Complexes of Molybdenum(III) with Sulphur-donor Ligands

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Reaction of $[Mo_2O_2Cl_2(H_2O)_6]$, (I), with ligands L gives complexes $[Mo_2O_2(H_2O)_xL_y]$ [L = *S*-methyl-L-cysteinato hydrochloride (x = 4, y = 2), (II), and 2-aminoethanethiolato hydrochloride (x = 6, y = 2) (III)], $[Mo_2(OH)_2L_4]$ [L = 4-mercaptotoluene-3-thiolato, (IV), and 2-aminobenzenethiolato, (V)], $[MoL_3]_2$ (VI; L = *NN*-diethyldithiocarbamato), and $[Mo_2OClL_3]$ (VII; L = 2-hydroxyethanethiolato). I.r., u.v., visible, n.m.r., and e.s.r. spectra and magnetic susceptibilities of the complexes are reported. Structures are proposed. The complexes are bi- or poly-nuclear. With bidentate thiols, sulphur bridges are formed between molybdenum atoms. In reactions with thiols, oxide bridges are readily replaced probably *via* initial protonation of bridging oxide. The complexes are discussed in the general context of molybdenum chemistry. The tendency to form sulphur-bridged complexes is greater with molybdenum(III) than with molybdenum(V). Sulphur bridges are less labile than oxygen bridges.

IN this paper we describe complexes obtained by reaction of the complex di-μ-oxo-bis[triaquachloromolybdenum(III)], $[Mo_2O_2Cl_2(H_2O)_6]$ (I),[1] with various sulphur compounds. The object was to extend our knowledge of molybdenum(III)–sulphur chemistry. Previous workers have reported rather poorly characterised polymeric molybdenum(III)–sulphur complexes prepared, for example, from reactions of the hexachloromolybdate(III) anion with chelating sulphur ligands,[2] and from molybdenum hexacarbonyl and disulphides.[3] Recently the *NN*-diethyldithiocarbamato-complex $[\{MoL_3\}_2]$ has been reported.[4] We were particularly interested in complexes which might contain oxomolybdenum(III) species since oxo-complexes of molybdenum-(V) and -(VI) are well known.[5] In an earlier paper[1] we showed that the Mo_2O_2 group, with two oxo-groups bridging the molybdenum atoms, occurs in oxomolybdenum(III) complexes with oxygen- and nitrogen-donor ligands, and that terminal oxide apparently is not found with molybdenum(III).

EXPERIMENTAL

Preparations.—All reactions and manipulations were carried out under a nitrogen atmosphere or *in vacuo*. Each preparation was carried out a number of times. Ligand : Mo ratios were *ca*. 3 : 1. Yields were *ca*. 100% except for complex (VI) (*ca*. 10%).

abchij-*Hexa-aqua*-dg-*dichloro*-ef-*di-μ-oxo-dimolybdenum*-(III), $[Mo_2O_2Cl_2(H_2O)_6]$ (I). This complex was prepared *via* electrolytic reduction of molybdenum(VI) in hydrochloric acid[1] (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%).

bchi-*Tetra-aqua*-ad,jg-*di*(S-*methyl*-L-*cysteinato hydrochloride*)-ef-*di-μ-oxo-dimolybdenum*(III)], $[Mo_2O_2\{MeSCH_2CH(NH_3^+Cl^-)CO_2\}_2(H_2O)_4]$ (II). A solution of *S*-methyl-L-cysteine hydrochloride (1·1 g) in water (20 cm³) was added to solid complex (I) (1·7 g) which dissolved to give a brown solution. The solution was left for 3 h and then acetone (300 cm³) was added dropwise. A tan coloured *precipitate* formed and was filtered off, washed with acetone, and dried *in vacuo* (Found: C, 15·3; H, 3·9; Cl, 10·9; Mo, 30·5; N, 4·1; S, 9·6. Calc. for $C_8H_{26}Cl_2Mo_2N_2O_{10}S_2$: C, 15·1; H, 4·1; Cl, 11·1; Mo, 30·1; N, 4·4; S, 10·0%).

