OXO-SPECIES OF MOLYBDENUM-(V) AND -(VI)

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MANY compounds of molybdenum-(V) and -(VI) are derived from oxo-species, $Mo_xO_y^{n+}$, with one or more oxygen atoms as terminal ligands (*i.e.*, bonded to only one molybdenum atom) or as bridging ligands (*i.e.*, bonded to two molybdenum atoms).[1] An essential feature is multiple bonding between the oxygen atom and the metal atom. Because of the strength of this multiple bond, the oxo-species occur in a range of compounds and persist through a variety of chemical reactions.

Currently there is increasing interest in the chemistry of the elements of the earlier transition groups which characteristically form oxo-species in their higher oxidation states.[2] Interest in oxomolybdenum compounds is centered on determination of structures and the interpretation of their vibrational and electronic spectra and their magnetic and chemical properties in terms of the Mo–O bonding interaction. Wider use of techniques for handling highly reactive, air- and moisture-sensitive compounds has led to a reinvestigation of known compounds and the preparation of new compounds. Also attracting some attention is the nature of the oxomolybdenum species in solution.

A representative selection of oxo-compounds of molybdenum-(VI) and -(V) is given in Table 1. The following oxo-species occur:

$$Mo^{VI}: MoO^{4+}\ MoO_2^{2+}\ MoO_3\ Mo_2O_5^{2+}$$

$$Mo^{V}: MoO^{3+}\ Mo_2O_3^{4+}\ Mo_2O_4^{2+}$$

There appears to be no molybdenum(V) compound in which the metal is bonded to more than one terminal oxygen. It is considered (see below) that the binuclear species, $Mo_2O_5^{2+}$ and $Mo_2O_3^{4+}$, have one oxygen bridge, and that the species $Mo_2O_4^{2+}$ has two oxygen bridges.

1. Structures and Physical Measurements

(a) Structures of Oxo-species.—Structures which have been determined by *X*-ray crystallography are MoO_3(dien) (I),[3] where dien is diethylenetriamine $H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$; $[Mo_2O_5(C_2O_4)_2(H_2O)_2]^{2-}$ (II);[4] $[MoO_3(C_2O_4)]^{2-}$ (III);[5] and Mo_2O_3(xanthate)$_4$ (IV),[6] where xan-

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[1] (*a*) N. V. Sidgwick, "Chemical Elements and Their Compounds", Oxford University Press, 1950, vol. 2, pp. 1032—1053; (*b*) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Wiley, 1962, pp. 776—800.

[2] (*a*) C. K. Jørgensen, "Inorganic Complexes", Academic Press, 1963, ch. 2; (*b*) J. Selbin, *J. Chem. Educ.*, 1964, **41**, 86; (*c*) J. Selbin, *Chem. Rev.*, 1965, **65**, 153; (*d*) J. Selbin, *Angew. Chem.*, to be published; (*e*) A. Carrington and M. C. Symons, *Chem. Rev.*, 1963, **63**, 443.

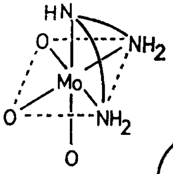
[3] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, 1964, **3**, 397.

[4] F. A. Cotton, S. M. Moorehouse, and J. S. Wood, *Inorg. Chem.*, 1964, **3**, 1603.

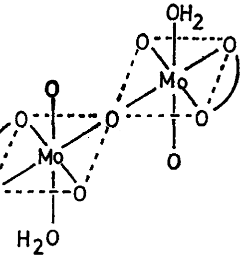
[5] L. O. Atomovniyan and G. B. Bokii, *Zhur. strukt. Khim.*, 1963, **4**, 576.

[6] A. B. Blake, F. A. Cotton, and J. S. Wood, *J. Amer. Chem. Soc.*, 1964, **86**, 3024.

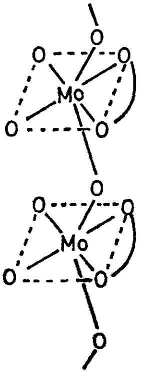
thate is EtOC(=S)S$^-$. Molybdenum is in distorted octahedral co-ordination and the oxygen ligands are mutually *cis*. The single oxygen bridges are linear and symmetrical except in the polynuclear oxalato-complex (III). Bonds to molybdenum from terminal oxygen are shorter (1·65—1·85 Å) than those from bridging oxygen (1·88 Å) and much shorter than Mo–O and Mo–N single bonds (*ca.* 2·33 Å). Those bonds between molybdenum and ligand atoms which are *trans* to multiple Mo–O bonds are exceptionally long, *e.g.*, in the xanthate complex (IV) the lengths of the Mo–S bonds decrease as they are *trans* to terminal oxygen > *trans* to bridging oxygen > *trans* to sulphur.[6]



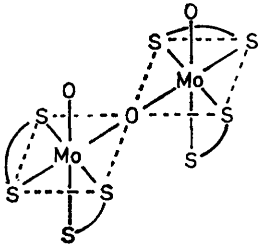
(I)



(II)



(III)



(IV)

Probable structures for the other compounds have been suggested on the basis of their stoicheiometries and the results of physical measurements with the assumption that molybdenum maintains a co-ordination number of six (apparent exceptions are "simple" compounds such as MoO_2Cl_2, which is tetrahedral in the vapour state,[7] and $MoOCl_3$. Such compounds may, however, be polymerised in the solid state).

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[7] A. F. Wells, "Structural Inorganic Chemistry", Oxford University Press, 1962, p. 387.

(b) The Molybdenum–Oxygen Bonding Interaction.—This has been treated for the ion $[MoOCl_5]^{2-}$ on the basis of a tetragonal structure with a short M–O bond [Figure (*a*)].[8a] The orbitals involved are: the Mo (*ds*) hybrid, Mo($5s + 4d_{z^2}$), and O(*sp*) giving a σ-bond and Mo($4d_{xz}$, $4d_{yz}$) and O($2p_x$, $2p_y$) giving two π-bonds. Chlorine forms σ-bonds with the molybdenum orbitals ($5s$–$4d_{z^2}$), ($5p_x$), ($5p_y$), ($5p_z$) and ($4d_{x^2-y^2}$). Mo($4d_{xy}$) is non-bonding. The important feature is π-donor bonding from oxygen to molybdenum giving a bond of order between two and three.

In compounds where more than one oxygen is bonded to molybdenum there is sharing of the metal d_π orbitals among the oxygens and so the extent of π-bonding between molybdenum and any one oxygen is less. Thus Mo–O bond lengths increase and stretching frequencies decrease as the number of terminal oxygens per molybdenum increases.[4] For di- and tri-oxo-species the *cis*-configuration is preferred because opportunities for π-bonding are greater than in the *trans*-configuration. An additional effect is a build up of charge on the metal atom as a result of the $p\pi \rightarrow d\pi$ bonding so that the presence of one π-bonded oxygen militates against π-bonding by a second.[4] The lengthening of bonds *trans* to multiple Mo–O bonds is probably also a consequence of this effect, the *trans* ligand experiencing electrostatic repulsion.

