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STRUCTURAL ASPECTS OF MOLYBDENUM(IV), MOLYBDENUM(V) AND MOLYBDENUM(VI) COMPLEXES

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CONTENTS

A. INTRODUCTION

The coordination chemistry of molybdenum in the oxidation states +4, +5 and +6 has received much attention recently due to the realization that molybdenum in these oxidation states is an essential trace element in a variety of redox enzymes. Several reviews describing the biochemistry [1,2] and chemistry [3—6] of molybdenum have appeared, but no comprehensive account of the structural chemistry of this element is available. The purpose of this article is to provide such an account.

This review covers the literature up to the middle of 1974, and will be con-

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cerned with molybdenum(IV, V and VI) complexes only. The binary compounds as well as the iso- or hetero-polyanions of molybdenum, which have been reviewed previously [6,7], will not be dealt with in this article.

The material in this review is arranged according to the metal oxidation state. For the +5 and +6 oxidation states compounds are grouped according to a repeating structural unit, while for the +4 oxidation state complexes are grouped according to coordination number. For each group of related complexes a representative example is described first in detail and then structural features of other complexes are examined provided they are significantly different*.

B. COMPLEXES OF $Mo^{(VI)}$

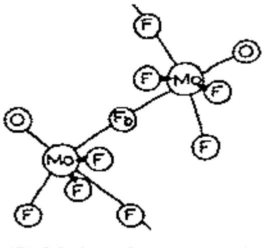
Except for a very few cases, $Mo^{(VI)}$ complexes contain one, two or three multiply bonded oxygen atoms. Thus, it is convenient to discuss the structural aspects of these complexes according to the number of terminal oxygen atoms present.

In quoting average bond lengths and angles, the standard deviations listed in parentheses will be estimated and not statistical values; however, for individual bond lengths and angles, the standard deviations listed will be from the referenced literature sources.

(i) Complexes with one terminal oxygen atom

$Mo^{(VI)}$ Complexes having one terminal oxygen atom are limited to the monooxo halides $MoOX_4$ (X = F, Cl), of which only the structure of $MoOF_4$ has been determined. The peroxo complexes which also contain one molybdenyl oxygen are described under a separate heading (Part B, Section (vi)).

In $MoOF_4$ [8] the molybdenum atom is coordinated in a distorted octahedral geometry to one terminal oxygen atom, O_t, and to five fluorine atoms. Two of the fluorine atoms bridge neighboring molecules with a Mo—F—Mo angle of 151° resulting in polymeric chains, (I). The short Mo—O_t distance of 1.64(1) Å is indicative of multiple bonding and is significantly shorter than



(I) Molecular geometry of $MoOF_4$.

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* Throughout this article differences in bond lengths and bond angles will be considered structurally significant when the magnitude of these differences is greater than three times the bond length and angle standard deviations.

the average Mo—O_t distance of 1.76 Å found in the tetrahedrally coordinated molybdate ion, MoO_4^{2-} [9]. The average molybdenum terminal fluorine distance of 1.86(2) Å agrees well with the Mo—F distance of 1.820(3) Å found by electron diffraction for MoF_6 [10]. The bridging fluorine atom *cis* to O_t has a Mo—F bond distance of 1.94(2) Å while that *trans* to O_t has a corresponding distance of 2.29(2) Å. The molybdenum atom is displaced 0.31 Å from the plane defined by the four fluorine atoms towards O_t.

(ii) Complexes with two terminal oxygen atoms

Relevant structural parameters for the known dioxo $\mathrm{Mo}^{(VI)}$ complexes are found in Table 1. All the known structures have a distorted octahedral geometry and a *cis* configuration for the two terminal oxygen atoms [11].

A representative example from this group of complexes is *cis*-dioxobis(di-*n*-propyldithiocarbamato)molybdenum(VI), (see Fig. 1) [12]. The coordination sites around the molybdenum atom are occupied by two terminal oxygen atoms and by four sulfur atoms. The two identical Mo—O_t distances are 1.695(5) Å and the O_t—Mo—O_t angle is 105.7(1)°. The two Mo—S distances *trans* to the O_t atoms are 2.651(2) Å, while those *cis* to the O_t atoms are significantly shorter, 2.451(2) Å.

Although most of the dioxo complexes reported are monomeric, in the solid state two examples of polymeric complexes have been reported. In the dioxodichloro complex $MoO_2Cl_2(H_2O)$, (II) [23] one of the two oxygen atoms, O_b, is weakly bound to a neighboring molybdenum atom in another molecule. Linear chains result from this bridging unit which contrast the zig-zag fluorine-bridged chains found in $MoO_2F_3^-$. (III) [24,25]. However, in both these structures the dimensions of the MoO_2 moiety are similar to those observed for the monomers.

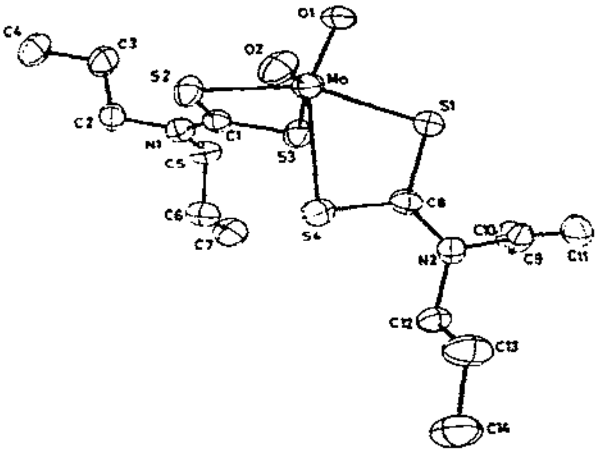


Fig. 1. Molecular structure of $MoO_2(S_2CN(C_3H_7)_2)_2$. (Reproduced with permission from the authors of ref. 12.)

TABLE 1

Relevant structural parameters for *cis*-dioxo Mo$^{(VI)}$ complexes[a]

Complex	Mo—O_t (Å)	O_t—Mo—O_t (deg)	Mo—C[b] (Å)	Mo—T[c] (Å)		Refs.
A. Monomeric complexes						
1. MoO_2Br_2(dipy)	1.83(2)	103(1)	Br—2.78(1)	N—	2.45(2)	13
	1.64(2)		Br—2.46(1)	N—	2.26(2)	
2a. $MoO_2(acac)_2$[d]	1.72(2)	111(1)	O— 1.98(2)	O—	2.24(2)	14
	1.64(2)	104(1)		O—	2.15(2)	
2b. $MoO_2(acac)_2$	1.69	105	O— 1.98	O—	2.19	15
3. $MoO_2Cl_2(DMF)_2$	1.68(1)	102(1)	Cl—2.34(1)	O—	2.20(1)	16
4. $MoO_2(C_9H_6NO)_2$	1.72(2)	104(1)	O— 1.98(2)	N—	2.32(2)	17
5. $MoO_2F_4^{2-}$	1.71(2)	95(1)	F— 1.94(1)	F—	1.97(2)	18,19
6. MoO_2(Et-dtc)$_2$	1.63(2)	114(2)	S— 2.44(1)	S—	2.63(1)	20
7. MoO_2(Pr-dtc)$_2$	1.696(5)	105.7(1)	S— 2.451(2)	S—	2.651(2)	12
8. $MoO_2(C_{15}H_{11}O_2)_2$	1.696(8)	104.8(4)	O— 1.992(2)	O—	2.166(9)	22
B. Polymeric complexes						
9. $MoO_2Cl_2(H_2O)$[e]	1.72(8)	105(3)	Cl—2.34(1)	H_2O,O_b'—	2.23(4)	23
10. $MoO_2F_3^{-}$	1.68(6)	104	F— 1.89	F—	2.11	24,25

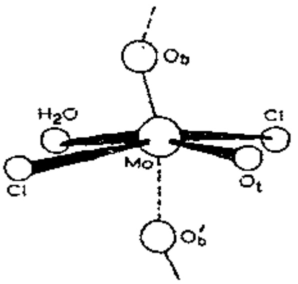
[a] Standard deviations are in parentheses.

[b] Atoms *cis* to O_t are listed next to the bond distance.

[c] Atom *trans* to O_t is listed next to the bond distance.

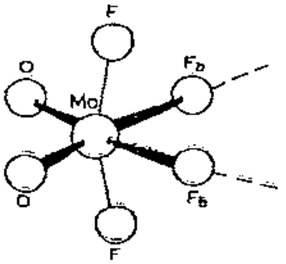
[d] Two independent molecules are in the unit cell, each differing slightly in dimensions.

[e] O_b in (II) is structurally similar to O_t.



(II) Structure of the polymeric $MoO_2Cl_2(H_2O)$ molecule.

Examination of Table 1 reveals a considerable variation in analogous structural parameters between complexes; for example, the $Mo—O_t$ bond lengths vary between 1.63 and 1.83 Å while the $O_t—Mo—O_t$ bond angles vary between 95 and 114°. It is believed that these variations are not significant but rather reflect the large discrepancy factors associated with these structures. It appears, however, that the most reasonable values for the $Mo{=}O_t$ distance and for the $O_t{=}Mo{=}O_t$ angle are 1.69 ± 0.01 Å and 105 ± 1°, respectively.



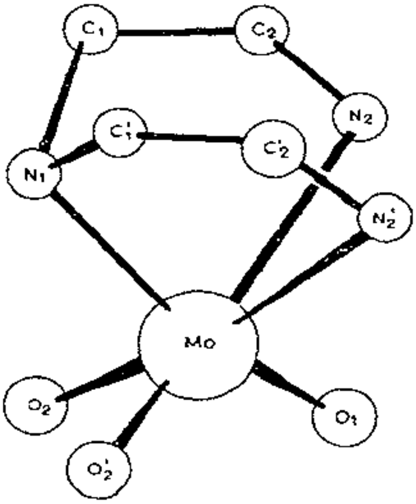
(III) Structure of the polymeric $MoO_2F_3^{=}$ anion.

(iii) Complexes with three terminal oxygen atoms

Three structures in which the molybdenum atom is coordinated to three terminal oxygen atoms have been reported, and in all cases these oxygen atoms are configured *cis* to one another. Relevant structural data for these complexes are found in Table 2.

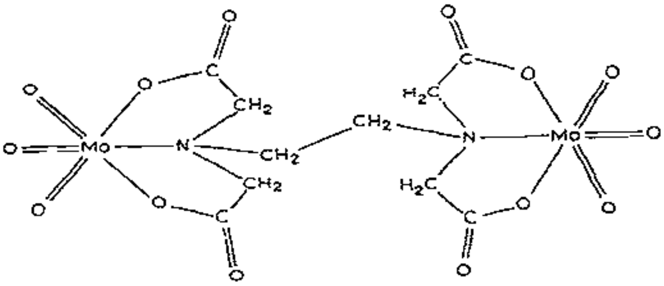
The molybdenum atom in MoO_3(dien) is coordinated in a distorted octahedral geometry to three O_t atoms and to three donor nitrogen atoms from the dien ligand, (IV) [26]. The three $Mo{=}O_t$ bond lengths are equivalent as are the three $Mo—N$ bond lengths; their respective average values are 1.736(7) Å and 2.326(5) Å. The average $O_t{=}Mo{=}O_t$ angle is 105.8° while the $N—Mo—N$ angles are all acute (73.1 and 80.0°). Thus, the molybdenum atom is located closer to the face defined by the three O_t atoms.