dg-*Di*(2-*aminoethanethiolato hydrochloride*)-abchij-*hexa-aqua*-ef-*di-μ-oxo-dimolybdenum*(III)–*methanol*, $[Mo_2O_2\{SCH_2CH_2(NH_3^+Cl^-)\}(H_2O)_6]$,MeOH (III). 2-Mercaptoethylaminium chloride (2 g) in methanol (20 cm³) was added to solid complex (I) (1·4 g). The suspension was heated under reflux for 15 h and cooled in ice to give a dark brown *solid* which was filtered off, washed with methanol and acetone, and dried *in vacuo* (Found: C, 9·9; H, 4·6; Cl, 12·0; Mo, 32·4; N, 4·9; S, 10·7. Calc. for $C_5H_{30}Cl_2Mo_2$-

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[1] P. C. H. Mitchell and R. D. Scarle, *J.C.S. Dalton*, 1972, 1809.

[2] L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Austral. J. Chem.*, 1965, **18**, 1549.

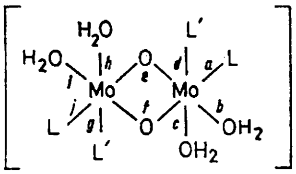
[3] (*a*) R. N. Jowitt and P. C. H. Mitchell, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 39; (*b*) D. A. Brown, W. K. Glass, and C. O'Daly, *J.C.S. Dalton*, 1973, 1311.

[4] D. A. Brown, B. J. Gordon, W. K. Glass, and C. J. O'Daly, *Proc. 14th Internat. Conf. Co-ordination Chem.*, Toronto, 1972, p. 646.

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

$N_2O_9S_2$: C, 10·2; H, 5·1; Cl, 12·1; Mo, 32·6; N, 4·8; S, 10·9%). The complex was readily soluble in water but insoluble in organic solvents.

dg-*Dihydroxo*-cf,he-*di*-μ-(4-*mercaptotoluene*-3-*thiolato*-SH,μ-S)-ab,ji-*di*(4-*mercaptotoluene*-3-*thiolato*-SH,S)*dimolybdenum*(III), $[Mo_2(OH)_2\{MeC_6H_3(S)SH\}_4]$ (IV). 3,4-Dimercaptotoluene (6 g) in ethanol (50 cm^3) was added to solid complex (I) (2·3 g). The resulting suspension was heated under reflux for 5 d. A black *solid* was filtered off, washed with ethanol, and dried *in vacuo* (Found: C, 39·5; H, 3·2; Mo, 23·0; S, 30·1. Calc. for $C_{28}H_{30}Mo_2O_2S_8$: C, 39·7; H, 3·5; Mo, 22·7; S, 30·3%). The complex was soluble in chloroform and benzene giving dark brown solutions.

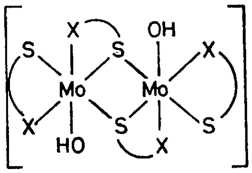


(A)

(I) L = H_2O, L' = Cl

(II) LL' = $MeSCH_2CH(NH_3^+Cl^-)CO_2^-$

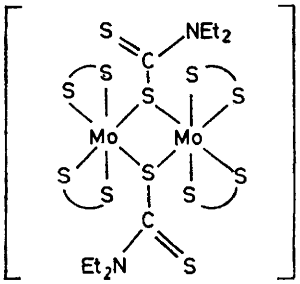
(III) L = H_2O; L' = $^-SCH_2CH_2NH_3^+Cl^-$



(B)

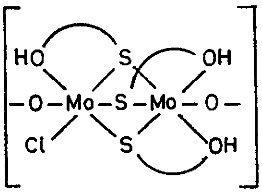
(IV) X = SH; SSH = $MeC_6H_3(S)SH$

(V) X = NH_2; SNH_2 = $H_2NC_6H_4S$



(C)

(VI) SS = Et_2NCS_2



(D)