For the linear bridged species, $K_2[Mo_2O_5(oxalate)_2(H_2O)_2]$[4] and $Mo_2O_3(xanthate)_4$[6] π-bonding has been discussed in terms of three-centre molecular orbitals. Combination of a d_π orbital of each molybdenum atom and a p_π orbital of the single bridging oxygen atom produces one bonding, one non-bonding, and one anti-bonding molecular orbital. In a molybdenum(v) complex the bonding and non-bonding molecular orbitals will each contain two electrons; in a molybdenum(vi) complex only the bonding molecular orbital will be occupied.

(c) Infrared Spectra.—Mo–O stretching frequencies are given in Table 1. Values for multiple bonds from terminal oxygen to molybdenum are in the range 850—1000 cm.$^{-1}$, the actual value depending on the nature of the oxo species, the oxidation state of molybdenum, and the other ligands.

(*i*) *The nature of the oxo-species.* For molybdenum(vi), Mo–O stretching frequencies tend to decrease in the order $MoO^{4+} > MoO_2^{2+} > MoO_3$ (Table 1) and similarly for molybdenum(v) $MoO^{3+} > Mo_2O_3^{4+} > Mo_2O_4^{2+}$ (*e.g.*, the bipyridyl complexes in Table 1). These trends correlate with the expected decrease in π-bonding in these species [cf. Section 1(b)].

For dioxo-species the number of infrared-active stretching modes depends on whether the terminal oxygens are *cis* or *trans*, *cis* having two active modes and *trans* one.[9] For example, in the cyclopentadienyl complexes $MoO_2Cl(C_5H_5)$ and $Mo_2O_5(C_5H_5)_2$ there are two Mo–O bands near 900 cm.$^{-1}$ but only one in $MoOCl_2(C_5H_5)$. The first two therefore have

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[8] (*a*) H. B. Gray and C. R. Hare, *Inorg. Chem.*, 1962, **1**, 363; (*b*) C. R. Hare, I. Bernal, and H. B. Gray, *ibid.*, p. 831.

[9] K. Nakamoto, "Infrared Spectra of Inorganic and Co-ordination Compounds", Wiley, 1963, pp. 77—78.

cis-MoO_2 groups.[10] The molybdenum(VI) complex $MoO_2(oxine)_2$ has an additional band in the 900 cm.$^{-1}$ region compared with the molybdenum(V) complex $Mo_2O_3(oxine)_4$ (Table 1) suggesting that the molybdenum(VI) compound has a *cis*-MoO_2 group.[11] The MoO_3 group with C_{3v} symmetry should also have two infrared-active Mo–O modes. Only one is observed in the compound MoO_3(dien) and it is thought that the two fundamentals are accidentally degenerate.[3]

The binuclear complexes have additional bands in the region 700—900 cm.$^{-1}$ and these (when they can be distinguished from other ligand vibrations) have been assigned to vibrations of the Mo–O–Mo bridge.[10,12,13]

(*ii*) *The oxidation state of molybdenum.* From Table 1 it appears that the Mo=O stretching frequencies are in a lower range for molybdenum(VI) than for molybdenum(V) compounds; but this is because the data are mainly for dioxo-compounds of molybdenum(VI) and monoxo-compounds of molybdenum(V). For analogous oxo-species of the two oxidation states there is little difference, *e.g.*, $MoOCl_3$, 1020;[14] $[MoOCl_4]^-$, 1000;[15] $MoOCl_4$, 997 cm.$^{-1}$.[16]

(*iii*) *Other ligands.* The Mo–O stretching frequency is sensitive to environment but there are few obvious correlations with the properties of other ligands. The stretching frequencies are particularly low in complexes of cyclopentadienyl and cyanide (Table 1). In a series of oxochloro-complexes (Table 1) the frequency decreases as the negative charge on the species increases: $MoOCl_3 > [MoOCl_4]^- > [MoOCl_5]^{2-}$. This is reasonable as the increasing negative charge should make the metal a poorer π-acceptor. A similar effect is observed for a series of carbonylate ions.[17]

The preceding account of molybdenum–oxygen bonding is based largely on the structural and infrared work of Cotton's group. Recently, in a paper which is a useful summary of this work, Cotton and Wing[18] have correlated the force constants of Mo–O bonds with the bond distances and estimated bond orders.

(d) Magnetic Properties.—The theoretical spin-only moments in Bohr magnetons are zero for molybdenum(VI) (d^0) and 1·73 for molybdenum(V) (d^1). A slight temperature-independent paramagnetism is observed for molybdenum(VI) compounds.[19,20] Magnetic moments close to 1·7 B.M.

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[10] M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 1964, 1567.

[11] P. C. H. Mitchell, unpublished observations.

[12] T. Dupusi and M. Viltange, *Compt. rend.*, 1962, **255**, 2582.

[13] P. C. H. Mitchell, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1967.

[14] D. A. Edwards, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1198.

[15] E. A. Allen, B. J. Brisdon, D. A. Edwards, G. W. A. Fowles, and R. G. Williams, *J. Chem. Soc.*, 1963, 4649.

[16] M. L. Larson and F. W. Moore, Paper submitted to the 149th meeting of the American Chemical Society, Detroit, 1965.

[17] Ref. 1(*b*), p. 621.

[18] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 867.

[19] (*a*) S. M. Horner and S. Y. Tyree, *Inorg. Chem.*, 1962, **1**, 122; (*b*) C. M. French and J. H. Garside, *J. Chem. Soc.*, 1962, 2006.

[20] Ref. 1(*b*), p. 706.

are observed for mononuclear molybdenum(v) complexes but the binuclear complexes may have much lower moments as a consequence of the coupling of electron spins on neighbouring molybdenum atoms (data in Table 1).[21,22]

The magnetic properties of the compound $(NH_4)_2MoOCl_5$ have been studied in some detail. The average magnetic moment over a wide temperature range is 1·67 B.M.[8b] A *g*-value of 1·947 has been obtained from the electron spin resonance (e.s.r.) spectrum of the compound in concentrated hydrochloric acid. This *g*-value of nearly two indicates that the orbital angular momentum is effectively quenched in the low-symmetry ligand field arising from the presence of the terminal oxygen ligand.[8b,23]

The magnetic properties of linear-bridged binuclear molybdenum(v) complexes have been discussed in the context of the complex Mo_2O_3(xanthate)$_4$.[6] Whether such a compound will be paramagnetic or diamagnetic appears to depend on the angle of twist of the two halves of the molecule about the oxygen bridge (the dihedral angle). When this angle is $\frac{\pi}{4}$ the most stable state is a triplet. As the angle decreases to zero the singlet becomes more stable leading to diamagnetism. In complexes with two oxygen bridges spin–spin interaction can occur through the bridges or possibly by direct formation of a metal–metal bond.[6,21,24]

