 03)	Mo–O(ter) 1 70 (0 03) Mo–O(ox) 2 11 (0.03) Mo–Mo 2 541 $\widehat{MoOMo}$ 83 5°	$P3_121$	3	C_s	65
$\{Na(NH_4)\ [MoO_3ox]\}_n$	2 230 and 1 878 (0 004)	Mo–O(ter) 1 82 (0 004) Mo–O(ox) 2 235 (0 004) $\widehat{MoOMo}$ 149°	$P2_1/c$	4	C_s	66
$Mo_2O_3(C_2H_5OCS)_4$	1.851 (0 03)	Mo–O(ter) 1 644 (0 03) Mo–S 2 50 (0 01) $\widehat{MoOMo}$ 180°	$P2_1$	2	C_s	67
$K_2[W_2O_3(O_2)_4(H_2O)_2]\ \ 2H_2O$	1 93 (0 02)	W–O(ter) 1 68 (0 02) $W–OH_2$ 2 35 (0 02) $\widehat{WOW}$ 139°	$P\bar{1}$	2	C_{2v}	68
$K_4[Re_2OCl_{10}]$	1 86 (0 005)	Re–Cl 2 38 (0 02) $\widehat{ReORe}$ 180°	$I4/mmm$	2	D_{4h}	69
$K_4[Ru_2OCl_{10}]$	1.80	Ru–Cl 2 34 $\widehat{RuORu}$ 180°	$I4/mmm$	2	D_{4h}	70
$K_4[Os_2O_6(NO_2)_4]$	2 08	Os=O 1.79 Os–N 2 16	$P2_1/c$	4	C_{2v}	71
$Cu_4OCl_6(Ph_3PO)_4$	1 905 (0 003)	Cu–O 1 89 (0 02) Cu–Cl 2 38 (0 01)	$P\bar{4}3m$	1	T_d	72

metal atoms and two $2p_\pi$ (p_y, p_z) orbitals from oxygen. Under D_{4h} symmetry these combine to give two sets of bonding, two of non-bonding and two of anti-bonding molecular orbitals The eight electrons from the ruthenium atoms and four from the oxygen will then fill up the bonding and non-bonding orbitals to give overall diamagnetism, and such a scheme will also account for the diamagnetism of the osmium analogues[73]. The scheme would however predict paramagnetism for $[Cr_2O(NH_3)_{10}]^{4+}$ and $[Re_2OCl_{10}]^{4-}$ (one unpaired electron per metal atom) whereas in both cases the moments at room temperature are less than this (*cf.* p. 495 and 502) [see Ref. (8) for another treatment of $[Re_2OCl_{10}]^{4-}$].

In the trinuclear ruthenium red complexes $[Ru_3O_2(NH_3)_{14}]^{6+}$ and $[Ru_3O_2(NH_3)_{14}]^{7+}$, which are believed to contain linear Ru–O–Ru–O–Ru units (p. 509) a molecular orbital treatment has been devised which is analogous to that for $[Ru_2OCl_{10}]^{4-}$; it satisfactorily explains the diamagnetism of the sextuply charged complex and the fact that $[Ru_3O_2(NH_3)_{14}]^{7+}$ has one unpaired electron per three metal atoms (p. 509). It also provides a partial assignment of the electronic absorption spectra of the compounds[74].

For the trinuclear species which contain coplanar triangular (M_3O) units in which the oxygen atom sits at the centre of an equilateral triangle [*viz.* in $[M_3O(OOCR)_6]^+$, where M = Cr, Fe, Ru and Al; in $[Ir_3O(SO_4)_9]^{10-}$ and the related nitrido species $[Ir_3N(SO_4)_6(H_2O)_3{}^{4-}]$ it has been suggested that a four-centre molecular orbital system encompasses the M_3O units, comprising the three metal t_{2g} orbitals which have the appropriate symmetry to overlap with the fourth atomic orbital, the p_z orbital on the central oxygen atom[74]. Again, the results are broadly in agreement with the electronic spectra[75] (p. 478) and vibrational spectra (p. 475) of such complexes.

(vii) Physical measurements

We have already reviewed, in Tables 2–5, the bond length data; comment on the values is made, when appropriate, in Part C.

(*a*) *Vibrational spectra*.—There has been considerable interest in the vibrational spectra of oxo complexes, mainly because the stretching and deformation modes associated with M–S (π-bonded) systems show characteristically sharp and intense bands in the Raman and the IR. Raman spectroscopy is particularly useful for obtaining information on the structures of oxo species in aqueous solution, since water has only a very weak Raman spectrum

Species containing $[MO_6]^{n-}$, $[MO_5]^{n-}$ *and* $[MO_4X_2]^{n-}$. Vibrational spectra of a number of transition metal complexes of these types have recently been studied. As mentioned previously (p. 461) it is unlikely that the hexa- and penta-species contain discrete $[MO_x]^{n-}$ ions, but most of them give strong Raman bands near 770 cm^{-1}, presumably to be associated with a symmetric M–O_x stretch. The complexes studied (using their empirical formulae), were $Na_5[ReO_6)$, $Ba_3[WO_6]$, $Ba_3[MoO_6]$, $Ba_5[OsO_6]_2$, $Ba_3[OsO_6]$, $K_3[ReO_5]$, $Na_3[ReO_5]$, and $K_3[OsO_5]$[41]. The tetraoxo species $Cs_2[OsO_4F_2]$, $K_2[OsO_4(OH)_2]$ and $Ba_3[ReO_4(OH)_2]_2$ have been studied by Raman and IR spectroscopy, and the results show that the anions have a *cis* configuration[41].

TABLE 6

VIBRATIONAL SPECTRA[a] OF $[MO_4]^{n-}$ COMPLEXES

Ion	*Method*[b]	ν_1 (A_1)	ν_2 (E)	ν_3 (F_2)	ν_4 (F_2)	*Sample*	*Ref*
$[TiO_4]^{4-}$	R	745	250			$Ba_2[TiO_4]$ (s)[c]	77
$[VO_4]^{3-}$	R	827	341	780	341	$K_3[VO_4]/H_2O$	78
$[CrO_4]^{2-}$	R	847	348	884	368	$K_2[CrO_4]/H_2O$	79
$[MoO_4]^{2-}$	R	897	318	841	318	$Na_2[MoO_4]/H_2O$	80
$[WO_4]^{2-}$	R	931	324	833	324	$Na_2[WO_4]/H_2O$	81
$[MnO_4]^-$	R	838	355	921	429	$K[MnO_4]/H_2O$	82
$[MnO_4]^{2-}$	IR	810		862	328	$K_2[MnO_4]$ (s)	83
$[MnO_4]^{3-}$	IR	836		770	348	$Na_3[MnO_4]$ (s)	83
$[FeO_4]^-$	R	912	325	912	325	$K[FeO_4]/H_2O$	80
$[ReO_4]^-$	R	971	332	916	332	$K[ReO_4]/H_2O$	81
$[FeO_4]^{2-}$	IR	778		800	320	$K_2[FeO_4]$ (s)	83
RuO_4	R	883	338	918	332	RuO_4 (liq)	84*a*
$[RuO_4]^-$	IR	826		848	282	$K[RuO_4]$ (s)	84
$[RuO_4]^{2-}$	R	810	330	836	330	$K_2[RuO_4]/H_2O$	84
OsO_4	R	964	338	953	334	OsO_4 (liq)	84

[a] Frequencies in cm^{-1}. [b] R = Raman, IR = infrared. All modes Raman active; F_2 mode also IR-active [c] s = solid

Tetraoxo anions, $[MO_4]^{n-}$. (See Table 6) The vibrational spectra of a wide range of tetrahedral species of this type have been measured, and the most recent values for the four fundamental modes for the T_d tetrahedron listed in Table 6. There has been considerable discussion on the interpretation of the spectra of $[MO_4]^{n-}$ species in solution respecting the positions of the deformation modes $\nu_2(E)$ and $\nu_4(F_2)$; in some cases only one band is found in the Raman spectra which may be ascribed to these. It has been variously claimed that, in species like $[MoO_4]^{2-}$, $[WO_4]^{2-}$, $[TcO_4]^-$ and OsO_4 that either ν_2 and ν_4 are coincident[81] or that ν_2 is too weak or too broad to be observed[80]; the author[84] inclines to the former view.

The force fields used include an orbital valency field[85], Urey–Bradley[86], a general valency force field (using a least squares method)[87] and a number of other force fields[88–90]. The difficulty with establishing a reasonable force field for tetraoxo molecules or ions is that there are only four fundamental frequencies from which the force constants are calculated, so gross approximations or assumptions have to be made on the values of the interaction constants. The situation would be greatly helped if data on $[M^{18}O_4]^{n-}$ species were available; so far there have been only incomplete studies on the IR spectra of $K[Mn^{18}O_4]$[91] and $Os^{18}O_4$[92].

The IR spectra of gaseous osmium tetroxide have been studied and Coriolis ζ constants obtained for this molecule[92]; there is some discussion of the interpretation of the results[93]. Coriolis ζ constants have also been calculated for RuO_4, $[TcO_4]^-$ and $[MoO_4]^{2-}$[84a,94].

TABLE 7

VIBRATIONAL SPECTRA[a] OF $[MO_3X]^-$ AND MOX_3 COMPLEXES

Complex	Method	A_1 (R, IR)			E (R, IR)			Ref
		ν_1 ν_{MO_3}	ν_2 ν_{MX}	ν_3 δ_{MO_3}	ν_4 ν_{MO_3}	ν_5 δ_{MO_3}	ν_6 δ_{MOX}	
$[CrO_3F]^-$	R	911	637	338	955	370	261	95
$[CrO_3Cl]^-$	R	907	438	295	954	365	209	96
ReO_3Cl^+	R	1001	435	293	960	344	196	97
ReO_3Br	R	997	195	350	963	332	168	97
$[OsO_3N]^-$	R, IR	897	1021	309	871	309	372	98
		ν_{MO}	ν_{MX_3}	δ_{MX_3}	ν_{MX_3}	δ_{MX_3}	δ_{MOX}	
VOF_3	R, IR	1060	720		805			99
$VOCl_3$*	R, IR	1035	408	165	504	249	129	100
$VOBr_3$*	R, IR	1025	271	120	400	83	212	101

[a] All spectra on samples in solution except* liquid.

Trioxo complexes. In Table 7 we list the fundamental modes of vibration for $[CrO_3F]^-$, $[CrO_3Cl]^-$, ReO_3Cl, ReO_3Br and $[OsO_3N]^-$; normal coordinate analyses for ReO_3Cl, ReO_3Br and $[ReO_3N]^{2-}$ have been carried out[102,103]. Studies have also been made of the vibrational spectra of the *cis* (1, 2, 3) trioxo species $K[OsO_3F_3]$, $K_3[WO_3F_3]$, $K_3[MoO_3F_3]$ and MoO_3 (dien)[41,42].

Dioxo complexes. (See Table 8). Both IR[106,107] and Raman[41] spectra of "osmyl" complexes, $[Os^{VI}O_2X_4]^{n-}$ (X = Cl, Br, CN, $\frac{1}{2}$ox, OH, NH_3) have been reported. IR[41,108] and some Raman[41] data have also been recorded on some *trans*-$[ReO_2X_4]^{n-}$ (X = CN, $\frac{1}{2}$en, py) complexes and *trans*-$[MoO_2(CN)_4]^{2-}$. In general, in such *trans* dioxo species, the symmetric MO_2 stretch is found near 880 cm^{-1} and the asymmetric MO_2 stretch near 800 cm^{-1} for osmium species, with values some 50 cm^{-1} lower for rhenium and molybdenum complexes; the

TABLE 8

VIBRATIONAL SPECTRA[a] OF GASEOUS MO_2X_2 SPECIES (C_{2v})

Complex	Method	A_1 (R, IR)				A_2(R) B_1 (R, IR)					Ref
		ν_1 ν_{MO_2}	ν_2 ν_{MX_2}	ν_3 δ_{MX_2}	ν_4 δ_{MX_2}	ν_5 τ	ν_6 ν_{MO_2}	ν_7 ρ_{MO_2}	ν_8 ν_{MX_2}	ν_9 ρ_{MX_2}	
CrO_2F_2*	R, IR	1006	727	304	(182)	(422)	1016	274	789	(259)	104
CrO_2Cl_2	R	984	465	357	144	216	994	230	497	263	105
MoO_2F_2	IR	987	692				1009		710		112
MoO_2Cl_2	IR	994	437				972		453		112
MoO_2Br_2	IR	991					969				112
MoO_2I_2	IR	972					950				112
WO_2Cl_2	IR	992	430				978		437		112
WO_2Br_2	IR	985					973				112
WO_2I_2	IR	980					960				112

[a] All spectra on gaseous samples except* liquid

TABLE 9

VIBRATIONAL SPECTRA[a] OF $MOX_5{}^{n-}$ AND MOX_4 SPECIES (C_{4v})

Complex	*Method*	*A_1 (R, IR)*					*E (R, IR)*				*Ref.*
		ν_1 ν_{MO}	ν_2 ν_{MX_4}	ν_3 $\nu_{MX'}$	ν_4 δ_{O-M-X}	ν_5 δ_{X-M-X}	ν_8 ν_{MX_4}	ν_9 δ_{O-M-X}	ν_{10} δ_{X-M-X}	ν_{11} $\delta_{X-M-X'}$	
$Cs_2[VOCl_5]$	IR	960	342	333	186		342	260	90		109
$[NbOF_5]^{2-}$*	R	945p	658p	613	288	264					110
$Cs_2[NbOCl_5]$	IR	928	330	320	231	180	325	217	168	85	111
	R	948p	345p		235						110
$Cs_2[NbOBr_5]$	IR	977	241		211	140	241	202	111		111
$Cs_2[CrOCl_5]$	IR	930	343	313	195	187	343	240	84		111
$Cs_2[MoOCl_5]$	IR	952	329	320	227	178	253			86	111
$Cs_2[MoOBr_5]$	IR	972 962	253	244	207	132		187	128	119	111
$MoOF_4$**	IR	1030	553	539			527 516				112
$Cs_2[WOCl_5]$	IR	957	333	309	230	174			164	84	111
$Cs_2[WOBr_5]$	IR	960	220		202	143			119		111
WOF_4	IR	1030	554	533 539			527 516				112

[a] All spectra on solids except **gases and *aqueous solution

δ_{MO_2} deformation mode lies near 350 cm^{-1} In *cis*-dioxo complexes such as *cis*-$[MO_2X_4]^{n-}$ (M = Mo^{VI}, W^{VI}, V^{V}; X = F, Cl), the symmetric and asymmetric MO_2 stretches are observed in both the Raman and the IR near 930 and 900 cm^{-1} with deformation δ_{MO_2} bands near 300 cm^{-1}[141]. A force field has been proposed for osmyl species[107].

In Table 8 we also list fundamental modes of vibration for a number of MO_2X_2 species; the chromium complexes are monomeric in the solid state and the molybdenum and tungsten polymeric as solids, but monomeric as gases.

Monooxo complexes (See Table 9) There are extensive IR studies on the $\nu_{M=O}$ stretching frequency in a number of vanadyl(IV)[60,113,114] complexes (*cf* p. 486), and some Raman and infrared data on $[MOX_5]^{n-}$ (M = V, Nb, Mo, W, X = Cl, Br) and $[MOX_4]^{n-}$ (M = Mo, W; X = Cl, Br, I) In general terminal M–O stretches in monooxo complexes appear in the range 900–1050 cm^{-1}, depending on the oxidation state of the metal and the nature of the X ligands; a frequency in this range is often used as diagnostic of a terminal M=O bond.

Vibrational spectra have also been measured of VOX_3 complexes (X = F, Cl, Br) (Table 7).

