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MOLYBDENUM

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CONTENTS

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INTRODUCTION

This review contains the literature on molybdenum published during 1982, essentially volumes 96 and 97 of Chemical Abstracts. Not included is the organometallic and carbonyl chemistry of molybdenum, however, certain of these compounds are discussed in Section 9 which deals with ^{95}Mo NMR spectroscopy.

1.1 MOLYBDENUM(VI)

1.1.1 Oxo-halide complexes

[MoO_2X_2] (X=Cl or Br) complexes have been isolated as monomers in low temperature matrices [1]. Prominent IR and UV-VIS bands have been assigned. The vibrational isotope effect on the antisymmetric stretching mode ν(Mo=O) leads to estimates of bond angles of 109°. In the quantitative assignment of the electronic spectra, the positions of the charge-transfer bands require lower values of optical electronegativities than are appropriate for octahedral complexes.

The preparation and characterization of complexes of bis-(η-cyclopentadienyl) and bis-(η-indenyl)Mo(VI) complexes [L_2MoOCl_2] with thio Schiff bases [2] and oximes [3] have been studied. The reaction with thio Schiff bases RCR_1=$NNHCS_2Me$ (R = Ph, R_1 = H(I); (R = Ph, R_1 = Me(II); R = R_1 = Ph(III); R = 2-HOC_6H_4; R_1 = H(IV); R = 2-$C_{10}H_6$, R_1 = H(V); R = 2-OHC_6H_4, R_1 = Me(VI)) yields 1:1 complexes. I, II, and III act as tridentate chelating ligands, coordinated through the *S* and azomethine *N* atoms; IV, V, and VI act as tridentate chelating ligands, coordinated through *S*, azomethine *N* and phenolic *O* atoms. The reaction with hydroxyoximes (salicylaldoxime, 2-hydroxy-5-methylacetophenon oxime, and 2-hydroxy-1-naphthaldioxime) has yielded [$L_2MoO(OX)$] complexes (OX^{2-} = oxime anion). The reactions with dioximes (α-benzildioxime, dimethylglyoxime, and 2,6-diacetylpyridinedioxime) have given complexes of the general formula [$L_2MoO(OXH)Cl$], where OXH is the dioxime anion.

The formation of relatively stable adducts of MoO_2Cl_2 with monodentate *N*-bases has been investigated by determination of the solubility and the integral heat of the solutions [4].

Air-oxidation of $MoCl_5$ in EtOH has formed Mo(VI) chloro-EtOH complexes [5]. These complexes are photoreduced to 5-, 4- and 3-valent Mo complexes when irradiated at a frequency corresponding to their charge-transfer band.

1.1.2 Dioxo complexes

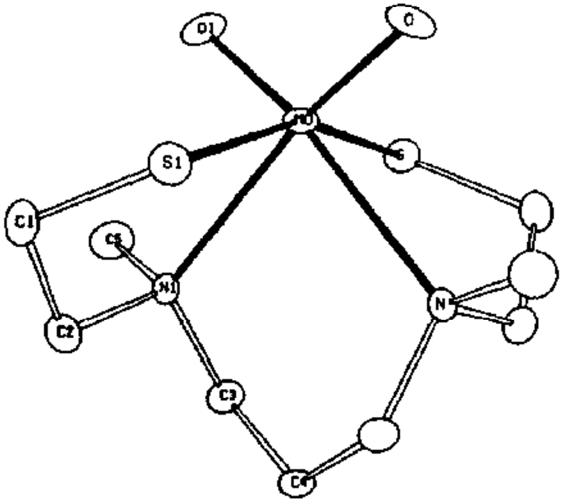
The reaction of $[MoO_2Br_2L]$ (L = bipy) with MeMgCl yields a $[MoO_2Me_2L]$ complex [6] whose structure closely resembles that of $[MoO_2Br_2L]$ [7], having the methyl groups mutually *trans*.

Molybdenum dioxo-complexes with thiocarbohydrazide, 1-carbamylthiocarbohydrazide, 1-thiocarbamylthiohydrazide and ammonium (1-amino-1-cyclopentene)dithiocarboxylate have been obtained, using MoO_2X_2 (X = halide), as the starting material [8].

Several Mo(VI) dioxo complexes with dithiocarbamate ligands have been synthesized [9,10]. The electrochemistry of diethyl dithiocarbamato-complexes in dichloromethane and dichloroethane shows two one-electron reduction steps, one to a $[MoO_2(R_2NCS_2)_2]^-$ complex and the second reduction to Mo(IV) and the free ligand [11]. Irradiation at 380 nm, into the lowest energy charge transfer band of this complex, has given the $[MoO_2(Et_2NCS_2)]$ and $Et_2NCS_2^{\cdot}$ radicals. A subsequent radical chain reaction in the dark leads, ultimately, to MoO_2 and $(Et_2NCS_2)_2$ [12]. The oxygen abstraction from these complexes by Ph_3E (E = N,P,As,Sb, or Bi) and Et_3N yields $[Mo_2O_3(Et_2NCS_2)_4]$ and Ph_3EO or Et_3NO [13].

Several Mo(VI) dioxo-complexes with Schiff bases derived from salicylaldehyde, salicylhydrazide, or benzoylhydrazide (= H_2L) with the general formula $MoO_2L\ H_2O$ or MoO_2L thf, have been prepared and characterized. The thf adducts are generally less stable than the H_2O adducts [14,15]. Mo(VI) complexes with aminopropanols [16] have been synthesized, as well as ternary complexes with oxalate - pyrocatechol ligands [17].

The crystal structure of the bis-(*N*-hydroxybenzamide)dioxomolybdenum-bis(*N*-dimethylformamide) complex has been determined; six oxygens are octahedrally, coordinated to the molybdenum [18]. The structures of four MoO_2Y complexes, where Y^{2-}, is a linear tetradentate ligand containing *N* and *S* donor atoms, have been reported for YH_2 = $HSCH_2CH_2NMe(CH_2)_nNMeCH_2CH_2SH$ (*n* = 2 or 3 **(1)** $HSC_6H_4NHCH_2CH_2NHC_6H_4SH$, or $HSCH_2CH_2NHCH_2CH_2SCH_2CH_2SH$ [19].



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1.1.3 Oxides

The structures of $[NBu_4]_2[Mo_6O_{19}]$ [20], $[PrNH_3]_6[Mo_7O_{24}].3H_2O$ [20], $[^iPrNH_3]_6[Mo_7O_{24}].3H_2O$ [21], $Na_2[NMe_4]_2[Mo_8O_{26}].2H_2O$ [22] and $[NH_4]_4[Mo_8O_{26}].5H_2O$ [23] have been determined. Ethylenedibisguanide dihydrosulphate($L.2H_2SO_4$ reacts in acid solution to form the insoluble salt, $[LH_6]_2H_4[Mo_8O_{26}]_3.6H_2O$ [24].

The structure of $[NBu_4]_2[Mo_2O_5L_2]$ (H_2L = 3,5-di-*tert*-butylcatechol) has been studied. Comparison of this structure to the neutral complex shows almost no difference in the $Mo_2O_5^{2+}$ region of the molecule. This result, together with the dimensions of the quinone ligands, shows that the charge difference is contained entirely within the quinones [25].

$Na_2[MoO_4]$ reacts with $BiCl_3$, in the presence of base, to give $Na_2[MoO_4(BiOCl)_n].2H_2O$ (n = 2,4, or 6), $[NH_4]_3[MoO_3Cl_3(BiOCl)_n].xH_2O$ (n = 1,2,4, or 6; x = 2, or 6), and $[pyH]_2[MoO_2Cl_4(BiOCl)_n].6H_2O$ [26].

A solution study has determined that the electroactive Mo(VI) species in neutral citrate medium is the 1:1 complex $[MoO_4HL]^{4-}$ (H_3L = citric acid). This complex is a rather weak one, with a formation constant of about 5×10^2 l mol^{-1} at 275K [27].

1.1.4 *Hydrazido complexes*

The oxohydrazido-complexes $[MoO(NNR_2)(S_2CNR'_2)_2]$ react with excess HX (X = Cl, Br, SPh, 0.5 1,2-$O_2C_6H_4$, or 0.5 2,3-$S_2C_6H_3Me$) to give the corresponding seven-coordinate $[MoX_2(NNR_2)(S_2CNR'_2)_2]$ complex; treatment of the product (X = Cl or Br) with $Na_2[S_2CNR'_2].3H_2O$ in methanol containing $Na[BPh_4]$, yields $[Mo(NNR_2)(S_2CNR'_2)_3][BPh_4]$. The complex $[MoO(NNMe_2)(C_9H_6No)_2]$, whose crystal structure has been determined, yields $NHMe_2$, NH_3 and Me_2NNH_2 on treatment with HCl [28].

$[Mo_2(OBu\text{-}tert)_6]$, in a hydrocarbon solvent, reacts with ≥ 4 equivalents of ArN_3 (Ar = Ph, 4-tolyl) to give $[Mo(OBu\text{-}tert)_2(NAr)_2]_2$, N_2, and *tert*-BuO· radicals. No intermediates have been detected in this reaction which brings about oxidative cleavage of the $Mo{\equiv}Mo$ bond. The crystal structure of the 4-tolylimido compound shows that each Mo atom is five-coordinate and the central $Mo_2O_4N_2N'_2$ skeleton may be viewed as two trigonal-bipyramidal units fused along a common equatorial-axial edge, through the agency of a pair of bridging imide ligands [29].

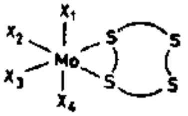
1.1.5 *Molybdenum(VI),(V),(IV),(III) complexes*

A series of corresponding molybdenum(VI),(V),(IV) compounds have been studied. The chemistry of the tetradentate N_2S_2 donor ligands *N*,*N'*-dimethyl-*N*,*N'*-bis(2-mercaptoethyl)ethylenediamine (LH_2) and *N*,*N*-dimethyl-*N*,*N'*-bis(2-mercaptoethyl)-1,3-propanediamine ($L'H_2$) with molybdenum in the (VI),(V), and (IV) oxidation states has been described. In

MeOH solution, molybdenum(VI)-oxo reagents combine with LH_2 or $L'H_2$ to give $[MoO_2L]$ or $[MoO_2L']$, respectively. Reduction of these complexes with HSPh in MeOH yields the corresponding dimeric complexes, $[Mo_2O_3L_2]$, and $H_2[Mo_2O_4L'_2]$. The more common mono-oxo-bridged molybdenum(V) dimer $[Mo_2O_3L'_2]$ may be prepared by the reaction of $[MoO_2L']$ with PMe_2Ph in dry thf. The molybdenum(V) species [MoOL] and [MoOL'] are obtained by treatment of the molybdenum(VI) species with an excess of PMe_2Ph in thf solution. It has also been possible to prepare the sulphido bridged dimers $[Mo_2S_4L'_2]^{2-}$ and $[Mo_2O_2S_2L'_2]^{2-}$. The IR, electronic, ^1H NMR spectroscopic and the electrochemical properties of these complexes have been reported and their reactivity towards substituted hydrazines has been studied [30].