(VII) SOH = SCH_2CH_2OH

cf,he-*Di*-μ-(2-*aminobenzenethiolato*-N,μ-S)-ab,ji-*di*(2-*aminobenzenethiolato*-N,S)-dg-*dihydroxodimolybdenum*(III)-*water*, $[Mo_2(OH)_2(H_2NC_6H_4S)_4],H_2O$ (V). 2-Aminobenzenethiol (7 cm^3) in ethanol (30 cm^3) was added to the solid complex (I) (2·0 g). The resulting suspension was heated under reflux for 3 d. A brown *solid* was filtered off, washed with ethanol, and dried *in vacuo* (Found: C, 38·8; H, 3·5; Mo, 26·1; N, 7·5; S, 17·2; H_2O, 2·7. Calc. for $C_{24}H_{28}Mo_2N_4O_3S_4$: C, 38·9; H, 3·8; Mo, 25·9; N, 7·6; S, 17·3; H_2O, 2·4%).

Bis-μ-(NN-*diethyldithiocarbamato*-S)-*bis*[*bis*(NN-*diethyldithiocarbamato*-S,S')*molybdenum*(III)], $[Mo_2(S_2CNEt_2)_6]$ (VI). A solution of sodium *NN*-diethyldithiocarbamate (6 g) in water (30 cm^3) was added to a solution of complex (I) (1·1 g) in water (20 cm^3) at pH 4 (acetic acid–sodium acetate buffer). The resulting mixture was heated for 2 h. A red *precipitate* was filtered off, washed with water, and ethanol (Found: C, 33·4; H, 5·3; Mo, 18·0; N, 7·6; S, 35·1. Calc. for $C_{30}H_{60}Mo_2N_6S_{12}$: C, 33·4; H, 5·5; Mo, 17·8; N, 7·8; S, 35·6%). The complex dissolved readily in chloroform and acetone giving orange-red solutions. It was obtained only under acidic conditions; there was no reaction between sodium *NN*-diethyldithiocarbamate and an aqueous suspension of complex (I).

Complex of molybdenum(III) *with* 2-*mercaptoethanol*, $[Mo_2O(Cl)(HOCH_2CH_2S)_3],2H_2O$ (VII). A solution of 2-mercaptoethanol (3 cm^3) in ethanol (30 cm^3) was added to solid complex (I) (1·2 g). The mixture was heated under reflux for 2 d to give a dark brown *solid* which was filtered off, washed with ice-cold ethanol, and dried *in vacuo* (Found: C, 13·9; H, 3·7; Cl, 7·0; Mo, 37·7; S, 19·0; H_2O, 6·5. Calc. for $C_6H_{19}ClMo_2O_6S_3$: C, 14·1; H, 3·7; Cl, 7·0; Mo, 37·6; S, 18·8; H_2O, 7·1%). The complex was insoluble in water and organic solvents.

Physical Measurements.—I.r. spectra for the complexes were recorded with Unicam SP 200 and Perkin-Elmer 457 spectrophotometers. U.v. and visible solution and reflectance spectra were recorded with a Unicam SP 700 C spectrophotometer. ^{1}H N.m.r. spectra were measured on a Perkin-Elmer 60 MHz instrument calibrated with tetramethylsilane. E.s.r. spectra were recorded with a Varian E3 spectrometer calibrated with diphenylpicrylhydrazyl. Magnetic susceptibilities were measured at room temperature with a Newport Instruments Gouy-balance system calibrated with cobalt(II) tetrathiocyanatomercurate(II).[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

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[6] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 1958, 4190.

TR1. Carbon, hydrogen, chlorine, nitrogen, and sulphur were determined microanalytically.

RESULTS AND DISCUSSION

Complexes Prepared.—By treating $[Mo_2O_2Cl_2(H_2O)_6]$, (I), with ligands (L) we have prepared new complexes $[Mo_2O_2(H_2O)_xL_y]$ [L = *S*-methyl-L-cysteinato hydrochloride (II; $x = 4$, $y = 2$), and 2-aminoethanethiolato hydrochloride (III; $x = 6$, $y = 2$)], $[Mo_2(OH)_2L_4]$ [L = 4-mercaptotoluene-3-thiolato (IV) and 2-aminobenzenethiolato (V)], $[\{MoL_3\}_2]$ [L = *NN*-diethyldithiocarbamato (VI)], and $[Mo_2OClL_3]$ [L = 2-hydroxyethanethiolato (VII)]. Complex (VI) was previously prepared by reacting molybdenum hexacarbonyl with tetraethylthiuram disulphide.[4] The complexes are formulated on the basis of analysis and physical measurements. The new complexes were insufficiently soluble or stable in solution for molecular-weight determinations.

