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2. MOLYBDENUM AND TUNGSTEN[†]

R. COLTON

CONTENTS

INTRODUCTION

The review on molybdenum and tungsten chemistry this year deals with the inorganic and coordination chemistry of the elements which was cited in Chemical Abstracts, Volumes 100 and 101. Thus most of the work published in 1984 and some published towards the end of 1983 will be reviewed. Organometallic chemistry, including carbonyl chemistry, is not formally included in the review, but reference is made to some papers of general interest.

[†] NO REPRINTS AVAILABLE.

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The arrangement of the material is similar to that in the review for last year. The primary criterion for ordering the presentation of material is oxidation state of the metals and within each oxidation state the order is determined by the type of donor atoms. With mixed ligand complexes the compounds are described in terms of the dominant ligand. The symbol M will be used where identical comments apply to both Mo and W.

2.1 MOLYBDENUM(VI) AND TUNGSTEN(VI)

2.1.1 Halides and halo complexes

The comparative redox properties of MoF_6, WF_6 (and UF_6) in MeCN at 298K have been compared with those of other redox couples using the electrochemical technique of cyclic voltammetry and also by carrying out redox reactions [1]. The order of oxidizing ability was found to be $UF_6 > MoF_6 > NO^+ >$ solvated $Cu^{2+} > WF_6$. The products of redox reactions, for example oxidation of Cu(I) by WF_6, were identified by spectroscopic methods, especially Raman spectroscopy.

A number of reactions of WF_6 have been examined [2] using ^{19}F NMR spectroscopy. Some typical reactions are

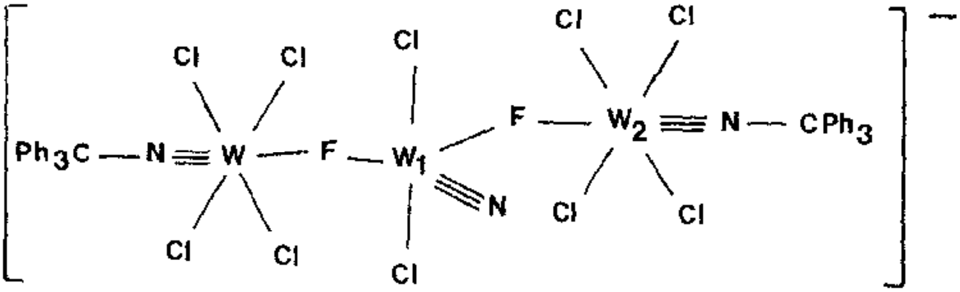
$$WF_6 + [WOF_6]^{2-} \longrightarrow [WOF_5]^- + [WF_7]^-$$

$$WF_6 + 2NEt_3 + H_2O\ (1:2:1) \longrightarrow [WOF_6]^{2-} + [WOF_5]^- + [WF_7]^-$$

$$[WOF_6]^{2-} + H_2O/NEt_3 \longrightarrow [WO_2F_4]^{2-}$$

The structure of WSF_4 in the gas phase has been determined by electron diffraction [3]. The data is consistent with a square pyramidal stereochemistry in which the tungsten atom is displaced out of the plane of the fluorines towards the sulphur atom. Bond distances are W=S = 2.104(7) and W-F = 1.847(3)Å. As reported in the review last year, WSF_4 in the solid state adopts a structure consisting of square pyramidal WSF_4 units linked by long W-F interactions *trans* to sulphur, so the electron diffraction data is nicely consistent with the solid state structure.

A remarkable reaction between $(AsPh_4)[WNCl_4]$ and triphenyl carbonium tetrafluoroborate, $(CPh_3)[BF_4]$, gave dark red crystals of $(CPh_3)[WNF_2Cl_2(Cl_4WNCPh_3)_2]$, and the structure of the anion is shown in (1). The anion can be regarded [4] as a distorted trigonal bipyramidal $[WNF_2Cl_2]^-$ unit coordinated to two molecules of Cl_4WNCPh_3, with these latter groups being generated by attack of $[CPh_3]^+$ on $[WNCl_4]^-$.



(1)

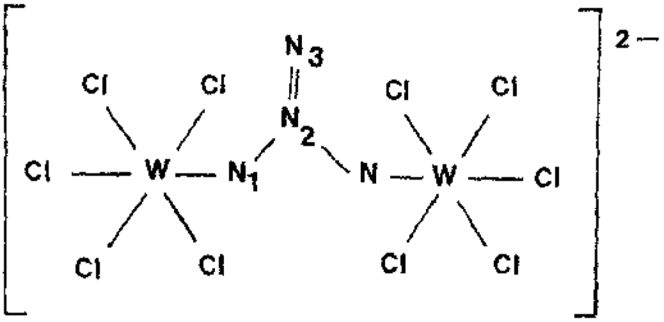
Bond distances are

W_1-N = 2.23(2) W_2-N = 1.67(3)
W_1-μF = 1.66(2) W_2-μF = 2.32(2)
W_1-Cl = 2.310(8) W_2-Cl = 2.311(5) - 2.368(9)Å
The angle at the bridging fluoro ligand is 163(2)°.

Partial thermolysis of $W(N_3)Cl_5$ (which gives rise to $WNCl_3$) in the presence of $AsPh_4Cl$ leads to the formation of the previously unknown tetraanionic isotetrazene bridging ligand according to the equation [5]

$$2AsPh_4Cl + W(N)Cl_3 + W(N_3)Cl_5 \longrightarrow (AsPh_4)[Cl_5W(\mu\text{-}N_4)WCl_5]$$

and the structure of the anion is shown in (2).



(2)

Bond distances are

$$W\text{-}N = 1.63(1)$$

$$W\text{-}Cl(\textit{trans}\ N) = 2.435\ (av) \qquad W\text{-}Cl(\textit{cis}\ N) = 2.232\ (av)$$

$$N_2\text{-}N_3 = 1.23(2) \qquad N_1\text{-}N_2 = 1.49\text{Å}\ (av)$$

The N_2-N_3 distance corresponds to a double bond, whilst that of N_1-N_2 is long for a single bond.

Reaction of WCl_6 with NO gave $WCl_3(NO)_4$ which on addition of donor ligands gave either $WCl_3(NO)L_2$ (L = PPh_3O, py) or $WCl_2(NO)_2L_2$ (L = PPh_3) [6]. In the presence of $EtAlCl_2$ all these tungsten nitrosyl complexes catalyzed the metathesis of pent-2-ene, but they showed a significantly lower activity than the corresponding molybdenum nitrosyl systems.

Somewhat surprisingly the reaction between *p*-tolyl azide and $MoCl_4(thf)_2$ formed an organoimido complex of Mo(VI)

$$MoCl_4(thf)_2 + p\text{-tolyl}N_3 \longrightarrow \textit{trans}\text{-}Mo(N\text{-}p\text{-tolyl})Cl_4(thf)] + N_2$$

A crystal structure determination revealed a short Mo-N bond length of 1.717(3)Å, suggesting considerable triple bond character and a very long Mo-O bond of 2.2343(27)A indicating a strong *trans* effect for the imido ligand. The Mo-Cl bond lengths are in the range 2.333-2.358Å [7]. The complex was reduced to Mo(V) compounds $Mo(N\text{-}p\text{-tolyl})Cl_3L_2$ with a variety of substrates (L = PPh_3, PEt_3; L_2 = bipy, dppe).

$WOBr_4$ is isostructural with $WOCl_4$, the structure in the solid state consisting of square pyramidal $WOBr_4$ units linked unsymmetrically via oxygen to form linear O-W-O-W chains [8]. Bond distances are W-O = 1.78(3) and 2.16(3) and W-Br = 2.444(2)Å.

Oxidation of $W_2(O^tBu)_6$ by iodine in toluene led to the isolation of *trans*-$WI_2(O^tBu)_4$ which has been fully characterized by an X-ray structural determination. Bond lengths are W-O = 1.840(4) and W-I = 2.28293(8)Å. This is the first W(VI)-I bond to be fully characterized and it is suggested by the authors that strong dative π-bonding from O to W (supported by the short W-O bond length) stabilizes the W-I bond [9].

2.1.2 Oxides, molybdates and tungstates

The standard molar enthalpy of formation of α-$MoO_3.H_2O$ at 298.15K has been redetermined by solution calorimetry to be $-(1037.8\pm0.9)KJmol^{-1}$ [10]. The molar heat capacity of MoO_3 has been measured over the temperature range 350-950K by adiabatic scanning calorimetry. Two heat capacity anomalies were detected at

808K and 857K with molar enthalpy changes of (88±21) and (60±36)$KJmol^{-1}$ respectively. The origin of these anomalies was thought to be slight movements of the distorted MoO_6 octahedra in the crystal lattice [11]. The laser Raman spectrum of solid MoO_3 has been observed and a normal coordinate analysis was carried out on the basis of C_{3v} symmetry [12]. The fundamental frequencies are A_1 814 and 282cm^{-1} and E_1 993 and 335cm^{-1}.

$MoO_3.H_2O$ reacted with refluxing methanol to give $Mo_2O_5(OMe)_2$, whereas reaction at 0°C gave $Mo_2O_5(OMe)_2.2MeOH$ which lost its methanol on heating. Reaction of either compound with water gave $MoO_3.0.5H_2O$ (identified by X-ray powder diffraction) and this is probably the most convenient method of synthesis of this compound. Two types of methoxide were indicated by the IR spectrum (possibly terminal and bridging) but the structures of the complexes are unknown. Thermal decomposition of the alkoxides led to the formation of Mo(V) residues [13].

The reduction of polycrystalline MoO_3 by heat treatment has been followed using EPR spectroscopy [14]. Two types of reduction product were observed, the first appeared after 5 minutes at 703K in vacuum and has been identified as Mo(V) in a distorted pyramidal configuration. A second signal, which appeared after about 8 minutes heating and which increased in intensity with time was assigned to Mo(V) in a distorted octahedral configuration.

The standard molar enthalpies of formation of a series of molybdates $K_2Mo_nO_{(3n+1)}$ have been determined by solution calorimetry [15]. The values are: $n = 1$, $\Delta H_f^o = -(1504.3\pm1.5)$; $n = 2$, $\Delta H_f^o = -(2298.7\pm1.7)$; $n = 3$, $\Delta H_f^o = -(3054.3\pm2.0)$; $n = 4$, $\Delta H_f^o = -(3824.7\pm2.1)$; $n = 8$, $\Delta H_f^o = -(6824.2\pm3.4)KJmol^{-1}$.

Formation constants of protonated mononuclear and polynuclear tungstates have been determined in NaCl solution at 95-290°C, $I = 0.1$-$5.1M$ and $[W] = 10^{-2}$ to $5 \times 10^{-4}M$. The important species are $[WO_4]^{2-}$, $[HWO_4]^-$ and H_2WO_4 together with polymeric species. The proportions of monomeric and polymeric species varied according to conditions with monomeric species becoming more important at low tungsten concentration, high temperatures and high ionic strengths [16].