Polynuclear complexes. The IR and far IR spectra have been measured of a number of binuclear complexes with single oxo bridges (*e g*. $[M_2OX_{10}]^{n-}$ (M = Os, Ru, Re; X = Cl, Br)[115] and Raman spectra of such species have also been measured[41]; force constant treatments have been proposed[116]. Spectra have also been measured of a few complexes containing two oxo bridges[41]. In general, in binuclear species containing linear M–O–M units, the asymmetric M–O–M stretch is found near 860 cm^{-1} and the corresponding symmetric mode is found in the Raman near 240 cm^{-1} (in analogous bridging nitrido complexes the asymmetric M–N–M mode is near 1080 cm^{-1} and the symmetric mode near 310 cm^{-1}, indicative of the greater π-bonding in metal–nitride rather than metal–oxide systems)[117]. A comparison of metal–oxo and metal–nitride vibrational frequencies has been tabulated. For systems containing bent M–O–M units the asymmetric M–O–M mode is found near 750 cm^{-1}, the symmetric near 500 cm^{-1} and the deformation mode near 200 cm^{-1} (for M = V, Cr, such values are very dependent on the mass of M).

Studies of the vibrational spectra of trinuclear complexes have recently been made; for $[Ru_3O_2(NH_3)_{14}]^{6+}$ and $[Ru_3O_2(NH_3)_{14}]^{7+}$ the infrared active Ru_3O_2 stretch occurs near 800 cm^{-1} and the symmetric stretch near 200 cm^{-1}; in complexes containing coplanar triangular M_3O units such as
$[M_3O(CH_3COO)_6(H_2O)_3]^+$
(M = Fe, Cr, Ru) and $[Ir_3O(SO_4)_9]^{10-}$ the asymmetric M_3O stretch is near 660 cm^{-1} and the symmetric M_3O mode near 190 cm^{-1} [118].

(*b*) *Electronic spectra.*—There have been no comprehensive studies on the electronic spectra of hexa-, penta- or substituted tetra-oxo species.

Tetraoxo anions, $[MO_4]^{n-}$. The electronic absorption spectra of most tetraoxo anions having d^0, d^1, or d^2 electronic configurations have been studied and assignments of charge transfer and crystal field bands made; most of the main band positions are listed in the review by Carrington and Symons[5]. As mentioned above (p. 465) the electronic spectra of such species have been useful as a check on the validity of the various theories of bonding in $[MO_4]^{n-}$ species; although the MO scheme of Wolfsberg and Helmholz[24] gives an approximate agreement between theory and observation for the spectra of d^0 ions, a better result is obtained by using Ballhausen and Liehr's scheme[25] or Gray and Viste's[28]. The most comprehensive papers on the electronic spectra of tetraoxo anions and their interpretations are those by Carrington and Schonland[26] (who use the Ballhausen and Liehr scheme) and Gray and Viste[28] (who use their own modification of the Ballhausen and Liehr scheme) Observations of the effects of pressure and environmental changes on the spectra of solid tetraoxo salts have been reviewed[5].

Dioxo species. Litt and Symons have interpreted the electronic spectra of $K_2[OsO_2(OH)_4]$ in terms of D_{4h} symmetry[44].

Monooxo species. The molecular orbital scheme proposed for bonding in vanadyl(IV), chromyl(V) and molybdenyl(V) species accounts well for the experimentally observed electronic spectra[56,57] although the agreement is not so good for $[MoOBr_5]^{2-}$ and $[WOX_5]^{2-}$ [58,59]: for the latter, a scheme involving π-bonding from the other ligands in the complex has been proposed[59]. The electronic spectra of a number of vanadyl(IV) species have been extensively studied[60]. There are also studies on vanadium-(V) and -(IV) monooxo species[59], single crystal polarised spectra of $[VOCl_5]^{3-}$ and $[MoOX_5]^{2-}$ (X = F, Cl, Br)[119], and solution spectra of $[TcOCl_5]^{2-}$ and $[ReOX_5]^{2-}$ (X = Cl, Br, I)[120].

Single crystal spectra of a number of monooxo species have been recorded; the subject has been reviewed[121].

Polynuclear species. The electronic absorption spectra of $[Ru_2OCl_{10}]^{4-}$ [74,122] $[Re_2OCl_{10}]^{4-}$ [123] and $[Cr_2O(NH_3)_{10}]^{4+}$ [124] have been recorded and assignments of bands proposed. For trinuclear species there are studies and assignments for $[Ru_3O_2(NH_3)_{14}]^{6+}$ [74] and $[Ir_3O(SO_4)_9]^{10-}$ [74,75] and recently the absorption spectra in the visible region of $[M_3O(CH_3COO)_6L_3]^+$ (L = H_2O, NH_3, py, DMSO, MeOH, EtOH; M = Cr, Fe) have been interpreted on the basis of ligand field theory for tetragonal fields[125].

(*c*) *Electron spin resonance spectra.* — *Tetraoxo anions.* Electron spin resonance spectra of paramagnetic tetraoxo anions have been as useful as electronic spectroscopy in assessing the worth of the various MO theories of bonding. Studies on d^1 systems ($[MnO_4]^{2-}$ [126], and $[NbO_4]^{4-}$ in a $CaWO_4$ lattice[127]) and d^2 ($[MnO_4]^{3-}$, $[FeO_4]^{2-}$ and $[RuO_4]^{2-}$) have been made[126].

Monooxo species. Ligand hyperfine structure has been observed in the ESR spectra of $[MOX_5]^{2-}$ (M = Cr, Mo, W; X = F, Br)[128]. Studies have also been made on $[CrOCl_5]^{2-}$ and $[CrOCl_4]^-$ and are consistent with the Hare and Gray molecular orbital scheme for monooxo species (p. 467)[129], though some of the assumptions in this study have been questioned[130,131]. ESR spectra have been used to study the species existing in solutions of molybdenum(V)–hydrobromic acid solutions[130], and three different complexes were detected. The extensive ESR studies which have been carried out on vanadyl(IV) species have been reviewed[114].

(*d*) *Magnetochemistry.*—(See Table 10). *Tetraoxo anions.* In addition to the data in Table 10, magnetic measurements over an unspecified range of temperatures have been made on the following salts (all were found to obey a Curie–Weiss law): $La[CrO_4]$ (1.76); $Y[CrO_4]$ (1.80); $Ba_3[CrO_4]_2$ (1.72); $Ba_2[CrO_4]$ (2 82); $K_3[MnO_4]$ (2.68, $\theta = 5°$); $Cs_3[MnO_4]$ (2.57, $\theta = 5°$) (magnetic moments at room temperatures in parentheses)[135].

Monooxo species. The room temperature magnetic moments of molybdenum(V) and tungsten(V) complexes are very close to the spin-only value of 1.73 B.M. This result is unexpected, since a large spin–orbit coupling leading to

TABLE 10

MAGNETOCHEMICAL STUDIES ON OXO COMPLEXES

Complex	*Range (°K) of study*	μ_{eff} *(T°K) (B.M.)*	θ *(°)*	*Ref.*
$Mg_2[VO_4]$	90–293	1.46 (293)		132
$(pyH)_2[VOCl_4]$	83–303	1.76 (300)	—10	133
$(pyH)_2[VOCl_4]\ 2H_2O$	77–301	1.23 (301)	— 4	133
$Cs_2[CrOCl_5]$	95–300	1.80	—14	134
$K_2[MoOCl_5]$	90–293	1.74 (300)	—27	133, 133*a*
$(NH_4)_2[MoOBr_5]$	90–293	1.72 (300)	—51	133, 133*a*
$Rb_2[MoOCl_4]$	90–293	1.74 (300)	— 0	58
$(pyH)\ [MoOBr_4]$	90–293	1.76 (300)	—16	133*a*
$Rb_2[WOCl_5]$	78–298	1.52 (298)	—16	133*a*
$Cs_2[WOBr_5]$	78–300	1.48 (300)	—20	133*a*
$Q[WOCl_4]^a$	82–298	1.43 (298)	— 2	133*a*
$Q[WOBr_4]^a$	80–301	1.37 (301)	—14	133*a*
$K_2[MnO_4]$	90–293	1.73 (293)		134*a*
$K_2[FeO_4]$	90–291	2.91 (291)		135

[a] Q = quinolinium

lower moments would be expected for these heavy elements. It appears likely that the spin–orbit coupling constant is lowered by the presence of the strongly π-donating oxo ligand[58].

Polynuclear complexes. According to the bonding theory of Dunitz and Orgel[73] (p. 470) $K_4[Re_2OCl_{10}]$ should have a magnetic moment corresponding to one unpaired electron per metal atom, and this should also be the case for $[Cr_2O(NH_3)_{10}]^{4+}$ salts. However, the potassium salt of the rhenium complex has a moment at room temperature of some 0.7 B.M. and the quinolinium salt is diamagnetic[136], it has been suggested that the large spin–orbit coupling constant of rhenium(VI) may have split the E_g level sufficiently for electron pairing to occur[136]. Another bonding scheme has also been proposed to explain the results for the rhenium complex[123]. In the case of the chromium species the moment at room temperature is close to 1.3 B.M. but the complex becomes diamagnetic at low temperatures[137]. Studies have also been made of the magnetic properties over a temperature range of the binuclear Schiff base complexes $[Fe\ base]_2O$ [138], and of the trinuclear species $[M_3O(OOCR)_6]^+$ (M = Cr, Fe)[139,140]; magnetic exchange integrals were evaluated.

(e) Nuclear magnetic resonance spectra — The chemical shift of ^{17}O in a number of tetraoxo complexes has been observed and a linear relationship deduced between the shifts and the lowest electronic transition for the molecule; the origin of the chemical shifts was discussed The complexes studied were $[VO_4]^{3-}$, $[CrO_4]^{2-}$, $[MoO_4]^{2-}$, $[WO_4]^{2-}$, $[TcO_4]^-$, $[ReO_4]^-$, RuO_4 and OsO_4 [141]. The chromate–dichromate equilibrium has been studied by ^{17}O resonance[142] and a

mechanism for the reaction discussed. It has been proposed that there is a relationship between the ^{17}O chemical shift and the degree of Cr–O π-bonding in $[CrO_4]^{2-}$, CrO_2Cl_2 and $[Cr_2O_7]^{2-}$, and that the latter retains a bent Cr–O–Cr unit in aqueous solution[143]. The exchange of water and coordinated water in aqueous solutions of vanadyl(IV) perchlorate has been studied by use of ^{17}O resonance techniques[144], and ^{17}O coupling with ^{55}Mn in $[MnO_4]^-$ studied[144a].

There seems little doubt that this technique, which has recently been reviewed[145], will become a most valuable one for structural and mechanistic studies on oxo complexes.

C. DESCRIPTIVE CHEMISTRY

In this section the oxo chemistry of the members of each periodic group will be summarised. Extensive reference will be made to standard texts or review articles on each element or group of elements, and these sources will be quoted at the head of the appropriate sections. The arrangement of material will be as follows; the elements are considered by their periodic Groups, IVa–VIII. General reviews on the chemistry of the elements will be given, followed by a very brief summary of the known oxides and oxohalides which fall outside the scope of this review. The ensuing discussion of oxo species falls under two categories: unsubstituted species [(*i*) $[MO_6]^{n-}$ and $[MO_5]^{n-}$; (*ii*) $[MO_4]^{n-}$; (*iii*) polyanions — a very brief section since most of such material will fall outside the scope of this review]; and substituted species [(*i*) tetraoxo species; (*ii*) trioxo; (*iii*) dioxo; (*iv*) monooxo; (*v*) polynuclear complexes]. Within each subsection the highest oxidation state of each element will be considered first.

(i) Group IVa (Ti–Zr–Hf)

The main sources of reference for these elements are the standard texts of Gmelin[146] and Pascal[147]; in addition Clark's monograph of titanium and vanadium is of considerable use[148].

(a) Oxides and oxohalides. — The dioxides MO_2 are the principal oxides; all three forms of TiO_2 (rutile, anatase, brookite) have been shown to contain TiO_6 octahedra, and the this is also likely to be the case with the zirconium and hafnium dioxides. A number of lower titanium oxides are known; principally Ti_3O_5, Ti_2O_3, TiO and Ti_2O, but a large number of other phases is known, in particular those intermediate between Ti_2O_3 and TiO[148] There seems to be no substantial evidence for the existence of lower oxides of zirconium and hafnium.

A large number of oxohalides is known for the three metals, many of empirical formula $MOX_2 \cdot nH_2O$ (X = F, Cl, Br, I). In the case of the zirconyl and hafnyl chlorides, $MOCl_2 \cdot 8H_2O$, X-ray analysis has shown that the complexes are in fact tetrameric, $[M_4(OH)_8(H_2O)_{16}]^{8+}$, with a square arrangement of metal atoms joined by double hydroxo bridges and an eight coordinate (Archimedaean antiprismatic) arrangement of ligands around the metal atoms. The structure (Fig 4) persists in aqueous solution[149]:

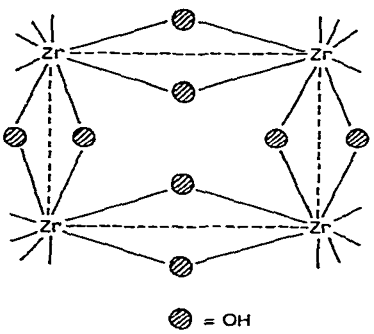


Fig 4. Structure of $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ in hydrated zirconyl chloride

(b) Unsubstituted oxo species.—Hexa- and penta-oxo complexes. The only reported examples are $Ba_3[TiO_5]$ and $Li_8[ZrO_6]^2$.

Tetraoxo complexes. For the three metals only the tetravalent state is involved for tetraoxo anions, *i.e.* they are all of the form $M_4{}^I[MO_4]$ and $M_2{}^{II}[MO_4]$ and are made by heating, to high temperatures, mixtures of the metal dioxides with alkali metal or alkaline earth oxides or carbonates. Although it is likely that the $M_4{}^I[MO_4]$ species do contain $[MO_4]^{4-}$ tetrahedra there is no direct evidence that this is the case. The alkali metal salts are instantly hydrolysed by water so there is no evidence for the existence of $[MO_4]^{4-}$ ions in aqueous solution. It is likely that most other tetraoxo salts of these metals contain MO_6 octahedra, although an X-ray crystal structure analysis has shown that $Ba_2[TiO_4]$ does contain discrete TiO_4 tetrahedra (*cf.* Table 2)[13]; the Raman spectrum of solid $Ba_2[TiO_4]$ has been measured[77]. Tarte has studied the infrared spectra of a number of orthosilicates which contain (TiO_4) units[150].

Polyanions. There appears to be no information on the existence of titanium polyanions in solution apart from the work on "titanyl" species dealt with below (p. 481). Both zirconium and hafnium dioxides are soluble to a limited extent in concentrated alkali, and although it has been proposed that the main species present in such solutions are $[M(OH)_5]^-$ and $[M(OH)_6]^{2-}$[151] it could well be that the species are $[MO_4]^{4-}$ or polyanions.

Meta-titanates $M_2{}^I[TiO_3]$ and -zirconates and -hafnates $M^{II}[MO_3]$ are known; these are really mixed metal oxides involving MO_6 octahedra. $Li[TiO_3]$ has a cubic structure; $M^{II}[TiO_3]$ have perovskite or ilmenite structures depending on the nature of M^{II}. Barium titanate, $Ba[TiO_3]$ has a perovskite structure (in fact there are five modifications of the compound, four of which are based on a perovskite structure) and is of importance in electronics on account of its ferroelectric and piezoelectric properties. Other oxo salts of these metals are $M^I{}_2[Ti_2O_5]$ (an X-ray crystal structure of the potassium salt shows that the titanium is five coordinate with infinite layers of Ti_2O_5 units[152]), $M^I{}_6[Ti_2O_6]$, $M^I{}_4[Ti_3O_8]$, $Na_2[Ti_3O_7]$, $M^I{}_2[M_2O_5]$ (M^I = alkali metal, M = Zr, Hf) *etc* , but none of these contains discrete anions.

