Table 23.3 Oxides of Group 6

Oxidation state:	+6	Intermediate	+4	+3
Cr	CrO_3	Cr_3O_8, Cr_2O_5, Cr_5O_{12}, etc.	CrO_2	Cr_2O_3
Mo	MoO_3	Mo_9O_{26}, Mo_8O_{23}, Mo_5O_{14}, $Mo_{17}O_{47}$, Mo_4O_{11}	MoO_2	—
W	WO_3	$W_{49}O_{119}$, $W_{50}O_{148}$, $W_{20}O_{58}$, $W_{18}O_{49}$	WO_2	—

23.3 Compounds of Chromium, Molybdenum and Tungsten[2,3,3a]

The binary borides (p. 145), carbides (p. 299), and nitrides (p. 418) have already been discussed. Suffice it to note here that the chromium atom is too small to allow the ready insertion of carbon into its lattice, and its carbide is consequently more reactive than those of its predecessors. As for the hydrides, only CrH is known which is consistent with the general trend in this part of the periodic table that hydrides become less stable across the d block and down each group.

23.3.1 Oxides[2,4]

The principal oxides formed by the elements of this group are given in Table 23.3 above.

CrO_3, as is to be expected with such a small cation, is a strongly acidic and rather covalent oxide with a mp of only 197°C. Its deep-red crystals are made up of chains of corner-shared CrO_4 tetrahedra. It is commonly called "chromic acid" and is generally prepared by the addition of conc H_2SO_4 to a saturated aqueous solution of a dichromate. Its strong oxidizing properties are widely used in organic chemistry. CrO_3 melts with some decomposition and, if heated above 220–250°, it loses oxygen to give a succession of lower oxides until the green Cr_2O_3 is formed.

Like the analogous oxides of Ti, V and Fe, Cr_2O_3 has the corundum structure (p. 243), and it finds wide applications as a green pigment. It is a semiconductor and is antiferromagnetic below 35°C. Cr_2O_3 is the most stable oxide of chromium and is the final product of combustion of the metal, though it is more conveniently obtained by heating ammonium dichromate:

$$(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + N_2 + 4H_2O^{\dagger}$$

When produced by such dry methods it is frequently unreactive but, if precipitated as the hydrous oxide (or "hydroxide") from aqueous chromium(III) solutions it is amphoteric. It dissolves readily in aqueous acids to give an extensive cationic chemistry based on the $[Cr(H_2O)_6]^{3+}$ ion, and in alkalis to produce complicated, extensively hydrolysed chromate(III) species ("chromites").

The third major oxide of chromium is the brown-black, CrO_2, which is an intermediate product in the decomposition of CrO_3 to Cr_2O_3 and has a rutile structure (p. 961). It has metallic conductivity and its ferromagnetic properties lead to its commercial importance in the manufacture of magnetic recording tapes which are claimed to give better resolution and high-frequency response than those made from iron oxide. Other more or less stable phases with compositions between CrO_2 and CrO_3 have been identified but are of little importance.

The trioxides of molybdenum and tungsten differ from CrO_3 in that, though they are acidic and dissolve in aqueous alkali to give salts of

[2] E. R. Braithwaite and J. Haber (eds.), *Molybdenum: An Outline of its Chemistry and Uses*, Elsevier, Amsterdam 1994, 662 pp.

[3] C. L. Rollinson, Chap. 36 in *Comprehensive Inorganic Chemistry*, Vol. 3, pp. 623–769, Pergamon Press, Oxford, 1973.

[3a] *Encyclopedia of Inorganic Chemistry*, Wiley, Chichester, 1994: for Cr see Vol. 2, pp. 666–78; for Mo see Vol. 5, pp. 2304–30; for W see Vol. 6, pp. 4240–68.

[4] M. T. Pope, Molybdenum oxygen chemistry, *Prog. Inorg. Chem.* **39**, 181–257 (1991); pp. 181–94 deals with oxides.

† In 1986 the initial drying of the dichromate in a rotary vacuum drier, resulted in a serious explosion in Ohio. The cause was not obvious but the presence of an organic contaminant must be a possibility.

the MO_4^{2-} ions, they are insoluble in water and have no appreciable oxidizing properties, being the final products of the combustion of the metals. MoO_3 and WO_3 have mps of 795 and 1473°C respectively (i.e. much higher than for CrO_3) and their crystal structures are different. The white MoO_3 has an unusual layer structure composed of distorted MoO_6 octahedra while the yellow WO_3 (like ReO_3 see p. 1047) consists of a three-dimensional array of corner-linked WO_6 octahedra. In fact, WO_3 is known in at least seven polymorphic forms and is unique in being the only oxide of any element that can undergo numerous facile crystallographic transitions near room temperature. Thus the monoclinic ReO_3-type phase (which is slightly distorted from cubic by W–W interactions) transforms to a ferroelectric monoclinic phase when cooled to −43°C, and transforms to another monoclinic variety above +20°C; there are further transitions to an orthorhombic phase at 325° and to a succession of tetragonal phases at 725°, 900° and 1225°.