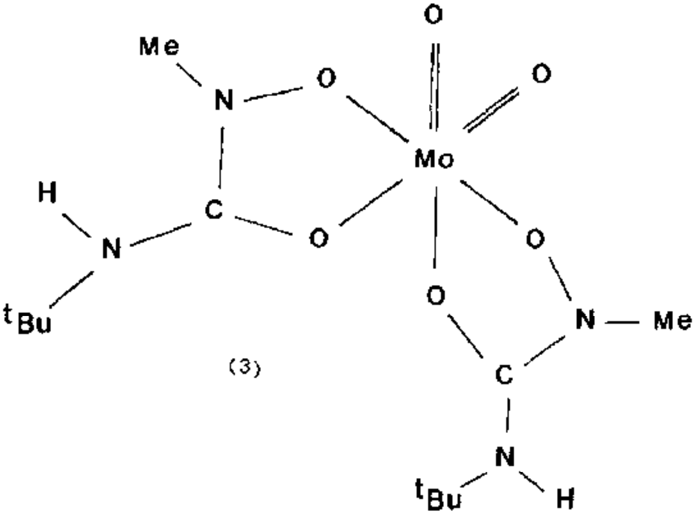
2.1.3 Monomeric oxo complexes

The crystal structure of $MoO(O_2)_2(bipy)$ has been determined and it is similar to that of the corresponding chromium complex. The stereochemistry about molybdenum is that of a distorted pentagonal bipyramid with the oxo group and one nitrogen of bipy being axial [17]. Bond distances are $M=O = 1.628(4)$, $Mo-N = 2.199(5)$ and $2.312(5)$, $Mo-O(O_2) = 1.912(5)$ and $1.953(4)$Å with the longer Mo-N bond axial and for the peroxo ligands the longer Mo-O bond is adjacent to the equatorial Mo-N bond.

Cis-dioxo and oxo-peroxo complexes of Mo(VI) with several organic ligands (bipy, 2,6-pyridinedicarboxylic acid etc) were distinguished by electrochemical techniques and the conversions dioxo $\rightleftarrows$ oxo-peroxo were accomplished electrochemically [18].

Complex formation between $[MoO_4]^{2-}$ and R,R-(+)-tartaric acid has been studied over a range of concentrations in aqueous and dmf solutions using ^{13}C and ^1H NMR spectroscopies. Four main species were identified, two (Mo:L = 1:1 and 1:2) are thought to contain ligands chelated through a carbonyl oxygen and an adjacent hydroxyl group, while the other two are thought to contain bridging tartaric acid moities [19].

The reaction of N-methylhydroxylamine with $[MoO_4]^{2-}$ in aqueous solution is known to give $MoO_2(MeNHO)_2$ containing two *O,N*-coordinated ligands. This complex has now been reacted with RCNO molecules (R = Et,Ph,^{t}Bu) to give $MoO_2[ON(Me)C(NHR)O]_2$ and the structure of the ^{t}Bu derivative is shown in (3).



(3)

Bond distances are [20]

$$Mo{=}O = 1.726(av)$$
$$Mo\text{-}O(N) = 1.98(1) \qquad Mo\text{-}O(C) = 2.23(1)\text{Å}$$

A Raman study of the interaction between the tungstate ion and thiomalic acid led to the conclusion that the major product was *cis*-WO_2L_2 with the ligand coordinated through sulphur and one of the oxygens of the adjacent carboxylate group [21].

A general treatment of the kinetics of the forward and reverse oxygen transfer reactions

$$Mo^{VI}O_2L_2 + X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mo^{IV}OL_2 + XO$$

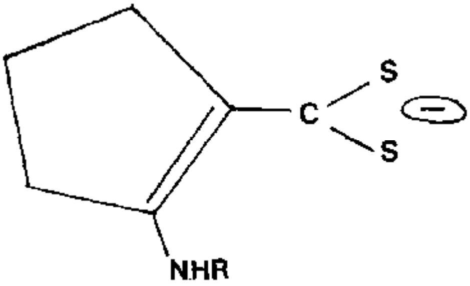
in the presence of the reversible dimerization equilibrium

$$Mo^{V}{}_2O_3L_4 \rightleftharpoons MoO_2L_2 + MoOL_2$$

has been developed and it allows the determination of rate constant data by spectrophotometric methods [22]. It has been applied to a number of systems with L = dtc and X = a phosphine. For the phosphines, the rate constant k_1 = 0.017(PPh_3), 0.23(PPh_2Et), 0.43($PPhEt_2$) increases monotonically with increasing phosphine neucleophilicity.

Complexes of 2-aminocyclopent-1-ene-1-carbodithioic acid and some *N*-alkylated derivatives (4) of Mo(VI) and Mo(V) have been prepared [23].

R = H,Et,Bu



(4)

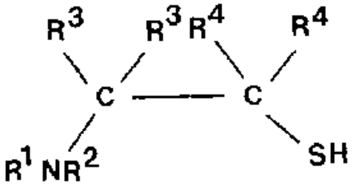
The complexes MoO_2L_2 are analogous to the corresponding $MoO_2(dtc)_2$ compounds and showed an irreversible one-electron reduction in dmf solution. Monomeric Mo(V) complexes of the type $MoOL_3$ were prepared from $[MoOCl_5]^{2-}$. These showed a quasi-reversible reduction to Mo(IV) but no product could be isolated using controlled potential electrolysis.

An electrochemical study has been made of *cis*-$MoO_2(O\text{-}N)_2$, *cis*-$MoOS(O\text{-}N)_2$ and *cis*-$MoS_2(O\text{-}N)_2$ (where HO-N = 1-hydroxypiperidine) and showed that reduction became progressively easier as oxygen was replaced by sulphur [24]. At room temperature and ordinary scan rates the reductions were irreversible, but cyclic voltammograms at low temperature and/or fast scan rates revealed a reversible one-electron reduction. The resulting monomeric Mo(V) complex quickly converted to an EPR silent species at room temperature.

The catalytic air oxidation of PPh_3 in dmf using $MoO_2(cys\text{-}OR)_2$ (cys-OR = *S*-deprotonated cysteine ester) has been investigated and it was found that the presence of water is essential for the reaction to proceed [25]. Studies with $H_2{}^{18}O$ showed the ^{18}O was incorporated into the PPh_3O formed, but a large excess of water stopped the catalytic activity. A monomeric Mo(V) species $MoO(OH)(cys\text{-}OR)_2$ is probably involved in the catalytic cycle.

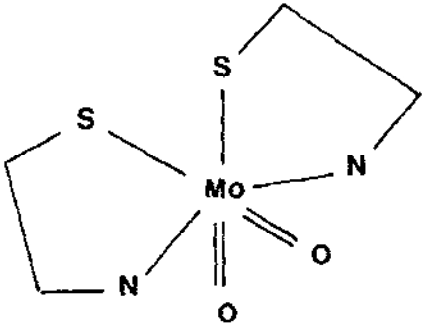
The crystal structure of $MoO_2(L\text{-}cys\text{-}OMe)_2$ (L-cys-OMe is the anion of the Me ester of L-cysteine) has been determined [26]. The stereochemistry about molybdenum is that of a distorted octahedron with *cis* oxo groups, *trans* thiolate groups and *cis* amino groups. Bond distances are Mo=O = 1.714(4), Mo-S = 2.414(2) and Mo-*N* = 2.375Å. The molecules crystallize with the configuration, but multinuclear (^1H, ^{13}C, ^{95}Mo) magnetic resonance studies show the presence of two isomers in solution which begin to interconvert on the NMR timescale at about 333K as shown by ^{95}Mo NMR studies.

A complete range of cysteamine methyl substituted derivatives of the type (5) have been synthesized where R^1-R^4 may be H or Me [27].



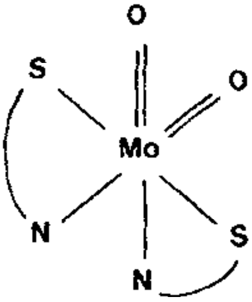
(5)

All the ligands react with $MoO_2(acac)_2$ to give MoO_2L_2 in which L is coordinated through nitrogen and the deprotonated sulphur. Some of these complexes adopt octahedral coordination about molybdenum, whilst others adopt a non-octahedral skew trapezoidal bipyramidal structure. ^1H and ^{17}O NMR studies suggest each complex retains the same structure in both solid and solution. Crystal structures of three examples with the non-octahedral structure are reported in another paper by the same group [28], the ligands used were $MeNCH_2CMe_2S^-$, $MeNHCMe_2CMe_2S^-$ and $Me_2NCH_2CMe_2S^-$. All the structures are similar and a generalized diagram is given in (6). The O-Mo-O angle varies between 120-122° and no group is *trans* to the oxo groups. The structure is best described as a skew trapezoidal bipyramid with short S-S contacts of 2.420-2.429Å.

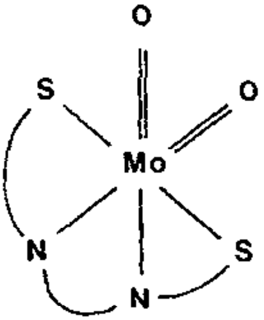


(6)

In an attempt to further investigate the steric factors which are thought to determine which configuration these six coordinate dioxo complexes adopt, the structures were determined of two complexes which were as similar as possible in the molybdenum coordination sphere [29]. The complexes chosen were $MoO_2[NH_2CMe_2CH_2S]_2$ and $MoO_2[SCMe_2CH_2NHCH_2CH_2NHCH_2CMe_2S]$ which give the same $O_2S_2N_2$ donor atom set as shown in (7) and (8).



(7)



(8)

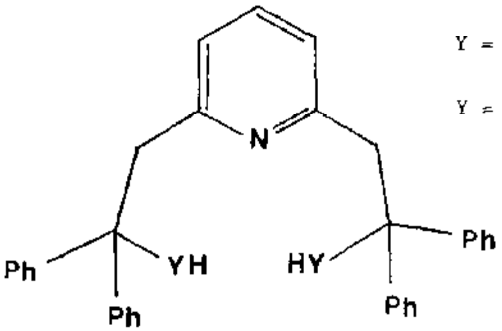
Bond distances are

Mo=O	1.705(3)	1.712(2)
Mo-N	2.325(3), 2.385(4)	2.316(3), 2.362(3)
Mo-S	2.402(1), 2.416(1)	2.404(1), 2.415(1)Å

Both complexes adopt very similar octahedral arrangements and small angular differences between them may be ascribed to the effects of the extra chelate ring. A major difference between these complexes and those described earlier with the skew structure is that the sulphur atoms are approximately *trans* in the octahedral complexes and approximately *cis* in the skew structures.

A series of complexes of the type MoO_2LD have been prepared where L is a tridentate *ONO* ligand derived from a Schiff base and D is a monodentate ligand such as H_2O, pyNO, thf, dmso. All the complexes contained *cis*-MoO_2 units and it was found that the separation between ν_{Mo-O}(sym) and ν_{Mo-O}(asym) was related to the basicity of L and the donor power of D [30].

Sulphite oxidase can transfer an oxygen atom from Mo(VI) to give Mo(IV) without this then combining with further Mo(VI) to give oxo-bridged Mo(V) dimers. In an attempt to mimic this feature of the action of this enzyme ligands of the type shown in (9) were prepared and reacted with $MoO_2(acac)_2$.



