Oxomolybdenum(III) Complexes

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Reaction of the molybdenum(III) compound $Mo_2O_2Cl_2(H_2O)_6$ with ligands, L, gave complexes $Mo_2O_2Cl_2(H_2O)_xL_y$ [L = 2,2'-bipyridyl and 4,4'-dimethyl-2,2'-bipyridyl (x = 2, y = 2), pyrrole and pyridazine (x = 4, y = 2), pyridine (x = 4, y = 3)], $Mo_2O_2(H_2O)_xL_y$ [L = acetylacetonate (x = 4, y = 2) and tartrate (2−) (x = 6, y = 1)], and an oxalato-complex $Mo_4O_3(C_2O_4)_3(H_2O)_{12}$. The complexes are formulated and structures proposed on the basis of analyses and physical measurements. The binuclear complexes contain the di-μ-oxo-dimolybdenum(III) group, MoO_2Mo, and the tetrameric oxalato-complex contains μ-hydroxo-μ-oxo-dimolybdenum groups, Mo(OH)OMo, linked by bridging oxalate. Earlier formulations of some of the complexes with terminal oxygen bonded to molybdenum are shown to be incorrect.

MANY years ago Wardlaw and his co-workers [1] prepared a series of molybdenum(III) complexes which were formulated as derivatives of an oxomolybdenum(III) cation MoO^+, *e.g.* the oxo-chloride $MoOCl,4H_2O$. To our knowledge these complexes have not been reinvestigated. In recent years there has been rather less work on the chemistry of molybdenum in oxidation state III, especially in an aqueous environment, than on molybdenum in higher oxidation states, especially V and VI.[2] However, because of suggestions that the III oxidation state of

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[1] W. Wardlaw, F. H. Nicholls, and N. D. Sylvester, *J. Chem. Soc.*, 1924, 1911; W. Wardlaw and R. L. Wormell *ibid.* 1924, 2370; W. Wardlaw and W. H. Parker, *ibid.*, 1925, 1311; W. Wardlaw and A. J. I. Harding, *ibid.*, 1926, 1592; W. Wardlaw and R. L. Wormell, *ibid.*, 1927, 130; W. R. Bucknall, S. R. Carter, and W. Wardlaw, *ibid.*, p. 512; W. Wardlaw and R. L. Wormell, *ibid.*, p. 1087.

[2] P. C. H. Mitchell, *Co-ordination Chem. Rev.*, 1966, **1**, 315.

molybdenum may be involved in catalysis by molybdoenzymes, *e.g.* xanthine oxidase[3] and nitrogenase,[4] and in the reduction of dinitrogen in model experiments,[5] a study of molybdenum(III) chemistry is timely. In the context of current work on oxo-complexes of the early transition metals[6] it is of interest to determine whether such complexes of molybdenum(III) have multiply bonded terminal oxygen as found for many complexes of the higher oxidation states. In this paper we report an investigation of an oxo-chloro-complex of molybdenum(III) and its reactions with oxygen- and nitrogen-donor ligands.

EXPERIMENTAL

Preparations.—All reactions and manipulations were carried out under nitrogen or *in vacuo*.

Di-μ-oxo-bis[triaquochloromolybdenum(III)], $Mo_2O_2Cl_2(H_2O)_6$ (I). A solution of molybdenum trioxide (45 g) in concentrated hydrochloric acid (130 ml) was reduced electrolytically using a smooth platinum cathode and a carbon anode at 1·5—2·0 A and 10—12 V for 2 days. Acetone was then run into the reduced solution and the resulting precipitate was filtered off, washed with acetone, and dried *in vacuo* (Found: Cl, 17·3; Mo, 47·5; H_2O, 26·3. Calc. for $H_{12}Cl_2Mo_2O_8$: Cl, 17·6; Mo, 47·6; H_2O, 26·8%).