Similar observations can be made for the $[(MoO_3)_2EDTA]^{4-}$ dimer [27]. In this molecule a crystallographic center of inversion bisects the ethylenic



(IV) Molecular geometry of $MoO_3(dien)$.

carbon atoms of the bridging EDTA ligand, (V). Each molybdenum atom is coordinated to two glycinato oxygen atoms (O_1) having an average Mo—O_1 bond length of 2.195 Å. The Mo—N distance is 2.399(5) Å while the average values for the Mo—O_t bond lengths and for the O_t—Mo—O_t bond angles are



(V) Sketch of the $[(MoO_3)_2EDTA]^{4-}$ anion.

1.740(6) Å and 105.6(4)°, respectively. As with $MoO_3(dien)$, the molybdenum atom is closer to the trigonal face defined by the three O_t atoms.

The structure of $MoO_3(C_2O_4)^{2-}$, (VI), is the least accurately determined of the three complexes [28]. The general features of this complex are similar to those reported above; however, the bond lengths and bond angles are much larger, Table 2, and therefore will not be used for comparative purposes.

On the basis of the structures described above it appears that the Mo—O_t distances and the O_t—Mo—O_t angles for the trioxo complexes of $Mo^{(VI)}$ should approximate 1.74 ± 0.01 Å and 106 ± 1°. Thus, the Mo—O_t bond

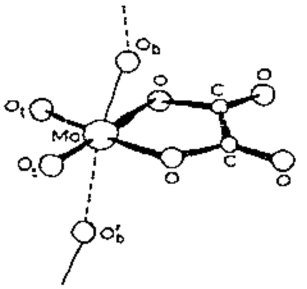
TABLE 2

Relevant structural parameters for *cis*-trioxo $Mo^{(VI)}$ complexes[a]

Complex	$Mo—O_t$ (Å)	Mo—Ligand (Å)	$O_t—Mo—O_t$ (deg)	Refs.
1. $MoO_3(dien)$	1.736(7)	N—2.324(5)	106(1)	26
2. $(MoO_3)_2EDTA^{4-}$	1.740(6)	N—2.399(5) O—2.195(6)	105.6(4)	27
3. $MoO_3(C_2O_4)^{2-}$[c]	1.85(1)	O—2.24(1)[b] O'_b—2.23(1)	114	28

[a] Numbers in parentheses are estimated standard deviations for averaged bond lengths.
[b] Oxalate oxygen.
[c] O_b in (VI) is structurally similar to O_t; the $Mo—O_b—Mo$ angle is 149°.

length depends primarily on the number of terminal oxygen atoms varying in the sequence $MoO_4 > MoO_3 > MoO_2 > MoO$ *.



(VI) Structure of the polymeric $MoO_3(C_2O_4)^{2-}$ anion.

Bonding of oxygen to molybdenum

From the structural survey presented thus far, it is obvious that oxygen plays a dominant role in $Mo^{(VI)}$ chemistry. The short $Mo—O_t$ distances observed in the above complexes compared to the $Mo—O_1$ distances suggest that the bonding is multiple in character. This is not surprising in view of the high positive charge on the molybdenum atom and the excellent π-donor qualities of the oxo anion. Thus, besides the σ interaction along the axis of the $Mo—O_t$ bond (Z-axis), two of the filled p orbitals of oxygen have the correct symmetry for overlap with the empty t_{2g} orbitals of the metal (p_x with d_{xy} and p_y with d_{zy}) [11,5,29]. The question of whether or not the $Mo—O_t$ interaction constitutes a triple bond has been discussed by Cotton [11]; the six electrons from oxygen are involved.

For the dioxo $Mo^{(VI)}$ complexes, the two terminal oxygen atoms are found

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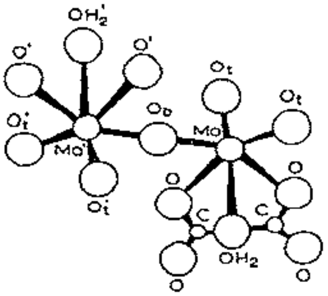
* The average $Mo—O_t$ distance in MoO_4^{2-} is 1.76 Å [9].

to have exclusively a *cis* configuration. This arrangement minimizes the electronic repulsions through the $d\pi$ system of the metal which would not occur if the atoms were *trans* to one another and had to compete for the same $d\pi$ orbitals. A simple extension of this theory to three terminal oxygen atoms would readily account for the *cis* configuration [5,11] observed in the trioxo complexes.

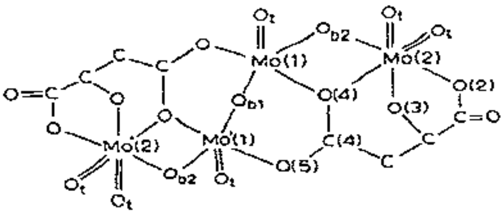
(iv) Oxo-bridged complexes

Although oxo-bridged complexes are more abundant in the +5 oxidation state, there are a few examples where molybdenum is in the +6 state as well. The two polymeric complexes $MoO_2Cl_2(H_2O)$ and $MoO_3(C_2O_4)^{2-}$ have already been described. Non-polymeric species include the oxalate complex $\{MoO_2(C_2O_4)(H_2O)]_2O\}^{2-}$, (VII) [30]. Here the bridging oxygen atom is located on a crystallographic inversion center which necessitates a linear Mo—O—Mo arrangement. The two O_t atoms are mutually *cis* having an average Mo—O_t bond length of 1.69 Å and an O_t—Mo—O_t bond angle of 106°. The bridging oxygen atom (O_b) is *cis* to the O_t atoms with a Mo—O_b bond length of 1.88(1) Å. The Mo—OH_2 distance is 2.33(2) Å while the two coordinated oxalato oxygen atoms have unequal Mo—O_1 bond lengths of 2.09(2) Å and 2.19(2) Å. The longer Mo—OH_2 and Mo—O_1 distances are associated with those atoms *trans* to the terminal oxygens.



(VII) Molecular geometry of the $\{[MoO_2(C_2O_4)(H_2O)]_2O\}^{2-}$ anion. (Atoms associated with the second oxalate ligand are deleted for simplicity.)

The crystal structure of the maleate complex $[Mo_4O_{11}(C_4H_3O_5)_2]^{4-}$, (VIII) [31], can best be described as two dimers linked by a non-linear oxygen bridge (Mo—O_{b1}—Mo angle of 152°). The complex has two different bridging oxygen atoms: O_b which is located on a crystallographic two-fold axis with a Mo—O_{b1} bond length of 1.91 Å, and O_{b2} which bridges Mo(1) and Mo(2) with a Mo—O_{b2}—Mo angle of 128° and an average Mo—O_{b2} bond length of 1.87 Å. The carboxylato oxygen, O(5), also aids in linking the two dimers by forming a weak Mo(1)—O(5) bond of 2.38 Å. The remaining Mo—O_1 bond lengths vary from 2.00 to 2.32 Å. Examining the molybdenum atoms, Mo(1)



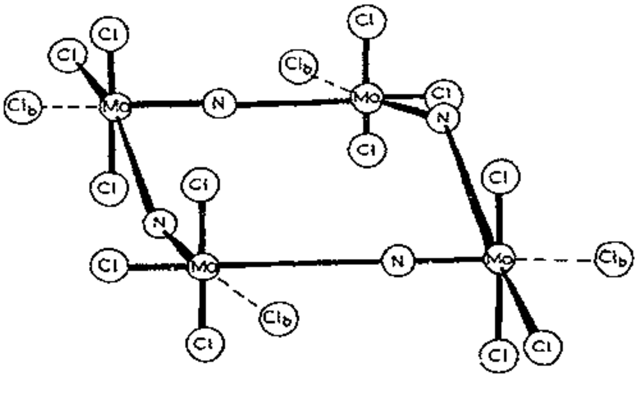
(VIII) Sketch of the $[Mo_4O_{11}(C_4H_3O_5)_2]^{4-}$ anion.

is five coordinate with one terminal oxygen atom while Mo(2) is six coordinate with two terminal oxygen atoms. Since no bond angles other than those described above were provided, no discussion of the geometry around each metal is possible; however, the Mo—O_t bond lengths are similar to others already described (the average Mo—O_t distance is 1.70 Å).

(v) Complexes without terminal oxygen atoms

Complexes with molybdenum in the +6 oxidation state that lack terminal oxygen atoms are quite rare. One class of such complexes are formed with the well known dithiolene [32,33] and diselenolene [34] ligands which impose a trigonal prismatic geometry on the metal. The structural aspects of the trigonal prismatic coordination are described in an excellent review by Eisenberg and interested readers are referred to that article [35].

Considering other complexes in this group, one interesting structure is that of the nitrido complex $MoNCl_3$, since N^{3-} is isoelectronic with O^{2-} [36]. The structure consists of $(MoNCl_3)_4$ tetrameric units interconnected by weak chlorine bridges, (IX) [37]. Within each tetrameric unit two types of nitrido bridges are present: one is linear (Mo—N—Mo angle of 178(1)°) and one is bent (Mo—N—Mo angle of 167(1)°). Both types of bridges are asymmetric having one short Mo—N bond of average length 1.66 Å, suggesting a multiply



(IX) Structure of the $(MoNCl_3)_4$ tetramer.

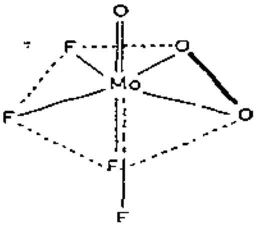
bonded nitrogen atom, and one longer Mo—N bond of average length 2.18 Å, suggesting a Mo$^{(VI)}$—N single bond. If the weakly bound chlorine atoms are considered, then the geometry around each molybdenum atom is a distorted octahedron; otherwise, the geometry can be described as a square pyramid with the closely bound nitride ligand in the apical position.

In the discussion of the Mo$^{(VI)}$ complexes, several structural features were found to be common. Since similar structural features will also appear in the Mo$^{(V)}$ and Mo$^{(IV)}$ complexes, they will be examined in greater detail later.

(VI) Peroxo complexes

Molybdenum salts are known to react with hydrogen peroxide to form a variety of complexes in which the peroxide to metal ratio is 1:1, 2:1, 3:1 and 4:1. The chemistry and syntheses of these peroxo complexes have been reviewed by Connor and Ebsworth; however, at the time of publication, 1964, virtually no structural information concerning these complexes was available [38]. Since then the structures of a number of complexes with peroxide to metal ratios of 1:1, 2:1 and 4:1 have been determined and they are summarized in Table 3.

Two independent structural determinations of the 1:1 complex $MoO(O_2)F_4^{2-}$ [39,40] established that the Mo$^{(VI)}$ atom is seven coordinate with a pentagonal bipyramidal geometry, (X); the axial positions are occupied by a terminal oxygen atom and by a fluorine atom. The short Mo—O$_t$ distance of 1.66 Å* demonstrates the multiple character of this bond. The average Mo—O$_1$ (peroxo) and Mo—F distances are 1.93 and 2.00 Å, respectively, while the peroxo O—O bond length is 1.40 Å. The molybdenum atom is displaced 0.2 Å from the pentagonal plane defined by the three fluorine atoms and by the peroxo group towards the terminal oxygen atom.



(X) Molecular geometry of the $MoO(O_2)F_4^{2-}$ anion.

Several structures with peroxide to metal ratios of 2:1 have been determined, and in all cases the molybdenum atom is again seven coordinate with a pentagonal bipyramidal geometry. A representative example is the oxalate complex $MoO(O_2)_2(C_2O_4)^{2-}$, (XI) [41]. The Mo—O$_t$, Mo—O (peroxo) and

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* A mean value from the two structures is listed in Table 3.