(c) Substituted oxo complexes. — No trioxo or dioxo complexes of these metals are known.

Monooxo species. Although there are many complexes of these metals which appear to contain (M=O) units, very few of these are monomers with terminal oxo ligands. Thus, in species like $[MO(SO_4)_2]^{2-}$ and $[MO(ox)_2]^{2-}$ (M = Ti, Zr, Hf) IR evidence suggests that there are infinite M–O–M–O chains, in the solids, though the structures of these species remain a subject for conjecture. Thus, in titanyl sulphate, $TiOSO_4 \cdot H_2O$, each titanium atom is bonded to one oxygen atom of each of three sulphate groups, to one water molecule (these Ti–O bond lengths are *ca* 1.97 Å) and to two oxygen chain ligands at 1.8 Å[153]. There is evidence from vibrational spectroscopy that $K_2[TiO(ox)_2]$ $2H_2O$ [148] and $K_2[TiOF_4]$[154] contain Ti–O–Ti .. chains; such chains are associated with very strong and broad absorption near 750 cm^{-1} in the IR.

Species which have been claimed to contain terminal M=O units include $(NEt_4)_2[TiOCl_4]$, TiOPc (Pc = phthalocyanine), $TiO(acac)_2$, $TiO[SbF_6]_2$ and $TiO[TiF_6]$, and there have also been suggestions that $[MO(NCS)_3]^- \cdot 2H_2O$ salts contain M=O terminal units (M = Zr, Hf) In the case of $(NEt_4)_2[TiOCl_4]$, made by reaction of $Ti_2OCl_6 \cdot 4CH_3CN$ with $(NEt)_4NCl$ in acetonitrile[155], preliminary X-ray crystal analysis indicates that there is indeed a terminal Ti=O unit in this compound (Ti–O 1.79 Å), and the structure of the anion is square pyramidal (Table 5)[45]. In the case of the phthalocyanine complex there is no direct structural evidence as yet The structures of $TiO(SbF_6)_2$, $TiO(TiF_6)$[156] rest on IR data, which are not conclusive in these cases; studies on $TiO(acac)_2$ suggest that this is dimeric[157]. The thiocyanates appear to contain only one coordinated water molecule[158]. The mineral fresnoite, $Ba_2[TiO]Si_2O_7$, contains $[Si_2O_7]^{6-}$ groups linked to TiO_5 square pyramidal units to give flat sheets, and in the TiO_5 pyramids there is a terminal Ti–O bond at 1 66 Å from the titanium, the basal oxygen atoms being 2 00 Å distant with the titanium atom displaced 0.59 Å from the basal plane towards the terminal oxygen atom[159]. Raman studies on solutions of titanium and zirconium dioxides in perchloric acid provide no evidence for the existence of mononuclear "titanyl" (TiO^{2+}) or "zirconyl" (ZrO^{2+}) species in solution[160]. The subjects of titanyl[7] and zirconyl[160] species have been reviewed.

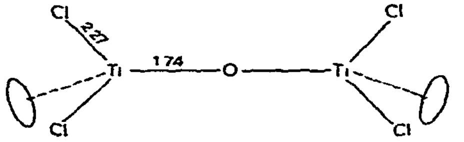


Fig 5 Structure of $[C_5H_5)_2TiCl]_2O$.

Polynuclear complexes. The cyclopentadienyl complex $[Cp_2TiCl]_2O$ has an oxo-bridged structure (Fig 5) with a linear Ti–O–Ti unit (Table 5)[61].

The Ti–O distance of 1.74 Å is short enough to suggest the presence of metal–oxygen π-bonding (in $TiOSO_4 \cdot H_2O$ the longer bridge distance of 1.80 Å, if the difference is indeed significant, is likely to arise from a lower degree of π-bonding in the case of titanyl sulphate, since in this the Ti–O–Ti system is not linear). The binuclear complex $(NEt_4)_2[Zr_2OCl_{10}]$ has been prepared by the action of $Zr_2OCl_6 \cdot 4CH_3CN$ on a solution of $(Et_4N)Cl$ in acetronitrile; the IR spectrum supports the formulation as a binuclear complex[161].

Polymeric titanium(VI) oxide alkoxides have been reported by Bradley *et al*; they take the form $Ti_{3(x+1)}O_{4x}(OR)_{4(x+3)}$, and are made by hydrolysis of titanium(VI) alkoxides. The compounds are high polymers, and the subject has recently been reviewed[12].

(ii) Group Va (V–Nb–Ta)

The main sources are the relevant volumes of Gmelin[146] and Pascal[147]. In addition there are specialist texts on vanadium[148,162] and on niobium and tantalum[163].

(a) Oxides and oxohalides. —The pentoxides are the most important oxides of the three elements. The vanadium in V_2O_5 has a distorted tetragonal pyramidal environment Thermodynamic data are available for the three oxides. Lower oxides which have been established include MO_2 (all three), V_2O_3 (there seems to be some uncertainty as to the existence of the niobium and tantalum analogues), MO (all three), and Nb_2O and Ta_2O. The oxohalides include MOX_3 ($M = V$, Nb, Ta; $X = Cl$, Br), VOF_3, $TaOF_3$, $NbOI_3$, $MOCl_2$ ($M = V$, Nb, Ta), VOF_2, $VOBr_2$, VOI_2, MO_2X ($M = Nb$, Ta; $X = F$, Cl, I), VO_2F, $[VOCl]_n$, $[VOBr]_n$, $V_2O_3Cl \cdot nH_2O$. The vanadium oxy-triahlides are monomeric (*cf.* below) but $NbOCl_3$ at least is polymeric in the solid state, with both chloro and oxo bridges (Nb–Cl ter. 2.24(0.02), Nb–Cl bridge 2 53(0 03), Nb–O 1 99(0 01) Å[164]).

(b) Unsubstituted oxo species.

Hexa- and penta-oxo complexes. The only examples appear to be $Na_5[VO_5]$ and $Ba_3[VO_5]$, the latter containing vanadium(IV)[2].

Tetraoxo complexes.

Orthovanadates, $[VO_4]^{3-}$. A considerable number of salts containing the orthovanadate ion are known; an X-ray study on pucherite, $Bi[VO_4]$, is given in Table 2. Salts of the form $M^I{}_3[VO_4]$ are made by fusion of the pentoxide with the alkali metal hydroxides but the sodium and potassium salts are only stable in aqueous solution in the presence of a very high concentration of base (> 10 M OH^-)[78]. Orthovanadates of the form $M^{II}{}_3[VO_4]_2$ and $M^{III}[VO_4]$ are also known. Both X-ray and spectroscopic[165,166] data suggest that most if not all of them contain $[MO_4]^{3-}$ tetrahedra.

Orthoniobates and orthotantalates. Few compounds containing $[NbO_4]^{3-}$ and $[TaO_4]^{3-}$ ions are known, and it appears that such species are not stable in aqueous solution even in the presence of a very large excess of base[78]. Salts of the form $M^I{}_3[NbO_4]$ (M = Li, Na, K) and $Na_3[TaO_4]$ can be made by fusion of the alkali metal carbonates with the pentoxides The mineral fergusonite, (Y, Yb) $[NbO_4]$ contains $[NbO_4]^{3-}$ tetrahedra in the scheelite structure (*cf.* Table 2)[15], but stibiotantalite, $Sb[TaO_4]$ and bismutotantalite, $Bi[TaO_4]$ contain MO_6 octahedra.

The ESR spectrum of $[Nb^{IV}O_4]^{4-}$ has been measured in a scheelite $Ca[WO_4]$ host lattice[127].

Polyanions. Polyoxo complexes of the Group Va elements have been reviewed[3,4].

Polyvanadates. A number of studies have been made of the polymerisation of $[VO_4]^{3-}$ which occurs in vanadate solutions containing the latter ion when the pH is decreased. It is generally considered that the principal steps are[4,167].

$$[VO_4]^{3-}+H^+ \leftrightarrow [HVO_4]^{2-}$$
$$2[HVO_4]^{2-} \leftrightarrow [V_2O_7]^{4-}+H_2O$$
$$[V_2O_7]^{4-}+H^+ \leftrightarrow [HV_2O_7]^{3-}$$
$$2[HV_2O_7]^{3-} \leftrightarrow [VO_3]_4{}^{4-} \text{ (or } [VO_3]_3{}^{3-})$$
$$[VO_3]_n{}^{n-}+H^+ \leftrightarrow [V_{10}O_{28}]^{6-}$$
$$[V_{10}O_{28}]^{6-}+H^+ \leftrightarrow [HV_{10}O_{28}]^{5-}$$
$$[HV_{10}O_{28}]^{5-}+H^+ \leftrightarrow [H_2V_{10}O_{28}]^{4-}$$
$$[H_2V_{10}O_{28}]^{4-}+14H^+ \leftrightarrow 10[VO_2]^{+}+8H_2O$$

Other intermediate steps are doubtless involved. There is some doubt as to whether the metaion $[VO_3]_n{}^{n-}$ is trimer or a tetramer[168,169]. It is likely to be cyclic (Fig. 6). Raman spectra of most of the above species have been measured[170]. The X-ray crystal structure of $K_2Zn_2[V_{10}O_{28}] \cdot 16H_2O$ is based on a 2–3–3–2 array of VO_6 octahedra, linked through the edges, giving eight terminal V=O groups and an idealised C_{2h} symmetry for the anion[171]. Other isopolyvanadates have been claimed, and there are also mixed vanadium(IV)–(V) isopoly complexes[172].

The X-ray crystal structure of $Cd_2[V_2O_7]$ shows that this has discrete $[V_2O_7]^{4-}$ anions (Table 5)[62]; the V–O–V unit is probably linear, though the

Raman spectra of $[Cr_2O_7]^{2-}$ and $[V_2O_7]^{4-}$ in solution are very similar[78], and dichromate in solution certainly has a bent Cr–O–Cr unit[143]. A number of metavanadates, $M^I[VO_3]$ and $M^{II}[VO_3]_2$ containing chain structures are known[173]. *Polyniobates and polytantalates* The simplest species claimed is $Ba_6[Nb_2O_{11}]^2$, but there is no evidence that this does in fact contain binuclear anions. Equally, the metaniobates and metatantalates $M^I[MO_3]$ and $M^{II}[MO_3]_2$ together with such species as $M^{II}{}_4[Nb_2O_9]$, $M^I{}_6[Nb_4O_{13}]$, $M^{II}{}_2[Ta_2O_7]$ and $M^{II}{}_4[Ta_2O_9]$ almost certainly contain sheet or chain polymeric anions.

In aqueous solution the main species present for niobates and tantalates are the hexamers $[M_6O_{19}]^{8-}$ [174], and X-ray crystal studies on $K_{14}[Nb_{12}O_{37}] \cdot 27H_2O$ and on $K_8[Ta_6O_{19}] \cdot 16H_2O$ indicate that both these salts contain hexanuclear anions, $[M_6O_{19}]^{8-}$ [175]. There is no evidence for the existence of the simple ortho-ions, $[MO_4]^{3-}$, in very alkaline solutions of niobates and tantalates.

(c) Substituted oxo complexes —

Trioxo and dioxo species. The salt $Na_3[VO_3] \cdot 10H_2O$ can be made from sodium sulphide and sodium pyrovanadate[176]. The only other trioxo species reported are $K_2[VO_3F_2]$ and $K[VO_3F]$, made from potassium fluoride–potassium metavanadate melts[177]; these are probably polymeric with *cis*-VO_2 units and bridging oxo ligands.

For dioxo species, Raman studies indicate that $(NH_4)_3[VO_2\,ox_2]$ and $K_3[VO_2F_4]$ both contain *cis*-VO_2 groups, as expected for these d^0 species[42]. It is also possible that the salts which are claimed[178] to contain $[V_2O_4(SO_4)_2]^{2-}$ anions do in fact contain *cis*-$[VO_2(SO_4)(H_2O)_2]^-$. It is said that $K_2[VO_2F_3]$ and $K_3[V_2O_4F_5]$ contain *cis* and *trans* VO_2 groups, respectively[179]. Organic derivatives of the form $[VO_2L_2]^-$, where L is a substituted quinoline ligand, may contain *cis*-VO_2 groups[180]. Other "dioxo" species such as $K_2[VO_2F_2]$[177], $[NbO_2F]^-$ and $[NbO_2F_2]^{2-}$ probably contain polymeric anions

Monooxo complexes.

Vanadium. A number of vanadium(V) monooxo species is known, but by far the greatest number and diversity of such species are found with vanadium(IV), the so-called "vanadyl" complexes

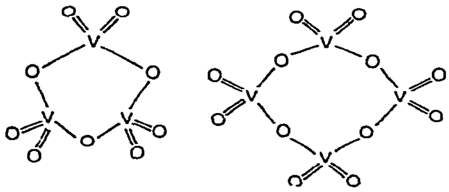


Fig. 6 Possible structures for trimeric and tetrameric $[VO_3]_n^{n-}$.

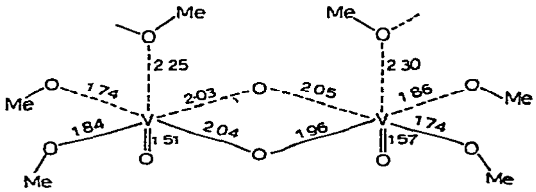


Fig. 7. Structure of $[VO(OMe)_3]_n$.

(1) *Vanadium(V).* Three oxotrihalides, VOX_3 (X = F, Cl, Br) are known. The fluoride can be made by the action of hydrofluoric acid in the cold on $VOCl_3$; the product is a yellowish white solid (m p. 300°, b.p. 480°) and is presumably polymeric. The trichloride is best made by heating a mixture of aluminium trichloride and vanadium pentoxide to 400° [181]; it is a lemon-yellow liquid m p. −79 5°, b.p. 127°) and is monomeric [the structure in the vapour phase has been determined by electron diffraction (Table 4)[30]]. The tribromide is a dark red liquid, and can be made by the action of bromine vapour on a mixture of vanadium pentoxide and carbon. Vibrational spectra of the three oxytrihalides have been measured (Table 7). Vanadium oxytrichloride forms a number of addition compounds of the form $VOCl_3 \cdot L$ and $VOCl_3 \cdot 2L$ with a variety of oxygen and nitrogen donor ligands[182], and it will also undergo a series of replacement reactions to give substitution products such as $VOCl(acac)_2$, $VO(OMe)_3$, $VOCl(OEt)_2$, *etc.*[162,183]. The X-ray crystal structure of $VO(OMe)_3$ shows this to be a linear polymer with distorted octahedral coordination about the metal atom, with a terminal V=O bond (1.57 Å) and a long V–O bond *trans* to it (2 30 Å) (Fig. 7)[184].

The compound $VO(NO_3)_3$ has been reported; it is made by the action of nitrogen pentoxide on vanadium pentoxide, and is probably polymeric since its IR spectrum shows the presence of bidentate nitrate groups[185]. The thiooxo salt $Na_3[VOS_3] \cdot 5H_2O$ [176] is probably monomeric.

Vanadium pentoxide dissolves in concentrated hydrofluoric acid to give $[VOF_4]^-$ or $[VOF_4(H_2O)]^-$ as the main solute species[160]; from such solutions salts can be isolated, *e g.* $K_2[VOF_5]$. The chloro species $[VOCl_5]^{2-}$ and $[VOCl_4]^-$ have recently been made from $VOCl_3$ and organic base chlorides, and the electronic spectra of the products recorded and interpreted[59]. Solutions of vanadium pentoxide in sulphuric acid are thought to contain $[VO(SO_4)_3]^{3-}$ and $[VO(SO_4)_2]^-$ [186]; in oleum the main species present is believed to be $VO(HSO_4)_3$ [187]. A variety of monooxo species of the form $[VO(OH)L_2]^{2-}$ and $[VO(OR)L_2]^{2-}$ have been reported (L being a substituted quinoline)[180]. A number of oxo–peroxo vanadium(V) salts of unknown constitution have been claimed[9].