Di-μ-oxo-bis[acetylacetonatodiaquomolybdenum(III)]*hydrate*, $[Mo_2O_2(C_5H_7O_2)_2(H_2O)_4]H_2O$ (II). This compound was prepared according to the procedure of Morgan and Castell[7] by heating the oxochloride (I) with acetylacetone in ethanol (Found: C, 23·1; H, 4·8; Mo, 37·6%; *M*, 600 ± 50. Calc. for $C_{10}H_{24}Mo_2O_{11}$: C, 23·45; H, 4·7; Mo, 37·5%; *M*, 512).

Oxalato-complex of molybdenum(III), $Mo_4O_3(C_2O_4)_3(H_2O)_{12}$ (III). Ammonium oxalate (1·05 g) in water (50 ml) was added to a suspension of the oxo-chloride (I) (1·50 g) in water (20 ml). The suspension was shaken for 1 h and a red solid was filtered off, washed with water, and dried *in vacuo* (Found: C, 7·8; H, 2·7; Mo, 41·6; H_2O, 24·0. Calc. for $C_6H_{24}Mo_4O_{27}$: C, 7·9; H, 2·6; Mo, 42·1; H_2O, 23·7%).

Tartrato-complex of molybdenum(III), $Mo_2O_2(C_4H_4O_6)(H_2O)_6$ (IV). A solution of potassium sodium tartrate (3·0 g) in water (25 ml) was added to the oxo-chloride (I) (4·06 g). The suspension was shaken for 1 h and a buff solid was filtered off, washed with water, and dried *in vacuo* (Found: C, 9·9; H, 3·1; Mo, 40·1. Calc. for $C_4H_{16}Mo_2O_{14}$: C, 10·0; H, 3·3; Mo, 40·0%).

Di-μ-oxo-bis[diaquochloropyridinemolybdenum(III)], *pyridine*, $[Mo_2O_2Cl_2(H_2O)_4(C_5H_5N)_2](C_5H_5N)$ (V). The oxo-chloride (I) was shaken for 2 days with pyridine (15 ml) and gave a dark yellow-brown solution which was evaporated to dryness of a vacuum line. An identical *product* was obtained after a reaction time of 7 days (Found: C, 29·6; H, 3·9; Cl, 11·7; Mo, 31·9; N, 6·6. $C_{15}H_{23}Cl_2Mo_2N_3O_6$ requires C, 29·8; H, 3·8; Cl, 11·75; Mo, 31·8; N, 7·0%).

Di-μ-oxo-bis[aquo(2,2′-*bipyridyl*)*chloromolybdenum*(III)], $Mo_2O_2Cl_2(C_{10}H_8N_2)_2(H_2O)_2$ (VI). A solution of 2,2′-bipyridyl (2·1 g) in ethanol (15 ml) was added to the oxo-chloride (I) (1·10 g). The resulting solution was heated under reflux for 18 h. A *solid* was precipitated by diethyl ether and this was filtered off and dried *in vacuo* (Found: C, 37·1; H, 2·9; Cl, 11·3; Mo, 29·95; N, 8·6. $C_{20}H_{20}Cl_2Mo_2N_4O_4$ requires C, 37·4; H, 3·1; Cl, 11·05; Mo, 29·85; N, 8·7%).

Di-μ-oxo-bis[aquochloro)(4,4′-*dimethyl*-2,2′-*bipyridyl*)-*molybdenum*(III)], $Mo_2O_2Cl_2(H_2O)_2(C_{12}H_{12}N_2)_2(H_2O)_2$ (VII). 4,4′-Dimethyl-2,2′-bipyridyl (2·7 g) was added to a suspension of the oxo-chloride (I) (1·5 g) in ethanol (50 ml) and the mixture was heated under reflux for 18 h. Ethanol (25 ml) was evaporated under reduced pressure and excess of the bipyridyl was filtered off. Ether was then added to the filtrate giving a dark *solid* which was filtered off, washed with acetone, and dried *in vacuo* (Found: C, 40·9; H, 4·1; Cl, 10·3; Mo, 27·5; N, 7·9. $C_{24}H_{32}Cl_2Mo_2N_4O_6$ requires C, 41·2; H, 4·0; Cl, 10·2; Mo, 27·5; N, 8·0%).

