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As, Si, etc.) which are able to act as ligands to a variety of transition metal cations as well as to organometallic groups such as SnR, AsR and Ti (η^5-C_5H_5).

2:18, tetrahedral. If acidic solutions of the 1:12 anions $[X^{V}M_{12}O_{40}]^{3-}$ ($X = P, As; M = Mo, W$) are allowed to stand, the 2:18 $[X_2M_{18}O_{62}]^{6-}$ ions are gradually produced and can be isolated as their ammonium or potassium salts. The ion is best considered to be formed from two lacunary, 1:9 ions fused together and is generally known as the Dawson structure.

1:6, octahedral. These are formed with larger heteroatoms such as Te^{VI}, I^{VII}, Co^{III} and Al^{III} and are usually obtained from slightly acidic (pH 4–5) aqueous solutions. They adopt the Anderson structure in which the hetero-atom coordinates to 6 edge-sharing MO_6 octahedra in the form of a hexagon around the central XO_6 octahedron. It is noticeable that tungsten forms this type of ion less frequently than does molybdenum, which again probably reflects a greater readiness of molybdenum to form large structures based solely on edge-sharing, rather than corner-sharing, of octahedra. This is further reinforced by the less common, 1:9 octahedral type which is based solely on edge-sharing octahedra and of which tungsten apparently forms none. The best characterized examples are $[Mn^{IV}Mo_9O_{32}]^{6-}$ and $[Ni^{IV}Mo_9O_{32}]^{6-}$, prepared by the oxidation of X^{II} molybdate solutions with peroxodisulfate, the kinetics of which have been investigated.(20)

Mild and reversible reduction of 1:12 and 2:18 heteropoly-molybdates and -tungstates produces characteristic and very intense blue colours ("heteropoly blues") which find application in the quantitative determinations of Si, Ge, P and As, and commercially as dyes and pigments. The reductions are most commonly of 2 electron equivalents but may be of 1 and up to 6 electron equivalents. Many of the reduced anions can be isolated as solid salts in which the unreduced structure remains essentially unchanged and the heteroatom is not normally involved; i.e. even $Fe^{III}W_{12}$ is reduced to $Fe^{III}W^{V}W^{VI}_{11}$ not to $Fe^{II}W_{12}$, although $Co^{III}W_{12}$ *is* reduced to $Co^{II}W_{12}$. 1- or 2-electron reductions evidently occur on individual M atoms, producing a proportion of M^{V} ions. Transfer of electrons from M^{V} to M^{VI} ions is then responsible for the intense "charge-transfer" absorption. In the highly reduced species, limited delocalization is probable.

23.3.4 Tungsten and molybdenum bronzes

These materials owe their name to their metallic lustre and are used in the production of "bronze" paints. They provide a further example of the formation of intense and characteristic colours by the reduction of oxo-species of Mo and W. The tungsten bronzes were the first to be discovered when, in 1823, F. Wöhler reduced a mixture of Na_2WO_4 and WO_3 with H_2 at red heat. The product was the precursor of a whole series of nonstoichiometric materials of general formula $M^{I}_{x}WO_3$ ($x < 1$) in which M^{I} is an alkali metal cation and W has an oxidation state between +5 and +6. Corresponding materials can also be obtained in which M is an alkaline earth or lanthanide metal. The alkali-metal molybdenum bronzes(21) are analogous to, but less well-known than, those of tungsten, being less stable and requiring high pressure for their formation; they were not produced until the 1960s. The lower stability of the molybdenum bronzes may be a consequence of the greater tendency of Mo^{V} to disproportionate as compared to W^{V}.

Tungsten bronzes can be prepared by a variety of reductive techniques but probably the most general method consists of heating the normal tungstate with tungsten metal. They are extremely inert chemically, being resistant both to alkalis and to acids, even when hot and concentrated. Their colours depend in the proportion of M and W present. In the case of sodium

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[20] S. J. DUNNE, R. C. BURNS and G. A. LAWRANCE, *Aust. J. Chem.* **45**, 1943–52 (1992).

