COORDINATION COMPOUNDS OF MOLYBDENUM*

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CONTENTS

A. INTRODUCTION

In recent years the chemistry of molybdenum compounds has attracted increasing attention because of their intrinsic chemical interest and their industrial and biological importance. Molybdenum exhibits a wide range of oxidation states and stereochemistries and forms complexes with most donor atoms. Individual molybdenum compounds or groups of compounds (e.g., molybdenum carbonyls and oxomolybdenum(V) complexes) have been important in the development of theories of bonding in co-ordination compounds and in the interpretation of their magnetic

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* (Abbreviations: Ph, C_6H_5; R, alkyl or aryl; tu, thiourea, $(NH_2)_2CS$; digly, diglyme, diethyleneglycol dimethyl ether, $(CH_3OCH_2CH_2)_2O$; py, pyridine; dien, diethylenetriamine, $NH_2CH_2CH_2NHCH_2CH_2NH_2$; diphos, 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$; diars, diarsine, *o*-phenylenebis(dimethylarsine), *o*-$C_6H_4(AsMe_2)_2$; bipy, 2,2′-bipyridyl.)

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and spectroscopic properties. Work on molybdenum compounds has been stimulated by current interest in the chemistry of the earlier-transition metals, by the wider application of techniques for handling highly reactive, air- and moisture-sensitive compounds[1], by recognition that molybdenum is essential for the activity of certain enzymes, e.g., xanthine oxidase[2] and nitrate reductase[3], and by the use of molybdenum compounds (e.g., molybdenum disulphide) as anti-wear additives and catalysts in the petroleum industry[4].

This article surveys the co-ordination chemistry of molybdenum with particular reference to recent work on well-characterised compounds. Oxo-species of molybdenum(V) and molybdenum(VI) have recently been reviewed and will not be discussed in detail here[5]. The solution chemistry of molybdenum is also excluded. (Of particular interest is the work of Haight *et al.* on the role of molybdenum(IV) in molybdate catalysed reactions[6].) No attempt has been made to include all molybdenum compounds mentioned in the literature but it is felt that the major areas of current interest in molybdenum co-ordination chemistry have been covered. There are no recent comprehensive accounts of molybdenum chemistry. Useful, but uncritical accounts of earlier work are available[7].

B. GENERAL SURVEY

Molybdenum is the second member of Group VIA of the Periodic Table and the fourth member of the second transition series. The valency-shell electronic configuration of the free atom in the ground state is $4d^5 5s^1$. Molybdenum differs from chromium, the first member of Group VIA, in two important respects: molybdenum exhibits more stable oxidation states than chromium and the higher oxidation states of molybdenum are more stable with respect to reduction and the lower oxidation states are less stable with respect to oxidation than those of chromium. This trend reflects the smaller ionisation potentials[8] for *d*-electrons and the larger ionic and covalent radii[7c] of molybdenum.

(*i*) *Oxidation states*

In its compounds molybdenum exhibits all oxidation states from -2 to $+6$. The lowest oxidation states, -2 to $+1$, occur in complexes with π-acceptor ligands, mainly carbon monoxide, cyclopentadiene and related compounds, nitric oxide, and unsaturated nitrogen-, phosphorus-, and arsenic-donor ligands. In these oxidation states molybdenum behaves as a class-B acceptor.

The best known compounds of molybdenum(II) are those containing the polynuclear ion $Mo_6Cl_8^{4+}$. Recently six- and seven-co-ordinate mononuclear complexes with π-acceptor ligands have been prepared.

In oxidation states $+3$ to $+6$ molybdenum forms a large number of complexes with nitrogen- and oxygen-donor ligands and with the lighter halogens. Complexes with sulphur-ligands are fairly common, but there are very few complexes with phosphorus- and arsenic-donors. In its higher oxidation states molybdenum behaves as a class-A acceptor.

The chemistry of the +6 and +5 oxidation states is dominated by oxo-molybdenum species (MoO^{4+}, MoO_2^{2+}, MoO_3, $Mo_2O_5^{2+}$; MoO^{3+}, $Mo_2O_3^{4+}$, $Mo_2O_4^{2+}$), with one or more oxygen atoms as terminal ligands (i.e., bonded to only one molybdenum atom) or as bridging atoms (i.e., bonded to two molybdenum atoms). An important feature is π-donation from oxygen to the metal giving a multiple bond[5]. This type of donor π-bonding occurs less readily as the formal oxidation state of the metal decreases and only a few, poorly characterised oxo-species of molybdenum(IV) and molybdenum(III) are known.

(*ii*) *Co-ordination numbers and structures*

The most-common co-ordination number is six giving octahedral and, in certain sulphur complexes (section E.(viii)), trigonal prismatic stereochemistries. In many compounds the metal attains six co-ordination through dimerisation or polymerisation. Co-ordination number four is not known and the only well-established example of co-ordination number five is for $MoCl_5$ in the vapour state. Co-ordination numbers greater than six are more common.

Polynuclear complexes are known for most oxidation states and many contain one or more Mo–Mo bonds.

(*iii*) *Magnetic properties*

Data for molybdenum complexes are included in a recent review article[9]. It should be noted that because of the large spin–orbit coupling constants (λ) of molybdenum(V) and molybdenum(IV), magnetic moments of their mononuclear octahedral complexes are expected to be much less than the spin-only values and to vary with temperature (ca. 1.0 and 1.8 B.M. respectively at 300 °K). The observed magnetic moments at 300 °K are 1.5–1.8 B.M. for Mo^{V} and 2.0–2.5 B.M. for Mo^{IV}. The deviations from the spin-only moments are less than expected because the spin–orbit coupling constants are reduced from the free-ion values through complex formation and because of the effect of asymmetric ligand fields in destroying orbital degeneracy. For octahedral low-spin molybdenum(II) (t_{2g}^4) and molybdenum(I) (t_{2g}^5) similar considerations apply except that the magnetic moments should be greater than the spin-only values (3.3 B.M. for Mo^{II} and 2.3 B.M. for Mo^{I} at 300 °K.)[9]. Observed and calculated magnetic moments for octahedral molybdenum(III) are close to the spin-only value. Co-ordination numbers seven and eight give ground states which appear to be orbitally non-degenerate and the complexes are either diamagnetic (Mo^{II}, Mo^{IV}) or have moments close to the spin-only value for one unpaired electron (Mo^{I}, Mo^{III}, Mo^{V}). Complexes of molybdenum(O) are diamagnetic. Bi- and polynuclear complexes usually have magnetic moments corresponding to less than 1.0 B.M. per Mo atom. Temperature-independent paramagnetism has been observed for spin-paired seven-co-ordinate molybdenum(II) and for molybdenum(IV). The magnetic properties of molybdenum complexes are much more complicated than is sometimes realised and caution is necessary in making deductions about structures, spin-states and even oxidation states.

(*iv*) *Electronic spectra*

Crystal-field (*d–d*) transitions are observed with complexes of the more electronegative ligands (halogens, saturated oxygen- and nitrogen-donors); but with ligands of low electronegativity, intense charge-transfer bands may cover the crystal-field transitions in the visible region. For a series of molybdenum(V) complexes with organic ligands the energies of the charge-transfer transitions decrease as the electron-donor character of the ligands increases suggesting ligand-to-metal charge transfer[10], whilst in molydenum(III) complexes the charge-transfer transitions are thought to be from metal-to-ligand[11].

Spectrochemical and nephelauxetic series based on the molybdenum(III) ion, have been obtained; these agree with the series for other metal ions[11,12].

(*v*) *Classification of complexes*

A strict classification of molybdenum complexes on the basis of donor atoms or oxidation states is not possible without extensive cross-referencing. Many complexes contain more than one type of ligand and their chemical properties may involve more than one oxidation state. Because of this, substituted carbonyls are grouped together (section C) and so are complexes derived from the molybdenum halides (section E.i). Other complexes are classified on the basis of ligand donor-atoms.

C. OXIDATION STATES −2 TO +1

Many complexes of molybdenum in these oxidation states are derivatives of molybdenum hexacarbonyl, $Mo(CO)_6$, but a few are known which do not contain carbon monoxide.

(*i*) *Molybdenum carbonyls and related compounds*

The chemistry of $Mo(CO)_6$ has been very extensively studied[13]. Up to three

CO groups may be replaced by monodentate ligands and up to four by certain bidentate ligands, but only rarely are all the CO groups replaced in substitution reactions. Complexes of organic ligands[6c] which have attracted much attention include π-complexes of cyclopentadiene (Cp), e.g., $Cp_2Mo_2(CO)_6$, $[CpMo(CO)_3]^-$, Cp_2MoCl_2; cycloheptatriene (C_7H_8), e.g., $(C_7H_8)Mo(CO)_3$; and benzene, e.g., $(C_6H_6)Mo(CO)_3$, $Mo(C_6H_6)_2$, $[Mo(C_6H_6)_2]^+$. Carbonyl anions are also known, e.g., $[Mo(CO)_5]^{2-}$ and $[Mo_2(CO)_{10}]^{2-}$.

Interest in molybdenum carbonyls and organometallic compounds has been concentrated in two areas: (*a*) structural and theoretical studies with particular reference to π-bonding in the hexacarbonyl and substituted carbonyls; (*b*) substitution and oxidation reactions giving new types of compound, compounds with unusual structures, and compounds of uncommon oxidation states.

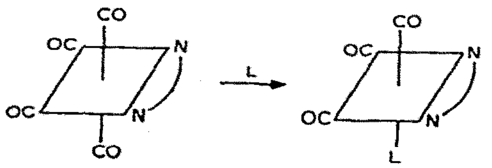
(*a*) *Structures and bonding*. That $Mo(CO)_6$ has a perfectly octahedral structure with linear Mo–C–O bonds has been shown by infrared, Raman, electron-diffraction, and X-ray measurements[13b]. The Mo–CO bond is described in terms of a σ-bond formed from the $d(e_g)$, s, and p orbitals of molybdenum and the (sp)-lone pair of carbon, and π-bonds formed by donation from the $d(t_{2g})$-orbitals of molybdenum to the anti-bonding π-orbitals of CO. The Mo–C bond has an order of more than one and the C–O bond an order of less than three. The order of the C–O bond decreases with increasing π-donation from the metal[14]. A molecular orbital treatment of $Mo(CO)_6$ has been given and used to interpret its electronic spectrum[15].

Replacement of CO by weaker π-acceptors causes a decrease in C–O stretching frequencies because of increased π-bonding between the metal and the *remaining* CO groups. The lowering is greatest in complexes of nitrogen- and oxygen-donors which lack π-acceptor orbitals, e.g.[16a], (diglyme)$Mo(CO)_3$, and[16b] (dien)$Mo(CO)_3$ and least in complexes of ligands which are good π-acceptors, e.g., in[16b] *cis*-$(PCl_3)_3Mo(CO)_3$. Measurements on a large number of tricarbonyls give the following order of decreasing C–O stretching frequencies (interpreted as decreasing π-acceptor ability of the ligands): $PCl_3 \sim AsCl_3 \sim SbCl_3 > Ph_3P \sim Ph_3As \sim Ph_3Sb \gg R_2S >$ tu $\sim$ digly $>$ py $\sim$ dien[13b,14,16].

For some tetracarbonyls, $Mo(CO)_4A$, the order is diphos > diars > bipy[17].

(*b*) *Some chemical reactions of molybdenum carbonyls.*

Substitution reactions. Substituted molybdenum carbonyls may be obtained directly from $Mo(CO)_6$ or by displacement of another substituent, e.g., from $C_7H_8Mo(CO)_3$. As CO groups are removed further substitution becomes more difficult. Thus diarsine displaces[18] two carbonyl groups at 150° and a further two at 200°. This effect is attributed to increased π-bonding between molybdenum and carbon monoxide as the number of CO groups decreases. In agreement, bipyridyl will displace only two CO groups from $Mo(CO)_6$ but diphos and diars, which are better π-acceptors, will displace four CO groups[17]. A further CO group is displaced from $Mo(CO)_4(bipy)$ by Ph_3P, Ph_2S or pyridine[19].



Displacement of an *axial*-CO group occurs because the bipyridyl causes more enhancement of metal–CO π-bonding in the plane than out of the plane.