Di-μ-oxo-bis[diaquochloropyridazinemolybdenum(III)], $Mo_2O_2Cl_2(H_2O)_4(C_4H_3N_2)_2$ (VIII). Pyridazine (1·3 ml) in ethanol (20 ml) was added to the oxo-chloride (I) (1·5 g). The suspension was heated under reflux for 6 h and a dark brown *solid* was filtered off, washed with ethanol, and dried *in vacuo* (Found: C, 18·05; H, 2·8; Cl, 13·8; Mo, 36·1; N, 9·9. $C_8H_{14}Cl_2Mo_2N_4O_6$ requires C, 18·2; H, 3·0; Cl, 13·5; Mo, 36·45; N, 10·6%).

Di-μ-oxo-bis[diaquochloropyrrolemolybdenum(III)], $Mo_2O_2Cl_2(H_2O)_4(C_4H_5N)_2$ (IX). Pyrrole (0·4 ml) in ethanol (20 ml) was added to the oxo-chloride (I) (1·5 g). The resulting solution was heated under reflux for 20 h and evaporated to dryness *in vacuo*. The product was a brown *solid* (Found: C, 19·3; H, 3·7; Cl, 14·0; Mo, 38·3; N, 5·3. $C_8H_{18}Cl_2Mo_2N_2O_6$ requires C, 19·2; H, 3·6; Cl, 14·2; Mo, 38·3; N, 5·6%).

Analyses.—Molybdenum was determined gravimetrically as molybdenum(VI) quinolin-8-olate after decomposing the complexes by heating with HNO_3–H_2SO_4 (1 : 1). Water was determined by heating the complexes in an atmosphere of nitrogen using a Stanton thermobalance model TR1. Carbon, hydrogen, chlorine, and nitrogen were determined microanalytically.

Physical Measurements.—I.r. spectra for the compounds were recorded over the ranges 650—4000 (Nujol mulls) and 250—650 cm^{-1} (potassium bromide discs) with a Unicam SP 200 and a Grubb-Parsons DM4 spectrophotometer respectively. U.v. and visible solution and reflectance spectra were recorded with a Unicam SP 700 spectrophotometer. Magnetic susceptibilities were measured on powdered samples at room temperature using a Gouy balance (Newport Instruments Ltd.) calibrated with cobalt mercury thiocyanate.

RESULTS AND DISCUSSION

Compounds Prepared.—By treating the compound $Mo_2O_2Cl_2(H_2O)_6$ (I) with the appropriate ligand (L) we have prepared two types of complex: (a) new complexes of nitrogen-donor ligands, $Mo_2O_2Cl_2(H_2O)_xL_y$ [L = 2,2′-bipyridyl (VI; $x = 2$, $y = 2$), 4,4′-dimethyl-2,2′-bipyridyl (VII; $x = 2, y = 2$), pyrrole (IX; $x = 4, y = 2$), pyridazine (VIII; $x = 4$, $y = 2$), and pyridine (V;

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[3] V. Massey, P. E. Brumby, and H. Komai, *J. Biol. Chem.*, 1969, **244**, 1682.

[4] R. Murray and D. C. Smith, *Co-ordination Chem. Rev.*, 1968, **3**, 429.

[5] N. T. Denisov, V. F. Shuvalov, N. I. Shuvalova, A. K. Shilova, and A. E. Shilov, *Doklady Akad. Nauk S.S.S.R.*, 1970, **195**, 879; *Nature*, 1971, **231**, 460.

[6] J. Selbin, *Angew. Chem.*, 1966, **78**, 736.

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

$x = 4$, $y = 3$); (b) complexes of oxygen-donor ligands, $Mo_2O_2(H_2O)_xL_y$ [L = acetylacetonate (II; $x = 4, y = 2$), tartrate (IV; $x = 6$, $y = 1$)] and the oxalato-complex $Mo_4O_3(C_2O_4)_3(H_2O)_{12}$ (III). The complexes are formulated on the basis of analyses and physical measurements. The oxidation state of molybdenum was shown to be III by titration with cerium(IV) or permanganate. The type (b) complexes have been prepared before [1,7] and our empirical formulae are in agreement with previous work. Our thermogravimetric analysis of the oxo-chloride (I), which has also been prepared before,[1] showed a water : molybdenum ratio of 3 : 1 whereas Wardlaw *et al.*[1] found 4 : 1.