[21] M. GREENBLATT, *Chem. Revs.* **88**, 31–53 (1988).

tungsten bronze the colour varies from golden yellow, when $x \sim 0.9$, through shades of orange and red to bluish-black when $x \sim 0.3$. Within this range of x-values the structure consists of corner-shared WO_6 octahedra[†] as in WO_3 (p. 1008), with Na^I ions in the interstices — in other words an M-deficient perovskite lattice (p. 963). The observed electrical conductivities are metallic in magnitude and decrease linearly with increase in temperature, suggesting the existence of a conduction band of delocalized electrons. Measurements of the Hall effect (used to measure free electron concentrations) indicate that the concentration of free electrons equals the concentration of sodium atoms, implying that the conduction electrons arise from the complete ionization of sodium atoms. Several mechanisms have been suggested for the formation of this conduction band but it seems most likely that the t_{2g} orbitals of the tungsten overlap, not directly (since adjacent W atoms are generally more than 500 pm apart) but via oxygen $p\pi$ orbitals, so forming a partly filled π^* band permeating the whole WO_3 framework. If the value of x is reduced below about 0.3 the resulting electrical properties are semiconducting rather than metallic. This change coincides with structural distortions which probably disrupt the mechanism by which the conduction band is formed and instead cause localization of electrons in t_{2g} orbitals of specific tungsten atoms.

23.3.5 Sulfides[(2)], selenides and tellurides

The sulfides of this triad, though showing some similarities in stoichiometry to the principal oxides (p. 1007), tend to be more stable in the lower oxidation states of the metals. Thus Cr forms no trisulfide and it is the di- rather than the tri-sulfides of Mo and W which are the more stable. However, tungsten (unlike Cr and Mo) does not form M_2S_3. Many of the compounds are nonstoichiometric, most are metallic (or at least semiconducting), and they exhibit a wide variety of magnetic behaviour encompassing diamagnetic, paramagnetic, antiferro-, ferri- and ferro-magnetic.

Cr_2S_3 is formed by heating powdered Cr with sulfur, or by the action of $H_2S(g)$ on Cr_2O_3, $CrCl_3$ or Cr. It decomposes to CrS on being heated, via a number of intermediate phases which approximate in composition to Cr_3S_4, Cr_5S_6 and Cr_7S_8. The structural relationship between these various phases can most readily be understood by reference to the NiAs–CdI_2 structure motif. Removal of all the M atoms from alternate layers of the NiAs structure (p. 555) yields the CdI_2 layer lattice (p. 1212). Between these two extremes, removal of a proportion of M atoms results in the above phases as follows: if one quarter of the Cr atoms are removed from *alternate* layers Cr_7S_8 results; if one third, Cr_5S_6 results; if two thirds, Cr_4S_6 (ie Cr_2S_3) results and if half, Cr_3S_4 results. Of these various phases Cr_2S_3 and CrS are semiconductors, whereas Cr_7S_8, Cr_5S_6 and Cr_3S_4 are metallic, and all exhibit magnetic ordering. The corresponding selenides CrSe, Cr_7Se_8, Cr_3Se_4, Cr_2Se_3, Cr_5Se_8 and Cr_7Se_{12} are broadly similar, as are the tellurides CrTe, Cr_7Te_8, Cr_5Te_6, Cr_3Te_4, Cr_2Te_3, Cr_5Te_8 and $CrTe_{\sim 2}$.

Of the many molybdenum sulfides which have been reported, only MoS, MoS_2 and Mo_2S_3 are well established. A hydrated form of the trisulfide of somewhat variable composition is precipitated from aqueous molybdate solutions by H_2S in classical analytical separations of molybdenum, but it is best prepared by thermal decomposition of the thiomolybdate, $(NH_4)_2MoS_4$. MoS is formed by heating the calculated amounts of Mo and S in an evacuated tube. The black MoS_2, however, is the most stable sulfide and, besides being the principal ore of Mo,

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[†] This corner-sharing in tungsten bronzes is to be compared with a mixture of corner and edge-sharing in molybdenum bronzes which presumably occurs, as in the case of the polymetallates, because the increased electrostatic repulsion entailed in edge-sharing is less disruptive when the smaller Mo is involved. The prevalence of edge-sharing is still more marked in the vanadium and titanium bronzes (pp. 987, 964) where the smaller charges on the metal ions produce correspondingly smaller repulsions.