The complex formation of dioxodichloromolybdenum(VI), oxotrichloromolybdenum(V), and tetrachloromolybdenum(IV) with the macrocyclic polythiaethers, 1,4,8,11-tetrathiacyclotetradecane (= ttp) and 1,4,7,10,13,16,-hexathiacyclooctadecane (= hto), have been studied and the new complexes $[MoO_2Cl_2$ (ttp)], $[MoO_2Cl_2$(hto)], $[(MoOCl_3)_2$(ttp)(thf)$_2]$, $[MoOCl_3$(ttp)], $[(MoOCl_3)_2$(hto)], $[MoCl_4$(ttp)], $[(MoCl_4)_2$(ttp)] and $[(MoCl_4)_2$(hto)] have been isolated. In these complexes, the bonding mode of the ligand is affected by the number of sulphur atoms, as well as the size of the ring of the macrocyclic polythiaether [31], as illustrated in (2).

Stable monomeric molybdenum(V),(IV), and (III) catechol complexes are formed by electrochemical reduction of the cis-dioxomolybdenum(VI) monomer $[MoO_2(cat)_2]^{2-}$ in aqueous buffers with a pH>9 and an excess of cathechol. The four oxidation states are interconvertable within a range of about 450 mV. The oxidation states were characterized by bulk solution electrochemistry, EPR spectroscopy, and visible spectroscopy linked to the electrochemical studies [32].



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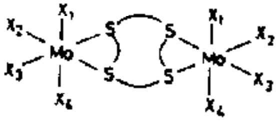

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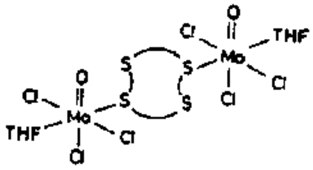

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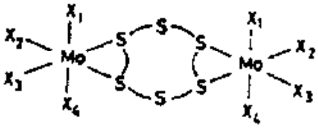

IV

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Electrochemical halfwave potentials and charge transfer absorption, EPR, and X-ray photoelectron spectral properties have been reported for a series of 8-coordinate molybdenum complexes with dithiocarbamate, thioxanthate, and 1,1 disubstituted ethylenedithiolate ligands. The complexes undergo reversible Mo^{VI}/Mo^{V} and Mo^{V}/Mo^{IV} electron transfers, with $E_{1/2}$ for a given charge transfer step spanning a range of 2 V for the ligands studied. Shifts in $E_{1/2}$ have been successfully correlated with parameters expressing the electron-donating or withdrawing capabilities of ligand substituent groups. Charge transfer absorption energies and molybenum(V) EPR signals experience relatively little change with the ligand structure. However, Mo $3d$ and S $2p$ XPES binding energies exhibit significant changes with ligand structure and correlate well with electrochemical half-wave potentials. [33].

Dioxomolybdenum(VI) and oxomolybdenum(V) complexes with tri- and tetradentate Schiff base ligands have been synthesized. The Schiff bases were prepared by condensation of salicylaldehyde, thiosalicylaldehyde, 2-hydroxyacetophenone, 3-carboxysalicylaldehyde, or acetylacetone with aminoalcohols, polymethylenediamines, or 2-phenylenediamines [34].

1.2 MOLYBDENUM(V)

1.2.1 *Oxo-halide complexes*

The complexes [$MoOCl_3$(trien)] and [$Mo_2O_4Cl_2$] have been prepared from [$trienH_4$][$MoOCl_5$] [35]. The reaction of $MoOCl_3$ and [$MoOCl_3(thf)_2$] with 1,3-bis(methylseleno)propane yields the *fac*-$MoOCl_3$ complexes [36]. With Schiff base ligands, possessing phenolic, imine, and various other side chain donors, the [$MoOCl_3(thf)_2$] starting material forms complexes of the type [$MoOCl_3(ligand)_2$]; the ligand generally binds as a neutral monodentate imine donor [37].

$MoCl_5$ reacts with [(Fe(salen))$_2$O] to form a compound having the molecular formula [Fe(salen)$_2$O($MoOCl_3$)$_2$)], in which the $MoOCl_3$ units are symmetrically coordinated to the oxygen atoms from salen [38]. [$MoOCl_3(thf)_2$] reacts with *N*,*N*'-ethylenebis-(thiophen-2-carbaldimine) (possessing an N_2S_2 set of donor atoms); 1,4,8,11-tetrathiacyclotetradecane (S_4), 2-mercaptobenzimidazole (N_2S) and 2-mercaptobenzothiazole (NS_2) to form the complexes [$MoOCl_3(N_2S_2)$], [($MoOCl_3$)$_2$(S_4)(thf)$_2$], [$MoOCl_3(N_2S)$] and [$MoOCl_3(NS_2)$], respectively [39].

EPR studies have indicated that [$MoOX_4L$]$^-$ (X = halide, L = dmf, Me_2CO, MeCN, or $MeNO_2$) react with 1,3-diones (HQ) to give complexes of the type, [$MoOQ_3$], [$MoOQX_2L$], [$MoOQ_2X$], and [$MoOQ_2L$]$^+$ [40].

The crystal structure of [$MoOCl_2$(HB(3,5-Me_2Pz)$_3$)] has been determined [41].

1.2.2 *Monomeric oxo complexes*

The electrochemical reduction of the (5,10,15,20-tetraphenylporphyrinato-

(2-))oxomethoxymolybdenum(V) complex in $[NBu_4][ClO_4]/CH_2Cl_2$ solution has been investigated. Five redox couples were found, in the potential range from +0.3V to -1.8V. Two of these couples, at -1.15V and -1.53V, correspond to the formation of the five coordinate anion radical $[(TPP)MoO]^-$ and dianion $[(TPP)MoO]^{2-}$. The other three couples involve six-coordinate complexes of molybdenum(V) and (IV), containing either $[ClO_4]^-$ or $[OCH_3]^-$ as the sixth axial ligand [42].

The synthesis and EPR characterization of monomeric, polymer anchored, molybdenum(V) complexes have been described. Tridentate Schiff bases derived from 5-X-salicylaldehyde (X = H or NO_2) and 4-amino-3-hydroxybenzoic acid served as ligands [43], the Schiff base ligand being covalently attached to an ester through the carboxylic acid function of the ligand. EPR results indicate that the electronic structure and the stereochemistry of the polymer-bound complex is essentially unchanged from that in the well characterized compound $[NEt_4][MoO(5\text{-}H\text{-}SAP)Cl_2]$. The polymer anchored molybdenum(V) complex is oxidized by $[NO_3]^-$ [44].

Solution studies on one monomeric and two dimeric molybdenum(V) complexes with 2-methyl-8-quinolinol as a ligand have been undertaken [45].

1.2.3 Monooxo-bridged dimers

The monooxo bridged dinuclear molybdenum(V) complexes $[Mo_2O_3(NCS)_4(bipy)_2]$, $[Mo_2O_3(NCS)_4(phen)_2]$ and $[Mo_2O_3(NCS)_2(8\text{-}O\text{-}quin)]$ have been prepared [46]. The structure of $[Mo_2O_3L_2]$, where L = *N,N'*-dimethyl, *N,N'*-bis(2-mercaptoethyl)ethylenediamine or *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)propylenediamine has been determined. The molecules possess a *trans*-planar $\{O{=}Mo{-}O{-}Mo{=}O\}^{4-}$ core and the ligand is tetradentate [47]. The reaction of $[MoO(S_2CNEt_2)_3][BF_4]$ and PPh_3 in MeOH under anaerobic conditions has been shown to give $[Mo_2O(S_2CNEt_2)_6][BF_4]$; this mixed oxidation state complex contains a new type of μ-oxo bridging between two Mo atoms, each having a formal oxidation state of 4.5 [48].

1.2.4 Dioxo-bridged dimers

The oxidation of $\{Mo_2O_4\}^{2+}$ by permanganate, $[MnO_4]^-$ in aqueous solution has been found to follow the equation:

$$2\ Mn^{VII} + 5(Mo^{V})_2 \rightarrow 2\ Mn^{II} + 10\ Mo^{VI}$$

Under pseudo first order conditions, the rate expression $d[MnO_4{}^-]/dt{=}/2k_{obs}[MnO_4{}^-]$ was found to be valid [49].

The reaction of $[Mo_2(OAc)_4]$ with 2-mercaptopyrimidine has been shown to form a green solid which has been transformed by dissolving in pyridine, in air, to yield a red-orange crystalline product, $[Mo_2O_3(py)(SN_2C_4H_4)_2]$ [50].

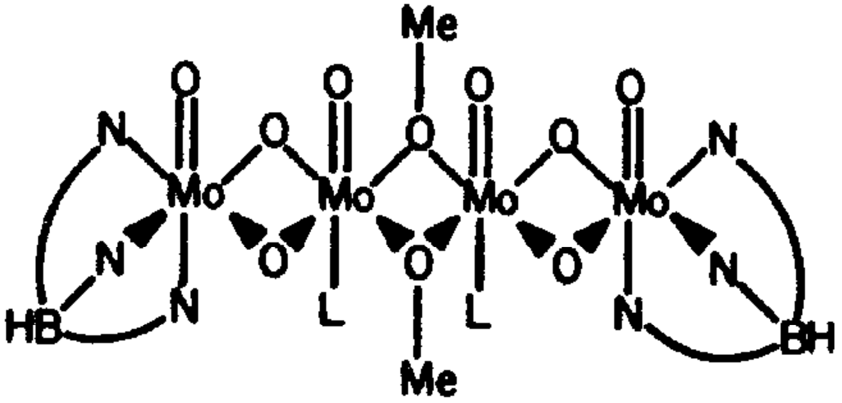
$[Mo_2O_4(L'H)_2]$ ($L'H_2$ = *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)propylenediamine) involves the Mo coordinated by the thiolate sulphur atoms of the L' ligand. The unusual feature of this structure is that the two amine nitrogen atoms are not coordinated, resulting in a 14-membered metal-chelate ring. One of the nitrogens of L'H is protonated, to produce a 6-membered H-N-C-C-C-N ring with a chair conformation and the ligand itself also assumes an overall chair conformation [47].

The structure of $[AsPh_4]_2[Mo_2O_4Cl_4].CH_2Cl_2.HCl$ [51] and of the tetramer **(3)** [52] have been determined. The molybdenum(V) tetramer is a dimer of dimers, with two $\{Mo_2O_4\}^{2+}$ centres joined together by two bridging methoxides.

1.2.5 Sulphur-bridged dimers

The μ-oxo-μ-sulphido(oxalato)molybdate(V) complex, $K_6[(Mo_2O_3\text{-}S(ox)_2)_2(ox)].10H_2O$ has been prepared and its structure has been determined. The molybdenum atoms in the dimer are bridged by one sulphur and by one oxygen atom and each molybdenum has a distorted octahedral environment [53].