TABLE 1

Infrared spectra. Main bands and assignments *

Compound		Water				
		ν(OH)	δ(OH)	Organic ligands	Mo_2O_2	ν(MoCl)
(I)	$Mo_2O_2Cl_2(H_2O)_6$	3250vs	1620s 1385s		710m 670s	388s
(II)	$[Mo_2O_2(acetylacetonate)_2(H_2O)_4]H_2O$	3300vs 3150vs	1615s	1550vs, 1375vs, 1278m, 1025m, 938w	675s	
(III)	$Mo_4O_3(oxalate)_3(H_2O)_{12}$	3150vs,b	1620sh 1400s	1695sh, 1670vs, 1303s, 905m, 785m	680s	
(IV)	$Mo_2O_2(tartrate)(H_2O)_6$	3250vs,b	1630s,b	1630s,b, 1550m, 1127m, 1075m	682s	
(V)	$[Mo_2O_2Cl_2(H_2O)_4(pyridine)_2]pyridine$	3280vs		1630w, 1600s, 1485m, 1445s, 1213m, 1065m, 752s, 690vs	675s	
(VI)	$Mo_2O_2Cl_2(H_2O)_2(bipyridyl)_2$	3230vs	1620m	1600s, 1472m, 1445s, 1385m, 1314w, 1150w, 768s, 725m	675s	
(VII)	$Mo_2O_2Cl_2(H_2O)_2$(4,4′-dimethyl-2,2′-bipyridyl)$_2$	3300vs		1613s, 1555m, 1488m, 1450m, 1417m, 1280m, 1240w, 1030s, 945s, 925w, 840m, 658m	670m	
(VIII)	$Mo_2O_2Cl_2(H_2O)_4(pyridazine)_2$	3200vs	1620m	1575s, 1445m, 1415m, 1385m, 1290w, 1035m, 975w, 765m	670s	
(IX)	$Mo_2O_2Cl_2(H_2O)_4(pyrrole)_2$	3200vs	1620s	3300vs, 1550m, 1442m, 1410m, 1090w, 1038m, 880w, 730s	690s	

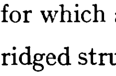
* Positions ($\bar{\nu}$/cm^{-1}) and relative intensities (vs, very strong; s, strong; m, medium; w, weak; b, broad; sh, shoulder). For assignments see refs. 9, 12 (water); 10 (Mo_2O_2); 14 (MoCl). For complexes (V)—(IX) ligand bands interfered with ν(MoCl) assignments. Assignments for organic ligands are based on comparisons with spectra of ligands and well characterised complexes.

General Properties of the Complexes.—The complexes were obtained as dark brown microcrystalline solids. The dry solids could be handled in air although they oxidised slowly (*ca.* 1 day). During exposure to air a band developed in their i.r. spectra at *ca.* 970—980 cm^{-1} which is in the region of Mo–O$_t$ stretching vibrations (where O$_t$ represents terminal oxygen) and indicates formation of an oxomolybdenum(V) species.[8] The oxochloride (I) was insoluble in water and slightly soluble in hot ethanol giving a yellow solution. Whereas the tartrato- and oxalato-complexes were insoluble in water and ethanol, the acetylacetonato-complex (II) and the type (a) complexes dissolved in these solvents in the cold. All complexes dissolved in concentrated hydrochloric acid giving red solutions.

Thermogravimetric Analyses.—In order to determine the water content of our complexes we carried out thermogravimetric analyses. Lattice water is expected to be released at a lower temperature than that of coordinated water,[9] the weight losses at the temperatures shown corresponding to the following numbers of water molecules per molybdenum atom: oxochloride (I), $3H_2O$ (180°); oxalato-complex (III), $1H_2O$ (130°) and $2H_2O$ (220°); tartrato-complex (IV), $1H_2O$ (130°) and $2H_2O$ (190 °C).