TABLE 3

Relevant structural parameters for peroxo complexes of molybdenum[a]

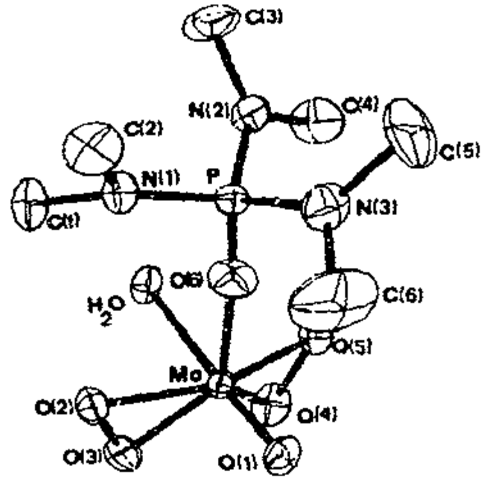
Complex	Mo—O$_t$ (Å)	Mo—O (peroxo) (Å)	Mo—Ligand (Å)	O—O (Å)	Mo displacement	Refs.
A. Monomeric complexes						
1. $(NH_4)_3F[MoO(O_2)F_4]$	1.67(2)	1.91(2)	F— 1.98(2)	1.36(3)	0.23	39
2. $K_2MoO(O_2)F_4$	1.64(2)	1.94(2)	F— 2.01(2)	1.44(3)	0.20	40
3. $K_2MoO(O_2)_2(C_4O_4)$	1.68(2)	1.94(1)	O— 2.08(1) O— 2.26(2)[c]	1.46(2)	0.35	41
4. $MoO(O_2)_2[OP(NMe_2)_3]H_2O$	1.662(5)	1.942(7)	O— 2.057(5) OH_2— 2.347(5)[c]	1.496(8)	0.40	42
5. $MoO(O_2)_2[OP(NMe_2)_3]py$	1.66(1)	1.93(2)	O— 2.04(1) N— 2.45(1)[c]	1.44(2)	0.39	42
6. $[Zn(NH_3)_4][Mo(O_2)_4]$		1.93(3)[b] 2.00(2)		1.55(5)		43
B. Bridged complexes						
7. $K_2\{[MoO(O_2)_2(H_2O)]_2O\}$	1.66(1)	1.96(1)	O_b— 1.93(2) OH_2— 2.44(1)	1.48(3)	0.40	44
8. $(pyH)_2\{[MoO(O_2)_2(H_2O)]_2O\}$	1.674(7)	1.964(8)	O_b— 1.917(7) OH_2— 2.445(7)	1.48	0.38	45
9. $(pyH)_2\{[MoO(O_2)_2(H_2O)]_2O\}$	1.669(6)	1.936(7)	$(OOH)_b$—2.047(6) $(OOH)_b$—2.391(6)[c]	1.46(1) 1.46(1)[d]	0.44	45

[a] Numbers in parentheses are estimated standard deviations for averaged bond lengths.

[b] There are two types of Mo—O (peroxo) bonds, see Part D, Section (i).

[c] *Trans* to O$_t$.

[d] Bridging hydroperoxo group.



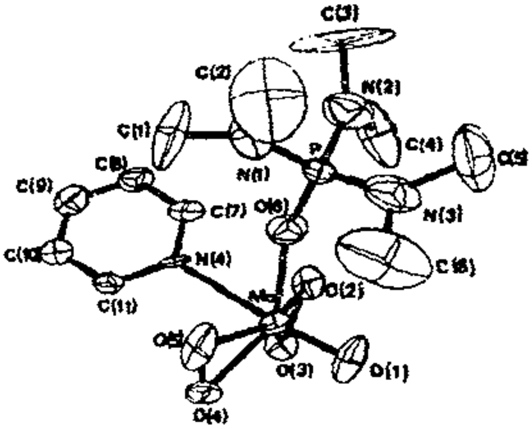
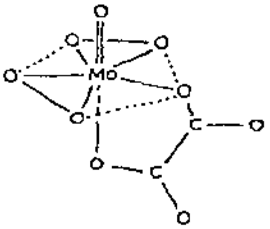


Fig. 2. Molecular structure of $MoO(O_2)_2[OP(NMe)_2)_3](H_2O)$. (Reproduced with permission from the authors of ref. 42.)

Fig. 3. Molecular structure of $MoO(O_2)_2[OP(NMe)_2)_3]py$. (Reproduced with permission from the authors of ref. 42.)

O—O distances are 1.68(2), 1.94(1) and 1.46(1) Å, respectively. The molybdenum atom is displaced 0.35 Å from the pentagonal plane towards O_t. In addition, the 2.26(1) Å Mo—O (oxalato) bond length *trans* to O_t is considerably longer than the corresponding 2.08(1) Å Mo—O (oxalato) bond length within the pentagonal plane. The structural parameters of the analogous complexes



(XI) Molecular geometry of the $MoO(O_2)_2(C_2O_4)^{2-}$ anion.

$MoO(O_2)_2[OP(NMe_2)_3]H_2O$, Fig. 2 [42], and $MoO(O_2)_2[OP(NMe_2)_3]py$, Fig. 3 [42], are very similar to those for $MoO(O_2)_2(C_2O_4)^{2-}$, Table 3.

2:1 Complexes that have bridging atoms are shown in Figs. 4 and 5. In the oxo-bridged complex $\{[MoO(O_2)_2(H_2O)]_2O\}^{2-}$ [44,45], the geometry of the molecule may be described as two pentagonal bipyramids sharing a common corner defined by the bridging oxygen atom. In $[MoO(O_2)_2(OOH)]_2{}^{2-}$ the two hydroperoxo groups bridge the two molybdenum atoms such that the anion consists of two pentagonal bipyramids sharing a common edge [45]. The bridge in the latter complex is not symmetrical resulting from

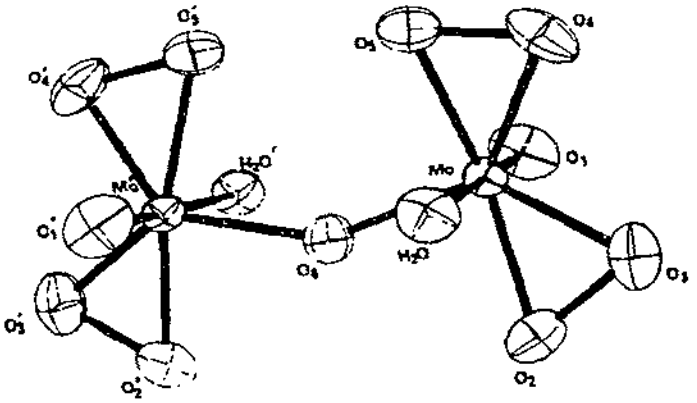


Fig. 4. Molecular structure of the $\{[MoO(O_2)_2(H_2O)]_2O\}^{2-}$ anion. (Reproduced with permission from the authors of ref. 45.)

the fact that one of the bridging oxygen atoms is *trans* to O_t while the other is *cis* to it.

From the above discussion several generalizations regarding the bonding and geometry of the 1:1 and 2:1 complexes can be made:

(i) The complexes are seven coordinate having pentagonal bipyramidal geometries.

(ii) The molybdenyl oxygen atom always occupies an axial position and the bond length *trans* to it is significantly longer than analogous bond lengths in the pentagonal plane.

(iii) Peroxo ligands always occupy coordination sites in the pentagonal plane.

(iv) The Mo—O (peroxo) bond length is independent of other donor atoms in the coordination sphere. Its average value is 1.94 ± 0.01 Å.

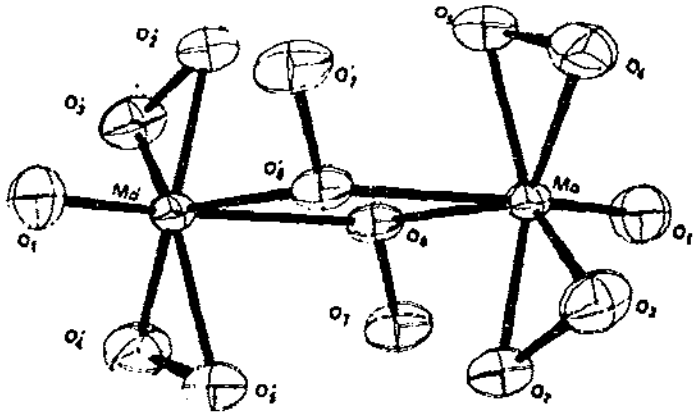


Fig. 5. Molecular structure of the $[MoO(O_2)_2(OOH)]_2^{2-}$ anion. (Reproduced with permission from the authors of ref. 45.)

(v) The average O—O distance of 1.44 ± 0.05 Å is similar to that observed for H_2O_2 vapor (1.47 Å).

(vi) The molybdenum atom is displaced 0.35—0.45 Å from the pentagonal plane towards O_t.

In the 4:1 complex, $Mo(O_2)_4^{2-}$, the molybdenum atom is eight coordinate with a distorted dodecahedral geometry [43]. The Mo—O (peroxo) and the O—O bond lengths, however, are similar to those for the 1:1 and 2:1 complexes. A more complete analysis of the geometric features of the molybdenum peroxo complexes will have to await the structural determination of a 3:1 complex.

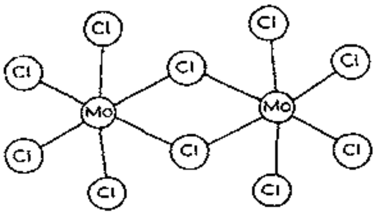
C. COMPLEXES OF $Mo^{(V)}$

Except for a few cases, $Mo^{(V)}$ complexes have one terminal oxygen atom per molybdenum. No monomeric complexes with two or more terminal oxygen atoms are known since these species characteristically dimerize and polymerize into compounds having one or more bridging oxygen atoms.

(i) Complexes without the oxo ligand

The best known complexes belonging to this category are the halides whose chemistry has been recently reviewed [46—48]. The structures of two molybdenum fluoride complexes appear in the literature. By the use of powder techniques, $NaMoF_6$ was found to be octahedral with Mo—F bond lengths of 1.74(3) Å [49]. The structure of MoF_5 [50], determined from two dimensional X-ray data, consists of tetrameric units with fluorine bridges as in the analogous NbF_5 complex [46—48,50]. The bridging Mo—F bond length is 2.06(4) Å while the terminal Mo—F bond lengths vary from 1.66 to 1.89 Å with an average value of 1.78 Å. In view of the large standard deviations associated with the Mo—F bond distances, the observed variations are not believed to be significant.

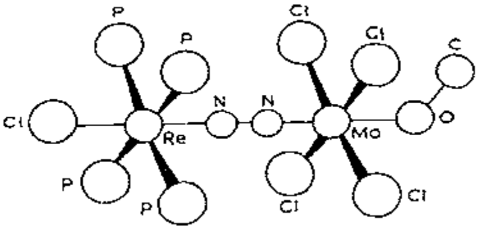
The pentachloro complex of molybdenum, $MoCl_5$, has been found to be a monomer in the vapor phase. This complex has a trigonal bipyramidal geometry as determined by electron diffraction techniques [51]. In the solid state, however, $MoCl_5$ dimerizes such that each molybdenum atom is six coordinate with two bridging chlorine atoms, (XII) [52]. The terminal Mo—Cl distance



(XII) Sketch of the $MoCl_5$ solid-state dimer.

of 2.24(1) Å compares favorably with the Mo—Cl distance found in the $MoCl_5$ vapor (2.27(2) Å). The average bridging Mo—Cl bond length is 2.53(1) Å and the Mo—Cl—Mo bond angle is 98.6°. The rather long Mo—Mo distance of 3.84(2) Å coupled with the paramagnetism of the complex strongly suggest that no metal—metal bonding occurs. The chlorine atoms perpendicular to the Mo—Mo vector are bent away from the terminal chlorine atoms. This configuration has been attributed to steric effects resulting in nearly equal Cl···Cl non-bonded distances [52].