Oxidation by halogens. Reactions in which some substituted molybdenum carbonyls are oxidised by halogens are summarised in Table I. Tetra- and tricarbonyls generally lose carbon monoxide to give dicarbonyls; but dicarbonyls react without further loss of carbon monoxide[16f,17,20–23]. Similar reactions occur with substituted chromium and tungsten carbonyls, the ease of displacement of CO increasing in the order[21,23] W < Mo < Cr.

TABLE I

OXIDATION OF SUBSTITUTED MOLYBDENUM CARBONYLS BY HALOGENS

Starting compound[a]	*Reagents*	*Products*	*Ref.*
$Mo(CO)_4(bipy)$	Br_2	$Mo^{II}(CO)_3(bipy)Br_2$	17
$Mo(CO)_4(diphos)$	Br_2 and I_2	$Mo^{II}(CO)_3(diphos)X_2$	20
$Mo(CO)_4(diars)$	Br_2, I_2	$Mo^{II}(CO)_3(diars)X_2$	21
	I_2, hot CCl_4	$Mo^{II}(CO)_2(diars)I_2$	22
	I_2, hot $CHCl_3$	$Mo^{III}(CO)_2(diars)I_3$	22
$Mo(CO)_4(dithia)$	Br_2 and I_2	$Mo^{III}(CO)_3(dithia)X_2$	16f
$Mo(CO)_3(\nu\text{-triars})$[b]	Br_2 and I_2	$[Mo^{II}(CO)_3(\nu\text{-triars})X]X$ and some $Mo^{II}(CO)_2(\nu\text{-triars})X_2$	23
$[Mo(CO)_3(\nu\text{-triars})Br]BPh_4$	LiCl in *n*-propanol	$Mo^{II}(CO)_2(\nu\text{-triars})Cl_2$	23
$Mo(CO)_2(diphos)_2$[c]	I_2	$[Mo^{I}(CO)_2(diphos)_2]I_3$	20
$Mo(CO)_2(diars)_2$	Br_2 and I_2	$[Mo^{II}(CO)_2(diars)_2X]X$	21

[a] dithia = 2,5-dithiahexane; ν-triars = 1,1,1-tris(dimethylarsinomethyl)ethane. For other ligand abbrevations see p. 315.

[b] The proportion of the dicarbonyl compound increases with increasing temperature. Similar reactions occur with $Mo(CO)_3$(1-triars) and $Mo(CO)_3$(*o*-triars) (1-triars = methyl-bis(dimethylarsino-3-propyl)arsine; *o*-triars = bis(*o*-dimethylarsinophenyl)methylarsine).

[c] The anion is the tri-iodide ion, I_3^-.

An important feature of these reactions is the formation of complexes of molybdenum(II) formulated, on the basis of physical measurements (conductivities in nitrobenzene, magnetic moments, and infrared spectra), with co-ordination number seven. A pentagonal bipyramidal structure with axial halogens has been proposed[21] for $Mo(CO)_3(diars)I_2$. The seven-co-ordinate complexes are spin-paired but have temperature-independent paramagnetic moments from 0.4 to 1.1 B.M.[23]

The existence of complexes of molybdenum(II) and (III) with co-ordination number seven has been rationalised with Nyholm's "nine-orbital rule" according to which transition metals in their complexes with polarisable ligands tend to utilise all nine valency orbitals (i.e., five $(n\text{-}1)d$, one ns, three np) for σ-bonding pairs, non-bonding pairs, and single electrons. The co-ordination number is limited by the number of σ-acceptor orbitals available[21]. In the spin-paired complexes of molybdenum(II) there are two non-bonding electron pairs, leaving seven σ-acceptor orbitals (d^3sp^3). Similarly molybdenum(III) (d^3 with one unpaired electron) has seven acceptor orbitals and so forms, e.g., $Mo(CO)_2(diars)I_3$ ($\mu = 1.40$ B.M.)[22]. However, low-spin molybdenum(I) (d^5) and molybdenum(II) (with two unpaired electrons) have only six acceptor orbitals and so form six-co-ordinate complexes, e.g., $[Mo^I(CO)_2(diphos)_2]I_3$ ($\mu = 1.66$ B.M.)[20] and $Mo^{II}(CO)_2(diars)I_2$ ($\mu = 1.98$ B.M.)[22].

Under vigorous conditions (e.g., excess halogen) carbon monoxide may be displaced completely:

$$Mo(CO)_6 \xrightarrow{Br_2} MoBr_4 \quad \text{(ref. 24)}$$

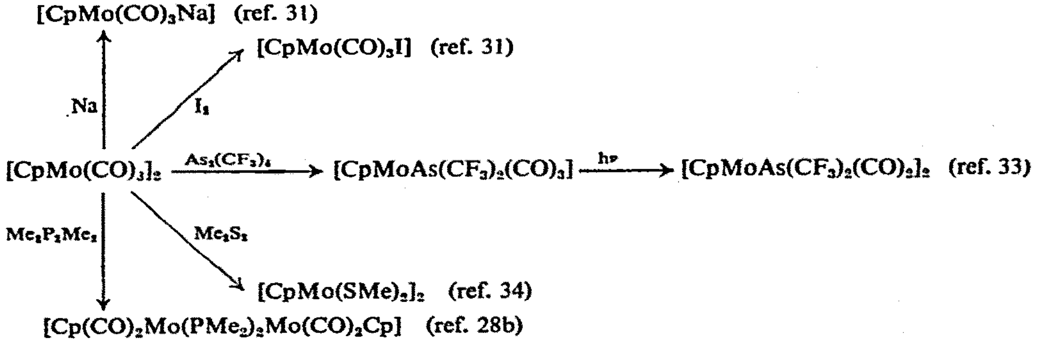
$$\begin{tikzcd} Mo(CO)_6 \arrow[r, "F_2,\ >50^\circ"] \arrow[dr, "F_2,\ -75^\circ"'] & MoF_6+MoO_3+COF_2 \\ & MoF_4+MoF_5 \quad \text{(ref. 25)} \end{tikzcd}$$

$$Mo(CO)_3(PPh_3)_3 \xrightarrow[\text{moist air}]{Br_2, CHCl_3} MoOBr_3(Ph_3PO)_2+MoO_2Br_2(Ph_3PO)_2 \quad \text{(ref. 26)}$$

$$Mo(CO)_4diars \xrightarrow{\text{excess } Br_2} MoBr_4diars \quad \text{(ref. 21)}$$

The compounds $Mo(CO)_3(Ph_3PO)_3$, *cis*- and *trans*-$Mo(CO)_4(PPh_3)_2$, $Mo(CO)_4(diphos)_2$ react similarly; analogous oxomolybdenum(V) complexes are also obtained by chlorine oxidation[26].

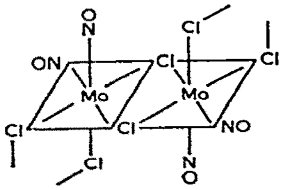
(*c*) *Compounds with Mo–Mo bonds.* There is a tendency for early-transition elements in oxidation states with unpaired electrons to dimerise through the formation of metal–metal bonds. This tendency can be rationalised by the inert-gas rule which is a special case of the nine-orbital rule[21]. Examples of low-valent molybdenum compounds with metal–metal bonds are the anion $[Mo_2(CO)_{10}]^{2-}$ which is diamagnetic[27] and isoelectronic with $[Mn_2(CO)_{10}]$ and the compound $[(Cp)_2Mo_2(CO)_6]$ obtained by the reaction of dicyclopentadiene[28] or cyclopentadienyl sodium[29] with $Mo(CO)_6$. The compound contains molybdenum formally in oxidation state +1, but is diamagnetic. The presence of the Mo–Mo bond has been shown by X-ray analysis, the molecule consisting of two $[CpMo(CO)_3]$ units united by a Mo–Mo bond of 3.22 Å[30]. Compounds containing mixed Mo–metal bonds have also been prepared, e.g., $Cp(CO)_3MoW(CO)_3Cp$ and $Cp(CO)_3MoFe(CO)_2Cp$ from $CpMo(CO)_3Na$ and $CpW(CO)_3I$ and $CpFe(CO)_2I$ respectively[31,32]. The metal–metal bond in $(Cp)_2Mo_2(CO)_6$ is fairly readily cleaved giving diamagnetic, bridged binuclear complexes:



(*ii*) *Nitrosyl complexes*

Rather few nitrosyl complexes of molybdenum are known; among these are the complexes[35] $[CpMo(CO)_2NO]$ and $K_4[Mo(CN)_5NO]$ (section E.(v)). Recently the compounds $[Mo(NO)_2Cl_2]$ and $[Mo(NO)_2(MNT)_2]$ have been prepared[36,37]. (MNT is the maleonitriledithiolate anion, $^-S–C(CN)=C(CN)–S^-$).

$Mo(NO)_2Cl_2$ is obtained as a dark-green solid from the reaction of $Mo(CO)_6$ with NOCl in dichloromethane. According to the infrared spectrum (N–O stretching frequency) the NO groups are *cis* and co-ordinated as NO^+. A polymeric structure with kinked chains is suggested:



Octahedral complexes $[Mo(NO)_2Cl_2L_2]$ are formed with L = Ph_3P, Ph_3As, pyridine, *p*-toluidine, cyclohexylamine, and Cl (from Ph_4AsCl) and, according to the infrared spectra, the NO^+ groups are *cis*[36] to one another.

With Na_2MNT in methanol, $Mo(NO)_2Cl_2$ forms a deep-green complex isolated as $(Ph_4P)_2[Mo(NO)_2(MNT)_2]$. The infrared spectrum is in accordance with *cis*-NO^+ groups and also suggests that in this compound MNT^{2-} functions as a π-acceptor (in contrast to its behaviour with high oxidation states with which it is a good donor, see section E.(viii))[37].

(*iii*) *Complexes of molybdenum(O) with nitrogen- and phosphorus-donors.*

Unstable, air-sensitive complexes in which molybdenum(O) is fully co-ordinated with N- and P-donors have been prepared, e.g., [Mo(bipy)$_3$] from [Mo(bipy)$_3$]Cl$_3$ and Li$_2$bipy in THF[38], [Mo(tripy)$_2$] from Mo(CO)$_6$ and 2,2',2"-tripyridyl[39], Mo(PP)$_3$ from [(C$_6$H$_6$)$_2$Mo] and o-C$_6$H$_4$(PR$_2$)$_2$ and also by reducing a mixture of MoCl$_5$ and the diphosphine in THF with lithium aluminium hydride[40], and Mo(PF$_3$)$_6$ from[39] (C$_6$H$_6$)$_2$Mo and PF$_3$. The existence of these complexes depends on the ability of the ligands to function as π-acceptors.

D. COMPLEXES OF MOLYBDENUM(II)

Molybdenum(II) may be stabilised in two ways: in mononuclear complexes with π-bonding ligands and through metal–metal bonding in polynuclear complexes with the more electronegative ligands. Unlike chromium(II), molybdenum(II), does not form a mono-nuclear aquo ion or complexes derived from it.

(*i*) *Mononuclear complexes*

Complexes of molybdenum(II) in which the metal is seven-co-ordinate have been described in Section C in connection with halogen oxidation of substituted molybdenum carbonyls.

Six-co-ordinate, low-spin complexes of molybdenum(II), Mo(diars)$_2$X$_2$ (X = Cl, Br, I) (μ = 2.8–2.9 B.M.), are obtained in a slow reaction (24 hours) between diars and an aqueous solution of molybdenum(III) and the appropriate halogen acid. The reaction appears to involve disproportionation[41] of molybdenum(III) to molybdenum(II) and (V).

(*ii*) *Polynuclear halogen complexes*

The halides of molybdenum(II), MoX$_2$ (X = Cl, Br, I), are polynuclear. X-ray analysis of the compounds [(Mo$_6$Cl$_8$)(OH)$_4$(H$_2$O)$_2$] 12 H$_2$O and [(Mo$_6$Cl$_8$)-Cl$_4$(H$_2$O)$_2$]6 H$_2$O has shown that the basic structural unit is the octa-μ_3-chlorohexamolybdenum(II) ion, [(Mo$_6$Cl$_8$]$^{4+}$, shown in Fig. 1(a). Eight chlorines are at the corners of a cube and six molybdenums at the face centres. Each molybdenum is in approximately square co-ordination with four chlorines and is also bonded to four other molybdenums 2.64 Å distant[42]. The metal atoms form an octahedral cluster[43].