is much the most important Mo compound commercially. In 1923 its structure was shown by R. G. Dickinson and L. Pauling (in the latter's first research paper) to consist of layers of MoS_2 in which the molybdenum atoms are each coordinated to 6 sulfides, but forming a trigonal prism rather than the more usual octahedron. This layer structure promotes easy cleavage and graphite-like lubricating properties, which have led to its widespread use as a lubricant both dry and in suspensions in oils and greases. It also has applications as a catalyst in many hydrogenation reactions and, even when the original catalyst takes the form of an oxide, it is likely that impurities (which often "poison" other catalysts) quickly produce a sulfide catalytic system. High-purity MoS_2 is normally prepared by heating the elements at 1000°C for several days. The reaction of anhydrous $MoCl_5$ and Na_2S offers a promising alternative.(22)

$$2MoCl_5 + 5Na_2S \longrightarrow 2MoS_2 + 10NaCl + S$$

It is so exothermic as to burst into flame on mixing, and is complete within seconds.

WS_3 and WS_2 are similar to their molybdenum analogues and all 4 compounds are diamagnetic semiconductors.

Selenides and tellurides are, again, broadly similar to the sulfides in structure and properties.

The oxygen atoms of $MO_4{}^{2-}$ can be replaced successively by sulfur, and all four thiometallates, MO_3S^{2-}, $MO_2S_2{}^{2-}$, $MOS_3{}^{2-}$ and $MS_4{}^{2-}$ have been prepared; the thiomolybdates a century ago. They are useful reagents for the preparation of metal-sulfur clusters, and act as ligands, usually chelating but also as bridging groups.(23)

$MSe_4{}^{2-}$ have also been known for a considerable time but are less familiar. They may be prepared conveniently by treating K_2Se_3 with $M(CO)_6$ in dmf.(24)

Remarkable physical properties are found in a series of ternary molybdenum chalcogenides, $M_xMo_6X_8$, known as Chevrel phases.(25) The first of these was $PbMo_6S_8$ but over 40 metals have been incorporated in the series, and both Se and Te analogues occur. These phases are black crystalline materials, prepared from the elements at temperatures of 1000–1100°C, and the $[Mo_6X_8]$ cluster, composed of an octahedron of Mo atoms face-capped by X atoms, is the basic structural unit (cf Mo, W dihalides, p. 1022). The clusters are linked because the otherwise free apical coordination site of each Mo is occupied by an X atom of an adjacent cluster, while the M_x atoms are intercalated in the channels between the clusters. That these bridges are strong, is evident from the observed intercluster Mo–Mo distances of only 310–360 pm compared to approx. 270 pm for Mo atoms within a cluster — which are not bridged. With $x = 0$, the metastable Mo_6X_8 (obtained by "deintercalation" of $M_xMo_6X_8$ with HCl, rather than by direct synthesis) has only 20 electrons per cluster (6×6 metal valence electrons less 2×8 used in bonding to X_8). This is 4 short of the 24 required for Mo–Mo single bonds along each of the edges of the cluster, and may be the cause of the observed trigonal distortion. Intercalation of M_x atoms provides up to 4 electrons which make good this deficit thereby strengthening and shortening the Mo–Mo bonds and reducing the distortion.[†] $PbMo_6S_8$ has 22 electrons per cluster. The electron "holes" facilitate conduction, and below 14 K it is a superconductor. This, and several other Chevrel phases retain their superconductivity in the presence of exceptionally strong magnetic fields, and attempts to produce technically acceptable superconductors by extruding filaments in a copper matrix have been

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[22] P. R. BONNEAU, R. F. JARVIS and R. B. KANER, *Nature* **349**, 510–2 (1991).

[23] M. A. GREANEY and E. I. STIEFEL, *J. Chem. Soc., Chem Commun.*, 1679–80 (1992).

[24] S. C. O'NEAL and J. W. COLIS, *J. Am. Chem. Soc.* **110**, 1971–3 (1988).