If either MoO_3 or WO_3 is heated *in vacuo* or is heated with the powdered metal, reduction occurs until eventually MO_2 with a distorted rutile structure (p. 961) is formed. In between these extremes, however, lie a variety of intensely coloured (usually violet or blue) phases whose structural complexity has excited great interest over many years.[5] Following the pioneer work of the Swedish chemist A. Magnéli in the late 1940s these materials, which were originally thought to consist of a comparatively small number of rather grossly nonstoichiometric phases, are now known to be composed of a much larger number of distinct and accurately stoichiometric phases with formulae such as Mo_4O_{11}, $Mo_{17}O_{47}$, Mo_8O_{23}, $W_{18}O_{49}$ and $W_{20}O_{58}$. As oxygen is progressively eliminated, a whole series of M_nO_{3n-1} stoichiometries is feasible between the MO_3 structure containing *corner*-shared MO_6 octahedra and the rutile structure consisting of edge-shared MO_6 octahedra. These are produced as slabs of corner-shared octahedra move so as to share edges with the octahedra of identical adjacent slabs. This is the phenomenon of crystallographic shear and occurs in an ordered fashion throughout the solid.[6] The situation is further complicated by the formation of structures involving (a) 7-coordinate, and (b) 4-coordinate, alongside the more prevalent 6-coordinate, metal atoms. The reasons for the formation of these intermediate phases is by no means fully understood but, although their "nonstoichiometric" M:O ratios imply mixed valence compounds, their largely metallic conductivities suggest that the electrons released as oxygen is removed are in fact delocalized within a conduction band permeating the whole lattice.

Reduction of a solution of a molybdate(VI), or of a suspension of MoO_3, in water or acid by a variety of reagents including Sn^{II}, SO_2, N_2H_4, Cu/acid or Sn/acid, leads to the production of intense blue, sometimes transient, and probably colloidal products, referred to rather imprecisely as *molybdenum blues*. They appear to be oxide/hydroxide species of mixed valence, forming a series between the extremes of $Mo^{VI}O_3$ and $Mo^{V}O(OH)_3$, but a precise explanation of their colour is lacking. Their formation can be used as a sensitive test for the presence of reducing agents. The behaviour of tungsten is entirely analogous to that of molybdenum and, as will be seen presently, the reduction of heteropolyanions of these metals produces similar coloured products which may be distinguished from the above "blues" as "heteropoly blues" (though this is not always done).

The dioxides of molybdenum (violet) and tungsten (brown) are the final oxide phases produced by reduction of the trioxides with hydrogen; they have rutile structures sufficiently distorted to allow the formation of M–M bonds and concomitant metallic conductivity and diamagnetism. Strong heating causes disproportionation:

$$3MO_2 \longrightarrow M + 2MO_3$$

[5] D. J. M. BEVAN, Chap. 49 in *Comprehensive Inorganic Chemistry*, Vol. 4, pp. 491–7, Pergamon Press, Oxford, 1973.

[6] See p. 148 of ref. 2.

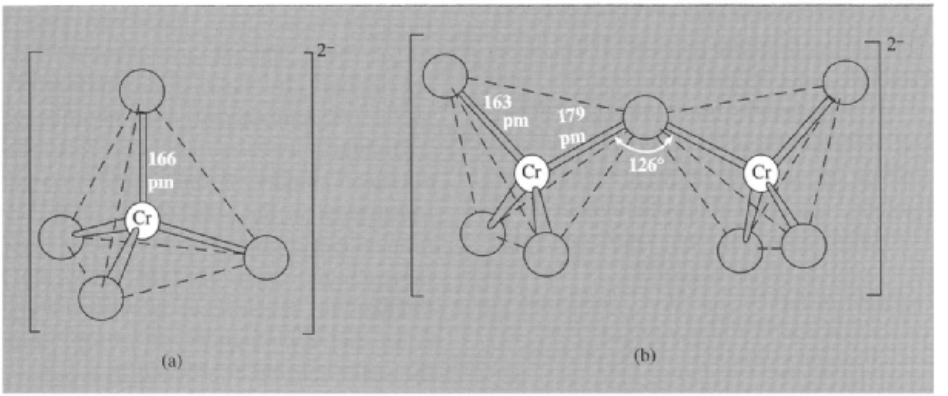


Figure 23.1 (a) CrO_4^{2-} ion, and (b) $Cr_2O_7^{2-}$ ion.

No other oxide phases below MO_2 have been established but a yellow "hydroxide", precipitated by alkali from aqueous solutions of chromium(II), spontaneously evolves H_2 and forms a chromium(III) species of uncertain composition. The sulfides, selenides and tellurides of this triad are considered on p. 1017.