The electronic structures of $[(MoO(cp))_2S_2]$, $[(MoS(cp))_2S_2]$ and $[Mo_2S_2(S_2C_2H_4)_2]^{2-}$ have been calculated by the parameter-free Fenske-Hall method [54]. Molybdenum(V) dimers with the general formula $[cp_2Mo_2S_4]$ have been synthesized and three different isomers isolated, one having four bridging sulphurs (**4**, A) and the other two bridging sulphurs (**4**, B and C) [55]. These



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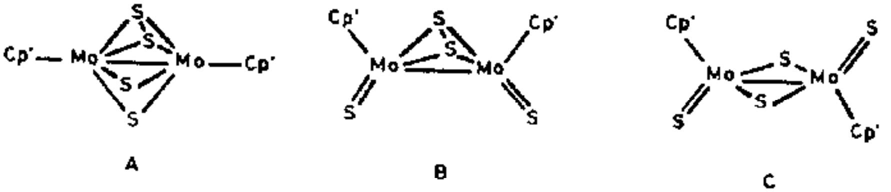
complexes have been used to synthesize bimetallic clusters of the composition $[cp_2Mo_2Co_2(\mu_3\text{-}S)_4(CO)_2]$ [56]. The complex with four bridging atoms has also been obtained with selenium, as have the two isomers with the general formula $[(cpMoO)_2(\mu\text{-}Se)_2]$ [57].



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1.2.6 Triply-bridged dimers

$[NBu_4][(Mo_2O_2Cl_5(SPh)_2]$ has been prepared by the reaction of $[NBu_4][MoOSPh_4]$ with stoichiometric amounts of HCl and characterized by single crystal X-ray structure analysis [58]. The dimeric anion is bridged by one chlorine and two oxygen atoms and each molybdenum has a pseudo-octahedral coordination geometry. The related compound $[Mo_2O_3(SPh)_2(S_2CNMe_2)_2]$ has been synthesized by the reaction of $[MoO_2(S_2CNMe_2)_2]$ with thiophenol in methanol and has also been characterized by X-ray crystallography. In this case, the triple bridge consists of two thiophenolate sulphur atoms and one oxo group, again giving each molybdenum a pseudo-octahedral environment. The complex, $[MoO(SCH_2CH_2CH_2S)_2]^-$ reacts with HN_3 in methanol to give $[Mo_2O_2(\mu\text{-}N_3)(SCH_2CH_2CH_2)_3]^-$. X-ray crystallography has shown that each molybdenum of the former anion have tetragonal pyramidal coordination with an apical oxo-group; the latter anion is an asymmetric dinuclear complex with a triple bridge comprising two dithiolate sulphurs and a bent azide group [59].

1.2.7 Non-oxo complexes

The compound $[Mo(S_2CNEt_2)_4]^+ [FeCl_4]^- (PhCH_2SSCH_2Ph)$ has been synthesized and its structure has been determined [60-62].

A series of eight-coordinate molybdenum(V) complexes with 1,1-disubstituted ethylenedithiolate, $[Mo(S_2C_2R_2)_4]^{3-}$, (where R = CN, or COOEt), dithiocarbamate, $[Mo(S_2CNEt_2)_4]^+$, and thioxanthate, $[MoS_2CS\text{-}\textit{tert}\text{-}Bu)_4]^+$, ligands have been studied. These complexes, with the exception of the last, exhibit a reversible Mo^V/Mo^{VI} oxidation and all of them manifest a reversible Mo^V/Mo^{IV} reduction. The half-wave potentials of these reversible processes span a range of +1.2V to -1.7V *vs.* SCE in CH_3CN or CH_2Cl_2 [63].

Tetranuclear, ferromagntic compounds of the formula $[MoN(S_2P)(OR)_2)]_4$ have been synthesized and characterized. The chiral molecule contains a nearly square and planar (MoN_4) ring, in which all bond distances are identical within experimental error. This portion of the structure contrasts markedly with the alternating triple and single bonds found in the lattice of $MoNCl_3$ [64].

An EPR investigation on the cation tetramesitymolybdenum(V) has been reported and the EPR parameters interpreted by means of a D_{2h} ligand field model [65].

1.3 MOLYBDENUM(IV)

1.3.1 Monomeric complexes

The crystal structure of $[MoO(PhCONNCOPh)(S_2CNMe_2)_2].C_2H_4Cl_2$ has been determined [66]. The approximate stereochemistry about the molybdenum is pentagonal bipyramidal; the four *S* atoms of the dithiocarbamate ligands and the nitrogen atom of the benzoyldiazene ligand occupy the equatorial positions; the axial sites are occupied by the terminal oxo group and the oxygen atom of the diazene ligand. Thus, the bidentate diazene ligand coordinates through *O* and *N* atoms to form a five-membered chelate ring. The structure of the $[MoO(S_2CPh)(S_3CPh)]$ complex has also been elucidated [67].

Molybdenum(IV) oxo complexes with tri- and tetradentate *O*,*N* and *S*-donor ligands have been synthesized. The complexes are of the type [MoOLL'], (where L = salicylaldehyde-2-hydroxyanil, or salicylaldehyde-2-mercaptoanil; L' = bipy or -phen) and [MoOL], (where L = *N*,*N*'-bis(2-mercapto-2-methylpropyl)-ehtylenediamine). These compounds may be electrochemically oxidized to the corresponding molybdenum(V) oxo complexes, also they may be reduced in a one-electron process [68]. A series of molybdenum(IV) complexes of the type $[MoCl_2L_2]$, where HL represents *N*-phenylsalicylideneimine and its derivatives, have been synthesized by the reaction of $[MoCl_2(acac)_2]$ or $[MoCl_4(CH_3CN)_2]$ with the Schiff base [69].

The substitution reactions of $[MoCl_4(CH_3CN)_2]$ with NaHS and $NaOCH_3$ have been studied [70]. The products of the reaction were found to be $[Mo(OCH_3)_4(CH_3CN)_2]$ and, possibly, $Na_4[MoS_4(CH_3CN)_2]$, respectively.

A kinetic study on the intramolecular rearrangements of heptacoordinate molybdenum(IV) complexes has been undertaken. The reaction of $[MoO(S_2CNR_2)_2]$ with ROOCN=NCOOR (R = Me or Et) proceeds *via* two successive steps, which consist of the formation of a monocapped trigonal prismatic intermediate, followed by intramolecular rearrangement, affording the final product with a pentagonal bipyramidal configuration. The entropy and volume of activation in the rearrangement for (R = Et) are both positive, which is in marked contrast to the negative values for a similar rearrangement of $[MoO(S_2CSPr^i)_2(MeOOCC{\equiv}CCOOMe)]$ [71].

$MoTe_2$ is oxidized in air to form Te_2MoO_7. Mild oxidation conditions give rise to an EPR signal characteristic of oxo-molybdenum(V) ions with a heterogeneous distribution in the solid. Higher temperatures promote, firstly, the formation of a broad signal typical of $TeMo_5O_{16}$ and, subsequently, the formation of Te_2MoO_7 which is EPR inactive [72].

A normal coordinate analysis has been carried out on the $[Mo(CN)_8]^{4-}$ ion in a crystalline environment. The frequencies of the 45 normal modes of the ion have been calculated with an average error of 1.3% or $4.4 cm^{-1}$ and all of the frequencies have been assigned. The investigation of the IR and Raman spectra of the solid $K_4[Mo(CN)_8].2H_2O$ has enabled the calculation of 10 force constants by use of a least square refinement [73].

1.3.2 Polymeric complexes

The compounds $[Mo_3O_2(OAc)_6(H_2O)_3]Br_2.H_2O$, with two capping oxygens [74], $[Mo_3O(CCH_2Me)(O_2CEt)_6(H_2O)_3]^+$ [75], and $[(CH_3)_4N][Mo_3O_4(SCN)_8(H_2O)].3H_2O$ [76] have been synthesized and their structure determined by X-ray crystallography.

$[Mo_2(NMe_2)_6]$ reacts with > 6 equivalents of *tert*-BuSH in hydrocarbon solvents, at room temperature, to give green crystals of the $[Mo_2(\mu\text{-}S)_2(tert\text{-}BuS)_4(HNMe_2)_2]$, which has been characterized by a single-crystal X-ray diffraction study [77]. Each molybdenum atom is in a distorted trigonal-bipyramidal environment, with respect to the atoms to which it is directly bonded, and the halves of the molecule are joined together by a pair of sulphido bridges, which form alternatively long (axial) and short (equatorial) bonds.

Trinuclear metal cluster ions of molybdenum undergo hydrolysis in aqueous solutions; the addition of various counterions such as Cl^-, Br^-, I^- and NCS^- to this solution, produce several hydrolysis products with different degrees of polymerization which have been crystallized, one of these compounds being $[H_3O][(Mo_3O_2(O_2CEt)_6(H_2O)_2)_2]Br_3.6H_2O$ [78].

1.4 MOLYBDENUM(III)

1.4.1 Monomeric complexes

The crystal structure of $[MoBr_3(\text{4-methylpyridine})_3]$ [79] and $[NH_4]_3[Mo(NCS)_6].H_2O.HCl$ [80] have been determined.

$AlMoCl_6$ has been prepared by three different methods and its reactions with liquid amines in methanol have been studied; these lead to the formation of octahedral $[MoCl_3L_3]$ (L = py, $PhNH_2$, or piperidine) complexes [81].

The reaction of $[MoCl(S_2CNEt_2)_3]$ with SO_2 in CH_2Cl_2 solution, under anaerobic, reducing conditions gives black crystals of $[Mo(S_2CNEt_2)_3(\eta^2\text{-}SO_2)]$, whose crystal structure has been determined, and a second product, which is believed to be $[Mo(S_2CNEt_2)_3(SOCl_2)]$ [82].

1.4.2 Polymeric complexes

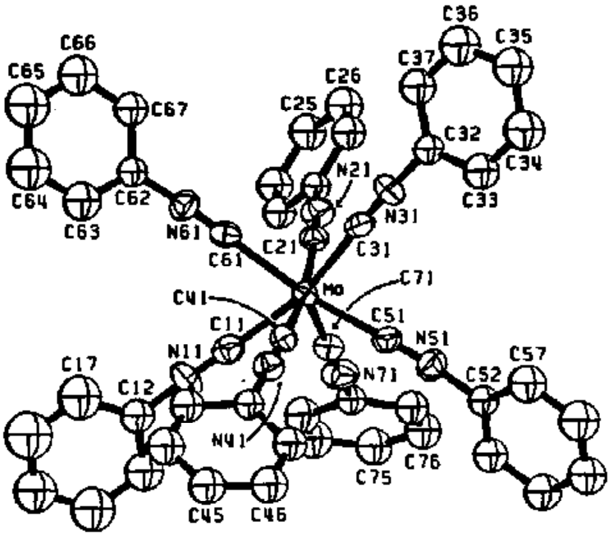
The confacial, bioctahedral complexes $[PPh_4][(Me_2S)Cl_2Mo(\mu\text{-}Cl)_3MoCl_2\ (SMe_2)]$ and $[(Me_2S)Cl_2Mo(\mu\text{-}Me_2S)(\mu\text{-}Cl)_2MoCl_2(SMe_2)]$ have been synthesized and their crystal structures determined [83].

