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7. MOLYBDENUM

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CONTENTS

The literature covered by this review is essentially that reported during 1979 and which appeared in Volumes 90 and 91 of Chemical Abstracts. This review describes work which has extended or improved the knowledge of the coordination chemistry of molybdenum. Therefore, although the organometallic and carbonyl chemistries of molybdenum are undergoing much development, papers relating to these topics have not been included, except when the study contained some aspect of inorganic interest. The material has been selected with the aim of producing a reasonably comprehensive account and has been organised according to the oxidation state of molybdenum in the compound of central interest; developments in those areas where delineation on the basis of oxidation state seems inappropriate have been summarised separately.

7.1 MOLYBDENUM(VI)

7.1.1 Molybdenum(VI) fluoride

Xα-scattered wave calculations have been performed to calculate the ionization energies for the valence electrons of [MoF_6] [1]. The heat of formation of liquid molybdenum(VI) fluoride has been determined by solution calorimetry, for the reaction between this compound and $NaOH/H_2O$, as -1593.3 kJ mol^{-1} [2]; this value differs from previous determinations. [MoF_6] has been shown to react with carboxylic acids at ca. 130°C to give trifluoromethyl compounds in good yields [3].

7.1.2 Oxo- and related complexes

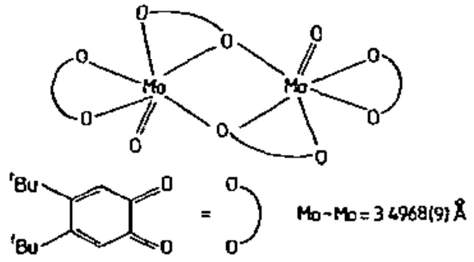
The reactions between $MoOCl_4$ and $Na[O_2CC(CF_3)_3]$, in various molar ratios, in dry CH_2Cl_2 have been shown to yield $[MoOCl_{4-n}\{O_2C(CF_3)_3\}_n]$ ($n = 1$–4) complexes; only the materials with $n = 3$ or 4 were isolated and these are volatile and moisture sensitive [4]. [$MoOCl(acac)_2$] has now been prepared by a novel O—Cl atom exchange between [$MoO_2(acac)_2$] and [$MoCl_2(acac)_2$]; [$MoOCl(acac)_2$] undergoes substitution when reacted with the free acid form of several ligands (LH = 8-hydroxy- or 8-mercaptoquinoline, $HS_2P(CHMe_2)_2$ or $L_2H_2 = (2\text{-HO-Ph-CH=N})_2(CH_2)_n$; $n = 2$ or 3) to yield the corresponding [$MoOClL_2$] complex [5]. A new synthetic route to [$MoOS_2(S_2CNR_2)_2$] (R = Me, Et or Pr) complexes has been described using Na_2S_4 or Na_2S; reactions of these complexes have been studied, including that with $MeOSO_2F$, which yields the corresponding $[MoO(SSMe)(S_2CNR_2)_2]^+$ complex [6].

[MoF_6] and Sb_2X_3 (X = S or Se) (3 : 1) react to give the corresponding amber coloured $MoXF_4$ compound and SbF_3; both of these molybdenum compounds are stable in vacuo but $MoSF_4$ is sensitive to moisture. The IR spectra of the materials show bands characteristic of both bridging and terminal fluoride ligands and therefore structures analogous to those of WXF_4 (X = O, S or Se) have been proposed [7].

The linewidths and chemical shifts of the ^{17}O NMR signals have been described for a series of mononuclear oxomolybdenum(VI) complexes; the chemical shift can be correlated with the force constant or length of the

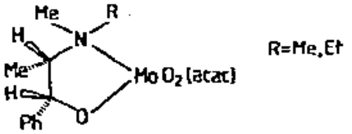
Mo—O bond and, it is suggested, each of these properties reflects the π-bond order. IR spectra have been obtained with ^{17}O and ^{18}O enrichment and confirmation of the assignment of Mo—O vibrational modes has been achieved [8].

The crystal structures of *cis*-$[MoO_2X_2(OPPh_3)_2]$ (X = Cl or Br) have been determined; the two complexes have the same ligand arrangement, with the Ph_3PO molecules bound *trans* to the oxido- groups and the halide ligands mutually *trans*. These authors also reported the crystal structure of *cis*-$[MoO_2(HL)_2] \cdot 2\ H_2L$ (where H_2L = butane-2,3-diol), in which the Mo—O distances were found to be 1.935(7) and 2.284(7) Å, respectively, for the deprotonated and protonated hydroxy functions [9]. A crystal structure determination of the 2,3-dimethyl-2,3-butanediol (H_2L') complex $[Mo_2O_3(L)_2(HL)_2]$ has established that each molybdenum atom is coordinated to two bidentate ligands, one of which is singly deprotonated and the other is doubly deprotonated; two intramolecular hydrogen bonds link the ligands attached to the different molybdenum atoms [10]. $[MoO_2(acac)_2]$ reacts with 3,5-di-*tert*-butyl catechol (1 : 2) in an aprotic medium to produce a purple, diamagnetic binuclear oxomolybdenum(VI)-catechol complex which, in moderately coordinating solvents, dissociates to a green monomer; both of these materials have a 1 : 2 Mo: catechol ratio. The purple complex reacts with $[Bu_4N]OH$ to give an orange binuclear molybdenum(VI) complex containing one catechol per molybdenum. Electrochemical and electronic spectral data have been obtained for these complexes and the former, together with some substitution reactions, suggest a versatile chemistry for this system [11]. The purple compound (1) has been obtained, by reacting $[Mo(CO)_6]$ with the ligand in refluxing toluene containing a trace of dioxygen, and characterised by X-ray crystallography [12]. The asymmetric epoxidation of simple olefins with an optically active peroxomolybdenum(VI) complex has been described [13].



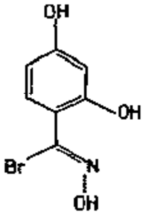
(1)

The complexes (2) have been prepared by stirring a mixture of $[MoO_2$-



(2)

(acac)$_2$] and the corresponding ligand (ca. 1 : 1) in a hydrocarbon solvent at 70—75° C; these materials have been utilised in the asymmetric oxidations of allylic alcohols [14]. A *cis*-dioxomolybdenum(VI) complex with 2,4-dihydroxyvalerophenone oxime (3) has been reported in which the ligand appears to be



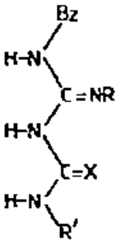
(3)

coordinated via the deprotonated *o*-hydroxy and *N* atoms of the oxime group [15]. [MoO$_2$L$_2$] · S (L = benzohydroxamate; S = solvent e.g. alcohol, MeCN or dmf) compounds have been obtained and characterised by IR spectroscopy, thermal decomposition studies, and X-ray crystallography; in the alcohol adducts, the R—O—H group is attached to a molybdenyl oxygen by a strong hydrogen bond [16]. Molybdate(VI) reacts with [NH$_3$OH]Cl at pH 6.5 to give [MoO$_2$(OH)$_2$(NH$_2$OH)$_2$] which, on washing with MeOAc, yields the oxime complex [MoO$_2$(OH)$_2$(Me$_2$C=NOH)$_2$] [17].

The crystal structure of [MoO$_2$(NCS)$_2$(hmpa)$_2$] has been determined; the thiocyanate ligands are *N* bound and are mutually *trans*, with Mo—N bonds of length ca. 2.06 Å [18]. In [MoO$_2$Cl$_2$(phen)], each nitrogen atom is approximately *trans* to an oxo-group and the Mo—N bonds are 2.308(3) Å in length [19].

The photolysis of bis(peroxo)molybdenum(VI) tetra-4-tolylporphyrin has been studied and the *cis*-[MoO$_2$(porphyrin)] complex spectroscopically characterised. This complex shows a high reactivity towards Ph$_3$P, forming Ph$_3$PO and [MoO(porphyrin)]; this ready oxygen atom transfer is proposed to arise because of the relief of steric strain within the molybdenum(VI) complex [20].

A large number of bi-, tri- or tetradentate Schiff base ligands, with *O*, *N* and/or *S* donor atoms, have been reported to complex to the *cis*-MoO$_2^{2+}$ moiety [21], as have the ligands (4) [22]. The dimensions of the coordination



(R=H, Ph;
R'=2-, or 4-tolyl
X=O,S)

(4)

sphere in *cis*-[MoO$_2$L] (LH$_2$ = (HSCH$_2$CH$_2$)$_2$NCH$_2$CH$_2$X; X = SMe or NMe$_2$)

complexes have been obtained by X-ray crystallographic and EXAFS studies; good agreement was achieved between the two approaches, with a mean difference of 0.012 Å for the values obtained for the length of the metal—ligand bonds [23]. The sulphur $2p_{3/2}$ binding energies of these latter, and related complexes involving cysteine and penicillamine, have been recorded. Free thioether and thiol ligands show similar sulphur 2*p* binding energies at ca. 163 eV. However, when complexed to molybdenum, the binding energy for the coordinated thiolate groups is appreciably below that for coordinated thioether groups. Therefore, XPES spectroscopy may allow for a clear distinction between thiolate and thioether coordination [24]; this could be of particular value for determining the ligands coordinated to molybdenum in biological systems (see Section 7.9). Reactions which may have some correspondence to the oxidations catalysed by the aldehyde and other molybdenum-containing oxidases have been described and discussed [25]. An important facility for the function of the molybdenum centres in these enzymes seems to be the possibility of ready transformations between monomeric molybdenum(VI), (V) and (IV) centres; this presumably requires relatively little structural reorganisation about the metal during these changes. In this context, the first structural comparison (5) between monomeric molybdenum(VI) and (V) complexes, having common (*S*, *N*) chelate ligands, is therefore of some importance. The major structural variation in the features common to both complexes is the Mo—N distances; Mo—N and Mo—N′ were refined as 2.382(9) and 2.374(9) Å for the molybdenum(VI) centre and 2.210(6) and 2.408(6) Å for the molybdenum(V) centre [26], whereas the lengths of the Mo—O and Mo—S bonds did not significantly differ from one complex to the other [26].

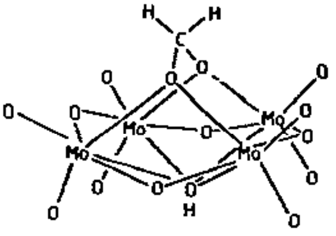
(X=O,Cl)

(5)

7.1.3 Molybdenum(VI) oxides and homonuclear polyanions

The products of evaporation of MoO_3 have been detected by mass spectrometry and tri-, tetra- and pentamers observed with heats of sublimation at 845—935 K of ca. 344, 397 and 471 kJ mol^{-1}, respectively [27]. In the presence of small quantities of water, MoO_3 reacts with amines to give alkyl ammonium salts of octa-, hepta- or mono-molybdates, depending upon the number of hydrogen bonds that the cation can form [28]. X-ray scattering measurements have been performed on solutions of lithium molybdate(VI) with varying acidities; the radial distribution curves obtained were considered to be consistent with the formation of either tetrahedral $[MoO_4]^{2-}$ or $[Mo_8O_{26}]^{4-}$ units [29]. A complete vibrational analysis has been performed for the $[Mo_7O_{24}]^{6-}$ ion with C_2 symmetry, and a good interpretation of the IR and Raman spectra for this ion was achieved [30].

The crystal structure of $[C_{12}H_{24}O_6]_2K_2[Mo_6O_{19}] \cdot H_2O$ ($C_{12}H_{24}O_6 \equiv$18-crown-6) has been determined; the anion is located between the two crown-ether complexed cations [31]. $[NBu_4]_2[Mo_2O_7]$ reacts with aldehydes (RCHO; R = H, Me, Ph, C_2H_3 or CF_3) in non-aqueous solution to form the corresponding $[NBu_4]_3[RCHMo_4O_{15}H]$ salt. An X-ray crystallographic study of the R = H compound has shown that it contains discrete $[CH_2Mo_4O_{15}H]^{3-}$ ions (6), in which (CH_2O_2) and OH groups are bonded by weak Mo—O (length >2.1 Å) linkages to opposite sides of an Mo_4O_{12} ring. This complex could be important as a model for the selective oxidation of propene to acrolein on an oxide catalyst surface [32]. $H_{12}Mo_5(CN)_8O_{16}$ has been obtained by the reaction of $K_4[Mo(CN)_8] \cdot 2\ H_2O$ with concentrated HNO_3 at 90°C; magnetic and spectral measurements suggest that $[Mo(CN)_8]^{4-}$ units are linked to Mo_4 polyhedra via *N*-bridging cyanide groups [33].