(e) **Electronic Spectra.**—The electronic spectrum of the $[MoOCl_5]^{2-}$ ion has been interpreted in terms of the orbital interaction described on page 103. The π-bonding from oxygen makes the molybdenum (d_{xz}, d_{yz}) orbitals antibonding [Figure (*b*)]. Three *d–d* transitions originating in the non-bonding (d_{xy}) orbital are possible.[8a] Two *d–d* transitions are observed (14·1 kK, to (d_{xz}, d_{yz}); 22·5 kK, to $(d_{x^2-y^2})$) but the third (to d_{z^2}) is covered by more intense charge-transfer transitions. The charge-transfer transitions involve excitation of an electron from the highest filled π-bonding molecular orbital (associated mainly with oxygen) to the *d*-orbitals. The observed and calculated spectra of $(NH_4)_2[MoOCl_5]$ as a solid and in concentrated hydrochloric acid are in good agreement.[8a]

Recent low-temperature measurements of the crystal spectra of the species $[MoOX_5]^{2-}$ (X = F, Cl, Br) have resolved the peak at 14 kK into a number of peaks which represent the progression of a vibrational mode superimposed on the electronic transition.[25,26]

The transition $(d_{xy}) \rightarrow (d_{x^2-y^2})$ gives the crystal field splitting parameter, *Dq*. It is interesting that the value of *Dq* for $[MoOCl_5]^{2-}$ (2250

[21] P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1962, 4570.

[22] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 1964, **6**, 37.

[23] K. DeArmond, B. B. Garrett, and H. S. Gutowsky, *J. Chem. Phys.*, 1965, **42**, 1019; ref. 1(*b*), p. 514.

[24] P. C. H. Mitchell, *J. Inorg. Nuclear Chem.*, 1963, **25**, 963.

[25] R. A. D. Wentworth and T. S. Piper, *J. Chem. Phys.*, 1964, **41**, 3884.

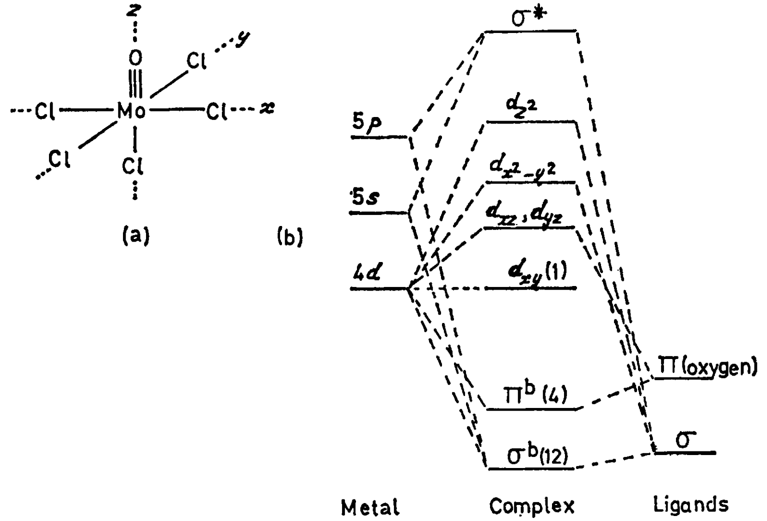
[26] (*a*) T. R. Ortolano, J. Selbin, and S. P. McGlynn, *J. Chem. Phys.*, 1964, **41**, 262; (*b*) J. Selbin and L. Morpurgo, *J. Inorg. Nuclear Chem.*, 1965, **27**, 673.

cm.$^{-1}$) is close to the value for $[MoCl_6]^{2-}$ (2200 cm.$^{-1}$) implying that the MoO^{3+} group presents an effective charge at the metal ion to the chlorines of about +4.[25]

The spectra of the binuclear complexes of molybdenum(V) (Table 1) also show peaks at 14 and 22—26 kK. The intensity of the second peak is enhanced on dimerisation (*e.g.*, the oxochloro-complexes in solution)[27] suggesting bridging in the *xy*-plane as this transition is localised in this plane.[8*b*,27]

Intense peaks due to ligand-to-metal charge-transfer transitions are observed in the visible spectra of some molybdenum(V) complexes (Table 1), *e.g.*, those with thiocyanate, bipyridyl, 8-hydroxyquinoline, and xanthate. The peaks shift to lower frequencies as the electron-donor character of the ligands increases.[21]

For molybdenum(VI) only ligand-to-metal charge-transfer transitions occur. The complexes are often white or yellow while analogous molybdenum(V) complexes are deeply coloured, *e.g.*, $MoO_2(oxine)_2$ yellow, $Mo_2O_3(oxine)_4$ black;[21,28] $MoO_2(CS_2NR_2)_2$ yellow, Mo_2O_3 $(CS_2NR_2)_4$ purple.[29] An obvious explanation is that the additional oxygen bonded to



(*a*) *The* $[MoOCl_5]^{2-}$ *ion and reference axes.* (*b*) *Orbitals for the* $[MoOCl_5]^{2-}$ *ion.* On the left are the molybdenum orbitals and on the right the π orbitals of oxygen and the σ orbitals of oxygen and chlorine. In the centre are the orbitals in the complex ion showing the splitting of the molybdenum *d*-orbitals and, in parentheses, the number of electrons in the orbitals. *d–d* transitions originate in the d_{xy} orbital and charge-transfer transitions in the π^b orbitals. The diagram is adapted from ref. 8*a*.

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[27] G. P. Haight, *J. Inorg. Nuclear Chem.*, 1962, **24**, 663.
[28] H. M. Stevens, *Analyt. Chim. Acta*, 1956, **14**, 126.
[29] L. Malatesta, *Gazzetta*, 1939, **69**, 408.