A recent communication has reported the preliminary structure of a mixed molybdenum—rhenium complex, $(PMePh_2)_4ClReN_2MoCl_4(OCH_3)$, in which a dinitrogen bridges the two metal atoms, (XIII) [53]. Of particular interest in this molecule is the short Mo—N and long N—N bond lengths of 1.89 and 1.21 Å. The short Mo—N distance, which suggests multiple bonding, is probably responsible for the lengthening and weakening of the N—N bond as manifested by a large shift to lower energy of the N—N infrared stretching frequency [54].



(XIII) Coordination about the Mo and Re atoms in $(PMePh_2)_4ClReN_2MoCl_4(OCH_3)$.

TABLE 4

Relevant bond lengths in $Mo^{(V)}$ oxo-halide complexes

Complex	$Mo—O_t$ (Å)	$Mo—C^b$ (Å)	$Mo—T^c$ (Å)	Refs.
K_2MoOF_5	1.67(3)	F— 1.88(7)	F— 2.03(1)	55
$(NH_4)[MoOBr_5]$	1.86(3)	Br—2.55(1)	Br— 2.83(1)	56
$(AsPh_4)[MoOBr_4(H_2O)]$	1.78(7)	Br—2.52(1)	OH_2—2.39(3)	57
$MoOCl_3$	1.63(4)	Cl—2.26(2) Cl—2.44(2)^d Cl—2.36(2)^d	Cl— 2.78(2)^e	58,59
$MoOBr_3$	1.65(1)	Br—2.41(1) Br—2.61(1)^d	O— 2.31(1)^e	60

[a] Standard deviations in parentheses.

[b] C represents the atoms *cis* to the terminal oxygen.

[c] T represents the atom *trans* to the terminal oxygen.

[d] A bridging atom.

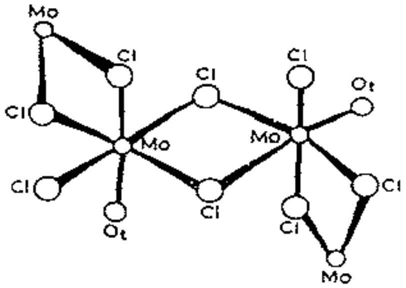
[e] A bridging atom *trans* to the terminal oxygen.

(ii) Monomeric and polymeric complexes with one oxo ligand per molybdenum

$Mo^{(V)}$ complexes containing one terminal oxygen atom are limited to the halides and pseudohalides. Important structural parameters are listed in Table 4.

The representative structure of $MoOF_5^{2-}$ [55] is similar to that of the $Mo^{(VI)}$ oxofluoride, $MoOF_4$ [8], described previously. The molybdenum atom in $MoOF_5^{2-}$ is six coordinate with a distorted octahedral geometry having the expected short Mo—O_t bond length of 1.67(2) Å. The fluorine atoms situated *cis* to O_t have an average Mo—F bond length of 1.88(7) Å which is significantly shorter than the Mo—F bond length of 2.03(1) Å for the atom *trans* to O_t. The molybdenum atom is displaced 0.11 Å from the plane defined by the four *cis* fluorine atoms towards O_t; this necessitates obtuse O_t—Mo—F (*cis*) angles of 94°.

The oxotrihalide complexes of $Mo^{(V)}$, $MoOX_3$[X=Cl,Br], are polymeric. In $MoOCl_3$ each molybdenum atom is in a distorted octahedral environment with bridging chlorine atoms, (XIV) [58,59]. One of the bridging chlorine atoms is symmetrically bound to two molybdenum atoms having a Mo—Cl bond length of 2.46 Å and a Mo—Cl—Mo bond angle of 103°. The second bridging chlorine atom, *trans* to the O_t atom of one molybdenum and *cis* to the O_t atom of the other, has asymmetric Mo—Cl bond lengths of 2.36(2) and 2.80(2) Å, and a Mo—Cl—Mo bond angle of 97°. The Mo—Cl (terminal) and Mo—O_t bond distances are respectively 2.26(2) Å and 1.63(4) Å. The molybdenum atoms in this complex are displaced 0.36 Å towards the terminal oxygen atoms, and the Mo—Mo distance, 3.84 Å, is similar to that found in $MoCl_5$ (vide supra). This large distance and the paramagnetism of the complex (μ = 1.65 BM)* strongly suggest that no metal—metal bonding occurs [46].



(XIV) Structure of the polymeric $MoOCl_3$ molecule.

Unlike the chloro complex, $MoOBr_3$ has oxygen atoms bridging dimeric units of Mo_2Br_6, (XV) [60]. The terminal Mo—Br and bridging Mo—Br_b bond

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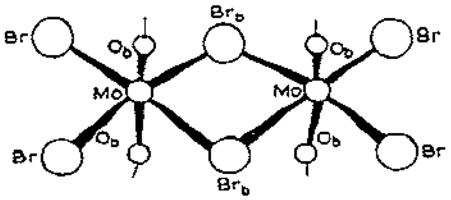
* Magnetic moment in Bohr Magnetons per Mo.



(XV) Structure of the polymeric $MoOBr_3$ molecule.

lengths are 2.41(1) and 2.61(1) Å, respectively, while the Mo—Br$_b$—Mo bond angle is 95°. The oxygen bridges perpendicular to the Mo_2Br_6 units have asymmetric Mo—O bond lengths of 1.65(1) Å and 2.31(1) Å. The molybdenum atoms are displaced 0.34 Å from the plane of the six bromine atoms towards the bridging oxygen atoms that have the shorter bond length. As in $MoOCl_3$, the Mo—Mo distance of 3.96 Å suggests that no metal—metal bonding occurs in this complex. The Mo—Mo distance via the bridging oxygen atom is 3.94 Å. Thus, this structure is best described as $Mo_2O_2Br_6$ structural units stacked such that the "terminal" oxygen atoms form dative bonds to the empty axial molybdenum coordination sites of neighboring molecules.

(iii) Bridged dimeric complexes

As noted above, $Mo^{(V)}$ has a great tendency to form dimeric compounds with either one or two bridging oxygen atoms. Recently complexes having two bridging sulfur atoms have been isolated and characterized.

TABLE 5

Relevant structural parameters for mono-oxygen-bridged complexes of the type $Mo_2O_3L_4$

	L		
	$S_2COC_2H_5$	$S_2P(OC_2H_5)_2$	$S_2CN(C_3H_7)_2$
Mo—O$_t$ (Å)	1.65(2)	1.85(1)	1.67(1)
Mo—O$_b$ (Å)	1.86(2)	1.86(1)	1.87(1)
Mo—S$_c$ (Å)[a]	2.49(1)	2.47(1)	2.48(4)
Mo—S$_b$ (Å)[b]	2.54(1)	2.547(5)	2.53(1)
Mo—S$_t$ (Å)[c]	2.70(2)	2.801(5)	2.68(1)
Mo—O—Mo (deg.)	178(4)	180[d]	178(1)
O$_b$—Mo—O$_t$ (deg.)	104(1)	103(1)	103(1)
Ref.	61	62	12

[a] *Cis* to the terminal and bridging oxygen atoms.
[b] *Trans* to the bridging oxygen atom.
[c] *Trans* to the terminal oxygen atom.
[d] A crystallographic inversion center is located on the bridging atom.

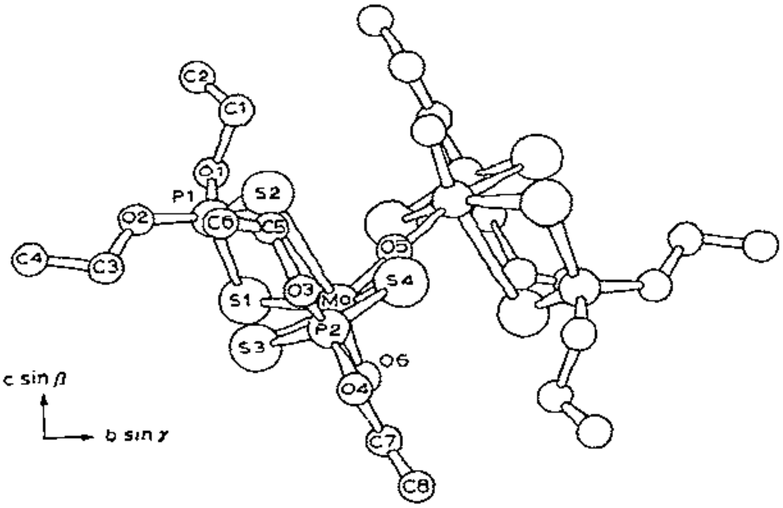


Fig. 6. Molecular structure of $Mo_2O_3(S_2P(OC_2H_5)_2)_4$. (Reproduced with permission from the authors of ref. 62.)

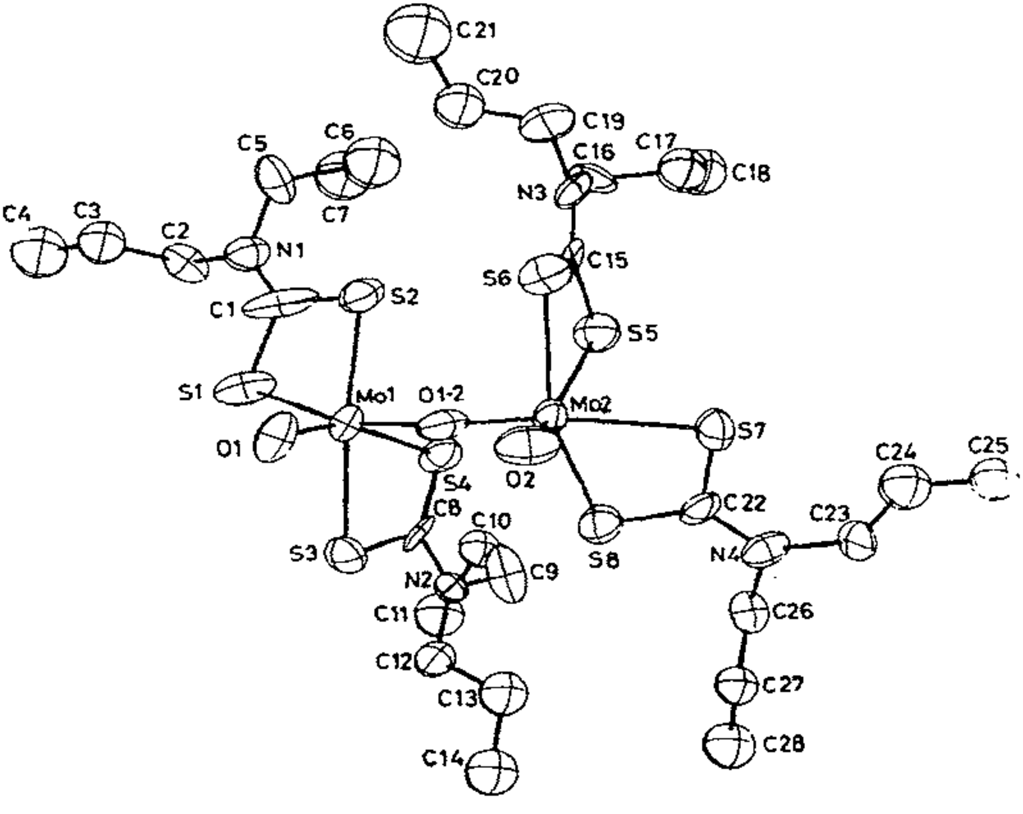


Fig. 7. Molecular structure of $Mo_2O_3(S_2CN(C_3H_7)_2)_4$. (Reproduced with permission from the authors of ref. 12.)