Structures and Physical Measurements.—Attempts to obtain crystals of the complexes suitable for *X*-ray crystallography were not successful. We were therefore forced to rely on physical measurements to reveal the main structural features. First we discuss general aspects of the structures and then propose a structure for each complex or group of complexes.

Oxidation State of Molybdenum.—Attempted oxidation-state determination by titration with cerium(IV) and potentiometric titration with potassium hexacyanoferrate(III) were unsuccessful because of slow non-quantitative oxidation of the sulphur ligands. In concentrated hydrochloric acid the complexes did not show molybdenum(V) e.s.r. signals. Since the complexes were prepared with careful exclusion of air and the thiol ligands are unlikely to effect reduction below molybdenum(III), we are confident that there was no change of oxidation state during the preparation of the complexes and that they are, therefore, complexes of molybdenum(III). Further evidence that the complexes contain the $[Mo_2O_2]^{2-}$ group was provided by their behaviour on oxidation. Complexes (III)—(VII) were stable in air as solids, (II) and (III) slowly oxidised (*ca.* 1 d). During exposure to air complexes (II) and (III), like other complexes containing the Mo_2O_2 group,[1] developed in their i.r. spectra a band at 970—980 cm^{-1} which is in the region of $Mo-O_t$ stretching vibrations (O_t represents terminal oxygen) and indicates formation of an oxomolybdenum(V) species.

Co-ordination Number of Molybdenum.—The majority of molybdenum(III) complexes are six-co-ordinate octahedral, although a few seven-co-ordinate low-spin complexes are known, *e.g.* $K_4[Mo(CN)_7]$ and $[Mo(CO)_2(diarsine)I_3]$.[7] We consider that with the type of ligand used in our present work molybdenum(III) is likely to remain six-co-ordinate and octahedral.

Bi- and Poly-nuclear Structures.—The complexes were not sufficiently soluble in suitable solvents or their solutions were too unstable for molecular-weight determinations. The complexes had magnetic moments (0·6—1·0 B.M. per Mo at *ca.* 295 K) much below the spin-only value for molybdenum(III) (3·88 B.M.), indicating magnetic interaction between adjacent molybdenum atoms either directly or through bridging atoms and hence bi- or poly-nuclear structures.* In their i.r. spectra, none of the complexes showed strong bands in the region of molybdenum–terminal-oxygen stretching vibrations (900—1 000 cm^{-1}) [5] and we consider that they do not contain terminal oxygen atoms.

Complexes (II) *and* (III). For the complexes with *S*-methyl-L-cysteinate hydrochloride, (II), and 2-aminoethanethiolate hydrochloride, (III), we propose structure (A). In their i.r. spectra the complexes had strong bands at 685 and 665 cm^{-1} respectively which we assign to the ν_3 mode of the Mo_2O_2 group.[1] That the organic ligands are present as their aminium chlorides with the NH_3^+ groups *not* co-ordinated is shown by the analytical data and the closely similar wavenumbers of the NH vibrations in the i.r. spectra of the free-ligand hydrochlorides and the complexes: ν(NH) for complex (II) occurred at 3 000 cm^{-1} (*cf.* ligand hydrochloride, 3 000 cm^{-1}), for (III) at 3 000 cm^{-1} (*cf.* ligand hydrochloride, 2 950 cm^{-1}); δ(NH) for complex (II) occurred at 1 500 cm^{-1} (*cf.* ligand hydrochloride, 1 495 cm^{-1}), for (III) at 1 485 cm^{-1} (*cf.* ligand hydrochloride, 1 490 cm^{-1}). In complex (II) *S*-methyl-L-cysteinate hydrochloride is bidentate through the carboxylate group, as shown by the decreased separation of the symmetric and antisymmetric CO_2 stretching modes for the complex (1 573 and 1 430 cm^{-1}) compared with the free ligand (1 590 and 1 425 cm^{-1}).[8] On the basis of the *g* values obtained from the e.s.r. spectra (see below), sulphur is not co-ordinated in complex (II) ($g_\perp$ 1·936, $g_\parallel$ 1·903) whereas the ionised thiol group is co-ordinated in complex (III) (*g* 1·991). In both complexes (II) and (III) the co-ordination sphere is completed by water molecules.