TABLE 1. *Some oxo-compounds of molybdenum-*(VI) *and* -(V)

Compound or complex ion	Infrared spectrum ν(Mo=O) (cm.$^{-1}$)*	Electronic spectrum ν_{max}(kK) (ϵ_{max})† or colour	Magnetic moment‡ (B.M., ~20°)
$MoOCl_4$	997[16]	green[16]	
MoO_2Cl_2		44·2(7000) 41(5000)[32]	
$[MoO_2Cl_3(H_2O)]^-$		44·2(7000) 34·5(5000)[32]	
$[MoO_2Cl_4]^{2-}$		44·2(7000) 32·3(5000)[32]	
$MoO_2Cl_2(PhCOCH_3)_2$	914[41]	White[41]	
$MoO_2Cl_2(Ph_3PO)_2$		Orange-yellow[19a]	0·32[19a]
$[MoO_2(oxalate)_2]^{2-}$	903[2b]		0·3[19b]
$MoO_2(acac)_2$	935[63] or 905[2b]	Yellow[63]	0·3[19b]
$[MoO_2(catechol)_2]^{2-}$	895[2b]	25·0(5560)[a]	
$MoO_2(oxine)_2$	926 899[b]	27·0 40·0[28]	0·26[11]
$MoO_2Cl(C_5H_5)$	920 887[10]	Yellow[10]	Dia.[10]
$[Mo_2O_5(oxalate)_2(H_2O)_2]^{2-}$	960 920[18]	Pale tan[4]	Dia.[4]
$Mo_2O_5(C_5H_5)_2$	930 920 898 850[10]	Yellow[10]	Dia.[10]
$[MoO_3(oxalate)(H_2O)]_n^{2n-}$	880 837[c]	White[c]	
$MoO_3(dien)$	839[3,18]	White[3]	
$[Mo_2O_6(EDTA)]^{4-}$	900 840[67]	White[67]	
$[MoOF_5]^{2-}$		12·3 13·1 21·2 22·0[25]	
$MoOCl_3$	1020[14]	13·7(20) 22·2(20)[14]	1·62[14]
$[MoOCl_4]^-$	1000[15] or 975[2b]	14·7 22·7[15]	1·7[15]
$[MoOCl_5]^{2-}$	967[d]	14·1(11) 22·5(10) 28·2(570) 32·2(5300) 41·7(3600)[8]	1·67[8]
$MoO(OH)Br_2·4H_2O$		14·9 21·7 27·0[35]	
$[MoOBr_4]^-$	985[2b]	14·3 20·8 24·2 26·3[35]	1·78[e]
$[MoOBr_5]^{2-}$		14·3(7) 21·3(560) 24·1(3200) 26·5(2500)[15]	1·7[15]
$MoOCl_3(Ph_3PO)_2$	967[19a]	13·5(19) 22·3(11)[f]	1·70[19a]
$MoOCl_3(MeCN)_2$	980[42]	13·7 19·0 26·0[42]	1·70[42]
$[MoOCl_4(MeCN)]^-$	990[f]	13·4(18) 22·5(17)[f]	1·68[f]
$MoOCl_3(bipy)$	979[24]	13·6 18·8 23·0[24]	1·87[24]
$MoOCl_3(oxine)$	935[2b]		
$MoOCl(oxine)_2$		16·9(1870) 26·1(3640)[21]	1·36[21]
$MoOCl_3(PPh_3)_2$	950[42]	Green[42]	1·72[42]
$MoOCl_2(C_5H_5)$	949[10]	Brown[10]	1·74[10]
$MoO(OH)(acac)_2·4H_2O$		20·4(5000)[21]	1·79[21]
$MoO(OH)(oxine)_2$		18·6(2280) 25·7(5000)[21]	1·79[21]
$[MoO(NCS)_5]^{2-}$	945[g]	12·8 19·2[g]	1·65[48]
$[MoO(CN)_4]^-$	929[2b]		
$Mo_2O_3Cl_4(bipy)_2$	966[24]	14·2 19·5 24·2[24]	0·84[24]
$[Mo_2O_3(NCS)_8]^{4-}$	950[g]	12·3 18·9[g]	

TABLE 1.—*continued*

Compound or complex ion	Infrared spectrum ν(Mo=O) (cm.$^{-1}$)*	Electronic spectrum ν_{max}(kK) (ϵ_{max})† or colour	Magnetic moment‡ (B.M., ~20°)
$Mo_2O_3(acac)_4$	961[64]	13·3 20·6(6236) 25·0(2068) 30·6(9672)[64]	Dia.[64]
$Mo_2O_3(xanthate)_4$	1236[6] or 1046[18] or 946[h]	Violet[29]	Dia.[29]
$Mo_2O_3(oxine)_4$	940[11]	18·5(5000) 25·0(10,000)[21]	0·66[21]
$Mo_2O_4(C_5H_5)_2$	925 901[10]	Yellow-brown[10]	Dia.[10]
$[Mo_2O_4(NCS)_6]^{4-}$	952[21]	13·4(75) 21·6(13,500) 31·0(19,000)[21, g]	0·1[48] or 0·6[21]
$Mo_2O_4Cl_2(bipy)_2$	952[24]	13·9 20·2 24·4[24]	0·47[24]
$[Mo_2O_4(ox)_2(H_2O)_2]^{2-}$	980[13]	20·4(41) 26·0(170) 32·8(3520) 38·9(3520)[13]	0·3[13]
$[Mo_2O_4(EDTA)]^{2-}$	940[67]	26·0(380) 33·6(9600)[21]	0·3[21]
$[Mo_2O_4Cl_4]^{2-}$			0·19[48]

*Stretching frequencies of bonds to terminal oxygen. †Frequencies of absorbance maxima (1 kK = 1000 cm.$^{-1}$) and molar extinction coefficients (where known). ‡In Bohr magnetons at room temperature.

Abbreviations: acac, acetylacetone anion; dien, diethylenetriamine; EDTA, ethylenediaminetetra-acetate; bipy, 2,2′-bipyridyl; ox, oxalate; dia., diamagnetic.

Reference numbers refer to those in the text. [a]G. P. Haight and V. Paragamian, *Analyt. Chem.*, 1960, **32**, 642. [b]R. J. Magee and A. S. Witwit, *Analyt. Chim. Acta*, 1963, **29**, 517. [c]Yu. Ya. Kharitonov and L. O. Atovmyan, *Izvest. Akad. Nauk, Otdel, Khim. Nauk*, 1965, 257. [d]C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1959, 3552. [e]P. Ray, *J. Indian Chem. Soc.*, 1930, 7, 741. [f]S. M. Horner and S. Y. Tyree, *Inorg. Chem.*, 1963, **2**, 568. [g]H. Wood and P. C. H. Mitchell, unpublished work. [h]See J. Selbin in ref 2*d*. The band at 1236 cm^{-1} is almost certainly not an Mo=O stretching frequency.

molybdenum(VI) in these compounds makes it a poorer electron acceptor than molybdenum(V): complexes in which molybdenum(VI) is fully co-ordinated with reducible ligands are deeply coloured, *e.g.*, $[MoS_4]^{2-}$ [1a] and Mo(toluene-3,4-dithiol)$_3$.[30]

2. Species in Solution

(a) **Molybdenum**(VI).—The species in strongly basic solutions is the colourless anion MoO_4^{2-}. In mineral acids the essential oxo-species appears to be the green cation MoO_2^{2+} which, depending on the particular acid, may be hydrated or complexed. At intermediate pH's polymeric species occur.[31]

Solutions of molybdenum(VI) in hydrochloric acid have been extensively

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[30] T. W. Gilbert and E. B. Sandell, *J. Amer. Chem. Soc.*, 1960, **82**, 1087.