(2) *Vanadium(IV).* A very large number[114] of vanadyl species is known; they take the form $[VOX_5]^{n-}$ (*e.g.* X = F, CN, NCS, H_2O); $[VOX_4]^{n-}$ (X = F, Cl); $[VOX_4(H_2O)]^{n-}$ (X = F, Cl, NCS); $VO(LL)_2$, $VO(LL)_2X$ and $VO(LL)X_3$ (LL = acac, ox, *o*-phen, bipy, MNT; X = H_2O, py, NCS, MeOH, F, Cl, Br).

Crystal structure analyses have been performed on a number of vanadyl complexes (Table 6)[46,47,114]. The structure[46] of $(NH_4)\,[VO(NCS)_4(H_2O)]$ is of particular interest; the water group is *trans* to the oxygen (V = 0 1.62 Å) and very distant from the metal ($V–OH_2$ 2 22 Å), a possible indication of a *trans* effect of the oxo ligand.

There have been many studies of the physical chemistry of vanadyl species. Measurements of the IR active V=O stretching frequency in some sixty vanadyl complexes show that $\nu_{V=O}$ lies in the range 910–1010 cm^{-1}, and attempts have been made to correlate shifts of this frequency with the σ and π properties of the other ligands present[60,113]. In vanadium(V) monooxo complexes the V=O stretch lies around 1060 cm^{-1}, higher than in the vanadium(IV) compounds as a result of the higher oxidation state of the metal atom. The only Raman work so far reported on vanadyl(IV) species is the work of Evans on $[VO(H_2O)_5]^{2+}$ in aqueous solution; two bands are observed, that at 1001 cm^{-1} being ascribed to the V=O stretch and that at 280 cm^{-1} to a symmetric V–OH_2 stretch[188]. The electronic spectra of vanadyl species have been reviewed by Selbin[114]. Most, but not all, of the results may be satisfactorily explained by the scheme of Ballhausen and Gray (p. 470)[56]. Although there has been much work on the ESR of vanadyl complexes, the results do not provide an unambiguous assignment of electronic energy levels[114]. Magnetic susceptibility data on the complexes indicate that the moment is close to 1.73 B.M., the spin-only value for a single unpaired electron[114].

Niobium and tantalum.

The established monooxo species are all of the pentavalent metals The halo species $[MOX_5]^{2-}$ (X = F, Cl, Br) are well known and can be made from the pentahalides or pentoxides in the appropriate acids. The IR spectra of these species have been measured and some assignments proposed (Table 9)[110 111]. The crystal structure of $K_2[NbOF_5]$ has been determined (Table 4)[48]. Salts of $[MOF_6]^{3-}$ can be made[189], and X-ray data suggest that the potassium salts contain seven coordinate $[MOF_6]^{3-}$ anions with the $[ZrF_7]^{3-}$ (C_{3v}) structure[49]. In aqueous solution, however, $K_3[NbOF_6]$ dissociates to give the $[NbOF_5]^{2-}$ ion. The Raman spectra of $K_3[NbOF_6]$ and $K_2[NbOF_5]$ species have been measured[190] The acid "heptafluoroniobate", $K_3H[NbOF_7]$, has been shown by X-ray studies to be a double salt, $K_2[NbOF_5] \cdot KHF_2$ [191]. Oxochloroniobates of the form $M^I[NbOCl_4]$, $M^I{}_2[NbOCl_5]$ and $M^I{}_3[NbOCl_6]$ can be obtained by heating $NbOCl_3$ and the alkali metal chloride together in sealed tubes; like the oxohexafluoroniobates, the oxohexachlorides are stable only in the solid state[192] The tantalum salts $M^I[TaOCl_4]$ have been obtained by heating the corresponding alkali metal hexachlorotantalates with antimony(III) oxide, and $M^I{}_2[TaOCl_5]$ (where M^I is pyridinium or quinolinium only) made from an alcoholic solution of tantalum pentachloride with the base[193]. Addition of alkali metal bromides to a solution of niobium pentoxide in hydrobromic acid yields $M^I{}_2[NbOBr_5]$, and salts of $[NbOBr_4]^-$ can be obtained in a similar way by using organic bases[194]. No oxotantalum bromide complexes seem to be known, and no oxoiodides of either metal.

There is a number of monooxo derivatives of organic ligands. Oxooxalates of the two elements have received some study[195] but there are still many obscurities in the system. One of the products of dissolving niobium pentoxide in oxalic acid is $[NbOox_3]^{3-}$; a recent X-ray study of the ammonium salt (Table 4) shows that the coordination about the niobium is pentagonal bipyramidal[50]. A number of monooxo complexes of niobium and tantalum with catechol, pyrogallol and other diols have been made[163], and it is likely that some of these, *e g.* $K_3[NbO(C_6H_4O_2)_3] \cdot H_2O$ may contain the metal in a seven coordinate stereochemistry. A number of oxo–peroxo complexes of the metals are known[9], but their formulae are not established.

Polynuclear complexes. A number of oxofluoro species are undoubtedly polymeric, *e.g.* the anions $[VO_2F_3]^{2-}$, $[VO_2F_2]^-$, $[Nb_3O_3F_{14}]^{5-}$, $[Nb_2O_5F]^-$, $[Nb_3O_6F_8]^{2-}$, but structural data are lacking. It is possible that $(NH_4)_4[V_2OS_6]$ contains a binuclear anion with a sulphur or oxygen bridge (the salt is made by the action of hydrogen sulphide on a solution of ammonium metavanadate in ammonia[176]). Raman spectra of the peroxy complex normally formulated as $K_4[V_2O_{11}]$ suggest that it may contain the anion $[V_2O(O_2)_4(H_2O)_2]^{4-}$ with a structure similar to that found for the anion in $K_2[W_2O(O_2)_4(H_2O)_2]$ (*cf.* Table 5 and p. 496)[68]. A few polymeric oxide alkoxides of Group Va metals are known, probably high polymers[12].

(iii) Group VIa (Cr–Mo–W)

Apart from Gmelin[146] and Pascal[147] there is a general review on the coordination chemistry of molybdenum[196], an account of the oxo chemistry of molybdenum(VI) and (V)[197], and a rather sketchy general review of the chemistry of tungsten[198].

(a) Oxides and oxohalides.—All three metals form trioxides MO_3, dioxides MO_2, sesquioxides M_2O_3, and the monoxides CrO and MoO are known A very large number of oxide phases between these formulae are known, particularly for chromium and molybdenum[147].

The subject of the oxohalides of the three metals has been reviewed[199]. The chromium species are CrO_2X_2 (X = F, Cl, Br) (these are monomers and are dealt with in more detail below (p. 491)), CrOX (X = F, Cl, Br), $CrOX_3$ (X = F, Cl), CrO_2ClF, and a wide range of oxochlorides with formulae such as $Cr_3O_6Cl_2$, Cr_3OCl_7, $Cr_4O_8Cl_7$, $Cr_5O_{10}Cl_6$, and $Cr_2OCl_4 \cdot 5H_2O$. For molybdenum and tungsten(VI) there are MOX_4 (X = F, Cl), MO_2X_2 (X = F, Cl, Br) and WO_2I_2 (these dioxo dihalides are polymeric in the solid state, unlike their chromium analogues, though they too are monomeric in the vapour phase — see Table 3); for the pentavalent metals there are $MOCl_3$, $MoOBr_3$, MoO_2Cl, and the tetravalent compound $MoOCl_2$ In $WOCl_4$ and $WOBr_4$ (solids) the oxygen atoms function as bridges between planar WX_4 units, (W–O 2 2 and 1 8 Å; W–Cl 2 28 Å; W–Br 2 45 Å)[200].

(b) Unsubstituted oxo complexes. — *Hexa- and penta-oxo species.* The compounds $M^{II}_3[MO_6]$ (M^{II} = Sr, Ba; M = Mo, W) and $Li_6[WO_6]$ have been reported for the hexavalent metals[2], and the vibrational spectra of $Ba_3[MoO_6]$ and

$Ba_3[WO_6]$ measured[41]. The pentaoxo species $M^I_4[MO_5]$ and $Ba_2[MO_5]$ (M^I = Li, Na; M = Mo, W) and $Na_5[CrO_5]$ have also been made[2].

Tetraoxo complexes

Chromium. The chromates, $[CrO_4]^{2-}$ are lemon-yellow or orange species made by oxidation of chromic salts in alkaline media. The potassium salt exists in two modifications, a red high-temperature form stable above 666° and the normal yellow low-temperature form, this latter being isomorphous with potassium manganate. The vibrational[79] (Table 6) and electronic[5] spectra of $[CrO_4]^{2-}$ have been measured. The temperature-independent paramagnetism (TIP) of potassium chromate has been studied and a theoretical interpretation of its origin given[201]. The ^{17}O magnetic resonance in chromates has been measured and the chromate–dichromate equilibrium studied with this technique (p. 478)[142,143].

Chromates are oxidising agents and are much more powerful in this respect than either molybdates or tungstates, a general situation for oxo complexes of first row elements compared with those of the second and third rows. Both chromates and dichromates are extensively used as oxidising agents. Acids cause protonation to $[HCrO_4]^-$ (the salt $KHCrO_4$ has been isolated), and this is followed by polymerisation to dichromate and the polychromates (see below). Concentrated halogen acids convert $K_2[CrO_4]$ to $K[CrO_3X]$, and the chromyl halides can be made from chromates and halogen acids. Reduction under controlled conditions leads to $[CrO_4]^{3-}$, $[CrO_4]^{4-}$ and, finally, to chromic salts. With hydrogen peroxide in alkaline solutions, $[CrO(O_2)_2(OH)]^-$ and $[Cr^V(O_2)_4]^{3-}$ salts may be formed; at very low temperatures the reaction yields the highly unstable, explosive $[Cr^{VI}(O_2)_4]^{2-}$ (it is noteworthy that the corresponding molybdenum(VI) and tungsten(VI) tetraperoxo species are chemically much more stable). IR spectra of chromato and molybdato cobaltamines show that these oxoanions may function as mono- and as bi-dentate ligands and this has been confirmed by an X-ray study of $(NH_4)_2[Zn(NH_3)_2(CrO_4)_2]$[201a].

Chromates(V) and (IV). Salts of the form $M^I_3[CrO_4]$ and $M^{II}_3[CrO_4]_2$ (M^I = Li, Na, K; M^{II} = Ba, Sr) have been obtained by reactions such as[202]

$$4K_2[CrO_4]+Cr_2O_3+5K_2O \xrightarrow{N_2,\ 700°} 6K_3[CrO_4]$$

and

$$4Ba[CrO_4]+2BaCO_3 \xrightarrow{N_2,\ 800°} 2Ba_3[CrO_4]_2$$

The salts are dark green and, in the case of the alkali metal species, deliquescent. Acid hydrolysis gives chromic salts and chromate, base gives hydrated chromium sesquioxide, and hydrogen peroxide gives a number of peroxo species. Magnetic measurements give a moment close to 1.7 B.M.[135] (*cf.* p. 477). Powder photographs show that $K_3[CrO_4]$ and $K_3[VO_4]$ are isomorphous.

Barium and strontium salts of $[CrO_4]^{4-}$ have been made by the reactions[202]:

$$Ba_3[Cr(OH)_6]+Ba(OH)_2 \xrightarrow{N_2,\ 1000°} 2Ba_2[CrO_4]+6H_2O+H_2$$

$$Sr[CrO_4]+Cr_2O_3+5Sr(OH)_2 \xrightarrow{N_2,\ 1000°} 3Sr_2[CrO_4]+5H_2O$$

X-ray measurements indicate that these blue-black solids do contain chromate(IV) tetrahedra; the barium salt has the barium titanate structure[202].

Molybdenum and tungsten. Salts of $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ are normally made by dissolving the trioxides in the appropriate alkali. The salts are usually colourless and chemically very stable. They are far weaker oxidising agents than the chromates. Vibrational[80,81] (Table 6) and electronic[5,28] spectra of $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ have been measured. Both molybdates and tungstates show a much greater tendency than chromate to polymerise in acid solution and it is for this reason that it is necessary to use a large amount of base during their preparations.

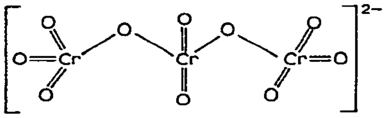
Barium salts of the $[MO_4]^{4-}$ anions can be obtained by the reaction[2]:

$$Ba[MO_4]+MoO_3+3Ba(OH)_2 \rightarrow B_2[MO_4]+3H_2O$$

Attempts to make these salts directly from the dioxides have not been successful

Polyanions.

Chromium Although the polymerisation of chromate(VI) in acid solution yields far fewer polymers than do such reactions with molybdates and tungstates there is still doubt as to the nature of the species present at low pH. The first product of acidification of $[CrO_4]^{2-}$ is the protonated ion $[HCrO_4]^-$, followed by $[Cr_2O_7]^{2-}$ (the dichromate ion), $[HCr_2O_7]^-$, and finally the polychromates $[Cr_3O_{10}]^{2-}$ and $[Cr_4O_{13}]^{2-}$. Of the latter two species little is known, and there is indeed considerable doubt as to whether the tetrachromate exists at all. Raman and IR spectra of the trichromate have recently been measured, however[203], and it is probable that the ion has the structure (4).



(4)

with tetrahedral coordination about the chromium atoms Diffusion studies have been made on the tri- and tetra-chromate ions[204].

The *dichromates* are important oxidising agents; most of them are orange and are made by acidification of the corresponding chromates. Raman, IR[205] and X-ray[61a] studies on $[Cr_2O_7]^{2-}$ have been reported, and the electronic spectra of a number of dichromates measured down to 20 °K[206].

Polymolybdates and polytungstates The polymerisation of $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ brought about by acidification of their aqueous solutions is a complex subject[3,4]; Keppert has given an excellent review of polytungstates[207].

The principal equilibria for molybdates are probably[208]:

$$[MoO_4]^{2-}+H^+ \leftrightarrow [HMoO_4]^-$$

$$7[MoO_4]^{2-}+8H^+ \leftrightarrow [Mo_7O_{24}]^{6-}+4H_2O$$

$$[Mo_7O_{24}]^{6-}+H^+ \leftrightarrow [HMo_7O_{24}]^{5-}$$

$$[HMo_7O_{24}]^{5-}+H^+ \leftrightarrow [H_2Mo_7O_{24}]^{4-}$$

and species such as $[Mo_8O_{26}]^{4-}$ and higher polymers may well be involved; these changes have been followed by a wide variety of physical methods[170,208]. The X-ray crystal structure of the ammonium and potassium salts of the $[Mo_7O_{24}]^{6-}$ ions show that there is a 2–3–2 array of MoO_6 octahedra of overall C_{2v} symmetry, while in $(NH_4)_4[Mo_8O_{26}] \cdot 4H_2O$ there is a 4–4 array of MoO_6 octahedra with an idealised D_{2d} symmetry for the anion[209]. In very acid solutions of molybdates *cis*-$[MoO_2X_4]^{2-}$ species are formed[110].

With tungstates it is thought that the principal equilibria are[207]:

$$6[WO_4]^{2-} + 7H^+ \leftrightarrow [HW_6O_{21}]^{5-}$$
$$2[HW_6O_{21}]^{5-} \leftrightarrow [W_{12}O_{40}]^{8-} + 2OH^-$$
$$2[HW_6O_{21}]^{5-} \leftrightarrow [W_{12}O_{42}]^{12-} + 2H^+$$

With protonation of the $[HW_6O_{21}]^{5-}$ ion as a side reaction:

$$[HW_6O_{21}]^{5-} + 2H^+ \leftrightarrow [H_3W_6O_{21}]^{3-}$$
$$2[H_3W_6O_{21}]^{3-} \leftrightarrow [H_2W_{12}O_{40}]^{6-} + 2H_2O$$

These changes have also been followed by a wide range of physical techniques[170,207]. The X-ray crystal structure of $Na_{12}[W_{12}O_{42}]$ shows that this has a centrosymmetric anion with a 3–6–3 array of linked WO_6 octahedra[210]. As with molybdenum, *cis*-$[WO_2X_4]^{2-}$ species are formed in very acid tungstate solutions[110].