The bonding in the Mo$_6$Cl$_8$$^{4+}$ cluster has been discussed in valence-bond[44,45] and in molecular-orbital terms[43,46]. The treatment most readily comprehensible in chemical terms is that due to Cotton and Haas[43]. They assume that

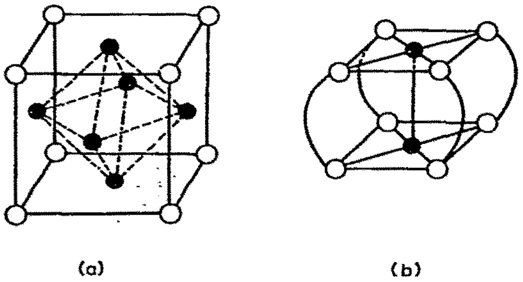


Fig. 1. Structures of (a) $[Mo_6Cl_8]^{4+}$ and (b) $[Mo(O_2CCH_3)_2]_2$. Closed circles represent molybdenum atoms. In (a) broken lines define the octahedral cluster of molybdenum atoms; Mo–Cl bonds are not shown. In (b) the oxygen atoms of carboxyl groups, Mo–O bonds, and the Mo–Mo bond are shown.

each molybdenum atom uses a d_{xy}-orbital, an s-orbital and the p_x- and p_y-orbitals to bind the four co-planar chlorines. The metal–metal bonding, using d_{z^2}, d_{xz}, d_{yz}, and $d_{x^2-y^2}$, is described in terms of molecular orbitals for the octahedral cluster. It is found that there are just sufficient strongly-bonding orbitals (A_{1g}, T_{1u}, T_{2g}, E_g, T_{2u}) to accommodate the 24 electrons of the cluster, thereby accounting for the diamagnetism and the stability of the cluster. Their treatment also shows the presence on each molybdenum of an empty, centrifugally-directed σ-orbital and so accounts for complexes of the type $(Mo_6Cl_8)L_6$.

The structures of the dihalides, Mo_6X_{12} ($X = Cl, Br, I$), have not been determined but they are thought to be polymeric, with $Mo_6X_8^{4+}$ clusters joined through halogen bridges[47].

The $Mo_6Cl_8^{4+}$ cluster will co-ordinate up to six ligands, one for each molybdenum, and a large number of complexes of the cluster are known. Examples include MX_4L_2 (where $M = Mo_6Cl_8$; $X = Cl, OH$; $L = py, NEt_3, H_2O, EtOH$), MX_6^{2-} ($X = Cl, Br, I, NCS$)[44,47], $[Mo_6X_8Y_6]^{2-}$ ($X = Br, I$; $Y = Cl, Br, I, OH$), $Mo_6X_8Y_4py_2$ ($Y = Cl, Br$)[47], $MCl_4(Ph_3EO)_2$ ($E = P, As$)[48], and MX_4L_2 (L = dimethylsulphoxide, dimethylformamide, methylsulphonate, $MeSO_3^-$). According to infrared studies the ligands in the last complex are bonded to $Mo_6Cl_8^{4+}$ through oxygen[49].

There have been some mechanistic studies of the reactions of chloromolybdenum(II) complexes. The rates of chloride exchange (using ^{36}Cl) and bromide substitution in $[Mo_6Cl_8]Cl_6^{2-}$ in water and moist ethanol are the same for both halides and independent of their concentrations suggesting that the reactions proceed through a common rate-determining step, probably aquation. No more than six chlorides may be replaced and there is no reaction with chlorides of the $Mo_6Cl_8^{4+}$ cluster[44].

Halogen in the ions $[Mo_6X_8(OH)_6]^{2+}$ ($X = Cl$[50], Br[51]), may be replaced by hydroxide giving species $[Mo_6X_{8-n}(OH)_n](OH)_6^{2-}$ ($n = 1, 2, 3$, etc.). There is evidence for a bimolecular rate-determining step, the rate being dependent on the molybdenum(II) and OH^- concentrations. A bimolecular process is reasonable since the chloro- and bromo-Mo^{II} structures are rigid, and a unimolecular process, involving distortion of the cluster to an activated complex of lower co-ordination number, would involve a very high activation energy. The rate is much less for the bromo complex than for the chloro complex suggesting the operation of steric factors: there is "more room" for S_N2 attack in the chloro compound than in the bromo compound[51].

(*iii*) *Binuclear carboxylates*

The compounds $[Mo(O_2CR)_2]_2$ have been obtained as yellow, diamagnetic solids by heating $Mo(CO)_6$ with various carboxylic acids. They are stable in the absence of air but give molybdenum blue in moist air. With pyridine the acetate gives[52] an adduct $[Mo(O_2CMe)_2py]_2$.

X-ray analysis of molybdenum(II) acetate[53] has shown that the structure is similar to that of cupric acetate with a short Mo–Mo bond of 2.11 Å (Fig. 1(b)).

E. OXIDATION STATES +3 TO +6

(*i*) *Binary halides and their derivatives*

(*a*) *Preparations.* The binary halides of molybdenum are listed in Table II which also gives preparative reactions and some of their properties[54–76]. Of particular interest is the reduction of $MoCl_5$ with benzene or chlorobenzene which has made $MoCl_4$ readily obtainable[67]. The best procedure for the preparation of MoF_5 is said[57] to be the reaction between MoF_6 and PF_3.

(*b*) *Structures and physical properties.* MoF_6 is octahedral with Mo–F = 1.840 Å, as indicated by an electron diffraction study of the vapour. The infrared and Raman spectra are also consistent with an octahedral structure[55]. MoF_5 is tetrameric in the solid (X-ray diffraction)[56]. Each molybdenum is in approximately octahedral co-ordination with four terminal fluorines (two at 1.85 and two at 1.70 Å) and two bridging fluorines (at 2.06 Å) (Fig. 2(a)). Molybdenum is also in octahedral co-ordination in solid MoF_3. According to Gutmann and Jack[60], X-ray analysis of MoF_3 indicates that the crystal has the cubic ReO_3 structure but a re-determination of the structure suggests a rhombohedral VF_3 structure[58]. It is possible that the compound studied by Gutmann and Jack was, in fact, an oxofluoride[58].

An electron diffraction study showed that, in the vapour, $MoCl_5$ is trigonal bipyramidal with all bond lengths equal (2.27 Å)[63]. Gillespie[77] considers that a re-investigation of the structure would be worthwhile since in most trigonal bi-

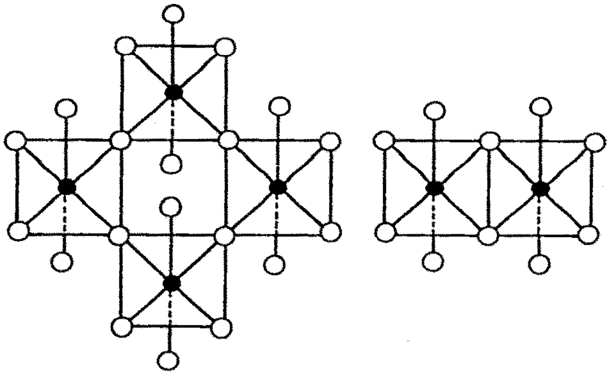
TABLE II

BINARY HALIDES

Compound	*Preparation*	*Properties and structure*[a] *(where known)*	*Ref.*
MoF_6	$Mo+F_2$	octahedral	54, 55
MoF_5	$Mo(CO)_6+F_2$	tetrameric (octahedral)	25, 56
	$Mo(CO)_6+MoF_6$		56
	MoF_6+Mo		56
	MoF_6+PF_3		57
MoF_4	Involatile residue in preparation of MoF_5		25, 56
MoF_3	MoF_5+Mo	octahedral	58, 60
	$MoBr_3+HF$		59
$MoCl_5$	$Mo+Cl_2$	trig. bipyramid vapour	61, 63
	MoS_2+CCl_4	dimeric (octahedral) solid; $\mu = 1.67$	62, 64, 65
$MoCl_4$	MoO_2+CCl_4	$\mu = 0.93$	66, 67
	$MoCl_5+C_6H_6$ or C_6H_5Cl		67
$MoCl_3$	$MoCl_5+H_2$	octahedral; $\mu = 0.67$	68, 69, 70
$MoBr_4$	$Mo(CO)_6+Br_2$	$\mu = 1.28$	24, 71
	$MoBr_3+Br_2$		71
$MoBr_3$	$Mo+Br_2$	octahedral; $\mu = 1.24$	70, 72, 73
MoI_3	$Mo+I_2$	$\mu = 1.4$	74
	$MoCl_5+HI$	or 1.85	75, 76
	$Mo(CO)_6+I_2$		76

[a] Magnetic moments (μ) in Bohr magnetons at *ca.* 20°.

pyramidal molecules the axial bonds are longer than the equatorial bonds. In the crystal, $MoCl_5$ is dimeric (X-ray diffraction) (Fig. 2(b))[64]. There are four terminal chlorines at 2.24 Å, two bridging chlorines at 2.53 Å, and a Mo–Mo bond of 3.84 Å. The molybdenum is in approximately octahedral co-ordination, the shape of the $MoCl_6$ octahedron being similar to that of MoF_6 in MoF_5. As in MoF_5 the bridging bonds are longer than the terminal bonds. $MoCl_5$ is monomeric in



(a) (b)

Fig. 2. Structures (not to scale) of[56] (a) $[MoF_5]_4$ and[64] (b) $[MoCl_5]_2$. Closed circles represent molybdenum atoms.

benzene[78] and in cyclohexane and carbon tetrachloride[79]. In $MoCl_3$[69] and $MoBr_3$[73] the molybdenum atom is also in octahedral co-ordination. The halide ions are hexagonal close-packed with the metal atoms in octahedral holes; there is distortion which brings pairs of metal atoms close together: in $MoCl_3$, Mo–Cl = 2.40 to 2.55 Å, Mo–Mo = 2.77 Å; in $MoBr_3$, Mo–Br = 2.57 Å, Mo–Mo = 3.30 Å.

Rather few physical measurements have been reported for the molybdenum halides. The electronic spectrum of $MoCl_5$ vapour shows rather-broad bands at 1.0, 15.2, 21.3, 27.8, 35.7, and >42.6 kK. Assignments are difficult because of the broadness of the bands and some dissociation to $MoCl_4$ and chlorine; the two highest frequency bands are assigned to charge-transfer transitions and the other bands to *d–d* transitions[79].

The magnetic moment of carefully-purified $MoCl_5$ has recently been redetermined over the range 83 to 333 °K. The value of 1.67 B.M.[65] is somewhat higher than previous values (1.52[80], 1.64[70]). Magnetic moments (where known) of the other halides are in Table II. The magnetic moments of the binary halides are less than the spin-only values and decrease with decreasing temperature. This is attributed to anti-ferromagnetism, the spin-exchange occurring via halogen bridges or through direct metal–metal bonding. It is noticeable that the deviation from the spin-only moments increases in the order $Mo^{V} < Mo^{IV} < Mo^{III}$ (correlating with the shorter Mo–Mo bonds in $MoCl_3$ and $MoBr_3$ compared with $MoCl_5$) and in the order I < Br < Cl.

(*c*) *Reactions of molybdenum halides.* These are summarised in Table III[81–98]. Reactions giving oxo-species of molybdenum(V) and (VI) have been reviewed and are not included here[5].

Addition reactions. Reactions of this type are common for the halides of molybdenum(IV) and molybdenum(III) but rare for $MoCl_5$. MoF_6 will add fluoride giving[81] MoF_7^- and MoF_8^{2-}. The number of ligands added is generally two for $MoCl_4$ and three for MoX_3 and the products are monomeric, paramagnetic, six-co-ordinate complexes except that with Ph_3AsO (but not, apparently, with Ph_3PO and Me_2SO), $MoCl_4$ gives[66] a diamagnetic, eight-co-ordinate complex, $MoCl_4(Ph_3AsO)_4$.