[25] R. CHEVREL, M. HIRRIEN and M. SERGENT, *Polyhedron* **5**, 87–94 (1986).

[†] An alternative interpretation, supported by evidence from relevant molecular compounds is that the distortions are the result of intercluster M–X interactions (see p. 1031)

promising. Apparently, no tungsten analogues are yet known.

23.3.6 Halides and oxohalides[2,3]

The known halides of chromium, molybdenum and tungsten are listed in Table 23.4. The observed trends are as expected. The group oxidation state of +6 is attained by chromium only with the strongly oxidizing fluorine, and even tungsten is unable to form a hexaiodide. Precisely the same is true in the +5 oxidation state, and in the +4 oxidation state the iodides have a doubtful or unstable existence. In the lower oxidation states all the chromium halides are known, but molybdenum has not yet been induced to form a difluoride nor tungsten a di- or

Table 23.4 Halides of Group 6 (mp/°C)

Oxidation state	Fluorides	Chlorides	Bromides	Iodides
+6	CrF_6 yellow (d > −100°)			
	MoF_6 colourless (17.4°) bp 34°	($MoCl_6$) black		
	WF_6 colourless (1.9°) bp 17.1°	WCl_6 dark blue (275°) bp 346°	WBr_6 dark blue (309°)	
+5	CrF_5 red (34°) bp 117°			
	MoF_5 yellow (67°) bp 213°	$MoCl_5$ black (194°) bp 268°		
	WF_5 yellow	WCl_5 dark green (242°) bp 286°	WBr_5 black	
+4	CrF_4 violet-amethyst[a]	$CrCl_4$ (d > 600°, gas phase)	$CrBr_4$?	CrI_4
	MoF_4 pale green	$MoCl_4$ black	$MoBr_4$ black	MoI_4?
	WF_4 red-brown	WCl_4 black	WBr_4 black	WI_4?
+3	CrF_3 green (1404°)	$CrCl_3$ red-violet (1150°)	$CrBr_3$ very dark green (1130°)	CrI_3 very dark green
	MoF_3 brown (>600°)	$MoCl_3$ very dark red (1027°)	$MoBr_3$ green (977°)	MoI_3 black (927°)
		WCl_3 red	WBr_3 black (*d* > 80°)	WI_3
+2	CrF_2 green (894°)	$CrCl_2$ white (820°)	$CrBr_2$ white (842°)	CrI_2 red-brown (868°)
		$MoCl_2$ yellow (*d* > 530°)	$MoBr_2$ yellow-red (*d* > 900°)	MoI_2
		WCl_2 yellow	WBr_2 yellow	WI_2 brown

[a] It is probable that previously reported green samples were largely CrF_3; O. Kramer and B. G. Müller, *Z. anorg. allg. Chem.* **621**, 1969–72 (1995).

tri-fluoride. Similarly, in the oxohalides (which are largely confined to the +6 and +5 oxidation states, see p. 1023) tungsten alone forms an oxoiodide, while only chromium (as yet) forms an oxofluoride in the lower of these oxidation states.

All the known hexahalides can be prepared by the direct action of the halogen on the metal and all are readily hydrolysed. The yellow CrF_6, however, requires a temperature of 400°C and a pressure of 200–300 atms for its formation, and reduction of the pressure causes it to dissociate into CrF_5 and F_2 even at temperatures as low as -100°C. The monomeric and octahedral hexafluorides MoF_6 and WF_6 are colourless liquids and the former is strongly oxidizing. Only tungsten is known with certainty to produce other hexahalides and these are the dark-blue solids WCl_6 and WBr_6, the latter in particular being susceptible to reduction.

Of the pentahalides, chromium again forms only the fluoride which is a strongly oxidizing, bright red, volatile solid prepared from the elements using less severe conditions than for CrF_6. MoF_5 and WF_5 can be prepared by reduction of the hexahalides with the metal but the latter disproportionates into WF_6 and WF_4 if heated above about 80°C. They are yellow volatile solids, isostructural with the tetrameric $(NbF_5)_4$ and $(TaF_5)_4$ (Fig. 22.4b, p. 990). Similarity with Group 5 is again evident in the pentachlorides of Mo and W, $MoCl_5$ being the most extensively studied of the pentahalides. These, respectively, black and dark-green solids are obtained by direct reaction of the elements under carefully controlled conditions and have the same dimeric structure as their Nb and Ta analogues (Fig. 22.4c, p. 990). WBr_5 can be prepared similarly but is not yet well characterized.