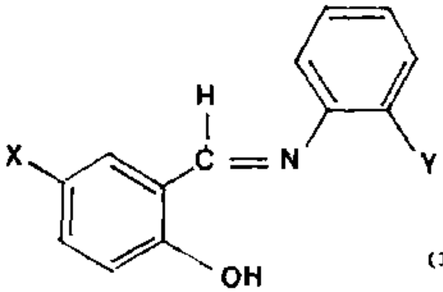
Y = O N-$(OH)_2$ anion $[N\text{-}O_2]^{2-}$

Y = S N-$(SH)_2$ anion $[N\text{-}S_2]^{2-}$

(9)

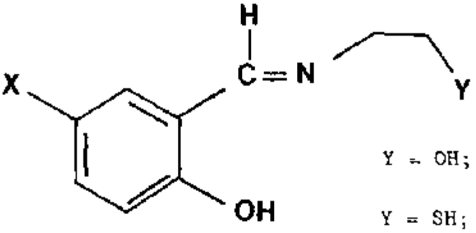
Reaction of N-$(OH)_2$ with $MoO_2(acac)_2$ in methanol gave $MoO_2(N\text{-}O_2)(MeOH)$ which on recrystallization from dmso gave $MoO_2(N\text{-}O_2)$(dmso). However reaction of N-$(SH)_2$ with $MoO_2(acac)_2$ gave $MoO_2(N\text{-}S_2)$ which in dmf did indeed transfer an oxygen to PPh_3 to yield $MoO(N\text{-}S_2)$(dmf) [31]. The molecular structure of $MoO_2(N\text{-}O_2)$(dmso) is distorted octahedral with *cis*-oxo ligands and dmso *trans* to one oxo group and the N-O_2 ligand is bonded in a *mer* configuration. Bond distances are Mo=O = 1.705(4)(av), Mo-O(dmso) = 2.382(3), Mo-O(N-O_2) = 1.902(3) and Mo-N = 2.417(4)Å. A crystal structure determination for $MoO_2(N\text{-}S_2)$ revealed a new stereochemistry for Mo(VI) as it is a trigonal bipyramid with the N-S_2 ligand occupying one axial and two equatorial positions. Bond distances are Mo=O = 1.694(4)(av), MO-S(eq) = 2.412(2), Mo-S(ax) = 2.419(2) and Mo-N = 2.244(7)Å.

A series of papers [32-34] have described a number of dioxomolybdenum(VI) compounds derived from the tridentate Schiff bases (10) and (11).



Y = OH; 5-X-SAP-H_2
Y = SH; 5-X-SSP-H_2
X = H,Br,Cl,NO_2,OMe

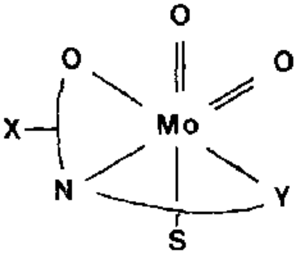
(10)



Y = OH; 5-X-SAE-H_2
Y = SH; 5-X-SSE-H_2
X = H,Br,Cl,NO_2,OMe

(11)

and the general structure of the complexes in solution is shown in (12).



(12)

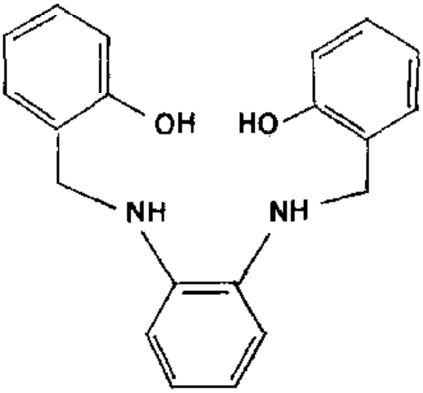
Electrochemical reduction of MoO_2L was irreversible, but although only E_p^{red} (rather than E^o) could be determined, there were correlations between E_p and the X-substituent and also with the substitution of sulphur for oxygen. The oxygen transfer reaction from these MoO_2L to $PEtPh_2$

$$MoO_2(5\text{-}XSSP) + PEtPh_2 \xrightarrow{k_1} MoO(5\text{-}XSSP) + OPEtPh_2$$

has been studied in dmf solution and for X = Br, Cl, H, OMe the rates showed a correlation with the irreversible reduction potentials. The applicable rate law for the oxygen transfer is

$$-d[MoO_2L]/dt = k_1[MoO_2L][PEtPh_2]$$

The ligand 2,2-[1,2-phenylenebis(iminomethylene)]bisphenol H_4L (13) reacted



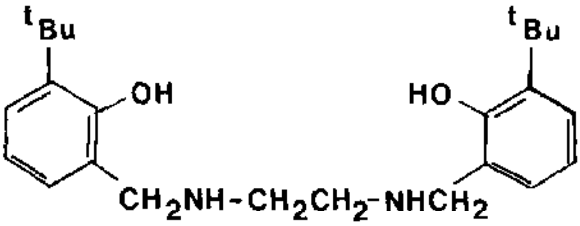
(13)

with $MoO_2(acac)_2$ to give *cis*-$MoO_2(H_2L)$ in which the ligand $[H_2L]^-$ was deprotonated at both phenol groups and acted as a tetradentate ligand. In contrast, reaction of H_4L with $[MoOBr_4]^-$ gave $Mo(HL)_2$ in which the ligand $[HL]^{3-}$ acted as a tridentate ligand through both nitrogens and one phenolic oxygen, with the other oxygen still protonated and uncoordinated. This was confirmed by a crystal structure analysis which showed the two coordinated oxygens *trans* and the equivalent nitrogen atoms on each ligand also mutually *trans*. Average bond distances were Mo-O = 1.975 and Mo-N = 2.023A [35].

Upon reduction, most *cis*-MoO_2L complexes give products which dimerize to give EPR silent oxo-bridged species

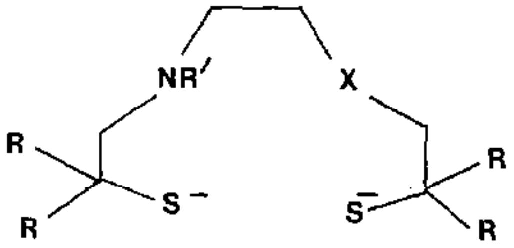
$$H_2O + 2MoO_2L \xrightarrow{2e^-} Mo_2O_3L_2 + 2OH^-$$

An attempt has been made to prevent the dimerization by using bulky groups. A series of *cis*-$Mo^{VI}O_2$ species were prepared with bidentate *NS*, tridentate *NOS* and tetradentate N_2O_2 and N_2S_2 ligands [36]. All gave irreversible one-electron reductions and the majority of the reduction products gave either no EPR signal or a very weak one. However, a few complexes with ^{t}Bu groups close to the *cis*-MoO_2 group did produce monomeric Mo(V) species upon reduction. The crystal structure of one of the Mo(VI) precursors with the deprotonated form of the ligand H_4L, shown in (14), was determined. The complex is octahedral with Mo=O = 1.708(6), Mo-O = 1.938(17) and Mo-N = 2.359(6)Å.



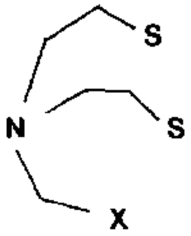
(14)

A number of linear and tripodal quadridentate ligands of the types (15) and (16) have been prepared and the complexes MoO_2L formed by their interaction



R = H,Me; R' = H,Me
X = NH,NMe,S

(15)



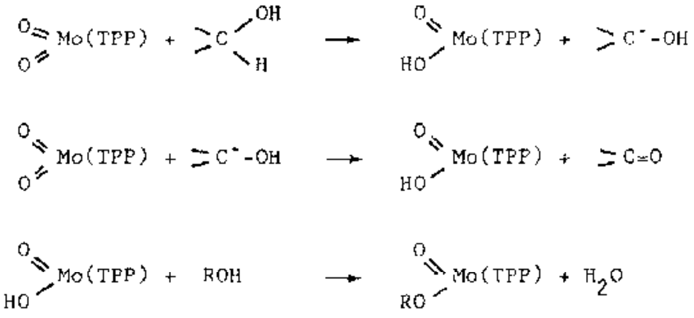
X = CH_2NH_2,CH_2NMe_2,CH_2NEt_2,
SMe,COO^-

(16)

with $MoO_2(acac)_2$ [37,38] and the structure of one of these has already been given in (8).

^{95}Mo NMR spectra have been measured for a series of *cis*-MoO_2LX complexes (L = $HB(3,5-Me_2pz)_3$; X = Cl,Br,NCS,OMe) and they show an inverse halogen effect, that is, the ^{95}Mo resonance of the bromo complex occurs at a higher frequency than that of the chloro complex (44ppm difference), although other types of Mo(VI) complex display a normal halogen dependence. The ^{95}Mo NMR spectra of other MoO_2L complexes were also reported (L = an N_2O_2, N_2S_2 or S_4 tetradentate ligand). These complexes are known to have distorted octahedral geometry and their chemical shifts cover a range of some 500ppm. There is however no simple correlation between structure and ^{95}Mo chemical shift [39].

Cis-$MoO_2(TPP)$ reacts with 2-propanol in the dark in the absence of oxygen at 60°C to give acetone (46%) and the molybdenum product was $OMo(O^iPr)(TPP)$. The stoichiometry of the reaction was always 1:2 so it does not proceed via a simple oxygen transfer which would be 1:1. In addition, MoO(TPP), which would be the product of such a transfer, was not detected and it was shown that this compound does not react with 2-propanol. The proposed mechanism is



However, it was shown that electrochemical reduction of $MoO_2(TPP)$ in the absence of chemical reducing agents did generate MoO(TPP) [40].

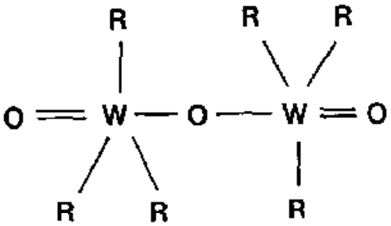
2.1.4 Dimeric and polymeric oxo complexes

Raman spectroscopic evidence has been reported for a dimeric oxo-bridged Mo(VI) species in acid solutions [41].

$Na_2[MoO_4]$ reacted with amino acids and pyridine carboxylic acids in HCl solution to give $Mo_2O_4(OH)_3L$ (HL = anthranilic and nicotinic acids, histidine), $Mo_2O_5(OH)L'$ (HL' = α and β-alanine, valine and *iso*-nicotinic acids) and $W_3O_8(OH)(H_2O)_4L''$ (HL" = nicotinic and *iso*-nicotinic acids, histidine). The compounds were characterized by IR and thermal stability studies [42].

Spectrophotometric and cryoscopic studies have indicated that three complexes exist in the Mo(VI)-lactic acid (H_2L) system at various pH's. They were isolated as their $[Co(en)_3]^{3+}$ salts and identified as $[MoO_2L_2]^{2-}$, $[Mo_2O_5L_2(H_2O)_2]^{2-}$ and $[Mo_2O_3(OH)_3L_2]^-$ [43].

Addition of excess water to $W(CCMe_3)(CH_2CMe_3)_3$ yielded air stable $W_2O_3(CH_2CMe_3)_6$. A crystal structure determination revealed a linear O-W-O-W-O system with trigonal bipyramidal coordination about W(VI) as shown in **(17)**.