Substitution and solvolytic reactions. Molybdenum pentachloride reacts vigorously with compounds containing an OH or NH group giving hydrogen chloride and substituted chloro complexes. The commonest products are of the type $MoCl_3L_2$ (L = OR, NRR′) which, according to their low magnetic moments and molecular weights, are dimeric[88,89]. Whether the carboxylates, $MoCl_3(O_2CR)_2$, are dimeric is not known[92]. An investigation of the mechanism of these substitution reactions would be of great interest since it is uncertain whether $MoCl_5$ reacts as a dimer or as a monomer or whether the substitution reactions are followed by dimerisation of the products. In discussing the reaction between $MoCl_5$ and carboxylic acids in carbon tetrachloride, Larson[92] suggests that $MoCl_5$ pre-

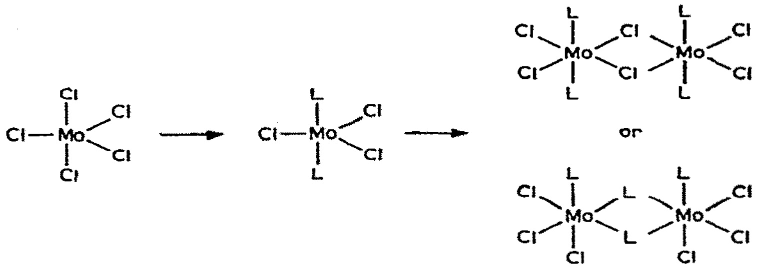
TABLE III

REACTIONS OF MOLYBDENUM HALIDES[a]

Halide and reaction	*Reagent*	*Product*[b]	*Ref.*
MoF_6; addition	MF in liq. IF_5	K_2MoF_8, Rb, $CsMoF_7$	81
	NOF, NO_2F	NO, NO_2MoF_7	82
MoF_6; reduction	NO, NOCl	$NO[MoF_6]$	82, 83
	PF_2	MoF_5	57
MoF_5; addition	NOF	$NO[MoF_6]$	83
MoF_4; addition	py, NMe_3, Me_2SO, Me_2NCHO	MoF_4L_2	84
$MoCl_5$; addition	Et_2O	$MoCl_5(Et_2O)_2$	85
	$POCl_3$	$MoCl_5(POCl_3)$	86
	PCl_5	$MoCl_5(PCl_5)$	87
	NMe_3	$MoCl_5(NMe_3)$	88
$MoCl_5$; substitution and solvolysis	conc. HCl, liq. SO_2	$MoOCl_3$, $MoOCl_5^{2-}$	5
	ROH, $-78°$	$[MoCl_3(OR)_2]_2$ (R = Me, Et, *n*-Pr)	89
	MeOH	$MoCl_3(OMe)_2$, $MoCl_2(OMe)_3$, $MoCl(OMe)_4$	90
	PhOH and *p*-CO_2H, $-CH_3$	$[MoCl_2(OPh)_3]_2$	10, 91
	$R \cdot CO_2H$	$MoCl_3(RCO_2)_2$	92
	Ph_3PO	$MoOCl_3(Ph_3PO)_2$	5
	NH_3 ($-33°$)	$MoCl_3(NH_2)_2$	88
	NH_3 (25°)	$MoCl(NH)(NH_2)_2$	88
	$NHMe_2$	$MoCl_3(NMe_2)_2(NHMe_2)$	88
	NHR_2	$[MoCl_3(NR_2)_2]_2$ (R = Et, *n*-Pr)	88
	NH_2R	$MoCl_3(NHR)_2(NH_2R)$ (R = *n*-Bu, *n*-Pr) and $[MoCl_2(NHR)_3]_2$ (R = *n*-Pr)	88
	NH_2R'	$[MoCl_2(NHR')_3]_2$ (R′ = Me, Et)	88
$MoCl_6$; reduction	NMe_3	$(NHMe_2)[MoCl_5(NMe_3)]$	88
	pyridine	$MoCl_4(py)_x$ ($x = 3, 4, 5$)	85, 93
	bipyridyl	$MoCl_4(bipy)$	94
	RCN	$MoCl_4(RCN)_2$ (R = Me, Et, *n*-Pr)	95
$MoCl_4$; addition	pyridine	$MoCl_4(py)_x$ ($x = 2, 3$)	67
	bipyridyl	$MoCl_4(bipy)$	94
	Ph_3AsO	$MoCl_4(Ph_3AsO)_4$	66
	thioxane	$MoCl_4$(*S*-thioxane)$_2$	96
$MoCl_4$; substitution	acetylacetone	$MoCl_2(acac)_2$	67
$MoCl_3$; addition	pyridine	$MoCl_3(py)_3$	97
$MoCl_3$; substitution	NH_3	$MoCl_2(NH_2)(NH_3)_2$	88
	bipyridyl	$[MoCl_2(bipy)_2]^+$-$[MoCl(bipy)_4]^-$	94
$MoBr_3$; addition	pyridine, γ-picoline	$MoBr_3L_3$	10, 96, 97, 98
	RCN	$MoBr_3(RCN)_3$	96
$MoBr_3$; substitution	NH_3	$MoBr(NH_2)_2(NH_3)_2$	88
	NH_2Me	$MoBr(NHMe)_2(NH_2Me)$	88
	$NHMe_2$	$MoBr_2(NMe_2)(NHMe_2)$	88
	bipyridyl	$[MoBr_2(bipy)_2]^+$-$[MoBr_4(bipy)]^-$	94
MoI_3; addition	pyridine	$MoI_3(py)_3$	76
MoI_3; substitution	bipyridyl	$[Mo(bipy)_3]^{3+}$ 3 I^-	94
MoI_3; reduction	diars	$Mo(diars)_2I_2$	76

[a] For ligand abbreviations see p. 315. [b] Reaction products are formulated as dimers where there is definite evidence (e.g., molecular weights, low magnetic moments).

serves its dimeric structure and that the axial chlorines react preferentially. However, the pentachloride appears to be monomeric (by the molecular weight) in benzene[78] and its electronic spectrum in cyclohexane and in carbon tetrachloride is the same as in the vapour (implying that it is also monomeric in these solvents)[79]. A more plausible interpretation is that replacement of the axial chlorines of a trigonal bipyramidal monomer first occurs and is followed by dimerisation. If this is the mechanism it seems likely that the dimeric reaction products contain nitrogen or oxygen rather than chlorine bridges:



Dimeric compounds $[MoCl_2L_3]_2$ are obtained from $MoCl_5$ and phenol and substituted phenols[10,91] and some amines[88]. A partial X-ray analysis of $[MoCl_2(OPh)_3]_2$ has shown the presence of bridging chlorines and a Mo–Mo bond of 2.8 Å, considerably shorter than in $[MoCl_5]_2$ (3.84 Å)[10]. It appears from the trend in the magnetic moments of the phenolate complexes (p-CO_2H > H > p-CH_3) that metal–metal interaction increases as the *para*-substituents become more electron-donating. This is reasonable because increased electron donation will cause a reduction of the residual charge on the metal atoms and so the repulsion between them will be reduced. Also, orbital expansion, leading to better orbital overlap in the metal–metal bond, will result from a decrease in the effective nuclear charge of the molybdenum atoms[10].

A qualitative feature of the substitution reactions is that the reactivity of $MoCl_5$ towards phenols (measured in terms of the vigour and speed of the reaction and the yield of product) increases as the *para*-substituent is[10] $CO_2H < H < CH_3$ and increases towards ammonia and amines (in terms of the number of Mo–Cl bonds broken) in the order[88] $NR_3 < NHR_2 < n\text{-}BuNH_2 < n\text{-}PrNH_2 < EtNH_2$, $MeNH_2 < NH_3$.

The deep colours of the phenolate complexes are due to charge-transfer transitions (ligand-to-metal), the energies decreasing as the electron-donor character of the *para*-substituent increases[10].

Substitution reactions are less common for the halides of molybdenum(IV) and molybdenum(III). Iodide is replaced more readily than chloride or bromide, e.g., with bipyridyl, $MoCl_3$ and $MoBr_3$ give complexes $[MoX_2(bipy)_2]^+[MoX_4(bipy)]^-$ but MoI_3 gives[94] $[Mo(bipy)_3]^{3+}3\,I^-$. This difference is in accordance with the class-A character of molybdenum(III).

(*d*) *Reduction with complex formation.* Reduction of $MoCl_5$ followed by complex formation is an important route to complexes of $MoCl_4$ with alkyl cyanides[95], pyridine[85,93,99] and bipyridyl[94]. The oxidation products of the organic ligands are not known except that with pyridine the product is probably the 1-4′-pyridyl-pyridinium ion[93,99]. Ligand-exchange reactions of the alkyl cyanide complexes of $MoCl_4$ have yielded many new complexes (see below). MoI_3 is not reduced by pyridine or bipyridyl but with diarsine a molybdenum(II) complex, $Mo(diars)_2I_2$, is obtained[76].

(*e*) *Ligand-exchange reactions.* Complexes $MoCl_4L_2$ and $MoCl_4B$ are formed in ligand-exchange reactions of $MoCl_4(RCN)_2$ (where L = pyridine, α-picoline, tetrahydrofuran, pentamethylene oxide, Ph_3PO, Ph_3P, Ph_3As, pyrazine, 2,6-dimethyl-pyrazine; B = bipy, 1,10-phenanthroline)[96]. Similar reactions occur with $MoBr_3(RCN)_3$ giving[96] $MoBr_3(RCN)L^2$ ($L = Ph_3P$, Ph_3As), $MoBr_3(MeCN)(bipy)$, $MoBr_3(pyrazine)_3$, and $MoBr_3(THF)_3$. Alkyl cyanides are not displaced by thioxane. The compound $MoCl_4(thioxane)_2$ (in which thioxane appears to be S-bonded) has been prepared[96] directly from $MoCl_4$.

These complexes of $MoCl_4$ and $MoBr_3$ are monomeric non-electrolytes. According to infrared data the substituents are *cis* in $MoCl_4(MeCN)_2$ and *trans* in $MoCl_4(PPh_3)_2$. The magnetic moments of the molybdenum(III) complexes are close to the spin-only value but the molybdenum(IV) complexes have low magnetic moments (2.2 to 2.7 B.M.). The electronic spectrum of $MoBr_3(RCN)_3$ is similar to that of $MoCl_6^{3-}$ as expected from the crystal-field order RCN > Cl > Br; crystal-field transitions are observed at *ca.* 15, 21, and 25 kK and charge-transfer transitions at higher frequencies. In the molybdenum(IV) complexes crystal-field transitions occur[96] at *ca.* 20 and 25 kK (also observed for $MoCl_6^{2-}$).

(*ii*) *Halide complexes*

(*a*) *Preparations.* The complexes are listed and preparative reactions outlined in Table IV[100–108]. Various features of these reactions are noteworthy. In reactions involving more than one halogen (MoF_6 and NaI[100], K_3MoCl_6 and Br_2[104], KI and $MoCl_5$[103]) the complex of the more electro-negative halogen is invariably obtained. In some reactions the product depends on the cation; MoF_8^{2-} with K^+ but MoF_7^- with[81] Rb^+ and Cs^+; salts of $MoBr_6^{2-}$ only with[103] Rb^+ and Cs^+, salts of $MoCl_6^{2-}$ from $MoCl_5$ and a chloride in liquid sulphur dioxide with only Rb^+ and Cs^+ (also formed in this reaction are salts of $MoOCl_4^{2-}$ which are the only products with pyH^+, $quinH^+$, and $Et_2NH_2^+$)[105,106]. Presumably lattice energy considerations are important in the formation of these compounds. It is not possible to obtain complexes of molybdenum(IV) by electrolytic reduction of molybdenum(VI) in aqueous solution since the reduction goes via molybdenum(V) to molybdenum(III).

TABLE IV

PREPARATION OF COMPLEX HALIDES

Compound	*Preparation*	*Ref.*
Molybdenum(VI)		
K_2MoF_8 and $(Rb,Cs)MoF_7$	See Table 3.	
Molybdenum(V)		
K_3MoF_8	MoF_6+KF in liq. SO_2	81
$MMoF_6$ (M = Na, K, Rb, Cs)	MoF_6+MI in liq. SO_2	100
$KMoCl_6$	Fuse $MoCl_5$ and KCl	101
Molybdenum(IV)		
Na_2MoF_6	MoF_6+excess NaI in liq. SO_2	102
K_2MoCl_6	$MoCl_5$+KCl in ICl	103
	[a]K_3MoCl_6+Br_2 (45°)	104
$(Rb_2,Cs_2)MoCl_6$	$MoCl_5$+MCl in liq. SO_2	105, 106
$(pyH)_2MoCl_6$	$MoCl_4(n\text{-}PrCN)_2$+(pyH)Cl in $CHCl_3$	106
$(Me_4N)_2MoCl_6\cdot\frac{1}{2}MeCN$	$MoCl_5$+$(Me_4N)Cl$ in MeCN	101a
$(Rb_2,Cs_2)MoBr_6$	$MoBr_3$+MBr+IBr (300°)	103
Molybdenum(III)		
K_3MoCl_6, $K_2MoCl_5(H_2O)$	Electrolytic reduction of Mo^{VI} in HCl	107
K_2MoCl_5	KI+$MoCl_5$	103
K_3MoBr_6, $K_2MoBr_5(H_2O)$	Electrolytic reduction of Mo^{VI} in HBr	108
$Rb_2Mo_2Br_9$	Rb_2MoBr_6+liq. NH_3	103
K_3MoI_6 (?, not isolated)	K_3MoBr_6+conc. HI	11

[a] That K_2MoCl_6 is formed is not certain as no analytical figures are given. At 450° the product is $MoCl_3$.