Complexes (IV) *and* (V).—For the complexes with 4-mercaptotoluene-3-thiolate, (IV), and 2-aminobenzenethiolate, (V), we propose structure (B). There were no i.r. bands which can be assigned to an oxygen-bridge system. Thus the bridging atoms must be provided by the organic ligands. In their i.r. spectra both complexes had bands which we assign to OH vibrations [(IV), ν(OH) at 3 400, δ(OH) at 1 620; (V), 3 420, 1 610 cm^{-1}]. For complex (V) the presence of lattice water was shown by thermogravimetric analysis; initial weight loss occurred at a temperature (100 °C) appropriate to lattice water [1] and corresponded to $0{\cdot}5H_2O$ per Mo. For complex (IV) there was no t.g.a. evidence for lattice water; the OH stretching vibration is high for co-ordinated water [1] but reasonable for co-ordinated hydroxide [*cf.* structure (B)].[9] Both complexes (IV) and (V) showed i.r. bands at 1 030—

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* 1 B.M. ≃ $9{\cdot}27 \times 10^{-24}$ A m^2.

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

[8] A. Kay and P. C. H. Mitchell, *J. Chem. Soc.* (*A*), 1970, 2421.

[9] K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' Wiley, New York, 1963, p. 201.

1 040 cm^{-1} which we assign to the bending vibration δ(M–O–H). Further evidence for co-ordinated hydroxide was provided by the n.m.r. spectra (resonance at τ 2·1, see below). According to the i.r. spectrum, the organic ligand in complex (V) is co-ordinated through the ionised thiol group and the amino-group. The S–H vibration observed for the free ligand (2 500 cm^{-1}) was absent from the spectrum of the complex and the NH vibrations were shifted for the complex [ν(NH) at 3 150, δ(NH) at 1 590 cm^{-1}] compared with the free ligand [ν(NH) at 3 300—3 400, δ(NH) at 1 615 cm^{-1}].

With complex (IV) a problem arises since overall charge neutrality requires that each molecule of ligand should carry only one negative charge, *i.e.* that only one thiol group should be ionised. Co-ordination of dimercaptotoluene through an ionised and un-ionised thiol group is unusual,[10] but seems inescapable in the present case. Even if the hydroxyl groups were in fact protonated, we could account for only two of the four protons. Some evidence for HS groups in complex (IV) was provided by the n.m.r. spectrum of its solution in $CDCl_3$. There were two sets of broad resonances in the spectrum of the dimercaptotoluene complex (III). The low τ set consisted of the aromatic proton resonances, which were virtually unshifted on complex formation, and a new resonance at τ 2·1 which we assign to a hydroxo-group bound to molybdenum.[11] The high τ set consisted of the methyl-group resonance and a new resonance at τ 7·45 which we assign to the protons of un-ionised thiol groups bound to molybdenum. In agreement with this assignment the integrated intensity ratios of the proton resonances at high ($2CH_3 + 2SH$) and low τ ($2C_6H_3 + OH$) were 8 : 7, corresponding to co-ordination of one hydroxide and two dimercaptotoluene monoanions per molybdenum. We conclude that dimercaptotoluene in complex (IV) behaves as a bidentate monoanion like aminobenzenethiol in the stoicheiometrically identical complex (V).