$R = CH_2CMe_3$

(17)

Bond distances are

W=O = 1.689(3), 1.726(10)
W-μO = 1.923(1), 1.977(10)
W-C = 2.127(14), 2.141(9)Å

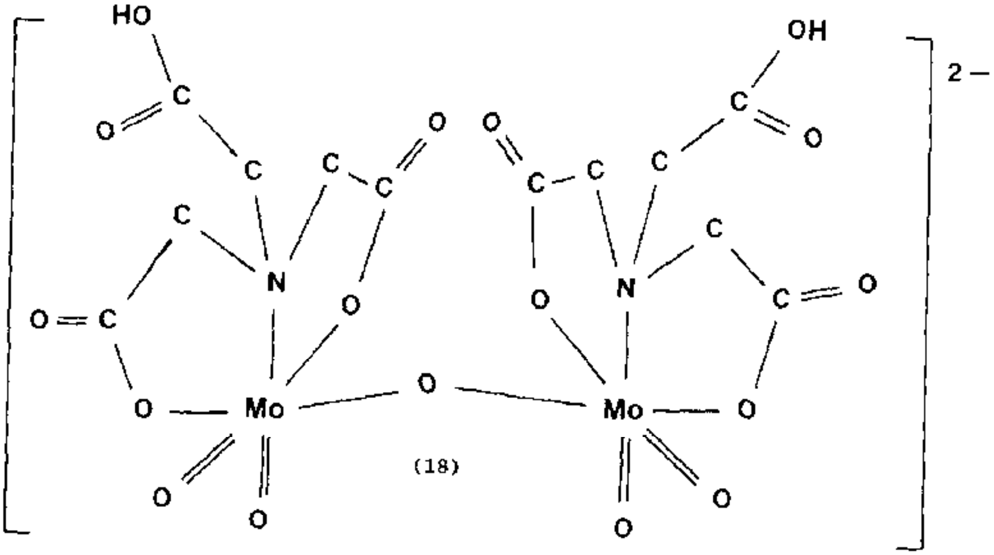
IR and Raman studies, including ^{18}O labelling, enabled identification of the stretching vibrations as follows (^{18}O values in parentheses) [44].

W=O (asym)	962(905) w	W=O (sym)	942(894) s
W-O-W (asym)	693(668) s	W-O-W (sym)	205cm^{-1}

Pyridine and nitrilotriacetic acid react with MoO_3 in aqueous solution at pH 7-8 to give $(pyH)_2[Mo_2O_5(ntaH)_2]$. A crystal structure determination showed a non-linear oxo bridge (167.0(2)°) with essentially octahedral coordination about molybdenum as shown in **(18)**. Bond distances are

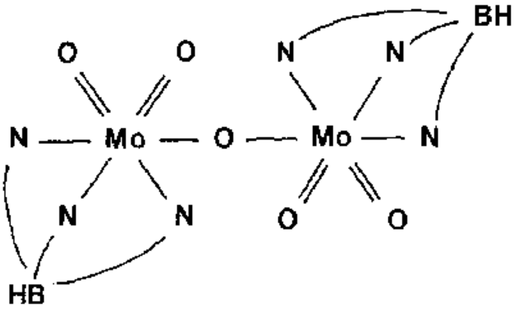
Mo=O = 1.683(3)-1.700(3)
Mo-μO = 1.876(6)
Mo-O(*trans* O_t) = 2.151(6)
Mo-O(*trans* O_b) = 2.072(2)
Mo-N = 2.413(3), 2.426(3)Å

The IR spectrum gave bands identified as stretches due to Mo=O at 945 and 920cm^{-1} and due to Mo_2O_2 at 783cm^{-1} [45].



(18)

Although the ligand $HB(3,5\text{-}Me_2pz)_3$ tends to stabilize monomeric complexes of molybdenum, a dinuclear species $Mo_2O_5[HB(3,5\text{-}Me_2pz)_3]_2$ has been isolated and its structure determined [46] to be that shown in (19) with the angle at the bridging oxygen being 167.1(2)°.



(19)

Bond distances are

Mo=O = 1.698(2)   Mo-μO = 1.889(1)

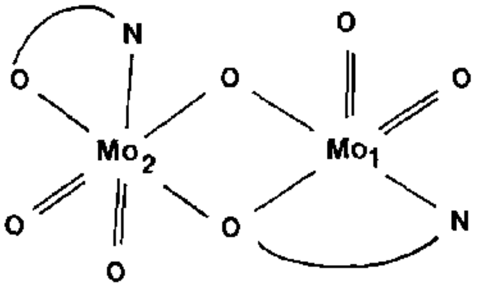
Mo-N(*trans*-μO) = 2.208(2)   Mo-N(*trans* oxo) = 2.316(2)Å

The crystal structure of a second form of the complex $Mo_3O_9(dmso)_4$ has been reported [47]. As with the polymorph described in the review for last year, the structure consists of chains containing the sequence $Mo_{tet}Mo_{oct}Mo_{oct}$ linked by single oxygen bridges, but the asymmetric unit is smaller and the angle at the bridging oxygen is $134.6(2)^{\circ}$ compared with the previously reported $145.1(4)^{\circ}$. This substance provides a nice example of the capacity of packing factors to determine the details of molecular geometry in crystals. Several insoluble polymeric complexes have been prepared by ligand exchange using solutions of MoO_3 in dmso [48]. Complexes isolated included $[MoO_3(pyNO)]_n$, $[MoO_3(py)]_n$ and $[MoO_3(Ph_3AsO)_{0.5}]_n$ whilst $[MoO_3(Ph_3AsO)]_n$ was prepared from $MoO_2(acac)_2$. Evidence concerning their structures was obtained from IR studies and X-ray powder diffractograms by comparison with 'white' and 'yellow' molybdic acids.

The thermal behaviour of $[Co(en)_3]^{3+}$ salts of monomeric $[MoO_2(OH)_2(ox)_2]^{4-}$ and the dimers $[Mo_2O_5(OH)_2(ox)_2]^{4-}$ and $[Mo_2O_5(OH)(ox)_2]^{3-}$ provided additional evidence for different types of linkage in the two dimers, supporting previous suggestions of a μ-oxo-μ-hydroxo double bridge arrangement in the monohydroxo complex [49].

The reactions of $MoO_2(acac)_2$ with aroylhydrazines, arylamines and aroylhydrazine Schiff bases have been described [50]. The products were characterized on the basis of IR studies and were formulated mainly as Mo(VI) dimers with two hydroxo bridges, although a few monomeric species were isolated.

The ligand 1-*n*-2-α-hydroxybenzylbenzimidazole (LH) reacted with MoO_2Cl_2 in dry EtOH to give $Mo_2O_5L_2$. X-ray analysis revealed an unusual asymmetric structure shown in (20).



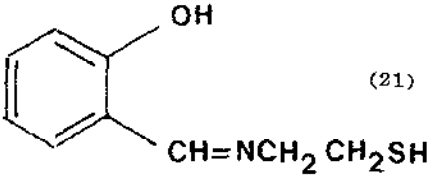
(20)

Bond distances are

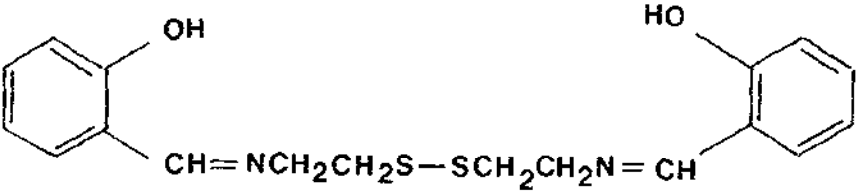
Mo_1-μO = 1.827(2) Mo_2-μO = 1.959(3)
Mo_1-μO(L) = 2.026(3) Mo_2-μO(L) = 2.358(3)
Mo_1=O = 1.694(3) Mo_2=O = 1.683(3), 1.699(3)
Mo_1-N = 2.141(3) Mo_2-N = 2.273(3)Å

The asymmetry arises because one of the bidentate ligands also uses its oxygen to coordinate to the second molybdenum so that one metal atom is five coordinate while the other is six coordinate. The structure is probably retained in solution since two ^{95}Mo NMR signals were observed [51].

Reaction of salicylaldehyde with 2-aminoethanethiol in methanol gave the products (21) and (22).

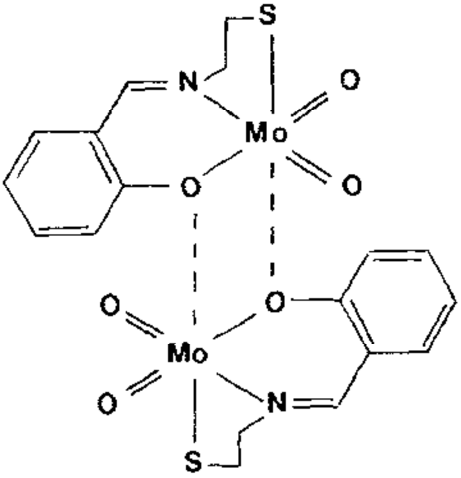


(21)



(22)

Reaction of (21) with $MoO_2(acac)_2$ gave a product which, on the basis of spectroscopic studies, was thought to have the structure (23) [52].



(23)

This compound forms 1:1 adducts with dmso, py etc. which cleave the phenoxide bridges to give monomeric *cis*-dioxo complexes [52]. Reaction of **(22)** with $MoO_2(acac)_2$ gave a product formulated as monomeric MoO_2L with the ligand acting as a tetradentate through N_2S_2.

A mixed molybdenum-tungsten tartrate complex has been identified using ^{13}C NMR spectroscopy. $[MoO_4]^{2-}$ with (+)-tartH_4 (1:1) in D_2O gave two singlets in the 13C NMR spectrum due to $\Delta,\Delta'[Mo_2O_4\{(+)\text{-tart}\}_2]^{4-}$ and the tungsten system gave a similar spectrum. A mixture of molybdate and tungstate gave close multiplets for each peak suggesting the presence of $[MoWO_4\{(+)\text{-tart}\}_2]^{4-}$ and the two homometallic species in approximately statistical proportions [53].

2.1.5 Complexes with oxygen donor ligands

It has been found that Mo(VI) alkylidynes containing electron withdrawing alkoxides of the type $Mo(CCMe_3)[OCMe_2(CF_3)]_3$ will catalytically metathesize dialkylacetylenes. It was suggested that earlier catalysts based on $Mo(CO)_6$ also involve a Mo(VI) alkylidyne species as the active catalyst [54]

2.1.6 Sulphides, thiomolybdates and thiotungstates

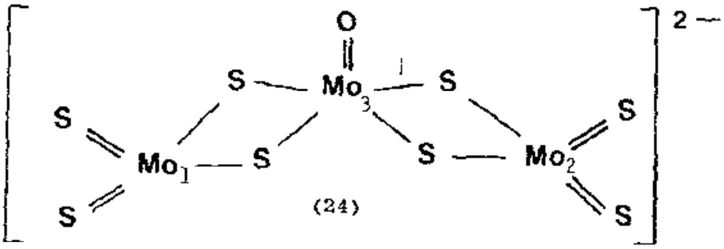
The structures of amorphous compounds of empirical formulae MoS_3 and $MoSe_3$ have been investigated using EXAFS [55]. Analysis of the metal EXAFS showed short metal-metal distances (Mo-Mo = 2.74; W-W = 2.79Å) as well as short S-S and Se-Se contacts. Although the structures could not be determined unambiguously, it was proposed that the compounds have a chain structure with dimeric $M_2(X^{2-})_4(X_2^{2-})$ repeating units (X = S,Se) with a triple bridge (one X^{2-} and one X_2^{2-}) between the metal atoms.

A simple preparation of good purity $Na_2[MoS_4]$ has been reported; it was made from the easily prepared $(NH_4)^+$ salt using aqueous NaOH at 0°C [56].

Molecular orbital studies have been carried out on $[MoS_4]^{2-}$ and $[Fe,Co(MoS_4)_2]^{n-}$ by the approximate, but parameter free, Fenske-Hall LCAO method. All the MO's of predominant *3d* character (Fe,Co) were found between the occupied orbitals on sulphur and the empty *4d* orbitals of molybdenum. In the redox series $[Co(MoS_4)_2]^{n-}$ (n = 2,3,4) no gross changes in orbital ordering occur [57].