The tetrahalides are scarcely more numerous or familiar than the hexa- and penta-halides, the 3 tetraiodides together with $CrBr_4$ and $CrCl_4$ being either of uncertain existence or occurring only at high temperatures in the gaseous phase. The most stable representatives are the fluorides: CrF_4 is an unreactive solid; MoF_4 is an involatile green solid; and WF_4 begins to decompose only when heated above 800°. $MoCl_4$ exists in two crystalline modifications: α-$MoCl_4$ is probably made up of linear chains of edge-shared octahedra, whereas β-$MoCl_4$ has a unique structure composed of hexameric cyclic molecules $(MoCl_4)_6$ generated by edge-shared $\{MoCl_6\}$ octahedra with Mo–Cl_t 220 pm, Mo–Cl_μ 243 and 251 pm and Mo$\cdots$Mo 367 pm. General preparative methods include controlled reaction of the elements, reduction of higher halides, and halogenation of lower halides. The tetrahalides of Mo and W are readily oxidized and hydrolysed and produce some adducts of the form MX_4L_2.

The trihalides show major differences between the 3 metals. All 4 of the chromium trihalides are known, this being much the most stable oxidation state for chromium; they can be prepared by reacting the halogen and the metal, though CrF_3 is better obtained from HF and $CrCl_3$ at 500°C. The fluoride is green, the chloride red-violet, and the bromide and iodide dark green to black. In all cases layer structures lead to octahedral coordination of the metal. $CrCl_3$ consists of a ccp lattice of chloride ions with Cr^{III} ions occupying two-thirds of the octahedral sites of alternate layers. The other alternate layers of octahedral sites are empty and, without the cohesive effect of the cations, easy cleavage in these planes is possible and this accounts for the flaky appearance. Stable, hydrated forms of CrX_3 can also be readily obtained from aqueous solutions, and $CrCl_3.6H_2O$ provides a well-known example of hydrate isomerism, mentioned on p. 920. In view of this clear ability of Cr^{III} to aquate it may seem surprising that anhydrous $CrCl_3$ is quite insoluble in pure water (though it dissolves rapidly on the addition of even a trace of a reducing agent). It appears that the reducing agent produces at least some Cr^{II} ions. Solubilization then follows as a result of electron transfer from $[Cr(aq)]^{2+}$ in solution via a chloride bridge to Cr^{III} in the solid, which leaves $[Cr(aq)]^{3+}$ in solution and Cr^{II} in the solid. The latter is kinetically far more labile than Cr^{III} and can readily leave the solid and aquate, so starting the cycle again and rapidly dissolving the solid.

The Mo trihalides are obtained by reducing a higher halide with the metal (except for the triiodide which, being the highest stable iodide, is best prepared directly). They are insoluble in water and generally inert. $MoCl_3$ is structurally similar to $CrCl_3$ but is distorted so that pairs of Mo atoms lie only 276 pm apart which, in view of the low and temperature-dependent magnetic moment, is evidently close enough to permit appreciable Mo–Mo interaction. Electrolytic reduction of a solution of MoO_3 in aqueous HCl changes the colour to green, then brown, and finally red, when complexes of the octahedral $[MoCl_6]^{3-}$, $[MoCl_5(H_2O)]^{2-}$ and $[Mo_2Cl_9]^{3-}$ can be isolated using suitable cations. The diversity of the coordination chemistry of molybdenum(III) is, however, in no way comparable to that of chromium(III).

