MOLYBDENUM COMPOUNDS

1. Introduction

The chemistry of molybdenum, Mo, is among the most diverse of the transition elements. In its compounds, molybdenum exhibits coordination numbers from four to eight, oxidation numbers from −II to VI, and numerous states of aggregation (nuclearity). Molybdenum forms binary compounds with many nonmetallic elements, and a number of these, namely the halides, oxides, sulfides, carbides, nitrides, and silicides, are of technological interest. In contrast to its congeners, chromium and tungsten, molybdenum is found naturally in the form of its sulfide molybdenite [1309-56-4], MoS_2. Similarly, in the enzymes in which molybdenum is found, the active site Mo is generally in a high sulfur environment. This thiophilicity of Mo also plays a role in a number of its technological uses.

In biology molybdenum is a component of fertilizer and nutrient formulations (see FERTILIZERS; MINERAL NUTRIENTS). Over 20 enzymes have been found to have molybdenum as a component of their active sites. The roles of molybdenum in nitrogen fixation (qv) and nitrate reduction establish this metal as a key element of a biological nitrogen cycle. In technology various solid and soluble molybdenum compounds have found use in lubrication (see LUBRICATION AND

LUBRICANTS); hydrodesulfurization, hydrogenation, and oxidation catalysis; anticorrosion and coatings (qv); flame and smoke retardancy (see FLAME RETARDANTS); and various forms of pigmentation.

The most important molybdenum oxidation states are VI, V, IV, III, II, and 0. The higher oxidation states are usually characterized by molybdenum binding to electronegative atoms, such as oxygen and the halogens. The lowest oxidation states are largely in the realm of organometallic chemistry, wherein the Mo is bound directly to the carbon atom of carbon monoxide (qv), to organic phosphines, and/or to a variety of unsaturated carbonaceous ligands.

2. Molybdenum(VI)

The chemistry of hexavalent molybdenum is very prominent in both biological and industrial systems. Oxygen coordination of molybdenum is most common in this oxidation state (1–3). Molybdenum trioxide [1313-27-5], MoO_3, is a key intermediate in the technological utilization of molybdenum (Fig. 1). In the refining of Mo, molybdenite ore, MoS_2, which contains tetravalent Mo, is first roasted in air to form impure MoO_3. The MoO_3 is then reduced to the metal with hydrogen from 500–1150°C. The trioxide melts at 795°C but sublimes significantly below that temperature. The structure of MoO_3 is a complex, layered arrangement in which each of the six-coordinate Mo(VI) atoms shares the face of an octahedron with another Mo(VI) atom. The MoO_3 reacts with base to produce a variety of molybdate salts, the simplest of which are of the form M_2MoO_4. Sodium molybdate [7631-95-0] is an example. These water-soluble salts serve as the starting materials for the synthesis of a wide variety of compounds.

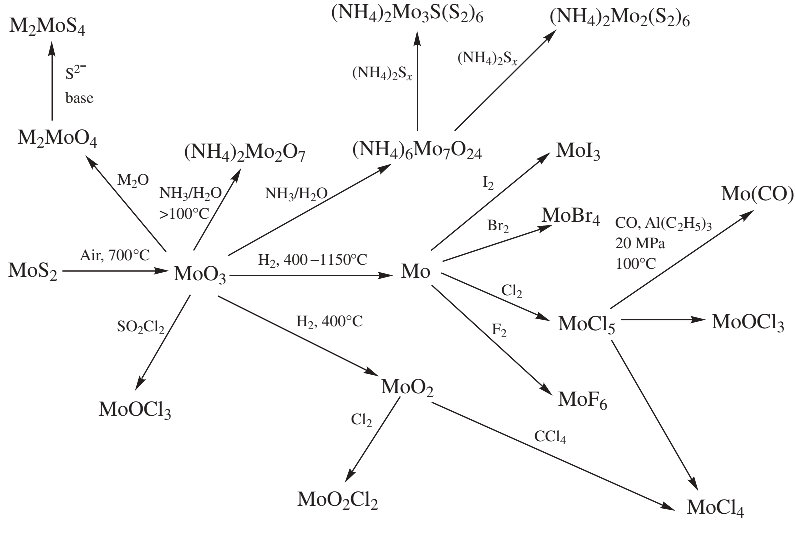
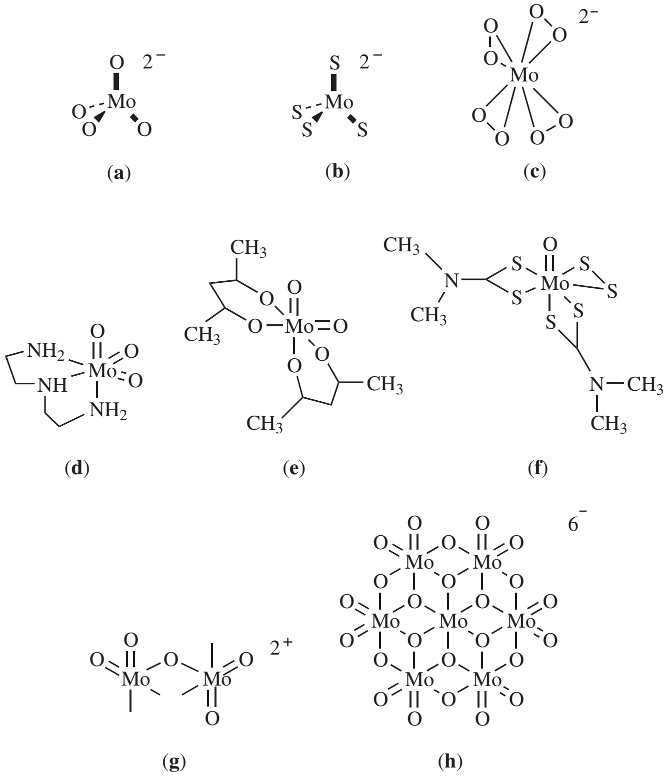


Fig. 1. Scheme for the preparation of technologically important compounds of molybdenum, where M=Li, Na, K, Rb, Cs, and NH_4. To convert MPa to psi, multiply by 145.



(a) (b) (c) (d) (e) (f) (g) (h)

Fig. 2. Representative structures for compounds of molybdenum(VI): (**a**) molybdate(VI), MoO_4^{2-}; (**b**) tetrathiomolybdate(VI), MoS_4^{2-}; (**c**) tetrakis(peroxo)molybdate(VI), $Mo(O_2)_4^{2-}$; (**d**) *cis*-trioxodiethylenetriaminemolybdenum(VI), (MoO_3(dien)), $C_4H_{13}N_3MoO_3$; (**e**) *cis*-bis-(acetylacetonato)dioxomolybdenum(VI), $MoO_2(C_5H_7O_2)_2$; (**f**) bis(dialkyldithiocarbamato)disulfidooxomolybdenum(VI), $MoO(S_2)(S_2CNR_2)_2$ (R = alkyl); (**g**) the dinuclear core structure for $Mo_2O^2+_5$ complexes; (**h**) heptamolybdate(VI), $Mo_7O_{24}^{6-}$.

The molybdate ion, $MoO_4{}^{2-}$, is a d^0, four-coordinate, tetrahedral anion. The structure (Fig. 2**a**) resembles that of other Group 6 (VIB) and Group 16 (VIA) ions, such as $CrO_4{}^{2-}$, $WO_4{}^{2-}$, $SO_4{}^{2-}$, and $SeO_4{}^{2-}$. The discrete dimolybdate ion [19282–23-6], $Mo_2O_7{}^{2-}$, exists in $N(C_4H_9)_4{}^+$ salts (see QUATERNARY AMMONIUM COMPOUNDS). Diammonium dimolybdate [27546-07-2], $(NH_4)_2Mo_2O_7$, available commercially as the tetrahydrate and prepared from MoO_3 and excess NH_3 in aqueous solution at 100°C, has an infinite chain structure based on MoO_6 octahedra. In aqueous solution the behavior of Mo(VI) is extremely pH-dependent (4). Above pH7 molybdenum(VI) occurs as the tetrahedral oxyanion $MoO_4{}^{2-}$, but below pH 7 a complex series of concentration-, temperature-, and pH-dependent equilibria exist. The best known of these equilibria lead to the formation of the heptamolybdate, $Mo_7O_{24}{}^{6-}$ (Fig. 2**h**), and octamolybdate, $Mo_8O_{26}{}^{4-}$, ions. Even larger aggregates may be present in solution and in salts. Both $Mo_{12}O_{37}{}^{2-}$ and $Mo_{36}O_{112}(H_2O)_{16}{}^{8-}$ have been isolated and crystallographically characterized (4). At sufficiently low pH in very dilute solutions, cationic forms such as $MoO_2{}^{2+}$ and MoO^{4+} are present.