Heating $(NH_4)_2[MoS_4]$ in MeCN/EtOH in the presence of $NaBH_4$ led to the formation of the $[MoO(MoS_4)_2]^{2-}$ anion and a crystal structure determination of the $(PPh_4)^+$ salt showed the structure in **(24)** [58].

Reaction of $CoCl_2$ and $(NH_4)_2[MoS_4]$ in dmf led to the isolation of $(PNP)_2(NEt_4)[Co(MoS_4)_2].2MeCN$ in which two $[MoS_4]^{2-}$ units are chelated to Co(II) [58]. Bond distances are Mo=S = 2.215(2) and Mo- S = 2.23(3)Å(av).



(24)

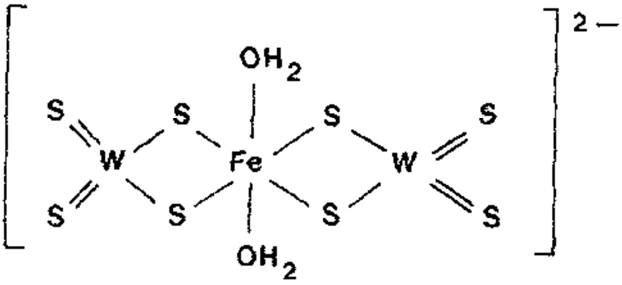
Bond distances are

$Mo_1{=}S = 2.138(4)$ $Mo_2{=}S = 2.135(4)$

$Mo_1{-}\mu S = 2.241(4)$ $Mo_2{-}\mu S = 2.248(4)$

$Mo_3{=}O = 1.763(9)$ $Mo_3{-}\mu S = 2.400(3){-}2.417(3)$Å

Similarly, reaction of $(NH_4)_2Fe(SO_4)_2$, $(NH_4)_2[WS_4]$ and NEt_4I in aqueous solution in the presence of succrose gave $(NEt_4)_2[Fe(H_2O)_2(WS_4)_2]$, the structure of which is shown in (25).

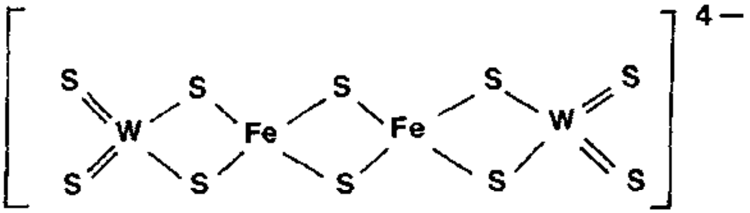


(25)

Bond distances are

$W{=}S = 2.174(3)(av)$ $W{-}\mu S = 2.218(2)$Å(av)

Reaction of $[Cl_2Fe(WS_4)_2]^{2-}$ with NaHS gave $[Fe_2S_2(WS_4)_2]^{4-}$ which contains a tetrametallic chain as shown in (26) [58].

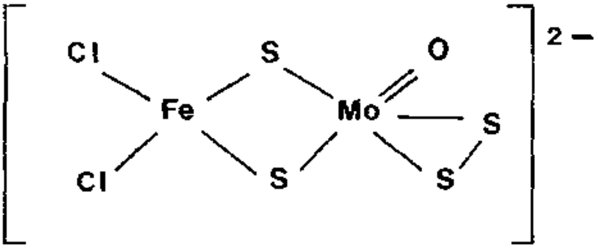


(26)

Bond distances are

W=S = 2.178(7)(av)   W-μS = 2.223(8)Å(av)

The reaction between $[Fe_3O(CH_3COO)_6(H_2O)_3]Cl$ and $(PPh_4)_2[MoS_4]$ in MeCN led to complete disruption of the iron cluster, cleavage of all Fe-O bonds and formation of the $[S_2Mo(O)(\mu\text{-}S)_2FeCl_2]^{2-}$ anion. The crystal structure of the MeCN adduct of the $(PPh_4)^+$ salt showed the anion to have the stereochemistry shown in (27) [59].



(27)

Bond distances are

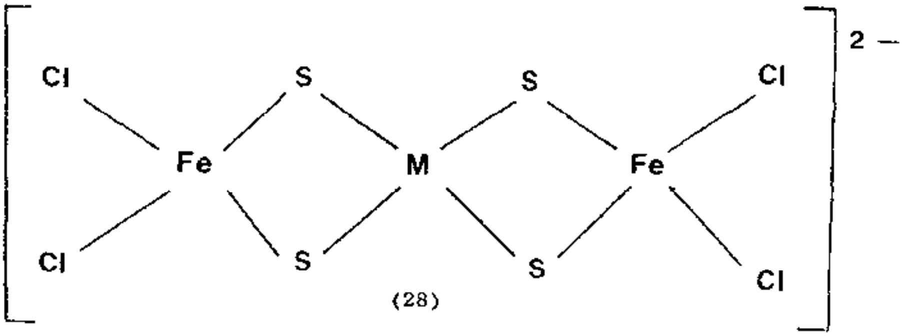
Mo=O = 1.671(5)   Mo-S = 2.385(3)

Mo-Fe = 2.746(1)   Mo-μS = 2.294(2), 2.312(2)

Fe-Cl = 2.261(2)   Fe-μS = 2.239(2)Å

As with the corresonding dmf adduct, there is significant folding of the anion at the bridging sulphurs (dihedral angle between FeS_2 and MoS_2 planes = 161^{o}) in contrast to the more usual planar arrangement. Since the folding occurs in two adducts, it is thought unlikely for it to be a result of packing factors.

Direct reaction of $FeCl_2$ and $[MS_4]^{2-}$ in MeCN in the presence of PPh_4Cl gave $(PPh_4)_2[Cl_2FeS_2MS_2FeCl_2]$ which are isostructural and have the configuration shown in (28).



(28)

Bond distances are

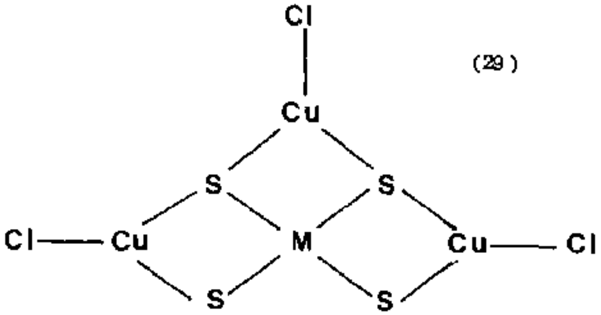
	M = Mo	M = W
M-Fe	2.775(av)	2.800(av)
M-S	2.205(3)	2.210(av)
Fe-S	2.295(av)	2.319(av)
Fe-Cl	2.221(3)-2.246(3)	2.221(2)-2.252(2)Å

The structure may be regarded as three edge sharing tetrahedra. IR, Moessbauer and UV spectra were studied. In dmf the equilibrium

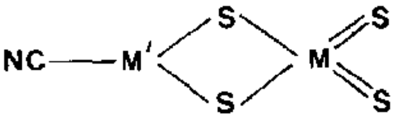
$$[Cl_2FeMS_4]^{2-} + FeCl_2 \rightleftharpoons [Cl_2FeS_2MS_2FeCl_2]^{2-}$$

was established. The complexes underwent one-electron electrochemical reduction followed by loss of chloride to give the $([Fe_2Cl_3S_2MS_2]^{2-})_n$ anions of unknown structure [60].

$(PPh_4)_2[MS_4]$ react with CuCl in MeCN to give the compounds $MS_4.3CuCl$ which were isolated in several isomeric forms [61]. However, they all have the same general structure with a CuCl group spanning three edges of the MS_4 tetrahedron as shown in (29).


(29)

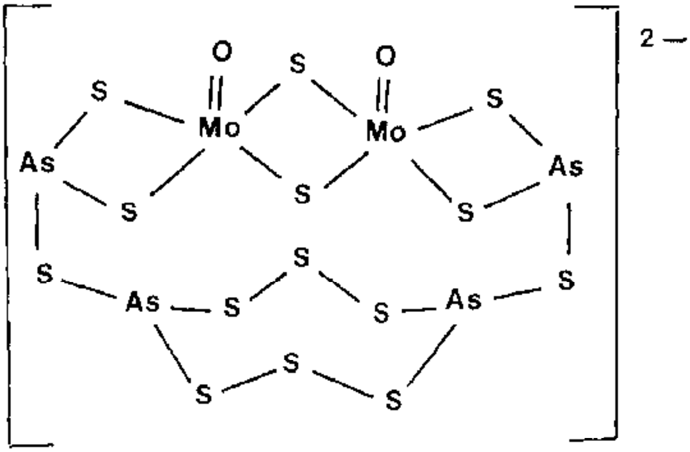
Addition of M'CN (M' = Cu,Ag) to solutions of $[MS_4]^{2-}$ generated $[(CN)M'S_2MS_2]^{2-}$ and $[(CNM'S_2MS_2M'(CN)]^{2-}$ while $[MOS_3]^{2-}$ gave $[(CN)M'S_2MSO]^{2-}$. The crystal structures of $(^{n}Pr_4N)[(CN)CuS_2MoS_2]$ and $(^{n}Pr_4N)[(CN)AgS_2WS_2]$ revealed discrete bimetallic anions as shown in (30) [62].


(30)

Bond distances are

	$[(CN)CuS_2MoS_2]^-$	$[(CN)AgS_2WS_2]^{2-}$
M...M'	2.624(1)	2.890(1)
M=S	2.150(2)	2.155(3)
M-μS	2.225(av)	2.227(2)
M'-μS	2.197(11), 2.217(2)	2.478(2)
M'-C	1.880(6)	2.093(11)Å

The interaction of realgar, As_4S_4, and $(PPh_4)_2[MoS_4]$ in MeCN gave, after recrystallization from dmso/EtOH, crystals of $(PPh_4)_2[Mo_2O_2As_4S_{14}]$ with the structure shown in (31) [63].



(31)

Bond distances are

Mo-Mo = 2.828(3)   Mo=O = 1.688(14), 1.718(11)

Mo-μS = 2.294(6)-2.320(5)   Mo-S = 2.441(5)-2.455(6)Å

2.1.7 Homonuclear polyanions

A Raman spectroscopic study of the formation of polymolybdates as a function of pH confirmed the presence of $[Mo_7O_{37}]^{2-}$ in solution and also identified $[Mo_6O_{19}]^{2-}$ and $[Mo_{12}O_{37}]^{2-}$ [64]. However, a different Raman study combined with light scattering measurements (to determine MW's) suggested that the aggregation sequence for molybdates is

$$\begin{tikzcd}
{[MoO_4]^{2-}} \arrow[r, leftrightarrows] & \text{heptamolybdate} \arrow[r, leftrightarrows] & \text{octamolybdate} \arrow[d, shift left] \\
& \text{protonated polymeric species} \arrow[r, leftrightarrows] & {[Mo_{36}O_{112}]^{8-}} \arrow[u, shift left]
\end{tikzcd}$$

and that all the equilibria were attained rapidly. Similar experiments for the tungstates suggested the sequence

$$[WO_4]^{2-} \rightleftarrows \text{Y-polytungstate} \rightleftarrows \text{paratungstate A} \rightleftarrows \Psi\text{-metatungstate} \rightleftarrows \text{paratungstate B}$$

and that these changes were slow (several days) to reach equilibrium [65].

^{95}Mo NMR spectra have been observed for a number of molybdates using samples enriched in the isotope. The resonances were in the range -18 to +140ppm (vs $[MoO_4]^{2-}$) as expected for Mo(VI) coordinated to oxygen. The line widths reflected the local symmetry ranging from 16Hz for tetrahedral sites to approximately 1000Hz in α-$[PMo_{12}O_{40}]^{3-}$ [66].