23.3.2 Isopolymetallates [4,7,8,9,9a]

Acidification of aqueous solutions of the yellow, tetrahedral chromate ion, CrO_4^{2-}, initiates a series of labile equilibria involving the formation of the orange-red dichromate ion, $Cr_2O_7^{2-}$:

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+$$

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+$$

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^-$$

$$HCr_2O_7^- \rightleftharpoons Cr_2O_7^{2-} + H^+$$

$$H_2CrO_4 \rightleftharpoons HCr_2O_7^- + H^+$$

However, estimates of equilibrium constants (see for instance, *Comprehensive Coordination Chemistry*, Vol. 3, p. 699) have been questioned and it appears that the concentration of $HCrO_4^-$ is much lower than was previously supposed, the ion being undetectable by Raman and uv-visible spectroscopic techniques.[9b] Because of the lability of these equilibria the addition of the cations Ag^I, Ba^{II} or Pb^{II} to aqueous dichromate solutions causes their immediate precipitation as insoluble chromates rather than their more soluble dichromates. Polymerization beyond the dichromate ion is apparently limited to the formation of tri- and tetra-chromates ($Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$), which can be crystallized as alkali-metal salts from very strongly acid solutions. These anions, as well as the dichromate ion, are formed by the corner sharing of CrO_4 tetrahedra, giving Cr–O–Cr angles very roughly in the region of 120° (Fig. 23.1). The simplicity of this anionic polymerization of chromium, as compared to that shown by the elements of the preceding groups and the heavier elements of the present triad, is probably due to the small size of Cr^{VI}. This evidently limits it to tetrahedral rather than octahedral coordination with oxygen, whilst simultaneously favouring Cr–O double bonds and so inhibiting the sharing of attached oxygens.

Sodium dichromate, $Na_2Cr_2O_7.2H_2O$, produced from the chromate is commercially much

[7] M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer Verlag, Berlin, 1983, 180 pp. Also Chap. 38 in *Comprehensive Coordination Chemistry*, Vol. 3, pp. 1028–58, Pergamon Press, Oxford, 1987.

[8] Polyoxometalate Symposium Report (Engl.), *Comptes Rendus Acad. Sci. IIc*, **1**, 297–403 (1998).

[9] M. T. Pope and A. Müller, *Angew. Chem. Int. Edn. Engl.* **30**, 34–48 (1991).

[9a] M. I. Khan and J. Zubieta, *Prog. Inorg. Chem.* **43**, 1–149 (1995).

[9b] V. G. Poulopoulou, E. Vrachnou, S. Koinis and D. Katakis, *Polyhedron* **16**, 521–4 (1997).

the most important compound of chromium. It yields a wide variety of pigments used in the manufacture of paints, inks, rubber and ceramics, and from it are formed a host of other chromates used as corrosion inhibitors and fungicides, etc. It is also the oxidant in many organic chemical processes; likewise, acidified dichromate solutions are used as strong oxidants in volumetric analysis:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O; \quad E^\circ = 1.33\ V$$

For this purpose the potassium salt $K_2Cr_2O_7$ is preferred since it lacks the hygroscopic character of the sodium salt and may therefore be used as a primary standard.

The polymerization of acidified solutions of molybdenum(VI) or tungsten(VI) yields the most complicated of all the polyanion systems and, in spite of the fact that the tungsten system has been the most intensively studied, it is still probably the least well understood. This arises from the problem inevitably associated with studies of such equilibria, and which were noted (p. 983) in the discussion of the Group 5 isopolyanions. It must also be admitted that, whilst the observed structures of individual polyanions are reasonable, it is often difficult to explain why, under given circumstances, a particular degree of aggregation or a particular structure is preferred over other possibilities.

When the trioxides of molybdenum and tungsten are dissolved in aqueous alkali, the resulting solutions contain tetrahedral MO_4^{2-} ions and simple, or "normal", molybdates and tungstates such as Na_2MO_4 can be crystallized from them. If these solutions are made strongly acid, precipitates of yellow "molybdic acid", $MoO_3.2H_2O$, or white "tungstic acid", $WO_3.2H_2O$ are obtained which convert to the monohydrates if warmed. At pHs between these two extremes, however, polymerization occurs and salts can be crystallized,[10] the anions of which are almost invariably made up of MO_6 octahedra. A plethora of physical techniques[7] has been used to characterize these species and unravel the complexity of their structures. Examination of the alkali metal (or ammonium) and alkaline earth salts, particularly by X-ray analysis, forms the basis of classical studies of the isopoly-molybdates and -tungstates in the solid state. Modern nmr techniques (especially pulsed Fourier transform) have increasingly been used to study the solutions themselves. Even so it is only with great difficulty that the structure of an ion, determined in the solid, can be confirmed in solution.

Important differences distinguish the molybdenum and tungsten systems. In aqueous solution, equilibration of the molybdenum species is complete within a matter of minutes whereas for tungsten this may take several weeks; it also transpires that whereas the basic unit of most isopolymolybdates is an MO_6 octahedron with a pair of *cis*-terminal oxygens, that of the isopolytungstates is more commonly an MO_6 octahedron with only one terminal oxygen. The two must therefore be considered separately.