Photolysis of $[(Mo(cp)H)_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5C_5H_4)]$ gives first *cis* and *trans* $[(Mo(cp)H)_2(\mu\text{-}\delta{:}\eta^5\text{-}C_5H_4)_2]$ and then $[(Mo(cp)_2(\mu\text{-}\delta{:}\eta^5C_5H_4)_2]$ [84]

1.5 MOLYBDENUM(II)

1.5.1 Monomeric complexes

The crystal structures of $[Mo(dppm)(CNMe)_5][PF_6]_2$ [85], $[Mo(dppe)(MeCN)_5][PF_6]_2$ [85], $[Mo(NC_6H_4Me)(S_2P(OEt)_2]_3$ [86], $[Mo(CNPh)_7][PF_6]_2$ [87], 5 and $[(OC)Mo(S_2CNMe_2)_2(diars)]$ [88] have been determined.



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The redox properties of the seven-coordinate cations $[Mo(CNR)_6X]^+$, $[Mo(CNR')_6I]^+$ and $[Mo(CNR)_7]^{2+}$ (R = alkyl, R' = aryl; X = Cl, Br, I, CN, or $SnCl_3$) have been investigated by cyclic voltammetry and controlled potential coulometry in CH_2Cl_2 solution [89]. All of these alkyl isocyanide complexes, with the exception of $[Mo(CN\text{-}\textit{tert}\text{-}Bu)_6(SnCl_3)]$, exhibit a quasi-reversible one-electron oxidation, to form seven-coordinate molybdenum(III) cations, and show also an irreversible reduction. The half-wave potentials increase in the order $[Mo(CNR)_4(CNHR)_2I]^+ < [Mo(CNR)_6X]^+$ (X = halide) $< [Mo(CNR)_6CN]^+ < [Mo(CNR)_7] < [Mo(CNR)_6(SnCl_3)]^+$, a trend that reflects the electron donor/acceptor properties of the ligands.

The synthesis of a series of bis(alkyne)bis(dithiocarbamato)molybdenum(II) complexes with terminal alkyl- and aryl-substituted alkynes have been reported [90]. Spectroscopic studies of solutions of molybdenum(II) trifluoroacetate in pyridine indicate that the solutions do not contain the axial bis-pyridine adduct, known in the solid state, but rather contain species with both bidentate and monodentate carboxylate ligands; ring opening and closing proceeds with an apparent free energy barrier (ΔG^*) of about 54 kJ/mol. [91].

1.5.2 *Polymeric complexes*

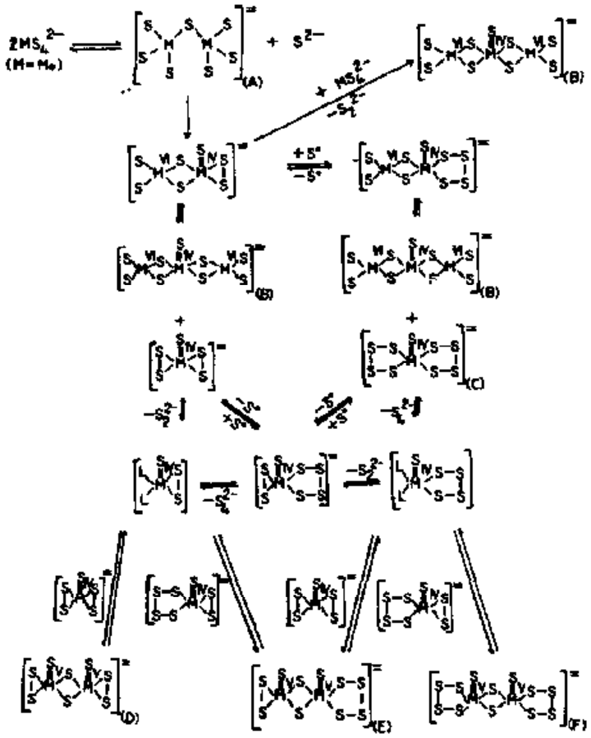
The cycloaddition of two $[Mo_2Cl_4(PPh_3)_2(MeOH)_2]$ and related molecules has produced a new type of tetrameric molybdenum cluster; $[Mo_4X_8L_4]$ (for X = Cl, Br, I and L = neutral donor ligand) have been fully characterised [92].

A synthetic procedure has been devised for the stepwise displacement of chloride by sulphide in the $[Mo_6Cl_8]^{4+}$ cluster, *via* reaction of Mo_6Cl_{12} with NaSH in refluxing pyridine [93]. The $[Mo_6Cl_7S]^{3+}$ cluster was isolated in two different salts containing the chloro anion $[(Mo_6Cl_7S)Cl_6]^{3-}$ and the structures were determined by X-ray crystallography.

1.6 MOLYBDENUM-SULPHUR-CLUSTERS

1.6.1 *Sulphur clusters*

The $[MoS_4]^{2-}$ anion reacts with elemental sulphur and active sulphur reagents, such as trisulphides or ammonium sulphides, to afford binary molybdenum sulphides. These materials appear to be the components of a complex equilibrium system, the position of which depends on the solvent system and the nature of the counter-ions present in solution (6). $[NEt_4]_2[(S_4)_2MoS]$ can be isolated from either MeCN or dmf solutions and the hydrolysis of this anion in these solvents has afforded $[(S_4)_2MoO]^{2-}$. In the presence of $[PPh_4]^+$, the $[Mo_2S_{10}]^{2-}$ and $[Mo_2S_{12}]^{2-}$ anions can be isolated from dmf solutions and the structures of these complexes have been determined by X-ray crystallography. In $[(S_4)_2MoS]^{2-}$ and $[(S_4)_2MoO]^{2-}$ the molybdenum is coordinated by two bidentate $S_4{}^{2-}$ chelates and a terminal sulphur or oxygen atom in a distorted square pyramidal arrangement in which the metal is situated above the basal plane. $[Mo_2S_{10}]^{2-}$ and $[Mo_2S_{12}]^{2-}$ have the $\{Mo_2S_4\}^{2+}$ core in common, as well as the tetrasulphide ligand attached to one molybdenum; the other molybdenum is either coordinated by a persulphido- or a tetrasulphido- group. These $\{Mo_2S_4\}^{2+}$ cores



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contain two $(Mo^{V}=S)^{3+}$ units, bridged asymmetrically by two sulphide ligands in the *syn*-configuration [94]. Addition of CS_2 to $[Ph_4]_2[(S_4)_2MoS]$ and $[PPh_4]_2[(S_4)Mo_2S_4(S_2)]$ has yielded the crystalline compounds $[PPh_4]_2[trans(CS_4)_2MoS]$.dmf and $[PPh_4]_2[cis\text{-}(CS_4)Mo_2S_4(CS_4)]$.0.5 dmf in high yields. The anion of the former contains the $(Mo^{IV}=S)^{2+}$ unit, coordinated by two nearly planar CS_4^{2-} ligands in a *trans* configuration and the geometry around the molybdenum is approximately square pyramidal, with the molybdenum atom situated above the equatorial plane. In the structure of the latter, the anion consists of a $\{Mo_2S_4\}^{2+}$ core in the *syn* configuration, with the CS_4^{2-} ligands coordinated to the Mo atoms in a *cis* configuration. The coordination geometry around each of the two Mo atoms is approximately square pyramidal [95].

The complex $[Mo_3S_8(N_2Me_2)_2]^{2-}$ has been synthesized by the reaction of $[Mo_2S_4(N_2Me_2)_2PPh_3]$ with LiSPh in CH_3CN. X-ray structure analysis of the $[PPh_4]^+$ salt has revealed the anion to be a linear molybdenum-trimer with two distinct coordination sites. The central metal atom enjoys pseudooctahedral geometry, through coordination of the *N* atoms of two end-on, linearly bound hydrazido(2-)-groups and to four bridging sulphido groups and crystallographic symmetry which gives a rigorously planar Mo_2S_4 unit, with *trans* hydrazido-groups. The terminal molybdenum atoms are tetrahedrally coordinated to two bridging and two terminal sulphido groups. The unusual Mo-N and N-N bond lengths of 2.13(1)Å and 1.16(2)Å, respectively, suggest that the $-NNMe_2$ ligands are best described as isodiazene groups [96].

$[PPh_4]_2[MoOS_3]$ and elemental sulphur in CH_3CN, or $[PPh_4]_2[MoS_4]$ in dmf solution react with O_2 to give $[PPh_4]_2[(S_2)OMoS_2MoO(S_3O_2)]$ which contains the novel trithiosulphate ligand [97]. $[Mo_3S_7(R_2PS_2)_3)][(R_2PS_2)]$ reacts with PPh_3 to form the coordinatively unsaturated, diamagnetic complex $[Mo_3S_4(R_2PS_2)_4]$ (R = Et, Pr, or Ph) [98]. The reaction of nonequivalent S_2^{2-} ligands in the tetranuclear anion of $[NH_4]_2[Mo(NO)_4(S_2)_4(S'_2)_2O].2H_2O$ with KCN in H_2O at 328-333K gives $K_8[Mo_4S_4(NO)_4(CN)_8].4H_2O$ [99]; $K_8[Mo_4S_4(CN)_{12}].4H_2O$ has also been prepared [100]. $[NH_4]_2[Mo(NO)_4(S_2)_6O].2H_2O$ may be conveniently prepared by the reaction of $[MoO_4]^{2-}$ with NH_2OH and H_2S in H_2O [101]. One of the products from the reaction of $[NH_4]_2[Mo_2O_7]$ with benzoin and P_4S_{10}, is the binuclear dithiolene complex $[Mo_2(S_2)(S_2C_2Ph_2)_4]$. An X-ray analysis of the structure has revealed that each molybdenum atom is coordinated by seven sulphur atoms, in an approximately monocapped-trigonal-prismatic arrangement. The two metal atoms are bridged by four sulphur atoms of a shared square face of the trigonal prisms; two of the bridging sulphur atoms are supplied by a bridging S_2 ligand and the other two are supplied by two bridging dithiolene ligands [102].

1.6.2 Iron-molybdenum-sulphur clusters

A special interest is directed towards Fe-Mo-S clusters because the active N_2 binding site in nitrogenases is believed to be such a cluster.