1. One bridging oxygen atom

Three structures of the general formula $Mo_2O_3L_4$ [L = $S_2P(OC_2H_5)_2$, $S_2COC_2H_5$ and $S_2CN(C_3H_7)_2$] [12,61,62] have been described. In each complex the molybdenum atom has a distorted octahedral geometry and a linear Mo—O_b—Mo′ bridge, Table 5. The two terminal oxygen atoms, which are invariably *cis* to the bridging oxygen, are in turn either *cis* or *trans* to one another, Figs. 6 and 7. The Mo—O_b and Mo—O_t bond lengths are 1.86(2) and 1.66(2) Å, and the terminal oxygen atoms are bent away from the Mo—O_b—Mo′ vector as seen in the O_b—Mo—O_t bond angle of 103°. A significant structural feature of these complexes is the variation in the Mo—S bond length for different ligand systems. Thus, in the ethyl xanthate complex $Mo_2O_3(S_2COC_2H_5)_4$ [61], the Mo—S distances range from 2.47 to 2.71 Å depending upon the position of the sulfur donor atom with respect to the bridging and terminal oxygen atoms. Similar observations have been made for $Mo_2O_3(S_2P(OC_2H_5)_2)_4$ [62] (Fig. 6) and for $Mo_2O_3(S_2CN(C_3H_7)_2)_4$ [12] (Fig. 7).

2. Two bridging oxygen atoms

Several complexes with two bridging oxygen atoms have been structurally characterized and important structural parameters are listed in Table 6. A representative example is the cysteine complex $Na_2Mo_2O_4(cysteine)_2.5H_2O$, Fig. 8 [63]. Each molybdenum atom is bound to two bridging oxygen atoms and to one terminal oxygen atom. The remainder of the coordination sphere is occupied by the tridentate cysteine ligand. The average Mo—O_b bond length is 1.93(2) Å, while the Mo—O_b—Mo′ and O_b—Mo—O_b′ bond angles are 83.4(6) and 93.2(6)°. The Mo_2O_2 bridge is non-planar having a dihedral angle of 151° between the Mo, O_b, O_b′ and Mo′, O_b', O_b planes. The molybdenum atoms are displaced 0.38 Å from the planes defined by the two bridging oxygen atoms and by the N and S donor atoms of the cysteine ligands toward the terminal oxygen atoms. The short Mo—Mo distance of 2.569(2) Å coupled with the diamagnetism of this complex suggest the presence of a metal—metal bond.

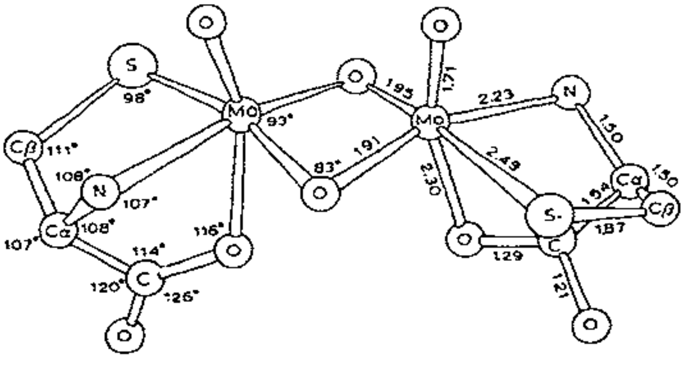


Fig. 8. Molecular structure of the $[Mo_2O_4(cysteine)_2]^{2-}$ anion. (Reproduced with permission from the authors of ref. 63.)

TABLE 6

Relevant structural parameters for $Mo_2B_2O_2$ (B = O,S) systems[a]

Complex	Mo—Mo (Å)	Mo—O_t (Å)	Mo—B (Å)	Mo—L (Å)
A. Dioxo-bridged complexes: B = O				
$Na_2Mo_2O_4$(cysteine)$_2$	2.569(2)	1.71(2)	1.93(2)	S— 2.490(6) N— 2.23(2) O*— 2.30(2)
$BaMo_2O_4(C_2O_4)_2(H_2O)_2$	2.541	1.70(3)	1.90(3)	O[b]— 2.13(4) OH_2—2.22(4)
Mo_2O_4(histidine)$_2$	2.552	1.71	1.92	N— 2.23 O*— 2.21
Mo_2O_4(cysteine ethyl-ester)$_2$[c]	2.562(3)	1.66(2)	1.93(2)	S— 2.380(8) N— 2.219(3)
$Mo_2O_4(S_2CN(C_2H_5)_2)_2$[d]	2.580(1)	1.678(2)	1.941(1)	S— 2.455(3)
B. Disulfido-bridged complexes: B = S				
$Mo_2S_2O_2$(cysteine-methyl-ester)$_2$[c]	2.804(4)	1.71(3)	2.30(1)	S— 2.38(1) N— 2.24(3)
$Mo_2S_2O_2$(histidine)$_2$	2.848(1)	1.676(9)	2.33(1)	N— 2.254(9) O*— 2.209(6)
$Cs_2Mo_2S_2O_2$EDTA[e]	2.799(1)	1.683(6)	2.294(1)	O— 2.111(9) N*— 2.448(8)
$Na_2Mo_2S_2O_2$(cysteine)$_2$	2.82(1)	1.62(3)	2.33(1)	S— 2.50(1) N— 2.27(3) O*— 2.37(3)
$(\pi\text{-}C_5H_5)_2Mo_2S_2O_2$	2.894(5)	1.679(6)	2.317(3)	C— 2.41
$(\pi\text{-}C_5H_5)_2Mo_2S_2(NC(CH_3)_3)_2$	2.920(1)	1.733(4)[f]	2.342(1)	C— 2.383
$Mo_2S_4(S_2CN(C_4H_9)_2)_2$[d]	2.801(2)	1.937(6)[g]	2.308(4)	S— 2.447(6)
$Mo_2S_2(SCN(C_3H_7)_2)_2$-$(S_2CN(C_3H_7)_2)_2$[h]	2.706(2)		2.242(2) 2.340(2)	S— 2.517(2) S— 2.536(2) S— 2.469(2) C— 2.069(7)

[a] Standard deviations are given in parentheses; B = bridging atom, L = ligand atom, * = atom *trans* to O_t.

[b] One oxalato oxygen atom is *trans* to O_t; however no significant difference in the two Mo—O (oxalato) bond lengths is observed.

[c] Five coordinate trigonal bipyramidal geometry.

[d] Five coordinate square pyramidal geometry.

The possible electronic repulsions between the Mo—Mo bond and the two Mo—O_t bonds are manifested in the obtuse Mo′—Mo—O_t angles of 100(1)°. The weakly bound carboxylato oxygen *trans* to O_t has a rather long Mo—O bond length of 2.30(2) Å. When cysteine ethyl ester is used as the ligand, a dimeric complex results in which each molybdenum atom is five coordinate

Mo—B—Mo (deg.)	B—Mo—B (deg.)	Mo—Mo—O_t (deg.)	Dihedral angle (deg.)	Mo displacement (Å)	Refs.
83.4(6)	96.2(4)	99.5(6)	151	0.38	63
84(1)	93(2)				64
83	94		153	0.34	65
83.0(6)	91.6(7)	102.5(6)	143.7		66
83.3(1)	91.9(1)			0.74	67
74.9(4)	101.8(5)	105(1)	149(1)		68
75.6(1)	103.0(1)	101.7(2)	159.7	0.30	69
75.2(1)	102.1(1)	100.5	152.3	0.37	70
75(1)	103(1)	100(1)	156	0.42	71
77.3(1)	102.7(1)	112.4(2)	180	0.0	72
77.1(1)	102.9(1)	109.3(1)	180	0.0	73
74.7(1)	101.8(6)	104.3(2)	148	0.72	74
72.3(1)	106.5(1)		160.7		75

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[e] The EDTA molecule is hexadentate, bridging the $Mo_2S_2O_2$ unit. A similar conformation has been reported for the analogous Mo_2O_4 complex in the solid state and in solution [76,77].

[f] The imido group occupies the O_t position.

[g] Terminal sulfur atom.

[h] A $Mo^{(IV)}$ complex.

with a distorted trigonal bipyramidal geometry [66]. Despite the change in coordination, the dimensions of the Mo_2O_4 unit remain unaffected. A recent structural determination of $Mo_2O_4(Et\text{-}dtc)_2$ [67], Fig. 9, shows that the geometry around each molybdenum atom in this complex is best described as a square pyramid in which two sulfur atoms and the two bridging oxygen

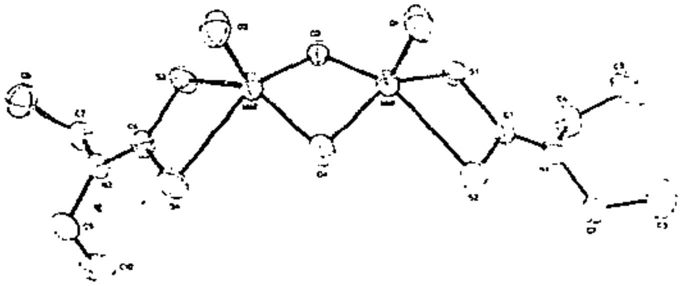
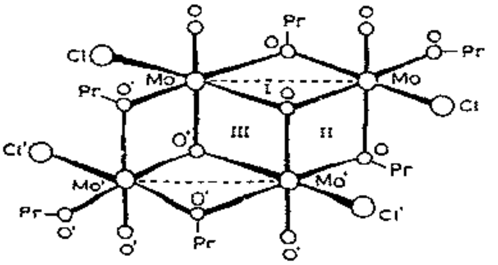


Fig. 9. Molecular structure of $Mo_2O_4(S_2CN(C_2H_5)_2)_2$. (Reproduced with permission from the authors of ref. 67.)

atoms define the basal plane. Each molybdenum atom is displaced 0.74 Å from this plane towards the terminal oxygen atom. Again there is no change in the dimensions of the Mo_2O_4 unit. From these structures one may observe that the structural features of the Mo_2O_4 dimeric unit are largely insensitive both to the nature of other donor atoms and to the geometry and coordination number of the metal, Table 6. Throughout this series of complexes the Mo—O_t bond lengths are short, ranging between 1.66 and 1.71 Å. Although this bond appears to be slightly longer for the six coordinate complexes, not enough structural information is presently available to be sure.

One further structure merits attention; a mixed valence molecule of formula $Mo_4O_6(OC_3H_7)_6Cl_4$, (XVI) [78], contains three dioxo bridges, I, II and III. Bridge I resembles the dioxo bridges discussed above, while bridges II and III



(XVI) Molecular geometry of $Mo_4O_6(OC_3H_7)_6Cl_4$.

are planar with *trans* molybdenyl oxygen atoms. The Mo—Mo distance of 2.669(2) Å (bridge I) is significantly longer than the value found in the other complexes containing the Mo_2O_4 unit. This lengthening is probably due to the fact that this complex contains two $Mo^{(V)}$ and two $Mo^{(VI)}$ atoms which necessitate a weaker Mo—Mo interaction.