Undoubtedly the first major polyanion formed when the pH of an aqueous molybdate solution is reduced below about 6 is the heptamolybdate $[Mo_7O_{24}]^{6-}$, traditionally known as the paramolybdate:

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

This may be crystallized from aqueous solution and, by the addition of diethylenetriamine, $(H_3dien)_2[Mo_7O_{24}].4H_2O$ has been obtained[11] as two distinct polymorphs. Both contain discrete $[Mo_7O_{24}]^{6-}$ ions but differ in the way these are packed in the crystals.

Anions with 8, and probably 16–18, Mo atoms also appear to be formed, before increasing acidity suffices to precipitate the hydrous oxide. It is clear from the above equation that the condensation of MoO_4 polyhedra to produce these large polyanions requires large quantities of strong acid as the supernumary oxygen atoms are removed in the form of water molecules. Careful

[10] *Inorganic Syntheses*, **27**, Chap. 3 pp. 71–135 (1990), gives several detailed preparations.

[11] P. ROMAN, A. LUQUE, A. ARANZABE and J. M. GUTIERREZ-ZORRILLA, *Polyhedron* **11**, 2027–38 (1992).

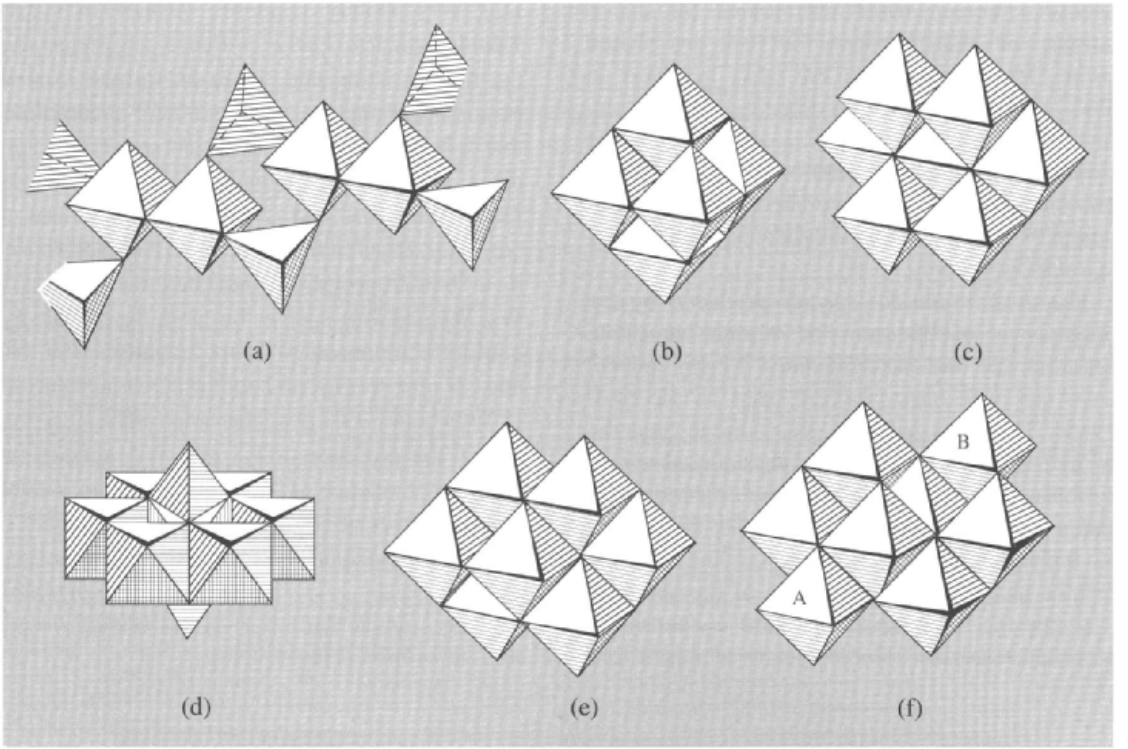


Figure 23.2 Idealized structures of isopolymolybdate ions. (a) Polymeric $[Mo_2O_7^{2-}]_n$ chain as found in the NH_4^+ salt. The $[NBu_4^n]^+$ salt contains discrete $[Mo_2O_7]^{2-}$ ions, comparable to $[Cr_2O_7]^{2-}$ (p. 1009) but with an M–O–M angle of 154° compared to 126°. (b) $[Mo_6O_{19}]^{2-}$ (the sixth octahedron is obscured). (c) Paramolybdate, $[Mo_7O_{24}]^{6-}$; this is the Anderson structure and can be viewed as an $M_{10}O_{28}$ structure (Fig. 22.3, p. 986) with a line of three octahedra removed. (d) α-$[Mo_8O_{26}]^{4-}$; a ring of six octahedra capped by two tetrahedra. (e) β-$[Mo_8O_{26}]^{4-}$ (one octahedron is obscured). (f) γ-$[Mo_8O_{26}]^{4-}$. One of the three terminal coordination positions in each octahedron A and B is unoccupied. Filling them with suitable ligands stabilizes this otherwise labile ion.