$[NEt_4]_2[FeL_2]$ (H_2L = *ortho*-xylyl-α,α'-dithiol) reacts with $[NEt_4]_2[MoS_4]$ in CH_2Cl_2 to give $[NEt_4]_2[L_2Fe(\mu\text{-}S)_2MoS_2]$, which has been characterized by IR, electronic, and EPR spectroscopy and cyclic voltammetry [103].

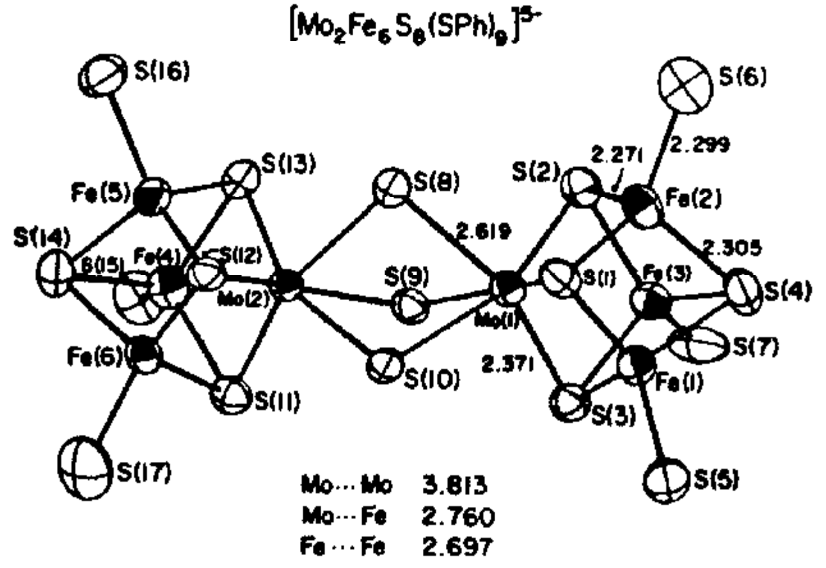
The complexes $[(4\text{-}CH_3C_6H_4S)_2FeS_2FeS_2MoS_2]^{3-}$ and $[(C_6H_5O)_2FeS_2MoS_2]^{2-}$ have been synthesized and their structures determined; these complexes have been used in EXAFS studies as models for the iron site(s) of the iron-molybdenum cofactor of nitrogenase [104].

The reactions of $AcGly_2(CysGly)_nCysGly_2NH_2$ (**A**; n = 1,2) with Fe^{II} and $[MoS_4]^{2-}$ in the presence of NEt_3 in dmso have been monitored by electronic spectroscopy. The spectra indicate $[MoS_4]^{2-}$-Fe interactions and a similar spectrum was obtained on treating $[Cl_2FeS_2MoS_2]^{2-}$ with **A** (n = 2) and Et_3N. Thus, it appears that the solution contains a complex with the FeS_2Mo chromophore [105]. The clusters $[FeCo_2MSAsMe_2cp(CO)_8]$ (M = Mo or W] result from the reaction of $[FeCo_2S(CO)_9]$ and $[cp(CO)_3MAsMe_2]$. The compounds have a tetetrahedral $FeCo_2M$ core with μ_2-$AsMe_2$ and μ_3-S bridges, as evidenced from the crystal structure analysis of the Mo-compound and, at room temperature, they add two molecules of CO to form the clusters $[FeCo_2MSAsMe_2cp(CO)_{10}]$ [106]. Treatment of $[(CO)_3FeS)_2]$ with $[(CO)_2cpMo{\equiv}Mocp(CO)_2]$ forms $[Fe_2Mo_2cp_2(\mu_3\text{-}S)_2(\mu_3\text{-}CO)_2(CO)_6]$, whose crystal structure has been determined and $[(cpMo(CO)_3)_2]$ [107].

N_2 can be reduced to NH_3 under the conditions of controlled potential electrolyses in the presence of $[Fe_4S_4(SPh)_4)]^{2-}$ or $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ in MeOH/thf or in H_2O. The maximum current efficiency in the reduction is 1.6% for the reduction of N_2 in MeOH/thf and the total yield of NH_3 based on the cluster is 195% for 4 days [108].

The electronic properties of certain components members of an electron transfer series formed by the double cubane clusters $[Mo_2Fe_6S_8(SR)_9]^{z-}$ (z = 2 to 5) and $[Mo_2Fe_6S_8(\mu_2\text{-}OMe)_3(SBu\text{-}tert)_6)]^{z-}$ (z = 1 to 5) have been elucidated.

The series is generated by one-electron reactions of $MoFe_3S_4$ subclusters, which are usually reversible as monitored by cyclic voltammetry; the 3-, 4-, and 5-members are the more stable derivatives and are produced in solution by electrochemical and chemical reactions. The crystal structure of $[NEt_4]_5[Mo_2Fe_6S_8(SPh)_9]$ (7) shows that the cluster retains the double cubane structure of the $[Mo_2Fe_6S_8(SR)_9]^{3-}$ species but with an increased Mo-Mo separation and subcluster dimensional changes consistent with ^{57}Fe Mössbauer measurements. The mean oxidation states of $Fe^{2.67}$ and $Fe^{2.33}$ are considered the most probable for the 3- and 5- clusters, respectively. At $T < 80K$, $[Mo_2Fe_6S_8(SR)_9]^{4-}$ possesses, on the ^{57}Fe Mössbauer time scale, inequivalent subclusters containing $Fe^{2.67+}$ and $Fe^{2.33+}$ and electronic absorption spectra and magnetic properties are consistent with this assignment. Collective spectroscopic and redox potential properties serve to demonstrate that electronic structural changes attendant upon the 3-/4- and 4-/5- electron transfer reactions of double cubanes are largely confined to subcluster Fe_3 portions and the associated S atoms. The assigned mean oxidation states of the metal atoms are intended as the best available estimates of charge distribution rather than precise descriptions [109].



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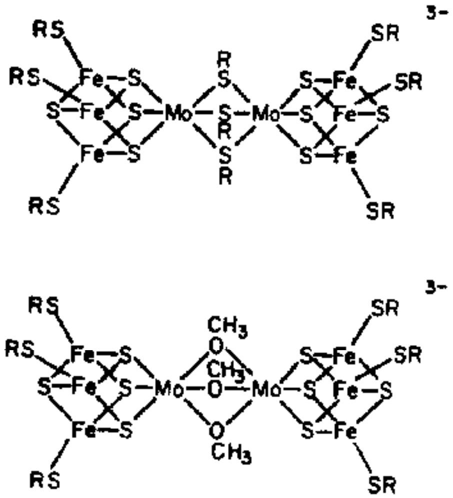
Reaction of the iron(III)-bridged double cubane clusters $[M_2Fe_7S_8(SEt)_{12}]^{3-}$ (M = Mo or W) with the 3,6-disubstituted catechols R'_2catH_2 in CH_3CN at ambient temperature results in bridge cleavage and formation of the new set of clusters $[M_2Fe_6S_8(SEt)_6(R'_2cat)_2]^{4-}$ (M = Mo or W; R' = Pr or $CH_2CH{=}CH_2$), which may be isolated in good yields as their $[NEt_4]^+$ salts. The structure of the centrosymmetric anion is that of a doubly bridged double cubane cluster; two $\{MoFe_3S_4(SEt_2)_2(R'_2cat)\}$ subclusters of unexceptional dimensions and containing a Mo-R'_2cat chelate ring are joined by two Mo(μ-SEt)Fe bridges. The bridge bond distances are 0.04-0.09Å longer than comparable terminal distances. In solution, the clusters undergo complete thiolate ligand substitution with arylthiols (RSH) affording $[M_2Fe_6S_8(SR)_6(R'_2cat)_2]^{4-}$ (R = Ph, p-tolyl, p-C_6H_4Cl), several of which have been isolated as $[NEt_4]^+$ salts. In coordinating solvents, such as dmso, Me_3CN and dmf at ambient temperature, the double cubanes are cleaved to single cluster solvates $[MFe_3S_4(SR)_3(R'_2cat)(solvent)]^{2-}$. ^1H NMR evidence indicates that all of the thiolate ligands are present as terminal Fe-SR groups; the M atom coordination is completed by a solvent molecule, which is in rapid exchange with the bulk solvent. Magnetic susceptibility and EPR spectral properties confirm an $S = 3/2$ groundstate. The EPR parameters are similar to those of the $S = 3/2$ spin system of FeMo-proteins and the FeMo-cofactor of the nitrogenases, suggesting an electronic similarity. The solvate/clusters undergo a single one-electron reduction at -1.1 to -1.5 V (vs. SCE). This property, together with the lability of coordinated solvent molecules, leads to the possibility that reducible nitrogenase substrates may be bound and activated by the M atom site [110].

The temperature variation of the effective magnetic moment from 1.9K to 300K, and the sensitivity to the strength of the applied magnetic field at 1.25 - 20.0 kG, has been reported for $[NR_4]_3[Fe_6M_2S_8(SR)_9]$ (R = Bu, M = Mo; R = Et, M = W) and $[NEt_4]_3[Fe_6M_2S_8(SPh)_6(OMe)_3]$ (M = Mo or W) (8). The EPR spectra at 4.2K for these systems have also been reported. These data are interpreted in terms of antiferromagnetic spin-coupling between two Fe^{II} and an Fe^{III} centre within a Fe_3MS_4 subunit, with an additional much weaker coupling between the subunits [111].



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1.7 COMPLEXES WITH NITROGEN LIGANDS

1.7.1 Nitrido complexes

Heating $[Mo_2(CO)_4cp_2]$ with ethyldiazoacetate results in the formation of $[Mo_3(N)O(CO)_4cp_3]$ which has been characterized by IR and ^1H NMR spectroscopy and the crystal and molecular structure of this compound has been determined. The molecule contains a nitrogen atom in a T-shaped arrangement bound to three molybdenum atoms [112].

1.7.2 Dinitrogen complexes

Because biological nitrogen fixation requires molybdenum, there is a special interest in inorganic molybdenum complexes which mimic the reactions of nitrogen fixing enzymes. One such complex is *trans*-$[Mo(N_2)(dppe)_2]$. The molybdenum K-edge EXAFS of the complex has been recorded and compared to that of *trans*-[$MoH_4(dppe)_2$]. On the basis of this analysis, one can detect that the N_2 complex contains coordinated nitrogen and the hydride complex does not, and it was possible to detect the correct Mo-N distance. This is significant because the molybdenum in both complexes is coordinated by four phosphorus atoms which dominate the EXAFS. A similar sort of interference is present in nitrogenase due to sulphur coordination of the molybdenum. Therefore, given adequate signal-to-noise ratio, the presence or absence of N_2 coordination to the molybdenum in the enzyme may be detected by EXAFS using existing data analysis techniques [113].