(*b*) *Structures and physical properties*. The complex ions in $NaMoF_6$[109] and K_2MoCl_6[103] are octahedral as indicated by X-ray analysis. (Mo–F = 1.74 Å; Mo–Cl = 2.31 Å). The binuclear ion $Mo_2Cl_9^{3-}$ is diamagnetic and is assumed to have a structure similar to that of $W_2Cl_9^{3-}$, i.e., two octahedrons joined by a common face, giving three chlorine bridges, and a metal–metal bond[110].

The magnetic moments of the complexes K_3MoCl_6 and $K_2MoCl_5H_2O$ are in the expected range, 3.7–3.8 B.M.[10,70,111,112]. Salts of the ions $MoCl_6^{2-}$ and $MoBr_6^{2-}$ have magnetic moments in the range 2.1 to 2.4 B.M. depending on the cation[101a,103,105,106]. The reduction below the spin-only value is attributed to spin–orbit coupling. The magnetic moments of the complexes M_2MoCl_6 (M = K, Rb, Cs, Tl) and M_2MoBr_6 (M = Rb, Cs) have been measured over the temperature range 80 to 290 °K, and plots of μ against temperature for the rubidium and caesium salts are in fair agreement with Kotani's theory for the t_{2g}^2 configuration[103]. Best values of the spin–orbit coupling constants (ζ_{nd}) are 450 cm^{-1} for the chloro-complexes and 500 cm^{-1} for the bromo-complexes (much less than the free ion value[9] for Mo^{4+} of 950 cm^{-1}). Salts of the ion MoF_6^- have magnetic moments around 1.7 B.M. The Curie–Weiss law is obeyed with rather large values of θ indicating anti-ferromagnetic interactions between the ions[113]. It should be noted that because of the large spin–orbit coupling constant for Mo^{5+} (ca. 1000 cm^{-1}) the t_{2g}^1 configuration should give moments much below the spin-only value. Evidently the spin–orbit coupling constant is considerably reduced in the complexes[9].

The electronic spectra of the molybdenum(III) halide complexes have recently been re-determined by Furlani and Piovesana[11] who give references to earlier work. The spectrum of K_3MoCl_6 in HCl $\gg 9$ *M* is the same as that of the solid; but at lower HCl concentrations the spin-allowed *d–d* bands are shifted to higher frequencies as a result of aquation and, between 1 and 2 *M* HCl, a spectrum attributed to $[MoCl_5(H_2O)]^{2-}$ is observed. The behaviour of the bromo-complex is similar. Spurious bands are sometimes observed as a result of slight oxidation of the molybdenum(III) solutions. The spectra show spin-forbidden transitions at *ca.* 10 kK (^2E_g, $^2T_{1g} \leftarrow {}^4A_{2g}$) and *ca.* 14 to 15 kK ($^2T_{2g} \leftarrow {}^4A_{2g}$) and spin-allowed crystal-field transitions at 17 to 21 kK ($^4T_{2g} \leftarrow {}^4A_{2g}$) and 20 to 26 kK ($^4T_{1g} \leftarrow {}^4A_{2g}$). The values of the crystal-field splitting parameter, Δ, and the nephelauxetic ratio, β, increase in the order I < Br < Cl. The spectra of salts of $MoCl_6{}^{2-}$ show crystal-field transitions at 21.51 ($^3T_{2g} \leftarrow {}^3T_{1g}$), 25.64 kK ($^3T_{1g}(P) \leftarrow {}^3T_{1g}$) and 27.78 (possibly $^3A_{2g} \leftarrow {}^3T_{1g}$)[106]. The value of Δ for $MoCl_6{}^{2-}$ is 22 kK. The spectrum of $KMoCl_6$ has a single asymmetric crystal-field band at 24.1 kK ($^2E_g \leftarrow {}^2T_{2g}$) giving $\Delta = 24.1$ kK[101a]. As expected Δ decreases in the order $Mo^V > Mo^{VI} > Mo^{III}$.

(*c*) *Chemical properties. Ligand exchange.* The hexahalide complexes are hydrolysed in water, the degree of hydrolysis decreasing from molybdenum(V) to molybdenum(III). Exchange reactions of K_3MoCl_6 have been useful in the preparation of organic complexes of molybdenum(III) (see below).

Oxidation–reduction. In aqueous solution the molybdenum(III) and molybdenum(IV) complexes oxidise rapidly in air. Molybdenum(III) is oxidised to molybdenum(V) by iron(III) and to molybdenum(VI) by Ce^{IV}. In the potentiometric titration curve of molybdenum(III) with Ce^{IV} there is no break corresponding to molybdenum(IV). It is clear that molybdenum(IV) is inaccessible as the chloro-complex in water[114].

Reduction of K_3MoCl_6 with diarsine has already been mentioned (p. 323).

(*d*) *Oxohalides and complexes.* Compounds of molybdenum(V) and molybdenum(VI) of this type are common[5]. Oxo-complexes of molybdenum(III), derived from MoO^+, have been described but there is no evidence (e.g., from infrared spectra) that they contain terminal oxygen. Wardlaw and Wormell[115] prepared complexes $MoOX \cdot xH_2O$ (X = F, Cl, Br). On the basis of chemical evidence they considered that the red and green forms of $MoOCl(H_2O)_4$ are *cis*- and *trans*-isomers respectively. The oxo-complexes of molybdenum(III) clearly need reinvestigation with modern techniques.

(*iii*) *Complexes with inorganic oxygen-donors*

A few, poorly characterised compounds with inorganic oxoanions are known, e.g., MoO_2SO_4[116], $MoO_2(NO_3)_2$[117], $K_4Mo(CO_3)_4 \cdot K_2CO_3 \cdot 2\,H_2O$[118]. The structure of $MoOPO_4$ has been determined[119].

(*iv*) *Complexes with inorganic nitrogen-donors*

Molybdenum, unlike chromium, has very little affinity for ammonia and the best-known molybdenum complexes with an inorganic nitrogen-donor are those with thiocyanate.

(*a*) *Complexes with* NH_3, NH_2^-, NH^{2-}, *and* N^{3-}. From a solution of $(NH_4)_2[MoCl_5(H_2O)]$ in liquid ammonia Wardlaw *et al.*[107b] obtained a complex $(NH_4)_2[MoCl_5(NH_3)]$ which rapidly hydrolyses in water. Rosenheim *et al.*[120] reported complexes $[MoCl_3(NH_3)_3]$, $[MoCl_2(NH_3)_4]Cl$, and $[Mo(NH_3)_6]Cl_3$; but, in view of recent work on the ammonolysis of molybdenum halides[88], their formulations are probably incorrect. Examples of ammonolysis products of the molybdenum halides include $[MoCl_2(NH_2)(NH_3)_2]$, $[MoBr(NH_2)_2(NH_3)]$ (from MoX_3 and liquid ammonia) and $[MoCl_3(NH_2)_2]$ and $[MoCl(NH)(NH_2)_2]$ (from $MoCl_5$)[88].

Various nitrido complexes of molybdenum(V) and molybdenum(VI) have been reported, e.g., $MoNCl_5^{3-}$,[121] MoO_3N^{3-},[122] and $MoNCl_3$[123]. The compound $MoNCl_3$ is obtained as dark brown crystals from the reaction of $MoCl_5$ and ClN_3. It is diamagnetic and the presence of a Mo–N multiple bond is shown by a band at 1045 cm^{-1} in the infrared spectrum. The force constant of this bond (7.86 mdynes/Å) is less than that of the MoO multiple bonds in $MoOCl_3$ (8.24) and $MoOCl_4$ (7.92). The compound is hydrolytically-unstable but gives an adduct with pyridine, $MoNCl_3(py)_3$[123].

(*b*) *Complexes with thiocyanate.* Thiocyanate complexes are formed by molybdenum in oxidation states +3, +4 and +5. Preparative reactions are given in Table V[124–126].

TABLE V

PREPARATION OF THIOCYANATE COMPLEXES

Compound	*Preparation*	*Ref.*
Molybdenum(V)		
$(pyH)_2MoO(NCS)_5$	$(pyH)_2MoOCl_5 + HNCS$; $(pyH)_4Mo_2O_4(NCS)_6 + HNCS$	124
$(Me_4N)_4Mo_2O_3(NCS)_8$	$(Me_4N)_2MoOCl_5 + NH_4NCS$	124
$(pyH)_4Mo_2O_4(NCS)_6$	$(pyH)_3MoOCl_5 + NH_4NCS$	124
$Mo(NCS)_5(Me_2CO)_2$ and $MoCl(NCS)_4(Me_2CO)_2$	$MoCl_5 + KNCS$ in acetone	125
Molybdenum(IV)		
$(pyH)_2Mo(NCS)_6$	$(pyH)_3Mo(NCS)_6 + Fe(CN)_6^{3-}$	126
Molybdenum(III)		
$M_3Mo(NCS)_6 \cdot x\,H_2O$ (M = K, NH_4, pyH)	$Mo^{III} + NCS^- + M^+$	107b

Preparations and chemical properties. Because of the instability of molybdenum(IV) in water the complex $(pyH)_2Mo(NCS)_6$ is prepared by triturating a suspension of $(pyH)_3Mo(NCS)_6$ with a concentrated aqueous solution of potassium ferricyanide[126]. A procedure[127] in which thiocyanate and pyridine are added to a 2 : 1 mixture of equimolar-solutions of molybdenum(III) and molybdenum(VI) (i.e., $2\ Mo^{III} + Mo^{VI} \rightleftharpoons 3\ Mo^{IV}$) gives mainly the molybdenum(V) complex[114].

In solution (e.g., ethanol, dioxan) the compounds are very susceptible to hydrolysis and the molybdenum(IV) complex disproportionates to molybdenum(III) and molybdenum(V). Its instability relative to molybdenum(III) and molybdenum(V) is similar to that of molybdenum(IV) with chloride and water (but quite different from the behaviour with cyanide ion which strongly stabilises molybdenum(IV))[114].

Physical properties. There are no X-ray structural data. Infrared data show that the thiocyanates are bound to molybdenum through nitrogen: the CN stretching frequencies for the molybdenum(V) and (IV) complexes[128] and the CN and CS[128,129] frequencies for the molybdenum(III) complexes occur in the appropriate range for N-bonded thiocyanate. Infrared data also show the absence of ligand-pyridine[130] and the presence in the molybdenum(V) complexes of terminal oxygen[10].

The magnetic moments of the molybdenum(III) complexes are close to the spin-only value[112b], but the moment of $(pyH)_2Mo(NCS)_6$ is low because of spin–orbit coupling[10]. The magnetic moment of $(pyH)_2MoO(NCS)_5$ is normal whilst the other molybdenum(V) complexes have low moments as a result of spin–spin interaction through oxygen bridges or a metal–metal bond[5].

In the electronic spectra of the oxomolybdenum(V) thiocyanate complexes the first crystal-field transition is observed as a weak broad peak near 12.5 kK, whilst ligand-to-metal charge-transfer transitions occur at higher frequencies[5]. Crystal-field transitions in the thiocyanates of molybdenum(IV) and molybdenum(III) are obscured by intense charge-transfer transitions[10,129]. The energies of the charge-transfer transitions increase in the order $Mo^{IV} < Mo^{V} < Mo^{III}$. The expected order in terms of the formal charges on the metal is $Mo^{V} < Mo^{IV} < Mo^{III}$; the reversal of molybdenum(IV) and (V) may be attributed to the effect of π-donation from oxygen in the oxomolybdenum(V) complexes[5].

(*v*) *Cyanide complexes*

The complexes are listed and preparative reactions and some of their properties are given in Table VI[131–143].