[31] (*a*) Y. Sasaki, I. Lindqvist, and L. G. Sillen, *J. Inorg. Nuclear Chem.*, 1959, **9**, 93; (*b*) J. Aveston, E. W. Anacker, and J. S. Johnson, *Inorg. Chem.*, 1964, **3**, 735.

investigated by ultraviolet and visible spectrophotometry,[32] solvent extraction,[32,33] Raman spectroscopy,[31b] and redox measurements for the Mo^{VI}/Mo^{V} couple.[34] A major species over the acid concentration range 1 to 12M appears to be MoO_2Cl_2; its maximum concentration is reached in 6M-HCl. Below 4M-HCl there is evidence of a dimeric species.[34] Above 7M-HCl a 3:1 (Cl:Mo) species is also present, but there is no evidence for a 4:1 species.[32]

Hydrobromic acid slowly reduces molybdenum(VI) giving bromo-complexes of molybdenum(V) and the ion Br_3^-. Equilibrium studies of this reaction indicate that the molybdenum-(VI) and -(V) species are both dimeric in HBr.[35]

(b) Molybdenum(V).—Solutions in hydrochloric acid have been studied mainly by spectrophotometry and magnetic measurements. Unfortunately the conditions used by different workers have often been different or not stated precisely and it is difficult to compare their results especially in connexion with polymerisation phenomena.

There is general agreement that the major species in HCl $\geqslant$ 10M is $[MoOCl_5]^{2-}$, the spectra[8,15,27,36] and magnetic properties[8,37] being identical with those of solid $(NH_4)_2[MoOCl_5]$. It is possible that the species $[MoOCl_4]^-$ is also present.

Dilution of the green solutions of molybdenum(V) in concentrated hydrochloric acid causes enhanced absorbance in the visible region (without change in the positions of maximum absorbance)[27] and reduced paramagnetism,[37] the maximum changes occurring in 5—6M-HCl. In 6M-HCl enhancement of the peak at 22·5 kK is proportional to the square of the molybdenum(V) concentration indicating formation of a dimer, $[Mo_2O_3Cl_8]^{2-}$ [27] or $[Mo_2O_3Cl_2]^{2+}$.[36a] The intensity of the e.s.r. spectrum (proportional to the concentration of a monomer, MoO^{3+})[8b] decreases almost to zero in going from 10 to 4M-HCl. The decrease is more rapid than would be expected from the total paramagnetic susceptibility (proportional to the concentration of all paramagnetic species)[37] and the difference is a maximum in 6M-HCl. It appears that the monomer is changing into another paramagnetic species (possibly $[Mo_2O_3Cl_8]^{2-}$) which reaches its maximum concentration in 6M-HCl.[8b] The nature of the diamagnetic species in dilute HCl ($\leqslant$ 2M) is uncertain. It has been formulated as a dimer with two oxygen bridges[27] and as a tetramer.[36a]

According to a spectrophotometric and conductometric study the species $MoOCl_3$, $[MoOCl_4]^-$, and $[MoOCl_5]^{2-}$ are formed in the reaction between molybdenum(V) and chloride in anhydrous formic acid.[36b]

[32] H. M. Neumann and N. C. Cook, *J. Amer. Chem. Soc.*, 1957, **79**, 3026.

[33] I. Nelidow and R. M. Diamond, *J. Phys. Chem.*, 1955, **59**, 710.

[34] A. R. Tourky and H. K. El Shamy, *J. Chem. Soc.*, 1949, 140.

[35] J. F. Allen and H. M. Neumann, *Inorg. Chem.*, 1964, **3**, 1612.

[36] (*a*) J. P. Simon and P. Souchay, *Bull. Soc. chim. France*, 1956, 1402; (*b*) E. Wendling, *ibid.*, 1965, 437; (*c*) E. Wendling and R. Rohmer, *ibid.*, 1963, 2550; (*d*) E. Wendling, R. Rohmer, and R. Weiss, *Compt. rend.*, 1963, **256**, 1117.

[37] L. Sacconi and R. Cini, *J. Amer. Chem. Soc.*, 1954, **76**, 4239.

In hydrobromic acid molybdenum(V), like molybdenum(VI), is thought to be dimeric, the main species in HBr $\geqslant$ 8M being $[MoOBr_4^-]_2$.[35] In contrast to hydrochloric acid, there is no evidence for an oxopentahalogeno-species. At lower concentrations of hydrobromic acid, 2:1 and 1:1 (Br:Mo) species, and bromine-free species are thought to be present; but the evidence for the nature of these species is not very convincing.[35] It is worth noting that the greatest changes in the spectra of solutions in HBr as in HCl occur in the acid concentration range 6—5M and it is possible that analogous changes are occurring in both media, *i.e.*, paramagnetic dimer $\rightleftharpoons$ diamagnetic dimer.

3. Oxohalides and Complexes

In this and the following sections specific compounds will be discussed. Structural work which has been referred to in Section 1 will not be discussed further.

Molybdenum-(VI) and -(V) form a large number of simple and complex oxohalides with the halogens except iodine. The main types are: $MoOX_4$ ($X = F, Cl$), MoO_2X_2 ($X = F, Cl, Br$), $MoOX_3$ ($X = Cl, Br$), $R_2[MoOX_5]$ ($X = F, Cl, Br$), $R[MoOX_4]$ ($X = Cl, Br$). (R is an alkali metal or ammonium, alkylammonium, pyridinium, or quinolinium cation.) Some poorly characterised complexes of molybdenum(VI) are also known.[38] There has been little work on the fluoro-compounds[39] and the simple oxobromides[40] and these will not be discussed here.

(a) "Simple" Oxochlorides.—The preparative chemistry and reactions of $MoOCl_4$, MoO_2Cl_2, and $MoOCl_3$ are summarised in Table 2. $MoOCl_4$ is less stable than MoO_2Cl_2 and is readily converted into $MoOCl_3$ and its derivatives, *e.g.*, when heated under nitrogen[40] or with excess of acetylacetone and pyridine (Table 2).[16]

MoO_2Cl_2 forms complexes $MoO_2Cl_2L_2$ (L = unidentate ligand) and MoO_2Cl_2L' (L' = bidentate ligand) with oxygen-donor organic ligands (*e.g.*, Ph_3PO, acetylacetone) which are diamagnetic and white (except for the triphenylphosphine oxide complex, Table 1) and less moisture-sensitive than the parent compound.[16,19,41]

$MoOCl_3$ similarly forms complexes $MoOCl_3L_2$ and $MoOCl_3L'$ with oxygen-donor and also with nitrogen- and phosphorus-donor ligands either by direct reaction[16,42] or indirectly from $MoOCl_3(MeCN)_2$,[42] $MoOCl_4$,[16] or $MoCl_5$ (cf. Table 2).[19a] Formation of the complexes $MoOCl_3(Ph_3PO)_2$ and $MoOCl_3(Me_2SO)_2$ from molybdenum pentachloride in methylene chloride or carbon tetrachloride involves oxygen abstrac-

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[38] Ref. 1(*a*), p. 1044.