(6)

7.1.4 Ternary oxides and heteronuclear polyanions

Chemisorption of dioxygen on MoO_3/MgO and MoO_3/Al_2O_3 at 25°C has been monitored by EPR spectroscopy and O^- and $[O_2]^-$ ions detected [34]. $MgMo_3O_{10} \cdot n\ H_2O$ (n = 7 or 10) and $Mg_2Mo_3O_{11}$ have been obtained after heating an aqueous mixture of MgO and MoO_3 under reflux; $MMo_3O_{10} \cdot x\ H_2O$ (M = Ca, x = 6; M = Sr, x = 4) have also been obtained and the TGA and IR spectral properties of these materials have been measured. $BaMoO_4$ and $BaMo_2O_7$ have also been reported [35]. The first heteropolyanions containing metal—metal bonds, for example $[(cp)Fe(CO)_2SnMo_{11}SiO_{39}]^{5-}$, have been claimed; these are derivatives of the Keggin-structure heteropolyanions $[M_{12}SiO_{40}]^{4-}$ (M = Mo or W) and $[W_{12}PO_{40}]^{3-}$, and have been prepared from the "unsaturated" $[M_{11}ZO_{39}]^{n-}$ (Z = Si, M = Mo or W, n = 4; Z = P, M = W, n = 3) Keggin fragments and transition metal complexes containing -$SnCl_3$ or -$GeCl_3$ [36]. X-ray crystallographic studies have shown that $Na_5HMo_5P_2O_{23}$-$(H_2O)_{11}$ contains discrete $[HMo_5P_2O_{23}]^{5-}$ units, each comprised of a ring of five $\{MoO_6\}$ octahedra and two $\{PO_4\}$ tetrahedra, one attached to each side of the ring [37]. α-Te_2MoO_7 contains molybdenum and tellurium in pseudo-octahedral environments; $\{MoO_6\}$ moieties are linked by edge-sharing into infinite chains which are connected through $[Te_4O_{10}]_n^{4n-}$ puckered layers [38]. The IR and electronic spectral properties of $[4\text{-}R\text{-}C_6H_4N_2][Mo_6IO_{24}]$ (R = Bu, MeO or NO_2) have been obtained [39] and the interference by iodide in the molybdate test for phosphate has been discussed [40].

$Na_6Mo_6V_2O_{26}(H_2O)_{16}$ has been studied by X-ray crystallography; the structure is comprised of $[Mo_6V_2O_{26}]^{6-}$ anions, linked together by sodium ions and water molecules into a three-dimensional framework. The anions have the expected structure, with a flat ring of six edge-sharing $\{MoO_6\}$ octahedra capped on either side of the central cavity by a $\{VO_4\}$ tetrahedron [41]. $K_{10}[MoNb_{12}O_{38}] \cdot 34\ H_2O$ has been reported [42]. The optical absorption spectra of single crystals and powder samples of $W_xMo_{1-x}O_3$ reveal fundamental absorption edges with gap energies of 2.77 eV (for WO_3) and 3.05 eV (for MoO_3), with a continuous shift of the absorption edge and simultaneous appearance of absorption tails for the ternary oxides. A theoretical interpretation has been advanced, based on an Anderson-localisation model with potential fluctuations due to Mo—W disorder [43]. $[NH_4]_3[FeMo_6O_{18}(OH)_6] \cdot 5\ H_2O$ has been prepared by the addition of $Fe(NO_3)_3 \cdot 9\ H_2O$ to a solution of $[NH_4]_6[Mo_7O_{24}]$ at 40°C and pH 3—3.5; $M_3[FeMo_6O_{18}(OH)_6] \cdot n\ H_2O$ (M = K, Rb or Cs; $n = 7$, 4 or 5, respectively) were prepared in a similar manner [44]. IR and ^1H NMR spectral data have been reported for some cobalt heteropolymolybdates [45], and IR and XPES data have been recorded for the series of heteropolyacid derivatives $M_xM'(OH)_6Mo_6O_{18} \cdot nH_2O$ ($x = 3$; M = K or NH_4, M' = Al, Ga, Cr, Fe, Co or Rh; $x = 4$, M = NH_4, M' = Mn, Co, Ni, Cu or Zn) and $[NH_4]_3Au(MoO_4)_3$ [46].

7.1.5 Tetraoxide, -sulphide and -selenide anions

The crystal structures of $(C_{12}H_{24}O_6)_2 \cdot K_2[MoO_4] \cdot 5\ H_2O$ ($C_{12}H_{24}O_6$ = 18-crown-6) [47] and $LaMBO_6$ (M = Mo or W) [48] have been determined and dimensions for the discrete $[MO_4]^{2-}$ tetrahedra in these lattices obtained. IR spectral data have been recorded for the complete set of lanthanide (Ln) salts $Ln[MoO_4][ReO_4]$ [49]; $[Cu(py)_4][MoO_4] \cdot 2\ H_2O$ has been prepared [50].

$X\alpha$-molecular orbital calculations have been carried out for the $[MoX_4]^{2-}$ (X = O, S or Se) ions and the data used to interpret their charge-transfer spectra [51]. A thorough analysis of the vibrational properties of $[MoS_4]^{2-}$ (and $[WS_4]^{2-}$) has been described [52]. These latter anions have been used as the starting materials for synthesis of mixed-metal—sulphur clusters and these studies are included in Section 7.7.

7.1.6 Molybdenum(VI)/molybdenum(V) oxides

The standard free energy of formation of Mo_4O_{11} has been determined as $(-2743 + 0.853T) \pm 5\ kJ\ mol^{-1}$, over the temperature range 840—1090K, by EMF measurements [53]. Large single crystals of MoO_{3-x} have been grown by physical vapour transport [54]. The crystal structure of the blue crystal-line salt, isolated following the photoreduction of $[(CHMe_2)NH_3]_6[Mo_7O_{24}]$, has been determined; this material contains the $[Mo_{13}O_{40}]^{4-}$ and $[H_4Mo_{12}O_{40}]^{4-}$ ions, both having the Keggin structure, randomly distributed over the anion sites in a 1 : 2 ratio [55]. The EPR spectra of the trianionic species obtained by electrochemical reduction of $[Mo_6O_{19}]^{2-}$ have been interpreted in terms of the formation of a localised MoO^{3+} centre, surrounded by oxide ions in C_{4v} symmetry [56].

7.2 MOLYBDENUM(V)

7.2.1 *Halide complexes*

Full details for the preparation of MoF_5, by the reduction of MoF_6 with Si powder in the presence of dry HF, have been published [57]. The structure and mobility of MoF_5 in liquid and glass phases have been studied by ^{19}F NMR spectroscopy; the data obtained are consistent with MoF_5 existing as a C_{4v} monomer in the liquid and condensing into infinite chains on solidification [58].

IR data have been presented for $[MoCl_6]^-$ [59] and complexes of the type $[Mo_2Cl_4L_2(\mu\text{-}L)_2]Cl_6$ (L = (4)) have been characterised [22].

7.2.2 *Monomeric complexes containing oxide and sulphide groups*

The dimensions of $[MoOCl_4(H_2O)]^-$, obtained from a crystal structure characterisation of $[NEt_4]_3[H_5O_2]_2[Mo_2Cl_8H][MoOCl_4(H_2O)]$ [60], are in reasonably good agreement with previous determinations. Various compounds containing $[MoOX_4(H_2O)]^-$ (X = Br or I) ions can be obtained in low yield by the reaction of $[Mo_2(OAc)_4]$ with aqueous HX in the presence of dioxygen. $[pyH]_5[MoOBr_4(H_2O)]_3 \cdot Br_2$, $[NEt_4][MoOBr_4(H_2O)]$, and $[NEt_4][MoOI_4\text{-}(H_2O)]$ have been prepared in this manner and their identities confirmed by X-ray crystallography [61].

The crystal structure of $Mo_2P_4O_{15}$ has been reported; this material consists of MoO^{3+} centres and $\{P_4O_{13}\}^{6-}$ units, with the molybdenum having a total of six oxygen atoms in its primary coordination sphere [62]. EPR studies indicate that similar centres are present in $[Mo_6O_{19}]^{3-}$ [56]. EPR and ^{31}P NMR studies of aqueous solutions containing $[NH_4]_2[MoOCl_5]$ and pyrophosphate, tripolyphosphate, or ATP have been recorded; the EPR spectra suggest that only 0.5—7.0% of the molybdenum is present as monomeric species [63].

The syntheses of the red and green isomers of $[MoOCl_3(bipy)]$ have been documented; the former is prepared when $[bipyH_2][MoOCl_5]$ is boiled in EtOH and the latter when this salt is boiled in MeCN [64]. These complexes, and their 1,10-phenanthroline counterparts, react with oxalic acid to produce the corresponding $[MoOCl(NN)(ox)]$ complex; these materials have been characterised by IR and electronic spectroscopy and magnetic and conductance data were also recorded [65]. The complexes $MoOCl_3L_2$ (L = 2-, 3- or

4-pyridine-monocarboxylic acid) have been prepared by heating $MoCl_5$ with the corresponding ligand in EtOH; the IR spectra of these non-electrolytes indicate that they contain L coordinated via the *N* atom [66]. The resonance Raman spectrum of two tetrapyrrole complexes of MoO^{3+} have been recorded and the information obtained suggests that the absorption at 455 nm is due to a π(pyrrole) → $d_{xz,yz}$ (Mo) charge-transfer transition, since the intensities of both ν(Mo=O) and ν(Mo—N) vibrations are enhanced as the wavelength of the exciting radiation approaches 455 nm [67].

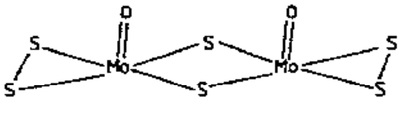
Oxomolybdenum(V) complexes of substituted quinolines and hydroxyquinolines have been prepared by the reaction of $[MoOCl_3(thf)_2]$ with the ligand and different types of complexes were observed, including $[MoOCl_3(ligand)]$ [68]. The crystal structure of $[LH_2][MoOCl_3L]$ (HL = 8-hydroxyquinoline) has been reported; the molybdenum atom is in a distorted octahedral environment, coordinated to three chlorine atoms *cis* to the oxide group, the other *cis* donor atom being the nitrogen of the bidentate hydroxyquinolate ligand [69]. The crystal structure of *cis*-$[MoOCl(SN)_2]$ (*SN* = 8-mercaptoquinolinate) has been obtained and compared to that of its *cis*-MoO_2^{2+} counterpart (see Section 7.1.2) [26]. The EPR parameters of the complex obtained when 8-mercaptoquinolinate reacts with molybdenum(V) in aqueous acid are very similar to signals obtained from the molybdenum centre of xanthine oxidase. The complex *cis*-$[MoOCl(SN)_2]$ is one of a group of oxomolybdenum(V) chloride complexes, for which frozen EPR data have been interpreted and discussed in relation to the molecular and electronic structures of the isomers formed in solution. As has been seen in earlier studies, the low symmetry complexes exhibit a non-coincidence of the principal components of the *g* and hyperfine tensors. This is probably caused by extensive mixing among the excited-state metal-based *d*-orbitals, although ligand spin—orbit coupling could also be a contributory factor. The complicated spin Hamiltonian precludes simple conclusions about molecular geometry and/or the nature of the donor atoms from EPR signals of molybdenum(V) centres [70]. In an attempt to reproduce the behaviour of the nitrate reductases, the reduction of nitrate by a number of monomeric molybdenum(V) complexes, including $[MoOCl_3L]$ (L = bipy or phen), $[MoOClL_2]$ (L = 8-hydroxyquinoline or 8-mercaptoquinoline), and $[MoOCl(CH_3OH)_xL']$ (L′ = *o*-(salicylidenimino)phenol, $x = 1$; L′ = *o*-bis(salicylidenimino)benzene, $x = 0$) have been studied. With the exception of these last two complexes, the molybdenum(V) centres reduce nitrate in a one-electron step, producing NO_2 and the corresponding *cis*-dioxomolybdenum(VI) compound. The mechanism for the reaction is consistent with earlier proposals that coordination of the nitrate group *cis* to the oxide of the molybdenum(V) centre is required for electron and oxygen transfer [71].

The reactions of $MoCl_5$ or $[MoOCl_4(dmf)]^-$ with thiols (RSH; R = Et or Am) in pyridine have been monitored by EPR and IR spectroscopy; $[MoSCl_{4-n}(SR)_n(py)]^-$ (n = 0—3, inclusive) and $[MoS(SR)_5]^{2-}$ were suggested as possible products [72].

7.2.3 Dimeric complexes containing oxide and sulphide groups

The crystal structure of a material containing $[Mo_2O_3(S_2CNEt_2)_4]$ molecules and (probably) $[H_5O_2]^+$ and $[Mo_2O_3(S_2CNEt_2)_4]^-$ ions have been reported. The paramagnetism and the EPR signals of the material have been attributed to the dimeric anion, which, as formulated, appears to contain molybdenum(V) and (IV); however, it is surprising that the EPR signals are characteristic of a monomeric complex, with six molybdenum hyperfine lines, rather than a dimeric complex with the unpaired electron shared equally between the two molybdenum centres, for which an eleven line hyperfine pattern should be evident [73]. Several $[Mo_2O_3Cl_4L_n]$ (L = substituted quinoline or hydroxyquinoline; n = 2 or 3) (and $[Mo_3O_5Cl_5L_3]$) complexes have been isolated, subsequent to the reaction between $[MoOCl_3(thf)_2]$ and the ligand [68]. $Na_6[Mo_2O_4(HP_3O_{10})_2] \cdot 6\ H_2O$ has been isolated in nearly quantitative yield from aqueous solutions of $[NH_4]_2[MoOCl_5]$ and tripolyphosphate (>1 : 1) at pH >4 [63].