adjustment of acidity, concentration and temperature, often coupled with slow crystallization, can produce solids containing many other ions which are apparently not present in solution. Mixtures abound, but amongst the distinct species which have been characterized are: the dimolybdate, $[Mo_2O_7]^{2-}$; the hexamolybdate, $[Mo_6O_{19}]^{2-}$; and the octamolybdate, $[Mo_8O_{26}]^{4-}$, for which there are α- and β-isomers. The latter is the one usually obtained from aqueous solutions, but large counter ions or non-aqueous solvents have been used to prepare the former. A third (γ), coordinatively unsaturated form containing two 5-coordinate Mo atoms has been suggested as an intermediate in the $\alpha \rightleftharpoons \beta$ equilibrium, and has been isolated[12] as the salt $[Me_3N(CH_2)_6NMe_3]_2[Mo_8O_{26}].2H_2O$. Stabilization of the γ-configuration is also possible by completing the octahedral coordination spheres of the 5-coordinate Mo atoms with suitable ligands such as pyridine or pyrazole.[13] Figure 23.2 depicts the structures of these ions and it can be seen that the basic units are

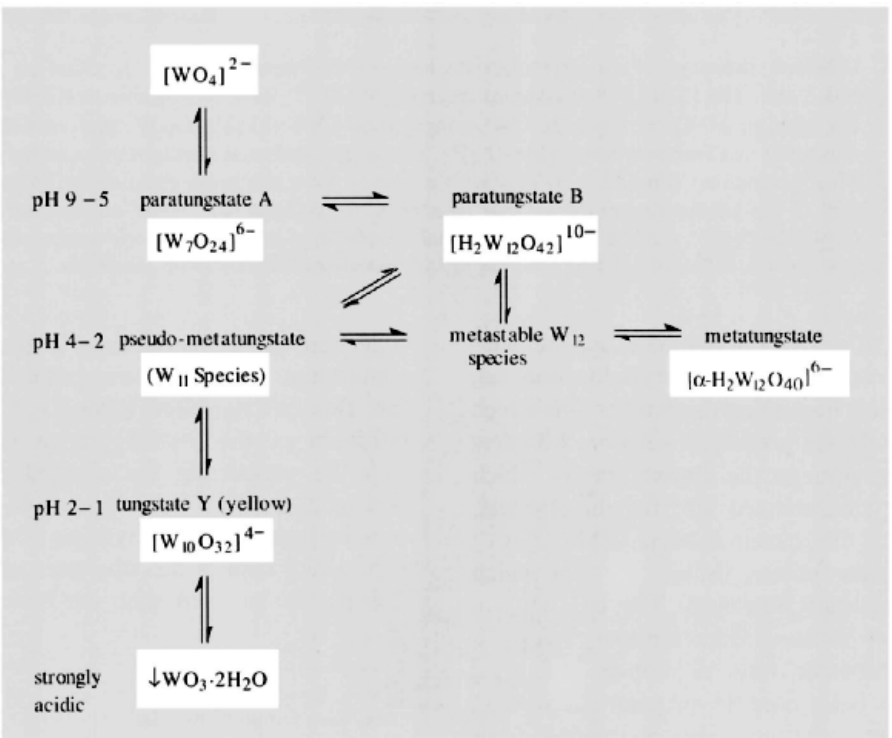
[12] M. L. NIVEN, J. J. CRUYWAGEN and J. B. B. HEYNS, *J. Chem. Soc., Dalton Trans.*, 2007–11 (1991).

[13] P. GILI, P. MARTIN-ZARZA, G. MARTIN-REYES, J. M. ARRIETA and G. MADARIAGA, *Polyhedron* **11**, 115–21 (1992).

MoO_6 octahedra which are joined by shared corners or shared edges, but not by shared faces. MoO_4 tetrahedra are also involved in $[Mo_2O_7^{2-}]_n$ and in a few other ions. The structure of $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$, one of the larger isopolyanions (but see Panel on p. 1015) consists predominantly of MoO_6 octahedra but includes, uniquely in the isopolymolybdates, MoO_7 pentagonal bipyramids.