(*a*) *Structures, bonding, and physical properties.* The octacyanomolybdate anion in $K_4Mo(CN)_8 \cdot 2\ H_2O$ has been shown by X-ray analysis to be dodecahedral. Mo–C distances are 2.04 to 2.24 Å (average 2.15 Å), C–N, 1.07 to 1.27 Å

TABLE VI

CYANIDE COMPLEXES

Compound	*Preparation*[a]	*Properties*[b]	*Ref.*
Molybdenum(V)			
$MoO(OH)(CN)_2(H_2O)_2$	$K_4[Mo(CN)_8]$+dil. HNO_3	red	131
$K_3[Mo(CN)_8]$	$K_4[Mo(CN)_8]+Ce^{IV}$ or Mn^{VII}	yellow, $\mu = 1.66$	10, 127, 132
$K_3[Mo(OH)_4(CN)_4] \cdot 2\ H_2O^c$	$MoO(OH)_3+KCN+EtOH$	blue, $\mu = 1.91$	133
Molybdenum(IV)			
$K_4[Mo(CN)_8] \cdot 2\ H_2O$	$Mo^{VI}+N_2H_4 \cdot 2\ HCl$, KCN	yellow, diamag.	70, 132
	$[Mo_2O_4(NCS)_6]^{4-}+KCN$		127, 134
	$K_3[Mo(CN)_8]+[Fe(CN)_6]^{4-}$		135
	$K_4[Mo(CN)_7]$ in air		136
$M_2[Mo(CN)_8R_2] \cdot 4\ H_2O$	see text	red	137
$K[Mo(CN)_5]$	Aq. $Mo^{VI}+KCN$	white, diamag.	136b
$K_4[Mo(OH)_3(CN)_5] \cdot x\ H_3O$	photolysis of $K_4[Mo(CN)_8]$	purple	138
$K_4[MoO_2(CN)_4]$	Aq. $Mo^{VI}+KCN$	red-brown, diamag.	136b
$K_4[Mo(OH)_4(CN)_4] \cdot 4\ H_2O^c$	$MoO(OH)_3+KCN+KOH$	red, diamag.	131, 133
$K_3[Mo(OH)_3(CN)_4(H_2O)] \cdot 2\ H_2O$	$MoO(OH)_3+KCN+EtOH$	blue	131
$K_2[Mo(OH)_2(CN)_4]$	photolysis of $K_4[Mo(CN)_8]$	blue	137
$K_3[MoS(OH)(CN)_4(H_2O)_2] \cdot 4\ H_2O$	$K_3[MoS(CN)_4(H_2O)_2]$+air	violet	139
$K_4[MoO_2(CN)_5(NO)] \cdot 3\ H_2O$	$K_4[Mo(CN)_5(NO)]$+air	yellow, diamag.	140
Molybdenum(III)			
$K_4[Mo(CN)_7] \cdot 2\ H_2O$	$K_3[MoCl_6]+KCN$, N_2	red, $\mu = 1.74$	10, 129, 136a
$K_2[Mo(CN)_5]$	$K_4[Mo(CN)_8]$+molten KCN	red, $\mu = 0.6$	141
$K_3[MoS(CN)_4] \cdot 2\ H_2O$	$Mo^{VI}+KCN+H_2S$	light blue	142
Molybdenum(II) or (O)[d]			
$K_4[Mo(OH)_2(CN)_5(NO)]$ or $K_4[Mo(CN)_5(NO)]$	$Mo^{VI}+H_2NOH+OH^-+KCN$	purple, diamag.	133, 143

[a] All reactions in aqueous solution. [b] Colour and magnetic moment (μ) in Bohr magnetons at ca. 20°. [c, d] The compounds may be identical: see text.

(average 1.15 Å), and N–N separations are 3.64 to 4.82 Å with an average of four longer distances at 4.75 Å and fourteen shorter at 3.98 Å. Strictly, the anion belongs to the point-group C_s, but, for a structure with averaged bond lengths and angles, the point-group is D_{2d}, the eight cyanides occupying the vertices of a dodecahedron with triangular faces (Fig. 3(a))[144]. Discussions of the structure and bonding have generally assumed D_{2d} symmetry. An alternative structure for eight-co-ordination is the square anti-prism (D_{4d} symmetry, Fig. 3(a)). The dodecahedral and anti-prismatic structures are both obtained by distortions of a cube (Fig. 3(a)). The structures of the other cyanide complexes have not been determined by X-ray crystallography. Because the infrared spectra of $K_4[Mo(CN)_8]$ and $K_3[Mo(CN)_8]$ are very similar it is assumed that the latter compound is also dodecahedral[145].

The bonding in the octacyanides is described from a valence-bond approach in terms of d^4sp^3 hybrids with one non-σ-bonding d-orbital occupied in molybdenum(V) by one electron and in molybdenum(IV) by two electrons in agreement with diamagnetism for the molybdenum(IV) compound[70,132] and one unpaired

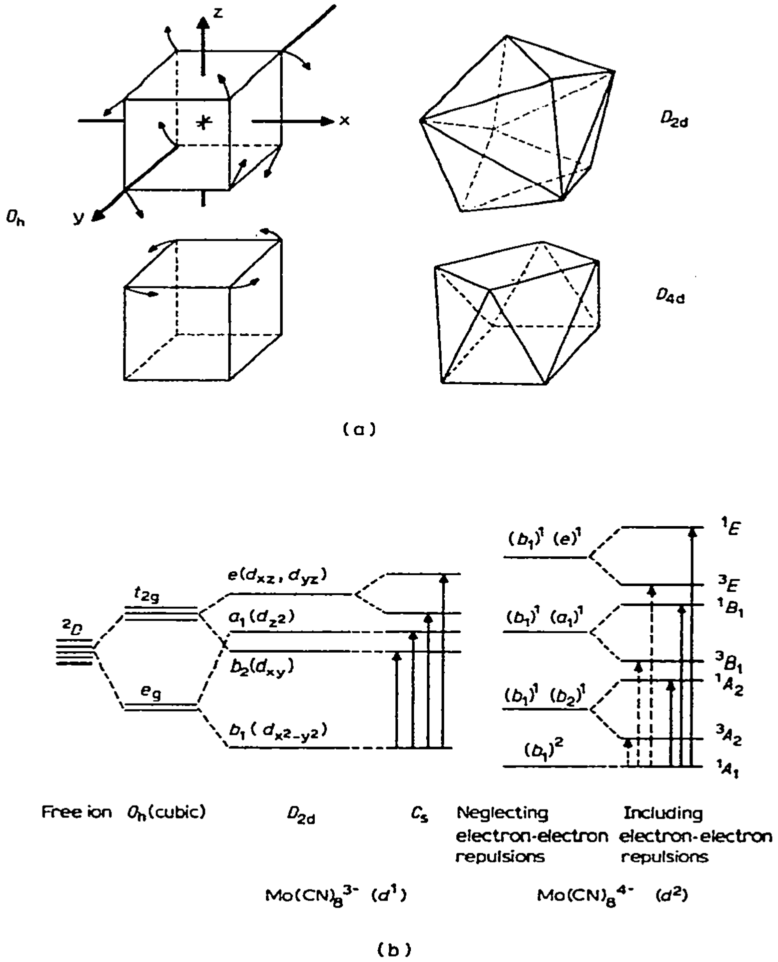


Fig. 3. (a) Distortions of a cube to a dodecahedron (top) and a square antiprism (bottom) (adapted from ref. 149). The reference axes pass through the face centres of the cube. (b) One-electron molecular-orbital energy level schemes for $[Mo(CN)_8]^{3-}$ (left) and $[Mo(CN)_8]^{4-}$ (right) (adapted from ref. 146h). Full vertical lines show spin-allowed *d–d* transitions, broken vertical lines spin-forbidden *d–d* transitions.

electron for molybdenum(V)[10,132]. More recent crystal-field and ligand-field descriptions show that one of the *d*-orbitals is strongly stabilised, $d_{x^2-y^2}$ for a dodecahedron and d_{z^2} for a square anti-prism[146]. Neither of these orbitals has the correct symmetry for σ-bonding. The $d_{x^2-y^2}$ orbital of the dodecahedron, but not the d_{z^2} orbital of the anti-prism, is capable of π-bonding with the anti-bonding (π^*) orbitals of the cyanides.

Energetically, there is very little difference between the dodecahedral and antiprismatic structures[147]. It is possible that the dodecahedral structure is slightly favoured by π-bonding involving the $d_{x^2-y^2}$ orbital. According to electron-spin resonance measurements on $[Mo(CN)_8]^{3-}$ enriched with ^{13}CN, there is extensive delocalisation of the unpaired electron of molybdenum(V) onto the carbon atoms[148]. Four of the cyanides are better disposed for π-bonding than the others and, in agreement with this, up to four cyanides may be replaced by hydroxide giving[146b] the ion $[Mo(CN)_4(OH)_4]^{4-}$. Against this it is argued that the effect of an electron pair in $d_{x^2-y^2}$ could be to cause an inhomogeneous swelling of the complex so that σ-bonding is loosened to an extent for which π-bonding cannot entirely compensate[147]. How these two descriptions are related is not clear.

Whether the $[Mo(CN)_8]^{4-}$ ion is dodecahedral or anti-prismatic in solution is uncertain. Raman[149], infrared[145,149] and electronic spectra[146e,f,g,h] have been interpreted with both models. Infrared data on $K_4Mo(CN)_8 \cdot 2\,H_2O$ are consistent with a dodecahedral structure for the solid but it appears that infrared and Raman spectroscopy cannot determine uniquely the structure of the ion in solution[149].

The structure of the molybdenum(III) complex $K_4Mo(CN)_7 \cdot 2\,H_2O$, is not known. Two possibilities are eight-co-ordination, dodecahedral (i.e., an anion $[Mo(CN)_7(H_2O)]^{4-}$) or seven-co-ordination, pentagonal bipyramidal (i.e., $[Mo(CN)_7]^{4-}$). The latter structure would be expected from the nine-orbital rule. The magnetic moment[10,129], corresponding to one unpaired electron, is consistent with both structures (for the pentagonal bipyramid an orbital doublet lies lowest)[150]. That the complex is readily and rapidly oxidised (unlike $Mo(CO)_2(diars)I_3$ and $K_4Mo(CN)_8$) suggests that one of the three d-electrons occupies a relatively unstable orbital and that the structures of the molybdenum(III) and molybdenum(IV) compounds are similar.

The structure of the compound $KMo(CN)_5$ is also unknown[136b]. The present writer has been unable to repeat the preparation of this compound — an experience shared by Figgis and Lewis[9].

The compound $K_2Mo(CN)_5$ also presents structural problems[141]. The oxidation number of the molybdenum, determined titrimetrically, is three and the compound appears to be monomeric in solution. C–N stretching frequencies are in the same range as for $K_4Mo(CN)_8$, but the low magnetic moment of the compound both in the solid state and in solution strongly suggest dimerisation with spin-pairing.

The purple pentacyanonitrosyl complex obtained by reducing with hydroxylamine an alkaline solution of molybdate and cyanide has been variously formulated as a complex of molybdenum(O), $K_4[Mo(CN)_5NO]$ (either with or without water of hydration)[143] and as an eight-co-ordinate complex of molybdenum(II)[133], $K_4[Mo(OH)_2(CN)_5NO]$. Co-ordination of nitric oxide as NO^+ is indicated by the N–O stretching frequency. According to Riley and Ho[143b] (whose work is the most convincing) the compound is very sensitive to air and moisture and the apparent presence of water or hydroxide is due to partial decomposition. The pure compound shows an N–O stretching frequency at 1455

cm^{-1}; a band at 1580 to 1590 cm^{-1} (assigned by Griffith *et al.*[133] as the N–O stretch) develops during exposure of the mulls to the atmosphere. The diamagnetism is consistent with molybdenum(O) and the rather low N–O frequency is understandable in terms of back donation from molybdenum(O) favoured by the zero formal charge on the metal.

Atmospheric oxidation of the purple complex gives[140] a yellow, diamagnetic molybdenum(IV) complex, $K_4[Mo(CN)_5O_2NO] \cdot 3H_2O$. The N–O stretching frequency (1580 cm^{-1}) is higher than in the purple molybdenum(O) compound, which is expected since molybdenum(IV) should be a poorer π-donor than molybdenum(O). (If the band at 1580 cm^{-1} is assigned as the N–O stretch in the purple molybdenum(O) or molybdenum(II) complex then it becomes necessary to explain why the frequency is the same in the molybdenum(IV) complex.)[140] Further work on these complexes seems called for.