Several salts, including $Cs_2[Mo_2O_2S_2L_2]$, $Cs_2[Mo_2O_2S_2Cl_4(H_2O)_2]$, $Cs_2[Mo_2S_2(C_2O_4)_2(H_2O)_2] \cdot 2\ H_2O$, and $Cs_6[Mo_4O_6S_2(C_2O_4)_5] \cdot H_2O$, have been isolated as products of the reaction between $Cs_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]$ and Cs_2L (where H_2L = dithiooxalic acid). X-ray crystallographic studies have established that the first three of these complexes contain a di-μ-sulphido $\{Mo_2O_2S_2\}$ core, whereas the last contains two μ-oxido-μ-sulphido $\{Mo_2O_3S\}$ moieties [74]. Raman and resonance Raman spectroscopic studies of dimers containing the $\{Mo_2(\mu\text{-}S)_2O_2\}$ core complexed by cysteinyl chelating ligands, have been reported. The strong Raman bands at 930—950 cm^{-1} and 420 cm^{-1} were assigned to $\nu(Mo{=}O)$ and $\nu(Mo{-}S(\mu))$ bridging modes, respectively, and the resonance Raman spectra indicate that the $Mo(\mu\text{-}S)_2Mo$ moiety gives rise to a broad electronic absorption [75]. $[Mo_2O_2S_2(S_2)_2]^{2-}$ (7) [76] and $[Mo_2(S_2)_6]^{2-}$ (8) [77,78] have been isolated and characterised by X-ray crystallography; further details concerning these complexes are provided in Section 7.7. $[Mo_2(S_2)_6]^{2-}$ reacts with $[S_2CNEt_2]^-$ in refluxing EtOH to yield $[Mo_2S_4(S_2CNEt_2)_2]$, the crystal structure of which has been determined [78]. The closely related complexes, $[Mo_2OS(\mu\text{-}S)_2(S_2CNR_2)_2]$ (R = Me or Et), have been synthesised by two methods: (i) dithionite reduction of $K_2[MoS_4]$ in aqueous solution containing $Na[S_2CNR_2]$ (2 : 3), followed by chromatographic purification; and (ii) bubbling H_2S through an anaerobic solution of $[Mo_2O_3(S_2CNEt_2)_2]$ in $CHCl_3$, with the resultant yellow precipitate being recrystallised from CH_2Cl_2/diethyl ether. The crystal structure of the diethyl-



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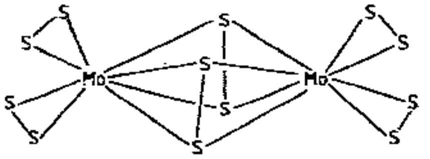
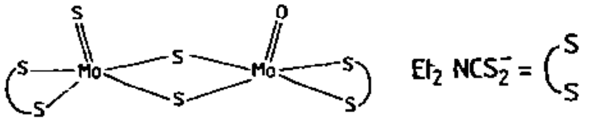


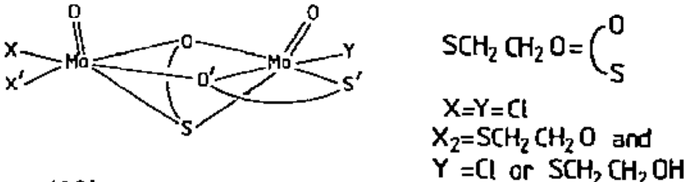
(8)

dithiocarbamate derivative (9) has been determined; although the terminal atoms are disordered, the other dimensions obtained, for example $r(\text{Mo—Mo})$ = 2.826(3); $r(\text{Mo—S}(\mu))$ = 2.32 Å and $\bar{r}(\text{Mo—S}_{\text{dtc}})$ = 2.47 Å, are typical of values obtained for the corresponding units in other structures. An interesting observation is that these materials react with $[CN]^-$ in refluxing $CHCl_3$, containing some moisture, to produce the corresponding $[MoO_2S_2(S_2CNR_2)_2]$ complex and $[SCN]^-$; this reaction may have some relevance to the cyanolysis of active xanthine oxidase which also forms $[SCN]^-$ [79].



(9)

The reactions of 2-hydroxyethanethiol and various bases, including Pr_3N, with $[MoOCl_4(H_2O)]^-$ or $[MoOCl_3(thf)_2]$ yield many products. The crystal structures of three such derivatives (10) have been determined and in each case the Mo—Mo separation is 2.734 ± 0.006 Å. The complexes $[Mo_2O_2(SR)_6Z]^-$ (R = $PhCH_2$ or Ph; Z = $PhCH_2S$, MeO, or Et_2N) are assigned a similar structure, with two thiolate groups and the ligand Z bridging across the molybdenum centres. $[Mo_2O_2(SCH_2Ph)_7]^-$ has been obtained by reacting $[MoOCl_3(thf)_2]$, $PhCH_2SH$, and NEt_3 in dmf, $[Mo_2O_2(SPh)_6(OMe)]^-$ by reacting $[MoOCl_3(thf)_2]$, PhSH, and Et_3N in MeCN/MeOH at 50—60°C for 18 h, and $[Mo_2O_2(SPh)_6(NEt_2)]^-$ may be isolated after Et_2NH is added to the solution obtained by reacting $[MoO(SPh)_4]^-$ with $FeCl_3$ [80]. The reaction of $[MoOCl_4(H_2O)]^-$ (or $[Mo_2O_2(SCH_2CH_2O)_2Cl_3]^-$), $HOCH_2CH_2SH$, H_2O, and a base, B (B = piperidine, morpholine, or pyrrolidine), leads to the formation of $[BH]_2[Mo_2O_3(SCH_2CH_2O)_3]$; the conformation and dimensions of the anion (11) were obtained from a crystal structure determination of the



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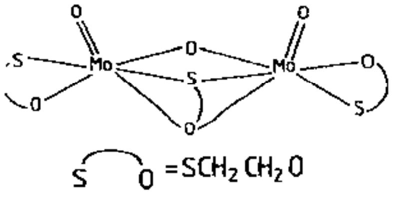


(11)

piperidinium salt; the Mo—Mo separation is 2.676(1) Å, some 0.10 Å shorter than the distance in (10), presumably because a bridging oxide is present rather than an alkoxide [81].

7.2.4 *Nitride and related complexes*

$MoNBr_2$ has been prepared by the thermolysis of $MoNBr_3$ in vacuo at 260°C. The material is a dark brown hygroscopic powder and $MoNBr_2 \cdot H_2O$ has been identified by mass spectrometry. The IR spectrum of the anhydrous material supports the presence of a Mo—N triple bond and the low magnetic moment of 0.65 μ_B is probably due to spin—spin interactions in the solid state [82]. $[(MoNCl_4)_2]$ has been prepared by reacting $MoCl_5$ with IN_3 or NCl_3. The IR, mass spectral, and magnetic (1.63 μ_B) data obtained for this material are consistent with a dimeric unit, linked by N—N bonds and involving Mo—N triple bonds [83].

The reactions of $MoCl_5$ and $[MoOCl_4(dmf)]^-$ with $PhNH_2$ in dmf have been monitored by EPR and IR spectroscopy, and the results interpreted in terms of the formation of the complexes $[Mo(NPh)Cl_{4-n}(NHPh)_n(dmf)]^-$ (n = 0—3, inclusive) and $[Mo(NPh)(NHPh)_5]^{2-}$ [72]. The majority of other studies which involved molybdenum—nitrogen multiple bonds are described in Section 7.8

7.2.5 *Octacyanomolybdate(V)*

Single crystal Q-band EPR spectra have been obtained for $[NBu_4]_3[Mo(CN)_8]$ and the observation that $g_\parallel > g_\perp$ is in contradiction of the simple crystal-field prediction of the sense of this anisotropy for the $[Mo(CN)_8]^{3-}$ ion with D_{2d} symmetry [84]. A kinetic study of the osmium catalyzed oxidation of tellurium(IV) by $[M(CN)_8]^{3-}$ (M = Mo or W) ions in an alkaline medium, has been reported [85].

7.3 MOLYBDENUM(IV)

7.3.1 *Chloride complexes*

Raman and IR spectroscopic data for $[MoCl_6]^{2-}$ have been described and discussed [59]. The reaction of gaseous HCl with [MoO(TTP)] (TTP = dianion of 5, 10, 15, 20-tetra-4-tolylporphyrin) forms $[MoCl_2(TTP)]$; the structure of the latter involves a planar porphyrin ring with the $Cl—\widehat{Mo}—Cl$ interbond angle 178.4(2)° and although the chloride ligands appear to be chemically equivalent, they are at different distances (2.347(4) and 2.276(4) Å) from the molybdenum atom [86]. The treatment of $[MoCl_4(PrCN)_2]$ with a dithiocarboxylic acid has been shown to be a general route to the preparation of molybdenum(IV) dithiocarboxylate complexes [87].

7.3.2 Oxides and chalcogenides

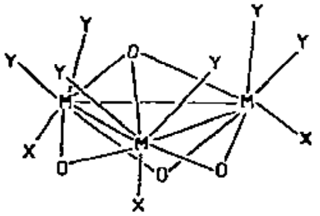
The free energy of formation of MoO_2 has been determined as (—571 + 0.1661 *T*) ± 1.1 kJ mol^{-1}, between 1070 and 1320K, by EMF measurements [53]. He(I) and $MgK_{\alpha 1,2}$ PE spectra of MoO_2 have been reported; with the former exciting radiation, a splitting of the molybdenum *4d* ionizations is manifest, in agreement with previous descriptions of the electronic structure of this material [88].

Thermodynamic properties have been obtained for MoS_2 between 298 and 1700K [89] and the mechanism of dissociation of this compound between 1113 and 1298K, to produce Mo_2S_3 and sulphur, has been studied by X-ray diffractometry [90]. Electronic spectral data have been obtained and analysed for single crystals of the 2*H*-polytypes of MoX_2 (X = S, Se or Te) [91].

7.3.3 Complexes with oxo groups

The structure of molybdenum(IV) in acidic aqueous media has been the subject of much discussion, with monomeric and dimeric molybdenum species having been proposed in earlier studies. An EXAFS study has now been accomplished and the data interpreted in terms of each Mo being surrounded by one Mo atom and two and four oxygen atoms at distances of 2.51, 1.96 and 2.20 Å, respectively. These results are compatible with the formation of $[(H_2O)_4Mo(\mu\text{-}O)_2Mo(H_2O)_4]^{4+}$ [92]. However, other complexes may be compatible with the EXAFS spectrum and, in view of the ready isolation of species containing $\{Mo^{IV}{}_3O_4\}$ moieties and the Mo—Mo and Mo—O distances observed therein (vide infra), it would be interesting to see the similarity between the EXAFS spectra and these clusters and the data obtained for the aqueous solutions. Molybdenum oxalate complexes, such as $K_2[Mo_2O(C_2O_4)_2(H_2O)_2(OH)_4]$ and $M_2[Mo_2O(C_2O_4)_2(OH)_6]$ (M = Ba, Pb, or Ag_2), have been prepared by reacting $K_2[MoCl_6]$ with oxalic acid (1 : 2—8) in aqueous solution; IR, EPR and TGA characteristics have been recorded and the anions are suggested to contain an Mo—O—Mo bridge [93].

Recent preparative and crystallographic studies have shown that there is an extensive chemistry of molybdenum(IV) and tungsten(IV) involving discrete trinuclear clusters, containing a triangular arrangement of the metal atoms with what appears to be a single bond spanning each metal—metal contact. The essentials of the structure may be represented by an $M_3O_4X_3Y_6$ framework (12). $Na_4[Mo_6O_8(edta)_3] \cdot 14\ H_2O$ has been obtained from a solution of



(12)

molybdenum(IV) in aqueous ethanoate buffer, upon the addition of Na_2-[H_2edta]. The red crystals obtained by the slow evaporation of this solution contain two equivalent trinuclear units connected by edta groups. Each trinuclear unit consists of an equilateral triangle of Mo atoms {$\bar{r}$(Mo—Mo) = 2.51(1) Å} capped by one μ_3-oxygen atom {$\bar{r}$(Mo—O) = 2.04(2) Å} and containing three μ_2-oxygen atoms {$\bar{r}$(Mo—O) = 1.93(1) Å}, one spanning each edge of the triangle. Each molybdenum atom is also coordinated by two carboxylate oxygen atoms and a nitrogen atom from one end of an $[\text{edta}]^{4-}$ ion; each end of each $[\text{edta}]^{4-}$ ion is attached to a different {Mo_3} cluster, so that two such clusters are connected by three edta groups [94]. $[Mo_3OCl_3(O_2CMe)_3(H_2O)_3]^{2+}$ is also constructed with the skeleton (12), but with chlorines in place of the μ_2-oxygen atoms and ethanoate groups spanning each edge of the {Mo_3} cluster [95].

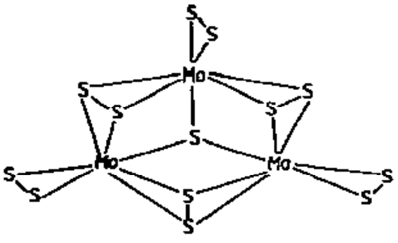
$K_4[MoO_2(CN)_4]$ reacts with dithiols ($H_2L = HSCH_2CH_2SH$ or toluene-3,4-dithiol) to form the corresponding $K_2[MoOL_2]$ complex; reaction of these with $Na[S_2CNEt_2]$ produces $[MoO(S_2CNEt_2)_2]$ [96]. In a further study of the ability of $[MoO(S_2CNR_2)_2]$ (R = Me or Et) complexes to bind unsaturated molecules (L = C_2H_2, C_2Ph_2 or PhC_2H), the IR and ^{1}H NMR spectra of the $[MoO(S_2CNR_2)_2L]$ adducts have been interpreted in terms of a seven coordinate, pentagonal bipyramidal structure, with L *cis* to the oxide group [97]. The crystal and molecular structure of ethoxo-oxido-bis(1,5,9,13-tetrathiocyclohexadecane)-μ-oxidodimolybdenum(IV) trifluoromethylsulphonate hydrate have been determined; the cation contains a linear O—Mo—O—Mo=O unit, with the two macrocycles coordinated as tetradentate ligands, one to each molybdenum, and staggered 43° relative to one another [98].

[MoO(TTP)] (TTP = dianion of 5,10,15,20-tetra-4-tolylporphyrin) has been shown to involve Mo—O and Mo—N bonds of length 1.656(6) and (average) 2.110(6) Å, respectively [86].