The crystal structure of $(NHEt_3)_3(H_3O)[Mo_8O_{26}].2H_2O$ has been determined. The anion has geometry similar to previous examples of this anion and all the cations and water molecules participate in a complex hydrogen bonding scheme [67]. The same anion has been isolated in a series of isomorphous $(3\text{-MePyH})^+$ and $(3\text{-EtpyH})^+$ β-octamolybdates of the type $(3\text{-MepyH})_n(3\text{-EtpyH})_{4-n}[Mo_8O_{26}]$ and the identity of the series was confirmed by X-ray crystallography for the compound n = 2 [68]. Reaction of py with $MoO_3.2H_2O$ gave either $(pyH)_4[Mo_8O_{26}]$ or $(pyH)_4[Mo_8O_{26}(py)_2]$. Recrystallization of the latter from dmso/py gave crystals of $(pyH)_4[Mo_8O_{26}(py)_2].2dmso$ whose structure was shown by X-ray crystallography to be similar to those of several other coordination compounds of polymolybdates of the type $[X_2Mo_8O_{26}]^{(2n-4)}$ (n = charge of X) consisting of two MoO_5X octahedra and four MoO_6 octahedra with the py's at opposite corners of the polymolybdate ensemble [69]. This is the first coordination compound of a polymolybdate with a donor atom other than oxygen. The Mo-N bond is long at 2.279(5)Å, and a similar weak bond was observed for corresponding oxygen donor coordination compounds.

Although the K^+, $(NBu_4)^+$ and $(HNBu_3)^+$ salts of the of the $[W_{10}O_{32}]^{4-}$ anion apparently gave different electrochemical responses, it has now been shown that this was due to medium and counterion effects and that they do indeed all contain the same $[W_{10}O_{32}]^{4-}$ ion which has been previously characterized in the solid state. The one-electron reduction product, $[W_{10}O_{32}]^{5-}$, has been prepared in solution by controlled potential electrolysis and its optical and low temperature EPR spectra recorded. It appears that the unpaired electron is localized in the equatorial sites [70]. A photochemical study under conditions of continuous irradiation at 323nm has been made of $(NBu_4)_4[W_{10}O_{32}]$ in MeCN. Blue colours due to photoreduction to W(V) were observed and $[W_{10}O_{32}]^{5-}$ was detected by EPR spectroscopy. Flash photolysis showed that this anion is protonated and the product then disproportionates

$$2[HW_{10}O_{32}]^{4-} \longrightarrow [H_2W_{10}O_{32}]^{4-} + [W_{10}O_{32}]^{4-}$$

Photocatalytic evolution of hydrogen was observed in the presence of a heterogeneous catalyst such as RuO_2, IrO_2 or platinum [71].

The compound $Tl_8Mo_{10}O_{34}$ was made by the interaction of Tl_2CO_3 and MoO_3. Its structure consists of discrete $[Mo_{10}O_{34}]^{8-}$ units consisting of eight MoO_6 octahedra joined by some edges in a double chain with a MoO_4 tetrahedron linked through a single vertex at one end of each chain at opposite sides of the polyanion [72].

The fluorinated polytungstates $[HW_{12}F_3O_{37}]^{4-}$, $[H_2W_{12}F_2O_{38}]^{4-}$, $[H_2W_{12}F_2O_{38}]^{5-}$, $[H_2W_{12}FO_{39}]^{5-}$ and $[H_2W_{12}FO_{39}]^{6-}$ are derived from the metatungstate and retain the Keggin structure. They were reported to undergo irreversible reductions by the introduction of 6, 12, 18 or 24 electrons per mole to give isostructural brown mixed valence W(VI)/W(IV) compounds. ^{19}F NMR spectroscopy was used to study these systems and it was shown that W_3O_{13} groups were reduced before $W_3O_{13}F$ groups [73].

2.1.8 Heteronuclear polyanions

Cis-$[Nb_2W_4O_{19}]^{4-}$ reacted with $[(C_5Me_5)RhCl]_2$ to give $(C_5Me_5)Rh(Nb_2W_4O_{19})$ in which the heteropolytungstate acted as a tridentate ligand through three oxygen atoms. The Nb and W atoms were disordered in the solid state showing the crystal to be a mixture of all three possible diastereomers. ^{17}O NMR studies showed a mixture of only two diastereomers in MeCN solution at 27°C, but all three were present at 79°C in the same solvent [74].

Two isomers of $[PtMo_6O_{24}]^{8-}$ have been found in the solid state, dependent upon the nature of the cation. $K_{3.5}[\alpha\text{-}H_{4.5}PtMo_6O_{24}]$ prepared at pH 2.5 contains the typical Anderson type anion with a central PtO_6 surrounded by a plane of MoO_6 octahedra sharing edges with PtO_6. However, the ammonium salt, $(NH_4)_4[\beta\text{-}H_4PtMo_6O_{24}]$ prepared at pH 5.4 shows the type of structure known for $[Mo_7O_{24}]^{6-}$ with the central PtO_6 octahedron surrounded by six MoO_6 octahedra which are not coplanar and which share corners as well as edges. This is the first example of isomerism in 1:6 heteropolymolybdates [75]. The anion in $K_6Na_2[PtW_6O_{24}].12H_2O$ has the ideal Anderson type structure [76].

The first polymolybdate containing mercury(I) has been prepared and its structure determined [77]. The anion in $K_5Cs_5[(Hg_2)_2WO(OH)(AsW_9O_{33})_2]$ consists of two β-type AsW_9O_{33} units linked by a WO_6 octahedron to form an open structure hinged at the WO_6 unit. The two Hg_2 units bridge the open end of the structure.

The absorption and emission spectra and the emission decay of the $[EuW_{10}O_{39}]^{9-}$ ion have been studied under a variety of conditions. In aqueous solution the complex maintains its integrity but is subject to equilibria involving water coordination to europium [78].

A number of polyphosphate ions containing rhenium of the types $[XW_{11}ReO_{40}]^{n-}$ (X = P,Si,B) and $[SiW_{10}Re_2O_{40}]^{n-}$ have been synthesized. The anions are of the Keggin or Keggin-β types and the value of n depends upon the oxidation state of rhenium (VII, VI or V) not tungsten. The compounds showed interesting reversible electrochemical behaviours which were associated with rhenium redox reactions [79].

Solid state ^{31}P and ^{29}Si NMR spectra have been used to characterize some heteropolytungstates. The ^{31}P resonance in the Keggin anion $[PMo_{12}O_{40}]^{3-}$ was sharp in both the static and MASS NMR spectra, but that of the Dawson type anion $[P_2Mo_{18}O_{62}]^{6-}$ showed a much greater chemical shift anisotropy and the MASS NMR spectrum was a doublet, although the structural significance of this observation is unknown. It was possible to identify degrees of tungsten substitution in $Cs_3[PMo_{11}WO_{40}]$ by ^{31}P MASS NMR spectra [80].

It has been shown that $[AsMo_{12}O_{40}]^{3-}$ can only be made from yellow $MoO_3.2H_2O$ and preparations using white $MoO_3.H_2O$ result in the formation of $[As_2Mo_{18}O_{62}]^{6-}$. ^{17}O NMR spectra of both types of anion were observed and were consistent with the known structures of these anions in the solid state [81].

IR and Raman studies have been carried out on $(NBu_4)^+$ salts of α- and β-$[XM_{12}O_{40}]^{n-}$ polyanions (X = Si,Ge,P,As). A good correlation between structural and vibrational data was observed for both Mo and W α-isomers and for tungsten β-isomers [82].

The previously unknown niobium member of the series $[SiW_9M'_3O_{40}]^{n-}$ has been synthesized and it dimerizes in acid solution to form a new type of heteropolyanion $[Si_2W_{18}Nb_6O_{77}]^{8-}$. The ^{183}W NMR spectrum was consistent with a proposed structure based on analytical data and IR spectra (especially evidence for a Nb-O-Nb vibration at 690cm^{-1}). The monomeric anion reacted with $[(C_5Me_5)Rh(MeCN)_3]^{2+}$ to give $[(C_5Me_5)Rh(SiW_9Nb_3O_{40})]^{5-}$ in which the rhodium was coordinated to a NbW_2 site [83].

In the presence of organic compounds, 1:12 heteropolytungstates are photosensitive at the oxygen to metal charge transfer bands in the UV and visible regions. Multi-electron reductions occurred with oxidation of the organic substrates. Photosensitivity varied in the order $[PW_{12}O_{40}]^{3-}$ > $[SiW_{12}O_{40}]^{4-}$ > $[FeW_{12}O_{40}]^{5-}$ > $[H_2W_{12}O_{40}]^{6-}$ which is the same order of increasing negative reduction potentials [84].

The great power of ^{183}W NMR spectroscopy in structural studies of heteropolytungstate anions has been demonstrated again, this time for a series of complexes based on the Wells-Dawson 2:18 structure [85]. The first γ-isomer of this structure, γ-$[As_2W_{18}O_{62}]^{6-}$ has been characterized. This isomer differs from the α-isomer by a 60° rotation of both end W_3O_{13} caps about the three-fold axis. α-$[P_2W_{12}Mo_6O_{62}]^{6-}$ has the tungstens in a boat like arrangement derived from the α-$[P_2W_{18}O_{62}]^{6-}$ structure. The complex previously formulated as α-$[P_2W_{16}Mo_2O_{62}]^{6-}$ is really α-$[P_2W_{15}Mo_3O_{62}]^{6-}$ with one W_3O_{13} cap of the parent replaced by Mo_3O_{13} [85].

The electrochemical reductions of the mixed phospho/molybdate/tungstate species $[P_2W_{18-n}Mo_nO_{62}]^{6-}$ have been investigated and it was found that the ease of the reduction depended upon the position of molybdenum in the polyanion (equatorial or cap positions) [86].

The anions in $Rb_8[As_2CoW_{20}O_{68}(H_2O)_2].10H_2O$ and $Rb_8[As_2ZnW_{20}O_{68}(H_2O)_2].12H_2O$ have the $[As_2W_{21}O_{69}(H_2O)_2]^{6-}$ structure with substitution of Co or Zn for one of the tungsten atoms in square pyramidal coordination in the equatorial belt of the parent anion [87].

The compound $Na_7[Nb_{15}W_{13}O_{80}]$ exhibits a new type of tunnel structure built up of pentagonal columns connected to each other directly and also via a string of MoO_6 octahedra parallel to the *c* axis. Four of the heavy metal sites were randomly filled by Nb or W, but the fifth was occupied only by niobium [88].

2.1.9 Ternary oxides

A temperature gradient flux growth method has been used to grow single crystals of the molybdenum bronzes $Li_{0.9}Mo_6O_{17}$ and $Li_{0.32}MoO_3$ and the new phase $Li_{0.04}MoO_3$ [89].

Me_2SnCl_2 and $Na_2[MoO_4]$ in aqueous solution are known to give Me_2SnMoO_4 and its structure has now been determined [90]. It is a three dimensional arrangement consisting of *trans*-$[Me_2SnO_4]$ units and tetrahedral MoO_4 units with every oxygen bridging between molybdenum and tin to form zigzag chains through the crystal. The average Mo-O bond distance is 1.75(1)Å.

LiW_3O_9F was prepared by the interaction of WO_3 and LiF at 680°C [91]. The structure is related to the hexagonal tungsten bronzes (HTB) and was described as a complex stacking of HTB layers with Li atoms in the hexagonal cavities.