[39] (*a*) Ref. 1(*a*), p. 1035; (*b*) G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 1958, 4390; (*c*) G. H. Cady and G. B. Hargreaves, *ibid.*, 1961, 1568.

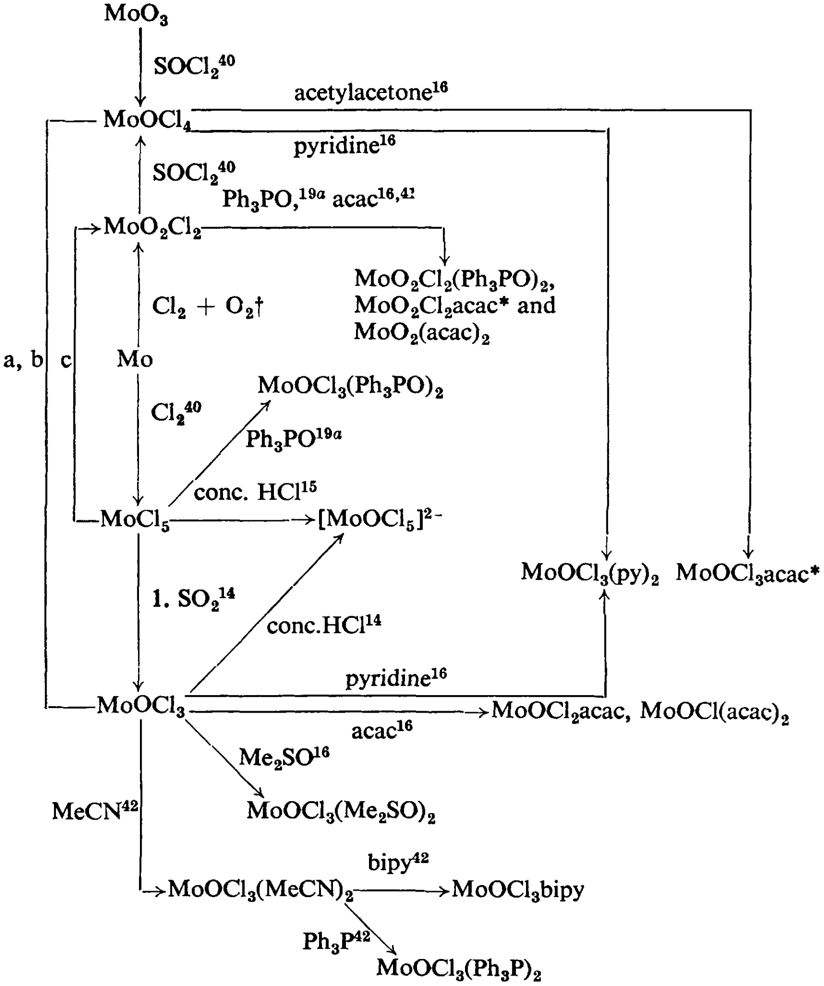
[40] (*a*) R. Colton, I. B. Tomkins, and P. W. Wilson, *Austral. J. Chem.*, 1964, **17**, 496; (*b*) R. Colton and I. B. Tomkins, *ibid.*, 1965, **18**, 447.

[41] H-L. Krauss and W. Hüber, *Chem. Ber.*, 1961, **94**, 2864.

[42] D. A. Edwards, *J. Inorg. Nuclear Chem.*, 1965, **27**, 303.

tion from the ligands, a process facilitated by the strength of the Mo–O bond.[19a] The complexes of $MoOCl_3$ are green solids with normal magnetic moments. Their electronic and infrared spectra are characteristic of compound containing the MoO^{3+} group. They are much less readily hydrolysed than $MoOCl_3$, the bipyridyl complexes being particularly stable.[16,19,42]

TABLE 2. *Preparations and reactions of molybdenum oxochlorides*



(a) Heat in nitrogen.[40] (b) Reflux with chlorobenzene.[16] (c) React with $SOCl_2$ in air.[40]
*These compounds have neutral acetylacetone as ligand.
†O. Ruff and F. Eisner, *Ber.*, 1907, **40**, 2933. Other reference numbers refer to those in the text.

(b) Oxochloro- and Oxobromo-complexes.—The complexes $R_2[MoOX_5]$ and $R[MoOX_4(H_2O)]$ (X = Cl, Br) may be prepared by electrolytic[43] or chemical[35,36a] reduction of a solution of molybdenum trioxide in concentrated halogen acid (HX) or by dissolving a compound of molybdenum(v) [*e.g.*, $MoCl_5$,[15] $MoO(OH)_3$ [44]] in concentrated halogen acid followed by addition of the appropriate halide (RX). Anhydrous complexes $R[MoOCl_4]$ have been prepared from molybdenum pentachloride and RCl in liquid sulphur dioxide, and $(pyH)[MoOBr_4]$ by treating the pentabromo-complex with sulphur dioxide.[15] It has been suggested that the $[MoOX_4]^-$ species are binuclear with halogen rather than oxygen bridges.[35]

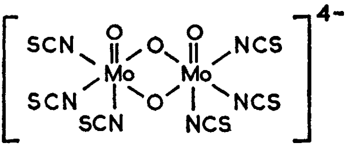
The chloro- and bromo-complexes are labile with respect to hydrolysis and replacement of halide [*e.g.*, the reactions of $(NH_4)_2[MoOCl_5]$with thiocyanate and organic ligands, Sections 4 and 5].

4. Oxoisothiocyanato-complexes

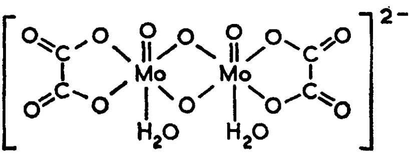
Isothiocyanato-complexes are known for molybdenum(v) but not for molybdenum(vi). The formation of a deeply coloured molybdenum(v) complex when an acidified molybdate solution is reduced by stannous chloride or cuprous chloride in the presence of thiocyanate is applied in the spectrophotometric determination of molybdenum.[45]

Ammonium thiocyanate and aqueous solutions of the complexes $R_2[MoOCl_5]$ yield either $R_4[Mo_2O_4(NCS)_6]$ (R = pyridinium, quinolinium) or $R_4[Mo_2O_3(NCS)_8]$ (R = Me_3NH, Me_4N). With boiling thiocyanic acid these compounds, and also the chloro-complexes, yield complexes $R_2[MoO(NCS)_5]$.[46]

The anion (V) in the compound $(pyH)_4[Mo_2O_4(NCS)_6]$ has been formulated as a dimer on the basis of the conductivity of the compound in nitrobenzene, its low magnetic moment, and its infrared spectrum (which shows the presence of terminal oxygen and *N*-bonded thiocyanate).[21,47] The octaisothiocyanate presumably has one oxygen bridge and the penta-isothiocyanate (magnetic moment = 1·65 B.M.)[48] is mononuclear.