The polymolybdate and heteropolymolybdate ions constitute a broad and commercially significant class. In these ions molybdenum is six-coordinate with octahedral geometry (4–8). Oxo (O^{2-}) groups bridge the Mo atoms and serve as terminal ligands on some of the Mo ions. When other atoms are present during the acidification of molybdate solutions, a series of heteropolymolybdates is formed. For example, cations such as Cr^{3+} or Co^{2+}, or anions such as PO_4^{3-} or AsO_4^{3-}, form the heteropoly anions $H_6CrMo_6O_{24}^{3-}$, $H_6CoMo_6O_{24}^{4-}$, $PMo_{12}O_{40}^{3-}$, and $AsMo_{12}O_{40}^{3-}$, respectively. The yellow ion, $PMo_{12}O_{40}^{3-}$, is analytically useful, being formed in the molybdenum test for phosphate ion. Poly- and heteropolymolybdate ions are used in the precipitation of dyes. The protonated forms of the ions are strongly acidic and many poly- and heteropolymolybdate compounds have catalytic activity that is attributable to their acid–base or redox properties.

The reduction of molybdate salts in acidic solutions leads to the formation of the molybdenum blues (9). Reductants include dithionite, stannous ion, hydrazine, and ascorbate. The molybdenum blues are mixed-valence compounds where the blue color presumably arises from the intervalence $Mo(V) \longrightarrow Mo(VI)$ electronic transition. These can be viewed as intermediate members of the class of mixed oxy hydroxides the end members of which are $Mo(VI)O_3$ and $Mo(V)O(OH)_3$ [27845-91-6]. MoO_3 and Mo(VI) solutions have been used as effective detectors of reductants because formation of the blue color can be monitored spectrophotometrically. The nonprotonic oxides of average oxidation state between V and VI are the molybdenum bronzes, known for their metallic luster and used in the formulation of bronze paints (see PAINT).

Reaction of the molybdate ion with organic ligands leads to a wide variety of (mostly) mononuclear Mo(VI) complexes (10,11). The largest number of these compounds contain the *cis*-MoO_2^{2+} core and four additional ligands, or one or two chelates, fill the remaining octahedral coordination sites. Examples, in addition to $MoO_2(acac)_2$ (Fig. 2**e**), are $(N(CH_3)_4)_2MoO_2(NCS)_4$, $MoO_2(dtc)_2$, and $MoO_2(CH_3)_2(bipy)$, where dtc = dialkyl dithiocarbamate and bipy = 2,2′-bipyridine. Complexes containing the MoO core, eg, $MoOS_2(dtc)_2$ (Fig. 2**f**), $MoOCl_2(dtc)_2$, $[MoO(dtc)_3]BF_4$, and $MoOCl_4$; the *cis*-MoO_3 core, eg, $MoO_3(dien)$ (Fig. 2**d**); or the dinuclear $Mo_2O_5^{2+}$ core (Fig. 2**g**), eg, $(NH_4)_2[Mo_2O_5(cat)_2]$, where cat = catecholate, are also known. The compounds MoO_2Cl_2 [13637-68-8], formed by the reaction of MoO_2 and Cl_2, and $MoO_2(acac)_2$ serve as useful starting materials for the synthesis of new Mo(VI) compounds.

Peroxo, O_2^{2-}, molybdate complexes are also well established in the chemistry of Mo(VI) (12). The prototypical complex is $Mo(O_2)_4^{2-}$ (Fig. 2**c**). The peroxo ligands are side-on coordinated to Mo to form a formally eight-coordinate structure, although the centroids of the O–O bonds form a tetrahedral array about Mo. Numerous complexes are known in which $MoO(O_2)^{2+}$ or $MoO(O_2)_2$ cores are present and additional ligands complete six- or seven-coordinate structures. One example is $K_2[MoO(O_2)_2C_2O_4]$. These complexes are of great interest because of their ability to transfer oxygen atoms to olefins, ie, act as peroxidation reagents, and to other organic molecules.

The tetrathiomolybdate ion [16330-92–0] (Fig. 2**b**), which has received great attention in the late 20th century, was first reported by Berzelius in

1838. The simple preparation from molybdate in basic aqueous solution occurs in high yield according to:

$$MoO_4^{2-} + 4\,S^{2-} \longrightarrow MoS_4^{2-} + 4\,O^{2-}$$

The red tetrathiomolybdate ion appears to be a principal participant in the biological Cu–Mo antagonism and is reactive toward other transition-metal ions to produce a wide variety of heteronuclear transition-metal sulfide complexes and clusters (13,14). For example, tetrathiomolybdate serves as a bidentate ligand for Co, forming $Co(MoS_4)_2{}^{3-}$. Tetrathiomolybdates and their mixed metal complexes are of interest as catalyst precursors for the hydrotreating of petroleum (qv) (15) and the hydroliquefaction of coal (see COAL CONVERSION PROCESSES) (16). The intermediate forms $MoOS_3{}^{2-}$, $MoO_2S_2{}^{2-}$, and MoO_3S^{2-} have also been prepared (17).

The tris(dithiolene) complexes of Mo can be formed by reaction of the corresponding dithiol and molybdate in acid solution. The intense green compound, $Mo(tdt)_3$, where tdt = toluene-3,4-dithiolate, possesses a trigonal prismatic six-coordination about Mo and has found great use in the analytical determination of molybdenum.

3. Molybdenum(V)

Molybdenum(V) compounds generally occur as mononuclear or dinuclear species. Molybdenum pentachloride [10241-05-1], $MoCl_5$, formed by combination of the elements, serves as a useful and reactive starting material (Fig. 1). $MoCl_5$ has a dinuclear structure (Fig. 3) in the solid state but is mononuclear in the gas phase. In solution or in the solid state the compound, actually Mo_2Cl_{10} (Fig. 3**a**), is readily hydrolyzed in air to form $MoOCl_3$ [13814-74-9]. The compound $MoOCl_3(thf)$, where thf is tetrahydrofuran, is also known.

Mononuclear Mo(V) compounds have a $4d^1$ electronic configuration, and the single unpaired electron gives rise to distinct magnetic and electron paramagnetic resonance (epr) signatures (see MAGNETIC SPIN RESONANCE) (10,18). The g and A values of the epr spectra are characteristic of the ligand donor set and the coordination geometry. This technique has been valuable in detecting the presence of the Mo(V) oxidation state in catalysts and enzymes. Mono oxo molybdenum(V) complexes such as $(NH_4)_2MoOCl_5$ are quite common (see also Fig. 3**b**).

Virtually all Mo(V) dinuclear complexes are diamagnetic and contain bridges between the two Mo atoms. The bridge can be a linear Mo–O–Mo linkage as in the $Mo_2O_3(NCS)_8{}^{4-}$ complex (Fig. 3**g**), which illustrates the $Mo_2O_3{}^{4+}$ core structure. Compounds such as $Mo_2O_3(acac)_4$ and $Mo_2O_3(dtc)_4$ also exist. More commonly, a double bridge is found in which the bridging atoms are oxo or sulfido ligands and a single molybdenum–molybdenum bond is also present. Here the Mo coordination sphere can be completed by a variety of nonoxo and nonsulfido ligands. The complexes $Mo_2O_4(NCS)_6{}^{4-}$ (Fig. 3**c**) and $Mo_2S_4(dtc)_2$ (Fig. 3**f**) present examples of the $Mo_2O_4{}^{2+}$ and $Mo_2S_4{}^{2+}$ core structures, respectively. Mixtures of $Mo_2S_4(dtc)_2$, $Mo_2O_4(dtc)_2$, and intermediate species with $Mo_2O_xS_{4-x}{}^{2+}$ cores and related dithiophosphate complexes are useful as additives in lubricant formulations.