The new compound $FeMoO_4Cl$ was made by the interaction of MoO_3, Fe_2O_3 and $FeCl_3$ in a sealed tube at 360°C for 18 hours, or alternatively, by reacting $Fe_2(MoO_4)_3$ and $FeCl_3$ at 350°C. The structure consists of layers of $FeMoO_4Cl$ units stacked along the *c*-axis, each layer containing linked tetrahedral MoO_4 and square pyramidal FeO_4Cl units. Unusual magnetic properties (μ = 4.96BM at 296K decreasing to 2.49BM at 66K) was interpreted in terms of Fe...Fe interactions via O-Mo-O pathways [92].

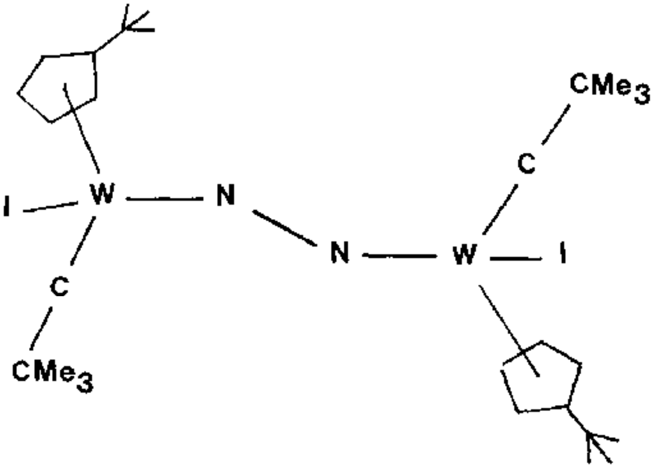
The structure of a new barium bronze, $Ba_{0.5}WO_3$, has been established by X-ray diffraction and high resolution microscopy studies. The lattice framework is built up of WO_6 octahedra sharing corners to form pentagonal tunnels in which the barium atoms are located [93].

The structures of two members of a new series of monoclinic sodium phosphate tungsten bronzes have been determined. The series is $Na_xP_4O_8(WO_3)_m$ and the compounds isolated were those with m = 2 and 6, that is $Na_xP_4W_8O_{32}$ and $Na_xP_4W_{12}O_{44}$. The framework consists of ReO_3-like slabs of WO_3 units linked by PO_4 tetrahedra giving distorted octahedral tunnels which accomodate the Na^+ ions [94].

2.1.10 Complexes with nitrogen and phosphorus donor ligands

The generation of ammonia by the hydrolysis of some polymer bound nitrido compounds has been studied. $MoNCl_3(bipy*)$, $MoNCl_2(bipy)(SCH_2Ph*)$ and $MoNCl(bipy)(S^tBu)(SCH_2Ph*)$ (* indicates polymer bound) were investigated and the amount of ammonia produced increased in the above order showing that the coordination of the thio group is important in the production of ammonia [95].

The complexes $[W(C_5Me_4{}^tBu)(CCMe_3)X]_2(\mu\text{-}N_2H_2)$ (X = Cl,I) have been synthesized and the structure of the iodo complex is shown in **(32)**.



(32)

Bond distances are

W-N = 1.932(7)   W-I = 2.714(1)

$W\text{-}C(CCMe_3)$ = 1.769(8)   N-N = 1.410(9)Å

The W-N-N angle is 131.66(50)°

The bond distances indicate that the ligand coordinates as a 1,2-hydrazido(2-) group rather than as a neutral diimine [96].

An improved synthesis of $WH_6(PMe_2Ph)_3$ from $WH_4(PMe_2Ph)_3$ and $Na[H_2Al(OCH_2CH_2OMe_2)_2]$ at -80°C has been reported. The corresponding molybdenum complexes MoH_6L_3 (L = Pcy_3, Pcy_2Ph, $P(^iPr)_3$, $P(^iPr)_2Ph$) were prepared from $MoCl_4(thf)_2$, L and $Na[H_2Al(OCH_2CH_2OMe_2)_2]$ in low yields as unstable oils which were characterized by ^1H and ^{31}P NMR studies. Attempts to prepare $[MH_9]^{3-}$ failed [97]. A neutron diffraction study on $WH_6(P^iPr_2Ph)_3$ has confirmed the capped trigonal prismatic structure with the phosphines occupying two eclipsed edge positions and one equatorial position. Bond distances are W-H = 1.718-1.745(3) and W-P = 2.424(2)-2.524(2)Å [98].

2.2 MOLYBDENUM(V) AND TUNGSTEN(V)

2.2.1 Halides and halocomplexes

An electron diffraction study of monomeric $MoCl_5$ in the gas phase at 115°C showed the presence of at least two forms. The C_{4v} square pyramidal form with Mo-Cl = 2.227(5)Å was the more abundant species with the D_{3h} trigonal bipyramidal form with Mo-Cl = 2.300(20)Å the less abundant. There was the possibility that a dimeric D_{4d} form (Mo-Mo = 2.600(38)Å) could also have been present [99].

Reaction of $MoCl_5$ in benzene solution with 1,9-nonanediamine and 1,10-decanediamine gave complexes formulated as $[Mo_2Cl_2(AA)_4]Cl_8$. They were diamagnetic and thought to contain halogen bridges [100].

TeF_6 (0.05 atm) reacted with Mo at 500-600°C to give $MoTeF_3$ which was condensed at -78°C and found to have the spin-only magnetic moment. At 0.4 atm pressure at 200-250°C the adduct $MoTeF_3.TeF_4$ was formed [101].

$MoOCl_3$ reacted with an excess of NMe_3 to give a small quantity of green $MoOCl_3.2NMe_3$ and a brown solid which analyzed to the same composition. The green crystals exhibited a strong IR band at 955cm^{-1} assigned to $\nu_{Mo=O}$, whilst the brown form showed several bands in the 950-990cm^{-1} region as well as further bands at 675 and 656cm^{-1} (absent in the green isomer) which were assigned to Mo-O-Mo vibrations, suggesting a polymeric structure [102].

Addition of either WCl_6 or $K[WCl_6]$ to the basic aluminium chloride/ 1-methyl-3-ethylimidazolium chloride ionic liquid produced $[WCl_6]^-$ in solution. Electrochemical studies in this solvent showed this ion to be reversibly reduced in two steps to $[WCl_6]^{2-}$ and $[WCl_6]^{3-}$. Studies on the oxidation of $[W_2Cl_9]^{3-}$ showed a reversible one-electron oxidation to $[W_2Cl_9]^{2-}$ followed by a second irreversible one-electron oxidation. On the longer coulometric timescale two electrons were transferred to give $[WCl_6]^{2-}$, thus suggesting an ECE mechanism for oxidation of $[W_2Cl_9]^{3-}$ on the longer timescale [103]. The electrochemistry of W(V) and W(IV) have also been studied in the molten LiCl/KCl eutectic by cyclic voltammetry [104]. Reduction of $[WCl_6]^-$ to $[WCl_6]^{2-}$ was reversible, but further reduction to W(II) was irreversible. W(II) disproportionated to W(IV) and W(0).

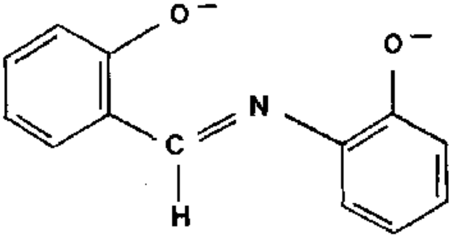
A study has been made of the ^{18}O exchange between water and $K[MoOCl_5]$ in hydrochloric acid solutions of various concentrations. The kinetics were highly dependent on acidity, $[Cl^-]$ and $[Mo]_t$. However, the kinetic rates were interpretable in terms of reversible formation of $[Cl_5Mo\text{-}O\text{-}MoCl_5]^{2-}$ in the most acidic media and the internal electronic rearrangement of the hydrolysis product $[MoO(OH)Cl_4]^-$ at lower chloride concentrations. It was concluded that $[MoOCl_5]^{2-}$ is the major species present even in 2M HCl provided $[Cl^-]$ is greater than 12M [105].

A spectrophotometric study of the aquation of $[MoOCl_5]^{2-}$ in HCl or $MeSO_3H$ solution showed the presence of an intermediate before the formation of $[Mo_2O_4]^{2+}$, but it could not be characterized. Evaporation of a solution of $K[MoOCl_5]$ gave crystals identified as $K[MoOCl_4(H_2O)]$ by X-ray diffraction. Although the ligand arrangement was *trans* octahedral, the Mo atom is displaced towards the oxo ligand so an alternative description would be square pyramidal with a weakly bonded water in the axial position. Bond distances are Mo=O = 1.637(5), Mo-H_2O = 2.325(3), Mo-Cl = 2.376(2)Å [106].

Reduction of $WSCl_4$ with C_2Cl_6 yielded $WSCl_3$ which reacted with PPh_4Cl in CH_2Cl_2 to give $(PPh_4)_2[W_2S_2Cl_8]$ which, judging by its IR spectrum, has a chlorine bridged structure. In contrast, iodide reduced $(PPh_3Me)[WSCl_5]$ to $(PPh_3Me)_2[WSCl_5]$ [107].

2.2.2 Monomeric oxo complexes

The structure of $(Ph_4As)[MoOCl_2L]$ (L = N-2-oxophenylsalicylideiminate (33)) has been determined [108].



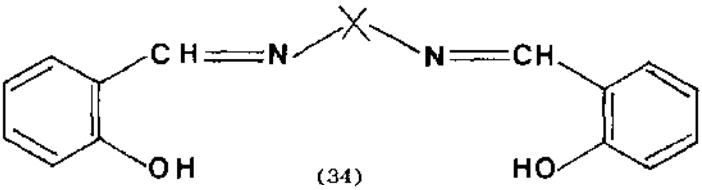
(33)

The molybdenum atom adopts a distorted octahedral arrangement with the planar tridentate ligand adopting a *mer* configuration with the terminal oxo ligand *trans* to the nitrogen of the tridentate. Bond distances are Mo=O = 1.673(3), Mo-O = 1.959(3), 1.9974(3), Mo-N = 2.298(4) and Mo-Cl = 2,371(1), 2.408(1)Å.

Mononuclear complexes of the type $MoXL_2$ (X = Cl,Br; LH = quinolin-8-ol, quinolin-8-thiol) were prepared by reacting the ligand hydrohalide with $(pyH)_2[MoOCl_5]$ or $(pyH)[MoOBr_4]$ in the presence of base. However, the reaction of quinolin-8-amine and water gave dinuclear $Mo_2O_3Cl_2L_2$ [109].

A series of monomeric complexes $MoOX(dtc)_2$ (X = F,Cl,Br,I; dtc = Et_2dtc, pipdtc,morphdtc) were prepared from MoO_3 in HCl solution, the appropriate hydrazinium halide and Na[dtc]. All were green and had magnetic moments corresponding to one unpaired electron [110,111]. The thermogravimetric behaviour of $MoOX(morphdtc)_2$ were examined. The first step at about 180°C involved loss of one morphdtc ligand, except for the iodo complex which lost iodide first. In all cases subsequent steps led to the formation of first MoS_3 and finally MoO_3 [111]. Similar compounds of the type $MoO(NCS)(dtc)_2$ were also prepared which IR studies indicated to contain *N* bonded thiocyanate [112,113]. Thermogravimetric studies indicated loss of thiocyanate and formation of MoS_3.