The kinetics of formation of $[MoO(OH)(CN)_4]^{3-}$, from $[Mo_2O_4L_2]^{n-}$ (L_2 = edta, $n = 2$; L = cys, $n = 1$; L = his, $n = 0$; L = cit, $n = 4$; L = HP_3O_{10}, $n = 6$) and cyanide in aqueous solution have been obtained [99]. $H_{12}Mo_5(CN)_8O_{16}$ is formed when $K_4[Mo(CN)_8] \cdot 2\ H_2O$ is reacted with concentrated HNO_3 at 90°C; the spectroscopic and magnetic properties of this material suggest that it comprises $[Mo(CN)_8]^{4-}$ ions linked to a tetramolybdate ion via *N*-bridging cyanide groups [33].

7.3.4 *Complexes with sulphide groups*

Reactions of molybdenum—sulphur compounds with cyanide have been investigated. MoS_2 reacts with cyanide in aqueous solution to form $[Mo_2(CN)_{12}S]^{6-}$. In this anion, each molybdenum has a pentagonal bipyramidal environment. The Mo atoms are linked by a μ_2-sulphide group, and the structure has overall C_{2v} symmetry; the Mo—$\widehat{\text{S}}$—Mo interbond angle is 169.5°, the Mo—S bond lengths are 2.173 Å and these values, together with the diamagnetic nature of the anion, are consistent with the Mo—S interactions having a bond order greater than one. The bridging sulphide is inert to attack by H^+, $[OH]^-$, or $[CN]^-$ [100, 101]. $[NH_4]_2[Mo_3S(S_2)_6]$ has been isolated as the precipitate of the reaction of aqueous $[MoO_4]^{2-}$ with $[NH_4]_2S_x$ at 90°C [77].

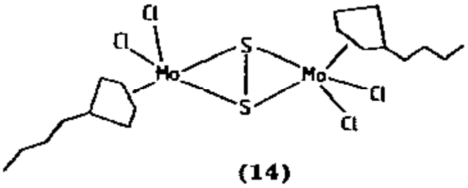


(13)

This anion has the structure (13), the central core having a notable resemblance to that of (12).

7.3.5 *Cyclopentadienyl complexes*

The metal—hydrogen bond enthalpies in $[(cp)_2MH_2]$ (M = Mo or W) molecules have been estimated as 251.4 and 305.2 kJ mol^{-1}, respectively [102]. $[(cp)_2MoCl_2]$ reacts with Na_2S_2 in EtOH to give $[(cp)_2MoS_2]$, together with $[(cp)_2MoS_4]$; the latter compound is favoured by an excess of Na_2S_2. The structure proposed for the former compound involves a sideways-bound persulphide group attached to a pseudotetrahedral molybdenum atom [103]. The crystal structure of $[Mo_2(Bu\text{-}cp)_2Cl_4(S_2)] \cdot 0.5\ CH_2Cl_2$ has been determined; the complex involves the two molybdenum and two sulphur atoms disposed towards the corners of a distorted tetrahedron (14) with Mo—Mo



(14)

and S—S separations of 2.937(1) and 2.019(3) Å, respectively. The crystal structures of $[MoCl_2(cp)(\mu_2\text{-}X)(\mu_2\text{-}SMe)_2MoCl(cp)]$ (X = OH or SMe) have been reported and the respective Mo—Mo separations, of 2.7267(1) and 2.852(2) Å may be indicative of direct metal—metal bonding interactions [104].

7.4 MOLYBDENUM(III)

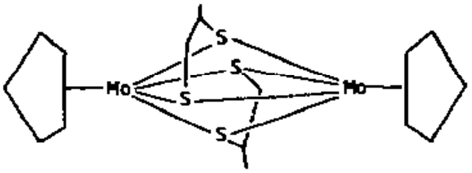
The majority of molybdenum(III) compounds reported this year contain metal—metal bonds and these will be described in Section 7.6.

Raman and IR data for $[MoCl_6]^{3-}$ have been interpreted [59], and the exchange interactions between pairs of Mo^{III} centres doped into CsMX$_3$ (M = Mg or Cd; X = Cl or Br) crystals have been shown to be antiferromagnetic with $J \leqslant 6$ cm^{-1} [105]. Further investigations of [Mo$_2$Cl$_9$]$^{3-}$ and related dimers have been reported [106]. From a solution prepared by dissolving [Mo$_2$(O$_2$CCH$_3$)$_4$] in 12 M HCl and heating to 70°C in air, followed by the addition of [NEt$_4$]Cl, deep yellow crystals of [NEt$_4$]$_3$[H$_5$O$_2$][Mo$_2$Cl$_8$H][MoOCl$_4$(H$_2$O)] have been obtained. This material has permitted the first precise structural characterisation of [Mo$_2$Cl$_8$H]$^{3-}$ to be achieved; the μ-H atom involves Mo—H bonds of 1.73 Å. The Mo—Mo separation is 2.375(2) Å, a contraction of some 0.28 Å from the value in [Mo$_2$Cl$_9$]$^{3-}$ [60]. [Mo$_2$Cl$_8$H]$^{3-}$ may also be obtained by treating [Mo$_2$(O$_2$CCH$_3$)$_4$] with HCl at a temperature below 60°C under anaerobic conditions [107] and the crystal structure of [pyH]$_3$[Mo$_2$Cl$_8$H], obtained in this manner, has been reported [108] and the dimensions of the anion found to be very similar to those reported earlier [60].

[Mo(acac)$_3$] has been shown by X-ray crystallography to have a molecular structure which approximates to D_3 symmetry and Mo—O bonds of average length 2.04(1) Å. The magnetic properties of this compound have been measured at temperatures down to 1.5K; in a magnetically dilute system the $^4A_2$ ground state is described by an $S = 3/2$ spin Hamiltonian with $g_{\parallel} = 1.94$, $g_{\perp} = 1.97$ and $D = -6.3$ (or +7.0) cm^{-1} [109]. [Mo(CO)$_6$] has been heated in wet dmf or dmso and products such as [Mo$_2$O$_3$(H$_2$O)$_5$(dmf)] or [Mo$_2$O$_3$(dmso)$_3$] obtained [110]. Electrocatalytic reductions of C$_2$H$_2$ in H$_2$O or dmf containing molybdenum(III) and citric acid have been investigated; the reactions lead to the formation of C$_2$H$_4$ and C$_2$H$_6$ and the catalytic activity has been attributed to binuclear complexes adsorbed onto the electrode and which facilitate electron transfer from the electrode to the substrate [111].

[Mo$_2$(CN)$_8$S$_2$]$^{6-}$ has been obtained as one product of the reaction between MoS$_2$ and cyanide in aqueous solution [100]. A range of molybdenum(III) complexes with tri- and tetradentate ligands have been prepared by reacting [NH$_4$]$_3$[Mo(NCS)$_6$] with the ligand; the complexes isolated include Mo(LH)L (H$_2$L = salicylidenethiosemicarbazone), MoL$'_3$ (HL$'$ = L-cysteine) and [MoL$''$(NCS)$_2$](NCS) (L$''$ = ethylenedibiguanide or piperazinedibiguanide). The magnetic moments (3.61—3.73 μ_B) and IR and electronic spectra of these complexes are consistent with their formulation as monomeric, pseudo-octahedral complexes [112].

[(cp)Mo(CO)$_3$]$_2$ or [(cp)Mo(CO)$_3$H] react with ethylene or propylene sulphide (RCH$_2$CH$_2$S; R = H or Me) to form [{cpMo(SC$_n$H$_{2n}$S)}$_2$] (n = 2 or 3, respectively). These complexes undergo two reversible one-electron oxida-



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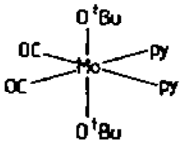


(16)

tions, at 0.13 and 0.79 V vs. SCE in MeCN. A product of the one-electron oxidation, $[\{cpMo(SC_3H_6S)\}_2][BF_4]$, has been characterised by X-ray crystallography; the cation (15) involves a metal—metal separation of 2.599(1) Å spanned by two 1,2-propanedithiolate ligands [113].

7.5 MOLYBDENUM(II)

The vast majority of the compounds containing molybdenum(II) involve a strong and direct metal—metal bond and these are described in the following section.

Mild carbonylation of $[Mo_2(OCMe_3)_6]$ in hexane/pyridine solution has been shown to lead to the formation of $[Mo(OCMe_3)_2(py)_2(CO)_2]$, which has the ligand arrangement depicted in (16). This molecule has values for the ν(C—O) stretching frequencies of 1908 and 1768 cm^{-1} and the average value, 1838 cm^{-1}, is the lowest yet observed for a pair of *cis*-carbonyl groups coordinated to a Mo^{II} centre [114]. The crystal structure of $[PPh_4]_2[Mo(NO)\{(CH_3)_2NCO\}(NCS)_4]$ has been reported; the dimethylcarbamide group binds in a sideways manner via its carbon and oxygen atoms $\{r(Mo—C) = 2.029; r(Mo—O) = 2.078$ Å$\}$ and the molybdenum has a distorted pentagonal bipyramidal coordination geometry [115]. The reactions of $[Mo_2(O_2CCH_3)_4]$ or $K_4[Mo_2Cl_8]$ with RNC (R = Me, CMe_3 or cych), to yield the corresponding $[Mo(CNR)_7]^{2+}$ ion, have been described and the structure of $[Mo(CNCH_3)_7][BF_4]_2$ determined; the geometry of this cation closely approximates to that of a capped octahedron, with Mo—C distances in the range 2.038(7)—2.16(1) Å. This complex is claimed as the first example of a homoleptic species with a capped octahedral structure [116].

7.6 COMPLEXES CONTAINING METAL—METAL BONDS

7.6.1 Molybdenum(V), (IV) and (III) dimers

Several of the molybdenum(V) dimers reported this year, for example $Cs_2[Mo_2O_2S_2(C_2O_4)_2(H_2O)_2]$, $Cs_6[Mo_4O_6S_2(C_2O_4)_5]\cdot H_2O$ [74], $[Mo_2O_2(SCH_2CH_2O)_2Cl_3]^-$ (10) [80], and $[Mo_2O_3(SCH_2CH_2O)_3]^{2-}$ (11) [81], have been shown to involve Mo—Mo separations of ca. 2.73 Å and would generally be considered to contain metal—metal single bonds, consistent with the diamagnetic nature of these systems. However, a definitive experimental characterisation of the electronic structure of such dimers has yet to be accomplished.

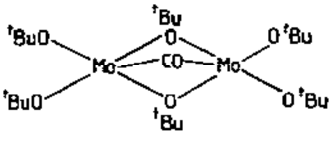
Molybdenum(IV) chemistry, neglected for so long, now appears to be more interesting, following the characterisation of $Mo_3O_4X_3Y_6$ (12), and related clusters [94,95], which involve metal—metal separations of ca. 2.52 Å. Other molybdenum(IV) complexes reported this year, and which can be presumed to involve a metal—metal bond, include $[MoCl_2(cp)(\mu_2\text{-}X)(\mu_2\text{-}SMe)_2MoCl(cp)]$ (X = OH or SMe) [104] and $[\{(cp)Mo(SC_3H_6S)\}_2][BF_4]$ (15) [113].

The interaction between pairs of molybdenum(III) atoms doped in $CsMX_3$ (M = Mg or Cd; X = Cl or Br) have been described [105], further studies of $[Mo_2Cl_9]^{3-}$ reported [106] and a marked reduction in the Mo^{III}—Mo^{III} separation noted, when a μ_2-chloride atom in $[Mo_2Cl_9]^{3-}$ is replaced by a μ_2-hydrogen atom [60,108]. The majority of the other systems containing Mo(III)—Mo(III) interactions reported this year, are best considered under the heading of metal—metal triple bonds.

7.6.2 Complexes with Mo—Mo triple bonds

A review of the complexes known to involve Mo—Mo and W—W triple bonds and their reactions has been presented [117]. An air- and heat-stable compound containing molybdenum—molybdenum triple bonds has been prepared by dissolving $K_4[Mo_2Cl_8] \cdot 2\,H_2O$ in H_3PO_4, mixing with CsCl in H_3PO_4, and allowing to stand for one week at room temperature. This compound, $Cs_2[Mo_2(HPO_4)_4(H_2O)_2]$, and the related material $[pyH]_3[Mo_2(HPO_4)_4]Cl$ contain a dimolybdenum aggregate spanned by four μ_2-(HPO_4) groups and, for the former, axial water molecules and, for the latter, axial chloride ions which form an infinite —Cl—Mo_2—Cl—Mo_2— chain. These Mo—Mo separations of 2.228 ± 0.005 Å seem consistent with a $\sigma^2\pi^4$ triple bond [118,119].