Complex (VI).—The dithiocarbamato-complex (VI) has the empirical formula [MoL_3] and, at first sight, we might expect it to be a straightforward mononuclear octahedral complex. However, dimerisation was indicated by the low magnetic moment and by *X*-ray data. From acetone, we obtained yellow-red crystals of the complex which proved to be a mosaic and unsuitable for a complete structure determination. The crystals were monoclinic ($a = 12{\cdot}98$, $b = 15{\cdot}11$, $c = 12{\cdot}29$ Å; $\beta = 98{\cdot}0°$). The density by flotation in dichloroethane–di-iodomethane was 1·859 g cm^{-3}. For two molecules in the unit cell the molecular weight is 1 193 which is consistent with a dimer with two molecules of acetone in the lattice, *i.e.* [$Mo_2(S_2CNEt_2)_6$],$2OCMe_2$ (*M* 1 196). Analysis and physical measurements showed that the only ligands are dithiocarbamate and so dimerisation must occur *via* bridging dithiocarbamate. Co-ordination of dithiocarbamate as a bidentate ligand is consistent with the i.r. spectrum [ν($N{=}CS_2$) at 1 520 and 1 500; ν(C–S) at 1 200 cm^{-1}].[12] However, that not all of the dithiocarbamate ligands are equivalent was suggested by splitting of the $N{=}CS_2$ vibration. We propose structure (C) with four bidentate dithiocarbamate groups and two unidentate groups which bridge the molybdenum atoms. An alternative and closely related structure with bidentate bridging ligands and seven-co-ordinate molybdenum(III) is possible. That complex (VI) has a particularly stable structure is shown by its preparation by two other methods: (*i*) from molybdenum hexacarbonyl and tetraethylthiuram disulphide;[4] (*ii*) from the oxomolybdenum(IV) complex [$MoO(S_2CNEt_2)_2$] [13] and triphenyldithiophosphorane {a disproportionation reaction which gave as the other product a new molybdenum(V) complex [$Mo_2O_4(S_2CNEt_2)$]}.[14]

Complex (VII).—The mercaptoethanol complex (VII) differs from the other complexes in containing chloride and, apparently, according to its i.r. spectrum, single oxo-bridges [$\nu_{asym}(Mo_2O)$ at 805 cm^{-1}, *cf.* analogous molybdenum(V) complexes,[7] 730—860 cm^{-1}]. If we regard oxide as similar to two chlorides, then the stoicheiometry of complex (VII) is similar to that of the 3-ethylthiopropane-1-thiolate complex [$Mo_2L_3Cl_3$].[2] We propose a polymeric structure (D) with repeating units containing three sulphur bridges linked by oxo-bridges. In agreement with a polymeric structure, complex (VII) is much less soluble in water and organic solvents than the dimeric mercaptoethanol complex of molybdenum(V), [$Mo_2O_4(SCH_2CH_2OH)_2$].[8] Thermogravimetric analysis of complex (VII) gave a weight loss at 90 °C corresponding to one lattice water per 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—5 000 cm^{-1}. Peak positions are given in Supplementary Publication No. SUP 21193 (4 pp.).* The spectra consisted of overlapping bands extending through the u.v. and visible regions and resulted in poorly resolved peaks and shoulders. We have discussed the electronic spectra of oxomolybdenum(III) complexes in a previous paper.[1] On the basis of their intensities, the absorption peaks fell into three groups: (*a*) very strong peaks ($\varepsilon > 10^4$ l mol^{-1} cm^{-1}) at wavenumbers $>$30 000 cm^{-1}; (*b*) medium-intensity peaks ($\varepsilon \approx 10^3$—10^4 l mol^{-1} cm^{-1}) at *ca.* 15 000—30 000 cm^{-1}; and (*c*) weak peaks ($\varepsilon <$ 20 l mol^{-1} cm^{-1}) at wavenumbers $>$15 000 cm^{-1}. We assign the group (*a*) to charge-transfer (c.t.) or internal-ligand transitions and (*c*) peaks to *d–d* transitions (which might be spin-forbidden transitions arising from singlet ground states of the bi- and poly-nuclear complexes).

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* For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full-size copies).

[10] A. Butcher and P. C. H. Mitchell, *Chem. Comm.*, 1967, 176.

[11] A. Kay and P. C. H. Mitchell, *J.C.S. Dalton*, 1973, 1388.

[12] R. N. Jowitt and P. C. H. Mitchell, *J. Chem. Soc.* (*A*), 1970, 1702.

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

[14] R. D. Searle and P. C. H. Mitchell, unpublished work.