Magnetic Properties.—After correction for diamagnetic contributions of the metal ion and ligands, the complexes had magnetic susceptibilities $\chi_{molar} = 0{\cdot}7$—$2{\cdot}0 \times 10^{-9}$ m^3 mol^{-1} at *ca.* 295 K corresponding to apparent magnetic moments $\mu = 0{\cdot}4$—$0{\cdot}6$ B.M. These magnetic moments are much below the spin-only value for molybdenum(III) (3·88 B.M.) indicating spin pairing between adjacent molybdenum atoms as found for many complexes of molybdenum(V).[8]

I.r. Spectra.—Positions of the main bands and assignments are in Table 1.

Molybdenum–oxygen vibrations. In the spectra of all our complexes we observed a strong broad band at 670—690 cm^{-1} which we assign [10] to vibrations of a molybdenum–oxygen–molybdenum bridging system. The spectrum of the oxo-chloride (I) in this region was similar to that of the molybdenum(V) complex $(Me_4N)_2[Mo_2O_4Cl_4(H_2O)_2]$ for which assignments have been made [10c] for a doubly bridged structure  $Mo\overset{O}{\underset{O}{<>}}Mo$, *viz.* ν_1, 729 cm^{-1}; ν_3, 705 cm^{-1}; and ν_4, 675 cm^{-1}. The intensity is greatest for the ν_3 band; the ν_1 and ν_4 bands appear as shoulders. The band centred at 670—690 cm^{-1} in the spectra of our complexes is assigned as ν_3 and, as expected, is at lower wavenumbers in the molybdenum(III) complexes than in the molybdenum(V) complexes. For the oxochloride (I) we assign a shoulder at 710 cm^{-1} as ν_1 but we were not able to resolve the ν_4 band. For our molybdenum(III) complexes with organic ligands the ν_3 band was broadened as a result of ligand vibrations and we were not able to resolve the ν_1 and ν_4 bands. There are no bands in the

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[8] P. C. H. Mitchell, *Quart. Rev.*, 1966, **20**, 103.

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

[10] (*a*) F. M. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 867; (*b*) D. J. Hewkin and W. P. Griffith, *J. Chem. Soc.* (*A*), 1966, **472**; (*c*) R. M. Wing and K. P. Callahan, *Inorg. Chem.*, 1969, **8**, 871.

region of molybdenum–terminal oxygen stretching vibrations (900—1000 cm^{-1}) [8,11] and we conclude, therefore, that there are no terminal oxygen atoms in the complexes.

O–H *Vibrations*. We assign bands in the range 3100—3300 cm^{-1} to O–H stretching vibrations of co-ordinated and/or lattice water.[9,12] Bands in the spectra of complexes which we consider to contain both co-ordinated and lattice water (II, III, and IV) were broader than in those which contain co-ordinated water only but we were unable to resolve the bands of co-ordinated and lattice water (the band of the latter is expected to be weak [12]). We assign bands at 1620 and 1385 cm^{-1} in the spectrum of the oxo-chloride (I) to bending vibrations of the water molecules. The remaining complexes have bands at similar wavenumbers but assignments are sometimes uncertain because of bands due to ligand vibrations. Splitting of the water bending vibration has been observed before and attributed to hydrogen-bonding interactions.[12]

TABLE 2

Electronic spectra *

	Compound	1	2	3	4	5	6
(I)	$Mo_2O_2Cl_2(H_2O)_6$ solid	37·0	29·5	26·0	22·0	15·0	10·5
(II)	$[Mo_2O_2(acetylacetonate)_2(H_2O)_4]H_2O$ solid	37·5	28·5	24·0	19·0	13·9	9·9
	solution (EtOH)					13·9(61)	9·9(27)
(III)	$Mo_4O_3(oxalate)_3(H_2O)_{12}$ solid	37·5	29·0	24·0			11·0
(IV)	$Mo_2O_2(tartrate)(H_2O)_6$ solid	37·8	30·4	25·4	19·0		10·0
(V)	$[Mo_2O_2Cl_2(H_2O)_4(pyridine)_2]$pyridine solid	37·0			Very broad		10·0
(VI)	$Mo_2O_2Cl_2(H_2O)_2(bipyridyl)_2$ solid	35·0	31·0	25·0	21·5		12·0
	solution (H_2O)						13·6(860)
(VII)	$Mo_2O_2Cl_2(H_2O)_2$(4,4′dimethyl-2,2′-bipyridyl)$_2$ solid	37·0	29·5	25·5	22·0		13·5
	solution (H_2O)						17·0(300)
(VIII)	$Mo_2O_2Cl_2(H_2O)_4(pyridazine)_2$ solid	37·0			Very broad		7·0
(IX)	$Mo_2O_2Cl_2(H_2O)_4(pyrrole)_2$ solid	36·0	29·5		21·5		13·0
	K_3MoCl_6 solid [a]	36·8		24·0	19·3	14·8	9·7
	solution (HCl) [b]			24·2(38)	19·4(23)	14·8(2)	9·5(1)