3. *Two bridging sulfur atoms*

Disulfido-bridged complexes of $Mo^{(V)}$ have been synthesized by a variety of methods using H_2S, MoS_4^{2-} and P_2S_5 [79,80]. A listing of the relevant

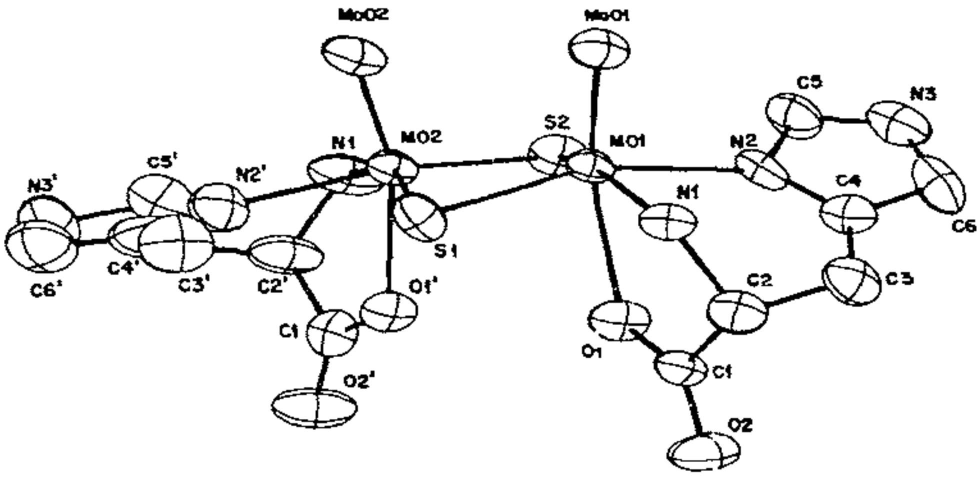
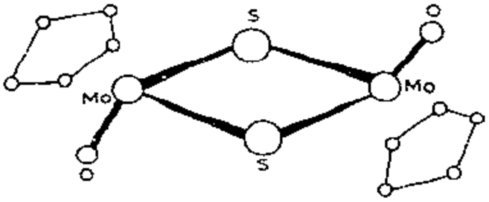


Fig. 10. Molecular structure of $Mo_2S_2O_2$(histidine)$_2$.

structural features of the known disulfido-bridged complexes is found in Table 6 and a representative example is the histidine complex, $Mo_2S_2O_2$(histidine)$_2$, Fig. 10 [69]. Each histidinato ligand coordinates to the molybdenum atom through the carboxylato oxygen, the α-amino nitrogen and the N(2) of the imidazole ring. The rest of the coordination sphere around each molybdenum atom consists of one terminal oxygen atom and two bridging sulfur atoms. The amino Mo—N and the imidazole Mo—N bond lengths of 2.263(9) and 2.241(8) Å are not significantly different from one another and are similar to those found in other $Mo^{(V)}$ complexes. The Mo—S bond length is 2.323(9) Å while the Mo—S—Mo and S—Mo—S bond angles are 75.6(1) and 103.0(4)°. The molybdenum atoms are displaced 0.30 Å from the plane defined by the two bridging sulfur atoms and by the four nitrogen atoms towards the terminal oxygen atoms. This spatial arrangement is a consequence of the multiply bonded terminal oxygen atoms which have Mo—O_t distances of 1.67(1) Å. The Mo—O (ligand) bond length of 2.210(6) Å, together with the other bond lengths and angles subtended at the molybdenum atom from the histidinato ligand, are not significantly different from those found in the analogous dioxo-bridged complex. Similar behaviour is observed in the cysteine [71] and cysteine methyl ester [68] complexes in which the bridging atoms have been changed from oxygen to sulfur. Thus, substituting sulfur for oxygen does not significantly affect the bonding between molybdenum and other donor atoms; only the dimensions and configuration of the $Mo_2B_2O_2$ (B = O,S) bridge itself are subject to change.

In the sulfur-bridged histidine complex, the Mo—Mo distance of 2.848(1) Å suggests metal—metal bonding; this is further supported by the diamagnetic behaviour of the complex. As similarly observed in the dioxo-bridged Mo_2O_4 unit, the Mo—Mo—O_t and Mo—Mo—L (L = ligand) angles are greater than 90° as predicted by the Nyholm—Gillespie model [81] (vide infra). This distribution of donor atoms around the molybdenum is not unique to the doubly-bridged complexes of the type $Mo_2B_2O_2$ (B = O, S), but is also observed in the mono-oxygen-bridged complexes described earlier. Finally, like the Mo_2O_4 unit, the $Mo_2S_2O_2$ bridge is not planar; a dihedral angle of 159.7° exists between the two planes defined by Mo,S,S and Mo′,S,S.

Two sulfido-bridged complexes in which planarity is imposed on the $Mo_2S_2O_2$ bridged units by a crystallographic center of inversion (requiring a *trans* configuration for the two terminal oxygen atoms) are $(\pi\text{-}C_5H_5)_2Mo_2S_2O_2$ (XVII) [72] and the analogous imine complex $(\pi\text{-}C_5H_5)_2Mo_2S_2(NC(CH_3)_3)_2$ [73]. In the latter complex the Mo—N distance of 1.733(4) Å suggests that the imido nitrogen atom is multiply bonded to the molybdenum; thus, this nitrogen atom can be viewed as substituting for the terminal oxygen atom.



(XVII) Molecular geometry of $(\pi\text{-}C_5H_5)_2Mo_2S_2O_2$.

As described earlier, the bridging oxygen atoms in Mo_2O_4 can be replaced by bridging sulfur atoms; treatment of $Mo_2S_2O_2(dtc)_2$ (dtc = dialkyldithiocarbamate) with P_2S_5 in boiling xylene results in the formation of a complex in which the terminal oxygen atoms have also been replaced by sulfur [80].

A drawing of the coordination sphere of $Mo_2S_4(Bu^n\text{—}dtc)_2$ is shown in Fig. 11 [74]. The geometry of this molecule is best described as two square pyramids sharing a common edge defined by the bridging sulfur atoms. The two basal planes form a dihedral angle of 152.9° and the two molybdenum atoms are displaced 0.72 Å from these planes toward the terminal sulfur atoms. The dimensions of the Mo_2S_4 bridge are similar to those of other complexes described above (Table 6); however, the terminally bound sulfur

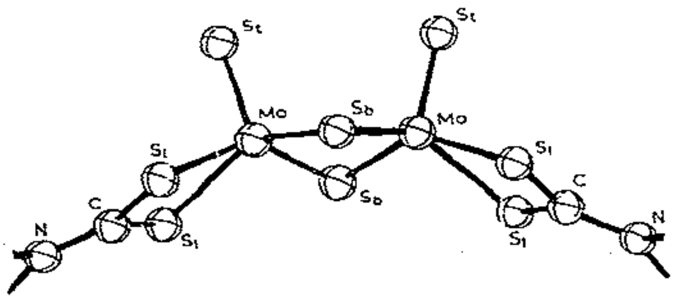


Fig. 11. Molecular structure of $Mo_2S_4(S_2CN(C_4H_9)_2)_2$.

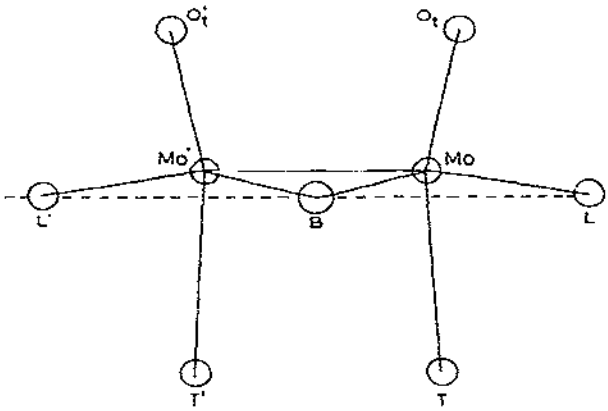


Fig. 12. Coordination about the molybdenum atoms in the doubly-bridged dimers. Projection is through the pairs of atoms labeled L′, B and L.

atoms are of particular interest. The 1.937(6) Å Mo—S_t bond length is shorter than any other Mo—S bond length found to date, and is approximately 0.5 Å shorter than a normal Mo—S single bond [61]. Similar decreases in bond length are also observed in going from a single to a multiply bonded oxygen atom [11]. Thus, it can be concluded that S_t is bound to the molybdenum atom with a bond order of at least two, in a way analogous to the molybdenyl oxygen.

4. *Summary of bridged structures*

Several generalizations concerning the geometry of bridged $Mo^{(V)}$ complexes can now be made:

(a) Atoms *trans* to the terminal oxygen atom always have bond lengths longer than expected. This lengthening is probably due to electronic factors such as the *trans* influence of the multiply bonded molybdenyl oxygen atom and/or steric effects including the minimization of non-bonded repulsions and ligand conformational requirements [69]. More structural studies will be needed to determine which factors predominate.

(b) Substituting sulfur atoms for the bridging oxygen atoms affects only the dimensions and configuration of the $Mo_2B_2O_2$ (B = O, S) bridge itself; the rest of the coordination sphere remains unperturbed. In addition, the dimensions of the $Mo_2B_2O_2$ (B = O, S) bridge are not affected by changes in the ligand donor atoms nor by changes in the geometry or coordination number of the metal.

(c) All the bridged complexes are diamagnetic. In the mono-oxygen-bridged complexes, spin pairing occurs via the bridging oxygen atom [61]. In the $Mo_2B_2O_2$ bridged complexes (B = O, S), the short Mo—Mo distances suggest a direct metal—metal bond [82].

(d) In the $Mo_2B_2O_2$ bridged complexes (B = O, S), neglecting metal—metal bonding, the molybdenum atoms are either five coordinate with a distorted trigonal bipyramidal or square pyramidal geometry, or six coordinate with a distorted octahedral geometry. In the latter case, the spatial arrangement of the donor atoms around the $Mo_2B_2O_2$ (B = O, S) bridge is depicted in Fig. 12. The six atoms Mo, Mo′, O_t, O_t', T and T′ (T signifies an atom *trans* to O_t) lie on a plane perpendicular to the plane defined by the bridging atoms, B, and by the ligand donor atoms, L (in the drawing these atoms are projected onto the Mo, Mo′ etc. plane). The Mo—Mo bond coupled with the tetragonal distortion brought about by the Mo displacement towards O_t are undoubtedly responsible for the observed dihedral angles between the Mo, B, B′ and Mo′B,B′ planes. The obtuse Mo—Mo—O_t and Mo—Mo—T bond angles can be thought to arise from the non-bonded repulsions between the Mo—Mo and the Mo—O_t or Mo—T bonds as predicted by the Nyholm—Gillespie model [81]. It is valuable to note in this connection that equivalent Mo—Mo—Cl angles in the $(MoCl_5)_2$ dimer described earlier are acute [52]. Here, with no metal—metal bond, the Nyholm—Gillespie model would predict a decrease in the Mo—Mo—Cl bond angle to a point governed only by inter- and intramolecular Cl···Cl non-bonded repulsions. This is in fact observed.

D. COMPLEXES OF $Mo^{(IV)}$

The chemistry of molybdenum in the +4 oxidation state, unlike that of the +5 and +6 oxidation states, is not dominated by the oxo ligand. In addition, $Mo^{(IV)}$ exhibits a wider range of ligand systems, coordination numbers, and geometries. Thus, it is more convenient to discuss the structural aspects of $Mo^{(IV)}$ according to coordination number rather than according to a repeating structural unit as was done with $Mo^{(V)}$ and $Mo^{(VI)}$.

(i) Coordination number 8

The geometry and chemistry of complexes with this coordination number have been fields of active research for a number of years. Since the general chemical, stereochemical and theoretical aspects of eight coordinate complexes have already been reviewed extensively, these subjects will not be discussed further [83,84].

Structurally, eight coordinate molybdenum complexes usually have dodecahedral geometries*. A listing of relevant structural details based on the notations of Hoard and co-workers [85] and on the suggestion of Lippard [86] are found in Table 7.