The most important species produced by the progressive acidification of normal tungstate solutions are the paratungstates which, indeed, were the only ones reported prior to the mid-1940s. They are generally less soluble than the normal tungstates and can be crystallized over a period of several days. Further acidification produces metatungstates which are rather more soluble but will crystallize either on standing for some months or on prolonged heating of the solution. It seems that comparatively rapid condensation produces relatively soluble species which, if left, will very slowly condense further into less-soluble species. Early evidence suggested that the first paratungstate, A, to be formed in solution is a hexamer but evidence later accumulated that a heptamer is produced, just as with molybdates. For instance, potentiometric data obtained from dilute (0.1 and 0.001 molar) solutions of $Na_2WO_4.2H_2O$ in the range pH 7.8–5 and treated by a "best-fit program", indicated the presence of W_6, W_7 and W_{12} species but with the W_6 always a minor component.[14] More recently, ^{183}W, ^{17}O and ^{1}H nmr spectra of 2 molar aqueous solutions of WO_3 and LiOH over the range pH 8–1.5 confirmed the presence of W_7 and W_{12} species but found no evidence of W_6; they revealed a complicated series of equilibria in which a variety of protonations played a crucial role, and involving

[14] J. J. CRUYWAGEN and I. F. J. van der MERWE, *J. Chem. Soc., Dalton Trans.*, 1701–5 (1987).



Reaction scheme for the condensation of tungstate ions in aqueous solution.

a W_{11} species of uncertain composition.[15] The much simplified reaction scheme at the foot of the previous page outlines the situation but it must be noted that concentration, temperature, rate of acidification and counter cation will all affect the details of a particular system.

Amongst the crystalline products obtained from aqueous solution are, $(NH_4)_{10}[H_2W_{12}O_{42}]$-$.10H_2O$, $Na_6[H_2W_{12}O_{40}].29H_2O$, $K_4[W_{10}O_{32}]$-$.4H_2O$ and $Na_6[W_7O_{24}].14H_2O$. The compound $Na_5[H_3W_6O_{22}].18H_2O$ has recently been precipitated by acetone from a non-equilibrated aqueous solution[15a] and the structure of the anion may be considered to be derived from that of $[W_7O_{24}]^{6-}$ (which is like that of its Mo analogue, Fig. 23.2c) by removal of an outer octahedron from the middle row of three. Another hexatungstate, $[W_6O_{19}]^{2-}$ isostructural with its Mo analogue, can be obtained from methanolic solutions. $Li_{14}(WO_4)_3(W_4O_{16}).4H_2O$ has also been crystallized from aqueous solution and shown to contain the discrete ion, $[W_4O_{16}]^{8-}$ though there is no direct evidence that this is present in solution. The structures† of these anions are described in Fig. 23.3.

Many attempts have been made to rationalize the structures and mechanisms of formation of polymetallates. Lipscomb observed that no individual MO_6 octahedral unit ever has more than two unshared, i.e. terminal oxygens (exceptions appear to be stable only in the solid state) and this has been explained on the basis of π-bonding between the metal and terminal oxygen atoms: more than two of these

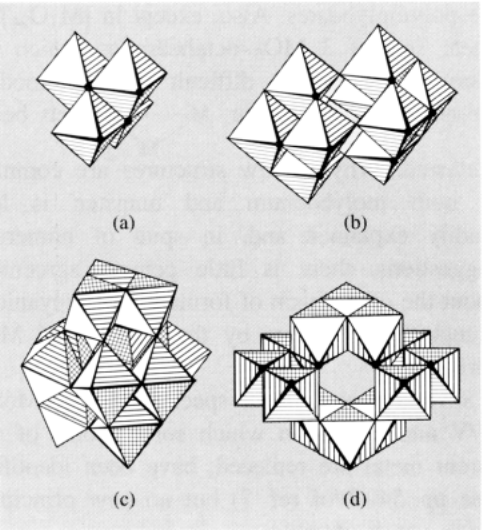


Figure 23.3 Idealized structures of isopolytungstate ions. (a) $[W_4O_{16}]^{8-}$ (b) $[W_{10}O_{32}]^{4-}$, composed of two identical W_5O_{16} groups. (c) The metatungstate ion, $[H_2W_{12}O_{40}]^{6-}$ (d) The paratungstate B ion, $[H_2W_{12}O_{42}]^{10-}$. As in the metatungstate, the protons appear to reside in the cavity of the ion but, unlike those of the metatungstate, exchange rapidly with protons from solvent water.

would so weaken and lengthen the *trans*-bonds holding the metal to the polyanion that it would become detached. Electrostatic repulsions between neighbouring metal ions will reinforce the distorting effect of M–O π-bonding, causing the metal ions to move off-centre in the MO_6 octahedra which are connected to each other. The effect increases as the mode of attachment changes from corner-sharing to edge-sharing. Thus, while the avoidance of unfavourably high, overall anionic charge favours edge-sharing as opposed to corner-sharing (thereby reducing the number of O^{2-} ions), the off-centre distortions become increasingly difficult to accommodate as the size of the polyanion increases. Ultimately edge-sharing is no longer possible, and this stage is reached by W^{VI} before it occurs with the smaller Mo^{VI}. Inspection of Figs. 23.2 and 23.3 shows the greater incidence of corner-sharing in the higher polytungstates than in

[15] J. J. HASTINGS and O. W. HOWARTH, *J. Chem. Soc., Dalton Trans.*, 209–15 (1992).