Assignment of group (*b*) is more difficult. These peaks could be assigned to c.t. transitions or to *d–d* transitions. In the latter case the rather high intensities would be a consequence of appreciable covalency in the molybdenum(III)–sulphur bonds. We consider it unprofitable to attempt more definite assignments of electronic transitions in complexes of the type under discussion and we question whether Brown *et al.*[3b] are correct in assigning all (or any) of the electronic transitions in certain polymeric sulphur complexes of molybdenum(III) and tungsten(III) to transitions from a $^4A_{2g}$ ground state of a d^3 ion in an octahedral field. The magnetic moments do not correspond to a quartet ground state and the intensities of the electronic transitions cast some doubt on their assignment as *d–d* transitions.

E.S.R. Spectra.—Although our complexes had low magnetic moments, we observed e.s.r. signals from the solids and their solutions. In view of current interest in e.s.r. spectra of molybdenum–sulphur complexes, especially in the context of the role of molybdenum in biological systems,[15] we list e.s.r. parameters in the Table.

E.s.r. spectra *

Complex	g	Solution	
		g_{av}	a(Mo)/G
(I) $[Mo_2O_2Cl_2(H_2O)_6]$	$g_\perp$ 1·941	1·963	
	$g_\parallel$ 2·007		
(II) $[Mo_2O_2\{MeSCH_2CH(NH_3{}^+Cl^-)$-$CO_2\}_2(H_2O)_4]$	$g_\perp$ 1·936		
	$g_\parallel$ 1·903		
(III) $[Mo_2O_2(SCH_2CH_2NH_3{}^+Cl^-)_2$-$(H_2O)_6]$,MeOH	1·991		
(IV) $[Mo_2(OH)_2\{MeC_6H_3(SH)S\}_4]$	2·003	2·004	31 †
(V) $[Mo_2(OH)_2(SC_6H_4NH_2)_4]$,$H_2O$	$g_\perp$ 2·003	2·013	32 ‡
	$g_\parallel$ 2·031		
(VI) $[Mo_2(S_2CNEt_2)_6]$		1·985	37·5 †
(VII) $[Mo_2OCl(SCH_2CH_2OH)_3]$,$2H_2O$	2·001		

* All spectra were measured at *ca.* 20 °C; *a* is the six-line molybdenum hyperfine splitting. † In chloroform. ‡ In *NN*-dimethylformamide.

We consider that the signals are due to molybdenum(III) species and not impurities, *e.g.* molybdenum(V), since they were observed for different preparations of the complexes; care was taken to avoid aerial oxidation of solids and solutions; species giving e.s.r. signals with the same parameters are formed by reduction of molybdenum(V) complexes; aerial oxidation of solutions of the complexes caused the signals to disappear; and solutions of the complexes, unlike molybdenum(V) complexes, in concentrated hydrochloric acid did not give signals characteristic of the $[MoOCl_5]^{2-}$ ion. Whether the signals arise from mono- or bi-nuclear species can, in principle, be decided from the relative intensities of the main and hyperfine satellite signals.[16] For mononuclear molybdenum(V) complexes, *e.g.* the $[Mo(CN)_8]^{3-}$ ion, we found that the relative intensities of the main and satellite peaks were *ca.* 3 : 1. For binuclear complexes the ratio was *ca.* 4 : 1. For the molybdenum(III) dithiocarbamate complex (VI), which gave particularly strong and well resolved spectra, the ratio was 3·8 : 1 and it seems, therefore, that the e.s.r.-active species is binuclear. We postpone further discussion pending a more thorough study of the e.s.r. spectra. With regard to the values of the e.s.r. parameters, we observe: (*a*) that molybdenum(III)–sulphur complexes, like molybdenum(V)–sulphur complexes, have higher *g* and lower *a* values than complexes with more electronegative ligands [*cf.* (I) and (II), Table]; and (*b*) molybdenum(III) complexes have higher *g* and lower *a* values than molybdenum(V) complexes with similar sulphur ligands.[15,17]

General Discussion.—We discuss here particular features of oxomolybdenum(III) complexes and the reactions described in this and our earlier paper [1] and comparisons especially with oxomolybdenum(V) complexes.