* Peak positions ($10^{-3}\bar{\nu}/cm^{-1}$) and, for solution spectra, extinction coefficients (ε/l mol^{-1} cm^{-1}) in parentheses.

[a] P. W. Smith and A. G. Wedd, *J. Chem. Soc.* (*A*), 1968, 1377. [b] C. Furlani and O. Piovesana, *Mol. Phys.*, 1965, **9**, 341.

The possibility that the complexes have co-ordinated OH-groups is not entirely eliminated by the spectra, but seems unlikely. Bands in the spectra of hydroxo-complexes in the region 1000—1200 cm^{-1} have been assigned to bending vibrations δ(M–O–H); [13] there are no bands in this region in the spectrum of the oxo-chloride (I) and for the other complexes bands may be assigned to vibrations of the organic ligands. Any bands due to O–H stretching vibrations of hydroxide would, of course, be covered by water bands in the region 3000—3500 cm^{-1}.

Organic ligands. That the organic molecules in the complexes are co-ordinated to molybdenum is indicated by shifts in the ligand bands in the spectra of the complexes from their positions in the spectra of the free ligands. For the pyridine complex (V) we suggest that one organic molecule is retained by the lattice and not co-ordinated, but there were no obvious differences in the i.r. spectra of the co-ordinated and lattice molecules presumably because the spectra are dominated by the former, or because the forces which hold the molecules in the lattice have the same effect on vibrations of the free ligands as those which bind the molecules to the metal. In the spectrum of the pyrrole complex (IX) there were bands at 3300 and 3200 cm^{-1}, one of which we assign to the O–H stretching vibration of water, and the other to the N–H stretching vibration of pyrrole (observed at 3370 cm^{-1} in unco-ordinated pyrrole). Thus reaction of pyrrole with the oxochloride (I) does not involve replacement of the hydrogen of the –NH group.

Molybdenum–chlorine vibrations.[14] We assign a band at 388 cm^{-1} in the far-i.r. spectrum of the oxo-chloride (I) to a molybdenum–chlorine stretching vibration. The occurrence of only one band is consistent with structures in which only one chlorine atom is co-ordinated to each molybdenum.

Electronic Spectra.—Reflectance spectra of the powdered solid complexes and solution spectra of some of the complexes were recorded in the range 45,000—5000 cm^{-1}. Peak positions are in Table 2. The spectra consisted of an intense broad band extending through the u.v. and visible regions with poorly resolved peaks and shoulders. Because of the difficulty of locating transitions precisely and of determining extinction coefficients a theoretical analysis of the spectra will not be attempted. In the spectra of the oxochloride (I) and the acetylacetonate (II) six peaks or shoulders could be distinguished from the general background absorption; they are numbered for convenience of reference as in Table 2. In the spectra of the complexes of oxygen-donor ligands (I)—(IV) peaks below 20,000 cm^{-1} (1 and 2) were of low intensity and so are assigned to '*d–d*' transitions. Absorption was much more intense above 20,000 cm^{-1} and peaks are assigned to charge-transfer and internal-ligand transitions. In the spectra of complexes of nitrogen-donor ligands (V)—

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[11] R. N. Jowitt and P. C. H. Mitchell, *J. Chem. Soc.* (*A*), 1969, 2632.