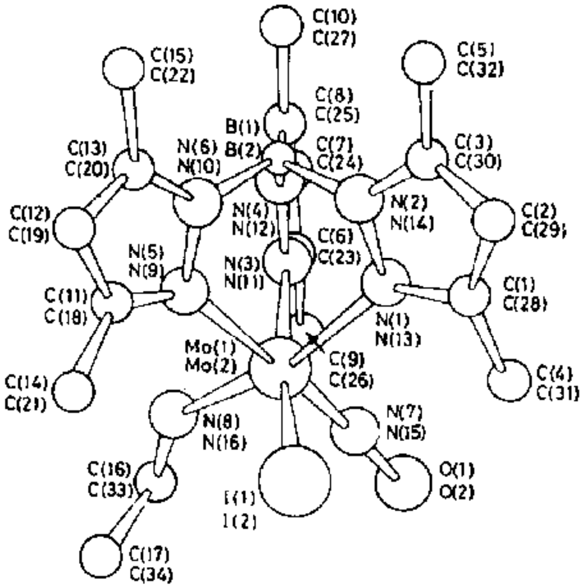
Irradiation of *trans*-[$Mo(N_2)_2(dppe)_2$] in the presence of RC_6H_4NCO (R = H, 4-Me or 4-Cl) in benzene gave the corresponding [$Mo(RC_6H_4NCO)_2(dppe)_2$] complex in good yield; IR data suggest a η^2-C,O coordination of the incoming ligand [114].

trans-[$Mo(N_2)_2(dppe)(PPh_2Me)_2$] reacts with anhydrous HBr in thf to give [$MoBr_3(dppe)(PPh_2Me)$], [NH_4]Br, 1.5 mols N_2, and [Ph_2MePH]Br, products which are analogous to those obtained in the reaction of *trans* -[$Mo(N_2)_2(triphos)(PPh_3)$] with HBr. Therefore, triphos does not dictate the pathway of the reaction. When *trans*-[$Mo(N_2)_2(triphos)(PPh_3)$] is reacted with H[$BF_4$] or [$Ph_3PH$][$BF_4$] the stable intermediate [$MoF(NNH_2)(triphos)(PPh_3)$][$BF_4$] may be isolated; this product, when treated with HBr, does not evolve NH_3 or N_2H_4. Other effects of the nature of the solvent and acid on reactions of these complexes have been studied [115].

1.7.3 Nitrosyl complexes

[Mo(NO)(terpy)(CN)(HNO)].H_2O has been synthesized and its crystal structure determined. The geometry about the molybdenum is a distorted pentagonal bipyramid with linear NO and CN groups in the axial positions, a tridentate terpyridine ligand and an *O,N*-coordinated HNO^{2-} ligand in an equatorial position [116].

The complexes [Mo(HBL_3)(NO)IL'] (L = 3,5-dimethylpyrazolyl; L' = NMe_2, NH_2, NHMe, NHEt, NHBu, $NHCH_2CHMe_2$, cyclohexylamino, $NHCH_2CH{:}CH_2$, or $NHCH_2Ph$) **(9)** have been prepared. Treatment of the complex for which L' = NH_2 with HCl and acetone in the presence of NEt_3 gave [Mo(HBL_3)(NO)Cl_2] or [Mo(HBL_3)(NO)I(N=CMe_2)].acetone, respectively. The crystal structure of the derivative for which L = NHEt has been determined; the molecule involves six-coordinate molybdenum with a linear Mo-N-O group and a short Mo-NHEt bond [117].



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The prochiral polypyrazolylborate complexes [R-B(3,5-X_2-pz)$_3$)Mo$(CO)_2$(NO)] (R = pz, X = H; R = H; X = CH_3) react with the optically active aminophosphines (L = $(C_6H_5)_2PNR'CH(CH_3)(C_6H_5)$; R = H or Me) to give the corresponding monosubstitution product [R-B(3,5-X_2-pz_3)$_3$Mo(CO)(NO)L], in which the metal atom is a new chiral centre. The separation of the diastereomers, differing only in their molybdenum configuration, by preparative liquid chromatography and fractional crystallization has been described [118].

Treatment of $[Mo(HBL_3)(NO)I_2]$ with one or two moles or $Ag[PF_6]$ in MeCN has afforded the paramagnetic (one-unpaired electron) complex $[Mo(HBL_3)(NO)(NCMe)_2][PF_6]$. The structure of this compound has been determined by X-ray crystallography and the six-coordinate geometry of the cation confirmed [119].

$[M(NO)Cl_3(MeCN)_2]$ (M = Mo or W) have been prepared by the reaction of $MoCl_5$ or WCl_6 with NO in the presence of CH_2Cl_2 and MeCN.$[W(NO)Cl_3L_2]$ (L = PPh_3, $AsPh_3$, tricyclohexylphosphine, or $OPPh_3$) and $[Mo(NO)Cl_3L_2]$ (L = PPh_3, $OPPh_3$, $AsPh_3$, dmf or dmso) have been synthesized by the reaction of $[M(NO)Cl_3(MeCN)_2$ and the corresponding L in CH_2Cl_2. In the reaction of $MoCl_5$ with NO, $[Mo(NO)Cl_2(CH_3CN)_3]$ has been obtained which, however, could not be isolated in the pure form. This compound reacts with an additional molecule of NO to give $[Mo(NO)_2Cl_2(MeCN)_2]$ [120].

trans-$[MX(NO)(dppe)_2]$ (X = NCO, H, or OH; M = Mo or W) have been prepared by treating the corresponding *trans*-$[M(N_2)(dppe)_2)]$ complex with $MeN(NO)CONH_2$ in thf (X = NCO), Et_2NNO in thf or thf/MeOH (X = H), or Et_2NNO in thf/K_2CO_3 (X = OH). The crystal structure of *trans*-$[Mo(OH)(NO)dppe)_2]$.2thf has been determined; the Mo-N-O system is linear with a long Mo-N distance (1.985Å) and a short MoOH distance (1.922Å). Complexes of the type *trans*-$[MX(NO)(dppe)_2]$ (X = N_3, Cl, Br, I and NCS) have been prepared by metathesis, and chemical oxidation of these systems has resulted in the isolation of $[(MX(NO)(dppe)_2]Y$ (Y = $[I_3]^-$, $[FeCl_4]^-$, $[CuCl_2]^-$, or $[BF_4]^-$), $[Mo(NO)(NCR)(dppe)_2][BF_4]$ and $[Mo(NO)(NCR)(dppe)_2][BF_4]_2$. Oxidation using $Ag[BF_4]$ in RCN (R = Me or Ph), and X_2 (X = Cl or Br) yielded $[MX_2(dppe)_2]$ [121].

A simple preparation of the complexes $[Mo(NO)(CO_4][AlCl_4]$ and $[MoCl(NO)(CO)_2(PPh_3)_2]$ has been described. The homogeneous system $[MoCl(NO)(CO)_2(PPh_3)_2]/RAlCl_2$ (R = Et or Me) represents a highly active, long lived catalyst for the metathesis of 2-pentene [122].

Stoichiometric reactions between $[cp_2Mo(NO)I]$ and equimolar amounts of AgY (Y = $[BF_4]^-$ or $[SbF_6]^-$) produce different nitrosyl complexes, depending upon the solvent used. In MeCN the monomeric cation $[(cp_2Mo(NO)(MeCN)]^+$ results, and can be isolated as its Y-salt in good yields. In aqueous acetone, the final isolable products are the trimetallooxonium salts, $[(cpMo(OH)_3O)]Y$, which probably result from the initial formation of the aquo cation $[cp_2Mo(NO)(H_2O)]^+$. The iodo analogue of this trimetallic hydroxo species has been prepared by treating an aqueous acetone solution of $[cpMo(NO)I_2]_2$ with AgY (1:2); in CH_2Cl_2 solution the Lewis acid-base adducts [cpM(NO)I].AgY form and precipitate in high yields for both M = W and Mo. These adducts react with the donor solvents in which they dissolve, in MeCN $[cp_2M(NO)(MeCN)]^+$ is formed and in aqueous acetone the trimetallooxonium salt is obtained. In none of the solvents investigated do the AgY salts transform $[cp_2Mo(NO)I]$ to $[cp_2Mo(NO)]^+$, this cation only being formed in low yield when excess $AlCl_3$ in CH_2Cl_2 is used as the iodide-abstracting reagent [123].

cis-$[M(R_2dtc)_2(NO)_2]$ complexes (M = Mo or W, R = Me, Et, Pr^i, or Bu) undergo a reversible one electron reduction to give the corresponding radical anion $[M(R_2dtc)_2(NO)_2]^{1-}$. EPR studies have shown that the unpaired electron is delocalized over both nitrosyl groups, but no metal hyperfine couplings were observed. Analysis of EPR spectra of frozen solutions of $[Mo(Et_2dtc)_2(^{15}NO)_2]^{1-}$ and $[Mo(Et_2dtc)_2(NO)_2]^{1-}$ has yielded anisotropic g and nitrogen hyperfine tensors for these complexes. In addition, the results demonstrate that the angle between the NO vectors remains essentially unchanged upon reduction of $[Mo(Et_2dtc)_2(NO)_2]$ [124].

The electrochemical behaviour of complexes of the type $[Mo(NO)_2Cl_2I_2]$ and $[Mo(NO)Cl_3I_2]$, which serve as catalyst precursors of olefin metathesis reactions, has been investigated. The localization of the odd electron in the one-electron reduction products has been determined by EPR spectroscopy. The mononitrosyl complexes containing the core $\{Mo(NO)\}^4$ are reduced at a more positive potential than the dinitrosyl complexes with the $\{Mo(NO)\}^6$ core. In the reduction of the former complexes, the electrons are accepted into a MO having predominantly metal *d*-character whilst, with the latter class of complexes, the electrons accepted during the reduction are accommodated in a π^*-NO based MO. A comparison of the electrochemical results with the catalytic activity of these complexes shows that the ability of the precursor complexes to form the catalytically active species depends on their substitution lability rather than their redox properties [125].

1.8 COMPLEXES WITH MULTIPLE METAL-METAL BONDS

1.8.1 Complexes with triple bonds

The preparation and characterization of the complexes of $[MoX_2R_4]$ (X = Br, Me, $OCHMe_2$, $OCMe_3$, or NMe_2; R = CH_2SiMe_3) have been reported. The pattern of ligand substitution may be 1,1-$X_2RMo{\equiv}MoR_3$ or 1,2-, $XR_2Mo{\equiv}MoR_2X$ depending upon the nature of X and the preparative route. The 1,1- and 1,2-$[Mo_2X_2R_4]$ compounds do not isomerize, demonstrating the existence of a high kinetic barrier to R- and X-group transfer between adjacent molybdenum atoms, but alkyl group transfer may occur during the substitution reaction. The reaction of 1,2-$[Mo_2Br_2R_4]$ with $Li[NMe_2]$ yields 1,1-$[Mo_2(NMe_2)_2R_4]$, whereas the reaction of 1,2-$[Mo_2Br_2R_4]$ with $HNMe_2$ affords 1,2-$[Mo_2(NMe_2)_2R_4]$. The formation of one isomer of $[Mo_2(NMe_2)_2R_4]$ must occur by kinetic control.