Reactions of complex (I), $[Mo_2O_2Cl_2(H_2O)_6]$. Three types of substitution reaction are possible, involving replacement of aqua, chloro-, and bridging oxo-groups. Which ligands are substituted depends on the nature of the incoming ligand. With neutral ligands (*e.g.* pyridine) one water molecule per molybdenum is substituted; with anionic bidentate ligands (*e.g.* pentane-2,4-dione) water and chloride are exchanged. For overall charge neutrality, co-ordination of a dianion (*e.g.* oxalate) must be accompanied by protonation probably at the oxo-bridges. Reactions of complex (I) with nitrogen- and oxygen-donor ligands do not lead to exchange of bridging oxide, but with thiols oxo-bridges are readily replaced by sulphur bridges [*cf.* complexes (IV), (V), and (VII)]. Elsewhere we have suggested that substitution of bridging oxide in molybdenum(V) complexes involves initial protonation of the oxo-group *via* an oxo-anion (*e.g.* phosphate) or a thiol already bound to molybdenum.[15] The reactions of the oxomolybdenum(III) complex (I) are consistent with this idea [*cf.* complexes (IV)—(VII)]. It is also significant that with the effectively unidentate thiol 2-aminoethanethiolate hydrochloride only chloride and not bridging oxide is replaced [*cf.* complex (III)]. Hydroxide formed by protonation of bridging oxide may remain co-ordinated to molybdenum(III) [*cf.* complexes (IV) and (V)] or may lead to further polymerisation *via* single oxo-bridges [*cf.* complex (VII)]. Once again we note that molybdenum(III), unlike the higher oxidation states, does not form complexes with terminal oxide. Since we expect molybdenum(III) to be a poorer π-acceptor than the higher oxidation states, it is entirely reasonable that HO groups bound to molybdenum(III) should be less acidic. With regard to the relative ease of substitution of different ligands of complex (I), the qualitative order is $H_2O \geqslant Cl > O$(bridge).

Sulphur-bridged complexes of molybdenum-(III) *and* -(V). Qualitatively the tendency to form sulphur-

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[15] P. C. H. Mitchell and R. D. Scarle, *Proc. Climax 1st Internat. Conf. Chem. and Uses of Molybdenum*, ed. P. C. H. Mitchell, Climax Molybdenum Co. Ltd., London, 1973, p. 140.

[16] J. F. Gibson in 'Electron Spin Resonance,' Specialist Periodical Report, Chem. Soc., London, vol. 1, 1973, p. 162. We are grateful to a referee for drawing our attention to this point.

[17] L. S. Meriwether, W. F. Marzluff, and W. G. Hodgson, *Nature*, 1966, 212, 465.

bridged complexes in solution under similar experimental conditions is molybdenum(III) > molybdenum(V) > molybdenum-(IV), -(VI). Molybdenum-(IV) and -(VI) have little tendency to form bi- or poly-nuclear complexes whether with oxygen or sulphur bridges. A striking illustration is the disproportionation reaction of the complex [$MoO(S_2CNEt_2)_2$] (see above) which gives a sulphur-bridged complex of molybdenum(III) and an oxo-bridged complex of molybdenum(V). Also molybdenum(III) with dithiocarbamate and mercaptoethanol gives sulphur-bridged complexes, whereas molybdenum(V) gives oxo-bridged complexes. The increase of affinity for sulphur relative to oxygen with decrease of oxidation state is in accordance with general trends.[18] It is now clear that sulphur-bridged systems are important in the chemistry of both molybdenum-(III) and -(V) and that sulphur bridges are less labile with respect to formation of mononuclear species than oxygen bridges.

The relatively greater stability of molybdenum sulphur-bridged species cannot be explained in terms of the molybdenum–sulphur bonding interaction since Mo–S bonds are weaker than Mo–O bonds.[18] We suggest that bridge breaking occurs less readily in the sulphur-bridged species because: (*i*) the proton affinity of sulphur is less than that of oxygen (hydrogen sulphide and thiols are stronger acids than water and alcohols); and (*ii*) sulphur offers greater steric resistance than oxygen to an incoming ligand which could be involved in bridge breaking. Currently we are investigating the formation and reactions of thio-bridged molybdenum complexes.

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[18] Ref. 12, p. 1.