$[Mo_2(OCMe_3)_6]$ in hydrocarbon solvents reacts with CO to form $[Mo(CO)_6]$ and $[Mo(OCMe_3)_4]$; an intermediate in this reaction, $[Mo_2(OCMe_3)_6(CO)]$ has been crystallised and structurally characterised (17). The metal—metal separation is 2.498(1) Å, and arguments have been presented in favour of this representing a rare example of a Mo—Mo double bond. A black paramagnetic material of empirical formula $Mo(OCHMe_2)_3CO$ has also been obtained which is believed to be composed of tetrameric molecules [120]. The reaction of $[Mo_2(OCMe_3)_6]$ with PF_3 yields the black, air-sensitive solid $[Mo_4(\mu_2\text{-}F)_4(OCMe_3)_8]$ (18); the related complex $[Mo_4(\mu_2\text{-}F)_3(\mu_2\text{-}NMe_2)(OCMe_3)_8]$ was also identified during analysis of the diffraction data and the presence of the



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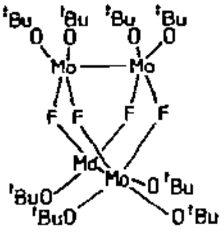
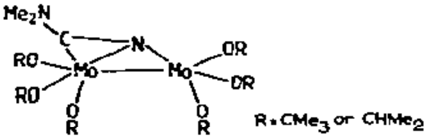
dimethylamide group attributed to incomplete alcoholysis of $[Mo_2(NMe_2)_6]$



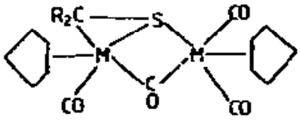
(18)

in the preparation of the starting material. These tetramers involve two short (2.26 Å) Mo—Mo approaches, corresponding to localized metal—metal triple bonds, and four long (3.75 Å), nonbonding, Mo—Mo distances; the cluster assembly arises, therefore, from the fluoride bridges rather than delocalisation of the metal—metal interactions over all four Mo atoms [121]. Dimethylcyanamide, Me_2NCN, adds across the Mo—Mo triple bond of $[Mo_2(OR)_6]$ (R = CMe_3 or $CHMe_2$) complexes to yield the corresponding $[Mo_2(OR)_6(NCNMe_2)]$ complex, the structure of which (19) has been assigned from IR



(19)

and ^1H NMR data. The latter studies also identified fluxional behaviour for the alkoxide and dimethylcyanamide groups. All the data obtained appear to be consistent with the view that the Me_2NCN group acts as a four-electron donor, in a manner analogous to that previously established for $[(cp)_2Mo_2(CO)_4(NCNMe_2)]$ [122]. Diaryl, arylalkyl, and cycloalkyl thioketones (R_2CS) react with $[(cp)_2M_2(CO)_6]$ (M = Mo or W) to form the corresponding complex (20) which, for the thiocamphor complex, involves an Mo—Mo separation of



(20)

3.145(1) Å. These compounds may also be prepared by reacting the thioketone with the triply bonded $[(cp)_2Mo_2(CO)_4]$ complex [123].

Solution, combustion, and other calorimetric studies on dimethylamide complexes of tantalum, molybdenum, and tungsten have been used, in combination with other thermodynamic data, to obtain the enthalpies of formation at 298K for monomeric and dimeric complexes. The transference of plausible values for $\bar{D}(M—NMe_2)$, from the monomeric complexes to the dimers, leads to a value for the D(Mo≡Mo) of 398 ± 18 kJ mol^{-1} (and D(W≡W) of 558 ± 20 kJ mol^{-1}) [124].

7.6.3 Complexes with Mo—Mo quadruple bonds

The standard enthalpies of formation at 298K of $[Mo_2(O_2CCH_3)_4]$, $[Mo_2(O_2CCH_3)_2(acac)_2]$ and $[CrMo(O_2CCH_3)_4]$, together with earlier data obtained for $[Mo(acac)_3]$, and the other necessary thermochemical data, have been used to obtain a value for D(Mo≡Mo) of 334 kJ mol^{-1} [125].

The electronic structure of complexes containing metal—metal quadruple bonds has attracted much attention during this year. A study of the Hartree—Fock instabilities in $[Mo_2(O_2CH)_4]$ calculations has been reported [126] and another Xα-calculation for $[Mo_2Cl_8]^{4-}$ has been reported; this latter study incorporated some valence bond concepts and obtained a better agreement with the experimental for the $\delta \rightarrow \delta^*$ excitation energy than hitherto achieved [127]. Another study of the polarised single crystal absorption spectrum of $[Mo_2(O_2CCH_3)_4]$ has provided evidence that the lowest energy absorption band, at 23 000 cm^{-1}, *is* the $\delta \rightarrow \delta^*$ transition [128]. The sterically hindered complex $[Mo_2Cl_4(PBu_3)_4]$ is highly emissive in 2-methylpentane, with emission lifetimes of 16 and 165 ns at room temperature and 77K, respectively; the results have been interpreted in terms of a very large splitting between triplet and singlet $\delta\delta^*$ excited states, with the emission corresponding to the (singlet) $\delta\delta^* \rightarrow \delta^2$ transition [129]. UVPES studies have been reported for gaseous $[Mo_2(O_2CR)_4]$ (R = H, Me, CF_3, or CMe_3), $[CrMo(O_2CCH_3)_4]$ [130], $[Mo_2(mhp)_4]$ (Hmhp = 6-methyl-2-hydroxypyridine), $[CrMo(mhp)_4]$, $[MoW(mhp)_4]$ and related molecules [131,132] and, with reference to such work, an electron diffraction study of $[Mo_2(O_2CCF_3)_4]$ has shown that there is no significant change in the molecular structure, in particular the Mo—Mo bond length, from solid to gas phase [133]. General agreement exists, in respect of the photoelectron spectral assignments, as to the location of the ionizations from the metal—metal δ- and π-bonding orbitals of the Mo_2^{4+} centre, however, no clear identification of the corresponding σ-ionization has yet been achieved. In another attempt to locate such an ionization, X-ray emission spectra, resulting from $MoL\beta_{2,15}$ or $ClK\beta_{1,3}$ excitation, and XPES data for $K_4[Mo_2Cl_8]$ have been combined to suggest that the δ, π and σ ionizations are separated by 2.1 and 1.7 eV, respectively [134]. Although these values are in reasonable agreement with Xα and ab initio molecular orbital predictions for $[Mo_2Cl_8]^{4-}$, they do not readily resolve the problem concerning the location of the metal—metal σ-ionizations in UVPES spectra of the $[Mo_2L_4]$ molecules. A comparison of the Raman stretching frequency of $[Mo_2(O_2CCH_3)_4]$ at ca. 400 cm^{-1}, for molybdenum with the normal isotopic abundances, with that for a 97.4% ^{92}Mo content, indicates that this mode is nearly a pure Mo—Mo stretching vibration [135].

The rate of ligand exchange between $[Mo_2(O_2CCF_3)_4]$ and $Na[O_2CCF_3]$ in MeCN has been measured using ^{19}F NMR spectroscopy; the rate shows a first-order dependence on the $[Mo_2(O_2CCF_3)_4]$ concentration but is independent of the concentration of $Na[O_2CCF_3]$ [136]. Details for the syntheses and reactions of a number of known complexes containing Mo—Mo quadruple bonds have been presented [107] and the preparation and characterisation of new complexes containing this interaction continues unabated. $[NH_4]_2[Mo_2(NCS)_8] \cdot x\ H_2O$ (x = 4 or 6) have been obtained by reacting $K_4[Mo_2Cl_8]$ and $[NH_4][NCS]$; these salts contain anions with virtual D_{4h} symmetry, approximately linear MoNCS units and a Mo—Mo bond of length 2.162(1)—2.177(1) Å. The visible absorption spectrum of the compounds contains an absorption centred at 14 500 cm^{-1}, which has been assigned as the $\delta \rightarrow \delta^*$ promotion of the metal—metal quadruple bond [137]. The reaction of $[Li(thf)]_4[Mo_2(CH_3)_8]$, dissolved in thf, with an excess of PhN(H)NNPh yields $[Mo_2(PhNNNPh)_4]$; X-ray crystallographic studies have confirmed that the molecules comprise four 1,3-diphenyltriazine ligands spanning a Mo—Mo separation of 2.083(2) Å [138]. $[Mo_2(O_2CCH_3)_4]$ reacts with the anion of *N*-(2-pyridylacetamide) to yield $[Mo_2(py\text{-}NC(O)CH_3)_4]$, in which the ligands are coordinated through both nitrogen atoms and span the shortest Mo—Mo approach yet identified of 2.037(3) Å [139]. Similarly, $[Mo_2(O_2CCH_3)_4]$ reacts with the anion of 4,6-dimethyl-2-mercaptopyrimidine (dmmp) to yield $[Mo_2(dmmp)_4]$, which involves Mo—Mo, Mo—N and Mo—S bonds of (average) length 2.083(2), 2.20 and 2.45 Å, respectively [140]. The corresponding 2,4-dimethyl-6-hydroxypyrimidine complex has been prepared by heating $[Mo(CO)_6]$ under reflux with the protonated ligand (dmhpH) in diglyme, as have the corresponding chromium and tungsten compounds; $[Mo_2(dmhp)_4]$ diglyme involves Mo—Mo, Mo—N and Mo—O bonds of (average) length 2.072(1), 2.156(5) and 2.081(4) Å, respectively [141]. $[Mo_2(gly)_4Cl_2]Cl_2 \cdot x\ H_2O$ (x = 2.67 or 3) have been obtained by allowing $K_4[Mo_2Cl_8]$ or $Cs_3[Mo_2Cl_8H]$ to react with glycine; these cations have the expected structure with bridging carboxylate groups, axial chloride ions, and a Mo—Mo separation of 2.108 ± 0.005 Å [142].

In addition to the above homoleptic complexes, a number of others have been reported which explore further the versatility of the coordination geometries possible for a dimetal centre. Full details of the isolation and crystal structure of $[AsPh_4][Mo_2(O_2CCH_3)_2Cl_4] \cdot 2\ S$ (S = MeOH or H_2O) have been published; the vibrational and electronic spectral characteristics of this anion are intermediate between those of $[Mo_2Cl_8]^{4-}$ and $[Mo_2(O_2CCH_3)_4]$, suggesting a continuity of assignment within these three complexes [143], consistent with the new interpretation of the electronic spectrum of $[Mo_2(O_2CCH_3)_4]$ [128]. $[Mo_2(O_2CCH_3)_2Cl_4]^{2-}$ has a *trans* arrangement of the bridging ethanoate groups and the corresponding arrangement has also been confirmed for the 4-methylpyridine(L) complexes, $[Mo_2X_4L_4]$ (X = Cl or Br) [144]. However, $[Mo_2(O_2CCH(NH_3)R)_2(NCS)_4] \cdot n\ H_2O$ (R = H, n = 1; R = $CH(CH_3)CH_2CH_3$, n = 4.5) involve a *cis* arrangement of the bridging carboxylate groups [145]. A comparison of the reactivity of the molybdenum(III) systems, MoX_3, $[Mo_2X_8H]^{3-}$ and $[Mo_2X_9]^{3-}$ (X = Cl or Br) has been made;

the first of these materials reacts with Me_2NH (in vacuo) or PR_3 (R = Et or Pr) (under N_2) to yield the respective $[Mo_2X_4L_4]$ complex [146]. A crystal structure determination of $[Mo_2Br_4(Ph_2PCH_2CH_2AsPh_2)_2]$ has shown that the bidentate ligands bridge the metal—metal bond and are mutually *trans*, with the As and P atoms disordered. The two approximately square $\{Br_2(P/As)_2\}$ ligand donor atom sets are rotated away from a completely eclipsed configuration by about 30°; that is, these sets are within about 15° of being completely staggered. This degree of twist is estimated to reduce the δ overlap by a factor of 0.5 from its maximum value but this appears to have relatively little effect on the metal—metal bond length which, at 2.167(4) Å [147], is strikingly similar to that in $[Mo_2(SO_4)_3]^{3-}$ (vide infra), in which the formal metal—metal bond order is 3.5. $[Mo_2(O_2CCH_3)_2(PMe_3)_2(CH_2Si(CH_3)_3)_2]$ has been shown to have a centrosymmetric structure with a *trans* arrangement of the bridging ethanoate groups and a metal—metal separation of 2.0984(5) Å [148]. The interaction between $MgAr_2$ (Ar = Ph, 2-$MeOC_6H_4$ or 4-FC_6H_4) and $[Mo_2(O_2CCH_3)_4]$ in the presence of PMe_3 has been shown to produce compounds such as $Mo_2(2\text{-}MeOC_6H_4)_4$, $Mo_2(O_2CCH_3)Ph_3(PMe_3)_3$, $Mo_2(O_2CCH_3)(4\text{-}FC_6H_4)_3(PMe_3)_3$ and $Mo_2(2\text{-}MeOC_6H_4)_4(PMe_3)_2$; these are all considered to involve aryl groups σ-bonded onto a quadruply bonded Mo—Mo moiety and possible structures have been presented on the bases of ^1H, ^{31}P and ^{13}C NMR spectral data [149].

Oxidations of compounds containing Mo—Mo quadruple bonds have been described [60, 107,108] and a new material containing the $[Mo_2(SO_4)_3]^{3-}$ ion has been characterised; $K_4[Mo_2(SO_4)_4]Cl \cdot 4\ H_2O$ was isolated from a solution of $K_4[Mo_2Cl_8]$ in 2 M H_2SO_4 and 0.3 M HCl, to which a small quantity of H_2O_2 had been added; the Mo—Mo bond length of 2.167(2) Å is not significantly different from that obtained previously for this ion and is considered to be representative of metal—metal bond order of 3.5 [150].

7.6.4 Molybdenum clusters

XPES data have been recorded for $\{Mo_6X_8\}X_4$ (X = Br or I), $\{Mo_6Br_8\}Br_4L_2$ (L = organic ligand), $[NEt_4]_2[\{Mo_6Br_8\}X_6]$ (X = Cl or Br) and $[NBu_4]_2[Mo_4I_{11}]$ and a distinction achieved between the bridging and terminal halogen environments [151].