Proton nuclear magnetic resonance has recently been used in the study of isopoly acids[211], and isopoly molybdates and tungstates of mixed oxidation states have been prepared[212].

(c) Substituted oxo complexes —

Tetraoxo species The complexes $K_3[CrO_4F]$[213], and $2NaOH \cdot Na_2[CrO_4]$[214], have been made; it is possible that the latter contains the $[CrO_4(OH)_2]^{4-}$ ion, in which case this would be the only example of a first row transition element tetraoxo complex expanding its coordination sphere in base.

Trioxo species. Chromium forms the red salts $M^I[CrO_3X]$, (X = F, Cl, Br, I), made from the halogen acids and dichromates[199]; detailed instructions for the preparation of $K[CrO_3Cl]$ from potassium chromate and chromyl chloride have been given[215]. Crystal structure data have been given on the potassium chloro salts (Table 3)[31] and their vibrational spectra have been measured (Table 7)[95,96]. Other chromium trioxo species which have been claimed include $[CrO_3(NH_2)]^-$, the alkyl species $[ROCrO_3]^-$ [216], and the iodato complex $[CrO_3(IO_3)]^-$ [217], (this latter salt has been subjected to X-ray analysis[217]). There is some doubt about the existence of $[CrO_3(NH_2)]^-$, a red substance made by passing ammonia through a suspension of $K[CrO_3Cl]$. It has been said that the product is not an amide but simply a mixture of potassium and ammonium chromates. There are a number of "addition" compounds of chromium trioxide with organic bases such as pyridine, picoline and quinoline, taking the form $CrO_3 \cdot 2L$, and it is thought that these may have a trigonal bipyramidal structure with the oxo ligands forming the equatorial plane[218]. Some species of the form CrO_3L can also be isolated with these organic bases.

Whereas the trioxo complexes of chromium are four or five coordinate, the only trioxo complexes of molybdenum or tungsten which are not octahedral are those formed with other strong π-donor ligands, *viz.* nitride and sulphide. The molybdenum nitrido complex $K_3[MoO_3N]$ can be made by the prolonged reaction of potassium amide and molybdenum trioxide in liquid ammonia, the salt is yellow and is very easily hydrolysed[219] The thio-salts $M^I_2[MO_3S]$ can be made by the action of alkali metal sulphides on the trioxides or $[MO_4]^{2-}$ salts under carefully controlled conditions[220]; IR spectra of a number of oxo–thio complexes of molybdenum, tungsten and vanadium have been recorded[221].

The trifluoro trioxo complexes of molybdenum and tungsten, $M^I_3[MO_3F_3]$, can be obtained from the trioxides, hydrofluoric acid and the alkali metal fluorides[222], or by fusion reactions[223]. Studies of the Raman and IR spectra of the potassium and ammonium salts in the solid state indicate that the anions have the expected *cis* (1, 2, 3) configuration, as does the isoelectronic $[OsO_3F_3]^-$ ion[41,42]. X-ray studies on MoO_3(dien), made from molybdenum trioxide and diethylenetriamine, show that this has the same type of structure with three mutually *cis* oxo ligands (Table 3)[32], and the same result is reached from study of its vibrational spectra[41]. The salt $Na_4[Mo_2O_6(EDTA)]$ is thought to have *cis* oxo ligands with a bridging EDTA ligand on the basis of preliminary X-ray data[224] and from studies of its vibrational spectrum[41]. It is likely that $(NH_4)_2[MoO_3F_2]$, made from ammonium molybdate, ammonium fluoride and ammonia, contains bridging oxo ligands and *cis* MoO_2 groups[42].

Dioxo species Most of these are tetrahedral for chromium and octahedral for molybdenum and tungsten.

Chromium. Two chromyl halides, CrO_2F_2 and CrO_2Cl_2 are well established, and there is some evidence for the existence of CrO_2Br_2 but none for CrO_2I_2. Chromyl fluoride can be made from chromium trioxide and hydrogen fluoride; it forms violet-red crystals and is probably polymeric in the solid state. The chloride is made from chromium trioxide and hydrogen chloride[215], and is a red liquid (f.p. −96 5°, b.p. 117°). The structure of the vapour has been determined by electron diffraction[30] (Table 3), and the vibrational spectra of chromyl fluoride and chloride obtained (Table 8)[104,105]. Chromyl bromide forms red crystals, very unstable at room temperatures, made by the action of hydrogen bromide on a solution of CrO_2Cl_2 in carbon tetrachloride. Other dioxo chromium species are $CrO_2(OAc)_2$ and CrO(OH) (OAc), made from acetic acid and chromium trioxide[225], the explosive $CrO_2(NCS)_2$, from $PO(NCS)_3$ and chromyl chloride in carbon tetrachloride[226], CrO_2ox, from chromium trioxide and oxalic acid, and $CrO_2(NO_3)_2$, made from the trioxide and nitrogen pentoxide (it is a dark red liquid, b.p. 64° at 0.7 mm)[185]. Some or all of these species (apart from CrO_2Cl_2)

could well have polymeric structures. It is though that $CrO_2(HSO_4)_2$ is the main species in solutions of chromates(VI) in oleum[187].

Molybdenum and tungsten

The dioxo complexes of molybdenum and tungsten(VI) contain *cis*-MO_2 groups while the few *trans* dioxo species are of the tetravalent metals, in accordance with expectation (p. 468).

(1) Cis-dioxo species Reaction of molybdates and tungstates with hydrofluoric acid gives the tetrafluoro salts $M^I_2[MO_2F_4]$[222,227], and studies of both the vibrational spectra[41,42,110] and ^{19}F nuclear magnetic resonance[228] suggest a *cis* arrangement of the oxo ligands; this has now been confirmed in the case of $K_2[MoO_2F_4] \cdot H_2O$ by a recent X-ray study[36b] (Table 3). The action of concentrated hydrochloric acid in excess on molybdates and tungstates yields $M^I_2[MO_2Cl_4]$ salts, and vibrational spectra also indicate that these have a *cis* dioxo group[41,42,110].

Both MoO_2Cl_2 and WO_2Cl_2 are polymeric in the solid state, but will react with a variety of mono- and bi-dentate ligands to give monomeric, octahedral species of the form $MoO_2Cl_2L_2$ and $MoO_2Cl_2(LL)$ ($L = Ph_3PO$, DMF, N,N-dimethylacetamide; LL = dialkyldithiocarbamates)[229] and $[MoO_2(LL)_2]^{n-}$ (LL = acac, ox, catechol, oxime, R_2NCS_2). IR spectra and dipole moments were determined for a number of these complexes and indicated the presence of *cis*-MO_2 units[229]. Fewer complexes have so far been prepared with tungsten, but WO_2Cl_2 will react with monodentate L ligands (Ph_3PO, DMF, MeCN) and bidentate (LL) ligands (bipy, phen) to give $WO_2Cl_2L_2$ and $WO_2Cl_2(LL)$; IR and electronic spectra were measured[230]. The X-ray crystal structure of $MoO_2Cl_2(Me_2NCHO)_2$ (the N,N-dimethylformamido complex) has recently been determined. The oxo ligands are *cis* to each other and the chloro ligands *trans*, the angle between the two doubly bonded oxo ligands being 103° [36b], compared with 95° in $K_2[MoO_2F_4] \cdot H_2O$[36a] (Table 3).

(2) Trans-dioxo species. The established *trans*-dioxo complexes of molybdenum and tungsten are the cyano complexes $M_4^I[MO_2(CN)_4]$, made by photolysis of the octacyano species, $[M(CN)_8]^{4-}$; IR and electronic spectra of the products have been recorded[231]. The vibrational spectra of $K_4[MoO_2(CN)_4]$ are consistent with a centrosymmetric D_{4h} structure[41], and a recent X-ray crystal structure of $NaK_3[MoO_2(CN)_4]$ confirms this[37] (Table 3). The Mo–O bond length is 1 834 (0.009) Å, significantly longer than the corresponding distances in the two *cis*-dioxo molybdates referred to above. The reason for this is probably that the *cis*-dioxo structure allows the use by the oxygen p_π orbitals of the three t_{2g} metal orbitals, whereas only two t_{2g} orbitals are available for this purpose in *trans*-dioxo species[41,42] (p. 468). It is also significant that it is possible to protonate *trans*-$[MO_2(CN)_4]^{4-}$ to $[MO(OH)(CN)_4]^{3-}$ (M = Mo, W)[231], whereas no such protonation of *cis*-dioxo species has yet been achieved.

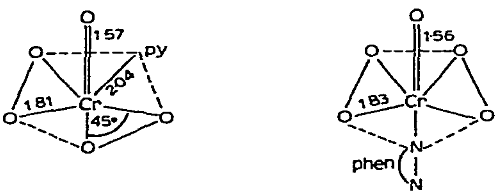
(3) Other dioxo species. There are references in the earlier literature to such "dioxo" species as (pyH) $[MoO_2Cl_2(H_2O)_2]$, $Li[MoO_2Br_2(H_2O)]$ aq., $(pyH)_2$-$[WO_2(NCS)_3]$, $(pyH)_2[MoO_2(NCS)_3]$, $Na_2[Mo_2O_4(EDTA)]$[41,197]; it appears, however, from measurements of magnetic properties and vibrational spectra, that such species are best formulated as dimers with a M—O—M bridge and one terminal oxo ligand per metal atom, *i e.* as $[M_2O_4X_6]^{n-}$ [41,197]. This type of structure is found in $Ba[Mo_2O_4\ ox_2(H_2O)_2]$[65], (Table 5 and p 497), and preliminary X-ray data suggest that $Na_2[Mo_2O_4(EDTA)]$ has such a structure[224]. In fact there are no *established* cases yet reported of monomeric dioxo species for metals having one or three *d* electrons.

The tetrahedral thio and selenido oxo species $[MoO_2S_2]^{2-}$, $[WO_2S_2]^{2-}$ and $[MoO_2Se_2]^{2-}$ have been made[220].

Monooxo species.

Chromium. The only chromium(VI) monooxo species known also have peroxo groups; like vanadium, it is the d^1 state of the metal (the pentavalent state for chromium, tetravalent for vanadium) which seems to provide the greatest number and diversity of such species. Peroxo oxo chromium(VI) complexes are listed by Connor and Ebsworth[9]. Those best established are the salts $M^I[CrO(O_2)_2X]$ (X = F, Cl, OH) and the complexes $CrO(O_2)_2$ (a very unstable blue species obtained by the action of hydrogen peroxide on acid solutions of dichromates — it is probably always solvated with one molecule of solvent), $CrO(O_2)_2py$ and $CrO(O_2)_2phen$. The X-ray structures of the pyridine (a)[51] (Table 5) and the phenanthroline[232] (b) complex have been determined (Fig 8). The pyridine complex is best described as a pentagonal pyramid, the two pyroxo groups and the pyridine occupying the basal plane with the oxo ligand axial[51], while in the phenanthroline complex there is a pentagonal bipyramidal coordination with an analogous arrangement[232] (Fig. 8).

Chromium(V) monooxo complexes are sometimes referred to as "chromyl" salts. The fluoro species $K[CrOF_4]$ can be obtained from the reaction between bromine trifluoride and potassium dichromate[233]. There are two series of chromyl chloro complexes, $M^I_2[CrOCl_5]$ (M^I = K, Rb, Cs, NH_4) The caesium salt is isomorphous with $Cs_2[NbOCl_5]$, and $R[CrOCl_4]$ (R = pyridinium, quinolinium);



(a) (b)

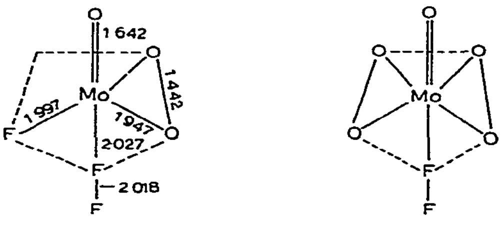
Fig 8 Structure of (a) $CrO(O_2)_2py$ and (b) $CrO(O_2)_2(o\text{-phen})$

both series are prepared by reduction of chromic trioxide with very concentrated hydrochloric acid at 0° in the presence of the appropriate chloride[234]. There has been much work on the electronic[56,57], IR[111] (Table 9) and electron spin resonance spectra[129–131] of these species, and magnetic data on $Cs_2[CrOCl_5]$ are given in Table 10[134]. Theoretical interpretations of the electronic spectra for chromyl complexes have been given (p. 476)[56,57].

The complexes $CrOCl_4$ L H_2O (L = pyridine, quinoline) can be made from chromium trioxide, hydrochloric acid and the ligand L[235].

Molybdenum and tungsten Here again the monooxo peroxo complexes are in the hexavalent state while most of the other monooxo species are of the d^1 pentavalent state metals. The peroxo complexes have been reviewed[9]; the best established are the fluorides $[MO(O_2)F_4]^{2-}$ and $[MoO(O_2)_2F_2]^{2-}$. These are made by the action of hydrogen peroxide on $[MO_2F_4]^{2-}$, and their vibrational[236] and ^{19}F nuclear magnetic resonance spectra[237] measured. The results suggested structures (a) and (b) (see Fig. 9), respectively, for the tetra- and di-fluoro complexes; a recently published[51a] X-ray crystal structure analysis of $K_2[MoO(O_2)F_4]\cdot H_2O$ confirms (a), *cf* Fig. 9 and Table 5. Other oxo–peroxo complexes of molybdenum and tungsten are the oxalates $[MO_2(O_2)\ ox(H_2O)]^{2-}$ and $[MO(O_2)_2\ ox]^{2-}$; the vibrational spectra of these suggest that the former contain *cis*-dioxo units, with both groups being seven coordinate[238] There are also rather unstable $[MoO(O_2)Cl_4]^{2-}$ salts (vibrational spectra of the caesium and ammonium salts suggest a seven coordinate structure like the analogous fluoro species)[236] and the salts $[MOF_5]^-$, which can be obtained from MF_6 and fluoride ion in moist solvents. Monothio species $[MO_3S]^{2-}$ can be made from molybdates and tungstates with hydrogen sulphide[220].

For the metals in their pentavalent conditions, salts of $[MOX_5]^{2-}$ and $[MOX_4]^-$ (X = Cl, Br) can be made by reaction of the trioxides with hydrochloric or hydrobromic acids in the presence of suitable reducing agents (*e g.* oxalic acid, hydriodic acid); electrolytic methods have been used[239] There have been several studies of the bonding[56–59] (p. 469), electronic[56–59,119], and vibrational spectra (Table 9)[111], ESR spectra[128,130], and magnetic properties (Table 10)[133,133a] of these species There has also been a considerable volume of work on the species



(a) (b)

Fig 9. Structure of anions in (a) $K_2[MoO(O_2)F_4]$ H_2O and (b) $K_2[MoO(O_2)_2F_2]$

existing in acid solutions of $[MoOCl_5]^{2-}$ and $[MoOBr_5]^{2-}$; if the concentration of HCl or HBr exceeds 10 M the mononuclear paramagnetic $[MoOX_5]^{2-}$ ions are the main solute species, but magnetic, ESR and spectroscopic data show that, as the acid concentration is reduced, both para- and dia-magnetic mono- and bi-nuclear species appear[130,197].