[15a] H. HARTL, R. PALM and J. FUCHS, *Angew. Chem. Int. Edn. Engl.* **32**, 1492–4 (1993).

† It is instructive to recall a particular problem facing early workers in establishing these structures by X-ray diffraction. Large scattering by the heavy tungsten atoms made it extremely difficult to locate the positions of the lighter oxygen atoms and this sometimes led to ambiguity in the assignment of precise structures (relative scattering $O/W = (8/74)^2 = 1/86$, cf. $H/C = (1/6)^2 = 1/36$). This is no longer a problem because of the greater precision of modern techniques of X-ray data acquisition and processing, but good-quality crystals are still necessary and these may be very difficult to produce.

the polymolybdates. Also, except in $[M_7O_{24}]^{6-}$, linear sets of 3 MO_6 octahedra on which the distortions are most difficult to accommodate are not found, triangular M--------M sets being preferred. Why so few structures are common to both molybdenum and tungsten is less readily explained and, in spite of numerous suggestions, there is little general agreement about the mechanism of formation of polyanions except that it occurs by the addition of MO_4 tetrahedra.

Several mixed metal species, Mo/W, Mo/V, W/V and W/Nb, in which some atoms of the parent metal are replaced, have been identified (see pp. 54–7 of ref. 7) but no new principles are as yet discernible.

23.3.3 Heteropolymetallates[7,8,9]

In 1826 J. J. Berzelius found that acidification of solutions containing both molybdate and phosphate produced a yellow crystalline precipitate. This was the first example of a heteropolyanion and it actually contains the phosphomolybdate ion, $[PMo_{12}O_{40}]^{3-}$, which can be used in the quantitative estimation of phosphate. Since its discovery a host of other heteropolyanions have been prepared, mostly with molybdenum and tungsten but with more than 50 different heteroatoms, which include many non-metals and most transition metals — often in more than one oxidation state. Unless the heteroatom contributes to the colour, the heteropoly-molybdates and -tungstates are generally of varying shades of yellow. The free acids and the salts of small cations are extremely soluble in water but the salts of large cations such as Cs^{I}, Ba^{II} and Pb^{II} are usually insoluble. The solid salts are noticeably more stable thermally than are the salts of isopolyanions. Heteropoly compounds have been applied extensively as catalysts in the petrochemicals industry, as precipitants for numerous dyes with which they form "lakes" and, in the case of the Mo compounds, as flame retardants.

In these ions the heteroatoms are situated inside "cavities" or "baskets" formed by MO_6 octahedra of the parent M atoms and are bonded to oxygen atoms of the adjacent MO_6 octahedra. The stereochemistry of the heteroatom is determined by the shape of the cavity which in turn depends on the ratio of the number of heteroatoms to parent atoms. Three major and a number of minor classes are found.

1:12, tetrahedral. These are found for both Mo and W but the latter are far more numerous and stable than the former. They occur with small heteroatoms such as P^{V}, As^{V}, Si^{IV} and Ge^{IV} which yield tetrahedral oxoanions, and they are the most readily obtained and best known of the heteropolyanions. Keggin[16] first determined the structure of the phosphotungstate, which was known to be isomorphous with the metatungstate, and his name is given to this structure type (Fig. 23.3c). The hetero-atom, or in the case of metatungstate a pair of protons, is situated in the tetrahedral inner cavity of the parent ion (Panel opposite). For the tungstates, Fe^{III}, Co^{II} and Zn^{II} derivatives are known, the second of which is of interest: it is readily formed, since tetrahedrally coordinated Co^{II} is not unusual, but oxidation yields $[Co^{III}W_{12}O_{40}]^{5-}$ in which the very unusual, high-spin, tetrahedral Co^{III} is trapped. Nor is tetrahedral coordination common for Cu^{II} but it is found in a recently reported[17] polyanion of this class containing both Cu^{II} and 2H as heteroatoms (giving an overall stoichiometry of $\{Cu_{0.4}(H_2)_{0.6}\}$ for the hetero "atom"). The structure of these compounds is now known as the α-Keggin structure since an isomeric β-Keggin structure has been identified for the heteropolyanions, "XMo_{12}" (X = Si, Ge, P, As) and "XW_{12}" (X = Si, Ge). Also β-$[H_2W_{12}O_{40}]^{6-}$ has been implicated in the isopolytungstate equilibria.[15] "Lacunary" ions, or their derivatives, are obtained by the nominal loss of one or more MO_6 octahedra (actually the stoichiometric loss of that number of MO

[16] J. F. Keggin, *Proc. R. Soc. A*, **144**, 75–100 (1934)

[17] H.-J. Lunk, S. Giese, J. Fuchs and R. Stösser, *Z. anorg. allg. Chem.* **619**, 961–8 (1993).