(ii) Coordination number 7

Reactions of $Mo^{(IV)}$ halides with tertiary phosphines have led to the isola-

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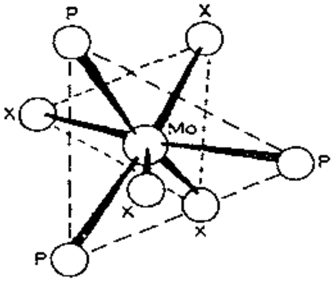
* The 4:1 peroxo to molybdenum complex, $Mo(O_2)_4$, is also dodecahedral.

tion of complexes of the type $MoX_4(PMePh_2)_3$ [X = Cl, Br], (XVIII), in which the seven coordinate molybdenum atom has a capped octahedral geometry [93,94]. Three halide ligands occupy the less sterically hindered un-



(XVIII) Sketch of the MoX_4(phosphine)$_3$ spatial arrangement.

capped face (Mo—Cl = 2.448(4) Å [93], Mo—Br = 2.560(5) Å, and Br—Mo—Br = 87°) [94], while the three phosphorous atoms define the face (Mo—P = 2.578(7) Å) which is capped by the remaining halogen atom (Mo—Cl = 2.339(3), Mo—Br = 2.425(7) Å). The Mo—X distance on the capped face is 0.11 to 0.13 Å shorter than analogous bond distances on the uncapped face. This shortening is reflected in the non-bonded distances between the halogen and phosphorus atoms (e.g., Br···P = 3.04 Å (capped face); Br···P = 3.18—3.22 Å (uncapped face) [94]). No obvious explanation exists for these observations at this time.

Reactions of $MoO(dtc)_2$ with unsaturated organic molecules such as diethylazodicarboxylate or tetracyanoethylene (TCNE) lead to the isolation of seven coordinate addition products [95]. The TCNE adduct of MoO(S_2CN-

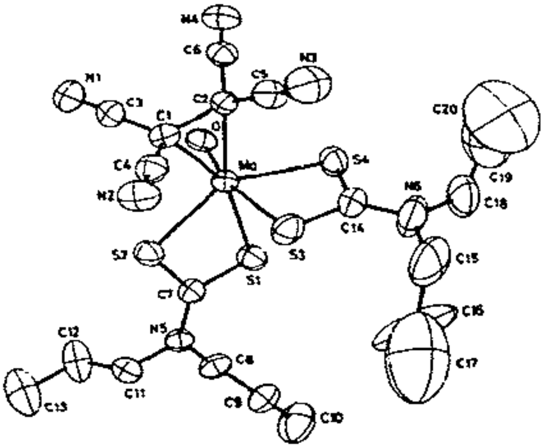


Fig. 13. Molecular structure of $MoO(S_2CN(C_3H_7)_2)_2$(TCNE). (Reproduced with permission from the authors of ref. 95.)

TABLE 7

Relevant structural details of 8-coordinate complexes[a]

Complex	Mo—A (Å)	Mo—B (Å)	θ_A (deg.)	θ_B (deg.)	Mo—A/Mo—B
1. $Mo(CN)_8^{4-}$	C 2.165	C 2.162	36.0	72.9	1.00
2. $Mo(CN)_8^{3-}$[c]	C 2.11	C 2.12	37.2	72.5	1.00
3. $(CH_3NC)_4Mo(CN)_4$[d]	C 2.177	C 2.148	35.7	75.7	1.01
4. $H_4Mo(PCH_3Ph_2)_4$	H 1.70	P 2.503	30.3	71.4	
5. "Most favourable"			35.2	73.5	1.03

[a] Notation based on Hoard; values in parentheses are normalized for the *a*, *m*, *b* and *g* edges.

[b] Dihedral angle between the two trapezoids which define a dodecahedron [86].

[c] A $Mo^{(V)}$ complex.

[d] Cyanide ligands occupy "A" sites, isocyanide ligands occupy "B" sites.

$(C_3H_7)_2)_2$, Fig. 13, has the molybdenum atom in a distorted pentagonal bipyramidal geometry similar to that observed in the peroxo complexes of $Mo^{(VI)}$ (see Part B, Section (v)) [96]. The terminal oxygen atom and a sulfur atom occupy the axial positions, while the three remaining sulfur atoms and the two carbon atoms of the TCNE ligand define the pentagonal plane. The Mo—O_t bond length of 1.682(4) Å is slightly, but not significantly longer than the Mo—O_t distance of the parent complex (1.664(8) Å, see Section (iv) [12]). The Mo—S distances vary from 2.419(2) to 2.486(2) Å for the sulfur atoms on the pentagonal plane while the Mo—S distance *trans* to O_t is 2.576(2) Å. The configuration of the TCNE ligand is similar to that found in other complexes containing this ligand. Other features of this complex include an average Mo—C bond length of 2.28(2) Å and an ethylenic C—C bond length of 1.473(9) Å. The lengthening of the C—C bond suggests π-back-donation from the metal and implies that this complex can be formulated as an oxidative addition product. This formulation is supported by the fact that hydrolysis of the diethylazodicarboxylate adduct of $MoO(dtc)_2$ leads to the production of both hydrazine dicarboxylate and the $Mo^{(VI)}$ complex $MoO_2(dtc)_2$.

(iii) Coordination number 6

Complexes of this coordination number have either octahedral or distorted octahedral geometries. A listing of relevant structural parameters is found in Table 8.

a (Å)	*m* (Å)	*g* (Å)	*b* (Å)	Dihedral angle (deg.)	Refs.
2.545 (1.18)	2.551 (1.16)	2.673 (1.24)	3.187 (1.47)		87,88
2.56 (1.21)	2.44 (1.15)	2.61 (1.23)	3.06—3.20 (1.45—1.51)	87.7	89
2.54 (1.17)	2.455 (1.13)	2.73 (1.26)	3.12 (1.44)	87.8	90,91
1.72 (1.17)	2.72 (1.17)	2.58 (1.24)	3.66 (1.49)	88.7 90.0	92 86

TABLE 8

Six coordinate $Mo^{(IV)}$ complexes

Complex	Mo—O (Å)	Mo—L[a] (Å)	Notes	Refs.
1. $K_3NaMoO_2(CN)_4$	1.834(9)	C— 2.22(1)	Terminal oxygen atoms are *trans* to one another	98
2. $K_4MoO_2(CN)_4$	1.828(14)	C— 2.18(2)		99
3. $MoOCl_2(PMe_2Ph)_3$	1.676(7)	Cl—2.551(3)[b] Cl—2.464(3)[c] P— 2.550(9)[d] P— 2.500(3)[e]	Blue isomer	100
4. $MoOCl_2(PEt_2Ph)_3$	1.801(9)	Cl—2.424(4)[b] Cl—2.482(4)[c] P— 2.567(5)[d] P— 2.522(4)[e]	Green isomer	101
5. $MoOCl(diphos)_2$	1.69	Cl—2.46[b] P— 2.57	Cl atom is *trans* to O_t, octahedral geometry	102
6. $MoCl_2(Sal—NMe)_2$[f]		Cl—2.388(2) O— 1.953(6) N— 2.137(8)	Cl atoms are *trans* to one another as are the two O atoms and the two N atoms	103

[a] L is the ligand donor type.

[b] *trans* to O_t.

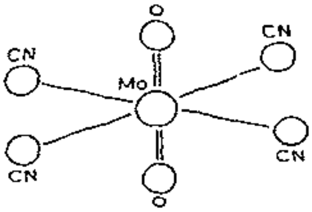
[c] *trans* to phosphorus.

[d] Average of two measurements.

[e] *trans* to Cl.

[f] Sal—*N*Me = *N*-methylsalicylaldimine.

The dioxo complex $MoO_2(CN)_4{}^{4-}$, (XIX) [98,99], which was originally thought to be the eight coordinate ion $Mo(OH)_4(CN)_4{}^{4-}$, has D_{4h} symmetry

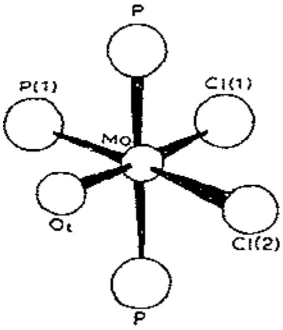


(XIX) Sketch of the $MoO_2(CN)_4{}^{4-}$ anion.

with the two O_t atoms *trans* to one another. This configuration is unlike the dioxo complexes of $Mo^{(VI)}$ where the O_t atoms are always *cis* to one another. It is believed that the preferred *trans* configuration for the d^2 $Mo^{(IV)}$ ion results from the fact that the tetragonal distortion imposed by the two O_t atoms pairs the electrons in the low-lying *dxy* orbital; this minimizes electronic repulsion with the good π-donor oxo ligands and allows for π-back-donation to the cyano ligands [11,98].

Butcher and Chatt described the synthesis of a number of tertiary phosphine oxo $Mo^{(IV)}$ complexes of the type $MoOX_2(PR_2Ph)_3$ [104]. Several of these complexes demonstrate isomerism in solution as evidenced by the irreversible color change from green to blue and by the accompanying shift in the infrared stretching frequency of the Mo—O_t group from 943 to 954 cm^{-1} [104]. Based on these observations Butcher and Chatt suggested that in one of the isomers the terminal oxygen atom is *trans* to a halide atom, while in the other it is *trans* to a phosphorus atom. The X-ray crystallographic studies have shown, however, that both the blue isomer of $MoOCl_2(PMe_2Ph)_3$ and the green isomer of $MoOCl_2(PEt_2Ph)_3$ have basically the same overall geometry with O_t *trans* to a chlorine atom, (XX) [100,101]. The structural differences in the isomers have been summarized by Muir [100,101,105]:

(1) In the blue isomer the Mo—O_t bond length is 1.67(7) Å, while in the



(XX) Spatial arrangement of atoms coordinated to molybdenum in $MoOCl_2(PMe_2Ph)_3$.

green isomer the corresponding Mo—O$_t$ distance is significantly longer, 1.801(9) Å.
(2) In the plane defined by O$_t$, Cl(1), Cl(2) and P(1), electrostatic repulsions between anionic ligands significantly distort the O—Mo—Cl(2) and P(1)—Mo—Cl(1) bond angles. These angles, ideally 90° for an octahedral complex, are 105.7(3) and 76.9(1)° in the blue isomer, and 98.9(3) and 81.5(1)° in the green isomer. These angular distortions minimize non-bonded interactions as observed in the O···Cl(2) and Cl(1)···Cl(2) distances of 3.33 and 3.41 Å in the blue isomer, and of 3.29 and 3.36 Å in the green isomer.
(3) The conformations of the organic substituents on the phosphine ligands are different in the two complexes which may be due to the different steric requirements of these ligands. In addition, the length of the Mo—Cl bond *trans* to O$_t$ varies by an amount proportional to the length of the Mo—O$_t$ bond; thus when the latter lengthens from 1.676(7) to 1.801(9) Å, the former shortens from 2.551(3) to 2.424(4) Å.

Due to the differences outlined above, which can mainly be ascribed to ligand repulsions, Chatt et al. have suggested that the blue—green isomerization be called "distortional isomerization" [105]. Whether this type of isomerization is confined to these examples or is more universal in nature awaits further structural and chemical investigations.