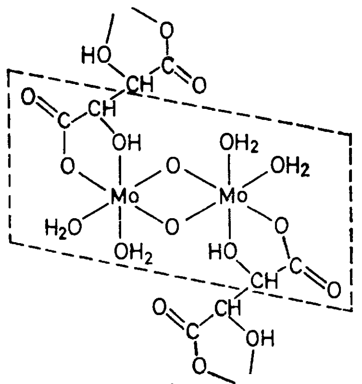
[12] I. Gamo, *Bull. Chem. Soc. Japan*, 1961, **34**, 760, 764.

[13] K. Nakamoto, 'Infra-red Spectra of Inorganic and Coordination Compounds,' Wiley, New York, 1963, p. 158.

[14] D. M. Adams, 'Metal-ligand and Related Vibrations,' Edward Arnold, London, 1967, p. 100.

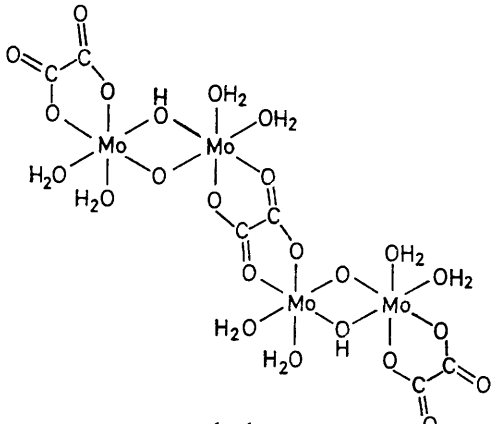
(X) absorption was intense (<5% transmittance) to 10,000 cm^{-1} and below and '*d–d*' transitions are covered. A number of features of the spectra are of interest.

(a) *Comparison with mononuclear molybdenum*(III). The spectrum of the $MoCl_6^{3-}$ ion has been assigned (see Table 2): peak (1) to a charge-transfer transition, peaks (3) and (4) to spin-allowed ligand-field transitions, peak (5) to a spin-forbidden ligand-field transition, and peak (6) to a spin-forbidden transition within the t_{2g}^3 configuration. For the oxo-chloride (I) and our oxygen-donor complexes (II)—(IV) the intensities of peaks (5) and (6) in the reflectance and solution spectra are greater than for the $MoCl_6^{3-}$ ion. The values of the extinction coefficients suggest that these peaks should be assigned to spin-allowed '*d–d*' transitions. According to their low magnetic moments our complexes are bi- (or poly-) nuclear and spin paired so the molybdenum atoms do not have the t_{2g}^3 configuration and a spin-forbidden transition within this configuration is not possible. Thus we assign peaks (5) and (6) in the spectra of our complexes to spin-allowed '*d–d*' transitions which are therefore at lower wavenumbers than those for the $MoCl_6^{3-}$ ion. The shift to lower wavenumbers of the ligand-field bands cannot be due to replacement of chlorine by oxygen since oxygen is higher than chlorine in the spectrochemical series. We suggest that the shift is a consequence of a π-bonding interaction between the bridging oxygen and molybdenum(III) in our complexes which causes splitting of the t_{2g} orbitals and thus makes available lower energy *d* orbitals to function as acceptor orbitals in '*d–d*' transitions, an effect similar to that of π-bonding from terminal oxygen in the spectra of vanadium(IV) and molybdenum(V) complexes.[8]



(C)

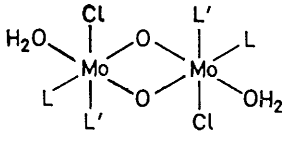
Tartrato-complex (VI), $[Mo_2O_2\{\frac{1}{2}tartrate(2-)\}_2(H_2O)_2]_n$



(D)

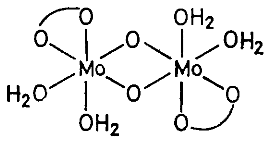
Oxalato-complex (III), $Mo_4O_2(OH)_2(C_2O_4)_3(H_2O)_8$

(b) *Comparison of* N- *and* O-*donors*. The main difference between the spectra of complexes containing N- and O-donor ligands is that the intense absorption extended to lower wavenumbers in the former (V)—(IX). Peak (6) in the spectra of the bipyridyl complexes (VI and VII) was shifted from its position in the solid when the complexes were dissolved in water and the extinction coefficients were greater than those expected for a '*d–d*' transition. Thus we assign the lowest wavenumber peaks in the spectra of complexes (V)—(IX) to a transition which is largely charge-transfer in character.