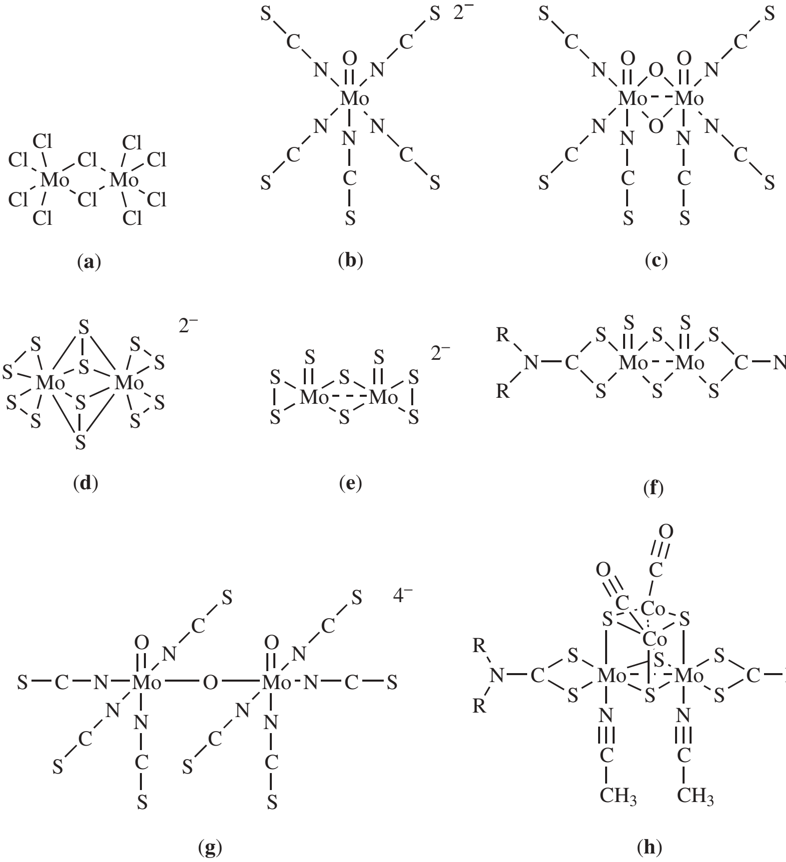


Fig. 3. Representive structures for compounds of molybdenum(V): (**a**) dimolybdenum dodecachloride [26814-39-1], Mo_2Cl_{10}, the dimer of molybdenum pentachloride; (**b**) pentakis(thiocyanato)oxomolybdenum(V), $MoO(NCS)_5^{2-}$; (**c**) $Mo_2O_4(NCS)_6^{4-}$; (**d**) $Mo_2(S_2)_6^{2-}$; (**e**) $Mo_2S_8^{2-}$; (**f**) $Mo_2S_4(S_2CNR_2)_2$; (**g**) $Mo_2O_3(NCS)_8^{4-}$; (**h**) $Mo_2Co_2S_4(S_2CNR_2)_2(CO)_2$-$(CH_3CN)_2$.

In many of the dinuclear complexes the Mo atom is five-coordinate, not counting the metal–metal bond. In a few examples such as in Mo_2O_4 $(Lcysteine)_2{}^{2-}$, the molybdenum is six-coordinate, not including the metal–metal bond. Also known are $Mo_2O_4(dtc)_2$ and $Mo_2O_2S_2(dtc)_2$. In general, the position trans to the terminal Mo oxo (or Mo sulfido) ligand is either empty or the ligand binds only weakly. If present, the trans ligand is kinetically labile, leading to facile substitution reactions.

Interestingly, the $Mo_2S_4{}^{2+}$ (Fig. 3**f**) core structure can be viewed as occupying six of the eight vertices of a distorted cube. Reaction of the dinuclear complexes having the $Mo_2S_4{}^{2+}$ core with appropriate metal ions leads to the planned assembly of $M_2Mo_2S_4$ thiocubane structures (19,20). When M=Co (Fig. 3**h**) the compounds are potential precursors for hydrodesulfurization catalysts (15).

The dinuclear ion $Mo_2(S_2)_6{}^{2-}$ (Fig. 3**d**) prepared from the reaction of molybdate and polysulfide solution (13) is a useful starting material for the preparation of dinuclear sulfur complexes. These disulfide ligands are reactive toward replacement or reduction to give complexes containing the $Mo_2S_4{}^{2+}$ core (Fig. 3**f**).

4. Molybdenum(IV)

Representative compounds for the +4 oxidation state are shown in Figure 4. The violet tetravalent molybdenum dioxide [18868-43-4], MoO_2, is formed by the reduction of MoO_3 with H_2 at temperatures below which Mo metal is formed or MoO_3 is volatile (ca 450°C). $MoCl_4$ [13320-71-3] is formed upon treatment of MoO_2 at 250°C with CCl_4 (see Fig. 1).

The most important compound of Mo(IV) is molybdenum disulfide [1317-33-5], MoS_2 (21). The layered structure of MoS_2 is reflected in the flat plate-like hexagonal gray-black crystallites found in natural and synthetic samples. The structure consists of pairs of close-packed layers of sulfur which are eclipsed with respect to each other. The close-packed sulfur surfaces are naturally hydrophobic, which facilitates the extraction of MoS_2 ore by flotation.

In the structure of MoS_2 molybdenum atoms occupy trigonal prismatic holes between the eclipsed sulfur layers with every other hole occupied. The molybdenum is thereby coordinated to six sulfur atoms from a trigonal prism the sides of which are nearly square. The commercial importance of MoS_2 in

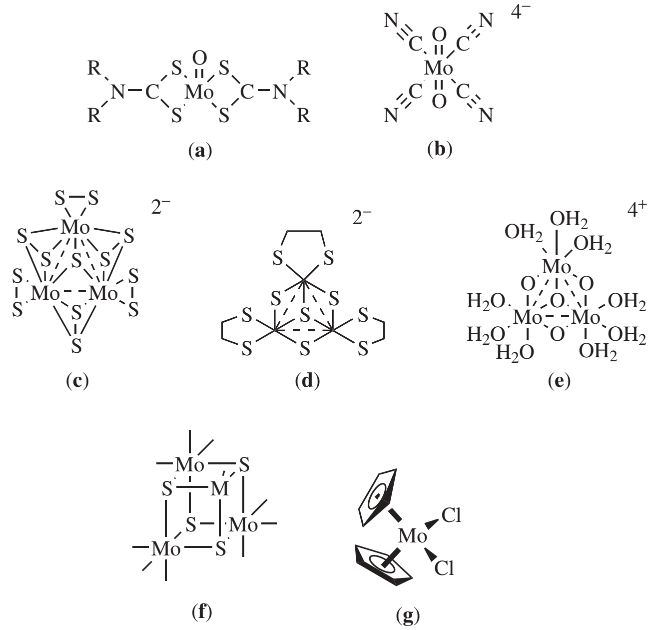


Fig. 4. Representative structures for compounds of molybdenum(IV): (**a**) bis(dialkyldithiocarbamato)oxomolybdenum(IV), $MoO(S_2CNR_2)_2$, where R = alkyl; (**b**) *trans*tetracyanodioxomolybdenum(IV), $MoO_2(CN)_4^{4-}$; (**c**) $Mo_3S_{13}^{2-}$; (**d**) $Mo_3S_4(SCH_2CH_2)_3^{2-}$; (**e**) $Mo_3O_4(H_2O)^4{+}_9$; (**f**) the $Mo_3M'S_4$ thiocubane core structure; (**g**) bis(cyclopentadienyl)-dichloromolybdenum(IV), Cp_2MoCl_2, where Cp = cyclopentadienyl.

lubrication and catalysis is a direct reflection of its solid-state structure. Molybdenum diselenide [12078-18-3], $MoSe_2$, and molybdenum ditelluride, $MoTe_2$, share the same basic structure but are not as important technologically. All the molybdenum dichalcogenides are semiconductors and have interesting photochemical, electrochemical, and photovoltaic properties (22).

The similarity of MoS_2 to graphite has been noted. Like elemental carbon, which has been found to form nanotubular structures, MoS_2 has also been found to form nested structures upon exposure to the electron beam in an electron microscope (23). Moreover, MoS_2 displays a variety of intercalation reactions typical of layered materials. Single-layer MoS_2 has been successfully prepared and manipulated (22).

The well-studied eight-coordinate octacyanide ion, $Mo(CN)_8{}^{4-}$, prepared by treatment of the oxo thiocyanate complexes of Mo(V) with KCN, has a reversible one-electron redox relationship with the Mo(V) species $Mo(CN)_8{}^{3-}$. Photolysis of $Mo(CN)_8{}^{4-}$ yields $MoO_2(CN)_4{}^{4-}$ (Fig. 4**b**) which has a *trans*-dioxo configuration. The principal type of oxo complex of molybdenum(IV) contains a single oxo ligand and has a distorted octahedral or tetragonal pyramidal, five-coordinate structure. One example is $MoO(S_2CNR_2)_2$ (Fig. 4**a**). The strong *trans*-activating effect of the oxo ligand causes the position trans to Mo–O (terminal bond) to be weakly binding and kinetically labile or empty.