Other monooxo species of molybdenum and tungsten include $MoOCl_3L_2$, $MoOCl_3(LL)$ (L = Ph_3PO, DMSO, MeCN, PPh_3; LL = bipy,oxine, acac)[197,229], $[MoO(NCS)_5]^{2-}$, and $MoOCl_2(C_5H_5)$[197], detailed physico-chemical studies have been made on $MoOX_3(\beta\text{-diketone})$ (X = Cl, Br) complexes[240]. Salts containing $[M^{IV}O(OH)(CN)_4]^{3-}$ have been made[231]. Monooxo species may well be present in solutions of MoO_3 and WO_3 in oxalic acid

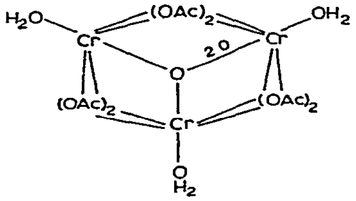
Polynuclear complexes.

Chromium. This forms two series of oxo-bridged polynuclear species, dimers and trimers. The dimers are typified by the ion $[Cr_2O(NH_3)_{10}]^{4+}$, made by aerial oxidation of chromium(II) ammines in ammonia[124] The salts are blue; studies of their magnetic properties (the moment at room temperature is less than that which would be expected for one unpaired electron per chromium atom)[137], electronic spectra[124] and infrared spectra of the normal and deuterated species[115] suggest that there is a linear Cr–O–Cr bridge Related complexes are $[Cr_2O(NH_3)_9X]^{3+}$ (X = F, Cl, NCS), $[Cr_2O(H_2O)_9(NH_3)]^{4+}$ [115 241], and the compounds $Cr_2O(NCS)_2(NH_3)_4(NCS)_2$ and $Cr_2O(NCS)_2py_4(NCS)_2$, in which there are thought to be one oxo and two thiocyanato bridges[242]. The bonding theory of Dunitz and Orgel[73] may be applicable to these complexes.

A number of trinuclear chromium(III) complexes have been made. These take the form $[Cr_3O(OAc)_6(H_2O)_3]^+$, $[Cr_3O(EtCOO)_6(H_2O)_3]^+$, $[Cr_3O(OAc)_6ox(H_2O)]^-$, $[Cr_3O(HCOO)_6]^+$, and $[Cr_3O(OAc)_6F_3]^{2-}$, they are often formulated in the earlier literature as aquo or hydroxo species, *e.g.* $[Cr_3(H_2O)_2(OAc)_6]^{3+} \cdot aq$, or $[Cr_3(OH)(OAc)_6(H_2O)]^{2+} \cdot aq$, and are made by the action of the appropriate carboxylic acid on chromium(III) oxide under controlled conditions[243]. An X-ray crystal structure study has shown that $[Cr_3O(OAc)_6(H_2O)_3]Cl \cdot 5H_2O$ has a structure (Fig 10) in which the three chromium atoms from an equilateral triangle with the oxygen atom at the centre, the four atoms being coplanar; six bridging acetato groups and three coordinated molecules give octahedral coordination to the chromium (Table 5)[63].

It seems likely that such a structure is to be found in the other trinuclear chromium species (and also in analogous iron, ruthenium and iridium complexes, *cf.* p. 509). Magnetic susceptibility measurements[139,140] have been made on such species and exchange coefficients calculated (p 478). The magnetic data, vibrational spectra[118] and electronic spectra[125] are consistent with this model, for which a theory of bonding has been proposed[74].

Some tetranuclear chromium(III) acetates are claimed in the earlier literature,



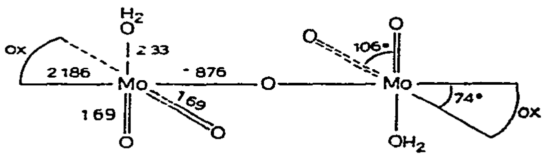
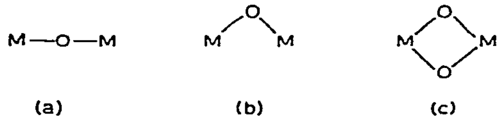


Fig 10. Structure of cation in $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl \cdot 5H_2O$
Fig 11 Structure of anion in $K_2[Mo_2O_5(ox)_2(H_2O)_2]$

e.g. $[Cr_4(OAc)_9]^{3+}$ and also the binuclear species $Cr_2O(OAc)_4 \cdot 2H_2O$, $Cr_2(OH)(OAc)_5$, *etc.* Their structures are unknown[244].

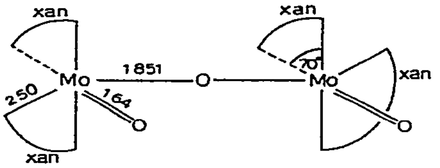
Molybdenum and tungsten Although there is undoubtedly a number of oxo bridged tungsten complexes the topic has been little investigated; molybdenum however has received more attention, and there are some valuable X-ray data. The three types of oxo bridged species encountered are (a) linear M–O–M, (b) bent M–O–M, (c) $\mu\mu'$, dioxo:



There are two X-ray structures of the first type. In $K_2[Mo_2O_5\ ox_2(H_2O)_2]$ which is a molybdenum(VI) complex, there are *cis*-MoO_2 units with terminal oxo ligands and one linear Mo–O–Mo oxo bridge. The Mo–O bridge length of 1.876 Å, although longer than the Mo=O (terminal) distance of 1.69 Å, is shorter than the Mo–O (oxalate) single bond distance of 2.10 Å (Fig. 9, Table 5)[64]. In the xanthate complex $Mo_2O_3(EtOCS_2)_4$ the molybdenum is pentavalent but the complex is diamagnetic due to spin-pairing through the oxo bridge[67]. The Mo–O bridge distance of 1.851 Å is very similar to that in the oxalato complex; the Mo=O terminal distance of 1.644 Å is slightly shorter than the terminal Mo=O lengths in the oxalate despite the lower oxidation state of the molybdenum[67] (Table 5) and this is due no doubt to the fact that there is only one terminal oxo ligand per metal in the xanthate (Fig. 12).

Examples of type (b), with bent M–O–M linkages, are afforded by $Na(NH_4)[MoO_3\ ox]$ and $K_2[W_2O(O_2)_4(H_2O)_2]$ The molybdenum oxalato complex is actually an infinite chain polymer, the chain being formed by bent Mo–O–Mo linkages. Here the Mo–O (bridge) distances alternate between 2.230 Å and 1.878 Å (similar to the bridging oxygen atoms in molybdenum trioxide). The *cis*-MoO_2 groups have Mo=O (terminal) distances of 1.82 Å (Table 5, Fig. 13)[66].

In $K_2[W_2O_3(O_2)_4(H_2O)_2]$ there is a bent W–O–W linkage in the binuclear anion; the angle is 139° and the W–O (bridge) distance 1.94 Å. This is again long since the W=O (terminal) length for the single oxo ligand per metal atom is



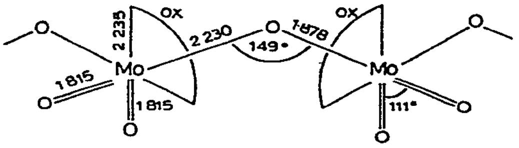


Fig 12. Structure of $Mo_2O_3(xan)_4$

Fig 13. Structure of anion in $[NaNH_4(MoO_3ox)]_n$

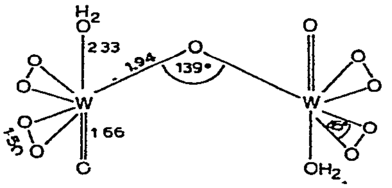
1.66 Å compared with 2 33 Å for the metal–water and 1.93 Å for the W–O (peroxo) length. The long W–OH_2 distance may be a manifestation of a *trans* effect by the doubly bonded W=O group (Table 5, Fig. 14)[68].

The only established examples of a $\mu\mu'$-dioxo linked system are provided by $Ba[Mo_2O_4\,ox_2(H_2O)_2]$, and by $Na_2[Mo_2O_4(cysteine)_2] \cdot 5H_2O$, both molybdenum(V) species. In the oxalate the two Mo–O bridge distances are 1.93Å with a small Mo–O–Mo angle of 83°; this rather strained angle is probably a result of the close Mo–Mo distance of 2.543 Å. The distance is short enough for substantial metal–metal bonding which probably accounts for the diamagnetism of the complex[65]. The Mo=O length for the single terminal oxo ligand per metal atom is 1.70 Å (Table 5, Fig. 15)[65].

In the cysteine complex the stereochemistry is similar (Table 5, Fig. 16)[63a].

Vibrational spectra of all the above species (with the exception of the xanthate complex) and of other binuclear species have been measured, and their stereochemistries rationalised on the basis of the availability of metal t_{2g} orbitals for receipt of electrons from oxygen p_π orbitals[41].

A number of other molybdenum binuclear species are known; thus Mo_2O_3-(acac)$_4$ and $Mo_2O_5(C_5H_5)_2$ are probably of type (a) with linear Mo–O–Mo bridges[197] whilst the $[Mo_2O_4X_6]^{n-}$ complexes referred to above are probably of



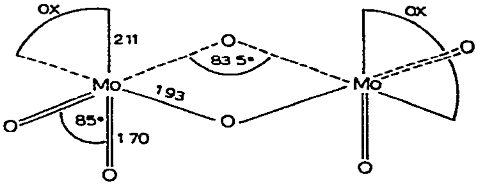


Fig 14 Structure of anion in $K_2[W_2O_3(O_2)_4(H_2O)_2]$

Fig 15 Structure of anion in $Ba[Mo_2O_4ox_2(H_2O)_2]$

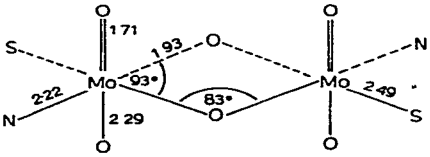
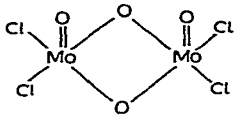


Fig 16 Structure of anion in $Na_2[Mo_2O_4(cysteine)_2]$ $5H_2O$.

type (c) with $\mu\mu'$-dioxo bridges[41,197]. It has been suggested, on the basis of infrared evidence, that MoO_2Cl_2 in solution has the binuclear structure (5)[245].



(5)

A polynuclear oxalato complex of molybdenum(IV), $[Mo_3O_4\,ox_3]^{2-}$ has been reported[246]. Recently the binuclear species $Cs_4[Mo_2O_3Cl_8]$ has been isolated from dilute solutions of $[MoOCl_5]^{2-}$ in hydrochloric acid with caesium chloride It is diamagnetic and thought to contain a bridging oxo ligand[247].

It has been shown that the tungsten complex previously reported as $K_2[W(OH)Cl_5]$, made by reduction of tungstate in hydrochloric acid with stannous chloride, is in fact binuclear, $K_4[W_2OCl_{10}]$. The potassium salt is not isomorphous with $K_4[Re_2OCl_{10}]$ which is known[69] to have a linear Re–O–Re bridge, and this together with IR and magnetic data suggests that the W–O–W bridge is bent. The magnetic moment μ_{eff} is 2.4 B M at 294° and 1.72 B M. at 70°; the electronic spectrum has a very intense band which is believed to arise from the presence of mixed oxidation states in the complex, and it has been concluded that it is best formulated as $[W^{V}W^{III}OCl_{10}]^{4-}$ [247].

(iv) Group VIIa (Mn–Tc–Re)

Apart from Pascal's text[147] there are two books on technetium and rhenium[248], and reviews on the chemistry of technetium[249] and rhenium[250].

(a) Oxides and oxohalides.—All three metals from heptoxides, M_2O_7; those of technetium and rhenium are polymers in the solid state All three form trioxides, MO_3, and dioxides, MO_2, and in addition manganese forms Mn_2O_3, Mn_3O_4, and MnO.

There appear to be no established oxohalides of manganese apart from MnO_3F (f p. −38°, b.p. 60°), but there are several of technetium and rheninium[10,248]. These take the form MO_3X (X = F, Cl) and ReO_3Br, MOX_4 (X = F, Cl) and $ReOBr_4$, MOX_3 (X = Cl, Br), $ReOF_5$, and ReO_2F_3 Those species which are mononuclear are considered in greater detail below. Both $ReOF_4$ and $TcOF_4$ are isostructural with $MoOF_4$, chains of octahedra being joined through *cis*-fluoro bridging ligands.

(b) Unsubstituted oxo complexes.—*Hexa- and penta-oxo species* No technetium compounds of this class have been made, and the only example so far discovered with manganese is $Na_5[MnO_5]$[2]. With rhenium, $M^{I}_5[ReO_6]$, $M^{II}_5[ReO_6]_2$,

$M^I_3[ReO_5]$ and $M^{II}_3[ReO_5]_2$ have been made[2,251], and vibrational spectra of the rhenium(VII) hexa- and penta-oxo compounds measured[41]. The rhenium(VI) species $Li_4[ReO_5]$ and $Li_6[ReO_6]$ are known; the latter exists in two crystal modifications[251].

Tetraoxo species.

Manganese. (1) The permanganates, $[MnO_4]^-$, are deep purple salts made by the oxidation of manganous salts, manganese dioxide or manganates in the presence of acid (in base, manganates(VI) normally result). The potassium salt has the barytes structure (Table 2)[19]. Vibrational spectra (Table 6)[82] and electronic spectra of $[MnO_4]^-$ have been studied and, in the latter case, energy levels assigned[28]. The effect of pressure on the electronic spectra of $[MnO_4]^-$ has been studied[252], and the temperature-independent paramagnetism of $K[MnO_4]$ discussed[201].

Permanganate is a very useful oxidising agent, in acid, neutral and alkaline solutions its oxidations are represented by the following equations, respectively:

$$[MnO_4]^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
$$[MnO_4]^- + 4H^+ + 3e^- \rightarrow Mn^{IV}O_2 + 2H_2O$$
$$2[MnO_4]^- + 2OH^- \rightarrow 2[MnO_4]^{2-} + H_2O + \tfrac{1}{2}O_2$$

Permanganate is sometimes used, like osmium tetroxide, for organic *cis*-hydroxylation reactions

(2) Manganates(VI). Manganates are best prepared by the action of excess alkali on permanganates; to obtain a pure product the reaction must be conducted in an atmosphere free from carbon dioxide[253]. The potassium salt forms bright green crystals when pure, but often appears darker due to a superficial film of permanganate. The crystal structure of $K_2[MnO_4]$ (Table 2)[20] shows that the Mn–O bond length is 0 03 Å longer than in $K[MnO_4]$[19], (the difference is significant since both determinations were of high accuracy). IR (Table 6)[83] electronic[5,254] and ESR[126] spectra, and magnetochemical studies (Table 10)[134a,253] of potassium manganate have been undertaken The rate of electron exchange between manganate and permanganate ion has been studied by NMR techniques[255].

(3) Hypomanganates, $[MnO_4]^{3-}$. These form bright blue salts, and are made by reduction of permanganate in excess alkali with sulphite[147]. The alkali metal salts are deliquescent and very easily hydrolysed. The electronic[5,254] and ESR[126] spectra of the ion have been measured.

The salts $Na_4[MnO_4]$ and $M^{II}_2[MnO_4]$ (M^{II} = Sr, Ba) have been reported[2], but it is not clear whether they contain tetrahedral anions.

Technetium and rhenium. Pertechnetates, $M^I[TcO_4]$ can be made from technetium heptoxide and the appropriate base, and *perrhenates* $M^I[ReO_4]$ can be obtained in similar fashion. As with their Group VI analogues, both pertechnetate and perrhenate ions are far weaker oxidising agents than permanganate. Vibrational (Table 6)[80,81], electronic[5,28] and ^{17}O magnetic resonance spectra[141] have been recorded for both ions. The rate of water exchange with perrhenate ion has been measured by two sets of workers, there being a certain amount of disagreement in the results[256]. In alkali, perrhenates form the $[ReO_4(OH)_2]^{3-}$ ion, but there is no evidence that pertechnetate expands its coordination sphere in this way The oxo species $[MOX_5]^{2-}$ can be made in halogen acids in the presence of reducing agents

Perrhenic acid can be made in solution by reaction of hydrogen peroxide with rhenium metal[257], and pertechnic acid can be made in a similar fashion (although aqueous solutions of pertechnic acid are colourless, the anhydrous solid, presumably $TcO_3(OH)$, is dark red[258]).