Hydroxocyanides. The literature on the hydroxocyanides is confused and a careful reinvestigation of these compounds would be worthwhile. Bucknall and Wardlaw[131] reacted molybdenum(V) hydroxide, $MoO(OH)_3$, with the theoretical amount of potassium cyanide and obtained a *blue* aqueous solution from which potassium hydroxide precipitated *red* crystals, $K_4[Mo(OH)_4(CN)_4]\ 4H_2O$. The *red* complex gave a *blue* aqueous solution from which ethanol precipitated *blue* crystals, $K_3[Mo(OH)_3(CN)_4(H_2O)]\ 2H_2O$. With excess KCN both compounds gave $K_4Mo(CN)_8$.

Adamson and Perumareddi[151] obtained a *blue* diamagnetic complex, $K_3[Mo(CN)_4(OH)_3(H_2O)]$ (apparently the anhydrous form of Wardlaw's blue compound) as the ultimate photolysis product of an aqueous solution of $K_4[Mo(CN)_8]$. Jakob *et al.*[137] considered the *blue* photolysis product to be $K_2Mo(CN)_4(OH)_2$, presumably an octahedral, paramagnetic complex of molybdenum(IV), which differs from Adamson's *blue* complex by one KOH and one H_2O. Since, according to Wardlaw, the hydroxo complexes are readily interconverted, it is possible that the nature of the solid obtained as the ultimate photolysis product is dependent on conditions of isolation and drying. Collenberg[138] exposed a solution of $K_4Mo(CN)_8$ in molar KOH to bright sunlight and isolated a violet compound, $K_4[Mo(OH)_3(CN)_5]\ x\ H_2O$.

Griffith *et al.*[133] apparently repeated Wardlaw's experimental work and obtained a *blue* complex with a magnetic moment of 1.91 B.M., slightly greater than the spin-only moment for molybdenum(V) or low-spin molybdenum(III). They formulated the complex with molybdenum(V), $K_3[Mo(OH)_4(CN)_4]\ 2\,H_2O$, or with molybdenum(III), $K_3[MoO_2(CN)_4(H_2O)_2]$. It is possible that this material is a mixture of Wardlaw's and Jakob's compounds.

Steele[136b] was unable to repeat the preparation of Wardlaw's red and blue complexes but obtained a *brown* complex, $K_4[MoO_2(CN)_4]$, by refluxing a solution of KCN and MoO_3. However, Golding and Carrington[146e] were able to prepare Wardlaw's *red* complex and gave it the same formula. They report its electronic spectrum in aqueous solution (a *d–d* transition at 20 kK and a charge-transfer transition above 42 kK).

Compounds with "eight(quasi-ten)-co-ordination". Compounds of the general formula $M_2[Mo(CN)_8R_2]\cdot 4\ H_2O$ (M = Cd, Mn; R = H_2O, NH_3, N_2H_4) separate as red crystals form aqueous solution[137]. Their aqueous solutions are stable in the dark but hydrolyse in light to $[Mo(CN)_4(OH)_2]^{2-}$. Hoard and Silverton[147] describe the molybdenum as having "eight(quasi-ten)-co-ordination" and suggest an antiprismatic structure with the two R groups located above and below the two square faces of the antiprism.

Electronic absorption spectra. There have been a number of attempts to interpret the electronic spectra of $K_3Mo(CN)_8$ and $K_4Mo(CN)_8$ using crystal-field and ligand-field theory and the original papers should be consulted for details[10,146e,f,g,h]. Adamson *et al.*[146h] give a useful critical account of earlier work. The splitting of the *d*-orbitals according to their ligand-field calculation is shown in Fig. 3(b) for D_{2d}(dodecahedral) and C_s symmetry. The effect of a reduction in symmetry from D_{2d} to C_s is to split the *e*-level into two *a*-levels. Peak positions and assignements are given in Table VII. There is good agreement between observed and calculated peak positions although not all possible transitions are observed.

TABLE VII

ELECTRONIC SPECTRA OF MOLYBDENUM CYANIDE COMPLEXES

$K_3[Mo(CN)_8]$[a]	$K_4[Mo(CN)_8]\cdot 2\ H_2O$[a]	$K_4[Mo(CN)_7]\cdot 2\ H_2O$[b]
25.8 $^2B_2 \leftarrow {}^2B_1$	19.6 $^3B_1 \leftarrow {}^1A_1$	19.8 *d–d*
32.0 $^2A_1 \leftarrow {}^2B_1$	23.2 $^1A_2 \leftarrow {}^1A_1$	26.3 *d–d*
36.8 39.8 $\Big\}$ $^2E \leftarrow {}^2B_1$	27.2 $^1B_1 \leftarrow {}^1A_1$	45.5 C–T
	32.45 $^1E \leftarrow {}^1A_1$	
	37.4 $^1E' \leftarrow {}^1A_1$	
	41.67 C–T	

[a] Peak positions in kK (1 kK = 10^{-3} cm^{-1}) and assignments from ref. 146h. C–T denotes a charge-transfer transition.
[b] From ref. 10.

Good agreement is also obtained by König[146g] assuming D_{4d} symmetry (i.e., the antiprismatic structure) but his assignments have been criticised[146h] because the strongest optical absorption is assigned to highly-forbidden two-electron jumps.

The spectrum of $K_4Mo(CN)_7\cdot 2H_2O$ has been measured but assignments have not been attempted. There are two *d–d* transitions and one charge-transfer transition.[10]

Magnetic measurements. The magnetic moments of the cyanide complexes are included in Table VII. The complexes are all low spin having one or no unpaired electrons.

The electron-spin resonance spectra of $K_3Mo(CN)_8$ and $Ag_3Mo(CN)_8$ as powders have a sharp single line at $g = 1.993$[146e], or 2.005 ± 0.005[146g], the sharpness suggesting that the g-tensor is isotropic. An electrostatic crystal field calculation gives $g = 1.92$, much less than the observed value, indicating extensive mixing of the d-orbitals and the cyanide orbitals[146e].

(*b*) *Chemical properties.* Some of the more important reactions of the complexes are apparent from Table VI.

Reactions of the cyanide ligands. With dimethyl sulphate two cyanides of $K_4Mo(CN)_8 \cdot 2\,H_2O$ are methylated and two are displaced giving $[Mo(CN)_4(CH_3NC)_2(H_2O)_2] \cdot 4\,H_2O$. With potassium cyanide this compound reverts to the octacyanide[152].

With BF_3, $K_4Mo(CN)_8$ behaves as a Lewis base giving $K_4Mo(CN)_8(BF_3)_8$ which contains cyanide bridges between molybdenum and boron atoms (i.e., $Mo{-}C{\equiv}N{-}BF_3$)[153].

Cyanide exchange and photolysis. Unlike many molybdenum complexes the octacyanides do not undergo rapid hydrolysis in water. $K_4Mo(CN)_8$ is inert with respect to exchange of ^{14}C-labelled cyanide in the dark.[154] Hydrolysis does, however, occur when an aqueous solution is irradiated by ultraviolet light, the colour changing from yellow through red and green to blue (cf. p. 338)[137,151,154,155]. High-intensity irradiation of aqueous $K_4Mo(CN)_8$ produces a transient red species formulated by Jakob *et al.*[137] as $[Mo(CN)_8(H_2O)_2]^{4-}$ and by Adamson and Perumareddi[151] as $[Mo(CN)_7OH]^{4-}$. They consider that the mechanism of photolysis is

$$R + HCN \rightleftharpoons Mo(CN)_8{}^{4-}; \quad R \rightarrow B$$

where R is the red intermediate and B the final blue product, $[Mo(CN)_4(OH)_3(H_2O)]^{3-}$.

Oxidation–reduction. Molybdenum(IV) is strongly stabilised in the octacyano complex with respect to both oxidation and reduction (presumably because for molybdenum(IV) the stable $d_{x^2-y^2}$-orbital is fully occupied). Oxidation to $K_3Mo(CN)_8$ requires powerful oxidising agents (Ce^{IV} and Mn^{VII})[127] and reduction to $K_2Mo(CN)_5$ requires[141] molten KCN. There is some reduction of $K_4Mo(CN)_8$ by potassium in liquid ammonia to an unidentified cyano complex which is extremely air-sensitive[156]. In contrast, the molybdenum(III) complex $K_4Mo(CN)_7 \cdot 2\,H_2O$ rapidly oxidises in air[136] and the molybdenum(V) complex is reduced by mild reducing agents (e.g., potassium ferrocyanide)[135].

$K_3Mo(CN)_8$ is highly photosensitive undergoing reduction to $K_4Mo(CN)_8$, and the solid and its solutions should be stored and handled in the dark[135]. Electron transfer between the ions $[Mo(CN)_8]^{3-}$ and $[Mo(CN)_8]^{4-}$ is very fast indicating that a true electron-transfer process is involved and not radical or ion exchange[157].

(*vi*) *Complexes with organic oxygen-donors*

Complexes of the molybdenum halides with oxygen-donors are described in section E.(iii) and the molybdenum(II) carboxylates in section D(iii). Complexes of molybdenum(III) with urea and *N*,*N*-dimethylformamide MoX_3L_3 (X = Cl, Br) and $[Mo(urea)_6]Br_3$, have also been prepared[12]. Of the remaining complexes the best known are those with acetylacetone and other β-diketones and with oxalate (Table VIII). With two exceptions these complexes are all derived from oxo-molybdenum species. The complexes of molybdenum(V) and (VI) have been reviewed[5].

TABLE VIII

COMPLEXES WITH ACETYLACETONE AND WITH OXALATE LIGANDS

Oxidation state	*Acetylacetone*	*Oxalate*	*Ref.*
+6	$MoO_2(acac)_2$	$NaNH_4[MoO_3(ox)\,(H_2O)_2]$	5
		$K_2[Mo_2O_5(ox)_2(H_2O)_2]$	5
		$(quinH)_2[MoO_2(ox)_2]$	5
+5	$MoO(OH)\,(acac)_2 \cdot 4\,H_2O$	$K_2[Mo_2O_4(ox)_2(H_2O)_2]$	5
	$MoO_2(acac)$		5
	$Mo_2O_3(acac)_4$		5
+4	$MoO_2(acacH)_2$	$MoO(ox)\,(H_2O)_3$	158, 163a
		$(NH_4)_2[Mo_3O_4(ox)_3(H_2O)_5]$	163b, 164, 165, 166
		$(NH_4)_4MO(ox)_4 \cdot 8\,H_2O$	118
+3	$Mo(acac)_3$	$Mo(OH)\,(ox)\,(H_2O)_3$	107b, 107c, 159, 161, 162
	$MoO(acac)_2 \cdot 2\tfrac{1}{2}H_2O$	$Mo_2O(ox)_2(H_2O)_6$	160, 163a
		$Mo_4O_3(ox)_3 \cdot 12\,H_2O$	163a

(*a*) *Acetylacetonates.* A diamagnetic molybdenum(IV) complex, MoO_2-$(acacH)_2$, was obtained as brown needles by reduction with zinc dust of a hot solution of $MoO_2(acac)_2$ in acetylacetone[158]. The compound was originally formulated $Mo(OH)_2(acac)_2$ but the infrared spectrum showed the absence of OH and suggested the presence of neutral acetylacetone. On treatment of the compound with aqueous alkali "molybdenum(IV) oxide monohydrate" separates quantitatively. Acetylacetone may be replaced by other β-diketones but not by CO, Ph_3P, Ph_3As and PhNC. Reduction of molybdenum(VI) to molybdenum(IV) in an oxygen environment is rather unusual and the evidence for molybdenum(IV) in this compound is not entirely convincing. The compound is described as having the same properties as the "black form" of molybdenum(VI) acetylacetonate prepared by Larson and Moore and shown later[159] to be a diamagnetic molybdenum(V) complex, $Mo_2O_3(acac)_4$.

The compound $MoO(acac)_2 \cdot 2\tfrac{1}{2}\,H_2O$ is obtained as brown crystals by heating acetylacetone and $MoOCl(H_2O)_4$ in ethanol, but the presence of terminal oxygen has not been proved. Aerial oxidation gives[160] green $MoO_2(acac)$.