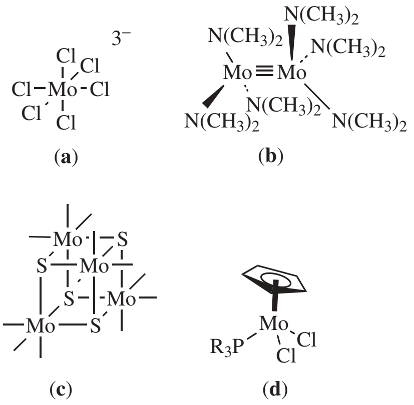
For molybdenum(IV), trinuclear species are common and often contain $Mo_3O_4{}^{4+}$ (Fig. 4**e**), $Mo_3S_4{}^{4+}$ (Fig. 4**d**), or $Mo_3S_7{}^{4+}$ (Fig. 4**c**) core structures (24). The ion $Mo_3S_{13}{}^{2-}$ prepared from the reaction of molybdate with polysulfide solutions (13) serves as a useful starting material for the formation of trinuclear sulfide bridged clusters which have threefold symmetric structures. The core structures for the $Mo_3O_4{}^{4+}$ (Fig. 4**e**) and $Mo_3S_4{}^{4+}$ (Fig. 4**d**) compounds (or mixed oxo–sulfido analogues) can be viewed as containing seven of the eight vertices of a distorted cube. Indeed, the sulfido structures readily react with metal ions to form complete "thiocubane" structures such as that shown in Figure 4**f** (25). The trinuclear clusters serve as precursors to and molecular analogues of MoS_2 (26).

Other molybdenum(IV) compounds include $Mo(NR_2)_4$, $Mo(OR)_4$, $MoCl_4(NC CH_3)_2$, $(NH_4)_2[MoCl_6]$, $Mo(S\text{-}t\text{-}C_4H_9)_4$, $Mo(dtc)_4$, $(NH_4)_2[MoS(S_2)_6]$, $[(C_6H_5)_4]_2 [MoS(S_4)_2]$, MoO(tpp), and MoO(pcn), where tpp = tetraphenylporphyrin and pcn = phthalocyanin.

5. Molybdenum(III)

Molybdenum(III) complexes include the molybdenum trihalides. Molybdenum trichoride [13478-18-7], trifluoride [20193-58-2], tribromide [13446-57-6], and triiodide [14055-75-5] are all known. The oxide dimolybdenum trioxide [1313-29-7], Mo_2O_3, and the seldom-studied sulfide analogue [12033-33-9], Mo_2S_3, are formally trivalent.

Molecular examples of trivalent molybdenum are known in mononuclear, dinuclear, and tetranuclear complexes, as illustrated in Figure 5. The hexachloride ion, $MoCl_6{}^{3-}$ (Fig. 5**a**) is generated by the electrolysis of Mo(VI) in concentrated HCl. Hydrolysis of $MoCl_6{}^{3-}$ in acid gives the hexaaquamolybdenum(III)



(a) (b) (c) (d)

Fig. 5. Representative structures for compounds of molybdenum(III): (**a**) hexacholoromolybdenum(III) ion, $MoCl_6^{3-}$; (**b**) hexakis(dimethylamido)dimolybdenum(III), $Mo_2(N(CH_3)_2)_6$; (**c**) the Mo_4S_4 thiocubane core structure; (**d**) dichlorocyclopentadienyl trialkylphosphinedichloromolybdenum(III), $CpMo(PR_3)Cl_2$, where Cp = cyclopentadienyl and R = alkyl.

ion, $Mo(H_2O)_6^{3+}$, which is obtainable in solution of poorly coordinating acids, such as triflic acid (17). Several molybdenum(III) organometallic compounds are known. These contain a single cyclopentadienyl ligand (Cp) attached to Mo (Fig. 5**d**) (27).

Dinuclear structures are known for molybdenum(III) in a series of air and moisture sensitive compounds containing multiple Mo–Mo bonds. Examples include $Mo_2(N(CH_3)_2)_6$ (Fig. 5**b**) and $Mo_2(CH_2Si(CH_3)_3)_6$ in which there is a strong Mo–Mo bond, presumably of triple-bond character (28).

The tetranuclear Mo_4S_4 (Fig. 5**c**) core structures are known with a variety of ligands including aqua, ammonia, cyanido, and a variety of cyclopentadienyl and chelating 1,1-dithiolate ligands (25). The core structures are of the thiocubane form and readily undergo redox reactions to form a variety of mixed valence species, eg, $Mo_4S_4(dtc)_6$, a Mo(III)/Mo(V) complex. Analogues containing the Mo_4O_4 core have been formed in solid-state structures of molybdenum oxide phosphate phases (29).

6. Molybdenum(II)

Divalent molybdenum compounds occur in mononuclear, dinuclear, and hexanuclear forms. Selected examples are shown in Figure 6. The mononuclear compounds are mostly in the realm of organometallic chemistry (30–32). Seven-coordinate complexes are common and include $MoX_2(CO)_3(PR_3)_2$, where X = Cl, Br, and I, and R = alkyl; $MoCl_2(P(CH_3)_3)_4$, heptakis(isonitrile) complexes of the form $Mo(CNR)_7^{2+}$ (Fig. 6**d**), and their chloro-substituted derivatives, eg, $Mo(CNR)_6Cl^+$. The latter undergo reductive coupling to form C–C bonds in the molybdenum coordination sphere (33).

The dinuclear compounds of molybdenum(II) have strong, quadruple, molybdenum–molybdenum bonds and eclipsed structures, such as those of $Mo_2Cl_8^{4-}$ (Fig. 6**a**) and $Mo_2(O_2CCH_3)_4$ (Fig. 6**b**). These quadruply bonded

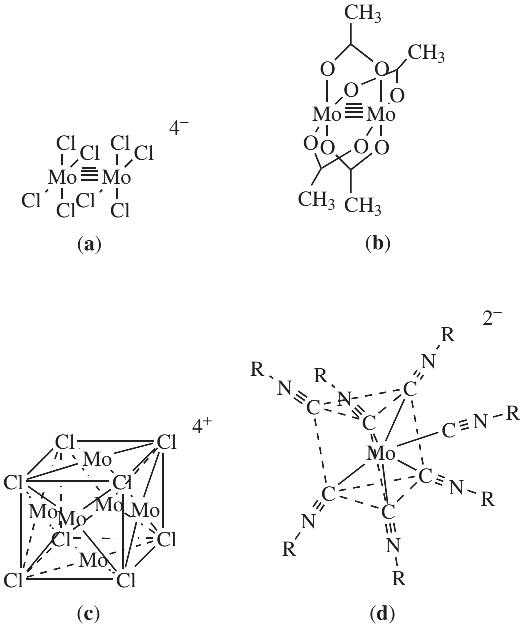


Fig. 6. Representive structures for compounds of molybdenum(II): (**a**) octachlorodimolybdenum(II) ion, $Mo_2Cl_8^{4-}$; (**b**) tetrakis(acetato)dimolybdenum(II), $Mo_2(O_2CCH_3)_4$; (**c**) the $Mo_6Cl^4{+}_8$ core; (**d**) heptakis(isocyanide)molybdenum(II), $Mo(CNR)^2{+}_7$, where R = alkyl.

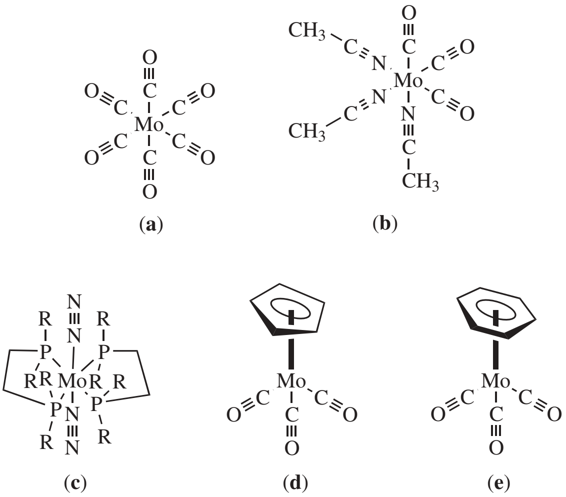
complexes have been intensely studied from the point of view of their structures, electronic structures, and reactivity (34,35).