The salt $Li_3[Re^VO_4]$ has been briefly reported[2].

Polyanions. Unlike Group IVa, Va and VIa oxo species but like those of Group VIII, the Group VIa species show little tendency to polymerise, though Raman and PMR spectra of aqueous solutions of $HReO_4$ at different concentrations suggest that some polymeric species are formed[259].

While Tc_2O_7 and Re_2O_7 have polymeric structures in the solid state, manganese heptoxide, Mn_2O_7, may be monomeric. It can be made by the action of sulphuric acid on permanganates, and is a liquid which appears to be red by transmitted light and green by reflected light[260]. It freezes at very low temperatures to green crystals; at −5° it is stable but at 0° slowly decomposes, and above 10° the decomposition may become explosive. It is an extremely powerful oxidising agent and will set fire to combustible substances

(c) Substituted oxo complexes. —

Tetraoxo species. Treatment of $Ba[ReO_4]_2$ with concentrated alkali gives the pale yellow $Ba_3[ReO_4[OH)_2]$, and studies of the Raman spectrum of this suggest that the anion has a *cis* configuration, like the isoelectronic $[OsO_4(OH)_2]^{2-}$ ion[41]. It has been suggested that first row tetraoxo anions do not expand their coordination spheres in alkali whereas second and third row elements do[261], and IR studies on films of a number of tetraoxo anions in alkaline solution support this view[83].

Trioxo species The three trioxo halides of rhenium, ReO_3X (X = F, Cl, Br) may be monomeric; they are made by the action of oxygen on the tetrahalides. Certainly the chloride and bromide are monomeric in the vapour state, since their structures have been determined by electron diffraction (Table 7)[97], and normal coordinate analyses on these molecules have been carried out[102].

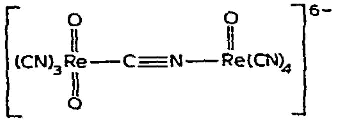
The thio species $[MO_3S]^-$ (M = Tc, Re) can be made from hydrogen sulphide on the $[MO_4]^-$ salts; IR spectra of the products were measured[262]. The yellow rhenium nitrido complex $K_2[ReO_3N]$ can be made by the reaction of potassium amide with rhenium heptoxide in liquid ammonia; its IR spectrum was recorded[263], and a normal coordinate analysis carried out[102]. Recently, $Cs_2[ReO_3Cl_3]$ has been made from solutions of perrhenic acid in hydrochloric acid with caesium chloride. Studies on the vibrational spectra of the salt suggest that the anion has C_{3v} symmetry with *cis* (1, 2, 3) oxo ligands, similar to other d^0 $[MO_3X_3]^{n-}$ species[264]. The compound $ReO_3(NO_3)$ can be obtained from ReO_3Cl and liquid nitrogen tetroxide; although IR spectra suggest that the nitrate is monodentate the compound is believed to be a polymer[265]. The green colour which appears when permanganates are dissolved in oleum is thought to be due to $MnO_3(HSO_4)$[187].

Dioxo species. None seems to be known for manganese or technetium, but there are a number for rhenium(V).

The only d^0 dioxo complexes reported are $K[ReO_2F_4]$, prepared by the action of bromine trifluoride on potassium perrhenate[266], and the dithio dioxo ion $[ReO_2S_2]^-$ [262]. The fluoro complex is likely to contain a *cis*-ReO_2 unit. The compound $K_2[ReO_2F_4]$ is said to be the product of the hydrolysis of $K_2[ReOF_6] \cdot 2HF$, but no analyses or any other supporting evidence were given for the formulation as a d^1 dioxo species[267].

The *trans*-dioxo rhenium(V) species $K_3[ReO_2(CN)_4]$[268], $[ReO_2\,en_2]Cl$[269], $[ReO_2py_4]Cl$[270] and $[ReO_2(NH_3)_4]Cl$[270] have been reported and their IR spectra measured[270]; the Raman spectra of the cyano and ethylenediamine complexes have also been measured[41]. These spectroscopic data support a *trans* streochemistry for the complex ion, and this is confirmed in the case of the cyanide by an X-ray crystal structure (Table 3)[38]. It is interesting to note that the Mo–O bond length[36a] in *cis* $K_2(MoO_2F_4)H_2O$ is 1 71 Å compared with 1 834 Å observed[37] in *trans*-$NaK_3[MoO_2(CN)_4] \cdot 6H_2O$ This bond lengthening in *trans*-dioxo complexes has been discussed above and arises from the restricted access of oxygen p_π orbitals to metal t_{2g} orbitals. Another consequence of this is that whereas rhenium monooxo bonds cannot be protonated, it is possible to protonate one (but not, of course, two) oxo ligands in $[ReO_2X_4]^{n-}$ to give $[ReO(OH)X_4]^{(n-1)-}$.

There is some evidence for the existence of $[ReO_2Br_2]^-$ and $[ReO_2(NCS)_2]^-$ ions[271], and it is claimed that the species in perrhenic acid–sulphuric acid mixtures is $[ReO_2(SO_4)_2]^-$ [272]. The compound obtained from reaction of $K_2[ReCl_6]$ and cyanide ion, once thought to be $K_4[ReO_2(CN)_4]$, has now been shown by spectroscopic and magnetic measurements to be a cyanide bridged dimer (6)[41]



$$\left[(CN)_3\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{Re}}}—C\equiv N—\overset{O}{\overset{\|}{Re}}(CN)_4\right]^{6-}$$

(6)

Monooxo species. None seems to be known for manganese. A few rhenium(VI) monooxo species are known but the majority are formed by the element in its pentavalent state.

Examples of rhenium(VI) monooxo species are $K_2[ReOF_6] \cdot 2HF$, a blue species made by the action of oxygen on a solution of $K_2[ReF_8]$ in hydrofluoric acid[267], the deep red, paramagnetic (μ_{eff} 1.6 B.M. at room temperatures) $R[ReOCl_5]$, made from $ReOCl_4$ in chloroform with an organic base chloride ($R = Ph_4As^+$, Et_2N^+); both IR and electronic spectra of these compounds were reported[273]. Although salts containing $[ReOCl_6]^{2-}$ have been claimed, a careful attempt to repeat these experiments failed and it now seems clear that salts of $[ReOCl_5]^{2-}$ had in fact been made[273].

A number of salts of $[ReOCl_5]^{2-}$ have been made[270], and there are corresponding bromo and iodo complexes[120]; the electronic spectra of $[ReOX_5]^{2-}$ and also of the recently prepared $[TcOCl_5]^{2-}$ have been measured and assignments proposed[120]. There is some doubt concerning the magnetic properties of certain salts of $[ReOCl_5]^{2-}$, some being said to be diamagnetic and others paramagnetic; the subject has been summarised by Grove and Wilkinson[270]. Protonation of $[ReO_2(CN)_4]^{3-}$ gives $[ReO(OH)(CN)_4]^{2-}$ [270], $[ReO_2py_4]^+$ will give $[ReO(OH)py_4]^{2+}$ [270], whilst $[ReO_2\,en_2]^+$ yields $[ReO(OH)en_2]^{2+}$ [269].

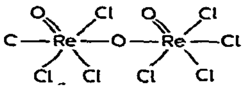
Phosphine complexes (*e g.* PEt_2Ph, PPh_3, PEt_3) and an arsine complex ($AsEt_2Ph$) of the form $ReOX_3(X_3)_2$ can be obtained from the tertiary phosphine or arsine with perrhenic acid in the appropriate acid ($X = Cl, Br, I$); IR spectra and dipole moments of many of the compounds were determined[274,275]. Detailed instructions for making $ReOX_3(PPh_3)_2$ and $ReOX_2(OEt)(PPh_3)_2$ have been given[257].

The square pyramidal species $[ReOX_4]^-$ ($X = Cl, Br, I$) can be made by reduction of potassium perrhenate with zinc in excess halogen acid; the products will take up a solvent molecule in the sixth coordination position to give such complexes as $[ReOBr_4(CH_3CN)]^-$ [276]. Crystal structure analyses of $(Ph_4As)[ReOBr_4(CH_3CN)]$[54] and $(Et_4N)[ReOBr_4(H_2O)]$[53] have been made (Table 4); in both cases the bromine atoms form the equatorial plane, and the rhenium atoms are displaced 0 33 Å out of this plane towards the oxo ligand.

The technetium(IV) complex $K_3[TcO(OH)(CN)_4]$ has been reported, but an alternative formulation as a seven coordinate hydroxo complex, $K_3[Tc(OH)_3(CN)_4]$, given for it[277].

Polynuclear species. The only established examples are with rhenium. The X-ray crystal structure of $K_4[Re_2OCl_{10}]$ (Table 5)[69] shows that this has an eclipsed D_{4h} centrosymmetric structure for the anion (*cf.* Fig. 3), with a linear Re–O–Re unit (Re–O = 1.86 Å). The rhenium atoms are displaced some 0 2 Å out of the Cl_4 planes towards the bridging oxo ligand; this may be due to a simple steric $O \cdot \leftrightarrow \cdot Cl$ repulsion (a similar effect has been observed in other oxo species, see above, and in $Cs_2[OsNCl_5]$[278] and $K_3[Ru_2NCl_8(H_2O)_2]$[279]. A molecular orbital scheme for bonding in the rhenium complex has been proposed[123]. Its vibrational spectrum[41] and magnetic properties[136,137] (p. 478) have been measured.

Complexes which may also contain Re^{IV}–O–Re^{IV} bridges are formed with carboxylates such as acetate and oxalate[280]. Although $K_4[Tc_2OCl_{10}]$ has been claimed it is now clear from X-ray analysis that the compound is in fact the monomeric $K_2[Tc(OH)Cl_5]$[281]; however, it is by no means unlikely that the $[Tc_2OCl_{10}]^{4-}$ ion could be made since the interconversion of $[Re_2OCl_{10}]^{4-}$ to $[Re(OH)Cl_5]^{2-}$ is very easy[280]. The exchange of $^{36}Cl^-$ with $[Re_2OCl_{10}]^{4-}$ has been studied[282]. Another binuclear oxo-chloro complex of rhenium, this time in the hexavalent state, is $[Re_2O_3Cl_8]^{2-}$, a diamagnetic species made from $ReOCl_4$ in chloroform with organic base chlorides. On the basis of IR and electronic spectra it was claimed that the structure was likely to be (7) or (8)[273] (see also the corresponding molybdenum compound[247], p. 498).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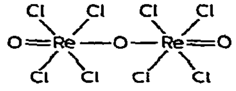
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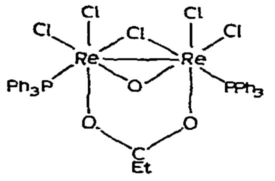
Two X-ray crystal structures have recently been reported of oxo-bridged carboxylates of rhenium(VI), $Re_2OCl_5(EtCOO)(PPh_3)_2$ (9)[283] and $Re_2OCl_3(EtCOO)_2(PPh_3)_2$ (10)[284].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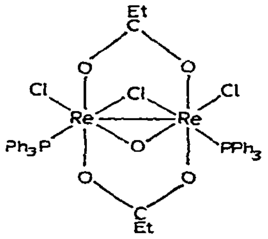
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These complexes are made from $ReOCl_3(PPh_3)_2$ and propionic acid, and both have very short Re–Re distances, 2 522(0.001) Å for (9), 2.541(0.001) Å for (10), in (9) the Re–O bridge distance is 1 896 (0.004) Å with a Re–O–Re angle of 83.8° while in (10) it is 2 095 Å with an angle of 82°. Re–Cl is 2.320 Å (9) and 2.357 (0.001) Å (10).

(v) Group VIII and Group Ib

The texts of Gmelin[146] and Pascal[147] have been used for the platinum group metals, and there is a recent monograph on the chemistry of osmium, ruthenium, iridium and rhodium[285], and a short review on osmium[286].

(a) Oxides and oxohalides — For iron, ruthenium and osmium the oxides are $M'O_4$, $M'O_3$, possibly M'_2O_5 and $M'O_2$ ($M' = Os, Ru$); M_2O_3, Fe_3O_4, MO ($M = Os, Ru, Fe$). For cobalt, rhodium and iridium there are $M'O_3$ and $M'O_2$ for iridium and rhodium, M_2O_3 and MO for all three metals, and Co_3O_4. For

nickel, palladium and platinum there are $M'O_2$ for palladium and platinum; and M_2O_3 and MO for all three metals. For copper, silver and gold there are MO and M_2O for all three metals.

There are no oxohalides of these metals apart from $[OsO_3F_2]_n$, $OsOF_5$, $OsOF_4$, $RuOF_4$, $OsOCl_4$, and Os_2OCl_6; reports of Os_2OCl_8 are apparently unfounded. Although $IrOF_4$ has been claimed it seems unlikely that the compound exists.

(b) Unsubstituted oxo complexes. —

Hexa- and penta-oxo species. Hexa- and penta-oxo complexes of osmium(VII) and (VI) have been made; $K_3[OsO_5]$, a black material prepared from potassium osmate and potassium superoxide, $M^I_5[OsO_6]$, made from lithium or sodium oxides and osmium metal in oxygen, $Li_6[OsO_6]$, made from $Li_5[OsO_6]$ and lithium oxide, and $Na_4[OsO_5]$, made by heating $Na_5[OsO_6]$[287]. An osmium(V) species, $Sr_2Cr^{III}[OsO_6]$ is also known[288]. The IR spectra of $Ba_5[OsO_6]_2$, $Ba_3[OsO_6]$ and $K_3[OsO_5]$ have been measured[41]. There have been reports of $Sr_4[MO_6]$ (M = Ir, Rh, Pt) but no preparative details were given[289] The existence of both $Ba_3[FeO_5]$ and $Ba_3[CoO_5]$ have been claimed[290].

Tetraoxo species.

First row elements.

(1) Iron. Three types of orthoferrate have been claimed with iron (VI), (V) and (IV) The iron(VI) species are the best established and are normally called the *ferrates*. The potassium salt, $K_2[FeO_4]$ can be obtained by oxidation of ferric hydroxide with hypochlorite[291]. The potassium salt forms dark purple crystals which appear very similar to those of the permanganate, and the aqueous solution (which is quite unstable) is a very deep purple The IR spectrum of the solid has been measured (Table 6)[84], and the electronic spectrum recorded[28,292]. The magnetic properties of the salt measured over a temperature range support a tetrahedral structure for the anion (Table 10)[135], as does the ESR spectrum[126].

The so-called "hypoferrates", $M^I_3[FeO_4]$ (M = Na, K) have been claimed; the potassium salt can be made by the action of potassium superoxide on ferric oxide, in an oxygen stream at 750°, or by the action of heat on the ferrate. The black crystalline salts are stable to 500° and are said to be stable in highly alkaline solutions[293]. The magnetic moment at room temperature is 3.85 B.M., and this together with X-ray powder patterns are said to demonstrate that they do contain tetrahedral anions[293], but some doubt has been cast on these results[5].

The black ferrates(IV) have been claimed; the barium salt is made by the reaction

$$Ba(OH)_2 + Ba_3[Fe(OH)_6] + 1/2O_2 \xrightarrow{900^\circ} 2Ba_2[FeO_4] + 7H_2O$$

and there are also sodium and strontium salts The barium salt has a similar X-ray powder pattern to $Ba_2[TiO_4]$ and so may contain the $[FeO_4]^{4-}$ anion[2]. An iron(III) salt, $Ba_5[FeO_4]_2$, has been claimed[2].