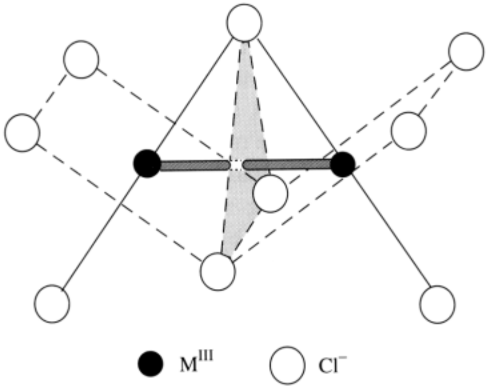

Figure 23.4 Structure of $[M_2Cl_9]^{3-}$ showing the M–M bond through the shared face of two inclined MCl_6 octahedra. See also Fig. 7.9, p. 240, for an alternative representation of the confacial bioctahedral structure.

By contrast, the tungsten trihalides (the trifluoride is not known) are "cluster" compounds similar to those of Nb and Ta. The trichloride and tribromide are prepared by halogenation of the dihalides. The structure of the former is based on the $[M_6X_{12}]^{n+}$ cluster (Fig. 22.6) with a further 6 Cl atoms situated above the apical W atoms. WBr_3, on the other hand, has a structure based on the $[M_6X_8]^{n+}$ cluster (see Fig. 23.5), but as it is formed by only a 2-electron oxidation of $[W_6Br_8]^{4+}$ it does not contain tungsten(III) and is best formulated as $[W_6Br_8]^{6+}$ $(Br_4{}^{2-})(Br^-)_2$, where $(Br_4{}^{2-})$ represents a bridging polybromide group. Electrolytic reduction of WO_3 in aqueous HCl fails to produce the mononuclear complexes obtained with molybdenum, but forms the green $[W_2Cl_9]^{3-}$ ion. This and its Cr and Mo analogues provide an interesting reflection of the increasing strength of M–M bonding in the order $Cr^{III} < Mo^{III} < W^{III}$. The structure consists of 2 MCl_6 octahedra sharing a common face (Fig. 23.4) which allows the possibility of direct M–M bonding. In the Cr ion the Cr atoms are 312 pm apart, being actually displaced in their CrO_6 octahedra away from each other. The magnetic moment of $[Cr_2Cl_9]^{3-}$ is normal for a metal ion with 3 unpaired electrons and indicates the absence of Cr–Cr bonding. In $[Mo_2Cl_9]^{3-}$ the Mo atoms are 267 pm apart and the magnetic moment is low and temperature dependent, indicating appreciable Mo–Mo bonding. Finally, $[W_2Cl_9]^{3-}$ is diamagnetic: the metal atoms are displaced towards each other, being only 242 pm apart (compared to 274 pm in the metal itself), consistent with a W–W triple bond (p. 1030).

Anhydrous chromium dihalides are conveniently prepared by reduction of the trihalides with H_2 at 300–500°C, or by the action of HX (or I_2 for the diiodide) on the metal at temperatures of the order of 1000°C. They are all deliquescent and the hydrates can be obtained by reduction of the trihalides using pure chromium metal and aqueous HX. All have distorted octahedral structures as anticipated for a metal ion with the d^4 configuration which is particularly susceptible to Jahn–Teller distortion[†]. This is typified by CrF_2, which adopts a distorted rutile structure in which

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[†] A theorem proposed by H. A. Jahn and E. Teller (1937) states that a molecule in a degenerate electronic state will be unstable and will undergo a geometrical distortion that lowers its symmetry and splits the degenerate state. *Jahn–Teller* distortions are particularly important and well-documented for octahedrally coordinated metal ions whose e_g (i.e. axial) orbitals are unequally occupied: $t_{2g}^3e_g^1$ (high-spin Cr^{II} and Mn^{III}), $t_{2g}^6e_g^1$ (low-spin Co^{II} and Ni^{III}) and $t_{2g}^6e_g^3$ (Cu^{II}). They are generally manifested by an elongation of the bonds on one axis, and may be ascribed to the d_{z^2} orbital containing 1

4 fluoride ions are 200 pm from the chromium atom while the remaining 2 are 243 pm away. The strongly reducing properties of chromium(II) halides contrast, at first sight surprisingly, with the redox stability of the molybdenum(II) halides. Even the tungsten(II) halides, which admittedly are also strong reducing agents (being oxidized to their trihalides), may by their very existence be thought to depart from the expected trend.