The dichloride of molybdenum(II) [13478-17-6], $MoCl_2$, contains $Mo_6Cl_8{}^{4+}$ core units (Fig. 6**c**) having chloride bridges in its solid-state structure. Similar or identical hexanuclear units are known in soluble species such as $Mo_6Cl_{14}{}^{2-}$ and other derivatives containing the $Mo_6Cl_8{}^{4+}$ core. These compounds have been under investigation because of their photochemical and photoluminescent activity (see PHOTOCHEMICAL TECHNOLOGY) (36,37). The hexanuclear clusters consist of octahedra of Mo embedded in cubes of chlorine. This structure is similar to that of solid-state Chevrel phase materials, which have cubes of sulfur in place of chlorine. The Chevrel phases have elicited great interest in light of their superconductivity and interesting magnetic properties (see MAGNETIC MATERIALS) (38). Related molecular clusters, such as $Mo_6S_8L_6$ where L is pyridine or $P(C_2H_5)_3$, have been reported (39).

Other molybdenum(II) compounds of interest include the nitric oxide complexes $Mo(NO)Cl_3$ and $Mo(NO)(dtc)_3$, *trans*-$MoH_2(dppe)_2$ where dppe = 1,2−bis(diphenylphosphino)ethane and $K_4[Mo_2(SO_4)_4]{\cdot}2H_2O$.

7. Molybdenum(0)

Molybdenum hexacarbonyl [13939-06-5] (Fig. 7**a**) is the starting material for the synthesis of most organometallic compounds of molybdenum. White crystalline



(a) (b) (c) (d) (e)

Fig. 7. Representive structures for compounds of molybdenum(0): (**a**) $Mo(CO)_6$; (**b**) tris(acetonitrile)tris(carbonyl)molybdenum(0); (**c**) bis(1,2−diphenylphosphinoethane) bis (dinitrogen) molybdenum(0), $[R_2PCH_2CH_2PR_2]_2Mo(N_2)_2$, where $R = C_6H_5$, also known as $Mo(dppe)_2(N_2)_2$, where dppe = 1, 2-diphenylphosphinoethane; (**d**) cyclopentadienyl tricarbonyl molybdenum(0) anion, $CpMo(CO)_3^-$, where Cp = cyclopentadienyl; (**e**) benzenetricarbonyl molybdenum(0), $(C_6H_6)Mo(CO)_3$.

$Mo(CO)_6$ is prepared by the reduction of $MoCl_5$ and Zn in the presence of a high pressure of carbon monoxide (see CARBONYLS). The hexacarbonyl melts at 150–151°C, but readily sublimes at lower temperatures and is soluble in nonpolar organic solvents. $Mo(CO)_6$ reacts readily in polar solvents such as acetonitrile to produce trisubstituted products such as $Mo(CO)_3(CH_3CN)_3$ (Fig. 7**b**), which serve as synthetically useful starting materials. Numerous other organometallic complexes have been prepared and structurally characterized. A few are shown in Figure 7 (31,32). A notable example is $Mo(CO)_3(PR_3)_2(H_2)$, one of the first examples of a coordinated dihydrogen complex (40). Many of the organometallic compounds of Mo display interesting organic reactivity, and some have been used as precursors for a variety of homogeneous and heterogeneous catalysts.

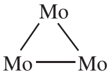
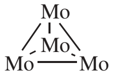
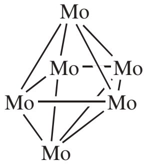
Molybdenum(0) also forms a variety of dinitrogen complexes (41), especially when there are phosphine ligands in the molybdenum coordination sphere (see Fig. 7**c**). This type of complex has been extensively studied because the coordinated dinitrogen is reduced to ammonia upon acidification.

Other molybdenum(0) compounds of interest include $MoCl_2(NO)_2$ and $MoCl_2(NO)_2$(bipy) where bipy = 2,2′-bipyridine. The compound $(C_5H_5)Mo(CO)_2NO$, similar in structure to Figure 7**d**, is also known.

8. Chemistry of Molybdenum Compounds

8.1. Metal–Metal Bonding. The degree of nuclearity exhibited as a function of the oxidation state of molybdenum is shown in Table 1. In the highest

Table 1. **Metal–Metal Bonding in Molybdenum Complexes and Clusters**

	Oxidation state				
Metal	Mo(VI)	Mo(V)	Mo(IV)	Mo(III)	Mo(II)
d-electron configuration	d^0	d^1	d^2	d^3	d^4
number of metal–metal bonds	0	1	2	3	4
formulation					
mononuclear or dinuclear	Mo	Mo—Mo	Mo═Mo	Mo≡Mo	Mo═Mo
polynuclear		Mo—Mo	 	 	
polynuclear geometry		linear	triangle	tetrahedron	octahedron

oxidation state, Mo(VI), the tendency is to form mononuclear or a wide variety of polynuclear complexes in which there are no molybdenum–molybdenum bonds. The absence of metal–metal bonding is attributable to the $4d^0$ electronic configuration of molybdenum, ie, there are no *d* electrons available for bonding. The Mo(V) complexes (Fig. 3), on the other hand, have a strong tendency to form dimers which have a single metal–metal bond. This is the result of the $4d^1$–$4d^1$ configurations of the two metal centers. The complexes in this case are usually also doubly or triply bridged by ligands such as oxide, sulfide, or halide. For Mo(IV) the $4d^2$ electronic configuration allows molybdenum to enter into two metal–metal bonds. Whereas dinuclear complexes containing a Mo–Mo double bond could be formed, a trinuclear structure in which each Mo atom is bound to two others in a triangular array is more often the observed case.

For Mo in the trivalent state, the $4d^3$ configuration leads to the possibility of three metal–metal bonds being formed per molybdenum. Some dinuclear structures in which the Mo atoms are triply bonded to each other in a relatively strong bond, generally in an unbridged complex, are known. Alternatively, each metal can achieve full binding capacity by binding to three other metals. This leads to the stabilization of a tetranuclear cluster in which Mo atoms are found at the corners of a tetrahedron. Because the faces of the tetrahedron are usually occupied by sulfur, or sometimes selenium or oxygen, the resulting overall structure is called a thiocubane. The four molybdenum and four sulfur atoms form a distorted cube (see Fig. 5**c**).

In the case of Mo(II), the $4d^4$ electronic configuration allows the formation of four metal–metal bonds. Such bonding can be accomplished in a dinuclear complex by the formation of a quadruple bond between the Mo atoms. Alternatively, the Mo atoms in Mo(II) compounds can form four metal–metal bonds by constructing an octahedral Mo_6 cluster in which each Mo atom is bonded to four molybdenum atoms. The resultant clusters are well known in certain Chevrel

Table 2. **Aqueous Ions of Molybdenum in Acid Solutions**

Molybdenum oxidation state	Ion	Color	Mo–Mo bonding
VI	MoO_2^{2+} and others	colorless	none
V	$Mo_2O_4(H_2O)_6^{2+}$	yellow	one single bond
IV	$Mo_3O_4(H_2O)_9^{4+}$	green	two double bonds
III	$Mo_4O_4(H_2O)_{12}^{4+}$		six single bonds
	$Mo(H_2O)_6^{3+}$	yellow	none
II	$Mo_2(H_2O)_8^{4+}$	red	quadruple

phases, such as $PbMo_6S_8$ [39432–49-0] (38), and in molecular clusters such as $Mo_6Cl_8{}^{4+}$ (37).

8.2. Halides of Molybdenum. The halides of molybdenum are solids that are quite reactive and useful starting points for further syntheses. Only fluoride supports the highest (hexavalent) oxidation state. Molybdenum hexafluoride [7783-77-9], MoF_6, and derivative salts containing $MoF_7{}^-$ exist. The highest Mo oxidation states for chloride, bromide, and iodide are V, IV, and III, respectively. The finding that MoF_6, $MoCl_5$, $MoBr_4$, and MoI_3 are, respectively, the highest halides formed for F, Cl, Br, and I is consistent with the ease of oxidation of the respective halides. The higher halides in the presence of higher oxidation states of molybdenum are susceptible to internal oxidation, eg, MoI_4 or MoI_5 would be unstable with respect to the formation of the MoI_3 and elemental iodine (I_2). The properties of the molybdenum halides have been described in some detail (42,43).