One Mo$^{(IV)}$ disulfido-bridged complex listed in Table 6 is $Mo_2S_2(SCN(C_3H_7)_2)_2(S_2CN(C_3H_7)_2)_2$, Fig. 14 [75]. This complex is formed by the oxidative-addition reaction of di-*n*-propyldithiocarbamate with the Mo$^{(II)}$ complex $Mo_2(O_2CCH_3)_4$. Of interest here is the short Mo—Mo distance of 2.705(2) Å which is accompanied by obtuse S$_b$—Mo—S$_b$ angles of 106.5(1)° and by correspondingly acute Mo—S$_b$—Mo angles of 72.3(1)°. The close contact between the molybdenum atoms and the accompanying angular changes within the

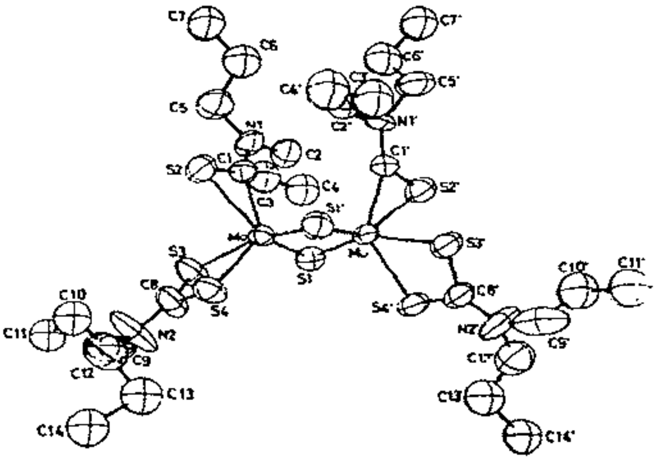


Fig. 14. Molecular structure of $Mo_2S_2(SCN(C_3H_7)_2)_2(S_2CN(C_3H_7)_2)_2$. (Reproduced with permission from the authors of ref. 75.)

bridge suggest that a stronger Mo—Mo bond is formed here than in the $Mo^{(V)}$ bridging unit $Mo_2S_2O_2$. The 2.069(7) Å Mo—C bond length in this complex is similar to that found in molybdenum carbene chemistry [75].

(iv) Coordination number 5

Several complexes of the type $MoOL_2$ ($L = S_2P(OC_2H_5)_2$ and S_2CNR_2) have been synthesized by Mitchell and co-workers [106]. The structure of the di-*n*-propyldithiocarbamato complex, $MoO(S_2CN(C_3H_7)_2)_2$, Fig. 15 [12], shows that the molybdenum atom has a square pyramidal geometry with the terminal oxygen atom in the apical position. The Mo—O_t bond length is 1.664(8) Å and the average Mo—S bond length is 2.413(5) Å. The molybdenum is displaced 0.83 Å from the basal plane defined by the four sulfur atoms towards O_t.

(v) Cyclopentadienyl complexes

In the +4 oxidation state molybdenum is associated with some interesting and varied organometallic chemistry, particularly with the cyclopentadienyl anion $C_5H_5^-$. The bis-cyclopentadienyl complexes of the type Cp_2MoL_2 are the best characterized and will be described first.

One of the earliest structurally characterized bis-cyclopentadienyl complexes was the dihydro complex Cp_2MoH_2, (XXI) [107], in which the two cyclopentadienyl rings are bent towards one another with a Cp—Mo—Cp an-

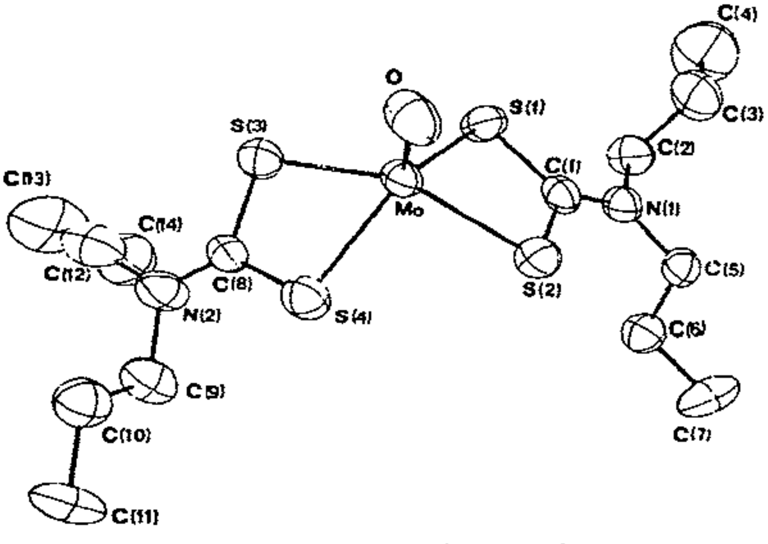
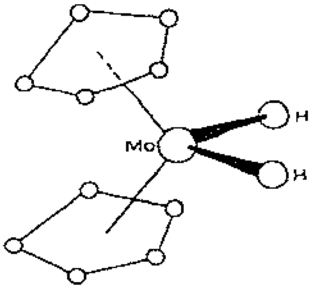


Fig. 15. Molecular structure of $MoO(S_2CN(C_3H_7)_2)_2$.(Reproduced with permission from the authors of ref. 12.)



(XXI) Structure of Cp_2MoH_2.

gle of 145.9°. This structural feature, now recognized as being characteristic of this class of complexes, and the L—Mo—L bond angle have led to several proposed bonding schemes [113,114].

The salient features of the bis-cyclopentadienyl complexes are the conformation of the Cp rings with respect to one another, and the angles defined by Cp—Mo—Cp and L—Mo—L. A listing of complexes stressing these features is found in Table 9. Observations concerning the geometries of these complexes have been described by Prout and co-workers [108—112] and are summarized below:

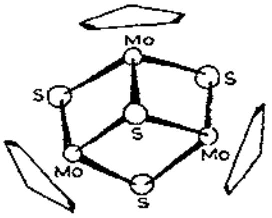
(1) The Cp rings are planar within experimental error and the individual C—C bond lengths within the rings do not vary.

(2) The molybdenum atom is situated almost directly over the centroid of the Cp rings with a Mo—Cp perpendicular distance of 1.92—2.00 Å. An exception to this generalization is found in Cp_2MoH_2.

(3) The exact angle of tilt (Cp—Mo—Cp) is independent of the nature of the other ligand donor atoms and appears to be a function of the crystal packing forces. The angles lie within the range 130.9—133.9°.

(4) Features of the Cp_2MoL_2 complexes are all alike except for the conformation of the rings. These conformations are independent of the nature of L as exemplified in the two cysteine structures listed in Table 9.

Cyclopentadienyl complexes with formulae other than Cp_2MoL_2 are also known. An interesting complex is the $Cp_3Mo_3S_4^+$ cluster, (XXII) [116]. In this complex three sulfur atoms individually bridge two molybdenum atoms



(XXII) Structure of the $Cp_3Mo_3S_4^+$ cluster.

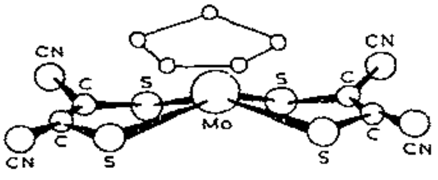
TABLE 9

Dicyclopentadienyl complexes of the type Cp_2MoL_2

Complex	Mo—Cp (Å)	Cp—Mo—Cp (deg.)	Mo—L (Å)
Cp_2MoH_2	1.89	145.9	H— 1.2
$Cp_2Mo(S_2C_6H_3CH_3)$	2.00	132.5	S— 2.433
$Cp_2Mo(SC_2H_4NH_2)$	1.99	130.9	S— 2.438(6) N— 2.211(15)
$H[Cp_2Mo(cysteine)]Cl$	1.98	133.7	S— 2.446(2) N— 2.256(7)
$H[Cp_2Mo(cysteine)]PF_6$	2.01	130	S— 2.46(1) N— 2.14 2.32(3)
$[Cp_2Mo(glycine)]Cl$	1.99	132	O— 2.10(1) N— 2.26(1)
$[Cp_2Mo(sarcosine)]Cl$	1.976	133.9	O— 2.10(2) N— 2.23(2)
$Cp_2Mo(\mu\text{-}SBu)_2FeCl_2$		133	S— 2.464(5)
$Cp_2Mo(SnBr_3)Br$			Br—2.605(9) Sn—2.691(4)

while the fourth sulfur atom bridges all three molybdenum atoms. Associated with the double-bridging sulfur atoms are an average Mo—S bond length and Mo—S—Mo bond angle of 2.293(6) Å and 75.6(6)°. Corresponding values for the unique triple-bridging sulfur atom are 2.314(4) Å and 74.8(1)°. The average Mo—Mo distance of 2.812(3) Å suggests the existence of metal—metal bonding while the 2.030(4) Å Mo—Cp (centroid) distance is typical of other complexes described.

One other interesting complex is $CpMo(mnt)_2^-$, (XXIII) [117]. Here the



(XXIII) Structure of the $CpMo(mnt)_2^-$ anion.

Mo—Cp (centroid) and Mo—S bond lengths are 2.000(4) and 2.407(4) Å, respectively. The molybdenum atom lies 0.911 Å above the best plane defined by the four sulfur atoms which is nearly parallel to the plane of the Cp ligand. If the Cp ring is considered to be a tridentate ligand, then the molybdenum atom is seven coordinate with a regular (3,4) or trigonal base tetragonal geometry.

L—Mo—L′ (deg.)	Comments	Refs.
	Eclipsed Cp ring, H positions uncertain	107
82	Staggered Cp rings	108
78.4(4)	Staggered Cp rings	109
77.0(2)	Staggered Cp rings, carboxylato group of cysteine forms H-bridge to neighboring molecule	110
80(1) 79(1)	Two independent molecules, Cp rings eclipsed, cysteine conformation unusual	110
74.1(5)	Eclipsed rings, glycine dimensions similar to other complexes	110
73.4(6)	Staggered Cp rings	110
72.6	Staggered Cp rings, Mo—Fe distance is 3.660(3) Å, not clear if metal—metal bonding occurs	111
80.2(1)	Cp rings have unreasonable temperature factors and cannot be described	112

E. SUMMARY

The molybdenum complexes that have been examined display a wide assortment of features. The oxo ligand is prominently found in $\mathrm{Mo}^{(V)}$ and $\mathrm{Mo}^{(VI)}$ chemistry, less so in $\mathrm{Mo}^{(IV)}$ chemistry. Frequently oxygen and halogen atoms serve as bridging agents in these complexes yielding assorted dimers, trimers, and polymers. Nitrogen and sulfur atoms also serve in this capacity. Metal—metal bonds are often associated with the d^2 $\mathrm{Mo}^{(IV)}$ and d^1 $\mathrm{Mo}^{(V)}$ di- and polymeric systems.

Oxygen atoms terminally coordinated to molybdenum are always observed to be multiply bonded. Regardless of oxidation state the Mo—$\mathrm{O_t}$ distances range between 1.66 and 1.74 Å with the larger values normally associated with a larger number of coordinated oxo ligands. With molybdenum in the +6 oxidation state the oxygen atoms are always *cis* to one another, while in the +4 oxidation state they are always *trans*.

Geometrically, octahedral or trigonal bipyramidal coordination is common to all of the oxidation states. Eight coordinate complexes, primarily of $\mathrm{Mo}^{(IV)}$, are dodecahedral. In addition to these coordination geometries, seven coordinate $\mathrm{Mo}^{(VI)}$ peroxide complexes are normally pentagonal bipyramidal while five coordinate $\mathrm{Mo}^{(V)}$ complexes are trigonal bipyramidal or square pyramidal. Both seven and five coordination numbers are common to complexes of $\mathrm{Mo}^{(IV)}$. With the former coordination number a capped octahedral coordination geometry is observed in addition to the pentagonal bipyramid.

The emergence of crystallography as a powerful molecular probe in recent years promises an increasingly rapid flow of structural reports in the future. Undoubtedly molybdenum complexes will receive considerable attention and reviews such as this one will require considerable revision and expansion.

ACKNOWLEDGEMENTS

We wish to thank Dr. R. Winograd for helpful discussions and for the preparation of this manuscript. Without his help this review would have taken several more months to finish.

NOTE ADDED IN PROOF

A novel triply-bridged $Mo^{(V)}$ dimer, $Mo_2O_3(oxine)_2(SCH_2CH_2O)$, has just been reported (J. Amer. Chem. Soc., 97 (1975) 1616). The two molybdenum atoms are bridged by one oxo ligand and by the sulfur and oxygen atoms of the 2-mercaptoethanol.

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