(A)

(I) L = L′ = H_2O
(V) L = H_2O, L′ = pyridine
(VI) LL′ = 2,2′-bipyridyl
(VII) LL′ = 4,4′-dimethyl-2,2′-bipyridyl
(VIII) L = H_2O, L′ = pyridazine
(IX) L = H_2O, L′ = pyrrole



(B)

Acetylacetonato-complex (II)

(c) *Comparison of ligands of different donor strength.* With our complexes of nitrogen donor ligands we are able to observe the effect on the lowest energy charge-transfer transition [peak (6)] of changing donor-strength (as indicated by pK_a values[15]) of structurally similar ligands. The general effect is that as the donor strength of the ligand increases (pyridine > pyridazine, 4,4′-dimethyl-2,2′-bipyridyl > 2,2′-bipyridyl) so peak (6) shifts to higher wavenumbers (see Table 2). The effect is similar to that observed for example with iron(II)[16] and the interpretation is that the first charge-transfer transition is of the metal→ligand type, *i.e.* from an orbital associated mainly with the metal to that associated mainly with the ligand, $M(d) \rightarrow L(\pi^*)$. In contrast the first charge-transfer transitions in complexes of molybdenum(V) and iron(III) with organic ligands are considered to be of the ligand→metal type.[17] It is interesting that the first charge-transfer transition for the pyrrole complex (X) is at a higher wavenumber than for the pyridazine and pyridine complexes although pyrrole is a poorer donor (pK_a −0·27) than pyridazine (pK_a 2·33)

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[15] 'Stability Constants,' Chem. Soc. Special Publ. No. 17, London, 1964.

[16] R. J. P. Williams, *Chem. Rev.*, 1956, **56**, 299.

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

and pyridine (pK_a 5·2). Presumably the π^*-acceptor orbital of pyrrole is at higher energy as a consequence of less ring conjugation than in pyridazine and pyridine.

Structures.—Attempts to grow crystals have not so far been successful and we have been unable to determine structures by *X*-ray crystallography. All our complexes contain molybdenum(III) in a bi- or poly-nuclear unit and in postulating structures we assume a co-ordination number of six for molybdenum.[2] For the oxo-chloride (I) and the complexes of nitrogen-donor ligands we suggest structure (A). Because of the *trans*-effect of oxide we assume that chloride avoids positions *trans* to bridging oxygen.[8] In our structure of the oxo-chloride (I) one water is *trans* to chlorine and we propose that this water molecule is more labile than the other two since only one water molecule per molybdenum atom is replaced by pyridine, pyridazine, and pyrrole even when these ligands are present in excess. For the acetylacetonato-complex (II) we suggest structure (B). For the tartrato- and oxalato-complexes (IV) and (III) it is difficult to suggest convincing structures; both complexes have $2H_2O$ per molybdenum atom. The fact that (III) and (IV) are insoluble in water indicates polymeric structures since they abound in hydrophilic groups and we therefore propose structure (C) for the tartrato-complex, tartrate(2−) ions acting as bridges between $Mo_2O_2(H_2O)_4$ units. Reaction of the oxo-chloride (I) with oxalate under various conditions (pH, temperature, oxalate concentration) always gave complex (III) so we have a single stable structural entity and not a mixture. A possible structure is (D) in which oxalate ions bridge binuclear molybdenum units giving a tetrameric structure (a structure containing bridging oxalate is known [18]). Overall charge neutrality requires that two of the bridging oxygen atoms are protonated.

One of us (R. D. S.) thanks the University of Reading for a Research Studentship.

[2/697 *Received, 24th March,* 1972]

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[18] M. G. B. Drew, G. W. A. Fowles, and D. F. Lewis, *Chem. Comm.*, 1969, 876.