A new molybdenum ternary oxide, $NaMo_4O_6$, has been obtained by the reaction of $Na_2[MoO_4]$, MoO_2, and ZnO (1 : 5 : 2) in a sealed molybdenum tube at 1100° C. The material is comprised of $[\{Mo_2Mo_{4/2}O_2O_{8/2}\}^-]_\infty$ cluster chains involving Mo_6 octahedra linked by edge sharing with an average Mo—Mo separation of 2.801 Å. The Na^+ ions are located in the channels between these chains and the dimensions observed for the cations' coordination imply that they are relatively loosely bound, thus suggesting that the material may function as a zeolite [152].

New clusters containing Mo_9, Mo_{12} and $(Mo_3)_\infty$ units have been obtained. These include $K_xMo_6S_8$ ($x \sim 1$), $K_2Mo_{15}S_{19} \equiv K_2\{Mo_6S_8\}\{Mo_9S_{11}\}$, $K_2Mo_9S_{11} \equiv$

$K_4\{Mo_6S_8\}\{Mo_{12}S_{14}\}$, and $K_2Mo_6S_6$, and X-ray diffraction data have been reported for these systems [153]. A new ternary molybdenum chalcogenide, $In_xMo_{15}Se_{19}$ (x = 2.9—3.4) has been discovered and shown to contain $\{Mo_6Se_8\}$ and $\{Mo_9Se_{11}\}$ clusters; limited substitution of sulphur or tellurium for the selenium of this system is possible [154]. MoI_3 and MoI_2 have been shown to react with elemental sulphur or selenium to produce the corresponding $Mo_3I_4X_7$ (X = S or Se) compound [155].

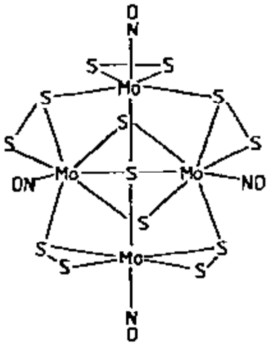
7.6.5 Heteronuclear molybdenum—metal bonds

Mo—Mg bonds of length 2.732 Å have been identified in $[\{MgBr(thf)_2\}\{(cp)_2MoH\}]$ [156]. Mo—Pt bonds have been characterised in $[Pt_2Mo_2(cp)_2(CO)_6(PR_3)_2]$ (R = Et or Ph) [157] and in *trans*-$[\{Pt(RNC)(RNHCOC_2H_5)\}\{Mo(CO)_3(cp)\}_2]$ (R = cych) [158]. The former of the Pt—Mo compounds have been prepared from *cis*-$[PtCl_2L_2]$ and $Na[Mo(CO)_3(cp)]$ and contains a planar, centrosymmetric rhombus of metal atoms, with asymmetrically bridging carbonyl groups spanning all four of the Pt—Mo distances, which are 2.81 Å in length; the latter compound has been obtained from *cis*-$[Cl_2Pt(CNR)(RNHCOC_2H_5)]$ and contains a Pt—Mo bond of length 2.889 Å and with a stretching frequency of 156 cm^{-1}.

7.7 MOLYBDENUM—SULPHUR COMPLEXES

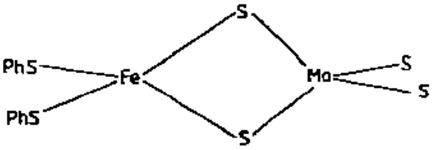
Molybdenum complexes with a terminal sulphide group are of some particular interest since EPR data for active xanthine oxidase, as compared to those for desulpho xanthine oxidase, are considered to be consistent with the presence of an Mo=S group for the former and an Mo=O group for the latter form of this enzyme [159]. This interpretation has received partial support following an EXAFS study of desulpho and a mixture of active and desulpho xanthine oxidase [160]. The conversion of the active to the desulpho form of xanthine oxidase may be achieved by treatment with CN^-, which yields CNS^-, and the corresponding reaction has been claimed for $[Mo_2S_4(S_2CNEt_2)_2]$ [100] and $[Mo_2OS_3(S_2CNR_2)_2]$ (R = Me or Et) [79]. Since monomeric molybdenum(V) complexes containing terminal sulphide groups are relatively rare, the report that the complexes $[MoSCl_{4-n}(SR)_n(py)]^-$ (n = 0—3, inclusive) and $[MoS(SR)_5]^{2-}$ (R = Et or Am) are readily obtained from the $MoCl_5$/RSH/py system [72] deserves further investigation.

Persulphide has also been suggested for the ligand of xanthine oxidase which loses sulphur on treatment with cyanide. Molybdenum—persulphide complexes are now well characterised and preparative routes for the formation of such complexes, possible modes of metal—ligand bonding, and salient structural features have been briefly reviewed [161]. Interesting new complexes containing Mo—(S_2) units include $[NH_4]_2[Mo_2(S_2)_6]\cdot 2H_2O$ (8) and $[NH_4]_2[Mo_3S(S_2)_6]$ (13) [77]. These compounds have been prepared by the reduction of $[MoO_4]^{2-}$ in aqueous solution with $[NH_4]_2S_x$; the latter material precipitates at 90° C and the former material can be obtained from the filtrate at room temperature [77,162]. $[NH_4]_6[Mo_7O_{24}] \cdot 4\ H_2O$ and $[NH_4][SCN]$ in aqueous solution react with $[NH_3OH]Cl$ to give a yellow suspension which, when heated for 1 h at 80° C and after the addition of $[NH_4]_2S_x$ solution, initially yields a dark precipitate and then, on cooling, orange-red crystals of $[NH_4]_4[Mo_4(NO)_4S_{13}] \cdot 2\ H_2O$. This anion (21) contains two equilateral triangular Mo_3 moieties joined by a common edge, with two triply bonded sulphur atoms normal to each triangle and, on the other side of the skeleton, another sulphur atom bonded to each of the metal atoms. one $[S_2]^{2-}$ unit functions as a bidentate ligand whilst the other four form asymmetrical bridges between two metal atoms. All of the metal atoms have a pentagonal bipyramidal coordination geometry [162,163]. The addition of aqueous H_2S to a warm, saturated solution of $[NH_4]_2[MoO_2S_2]$, followed by cooling to room temperature and addition of $[NMe_4]Cl$, leads to the formation of $[NMe_4][Mo_2O_2S_2(S_2)_2]$ (7) [76]. Other complexes containing Mo—(S_2) arrangements reported this year include $[MoOS_2(S_2CNR_2)_2]$ (R= Me, Et, or Pr) [6], $[(cp)_2MoS_2]$ [103] and $[(Bu\text{-}cp)_2Mo_2Cl_4(S_2)] \cdot 0.5\ CH_2Cl_2$ [104]. Typically, Mo—S and S—S bond lengths in persulphide complexes are ca. 2.38—2.45 Å and 2.03—2.09 Å, respectively, and the ν(S—S) stretching frequency occurs at ca. 530 cm^{-1} [161,162]. Molybdenum complexes containing $(S_n)^{2-}$ ($n > 2$) groups are less well-known; the structure of $[(cp)_2MoS_4]$ has been reported earlier and a preparative route to this complex has been described [103].



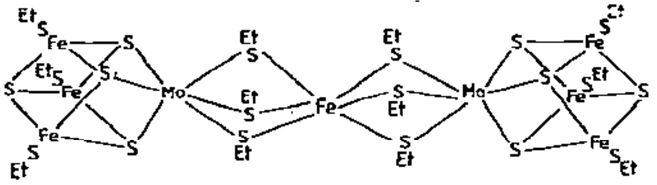
(21)

New molybdenum—sulphur, selenium or tellurium binary or ternary phases, which contain clusters of the metal atoms, have been prepared [153—155], see Section 7.6.4. Significant developments in molybdenum—iron—sulphur



(22)

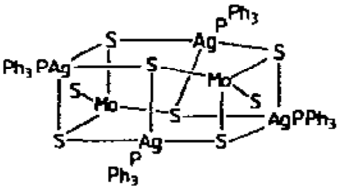
chemistry have followed the identification of a Mo—Fe—S cluster as an integral component of the molybdenum cofactor for the nitrogenase enzymes. Perhaps the simplest possible assembly of these atoms has been obtained in the anion of $[NEt_4]_2[(PhS)_2FeS_2MoS_2]$ (22). This complex has been obtained by reacting $[MoS_4]^{2-}$ with $[Fe(SPh)_4]^{2-}$ (1 : 1) in dmf; it contains an essentially planar central $\{Fe(\mu_2\text{-}S)_2Mo\}$ rhombus, the terminal and bridging Mo—S bond lengths are 2.15 and 2.25 Å, respectively, and the Mo—Fe separation is 2.750(4) Å [164]. A similar chelation of iron by $[MoS_4]^{2-}$ has been claimed for a product of the reaction between $[NMe_4]_2[MoS_4]$ and $[NMe_4]_2[Fe_4(\mu_3\text{-}S)_4(SCMe_3)_4]$ in MeCN/*N*-methylmethamide solution containing 2,4,6-trimethylpyridinium chloride. A black microcrystalline material was obtained, the analytical data for which were consistent with the formulation $[NMe_4]_6[Fe_4(\mu_3\text{-}S)_4(S_2MoS_2)_4]$ [165]. $\{Fe_3MoS_4\}$ cubane-like clusters readily self-assemble in reactions between $FeCl_3$, $[MoS_4]^{2-}$, and an excess of a thiolate anion in methanol solution. Several complexes are formed under these conditions and, by varying the reaction time and/or the nature of the cations introduced with $[MoS_4]^{2-}$, and with careful work-up, three different types of system have been crystallised. Each of these contain two $\{(RSFe)_3(\mu_3\text{-}S)_4Mo\}$ cubane-like clusters and the difference between them arises with respect to the nature of the bridging groups linking the two molybdenum atoms; $[NEt_4]_3[Fe_6Mo_2S_8(SEt)_9]$ [166] and $[Et_3NCH_2Ph]_3[Fe_6Mo_2S_8(SEt)_9]$ [167] contain a set of three (μ_2-SEt) groups, $[NEt_4]_3[Fe_6Mo_2S_9(SEt)_8]$ [167] contains one (μ_2-S) and two (μ_2-SEt) groups, and $[Me_3NCH_2Ph]_3[Fe_7Mo_2S_8(SEt)_{12}]$ [168] involves a $(\mu_2\text{-}SEt)_3Fe(\mu_2\text{-}SEt)_3$ bridging arrangement (23). The internal dimensions of the $\{Fe_3MoS_4\}$ clusters remain essentially invariant from compound to compound and, with Mo—Fe distances of length 2.72 ± 0.01 and Mo—S bonds of length 2.35 ± 0.01 Å, closely resemble the environment suggested for molybdenum in nitrogenase on the basis of the EXAFS measurements. Mössbauer studies indicate that all the iron atoms of the clusters are essentially equivalent, with an average oxidation state of 2.50 ± 0.17 and thus the molybdenum has an oxidation state of between III and IV. The complexes undergo two reversible one-electron reductions, at potentials separated by only 200 mV and thus they have a possible functionality as two-electron storage and transfer mediators. The central iron atom of (23) has a Mössbauer isomer shift typical of Fe(III) and electrochemical studies have suggested that the first reduction of this complex is localised on this atom; exploration of



(23)

the reaction system $FeCl_3/[NBu_4]_2[MoS_4]/PhCH_2SH$ in MeOH has resulted in the isolation of $[NBu_4]_4[Fe_7Mo_2S_8(SCH_2Ph)_{12}]$, the Mössbauer spectrum of which indicates that the only significant change from (23) is the presence of an Fe(II) atom. The Mo—Mo separation in $[Fe_6Mo_2S_8(SEt)_9]^{3-}$ of 3.67 Å is long for a bridge spanned by three μ_2-SR groups (cf. the value of 2.983(1) Å in $[(OC)_3Mo(\mu_2\text{-}SR)_3Mo(\eta^7\text{-}C_7H_7)]$ for R= CMe_3 or Bu, respectively [169]); this separation shortens to 3.31 Å when one of the μ_2-SEt groups is replaced by a μ_2-S group. These long bridging distances might be indicative of some strain or steric hindrance; however, it has not yet proved possible to isolate a system containing a single $\{Fe_3MoS_4\}$ moiety. This is all the more surprising given the ready thiolate exchange demonstrated for bridging (and terminal) thiolate groups of $[Fe_6Mo_2S_8(SEt)_9]^{3-}$ which, on treatment with an excess of $HOCH_2CH_2SH$, yields $[Fe_6Mo_2S_8(SCH_2CH_2OH)_9]^{3-}$. The latter complex is water-soluble and should be of value for the mediation of electron transfer processes in aqueous media [170].

$[\{Mo_2S_8Ag_4\}(PPh_3)_4]$ (24) has been prepared by extracting an aqueous solution of $[NH_4]_2[MoS_4]$ with a solution of PPh_3 and $Ag[NO_3]$ in CH_2Cl_2. $[MoS_4]^{2-}$ acts as a terdentate ligand and, as expected, the terminal Mo—S bonds (2.11 Å) are significantly shorter than those involving the chelate arrangement (2.23 Å) [171].