8.3. Aqueous Chemistry. Molybdenum has well-characterized aqueous chemistry in the five oxidation states, VI, V, IV, III, and II. A listing of aqua ions is given in Table 2. Except for the Mo(VI) species all of the aqua ions are only soluble or stable in acidic media (17). The range of aqueous ions known for molybdenum is far broader than that of other elements.

9. Biological Aspects

Molybdenum, recognized as an essential trace element for plants, animals, and most bacteria, is present in a variety of metallo enzymes (44–46). Indeed, the absence of Mo, and in particular its co-factor, in humans leads to severe debility or early death (47,48). Molybdenum in the diet has been implicated as having a role in lowering the incidence of dental caries and in the prevention of certain cancers (49,50). To aid the growth of plants, Mo has been used as a fertilizer and as a coating for legume seeds (51,52) (see FERTILIZERS; MINERAL NUTRIENTS).

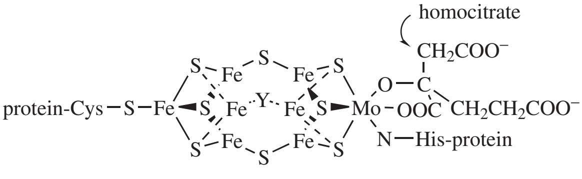
Environmentally, the presence of molybdenum has been of concern only in isolated instances (53). Reports of molybdenum toxicity have been rare (54). Molybdenum is involved in copper–molybdenum antagonism wherein excess molybdenum in the soil elicits a copper (qv) deficiency in animals (especially ruminants) that graze on the vegetation (55). Conversely, excess copper in the soil induces a molybdenum deficiency in ruminant animals that graze on the vegetation (see FEEDS AND FEED ADDITIVES, RUMINANT FEEDS). The problem is exacerbated in soils that have high levels of sulfate. The mechanism of the toxicity is understood. The anaerobic rumen of the affected animals contains a population of sulfate-reducing bacteria that reduces the soil sulfate to hydrogen sulfide (sulfide ions in solution). The sulfide ions react with molybdates to form thiomolybdates, which are known to be excellent ligands for copper. The resultant copper molybdenum compounds are insoluble and therefore the elements in them are not available to satisfy the nutritional needs of the animals. Fortunately, supplementation with the deficient element, eg, copper, alleviates the toxic effects.

Molybdate is also known as an inhibitor of the important enzyme ATP sulfurylase where ATP is adenosine triphosphate, which activates sulfate for participation in biosynthetic pathways (56). The tetrahedral molybdate dianion, $MoO_4{}^{2-}$, substitutes for the tetrahedral sulfate dianion, $SO_4{}^{2-}$, and leads to futile cycling of the enzyme and total inhibition of sulfate activation. Molybdate is also a co-effector in the receptor for steroids (qv) in mammalian systems, a biochemical finding that may also have physiological implications (57).

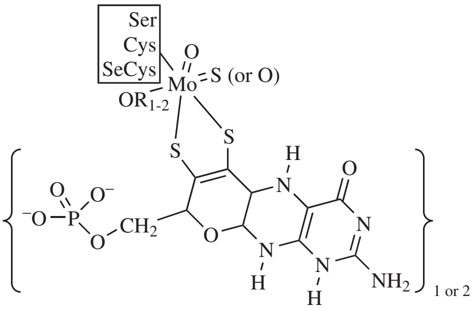
The clearest manifestation of molybdenum in biology is its presence in over 20 enzymes which participate in a wide variety of redox processes (44–46). Some of the Mo enzymes and their occurrence are as follows:

Enzyme	Occurrence
Nitrogen metabolism	
nitrogenase	bacteria (including symbionts)
nitrate reductase	plants, fungi, algae, bacteria
trimethylamine *N*-oxide reductase	bacteria
xanthine oxidase	cow's milk, mammalian liver, kidney
xanthine dehydrogenase	chicken liver, bacteria
quinoline oxidoreductase	bacteria
picolinic acid dehydrogenase	bacteria
Carbon metabolism	
aldehyde oxidase	mammalian liver
formate dehydrogenase	fungi, yeast, bacteria, plants
carbon monoxide oxidoreductase	bacteria
formylmethanofuran dehydrogenase	bacteria
Sulfur metabolism	
sulfite oxidase	mammalian liver, bacteria
dimethyl sulfoxide (DMSO) rectuctase	bacteria
biotin sulfoxide reductase	bacteria
tetrathionite reductase	bacteria
Others	
arsenite oxidase	bacteria
chlorate reductase	bacteria

The enzyme nitrogenase (58) catalyzes the reduction of dinitrogen to ammonia. The process known as nitrogen fixation (qv) is of critical importance to crops such as soybeans and other legumes (see SOYBEANS AND OTHER OIL SEEDS). Nitrogenase is found in the symbiotic bacteria that live in root nodules of legumes. These bacteria reduce atmospheric dinitrogen to ammonia, which is incorporated into the metabolic pathways of both the bacterium and the plant to synthesize proteins (qv), nucleic acids (qv), and other biomolecules that contain nitrogen. The crystal structure (59) of the iron–molybdenum protein of nitrogenase reveals an iron–molybdenum cluster (FeMoco) of unusual structure, which is the active site responsible for reduction of N_2 in the enzyme.



FeMoco



The remaining Mo enzymes all contain the molybdenum co-factor (Moco) which is chemically, biochemically, and genetically distinct from the nitrogenase co-factor, FeMoco. In Moco the molybdenum is bound by a pterin-enedithiolate ligand (60). The Moco enzymes (61,62) catalyze such important reactions as the oxidation of sulfite to sulfate; the reduction of nitrate to nitrite; the oxidation of xanthine to uric acid, ie, the last step in purine metabolism in humans; and quinoline hydroxylation which is crucial for the biodegradation of petroleum residues. The sulfite oxidation reaction is critical in human metabolism. Sulfite is toxic and must be removed from the body as it is produced metabolically or ingested. Children born without the sulfite oxidase activity are severely compromised and generally do not survive (47). The nitrate reduction reaction is critical to plant health, as all plants that do not harbor nitrogen-fixing symbionts require this enzyme as the first step in their assimilation of inorganic nitrogen. Molybdenum clearly plays a principal role in the biological nitrogen cycle.

Most of the Moco enzymes catalyze oxygen atom addition or removal from their substrates. Molybdenum usually alternates between oxidation states VI and IV. The Mo(V) state forms as an intermediate as the active site is reconstituted by coupled proton–electron transfer processes (62). The working of the Moco enzymes depends on the oxo chemistry of Mo(VI), Mo(V), and Mo(IV).

Although molybdenum is an essential element, excess levels can have deleterious effects. The LD_{50} and TLV values of the most common Mo compounds are listed in Table 3 (63,64). In general the toxicity of Mo compounds is considered to be low. For example, MoS_2 has been found to be virtually nontoxic even at high levels. Certain Mo compounds such as $MoCl_5$ and $Mo(CO)_6$, have higher toxicity

Table 3. **Toxicity of Molybdenum Compounds**[a]

Compound	Molecular formula	LD_{50} (rat, oral), mg/kg	TLV(TWA),[b] mg/m^3
ammonium heptamolyb-date	$(NH_4)_6Mo_7O_24H_2O$	333	
molybdenum trioxide	MoO_3	2689	5
sodium molybdate	Na_2MoO_4	4000	5
molybdenum disulfide, molybdenite	MoS_2	nontoxic[c]	

[a] Refs. 63 and 64.

[b] On the basiis of weight of Mo.

[c] Rates ingesting 500 mg/d for 44 days showed no toxic signs.

because of the chemical nature and reactivity of these compounds rather than the Mo content. Supplementary dietary Cu^{2+}, thiosulfate, methionine, and cysteine have been shown to be effective in alleviating Mo toxicity in animals.