Of the various preparative methods available for the dihalides of Mo and W, thermal decomposition or reduction of higher halides is the most general. The reason for their enhanced stability lies in the prevalence of metal–atom clusters, stabilized by M–M bonding. All 6 of these dihalides (Mo and W do not form difluorides) are isomorphous,(26) with a structure based on the $[M_6X_8]^{4+}$ unit briefly mentioned above for WBr_3 (see also Chevrel phases p. 1018). It can be seen (Fig. 23.5) that in this cluster each metal atom has a free coordination position. In the dihalides themselves, these positions are occupied by $6X^-$ ions, 4 of them bridging to other $[M_6X_8]^{4+}$ units, giving the composition $[M_6X_8]X_2X_{4/2} = MX_2$. Although precise details of the bonding scheme are not settled it is clear that in each cluster the 6 metals contribute $6 \times 6 = 36$ valence electrons of which 4 are transferred to the counter anions, so producing the net charge, and 8 are used in bonding to the 8 chlorines of the cluster. Twenty-four electrons remain which can provide M–M bonds along each of the 12 edges of the octahedron of metal atoms accounting for the observed diamagnetism. Unlike the M_6 clusters of the "electron-poor" elements of groups 3, 4 and 5 (pp. 950, 965 and 992) the incorporation of interstitial atoms offers no additional stability and is not observed.

The six outer halide ions are readily replaced, leaving the $[M_6X_8]^{4+}$ core intact throughout a variety of substitution reactions. The eight core halogens are far less labile, but prolonged heating (16 h at 500C) of $[Mo_6Cl_8Br_4]^{2-}$ for instance, has been shown(27) by ^{19}F nmr spectroscopy to yield a mixture containing all 22 possible isomers of the $[Mo_6Br_nCl_{8-n}]^{4+}$ cluster. Oxidation of WBr_2 with Br_2 yields brownish-black crystals of the molecular cluster compound W_6Br_{14} in which a non-bridging Br completes the coordination sphere of each metal atom in the $\{W_6Br_8\}$ core.(27a)

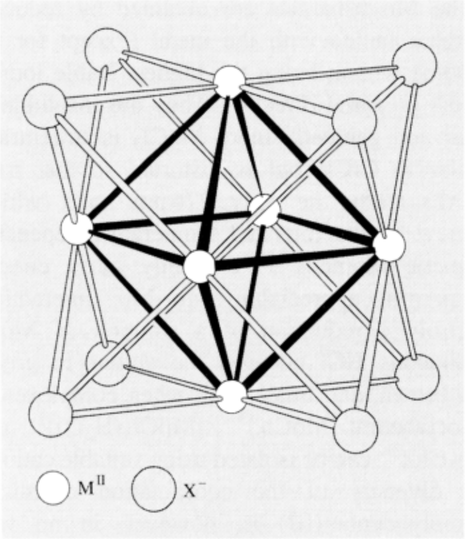

Figure 23.5 $[M_6X_8]^{4+}$ clusters with X bridges over each face of the octahedron of metal ions.

The oxohalides of all three elements (Table 23.5) are very susceptible to hydrolysis and their oxidizing properties decrease in the order Cr > Mo > W. They are yellow to red liquids or volatile solids; probably the best known is the deep-red liquid, chromyl chloride, CrO_2Cl_2. It is most commonly encountered as the distillate in qualitative tests for chromium or chloride and can be obtained by heating a dichromate and chloride in conc H_2SO_4; it is an extremely aggressive oxidizing agent. The Mo and W oxohalides

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electron more than the $d_{x^2-y^2}$, so preventing ligands on the z-axis approaching as close as those on the x and y

[26] An amorphous form of $MoCl_2$ is also known, whose spectroscopic properties suggest the presence of tetranuclear units; see W. W. BEERS and R. E. MCCARLEY, *Inorg. Chem.* **24**, 472–5 (1985).

[27] P. BRÜCKNER, G. PETERS and W. PREETZ, *Z. anorg. allg. Chem.* **619**, 551–8 (1993).

[27a] J. SASSMANSHAUSEN and H.-G. VON SCHNERING, *Z. anorg. allg. Chem.* **620**, 1312–20 (1994).

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