(2) Cobalt. Reaction of cobaltous hydroxide with barium hydroxide at 1050° yields the red-brown $Ba_2[Co^{IV}O_4]$[290], and the bright blue deliquescent $Na_3[CoO_4]$ and $K_3[CoO_4]$ have been isolated. The magnetic moment of 2.01 B.M. at 300° is said to be consistent with high-spin cobalt (V)[294]. The salt $Li_6[CoO_4]$ has also been claimed[2].

(3) Nickel. Both $Ba_2[NiO_4]$[2] and $Ba_3[NiO_4]$[295] are reported; the latter at least is known to be a mixed metal oxide with a distorted rock-salt type of structure[295].

Second row elements.

(1) Ruthenium. There are three well-established tetraoxo species of ruthenium(VIII), (VII) and (VI).

Ruthenium tetroxide, RuO_4, is a yellow crystalline solid (m.p 25 4°, b.p. 40°), made by oxidising potassium ruthenate or perruthenate with chlorine or acid permanganate[296]. It has a sharp and characteristic smell, not unlike that of osmium tetroxide. There have been a number of studies recently on the vibrational spectra of the solid, liquid, aqueous solution and vapour, and force constant calculations have been carried out with the results shown in Table 6[84a]. Electronic spectra have also been measured[28,297], and the thermochemistry of the compound reviewed (together with that of other ruthenium oxides)[298]. The compound is a very powerful oxidising agent, and on that account should be handled with considerable care. Halogen acids reduce it to $[RuX_6]^{2-}$, probably *via trans*-$[RuO_2X_4]^{2-}$ species, while with most other ligands it will give ruthenium(III) or ruthenium(II) complexes. Gentle reduction gives $[RuO_4]^-$ and $[RuO_4]^{2-}$. There is no substantial evidence for the formation of species of the type $[MO_4X_2]^{n-}$ given by osmium(VIII) and rhenium(VII).

The perruthenates, $[RuO_4]^-$, are made by careful oxidation of ruthenates with chlorine or by reaction of ruthenium metal with alkaline oxidising fluxes[296]. The potassium salt forms small black crystals which decompose above 400° to potassium ruthenate and ruthenium dioxide. The X-ray crystal structure (Table 2)[21] shows the anion to be tetrahedral with only slight distortion (the salt is not isomorphous with potassium permanganate). IR[84] and electronic spectra of $[RuO_4]^-$ ion have been studied, and there is some evidence that in alkaline solutions there may be species such as $[RuO_4(OH)_2]^{3-}$ [299].

The ruthenates, $[RuO_4]^{2-}$, are normally made by reaction of ruthenium metal or ruthenium salts with potassium nitrate and hydroxide[296]. The potassium salt is deep red and gives a deep red solution. The vibrational spectrum (Table 6)[84], electronic spectrum[28,299] and ESR spectrum have been measured. It is likely that "ammonium ruthenate, $(NH_4)_2$ $[RuO_4]$", is in fact a bridged μ-nitrido complex[117].

(2) *Rhodium.* Potassium rhodate, $K_2[RhO_4]$, is said to be formed as a blue salt when chlorine is passed into a solution of rhodium dioxide or sesquioxide in alkali; a blue barium salt has been made which had a magnetic moment corresponding to one unpaired electron per metal atom[5]. Strontium and calcium salts approximating in formula to $M^{II}[RhO_4]$ have been made:

$$Rh+2SrCO_3+O_2 \xrightarrow{\text{air, }1200°} Sr_2[RhO_4]$$

though both compounds are somewhat oxygen-deficient[300].

Third row elements.

(1) *Osmium.* The only example is osmium tetroxide, but this is one of the most important compounds of the metal.

Osmium tetroxide, OsO_4, is a yellow crystalline solid (m p. 40.6°, b p. 131.2°), prepared by oxidising the metal or almost any osmium compound with nitric acid[296]. The solid has a considerable vapour pressure at room temperatures and the compound should be handled with care Electron-diffraction measurements on the vapour show the molecule to be tetrahedral (Table 2)[22] and the X-ray crystal structure of the solid has also been determined[23]. Vibrational spectra of the solid, liquid, solution and gas have been determined and force constant treatments applied (Table 6)[84,94]. The electronic spectrum has been measured[28], and also the ^{17}O magnetic resonance[141], and thermodynamic data for the molecule reviewed[298]. With halogen acids HX, *trans*-$[OsO_2X_4]^{2-}$ and $[OsX_6]^{2-}$ are formed; with ammonia, $OsO_4 \cdot NH_3$ is formed in the dry, while in aqueous solution $[OsO_4(OH)_2]^{2-}$ and $[OsO_3N]^-$ are formed. Reactions with ligands give osmium(IV), (III) or (II) complexes.

(2) *Iridium.* Ill-defined iridates(VI) of the form $K_2O\ nIrO_3$ have been claimed. Reaction of iridium dioxide with calcium or strontium carbonates gives $M^{II}_2[IrO_4]$[300]:

$$2CaCO_3+IrO_2 \xrightarrow{\text{air, }1000°} Ca_2[IrO_4]$$

(c) Substituted oxo complexes.—

Tetraoxo species. These are confined to osmium and ruthenium. Both osmium and ruthenium tetroxides form unstable 'addition' compounds with ammonia gas $OsO_4 \cdot NH_3$, an orange species whose IR spectrum suggests a square based pyramidal structure[301], $OsO_4 \cdot py$ and some adducts with organic molecules, $RuO_4 \cdot NH_3$, RuO_4py_2 (this latter species, however, may be $Ru(OH)_4py_2$), $RuO_4 \cdot PF_3$ and $(RuO_4)_2 \cdot PF_3$.

Salts of $[OsO_4(OH)_2]^{2-}$ and $[OsO_4F_2]^{2-}$ can be isolated from aqueous solutions of osmium tetroxide with hydroxo or fluoro ions, and studies of the vibrational spectra of the products suggest a *cis* configuration for the complex anion[41]. There is also evidence for the existence of $[OsO_4(OH)(H_2O)]^-$ and for $[RuO_4(OH)_2]^{3-}$.

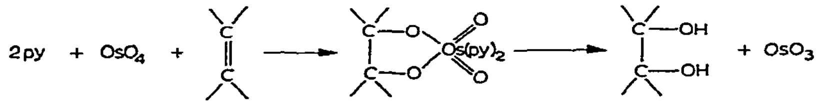
Trioxo complexes. Reaction of osmium tetroxide with aqueous ammonia yields the $[OsO_3N]^-$ ion, normally studied as the sparingly soluble potassium salt[302]. The complex anion has recently been studied by X-ray methods and confirms the C_{3v} distorted tetrahedral arrangement; the $Os{\equiv}N$ distance is even shorter than $Os{=}O$ (Table 3)[35a]. The vibrational spectra have been measured[303]. Reaction of osmium tetroxide with *tert*-butylamine gives $OsO_3(NMe_3)$, and an IR spectrum (with some rather dubious assignments) reported[302].

The action of bromine trifluoride on a mixture of osmium tetroxide with potassium bromide yields $[OsO_3F_2]_n$ (presumably a dimer with fluoro bridges) and $K[OsO_3F_3]$ The vibrational spectra of the latter indicate the expected *cis* (1, 2, 3) arrangement (1) of oxo ligands[41].

Dioxo complexes. Although there have been reports of $[IrO_2]^{2+}$ and $[RhO_2]^+$ species[285] these have yet to be substantiated. One ruthenium dioxo complex, $Cs_2[RuO_2Cl_4]$, made by the action of hydrochloric acid and caesium chloride on ruthenium tetroxide is known. The IR spectrum suggests that there is a *trans* configuration for the anion[285]. The species formulated as $RuO_2(NH_3)_2Cl_2$ is now known to be a μ-nitrido complex[117].

A number of osmium dioxo complexes are known, normally called 'osmyl' species They are all of osmium(VI), taking the form $[OsO_2X_4]^{n-}$ (X = Cl, Br, 1/2 ox, OCH_3, OH, SO_3, NH_3) and $[OsO_2(OH)_2X_2]^{2-}$ (X = Cl, Br, 1/2 ox)—these latter species[106] were formerly believed to contain $[OsO_3X_2]^{2-}$ ions. They all have *trans*-dioxo units and the vibrational spectra of most of them have been measured[41,106].

The X-ray crystal structures of $K_2[OsO_2Cl_4]$[39] and $K_2(OsO_2(OH)_4]$ (Table 3)[40] confirm this. The electronic spectrum of 'potassium osmate', $K_2[OsO_2(OH)_4]$ has been measured (this compound is formulated in the older literature as $K_2[OsO_4]\cdot 2H_2O$ but was re-formulated as containing *trans*-$[OsO_2(OH)_4]^{2-}$ by Lott and Symons on the basis of the electronic spectrum and the diamagnetism of the complex[44]). Schemes for bonding in osmyl complexes have been proposed[43,44]. It is likely that cyclic osmium(VI) esters are formed as intermediates during *cis*-hydroxylation reactions between olefins and osmium tetroxide. The main steps of the reaction, which is widely used in organic chemistry where a smooth and specific *cis*-hydroxylation is required, are probably:



Monooxo complexes. Species of this type are very rare for this group of elements. Undoubtedly the oxotetrahalides of osmium and ruthenium are monomeric in the gas phase, but in the solid state they are polymeric with halogen bridges.

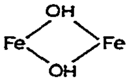
The only complex which is known to be a monomer at room temperatures in this group is $OsOF_5$, a green crystalline solid (m p. 59.8°) made by fluorination of osmium dioxide at 200°. The ESR spectrum of a solution of the substance was measured[304]. There is also a report of $(NO)^+[OsOF_5]^-$.

Although it has been claimed that the green reaction product of $OsOCl_4$ and caesium chloride at low temperatures is $Cs_2[OsOCl_6]$, this has not been established beyond doubt since the product was certainly contaminated with $Cs_2[OsO_2Cl_4]$.

Species such as $[IrO(OH)]^+$ and $[RhO]^{3+}$ have been claimed but there is no good evidence as yet for their existence. There is however evidence for the existence of 'ruthenyl' species in aqueous solutions of ruthenium tetroxide with perchloric acid; these are probably $[RuO(H_2O)_5]^{2+}$ [305].

Polynuclear complexes.

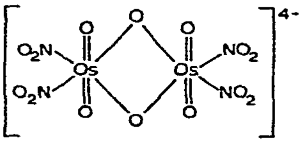
Binuclear. Iron(III) forms a series of binuclear complexes with a number of ligands, and such species contain either a Fe–O–Fe bridge or a diol system,



Systems which have been shown to contain the first type of linkage are [Fe $base_2$]O (the base being of the Schiff type)[138] and a number of *o*-phenanthroline and bipyridyl iron (III) species probably have a similar structure[139]. Magnetic susceptibility measurements were made over a temperature range on these species and magnetic exchange intergrals evaluated; a qualitative molecular orbital scheme was proposed to account for the results[138].

Ruthenium and osmium: the complex anions $[M_2OX_{10}]^{4-}$ (X = Cl, Br) are made by the reduction of the tetroxides with hydrochloric acid under carefully controlled conditions; a new preparation for $K_4[Ru_2OCl_{10}]$ using ruthenium and potassium chlorate has recently been described[306]. The X-ray crystal structure of $K_4[Ru_2OCl_{10}]$ shows that this has a D_{4h} centrosymmetric structure for the anion as has $K_4[Re_2OCl_{10}]$ (*cf.* Table 5 [70] and Fig. 3). The Ru–O distance of 1.80 Å is clearly indicative of some metal–oxo multiple bonding. The complex is diamagnetic; this and the electronic spectrum[74,122] have been interpreted on the bonding theory of Dunitz and Orgel already described (p. 471)[73]. Vibrational spectra of these and other binuclear complexes containing linear M–O–M bonds have been measured[41], and the results compared with those for analogous linear M–N–M systems[117]; force constants have been evaluated for these systems on a simple valence force field model [41,116].

A rare example of a $\mu\mu'$-dioxo system is $K_4[Os_2O_6(NO_2)_6]$, formulated in the early literature as an 'oxy-osmyl' complex $K_2[OsO_3(NO_2)_2]$ and then reformulated by the author (who had at his disposal the modern wonders of infrared spectroscopy) as $K_2[OsO_2(OH)_2(NO_2)_2]$[106]; it is in fact binuclear (11), as X-ray studies now show (Table 5)[71].

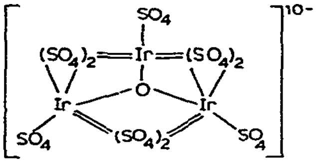


(11)

Newly primed with this knowledge it was possible to re-interpret the vibrational spectrum[41].

Trinuclear. Two types have been distinguished with these metals: triangular trinuclear and linear trinuclear.

The complexes which are believed to contain triangular M_3O units (the three metal atoms at the vertices of an equilateral triangle with the oxygen at the centre, the four atoms being coplanar) are $[Fe_3O(CH_3COO)_6(H_2O)_3]^+$ and the ruthenium complex $[Ru_3O(CH_3COO)_6(H_2O)_3]^+$. Magnetic susceptibility data determined over a temperature range support the trinuclear formulation for the iron complexes[139] as do the vibrational spectra[41], and both methods suggest that the iron species retain this triangular structure in aqueous solution[41,139]. Furthermore, the iron acetato complex $[Fe_3O(CH_3COO)_6(H_2O)_3]Cl \cdot 5H_2O$ is isomorphous with[63], and has very similar unit cell constants to, the corresponding chromium species, the structure of which has been determined by X-ray methods (Table 5 [63]; Fig. 10). A compound which probably has a related structure is $K_{10}[Ir_3O(SO_4)_9]$, made by boiling $(NH_4)_3[IrCl_6]$ with sulphuric acid. The complex has a single unpaired electron per three metal atoms, consistent with the bonding predictions for a triangular system of the chromium iron and ruthenium acetate complexes (12); it is likely that the diamagnetic nitrido species $K_4[Ir_3N(SO_4)_6(H_2O)_3]$ (13) has a similar type of structure[74]. This is supported by measurements of electronic[74,75] and vibrational spectra[117,118].



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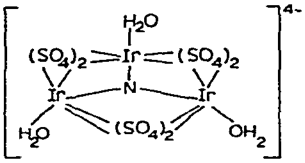

(13)

In the ruthenium red complex, $[Ru_3O_2(NH_3)_{14}]^{6+}$ (made by oxidation of ruthenium (III) or ruthenium (II) ammines) it has been proposed that there is a linear Ru–O–Ru–O–Ru skeleton[307]; this is consistent with the diamagnetism of the complex and its electronic spectrum[74]. A similar structure has been proposed for the brown oxidation product of ruthenium red, $[Ru_3O_2(NH_3)_{14}]^{7+}$ [307]. Vibrational spectra of the complexes have been measured[118].

Finally, the tetranuclear copper(II) complex $Cu_4OCl_6(Ph_3PO)_4$, is interesting as being a transition metal analogue of the tetranuclear basic acetates of beryllium and zinc. In the copper complex the oxygen atom is at the centre of a tetrahedron of copper atoms, and chlorine ligands span the six sides of the tetrahedron (Table 5, Fig. 17)[72].

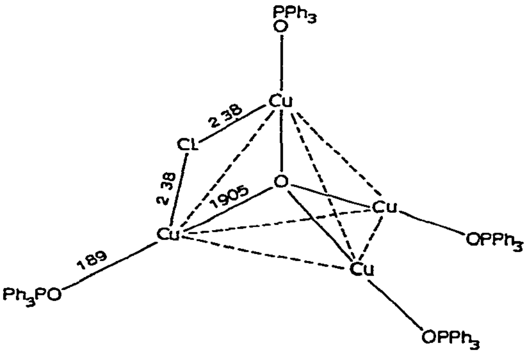

Fig 17 Structure of $Cu_4OCl_6(Ph_3PO)_4$, for clarity, only one of the six chlorine ligands which span the sides of the tetrahedron is shown

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