10. Economic Aspects

Table 4 gives United States information on consumption by end use for 1997 and 1998. Oxide was the chief form of molybdenum used by industry particularly in stainless and alloy steel, cast iron, and superalloys. Some of the oxide was, however, converted to other molybdenum products such as ferromolybdenum, high purity oxide, ammonium and sodium molybdenate and metal powder (65). The diversity of molybdenum compounds, coupled with potential environmental advantages and reduced costs of molybdenum relative to the noble metals leads to projections for the increased use of molybdenum, especially in catalysis (66). Roughly 30% of the molybdenum processed goes into compounds with nonmetallurgical used. Most of the bulk molybdenum chemicals, eg, MoO_3, Na_2MoO_4, $(NH_4)_2Mo_2O_7$, $(NH_4)_6Mo_7O_{24}$, and MoS_2, sell for \$6–9/kg (67). For example, the average 1998 price for molybdic oxide was \$5.87/kg and for ferromolybdenum was \$8.32/kg

11. Uses

In most of the nonmetallurgical uses of molybdenum compounds the metal is coordinated by oxygen or sulfur ligands. Molybdenum nitrides, carbides, and silicides are, however, coming under increasing study for various applications. Roughly 75% of all molybdenum compounds are used as catalysts in the petroleum and chemicals industries.

11.1. Lubrication. Molybdenum is found naturally mostly as the disulfide, MoS_2. Once purified, the graphite-like layered structure and the thermal and oxidative stability of MoS_2 make it extremely useful as a lubricant or lubricant component. MoS_2 is used directly as a solid or in coatings (qv) that are bonded onto the metal surface by burnishing; by vapor deposition, eg, sputtering; or by bonding processes that use binders, solvents, and mechanochemical

Table 4. **U.S. Reported Consumption, by End Uses, and, Consumer Stocks of Molybdenum Materials**[a]

		(Kilograms, contained molybdenum)				
End use	Molybdic oxides	Ferro molybdenum[b]	Ammonium and sodium molybdate	Molybdenum scrap	Other	Total
1997:						
Steel						
Carbon	626,000	307,000	–	–	76,500	1,010,000
High-strength low-alloy	586,000	293,000	–	–	–	879,000
Stainless and heat-resisting	3,410,000	455,000	–	–	90,000	3,950,000
Fully alloy	2,400,000	1,990,000	–	–	27,900	4,420,000[c]
Tool	1,010,000	88,700	–	[c]	18,800	1,120,000[d]
Total	8,030,000	3,140,000	–	–	213,000[c]	11,400,000[c]
Cast irons (gray, malleabale, ductile iron)	180,000	806,000[c]	–	–	28,600	1,010,000[c]
Superalloys	W	W	–	[d]	1,180,000	1,180,000
Alloys (other than steels, cast irons, superalloys):						
Welding materials (structural and hard-facing)	–	39,500[a]	–	[f]	416[c]	39,900[c]
Other alloys	–	W	–	–	78,000[c]	78,000[c]
Mill products made from metal powder[g]	–	–		–	2,250,000	2,250,000
Cemented carbides and related products[h]	–	–	–	–	156	156
Chemical and ceramic uses:						
Pigments	W	–	W	–	–	W
Catalysis	971,000	–	W	–	W	971,000
Other	W	–	–	–	29,200[c]	29,200
Miscellaneous and unspecified uses:						
Lubricants	–	–	–	–	285,000[c]	285,000[c]
Other	1,140,000	191,000[c]	1,290,000	–	179,000[d]	2,800,000[c]
Grand total	10,300,000	4,170,000	1,290,000	–	4,240,000	20,000,000
Stocks, December 31, 1997	761,000[c]	202,000	52,400	35,000	172,000	1,220,000
1998:						
Steel:						
Carbon	503,000	280,000	–	–	39,600	822,000
High-strength low-alloy	505,000	146,000	–	–	–	651,000
Stainless and heat-resisting	3,060,000	664,000	–	[i]	89,300	3,810,000
Full alloy	2,260,000	2,010,000	–	–	27,900	4,290,000

Table 4. (*Continued*)

	(Kilograms, contained molybdenum)					
End use	Molybdic oxides	Ferro molybdenum[b]	Ammonium and sodium molybdate	Molybdenum scrap	Other	Total
Tool	650,000	87,800	–	[d]	19,400	757,000
Total	6,970,000	3,190,000	–	–	176,000	10,300,000
Cast irons (gray, malleable, ductile iron)	241,000	843,000	–	–	27,700	1,110,000
Superalloys	981,000	W	–	–	1,220,000	2,200,000
Alloys (other than steels, cast irons, superalloys):						
Welding materials (structural and hard-facing)	–	37,700	–	–	375	38,100
Other alloys	W[f]	96,000	–	–	79,600	176,000
Mill products made from metal powder[g]	–	–		–	2,410,000	2,410,000
Cemented carbides and related products[h]	–	–	–	–	93	93
Chemical and ceramic uses:						
Pigments	W[f]	–	W[f]	–	–	W[j]
Catalysts	967,000	–	W[f]	–	W[f]	967,000
Other	W[f]	–	–	–	29,400	29,400
Miscellaneous and unspecified uses:						
Lubricants	–	–	–	–	231,000	231,000
Other	11,800	84,400	1,170,000	–	179,000	1,440,000
Grand total	9,170,000	4,250,000	1,170,000	–	4,350,000	18,900,000
Stocks, December 31, 1998	873,000	393,000	46,700	19,300	839,000	2,170,000

[a] Data are rounded to three significant digits; may not add to totals shown.

[b] Includes calcium molybdate.

[d] Revised.

[c] Data are rounded to three significant digits; may not add to totals shown.

[e] Included in "Other" of "Superalloys" category.

[f] Included in "Other" of "Welding materials" category.

[g] Includes construction, mining, oil and gas, metal working machinery.

[h] Includes ingot, wire, rod, and sheet.

[i] Included in "Other" of "Stainless and heat-resisting" category.

[j] W Withheld to avoid disclosing company proprietary data; included in "Other" of the "Miscellaneous and unspecified uses category.

procedures. Sputtered MoS_2 films have been found to have remarkably low friction coefficients (68) (see THIN FILMS). As a solid lubricant, MoS_2 is preferable to graphite in applications that involve high pressure, high vacuum, and radiation exposure. MoS_2 has been found effective in the lubrication of ceramic and polymer, as well as metal surfaces. Extensive use has been seen in high vacuum applications, including space vehicles where MoS_2 is the most widely used lubricant (69). Solid MoS_2 is a component of self-lubricating polymers and rubbers, and is often suspended in greases, pastes, and oils (70). MoS_2 is considered an intrinsic lubricant. Unlike graphite to which MoS_2 is often compared, no additives or adsorbates are required for efficacy.

More recently, molecular molybdenum-sulfur complexes and clusters have been used as soluble precursors for MoS_2 in the formulation of lubricating oils for a variety of applications (71). Presumably, the oil-soluble molybdenum–sulfur-containing precursors decompose under shear, pressure, or temperature stress at the wear surface to give beneficial coatings. In several cases it has been shown that the soluble precursors are trifunctional in that they not only display antifriction properties, but have antiwear and antioxidant characteristics as well. In most cases, the ligands for the Mo are of the 1,1-dithiolate type, including dithiocarbamates, dithiophosphates, and xanthates (55,72).

11.2. Hydrodesulfurization and Hydrotreating Catalysis. Hydrotreating is used to remove sulfur, nitrogen, oxygen, and metals, mostly vanadium and nickel, from petroleum fractions. In hydrodesulfurization, the hydrogenolysis of C–S bonds in organosulfur compounds, such as thiophene, benzo-, or dibenzothiophene, yields H_2S and a corresponding hydrocarbon. In hydrodenitrogenation, the hydrogenolysis of C–N bonds in organic molecules, eg, pyridines, and carbazoles, yields ammonia (qv) and the hydrocarbon. Related hydrogenating processes lead to the saturation of aromatics and coal liquefaction (see COAL CONVERSION PROCESSES) **(16)**. An important attribute of the catalysts for these processes is sulfur tolerance. The metal most closely associated with all the processes in use is molybdenum. Molybdenum sulfide catalysts are not only sulfur-tolerant but actually require sulfur for their activity.

The industry mainstay for the hydrodesulfurization of petroleum is the cobalt–molybdenum (co–moly) on alumina catalyst (73,74) 1993. The classic preparative technique involves wet impregnation of molybdates on alumina to produce a molybdenum oxide on alumina. Subsequent treatment using (usually divalent) cobalt leads to a cobalt oxide coating. This material is then sulfided using H_2S–H_2 or organosulfur compounds. Increasingly, presulfided (passivated) catalysts, preferred for their convenience and for environmental considerations, are being used (75). Environmental considerations leading to tighter sulfur specifications on petroleum products should lead to an increase in the use of molybdenum catalysts. Moreover, the recycling of spent catalyst should grow in importance as environmental trends disallow classical methods of disposal (see CATALYST REGENERATION, METAL CATALYSTS).