(V)



(VI)

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[43] (*a*) R. G. James and W. Wardlaw, *J. Chem. Soc.*, 1927, 2145; (*b*) F. G. Angell, R. G. James, and W. Wardlaw, *ibid.*, 1929, 2578.

[44] W. G. Palmer, "Experimental Inorganic Chemistry", Cambridge University Press, 1959, p. 408.

[45] A. I. Vogel, "Quantitative Inorganic Analysis", Longmans, 1962, p. 903.

[46] R. G. James and W. Wardlaw, *J. Chem. Soc.*, 1928, 2726.

[47] P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1960, 1912.

[48] W. Klemm and H. Steinberg, *Z. anorg. Chem.*, 1936, **227**, 193.

The first crystal-field transition in the isothiocyanate complexes occurs as a broad, weak peak near 12·5 kK but the second is covered by an intense change-transfer peak (SCN→Mo) at 21 kK which is responsible for the deep colour of the compounds.

In spite of a large amount of work the nature of the analytical species absorbing near 21 kK is still uncertain. It has been variously formulated as $MoO(NCS)_3$,[49] $[Mo(NCS)_4]^+$,[50] $[MoO(NCS)_5]^{2-}$ or $Mo(NCS)_5$,[51] and $[Mo_2O_2(OH)(NCS)_3]^{2+}$.[52] It is in equilibrium with other species absorbing near 19·6 kK[50,51,53] and 23·5 kK[49] and with a colourless species,[49] the proportion of each depending on the acidity and the thiocyanate concentration.

5. Complexes with Organic Ligands

The oxo-species of molybdenum behave as Class (*a*) acceptors and form a large number of complexes with nitrogen- and oxygen-donors. They have some affinity also for sulphur-donors.

(a) Complexes with Nitrogen-donors.—(*i*) *Amines.* The molybdenum(VI) complex MoO_3(dien) (cf. p. 101) (dien = diethylenetriamine,$H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$) precipitates when ethanol is added to a solution of molybdenum trixode in aqueous dien. With ethylenediamine and triethylenetetramine solids of variable composition, probably containing polymolybdates, were obtained.[54]

(*ii*) 2,2′-*Bipyridyl.* Reaction of bipyridyl with molybdenum pentachloride or $(NH_4)_2MoOCl_5$ gives complexes $MoOCl_3$(bipy), $Mo_2O_3Cl_4$(bipy)$_2$, and $Mo_2O_4Cl_2$(bipy)$_2$.[24] The first has also been prepared from bipyridyl and $MoOCl_3(MeCN)_2$.[42] The solids are insoluble in water and common organic solvents and resistant to hydrolysis and aerial oxidation. The electronic spectra of the complexes (Table 1) show the two crystal-field transitions characteristic of oxomolybdenum(V) complexes. The intensity of the second transition is greater in the two binuclear complexes (cf. p. 106). Bipyridyl-to-molybdenum charge-transfer transitions are also observed.[24]

(b) Complexes with Oxygen-donors.—Complexes with pyridine *N*-oxide, triphenyl and triarsine oxides, and with dimethyl sulphoxide have already been mentioned (p. 110). Other well characterised complexes are those with the oxalate and acetylacetone anions.

(*i*) *Oxalate.* The white molybdenum(VI) complexes are of three types: $NaNH_4[MoO_3(C_2O_4)],2H_2O$,[55] $K_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$,[4] and (quinH)$_2$-

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[49] D. D. Perrin, *J. Amer. Chem. Soc.*, 1958, **80**, 3540.

[50] Hsu Pao-Yun and Chang Wei-Chin, *Acta Chim. Sinica*, 1958, **24**, 258.

[51] A. K. Babko, *J. Gen. Chem.* (*U.S.S.R.*), 1947, **17**, 642.

[52] P. Souchay, M. Cadiot, and M. Duhameaux, *Compt. rend.*, 1965, **260**, 186; M. Duhameaux and M. Cadiot, *ibid.*, p. 1153.

[53] C. E. Crouthamel and C. E. Johnson, *Analyt. Chem.*, 1954, **26**, 1284.

[54] W. F. Marzluff, *Inorg. Chem.*, 1964, **3**, 395.

[55] A. Rosenheim and A. Bertheim, *Z. anorg. Chem.* 1903 **34**, 436.

$[MoO_2(C_2O_4)_2]$ (quin = quinoline).[56] The first and last are obtained from aqueous solutions of molybdenum trioxide in oxalic acid and the second by aerial oxidation of the molybdenum(V) complex $K_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]$. For structures, see p. 101.

The brown molybdenum(V) complex $Ba[Mo_2O_4(C_2O_4)_2(H_2O)_2],3H_2O$ is precipitated when barium chloride is added to an aqueous solution of $(NH_4)_2[MoOCl_5]$ and oxalic acid. The corresponding potassium and pyridinium salts are also known.[43a,57] These complexes have also been prepared by reducing with hydrazine hydrochloride an aqueous solution of a molybdate and oxalic acid.[58] Aqueous solutions of the potassium salt are slowly oxidised in air and the oxalate groups dissociate in dilute acids. On the basis of the electrical conductivity of the potassium salt in water, and the infrared spectrum, diamagnetism, and thermogravimetric analysis of the solid, the complex anion is formulated[13] as a dimer with two oxygen bridges (VI).*

(*ii*) *Acetylacetone* Orange-yellow crystals of the complex $MoO_2(acac)_2$ are obtained by the addition of nitric acid to a solution of ammonium paramolybdate and acetylacetone[59] and by refluxing acetylacetone with molybdenum trioxide.[60] The compound is insoluble in water but dissolves in chloroform and benzene.

Three types of complex are known for molybdenum(V): $MoO_2(acac)$, obtained by aerial oxidation of the molybdenum(III) compound $MoO(acac),2\frac{1}{2}H_2O$;[61] $MoO(OH)(acac)_2,4H_2O$, obtained by heating $(NH_4)_2[MoOCl_5]$ with acetylacetone;[24,62] and $Mo_2O_3(acac)_4$, obtained by the reaction of an aqueous solution of $(NH_4)_2[MoOCl_5]$ with acetylacetone and by aerial oxidation of $Mo(acac)_3$.[63,64] The first is green and soluble in water and organic solvents. The last two are insoluble in water but dissolve in methylene chloride, chloroform, and benzene.