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7.8 MOLYBDENUM—NITROGEN COMPLEXES

7.8.1 Nitrosyls and thionitrosyls

Molybdenum(VI) oxoanions are known to react with NH_2OH in alkaline or acidic solution to give yellow products and the first characterisation of a product of such a reaction has now been achieved, following the addition of bipy to these solutions. $[Mo(bipy)(H_2NO)_2(NO)]Cl$ was the complex obtained, and an X-ray crystallographic study has shown that it involves a pentagonal bipyramidal coordination about the molybdenum, comprising one bipy and two hydroxylamido-*O,N* ligands, all of which are bidentate, and a nitrosyl ligand, the Mo—N—O arrangement for which is approximately linear [172]. The corresponding reaction in the presence of terpy leads to the formation of $[Mo(terpy)(H_2NO)(H_2O)(NO)]^{2+}$ which, on the basis of its diamagnetic nature, and IR spectrum, and the structure of the bipy complex, has been assigned a pentagonal bipyramidal structure; the water molecule of this complex may be replaced by cyanide [173]. Ammonium paramolybdate reacts with an excess of $[NH_3OH]X$ (X= Cl or Br) in glacial CH_3CO_2H/aqueous py to yield $[MoO_2(NO)_2(py)_2X_2]$; ligand exchange reactions have been demonstrated and the complexes $[MoO_2(NO)_2(bipy)X_2]$ and $[MoO_2(NO)_2(bipy)_2]^{2+}$ have also been reported [174]. Similar reactions in the presence of $Na[S_2CNEt_2]$/dmf or Hacac/dmf have yielded $[Mo(NO)_2(S_2CNEt_2)_2]$ or $[Mo(NO)_2(acac)_2]$, respectively [175]. $[Mo(NO)_2Cl_2(H_2O)_2]$ has been obtained by reacting MoO_3, in aqueous acidic solution with $Na_2[CO_3]$, followed by reduction with tin and treatment with NO. $Cs_2[Mo(NO)_2Cl_4]$, and the corresponding $[LLH_2]^{2+}$ (LL = bipy or phen) salts, have been prepared by addition of CsCl or LL to $[Mo(NO)_2Cl_2(H_2O)_2]$ in concentrated HCl; these $[LLH_2][Mo(NO)_2Cl_4]$ salts are converted at 140° C, under an atmosphere of CO_2, to the corresponding $[Mo(LL)(NO)_2Cl_2]$ complex. $[Mo(NO)_2Cl_2(H_2O)_2]$ reacts with $Tl_2[CO_3]$ to form $Tl_2[Mo_2(NO)_2(OH)_4]$ [176].

Nitrosyl complexes of molybdenum bonded to dithiocarbamate groups have been prepared and characterised by ^1H NMR and IR spectroscopy. These include $[Mo(NCO)X(S_2CNEt_2)_2(NO)]^-$ (X = Cl, $[N_3]$ or [NCS]), $[Mo(NCO)(S_2CNEt_2)(NO)]_2 \cdot N_2H_4$ and $[Mo(NCO)L(S_2CNEt_2)(NO)]$ (L= dmso, NH_3 or py); the assignment of the nitrosyl IR bands in *cis*-$[Mo(S_2CNEt_2)_2(NO)_2]$ and $[Mo(NCO)(dmso)(S_2CNEt_2)(NO)]$ has been achieved with the assistance of ^{15}N labelled NO [177]. $[NO][PF_6]$ reacts with $[Mo(diars)(CO)_4]$ to form *mer*-$[Mo(diars)(CO)_3(NO)][PF_6]$; this compound reacts in refluxing propanone to form $[Mo(diars)(CO)_2(NO)(O_2PF_2)]$, with halide (X= Cl, Br or I) ions to yield $[Mo(diars)(CO)_2X(NO)]$, and with $[Me_2NCS_2]^-$ ions to form $[Mo(diars)(CO)(NO)(S_2CNMe_2)]$ [178]. X-ray crystal structures have been reported for *trans*-$[\{(cp)Mo(NO)(SEt)\}_2]$ and *cis*-$[\{(cp)Mo(NO)(SCHMe_2)\}_2]$; in each case the molecule contains a planar Mo_2S_2 central portion with terminal NO and cp ligands [179]. The preparations of $[(cp)Mo(NO)_2R]$ (R= Et or Ph) have been documented [180].

$[Mo(NO)_2(TTP)] \cdot C_6H_6$ (TTP = meso-tetra-*p*-tolylporphyrin) has been isolated following the Zn/Hg reduction of $[MoCl_2(TTP)]$ under an atmosphere of NO. Elution of this compound from an Al_2O_3 chromatography column with CH_2Cl_2 containing traces of MeOH, led to the formation of $[Mo(NO)(MeOH)(TTP)] \cdot C_6H_6$; the latter compound is red and paramagnetic (1.71 μ_B, $g = 1.968$) and is converted to the former, green, diamagnetic compound by treatment with NO. Both of these compounds have been characterised by X-ray crystallography; the former has a *cis* arrangement of NO groups, with $N-\widehat{Mo}-N = 78.4(5)°$, and with the Mo atom situated 0.99 Å above the plane of the porphyrin ring, whereas the latter has a *trans* arrangement of the NO and MeOH groups and the Mo is only 0.28 Å out of the plane of the porphyrin ring [181]. Complexes of the type $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)XY]$ (X = I or OR, R = alkyl; Y = NNR′, R′ = OH, alkyl, NH_2, NMe_2, NMePh, NHPh, CH_2CH_2OH or Me_2CN) have been prepared and extensively characterised [182]. NO reacts with $[Mo_2X_4L_4]$ (X = Cl or Br; L = $PEtPh_2$, PEt_3 or PBu_3) or $[Mo_2X_4(LL)_2]$ (X= Cl or NCS; LL= dppe or dppm) in CH_2Cl_2, cleaving the metal—metal bond, to give the corresponding $[Mo(NO)_2X_2L_2]$ or $[Mo(NO)_2X_2(LL)]$ complex [183]. Details of the preparation and structure of $[NH_4]_4[Mo_4(NO)_4S_{13}] \cdot 2\,H_2O$ [163] have been given in Section 7.7.

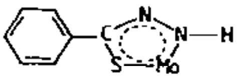
A full account has been published of the reactions of $[MoN(S_2CNR_2)_3]$ with elemental sulphur or propylene sulphide to give the corresponding $[Mo(NS)(S_2CNR_2)_3]$ compound in high yield. These compounds are yellow and diamagnetic [184]; $[Mo(NS)(S_2CNEt_2)_3]$ involves a pentagonal bipyramidal geometry about the molybdenum with the thionitrosyl group in an axial position, with an $Mo—\hat{N}—S$ interbond angle of 172.0(7)° [185].

7.8.2 *Dinitrogen, diazenide, imide and related complexes*

Preparations of the $[Mo(N_2)_2L_4]$ ($L = PMePh_2$ or L_2 = dppe) complexes have been reported [186]; N 1*s*, P $2p_{3/2}$ and Mo $3d_{5/2}$ XPES spectra have been obtained for these complexes and the two N 1s signals found to have a separation of 1.3—1.4 eV [187]. The ^{15}N NMR spectra of *trans*-$[Mo(^{15}N_2)_2(dppe)_2]$ and *cis*-$[Mo(^{15}N_2)_2(PMe_2Ph)_4]$ have been reported and the assignment of the resonances discussed in the light of $J(^{15}N^{31}P)$ values [188].

Gaseous HCl, when bubbled through a suspension of *cis*-$[M(N_2)_2(PMePh_2)_4]$ or *trans*-$[M(N_2)(PPh_2Me)_4]$ (M = Mo or W) gives, in contrast to similar reactions with H_2SO_4 in MeOH, moderate quantities of hydrazine in preference to ammonia. A preliminary crystallographic characterisation of an intermediate of this reaction has established a linear M—N—N skeleton favouring the $—\overset{+}{N}H_3$, as opposed to the $—NH—NH_2$, arrangement [189]. The hydrazide complexes $[MF(NNH_2)(dppe)_2][BF_4]$ (M = Mo or W) undergo a condensation reaction with aldehydes and ketones to form the corresponding $[MF(NN{=}CRR')(dppe)_2][BF_4]$ (R, R' = H or alkyl; or $RR' = (CH_2)_5$) compound in good yield [190]. *Trans*-$[Mo(N_2)_2(dppe)_2]$ reacts with ethyl haloethanoates to give the corresponding $[MoX(N_2CH_2CO_2Et)(dppe)_2]$ (X = Cl, Br or I) complex which, on treatment with $H[BF_4]$, undergoes protonation at the *C*-bound nitrogen to form the $[MoX\{N_2H(CH_2CO_2Et)\}(dppe)_2][BF_4]$ salt [191]. The reaction of $[MoO_2(S_2CNR_2)_2]$ with a hydrazine, $QNHNH_2$ (Q = alkyl, aryl or alkoxycarbonyl) (1 : 2), in the presence of one equivalent of $Na[S_2CNR_2]$, forms the corresponding $[Mo_2(N_2Q)(S_2CNR_2)_3]$ complex in 70—80% yield; when the $Na[S_2CNR_2]$ is omitted and five equivalents of the hydrazine hydrochloride are used, the corresponding $[Mo(N_2Q)_2(S_2CNR_2)_2]$ complex is obtained, probably via an intermediate $[Mo(N_2H_2Q)(N_2Q)(S_2CNR_2)_2]$ complex. The $[Mo(N_2Q)(S_2CNR_2)_3]$ complexes can be protonated, alkylated or arylated at the diazenido-nitrogen remote from the metal [192]. Condensations of $[MoO_2(LL)_2]$ complexes with $ArNHNH_2$ have been shown to lead to the formation of the corresponding $[Mo(N_2Ar)(LL)_2]$ (LL = oxinate), $[Mo(NNHAr)(LL)_2]$ (LL = thiooxinate) or $[Mo_2(NNAr)_3(LL)_4]$ ($LL = R_2NCS_2$) complexes; these molybdenum(VI) starting materials are effective in dehydrogenating hydrazobenzene to form azobenzene, and the complexes formed would appear to be relevant to this function [193].

The crystal structure of [$Mo(NNPh_2)(S_2CNMe_2)_2$] has been determined; the molybdenum has a distorted octahedral environment with a *cis* arrangement of the hydrazide ligands; the dimensions obtained, *r*(Mo—N) = 1.790(8), *r*(N—N) = 1.31(1) Å and Mo—$\widehat{N}$—N = 169.9(8)°, are consistent with a π-system extending over the Mo—N—N arrangement [194]. [$Mo(N_2C_6H_4X)(S_2CNMe_2)_3$] (X = a range of 2-, 3- and 4-substituents) complexes display a reversible one-electron oxidation at a potential which is dependent upon the nature of X. The EPR spectra of the stable cationic molybdenum(V) species generated in this manner indicate that the HOMO has mainly metal character for X = H ($\bar{g}$ = 2.009 and $\bar{A}$ = 2.8 mT). Electron withdrawing substituents (X) stabilise this orbital, i.e. $E_{1/2}{}^{ox}$ becomes more positive, and the potential shows a linear correlation with the Hammett σ-parameter of X. There is no evidence for reduction of these complexes before −2.4 V (vs. S.C.E.), and therefore the LUMO is at least ca. 290 kJ higher in energy than the HOMO. These complexes display a charge-transfer absorption at ca. 415 nm which shows little variation with X. Therefore, it appears that the electronic effects of X are transmitted to affect both HOMO and LUMO equally [195]. The aroylhydrazines, $RCONHNH_2$ (R = Ph, 4-ClC_6H_4, 2- or 4-$NO_2C_6H_4$, or 1-$C_{10}H_7$), react with [$MoOCl_2(PR'_3)_3$] (PR'_3 = PMe_2Ph, PEt_2Ph, PPr_2Ph, $PMePh_2$ or PEt_3) to give the corresponding red [$MoCl(N_2COR)(NHNCOR)(PR'_3)_2$] compound. The structure of [$MoCl(N_2COPh)(NHNCOPh)(PMe_2Ph)_2$] has been determined and each molecule observed to contain a unidentate diazenide ligand, *r*(Mo—N) = 1.78(1) Å, and a chelating benzoyldiazene ligand, *r*(Mo—N) = 1.945, *r*(Mo—O) = 2.131 Å [196]. [$MoO_2(acac)_2$] or $Na_2[MoO_4]$ react with thioaroylhydrazines, RNHNHCSR' (R = H, R' = Ph, 4-MeC_6H_4 or 4-$MeOC_6H_4$; R = Ph, R' = $PhCH_2$, 1-$C_{10}H_7$, 4-MeC_6H_4 or 4-$MeOC_6H_4$) to form dark green or black [$Mo(RN_2CSR')_3$] complexes. The structure of [$Mo(HN_2SCPh)_3$] · dmf has been determined and shown to involve the bidentate coordination (25), with the molybdenum coordinated by a distorted trigonal prismatic {S_3N_3} arrangement [197]. The complexes (26) have been reported and their ^1H



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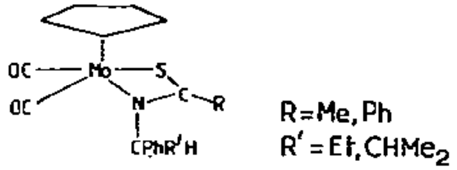

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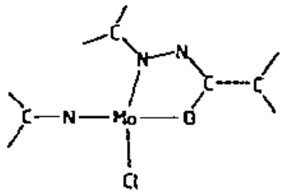
NMR properties discussed in terms of the electronic environment of the metal atom [198]. The first examples of molybdenum coordinated to hydroxylamine derivatives have been reported [172,173] (see Section 7.8.1). $[MoO_4]^{2-}$ reacts with MeNHOH at pH 6 to form [$MoO_2(MeNHO)_2$]; the coordination sphere of this molybdenum comprises a *cis*-dioxide grouping, *r*(Mo—O) = 1.700(8) and 1.728(8) Å, and two *N,O*-bonded *N*-methyloximate groups, *r*(Mo—O) = 1.961(9) and 1.964(9) Å; *r*(Mo—N) = 2.130(10) and 2.119(11) Å [172].