Variable temperature ^1H NMR spectroscopic studies for 1,1- and 1,2-$[Mo_2(NMe_2)_2R_4]$ compounds have provided the first observation of rotation about the $Mo{\equiv}Mo$ bond. The energy barriers to rotation are reconcilable with steric restraints. By contrast, the barriers to rotation about Mo-N bonds in the 1,1- and 1,2-$[Mo_2(NMe_2)_2R_4]$ compounds are $\Delta G^*/kJmol^{-1} = 48 \pm 2$ and 63 ± 2, respectively, and the difference has been rationalised in terms of electronic factors.

The structure of 1,2-$[Mo_2(OCMe_3)_2R_4]$, determined by a single crystal X-ray diffraction study, has revealed a staggered ethane-like (C_{2h}) *anti*-MoO_2C_4 central skeleton [126].

The neutral compounds $[M(bipy)_3]$ and $[M(phen)_3]$ can be made conveniently and in high yield by sodium amalgam reduction of the metal chlorides, for M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, or Re, or their adducts, in thf containing bipy or phen. Also the Cr and Mo compounds can be obtained from the dimeric acetates $[M_2(CO_2Me)_4]$ [127].

1.8.2 *Complexes with quadruple bonds*

Evidence for a *trans* influence in $[(Me_3CCO_2)_2Mo_2R_2(PMe_2Et)_2]$ (R = CH_2CMe_3, CH_2SiMe_3, Me, Cl, Br, I, $N(CHMe_2)_2$ or $OSiMe_3$) and similar compounds has been obtained from X-ray crystallography and ^{31}P-^{31}P coupling constants. The order deduced, alkyl > halide > amide > siloxy, agrees with results available from platinum(II) square planar chemistry. The kinetic data for phosphine exchange reactions of these complexes are also indicative of a *trans* effect, with rates for R = alkyl being about 10^2 times faster than the corresponding siloxides [128].

Addition of CO_2 or 1,3-diaryltriazines to 1,2-$[Mo_2R_2(NMe_2)_4]$ (R = Me or CH_2SiMe_3) compounds yields the corresponding $[Mo_2R_2(O_2CNMe_2)_4]$ or $[Mo_2R_2(NMe_2)_2(ArN_3Ar)_2]$ compound with retention of the Mo-Mo triple bond, whereas related reactions, for R = Et, $CHMe_2$ or *n*-, *sec*-, or *tert*-C_4H_9, yield Mo-Mo quadruply bonded compounds $[Mo_2(O_2CNMe_2)_4]$ and $[Mo_2(ArN_3Ar)_4]$ by reductive elimination (*i.e.* alkyl group disproportionation) of alkene and alkane. Observations of the products of reactions of CO_2 with deuterium labelled compounds have established that reductive elimination occurs by an intramolecular reaction, in which a β-hydrogen atom of one Et-ligand is transferred to the α-carbon of the other Et or alkyl group. The insertion of CO_2 into Mo-NMe_2 bonds proceeds *via* an amine-catalyzed sequence: $Me_2NH + CO_2 \longrightarrow Me_2CO_2H$; Mo-$NMe_2$ + $HOOCNMe_2 \longrightarrow MoO_2CNMe_2 + HNMe_2$. The replacement of NMe_2 groups by either O_2CNMe_2 or ArN_3Ar ligands involves a protolysis which is common for metal dimethylamides. In the present instance, the reactions involving $[Mo_2(Et_2)_4(NMe_2)_4]$ are considered to proceed through intermediates of the formula $[Mo_2Et_2(NMe_2)_2L_2]$ (L = O_2CNMe_2 or ArN_3Ar (with Ar = Ph or 4-tolyl). The carbamato intermediate has only been detected by ^1H NMR studies, but the 4-tolyltriazenido compound has been isolated and its crystal structure determined. The molecule has a virtual, but not crystallographically imposed C_2 symmetry and the $Mo\equiv Mo$ bond is bridged by *cis*-triazenido ligands, which afford sufficient flexibility to allow a noneclipsed geometry with respect to each half of the molecule. Each molybdenum is coordinated to three nitrogen atoms and one carbon atom which lie roughly in a plane [129].

The homologous compounds $[M_2Cl_4(PR_3)_4]$ (M = Mo or W) have been used in a combined theoretical and experimental study to compare the electronic structures of quadruple bonds between Mo atoms and between W atoms. The theoretical work has been carried out by the SCF-X_α-SW method on the model systems with R = H, but in all other respects, using the experimentally measured bond lengths and angles for the compounds with R = CH_3. Relativistic corrections have been made for both compounds, but were significant only for tungsten. The PMe_3 compounds were used for HeI and HeII gas phase PES. For both PMe_3 compounds the highest filled orbital is considered to be the M-M δ-bonding orbital and the measured ionization energies are 6.44 and 5.81 eV for the Mo and W compounds, respectively. The next observed ionization at 7.70 eV (Mo) and 7.05, 7.45 eV (W) has been assigned to the M-M π-bonding orbitals. The spin-orbit splitting of the W-W π-peak shows features attributed to mixing of σ,π and δ components by the spin-orbit coupling operator. Other ionizations have been assigned to M-P bonding electrons at 8.41 eV (Mo) and 8.36 eV (W). The W-W bonding appears to be weaker than the Mo-Mo bonding and in general the results of this study are consistent with the greater reactivity (*i.e.* lower chemical stability) of the W-W quadruple bond as compared to the Mo-Mo quadruple bond [130].

1.9 ^{95}Mo NMR SPECTROSCOPY

^{95}Mo NMR has become an increasingly useful tool in the characterization of molybdenum complexes [131-151]. The ^{95}Mo nucleus is preferred to the ^{97}Mo nucleus because of its higher abundance (15.72% *vs.* 9.46%) and smaller quadruple moment (0.12 *vs.* 1.1). The chemical shift range for ^{95}Mo spans 7000 p.p.m. so far [144]. ^{95}Mo NMR is a sensitive probe for the coordination sphere of molybdenum and can distinguish between diastereomers. Because of overlapping ranges no general information about the oxidation state of the Mo can be deduced from the ^{95}Mo NMR chemical shift alone.

The ^{95}Mo NMR spectra of a series of complexes [Mo(CO)$_{6-n}$L$_n$] (n = 1-3, L = N, P, As or Sb donor ligand) have been determined. The relative chemical shifts, which occur in the range -1093 to -1867 p.p.m. have been explained in terms of a symmetry modified ΔE contribution to the Ramsey formalism [147]. The systematic study of these complexes shows that replacement of carbonyl groups of [Mo(CO)$_6$] by other ligands leads generally to a downfield chemical shift, with the greatest shift occuring for acetonitrile and piperidine. An upfield trend in chemical shift in the order PPh$_3$< AsPh$_3$< SbPh$_3$ was found for both the [Mo(CO)$_5$L] and [Mo(CO)$_4$L$_2$] series. Coupling constants are higher for the species containing P(OPh)$_3$ as ligand than those involving phosphine ligands [143]. Another study of these [Mo(CO)$_{6-n}$L$_n$) complexes has been accomplished for L = P(OCH$_3$)$_3$ n = 1-5; L = P(OC$_2$H$_5$)$_3$ n = 1-3; L = PF$_3$ n = 1, including isomers (*cis*, *trans*, *fac*, *mes*) [149].

[cp(CO)$_2$LMoHgX] (L = CO, P(OMe)$_3$, or PPh$_3$; X = Cl, Br, I, S$_2$COEt, S$_2$P(OEt)$_2$, S$_2$CNEt$_2$ or Mo(CO)$_3$cp) have been studied by multinuclear NMR spectroscopy. The chemical shifts for the ^{95}Mo resonances have been found in the range from -1706 to -1939 p.p.m. [151]. A systematic study has been made of the effects of substituent-induced chemical shifts in [cp(CO)$_3$Mo(CH$_2$C$_6$H$_4$R)] compounds. The cp(CO)$_3$MoCH$_2$- group is a reasonably strong resonance donor (s_r = -0.21) and weak inductive donor (s_i = -0.07) and the ^{95}Mo chemical shifts are extremely sensitive to the effects of distant substituents (range *ca.* 40 p.p.m.). Since the shift correlates with substituent constants in this series, it is suggested that the chemical shift is controlled by the paramagnetic term for this spin 5/2 nucleus [148].

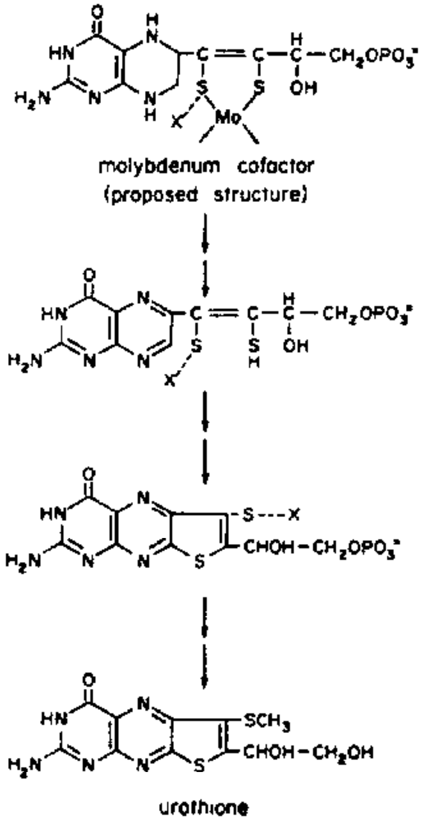
^{95}Mo NMR signals of the molybdenum(IV)-aquo ion in 4-toluenesulphonic and methylsulphonic acid, and those of molybdenum(IV) complexes containing oxalate, EDTA, and methyliminodiacetate ligands whose solid structures are based on the {Mo$_3$O$_4$}$^{4+}$ cluster, fall in the narrow chemical shift range of 990 - 1162 p.p.m. This observation indicates that the ^{95}Mo nucleus is in a similar chemical environment in each of the species examined and, taken with other evidence, allows formulation of the Mo(IV) aquo ion as [Mo$_3$O$_4$(H$_2$O)$_9$]$^{4+}$. In hydrochloric acid media, two ^{95}Mo resonances are detected in the above range. For the methylsulphonic acid, hydrochloric acid, and EDTA systems, additional resonances attributed to $\{Mo^{V}{}_2O_4\}^{2+}$-based species appeared over a period of several days [146].

^{95}Mo NMR spectra for two related series of six-coordinate dioxomolybdenum(VI) complexes with tridentate Schiff bases have been obtained. The complexes show chemical shifts of +26 and +47 p.p.m., with linewidths from 160 to 1170 Hz. The chemical shifts reflect the fine tuning of the electronic effects exerted on the molybdenum by the tridentate ligand by changing the substituent on the salicylaldehyde moiety. The observed trend is slightly different in each series with the complex having an electron-donating methoxy substituent being least shielded [150]. Various trioxo-molybdenum(VI) complexes have also been studied by ^{95}Mo NMR spectroscopy. The shifts of these complexes were found to be identical within experimental error [144].