(c) **Complexes with Oxygen- and Nitrogen-donors.**—Important complexes are those with the anions of ethylenediaminetetra-acetic acid ($EDTAH_4$) and 8-hydroxyquinoline (oxine).

(*i*) $EDTAH_4$. The reaction between molybdenum-(VI) and -(V) and $EDTAH_4$ has been investigated polarographically and spectrophoto-

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[56] H. M. Spittle and W. Wardlaw, *J. Chem. Soc.*, 1931, 1748.

[57] H. M. Spittle and W. Wardlaw, *J. Chem. Soc.*, 1928, 2742.

[58] G. A. Barbieri and A. Malaguti, *Mem. Accad. Sci. Ist. Bologna*, 1951, **9**, 3; G. Cavicchi, *Gazzetta*, 1963, **83**, 402.

[59] M. M. Jones, *J. Amer. Chem. Soc.*, 1959, **81**, 3188.

[60] W. C. Fernelius, K. Terada, and B. E. Bryant, *Inorg. Synth.*, 1960, **6**, 147.

[61] G. T. Morgan and R. A. S. Castell, *J. Chem. Soc.*, 1928, 3252.

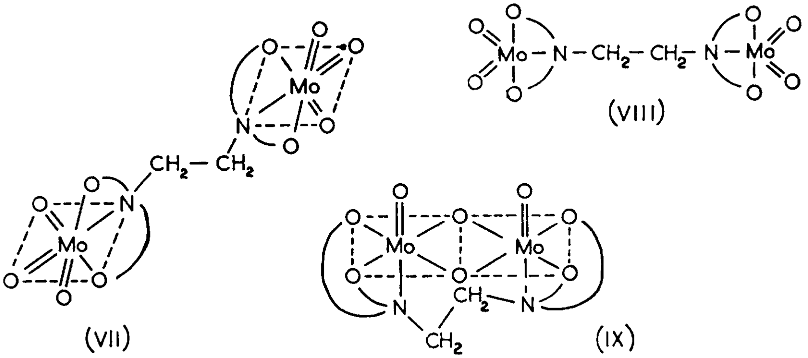
[62] A. Rosenheim and C. Nernst, *Z. anorg. Chem.*, 1933, **209**, 216.

[63] M. L. Larson and F. W. Moore, *Inorg. Chem.*, 1962, **1**, 856.

[64] M. L. Larson and F. W. Moore, *Inorg. Chem.*, 1963, **2**, 881.

* [*Note added in proof.*—The structure of the oxalato-complex $Ba[Mo_2O_4(C_2O_4)_2(H_2O)_2],3H_2O$ has now been published (F. A. Cotton and S. M. Morehouse, *Inorg. Chem.* 1965, **4**, 1377) and confirms the proposed structure. The complex anion is a dimer with two oxygen bridges and a Mo—Mo bond of 2·541Å.]

metrically,[65] and by proton magnetic resonance.[66] Complexes with a Mo:EDTA^{4-} ratio of 2:1 are formed. From the aqueous solutions a white molybdenum(VI) complex, $Na_4[Mo_2O_6(EDTA)],8H_2O$, and a brown molybdenum(V) complex, $Na_2[Mo_2O_4(EDTA)],H_2O$, have been isolated. Aqueous solutions of the molybdenum(V) complex are stable in air. According to their infrared spectra[67] both complexes contain terminal oxygen. A possible structure of the molybdenum(VI) complex is shown as (VII) (where the $N{\cdot}CH_2{\cdot}CO_2^-$ group is represented as NO); the stereochemistry of each molybdenum is similar to that in the complex MoO_3-(dien). A similar structure (VIII) for the molybdenum(V) complex has been proposed[65] but is unlikely in view of the diamagnetism of the compound,[21] a co-ordination number of less than six for molybdenum, and the suggestion of a MoO_2 group. A more plausible structure which overcomes these objections, accounts for the stability of the compound, and is feasible on the basis of a molecular model, is suggested in (IX) where the N–C–C–N unit bridges a Mo_2O_4 group.


(VII) (VIII) (IX)

(*ii*) 8-*Hydroxyquinoline*. Quantitative precipitation of molybdenum(VI) as the yellow complex, $MoO_2(oxine)_2$, is an established analytical procedure.[68] The compound is insoluble in water but dissolves slightly in methylene chloride, chloroform, and dimethylformamide.[69]

The molybdenum(V) complexes, $MoO(OH)(oxine)_2$ and $Mo_2O_3(oxine)_4$, are precipitated when oxine is added to an aqueous solution of molybdenum(V).[21,28,70] With $(NH_4)_2[MoOCl_5]$ in ethanol the complex $MoOCl(oxinate)_2$ is obtained.[21] These complexes are soluble in polar organic solvents and stable in air. The deep colours of the molybdenum(V) complexes are due to a ligand-to-metal charge-transfer transition near 18·5 kK.

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[65] R. L. Pecsock and D. T. Sawyer, *J. Amer. Chem. Soc.*, 1956, **78**, 5496.

[66] S. I. Chan, R. J. Kula, and D. T. Sawyer, *J. Amer. Chem. Soc.*, 1964, **86**, 377.

[67] D. T. Sawyer and J. M. McKinnie, *J. Amer. Chem. Soc.*, 1960, **82**, 4191.

[68] Ref. 45, p. 506.

[69] A. I. Busev and Chang Fan, *Zhur. analit. Khim.*, 1960, **15**, 455.

[70] A. I. Busev and Chang Fan, *Talanta*, 1962, **9**, 107; J. T. Spence and E. R. Perlen, *Inorg. Chem.*, 1962, **1**, 277.

Complexes with substituted oxines and with 8-mercaptoquinoline are also known.[21,70,71]

(d) Complexes with Sulphur-donors.—Solutions of molybdates are reduced by the bidentate sulphur-donor ligands (L′) monoalkyldithiocarbamate ($RNH{\cdot}CS_2^-$), alkyl xanthate ($ROCS_2^-$, cf. p. 102),[29] and dialkyldithiophosphate [$(RO)_2PS_2^-$][72] giving deep purple diamagnetic molybdenum(v) complexes, $Mo_2O_3L'_4$. The complexes are stable in air. They are insoluble in water but dissolve in organic solvents. With dialkyldithiocarbamates ($R_2NCS_2^-$), which are not reducing agents, molybdates form orange-yellow complexes, $MoO_2(R_2NCS_2)_2$, which are reduced by sulphur dioxide to molybdenum(v) complexes, $Mo_2O_3(R_2NCS_2)_4$.[29]

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[71] J. Bankorskis, E. Svarles, and A. Ievins, *Zhur. analit. Khim.*, 1959, **14**, 331.
[72] G. Spengler and A. Weber, *Chem. Ber.*, 1959, **92**, 2163.