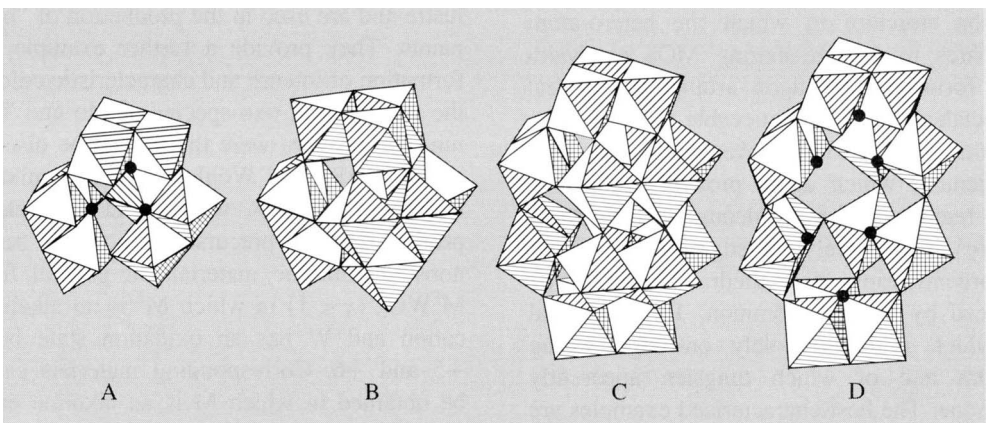
Large Polymetallates

With the objective of producing model systems to mimic the metal oxide surfaces of catalysts, a great deal of effort has been devoted to the preparation of large polymetallate structures.

The α-Keggin structure of $[PW_{12}O_{40}]^{3-}$ and the metatungstate, $[H_2W_{12}O_{40}]^{6-}$ can be seen (Fig 23.3) to be composed of four identical "tritungstate" or W_3 groups. Each of these is made up of three edge-sharing WO_6 octahedra, and the four groups are linked to each other by corner-sharing so as to enclose the heteroatom. This is more clearly seen in A where one of the W_3 groups has been omitted and the oxygens which are nearest neighbours to the heteroatom are marked by dots. The β-Keggin structure, B, is derived from the α-form by rotation of one W_3 group (in this case the top one) through 60°. In principle, similar rotation of the other three W_3 groups would yield γ, δ and ε isomers.

The Dawson structure, C, can be visualized as being formed by removing the three basal octahedra from each of two α-Keggin ions which are then fused together. By omitting the four octahedra at the front, the oxygens associated with the 2 heteroatoms can be seen more clearly (D).

Still larger heteropolyanions are possible by using As^{III} as the heteroatom. The lone-pair of electrons of this atom makes it too large to fit inside the Keggin ion, and the lacunary $[AsW_9O_{33}]^{9-}$ is formed instead. By judicious use of this as a "building block," $[As_4W_{40}O_{140}]^{28-}$ has been prepared. Similar use of $[P_2W_{12}O_{48}]^{12-}$, produced by degrading the Dawson structure by raising the pH, has yielded[18] $[P_4W_{48}O_{184}]^{40-}$.



The largest polymetallates so far reported, however, are the mixed valence (Mo^{VI}, Mo^{V}) nitrosyls obtained by the more straightforward, if less systematic, method of heating acidified aqueous solutions of MoO_4^- and NH_2OH with VO_3^-. Depending on concentration and whether the solutions are refluxed or heated without stirring, a variety of products has been obtained[19] including the mixed metal $[Mo_{57}V_6O_{183}(NO)_6(H_2O)_{18}]^{6-}$ and the spectacular $[Mo_{154}O_{420}(NO)_{14}(H_2O)_{70}]^{n-}$ ($n = 25 \pm 5$). Both are dark blue and are composed of edge- and corner-sharing MoO_6 octahedra and $\{Mo(NO)O_6\}$ pentagonal bipyramids, along with $V^{IV}O_6$ octahedra in the case of the former. The latter has the overall shape of a car (automobile) tyre and, in spite of its large molar mass, its large surface area, bristling with H_2O and OH ligands, renders it readily soluble in water from which it can be recrystallized without decomposition in the absence of air.

units). The hetero atom is then held in an open "basket" rather than being totally enclosed. The most numerous of such ions[9] are the Keggin derivatives, $[XM_{11}O_{39}]^{n-}$ (M = Mo, W; X = P,

[18] Y. JEANNIN, G. HERVE and A. PROUST, *Inorg. Chim. Acta* **198–200**, 319–36 (1992).

[19] S.-W. ZHANG, G.-Q. HUANG, M.-C. SHAO and Y.-Q. TANG, *J. Chem. Soc., Chem. Commun.*, 37–8 (1993). A. MÜLLER, E. KRICKEMEYER, J. MEYER, H. BOGGE, F. PETERS, W. PLASS, E. DIEMANN, S. DILLINGER, F. NONNENBRUCH, M. RANDERATH and C. MENKE, *Angew. Chem. Int. Edn. Engl.* **34**, 2122–4 (1995).

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