The active hydrotreating catalyst appears to have MoS_2-like aggregates as the active species, with the edges of the MoS_2 responsible for the catalytic activity (73). The cobalt, which is said to be a promoter of MoS_2 activity, is associated with the edges of the MoS_2 in groupings that are sometimes referred to as the CoMoS phase (76). Alternative approaches to making the CoMo catalysts are being developed including the use of specific precursors that already contain Co, Mo, and S in a single compound (15). Low valent Co compounds such as $Co_2(CO)_8$ have been found to promote MoS_2 activity by binding directly at the edge surfaces (77).

11.3. Oxidation Catalysis. The multiple oxidation states available in molybdenum oxide species make these excellent catalysts in oxidation reactions. The oxidation of methanol (qv) to formaldehyde (qv) is generally carried out commercially on mixed ferric molybdate–molybdenum trioxide catalysts. The oxidation of propylene (qv) to acrolein (78) and the ammoxidation of propylene to acrylonitrile (qv) (79) are each carried out over bismuth–molybdenum oxide catalyst systems. The latter (Sohio) process produces in excess of 3.6×10^6 t/yr of acrylonitrile, which finds use in the production of fibers (qv), elastomers (qv), and water-soluble polymers.

The addition of an oxygen atom to an olefin to generate an epoxide is often catalyzed by soluble molybdenum complexes. The use of alkyl hydroperoxides such as *tert*-butyl hydroperoxide leads to the efficient production of propylene oxide (qv) from propylene in the so-called Oxirane (Halcon or ARCO) process (80).

In addition to these principal commercial uses of molybdenum catalysts, there is great research interest in molybdenum oxides, often supported on silica, ie, MoO_3–SiO_2, as partial oxidation catalysts for such processes as methane-to-methanol or methane-to-formaldehyde (81). Both O_2 and N_2O have been used as oxidants, and photochemical activation of the MoO_3 catalyst has been reported (82). The research is driven by the increased use of natural gas as a feedstock for liquid fuels and chemicals (83). Various heteropolymolybdates (84), MoO_3-containing ultrastable Y-zeolites (85), and certain mixed metal molybdates, eg, $MnMoO_4$, $Fe_2(MoO)_3$, photoactivated $CuMoO_4$, and $ZnMoO_4$, have also been studied as partial oxidation catalysts for methane conversion to methanol or formaldehyde (81) and for the oxidation of C-4-hydrocarbons to maleic anhydride (86). Heteropolymolybdates have also been shown to effect ethylene (qv) conversion to acetaldehyde (qv) in a possible replacement for the Wacker process.

11.4. Other Catalytic Applications. Molybdenum disulfide is used as a catalyst for the decomposition of NaN_3 and other alkali and alkaline-earth azides. This leads to rapid N_2 production, useful in the rapid inflation of airbags in passive automotive restraint systems. Molybdenum compounds are also under continued study for the catalysis of a wide variety of reactions (87), including hydrogenation; hydrogenolysis; dehydrogenation; olefin metathesis, including ring-opening metathesis polymerization (ROMP); olefin, and especially, alkyne polymerization; dehydration; hydration, eg, isobutene to *tert*-butanol; hydrolysis; isomerization of alkanes (*n*-pentane to isopentane, cyclohexane to methylcyclopentane); water gas shift; Fischer-Tropsch synthesis of alcohols; naphtha reforming; and methanation. The varied chemistry of molybdenum is clearly reflected in the diverse array of reactions catalyzed by the compounds of this element.

11.5. Advanced Structural and Heating Materials. Molybdenum silicide [12136-78-6] and composites of $MoSi_2$ and silicon carbide, SiC, have properties that allow use as high temperature structural materials that are stable in oxidizing environments (see COMPOSITE MATERIALS; METAL-MATRIX COMPOSITES). Molybdenum disilicide also finds use in resistance heating elements (88,89).

11.6. Anticorrosion Agents. Sodium molybdate is finding increasing use in corrosion inhibition in cooling systems (see CORROSION AND CORROSION CONTROL), automotive antifreeze (see ANTIFREEZES AND DEICING FLUIDS), and cutting fluids. A big incentive in air conditioning cooling towers involves the replacement of the relatively toxic chromate ion with the far less toxic molybdate ion. Molybdate, a component of vitamin preparations and fertilizers, is generally considered to be a nutrient rather than a toxin (90). The mechanism of corrosion protection presumably involves adsorption of the molybdate on the internal surface of the tower to form mixed metal molybdate phases that resist corrosion (91).

11.7. Coatings, Paints, and Pigments. Various slightly soluble molybdates, such as those of zinc, calcium, and strontium, provide long-term corrosion control as undercoatings on ferrous metals (91–93). The mechanism of action presumably involves the slow release of molybdate ion, which forms an insoluble ferric molybdate protective layer. This layer is insoluble in neutral or basic solution. A primary impetus for the use of molybdenum, generally in place of chromium, is the lower toxicity of the molybdenum compound.

Molybdate orange and red are pigments (qv) that contain lead(II) molybdate [10190-55-3], $PbMoO_4$, formulated in mixed phases with $PbCrO_4$ and $PbSO_4$. The mixed phase is more intensely colored than any of the component phases. Concerns about lead content are lessening the use of these materials (see also PAINT). Various organic dyes are precipitated with heteropolymolybdates. This process allows the fixation of the dye in various fabrics. The molybdenum anion generally imparts light stability to the colorant as well (92).

11.8. Other Industrial Uses. *Flame and Smoke Retardants.* Molybdenum compounds are used extensively as flame retardants (qv) (94,95) in the formulation of halogenated polymers such as PVC, polyolefins, and other plastics; elastomers; and fabrics. An incentive for the use of molybdenum oxide and other molybdenum smoke and flame retardants is the elimination of the use of arsenic trioxide. Although hydrated inorganics are often used as flame retardants, and thought to work by releasing water of crystallization, anhydrous molybdenum oxides are effective. Presumably the molybdenum oxides rapidly form surface char, providing a barrier that prevents additional thermal or oxidative damage. The molybdenum is apparently not volatilized in the process.

Pyrotechnics. Molybdenum-containing formulations are used in delay elements of pyrotechnic display devices (see PYROTECHNICS) (96).

Battery Electrodes. Molybdenum disulfide in amorphous form and molybdenum trisulfide [12033-29-3] are useful as electrodes in Li batteries (qv). The lithium presumably intercalates between the molybdenum sulfide layers during charging, and then deintercalates upon discharging (97).

11.9. Biological Usage. *Soil Nutrient.* Molybdenum has been widely used to increase crop productivity in many soils worldwide (see FERTILIZERS). It is the heaviest element needed for plant productivity and stimulates both nitrogen fixation and nitrate reduction (51,52). The effects are particularly significant in leguminous crops, where symbiotic bacteria responsible for nitrogen fixation provide the principal nitrogen input to the plant. Molybdenum deficiency is usually more prominent in acidic soils, where Mo(VI) is less soluble and more easily reduced to insoluble, and hence unavailable, forms. Above pH 7, the soluble anionic, and hence available, molybdate ion is the principal species.

Biomedical Uses. The molybdate ion is added to total parenteral nutrition protocols and appears to alleviate toxicity of some of the amino acid components in these preparations (see MINERAL NUTRIENTS) (98). Molybdenum supplements have been shown to reduce nitrosamine-induced mammary carcinomas in rats (50). A number of studies have shown that certain heteropolymolybdates (99) and organometallic molybdenum compounds (100) have antiviral, including anti-AIDS, and antitumor activity (see ANTIVIRAL AGENTS; CHEMOTHERAPEUTICS, ANTICANCER).

The isotope molybdenum-99 is produced in large quantity as the precursor to technetium-99*m*, a radionucleide used in numerous medical imaging procedures such as those of bone and the heart (see MEDICAL IMAGING TECHNOLOGY). The molybdenum-99 is either recovered from the fission of uranium or made from lighter Mo isotopes by neutron capture. Typically, a Mo-99 cow consists of $MoO_4{}^{2-}$ adsorbed on a lead-shielded alumina column. The $TcO_4{}^{-}$ formed upon the decay of Mo-99 by β-decay, $t_{1/2} = 66$ h, has less affinity for the column and is eluted or milked and either used directly or appropriately chemically derivatized for the particular diagnostic test (101).

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EDWARD I. STIEFEL
ExxonMobil Research and Engineering Company