The complexes $[\mathrm{MoOCl_2(PR''_3)_3}]$ ($\mathrm{PR''_3}$ = $\mathrm{PMe_2Ph}$ or $\mathrm{PEt_2Ph}$) react with the substituted hydrazines, RCONHNHR′ (R′ = Ph, 4-$\mathrm{ClC_6H_4}$, 4-$\mathrm{MeOC_6H_4}$, Et, Pr, $\mathrm{CHMe_2}$ or $\mathrm{PhCH_2}$; R′ = Ph, 4-$\mathrm{ClC_6H_4}$, 4-$\mathrm{MeOC_6H_4}$, 1-$\mathrm{C_{10}H_7}$ or Me), to give the corresponding $[\mathrm{MoCl_2(NR')(R'N_2COR)(PR''_3)}]$ complex. The crystal structure of $[\mathrm{MoCl_2(NC_6H_4Me\text{-}4)(4\text{-}MeC_6H_4N_2COPh)(PMe_2Ph)}]$ has been determined; this molecule contains the arrangement (27), with a planar metal—diazene chelate system and an essentially linear M—N—C skeleton for the metal—imine group; the Mo—N distances are 1.984(8) Å for the former and 1.726(9) Å for the latter and both are considered to involve multiple metal—ligand bonding interactions [199]. The first bisimide complex of molybdenum $[\mathrm{Mo(NPh)_2(S_2CNEt_2)_2}]$ has been prepared by allowing an excess of phenyl azide to react with $[\mathrm{Mo(CO)_2(S_2CNEt_2)_2}]$ in dry $\mathrm{CH_2Cl_2}$. This complex completes the series $[\mathrm{MoO_{2-\mathit{n}}(NR)_{\mathit{n}}(S_2CNR_2)_2}]$ (n = 0—2). $[\mathrm{Mo(NPh)_2(S_2CNEt_2)_2}]$ is monomeric with a distorted octahedral geometry; one imide group is bent at the nitrogen atom, with Mo—$\hat{\mathrm{N}}$—C = 139.4(4)° and r(Mo—N) = 1.789(4) Å, and the other is nearly linear, with Mo—$\hat{\mathrm{N}}$—C = 169.4(4)° and r(Mo—N) = 1.754(4) Å. The associated structural data indicate that a linear ligand exerts little *trans* influence, whereas the bent one has a significant *trans* influence [200]. Reaction of an arylazide with $[\mathrm{MoO(S_2CNEt_2)_2}]$ yields $[\mathrm{MoO(NR)(S_2CNEt_2)_2}]$ which reacts with HCl or MeBr to form $[\mathrm{Mo(NR)X_2(S_2CNEt_2)_2}]$ (X = Cl or Br, respectively); other reactions of these complexes have been described and a plausible mechanism for the protonation of complexes containing the $\mathrm{MoO_2}$, MoO(NR) and $\mathrm{Mo(NR)_2}$ fragments has been presented [201].



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7.9 MOLYBDOENZYMES AND CHEMICAL ANALOGUES

Knowledge concerning the structure and nature of the molybdoenzymes is presently undergoing rapid development and the following appear to be representative of the studies reported recently.

Several reviews concerning the genetic requirements, structure and function of the nitrogenases have appeared [202—204]. The nature of the Mo—Fe—S and Fe—S centres of the molybdoferredoxin of nitrogenase has been investigated by several spectroscopic techniques. CD and MCD spectra have been reported for both of the proteins of nitrogenase and the properties observed for the molybdoferredoxin could not be explained solely in terms of contributions from known $\{\mathrm{Fe_4S_4}\}$ or $\{\mathrm{Fe_2S_2}\}$ clusters [205]. Oxidation of the molybdoferredoxin of nitrogenase can be achieved with thionin, and EPR spectroscopy indicates that this proceeds in two distinct phases; in the first phase four electrons are removed without loss of the signal characteristic of the $S = 3/2$ (M, or Mo—Fe—S, cluster), in the second phase, the removal of two electrons occurs and the $S = 3/2$ signal disappears. Analyses of the Mössbauer data obtained for this protein indicate that it contains 30 iron atoms; 12 belong to two apparently identical M-type clusters which have three distinct oxidation levels — M^{OX}, obtained upon thionin or O_2 oxidation, M^N, the $S =$ 3/2 level, and M^R, obtained under dinitrogen fixing conditions. The other 16 iron atoms are associated with four iron (P-type) clusters, which may be $\{Fe_4S_4\}$ clusters but, if so, have atypical spectral properties [206]. The Mössbauer spectrum of the molybdoferredoxin from the nitrogenase of *Azotobacter vinelandii* has been recorded in magnetic fields of ≤50 Gauss. The spectra from the M-type centres in the $S = 3/2$ state were resolved into 6 subcomponents, suggesting that the Mo—Fe—S cofactor probably contains 6 iron atoms in a spin-coupled cluster [207]. A Fourier-transform ^{19}F NMR method has been used to identify the Fe—S cores extended from this protein; the results obtained indicate that at least two $\{Fe_4S_4\}$ clusters are obtained from both the reduced and the thionin-oxidized form of the protein, plus one $\{Fe_2S_2\}$ cluster from the oxidized protein. However, the removal of these Fe—S cores was considered to be incomplete. The Mo—Fe—S cofactor was not extracted under the extrusion conditions, which involved treatment of the protein in hmpa/H_2O (4 : 1) with 4-$CF_3C_6H_4SH$ [208]. Acid/base treatment of the molybdoferredoxin of the nitrogenase from *Clostridium pasteurianum* results in the formation of several low molecular weight compounds containing molybdenum. These have been separated by gel chromatography and their analytical and electronic spectral properties are comparable to those of thiomolybdate anions. Therefore, it has been proposed that the Mo—Fe—S cofactor contains a sulphide complex of molybdenum coupled to an Fe—S cluster [209]. The synthetic attempts to prepare such species are summarized in Section 7.8 and it is clear that, although much interesting chemistry has been developed in these studies, no realistic model of the Mo—Fe—S cofactor of nitrogenase has yet been reported.

Sulphite oxidase is the simplest of the molybdoenzymes. The native enzyme, from rat liver, has a molecular weight of ca. 120 000 and is a dimer composed of two subunits, each of which contains one molybdenum and one haem centre; these are segregated in independently-folded domains of the subunit which are linked by a flexible portion of the protein (the "hinge" region). This subunit can be cleaved into molybdenum and haem domains by proteolysis with trypsin, chymotrypsin, or papain; these cleave the hinge region at different points and the molecular weights of the fragments obtained imply that this region contains ca. 30 amino acid residues. The molybdenum domain associates to a dimeric unit of molecular weight ca. 100 000, whereas the haem domain can be isolated as a monomer of molecular weight ca. 10 000. CD spectroscopic studies indicate that no basic structural change of the protein occurs upon cleavage [210]. The cleavage is easier to accomplish for the oxidised form of the enzyme than for the reduced form [211].

The redox potentials for the molybdenum centre of the nitrate reductase from *Escherichia coli* K12 at pH 7.14 have been determined by an EPR method as +180 and +220 mV, for the Mo^{IV}/Mo^{V} and Mo^{V}/Mo^{VI} couples, respectively [212]. The similarity in these values is consistent with the requirement that this centre transfers two electrons to the nitrate ion. The properties of the nitrate reductases have been reviewed and a scheme for their function has been proposed [213].

A new substrate for xanthine oxidase has been observed. Milk xanthine oxidase slowly catalyses the conversion of ethylene glycol to glycolic and oxalic acids, whereas the desulpho form of the enzyme produces only glycolic acid [214]. Chicken liver xanthine dehydrogenase is a dimer of molecular weight ca. 150 000, each subunit of which contains 1 molybdenum, 1 FAD and two distinct $\{Fe_2S_2\}$ clusters (cf. extrusion experiments for milk xanthine oxidase [208]). Proteolytic cleavage of these sub-units has been achieved at three distinct sites and a catalytically active fragment of molecular weight ca. 65 000, devoid of FAD but containing molybdenum and both $\{Fe_2S_2\}$ centres, has been isolated [215]. The EPR characteristics of xanthine oxidase have been reviewed [159] and significant new developments in the characterisation of the structure and function of this enzyme have been achieved using this technique. In the reduced, functional form of milk xanthine oxidase, the molybdenum(V) centre interacts with two enzyme-bound protons which are exchangeable with the solvent protons; these protons are coupled to the metal with average hyperfine coupling constants of 1.4 and 0.3 mT. The enzyme also contains an anion binding site immediately adjacent to the molybdenum, as seen by the effect of $[NO_3]^-$ on the molybdenum(V) EPR signals. It is suggested that, in the Michaelis complex, the substrate molecule probably occupies this site and is bound to the molybdenum via the N-9 atom. During the turnover of the enzyme, the hydrogen atom from the C-8 atom and two electrons are transferred to the molybdenum; concomitantly, it is proposed that the carbonium ion of the xanthine residue reacts with a nucleophile, and that the subsequent hydrolysis of this product releases uric acid [216,217]. EPR evidence has also been obtained for the coordination of an oxygen atom to molybdenum in functional xanthine oxidase; ^{17}O incorporation can be achieved by dissolving the enzyme in water and the molybdenum(V) signal manifests moderately strong hyperfine coupling of ca. 1.6 mT with this atom. The possibility that this oxygen is present as an Mo—O—H group, the proton of which produces the hyperfine splitting of 1.4 mT, has been considered [218]. However, similar molybdenum(V)—oxygen and/or —hydrogen coupling constants have not yet been observed in chemical systems. Comparisons of the EPR characteristics of the non-functional, desulpho form of xanthine oxidase with those of the active enzyme indicate many similarities. Differences, including redox potential, pK variations, and functionality, have been interpreted on the basis of the proposition that the significant difference between them is that, in their oxidised state, the active and the desulpho forms possess an Mo=S and an Mo=O group, respectively [219].

This latter conclusion has received partial support from the EXAFS spectra, associated with the K-absorption edge of molybdenum, obtained for desulpho and a mixture of desulpho and active oxidised xanthine oxidase. These data indicate that the immediate environment of the molybdenum is different in the two forms of the enzyme and the difference is consistent with an Mo=O group $\{r(\text{Mo—O}) \simeq 1.7$ Å$\}$ in the desulpho form being replaced by an Mo—S group $\{r(\text{Mo—S}) \leqslant 2.3$ Å$\}$ in the active form [160]. The other atoms bound to molybdenum in both forms of the enzyme appear to be predominantly sulphur at a distance of $\geqslant$2.4 Å. Another EXAFS study of a mixture of the desulpho and active forms of xanthine oxidase concluded that, on average, the molybdenum is coordinated to ca. two Mo=O groups $\{r(\text{Mo—O}) = 1.71$ Å$\}$, ca. two sulphur atoms at 2.54 Å and ca. one at 2.84 Å [220]. An EXAFS study of oxidised and reduced forms of sulphite oxidase has been reported. The data obtained for the oxidised enzyme were interpreted in terms of a molybdenum environment similar to that in desulpho xanthine oxidase (vide ultra) with ca. two Mo=O bonds of length 1.71 Å, plus ca. two sulphur atoms at 2.42 Å and ca. one sulphur atom at ca. 2.84 Å. Reduction, to what is generally assumed to be the molybdenum(IV) level, resulted in the loss of one oxide ligand from, and the incorporation of an additional sulphur atom and possibly a nitrogen atom to the coordination sphere of the molybdenum; distances (and occupation numbers) obtained were $r(\text{Mo—O}) = 1.69$ (1.0), $r(\text{Mo—S}) = 2.38$ (3.3), $r(\text{Mo—S}') = 2.85$ (0.9) and $r(\text{Mo—N}) = 2.06$ Å (1.6) [221]. Although these EXAFS studies represent a considerable improvement in the understanding of the nature of the molybdenum centres in sulphite and xanthine oxidase, further work is necessary before the conclusions can be regarded as definitive; in this connection, a suggested reinterpretation [222] of the EXAFS data, reported earlier for the molybdenum centre in nitrogenase, may have some relevance.

Developments in the chemistry of molybdenum systems, which in some way mimic the reactions catalyzed by the various molybdoenzymes, have been reported. Stoicheiometric combinations of the reduced peptide chains A and B of bovine insulin with $[\text{MoO}_4]^{2-}$ have been shown to reduce C_2H_2 at virtually the same rate, but with a lower selectivity, as the iron—molybdenum cofactor of nitrogenase, with $\text{Na}[\text{BH}_4]$ as reductant. It is suggested that the formation of catalytically active complexes occurs through the interaction of molybdenum with the six cysteinyl and two histidinyl residues of the reduced insulin peptides [223]. Similar observations have been made for the reduction of N_2 by these systems; the latter reduction is stimulated by ATP and significantly inhibited by CO. A conclusion drawn from these and related studies is that the substrate reductions of nitrogenase are typical of reactions which occur at mononuclear molybdenum centres and non-haem Fe—S or Mo—S—Fe clusters are not required for the simulation of nitrogenase reactions in artificial systems [224].

The reactions of monomeric molybdenum(V) complexes with nitrate [71] have been described earlier (Section 7.2.2). Oxygenation of aldehydes, tertiary phosphines, or tertiary phosphites have been reported to be catalyzed by [MoO_2(ethyl-L-cysteine)$_2$]; the aldehyde oxidation was considered to be radical in character but those for the phosphines or phosphites involved oxygen transfer [225]. Benzaldehyde has been characterised as a *C,O*-bonded bidentate ligand in the complex [{$C_6H_5C(C_5NH_4)NH(Me)$}(cp)COMo-($OCHC_6H_5$)] [226].

7.10 ACKNOWLEDGEMENTS

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