1.10 MOLYBDOENZYMES

The molybdenum-containing cofactor, common to a variety of molybdoenzymes, has been shown to contain a novel pterin. The pterin has been isolated from sulphite oxidase from several sources, xanthine-oxidizing enzymes from milk and chicken liver, and nitrate reductase of *Chlorella vulgaris* after denaturation of the proteins in the presence of I_2. Investigation of the anionic nature of the isolated pterin has revealed that it is a monophosphate ester susceptible to cleavage by alkaline phosphatase. Quantitative analyses show that one molecule of the pterin phosphate is associated with each molybdenum atom in sulphite oxidase. Studies to date have shown that the pterin is present in a reduced form in sulphite oxidase and xanthine dehydrogenase, and that *in situ* oxidation of the pterin leads to inactivation of sulphite oxidase [152].

The sulphur-containing pterin, urothione, which has been characterized earlier [153], has been isolated from human urine. The permanganate oxidation product of urothione has been described as pterin-6-carboxylic-7-sulphonic acid and is identical to the pterin obtained from the cofactor, when it is isolated aerobically in the absence of I_2 or KI. Because urothione also contains a periodo-sensitive glycol substituent, a structural relationship has been suggested (10). The finding that urine samples from patients deficient in the molybdenum cofactor are devoid of urothione demonstrates a clear metabolic link between the two molecules [154].



(10)

The EPR spectra of molybdenum(V) centres in enzymes and in chemical complexes have been classified in two types of plotting (g_3-g_1) as a function of g_3. Type 1 has a wider g-anisotropy than Type 2. Most of the EPR signals of the native molybodenzymes fall within Type 2, whereas many molybdenum(V) complexes with one or two thiolate ligands and inactivated molybodenzymes are classified as Type 1 or Type 2'. Comparison of the EPR parameters of molybdenum(V) complexes whose structures are known suggested that Type 1 complexes have an octahedral structure and Type 2 complexes have a square pyramidal structure. Type 1 complexes seem to be more strongly affected by the delocalisation of the unpaired electron (coordination donor effect) than Type 2 [155].

1.10.1 Xanthine oxidase

Xanthine oxidase is the most widely studied molybdenum enzyme. The effect of using ^{17}O labelled water (24-50% enriched) as solvent on the molybdenum(V) EPR spectra of different reduced forms of xanthine oxidase has been investigated. All the molybdenum(V) EPR signals were affected and the number of coupled oxygen atoms may be determined by an estimation of the fraction of the spectrum that remains unchanged by the isotope at a known enrichment. For a species having two coupled oxygen atoms, the use of two different isotope enrichments permits elimination of the contribution of the two singly substituted species. These studies have led to the conclusion that not only the strength of the hyperfine coupling of oxygen ligands of molybdenum, but also their number and exchangeability with the solvent, vary from one reduced form of the enzyme to another. The inhibited species from active xanthine oxidase has two weakly coupled oxygens ($A(^{17}O)_{av}$ = 0.1-0.2 mT) that do not exchange with the solvent. A cyclic structure is proposed for this species, in which two oxygen ligands of molybdenum are bonded to the carbon of the formaldehyde, or other alcohol or aldehyde molecule, that reacted in producing the EPR active species [156].

EPR spectroscopy has also been used to examine each of the six possible pairwise interactions between electron-carrying centres in the xanthine oxidase molecule. In addition to the Mo-$(Fe/S)_I$ magnetic interaction, positive evidence has been obtained for interactions between $(Fe/S)_I$ and $(Fe/S)_{II}$, FAD and $(Fe/S)_{II}$, and FAD and $(Fe/S)_I$. No interaction has been detected between the Mo and $(Fe/S)_{II}$ or between FAD and Mo. The following approximate distances between the electron carrying prosthetic groups of milk xanthine oxidase have been estimated: Mo-$(Fe/S)_I$, 11A; $(Fe/S)_I$-$(Fe/S)_{II}$, 15A; FAD-$(Fe/S)_I$, 16A; FAD-$(Fe/S)_{II}$, 16A [157].

Potentiometric titrations have been performed for native and desulpho milk xanthine oxidase at 298 K a pH range of 5.7-10.9. The potentials of the FAD and Fe/S centres, as well as the molybdenum centre, of xanthine oxidase were examined as a function of the pH. Protonation accompanies Mo^{VI} reduction to both the Mo^V and Mo^{IV} states. The Mo^V centre remains protonated from pH 5.7 to 10.9. The intrinsic electron affinity of the molybdenum centre is not significantly altered when a terminal sulphur ligand of the Mo was replaced by oxygen, even though the enzyme was rendered nonfunctional. However, the affinity for protons of the Mo^{IV} state was substantially different in the two forms. It is this effect which makes the observed Mo^V/Mo^{IV} redox potential so negative at alkaline pH in the desulpho enzyme. Evidence has also been obtained for a specifically tight binding of uric acid (the product of xanthine oxidation) to the Mo^{IV} oxidation state of the native enzyme. Thus, the order of reduction of various centres can be altered by manipulation of pH, and uric acid can significantly shift the potential for the enzymic Mo^V/Mo^{IV} couple, whilst not affecting that for the Mo^{VI}/Mo^V couple [158]. Another series of potentiometric titrations has been carried out for xanthine oxidase at room temperature from pH 6.1-9.9. The reduction of the two Fe/S centres have been monitored by CD, and that of the FAD and Mo centres by EPR. The Fe/S centres have a protonable group whose pK_a changes with the reduction state. The flavin and the molybdenum centres show varying behaviour but, in all cases, electron addition is accompanied by protonation. The sequence for FAD is reduction, protonation, reduction, protonation. For the centre which gives rise to the "rapid" molybdenum(V) EPR signal, the sequence is protonation, reduction, protonation, and reduction. For the centre which gives rise to the "slow" molybdenum(V) EPR signal, the sequence is protonation, reduction, and protonation. The behaviour of both of these centres have significant temperature dependence [159].

The stoichiometry of electron addition to xanthine oxidase has been reexamined by reductive titration with sodium dithionite, and anaerobic reoxidation with cytochrome *c* and phenanzine methosulphate of the dithionite- or photoreduced enzyme. 8.0 ± 0.1 reducing equivalents are taken up (or given up) by the enzyme, a value two equivalents greater than expected on the basis of the known oxidation/reduction centres in the enzyme. The reaction of reduced xanthine oxidase with (^{14}C)iodoacetate indicates that, in the reduced form of the enzyme, additional cysteine residues are available for the reaction. These results, in conjunction with the observation that the reaction of the oxidized enzyme with sulphite results in the appearance of an additional equivalent of thiol capable of reacting with 5,5'-dithiobis-(2-nitrobenzoic acid) or iodoacetate, indicate the presence of a disulphide linkage in the enzyme that can be reduced chemically by dithionite or photochemically by employing EDTA and 5-deazaflavin. However, neither xanthine nor lumazine is capable of reducing this oxidation/reduction centre, suggesting that the disulphide does not play a role in the catalytic reactions of the enzyme. These results resolve discrepancies in the literature which indicated that greater than six reducing equivalents were consistently needed to bring about the complete reduction of xanthine oxidase [160].

1.10.2 Sulphite oxidase

Reduction of sulphite oxidase by sulphite at low pH values in *mes*(4-morpholine-ethanesulphonic acid) buffer has given rise to a new molybdenum(V) EPR spectrum which is different from that obtained by photoreduction of the enzyme in the same medium. The spectrum is attributed to a sulphite complex of the enzyme, showing *g*-values of 2.000, 1.972 and 1.963. The complex is analogous to that with the inhibitor phosphate, in that it gives rise to no observable hyperfine coupling of the molybdenum(V) with exchangeable protons (161).

1.10.3 Nitrate reductase

The molybdenum-containing cofactor content of cultured cells in *Nicotiana* *tabacum* has been estimated by the ability of the acid- and heat-treated extract to restore NADPH-nitrate reductase activity of *Neurospora crassa*. Addition of nitrate to wild-type cells grown on amino acids caused a rapid increase in cofactor activity, concomitant with the induction of NADPH-nitrate reductase activity [162].

1.10.4 *Aldehyde oxidase*

The molybdenum(V) EPR spectra from reduced forms of aldehyde oxidase have been obtained and compared with those from xanthine oxidase. The inhibited and desulpho-inhibited signals from aldehyde oxidase have been fully characterized, and parameters were obtained with the help of computer simulations. The value of these parameter differed slightly, but significantly, from the corresponding parameters for the xanthine oxidase signals. "Rapid" Type-1 and Type-2 and "slow" signals have been obtained from aldehyde oxidase, but were not fully characterized. From the general similarities of the molybdenum(V) EPR signals from the two enzymes, it is concluded that the ligands of the molybdenum must be identical and that the overall coordination geometries must be very similar. The striking differences in substrate specificity must relate primarily to the structural differences in a part of the active centre concerned with substrate binding and not involving the catalytically important Mo site [163].

1.10.5 *Nitrogenase*

The 289 amino acid-residue sequence of the Fe-protein from the *Azotobacter vinelandii* nitrogenase complex has been determined using peptides derived from trypsin, *Staphylococcus aureus* protease and cyanogen bromide cleavage [164].

The sulphur content of *N*-methylformamide solutions of the FeMo-cofactor from *Clostridium pasteurianum* nitrogenase has been determined to be 11.9 ± 0.9 mole per mole of molybdenum. This value was determined radiochemically, using FeMo-cofactor isolated from the FeMo-protein from bacteria grown on $^{35}SO_4$. A total of 3.2 ± 0.2 mole of sulphur per mole of molybdenum was found to be present in cysteine and methionine, probably arising from contaminating proteins not intrinsic to the cofactor. Combined with other evidence, these results lead to an updated stoichiometry of $MoFe_6S_{8-9}$, not $MoFe_6S_4$ as previously thought, for the FeMo-cofactor [165].

The crystalline FeMo-protein of the *Azotobacter vinelandii* nitrogenase has been denatured by exposure to air or oxygen, but not degraded, to release Mo- and Fe-containing fragments. The FeMo-cofactor extracted from the protein reactivated the denatured protein and partially or completely restored its C_2H_2-reducing activity. The efficiency of reactivation decreased with increasing exposure of the protein to air or oxygen. Oxygen-exposed cofactor did not reactivate the denatured Mo-Fe protein, indicating that the FeMo-cofactor is probably the first component denatured upon air- or oxygen-exposure of the nitrogenase protein [166].

Mechanisms of nitrogenase-catalyzed reductions have been explained by using a dicubane cluster model and involving the coordination of substrates with terminal triple bonds [167].

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