$Mo(acac)_3$ has been prepared by heating[107c] $(NH_4)_2MoCl_5(H_2O)$ or[159,161] K_3MoCl_6 with acetylacetone and by refluxing acetylacetone with[159] $Mo(CO)_6$. Complexes with other β-diketones were later obtained from the hexacarbonyl[162]. The compound oxidises rapidly and exothermically in air to[159] $Mo_2O_3(acac)_4$. It does not react with water, benzophenone, pyridine or tripenylphosphine, but with carbon tetrachloride it gives chloromolybdenum materials of variable composition[159]. The magnetic moment (3.8 B.M.) is normal and the electronic spectrum shows charge-transfer peaks at 27 and 23.3 kK[162].

(*b*) *Oxalato complexes.* Various oxalato complexes of molybdenum(III) were prepared by Wardlaw *et al.* from solutions of[107b] $(NH_4)_2MoCl_5(H_2O)$ or[163] $Mo(OH)_3$ and oxalates (see Table VIII).

Aerial oxidation of solutions of molybdenum(III) oxalates gives molybdenum(IV) complexes of empirical formula[163a] $MoO(C_2O_4)(H_2O)_3$. A red-violet salt, $M_2[Mo_3O_4(C_2O_4)_3(H_2O)_5]$ ($M = K$, pyH), has also been isolated[163b]. A detailed spectrophotometric and titrimetric investigation[164] of the oxidation has shown that molybdenum(V) is formed initially and that the species $[Mo_3O_4(C_2O_4)_3]^{2-}$ arises from a slow reaction between molybdenum(V) and molybdenum(III). In the polarographic reduction of a solution of molybdenum(IV) oxalate only two waves are observed ($Mo^{VI} \rightarrow Mo^{V}$ and $Mo^{V} \rightarrow Mo^{III}$) but for solutions of molybdenum(III) oxalate which have been oxidised in air a third wave, attributed to $Mo^{IV} \rightarrow Mo^{III}$, is observed. Aqueous solutions of the molybdenum(IV) complex are stable in air for long periods. Saturation of the solution with HCl gas gives a chlorooxalato complex of molybdenum(IV). This behaviour is quite different from that of other molybdenum(IV) compounds (e.g., $K_4Mo(CN)_8$) which disproportionate in concentrated hydrochloric acid to molybdenum(III) and molybdenum(V)[165]. Stabilisation of molybdenum(IV) by oxygen-donors is unusual and it is possible that the basic structural unit is a trinuclear cluster $[MoO(C_2O_4)(H_2O)_3]_3$ with metal–metal bonds and oxygen bridges and with one oxalate and one or more water molecules co-ordinated to each molybdenum. Such a structure is consistent with the diamagnetism[166], stability and slow rate of formation of the complex.

The complex $(NH_4)_4[Mo(C_2O_4)_4] \cdot 8\,H_2O$ is said to be formed by electrolytic reduction of ammonium molybdate in the presence of oxalic acid. It is brown and diamagnetic and apparently contains eight-co-ordinate molybdenum(IV)[118].

(*vii*) *Complexes with organic nitrogen-, arsenic- and phosphorus-donors and with "oxine" and EDTA*

Molybdenum forms rather few complexes in which these are the only donor atoms. Substituted carbonyls are described in section C, complexes of molybdenum halides in section E.(i), and molybdenum(II) complexes of phosphorus and arsenic donors in section D. Complexes of these donors with oxo-species are also known[5], e.g., $MoOCl_3(MeCN)_2$, $MoOCl_3(bipy)$, $Mo_2O_3Cl_4(bipy)_2$, $Mo_2O_4Cl_2(bipy)_2$, $MoO_3(dien)$, $MoOCl_3(PPh_3)_2$.

(*a*) *Pyridine and substituted pyridines.* No complexes of the type $Mo(py)_6$ are known; but the bidentate ligand 2-aminomethyl-pyridine (amp) forms a complex $[Mo(amp)_3]^{3+}$ with aqueous molybdenum(III) which may be crystallised as the yellow perchlorate salt (μ = 3.7 B.M.)[167].

(*b*) *2,2′-bipyridyl and 1,10-phenanthroline.* By reacting 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen) with $(NH_4)_3MoCl_6$, Steele[168] obtained dark red complexes $[Mo(bipy)_3]X_3$ and $[Mo(phen)_3]X_3$ (X = Cl, Br, I) with magnetic moments of 3.7 to 3.8 B.M. From MoI_3 and excess bipyridyl, Carmichael *et al.*[94] obtained a crimson compound $[Mo(bipy)_3]I_3$ (μ = 3.93) but they were unable to prepare the corresponding chloride and bromide salts and, instead, obtained compounds $[MoX_2(bipy)_2]^+[MoX_4(bipy)]^-$ (X = Cl, Br) (crimson, μ = 3.62 B.M.). Furlani and Piovesana[11] were also unable to prepare tris(bipyridyl) complexes and obtained compounds $BH[MoCl_4B]$ (B = bipy or phen) (brown solids, 1 : 1 electrolytes in nitromethane). Their formulae are based on analyses for chlorine only. Herzog and Schneider[38] appear to have prepared a compound $[Mo(bipy)_3]Cl_3$ since they describe its reduction to $Mo(bipy)_3$. The bipyridyl and phenanthroline complexes of molybdenum(III) are stable to oxidation. Stabilisation of molybdenum(III) by π-acceptor ligands is, of course, expected.

(*c*) *Phosphorus- and arsenic-donors.* Complexes of the higher-oxidation states with these donors are rare. A molybdenum(IV) complex, $MoBr_4(diars)$, (orange-brown, μ = 1.96 B.M.) is formed by the action of excess bromine on $Mo(CO)_4(diars)$[21].

(*d*) *Oxine and EDTA derivates.* With 8-hydroxyquinoline (oxine) and ethylenediaminetetraacetate ($EDTA^{4-}$), molybdenum(VI) and molybdenum(V) form complexes[5]:

$[MoO_2(oxine)_2]$ $[MoO(OH)(oxine)_2]$ $[MoOCl(oxine)_2]$ $[MoOCl_3(oxine)]$ $[Mo_2O_3(oxine)_4]$

$Na_4[Mo_2O_6(EDTA)] \cdot 8\,H_2O$ $Na_2[Mo_2O_4(EDTA)] \cdot H_2O$

No complexes of molybdenum(IV) with these ligands are known. A complex of molybdenum(III) with oxine is formed by heating $Li_3MoCl_6 \cdot LiCl \cdot 9\,H_2O$ with a solution of oxine in ethanol. On the basis of elementary analyses the compound was assigned the rather unusual formula $Mo_4(oxine)_5Cl_7(H_2O)_7$. To explain the low magnetic moment (1.2 B.M.) a bridged structure involving eight-co-ordination is suggested[169].

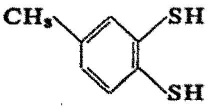
(*viii*) *Complexes with sulphur-donors*

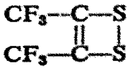
Although molybdenum in its higher oxidation states has class-A character, it does have some affinity for sulphur-donor ligands. The sulphides, Mo_2S_3, MoS_2, Mo_2S_5, and MoS_3 are well known[7]. A recent X-ray analysis of Mo_2S_3 has shown that the sulphur atoms form a distorted close-packed array with the metal atoms displaced 0.34 Å from the centres of octahedral holes and metal–metal bonds of 2.85 Å[170]. In MoS_2 the metal atom is surrounded by six sulphurs at the vertices of a trigonal prism. MoS_3 is amorphous[171].

Molybdates react with hydrogen sulphide with successive replacement of oxygen by sulphur; deep-red tetrathiomolybdates may be isolated[172] as ammonium or alkylammonium salts, R_2MoS_4.

Numerous colour reactions of molybdates with organo-sulphur compounds are described in the analytical literature but the compounds formed have generally not been well characterised. The reaction of cysteine, $CH_2(SH)CH(NH_2)COOH$, with molybdenum(VI) and molybdenum(V) in aqueous solution has been studied spectrophotometrically. With molybdenum(VI) the ligand : metal ratio varies from 3 : 1 to 1 : 1 but with molybdenum(V) only the 1 : 1 complex is formed. It is thought that co-ordination is through the ionised mercapto- and either the amino or carboxyl group[173]. The structure of the complex $Mo_2O_3(\text{xanthate})_4$ has recently been determined[5,174]. Some well-characterised complexes in which molybdenum is fully co-ordinated with sulphur are described below.

Complexes with 1,2-dithiols. Recently there has been widespread interest in tris-complexes of molybdenum and other transition metals with ligands of the type R—C(SH)=C(SH)–R where R = CF_3[175], C_6H_5[176], CN[177] and with toluene-3,4-dithiol, (H_2tdt, I)[178]. Complexes of toluene-3,4-dithiol with molybdenum(VI) and (IV) were first prepared by Gilbert and Sandell[178a], and formulated $Mo(tdt)_3$ and $Mo(tdt)_2(H_2tdt)$ or $Mo(tdt)(Htdt)_2$ respectively. The complex $[Mo(CF_3\text{–}C(S)\text{–}C(S)\text{–}CF_3)_3]$ (abbreviated to $[Mo(SS)_3]^{\circ}$) has been obtained as black crystals by refluxing $[Mo(CO)_6]$ with bis(trifluoromethyl)dithietene(II) in methylcyclohexane[175a].


I


II

The complex is reduced by hydrazine in ethanol to a blue complex, $[Mo(SS)_3]^{2-}$, isolated as the $[Ph_4As]^+$ salt. Both compounds are diamagnetic. They react in solution to give a singly-charged complex, $[Mo(SS)_3]^{1-}$, isolated as the $[Ph_4As]^+$ salt which has one unpaired electron. The electron-spin resonance spectrum of this compound suggests that the unpaired electron resides in a molecular orbital which is principally ligand in character. It appears that in all three compounds molybdenum is formally in the +4 oxidation state and that the electronic configurations (including a ligand orbital, *L*) are[175b]: $[Mo(SS)_3]^{\circ}$, d^2L°; $[Mo(SS)_3]^{1-}$, d^2L^1; $[Mo(SS)_3]^{2-}$, d^2L^2. Other tris-dithiolato complexes undergo similar redox reactions[178b].

The rhenium complex, $Re(PhC(S){=}C(S)Ph)_3$, has been shown by X-ray analysis[179] to have a trigonal prismatic structure (D_{3h}-symmetry Fig. 4) and it seems likely that other tris(dithiolato) complexes also have this structure.

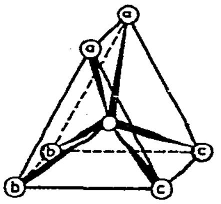
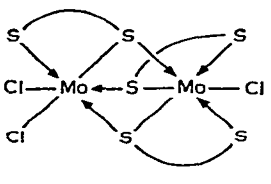
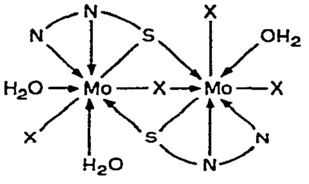


Fig. 4. Trigonal prismatic coordination. In the compound $Re(PhC(S){=}C(S)Ph)_3$ the bidentate ligands are bonded to the metal atom through pairs of sulphur atoms aa, bb, and cc[179].

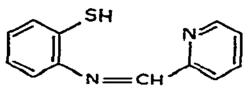
Complexes of molybdenum(III) with multidentate sulphur-ligands[169]. With a number of sulphur-ligands molybdenum(III) gives complexes which are non-electrolytes and have low magnetic moments (0.3–1.6 B.M.). It is possible that the complexes are dimerised through thiol bridges, and that in most of the compounds the molybdenum is eight-co-ordinate. Examples of proposed structures are shown below (the complex (I) with 3-ethyl-thiopropane-1-thiol, $EtSCH_2CH_2CH_2SH$; and the complex (II) with *N*-2-mercapto-phenylene-2′-pyridylmethyleneimine (III)) but they must be regarded as tentative until X-ray structural determinations have been carried out.



(I)



(II) (X = Cl, Br)



(III)

With thiourea and substituted thioureas, molybdenum(III) forms complexes with normal magnetic moments (e.g., $[Mo(NH_2CSNH_2)_3Cl_3]$, $\mu = 3.71$ B.M.) and with low moments (e.g., $[Mo_2(NH_2CSNH_2)_3Cl_6]$, $\mu = 0.59$ B.M.). It is suggested that the complexes with low moments are dimeric with three halogen bridges[180].

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