EPR and halide concentration studies have been carried out on a series of Mo(V) complexes of the types *trans*-[MoOL(MeOH)]Br and [MoO(SALPN))Cl] in dmf where L is the Schiff base ligand shown in (34). There were complex equilibria between monomeric and polynuclear species in solution although the bromo system was dominated by monomeric species and the SALPN chloro system was dominated by polynuclear species. Electrochemical studies were carried out but detailed interpretation of the data was rendered impossible by the complex equilibria [114].


(34)

A number of complexes of the type MoO(SR)L (R = Ph,*p*-tolyl; L = the dianion of a quadridentate Schiff base ligand) have been previously prepared by the reaction of RSH and NEt_3 with MoO(Cl)L in MeCN. Their EPR spectra have now been reported and they revealed the presence of both *cis* and *trans* isomers [115].

The molybdenum(V) tetraphenylporphyrins MoO(TPP)X (X = NCS,F,Cl,Br) in a glassy matrix of 2-Methf at 77K are reduced by γ-irradiation to give $[MoO(TPP)X]^-$, but on warming this anion decomposed to MoO(TPP). Optical and EPR spectroscopies were used to monitor these reactions [116]. Reaction of MoO(TPP)Br with ROH (R = Me,Et) in CH_2Cl_2 at 25°C proceeded through two steps to give [MoO(TPP)(ROH)]Br and MoO(TPP)(OR)]. In the presence of the superoxide ion the reaction gave only MoO(TPP)(OR) through two competitive routes in which the superoxide acted as a proton acceptor and a reducing agent. Again, optical and EPR spectroscopies were used to follow the reactions [117]. A different reasearch group has studied MoO(TPP)(OMe) in thf by picosecond absorption spectroscopy. Two excited states were observed with lifetimes of 2-9ps and 4±1ns [118]. Unusual resonance Raman effects have been observed for MoO(TPP)(NCS). Excitation at 530.9nm gave strong enhancement of of the in-plane depolarized B_{1g} and B_{2g} modes, but excitation into the higher energy transition at 406.7nm gave strong resonance enhancement of the polarized A_{1g} and inversely polarized A_{2g} modes and very weak scattering of the depolarized B_{1g} and B_{2g} modes [119].

2.2.3. *μ-oxo, μ-sulphido complexes*

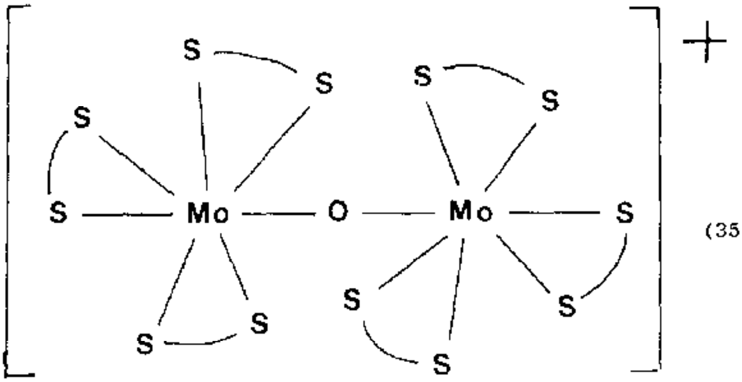
A Raman study on solutions of Mo(V) in hydrochloric acid solutions showed that they contain $[MoOCl_5]^{2-}$ at high acidity, a dimer with the O-Mo-O-Mo-O core at 3-5M HCl and a species with the O-MoO_2Mo-O core in 1M HCl [120].

Two series of dinuclear W(V) dithiocarbamate complexes have been prepared by the interaction of $Na_2[WO_4]$ with $[morphdtc]^-$ or $[pipdtc]^-$ using sodium dithionite as the reducing agent. The complexes were $W_2O_3(dtc)_4$ at pH 5 (HOAc) and $W_2O_4(dtc)_2$ at pH 2 (HCl). These were formulated as mono- and dioxo bridged species respectively. Treatment with H_2S after the acidification step gave $W_2O_2S_2(dtc)_2$ and $W_2O_3S(dtc)_2$ which contain disulphido and oxosulphido bridges respectively. All the complexes exhibited low magnetic moments, suggesting considerable spin pairing between the tungsten atoms [121].

Reaction between PPh_3 and $[MoO(Et_2dtc)_3]BF_4$ led to oxygen abstraction and formation of $[Mo_2O(Et_2dtc)_6]BF_4$. This complex has a single unpaired electron in the solid and in solution and a crystallographic study revealed a structure with an almost linear oxo bridge and pentagonal bipyramidal coordination about molybdenum as shown in (35). All evidence suggested that the unpaired electron was delocalized over both molybdenum centres. A quasi-reversible one-electron reduction gave the corresponding Mo(IV) dimer in solution although it was not isolated

$$[Mo_2O(Et_2dtc)_6]^+ \quad \overset{+e^-}{\rightleftharpoons} \quad Mo_2O(Et_2dtc)_6$$

The electrochemical interconversion of $[Mo(V)]_2$ and $[Mo(III)]_2$ aquo ions, although quantitative on the timescale of coulometry, is highly asymmetrical on the cyclic voltammetric timescale such that the current due to oxidation of Mo(III) is small , and the separation of the oxidation and reduction responses is large. A slow chemical step, probably conversion of an aquo group to hydroxo



(35)

Bond distances are

$$\text{Mo-O} = 1.848(2)$$
$$\text{Mo-S(ax)} = 2.526(2) \qquad \text{Mo-S(eq)} = 2.484(3)\text{-}2.579(2)\text{Å}$$

(or oxo) is thought to be responsible for the anomalous electrochemical behaviour [123].

The reaction between $[Mo_2O_4]^{2+}$ and Ce(IV) in $HClO_4$ solution has been studied by stopped flow techniques [124]. The reaction is rapid and quantitative and the stoichiometry corresponds to

$$[Mo_2O_4]^{2+} + 2Ce(IV) + 8H^+ \longrightarrow 2Mo(VI) + 2Ce(III) + 4H_2O$$

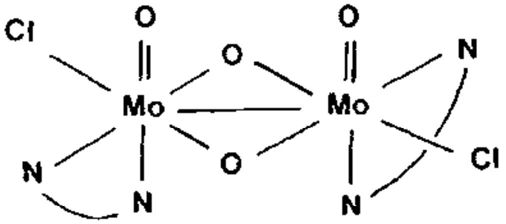
The observed pseudo first order rate law ([Mo(VI)>>[Ce(IV)] is

$$-d[Ce(IV)]/2dt = k_2[Mo_2O_4{}^{2+}][Ce(IV)]$$

where $k_2 = k_{2h}K_h/([H^+] + K_h)$ with $k_{2h} = 2.73 \times 10^4 M^{-1}S^{-1}$ and $k_h = 0.46M$.

Oxidation of $MoCl_4(bipy)$ with O_2 in EtOH/HCl and recrystallization from CH_3NO_2 gave crystals of $[Mo_2O_4(bipy)_2].CH_3NO_2$ which has a non-planar Mo_2O_2 core with the oxo groups on the same side of the molecule as shown in (36).

Tungsten(IV) complexes of the type $W_2Cl_4(\mu\text{-}OR)_2(OR)_2(ROH)_2$ react with certain ketones to give ditungsten(V) complexes containing α-diol ligands derived from the ketone [126]. The structure of the compound $W_2Cl_4(\mu\text{-}OEt)_2[Me_2C(O)C(O)Me_2]_2$ is shown in (37). The structure of $W_2Cl_4(\mu\text{-}OEt)_2[MeEtC(O)C(O)MeEt]_2$ was found to be very similar. These are the



(36)

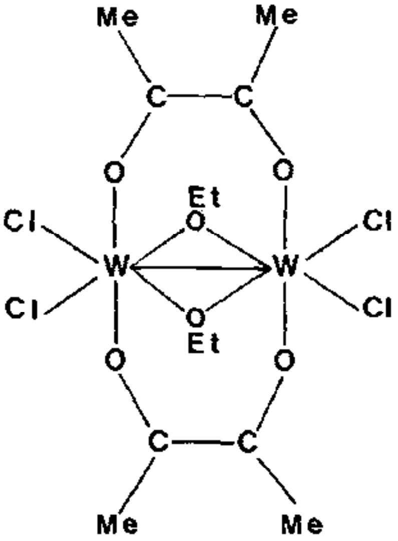
Bond distances are

Mo-Mo = 2.565(1)

Mo=O = 1.607(7),1.651(7) Mo- O = 1.915(5)-1.957(6)

Mo-Cl = 2.447(3),2.492(2) Mo-N = 2.266(8)-2.304(7)Å

The Mo-Mo distance indicated a strong metal-metal interaction [125].



(37)

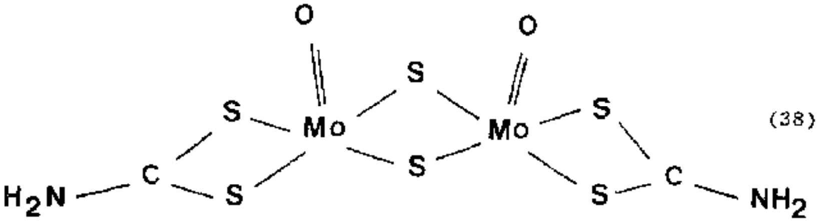
Bond distances are

W-W = 2.701(1) W-Cl = 2.363(av)

W-O = 1.82(av) W-μOEt = 2.05Å(av)

first reported examples of two ketones coupling to form a pinacol using a double bonded metal system (which is converted to a single bond in the reaction) as the source of electrons.

A Mo(V) complex of the parent dithiocarbamate, $[S_2CNH_2]^-$, has been prepared [127]. Reaction between Mo(VI) and $(NH_4)[S_2CNH_2]$ gave $[Mo_2O_2S_2(dtc)_2].2MeCN$ after recrystallization from MeCN. The crystal structure determination showed bridging sulphides and the stereochemistry about each molybdenum was square pyramidal as shown in (38).



(38)

Bond distances are

Mo-Mo = 2.820(1)   Mo=O = 1.677(3)

Mo-μS = 2.324(1)   Mo-S(dtc) = 2.460(1)Å

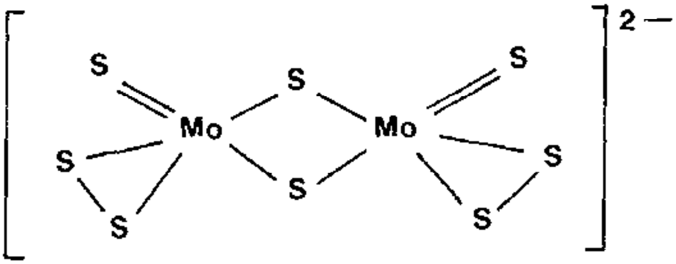
(Presumably the structures of the complexes noted in reference 121 are similar). The C-N stretch occurred at 1455cm^{-1}, compared with 1480-1550cm^{-1} for dialkyldithiocarbamate complexes. Electrochemical studies showed no oxidation responses, but an irreversible two-electron reduction occurred in dmso or MeCN which involved loss of $[dtc]^-$.

The remarkable reaction

$$2[MoS_4]^{2-} + RSSR \longrightarrow [Mo_2S_8]^{2-} + 2RS^-$$

has been reported in which $[MoS_4]^{2-}$ reacted with an oxidant to give a reduced Mo(V) species and an oxidized form of the ligand via an internal redox reaction [128]. The structure of the $[Mo_2S_8]^{2-}$ anion in the $(PPh_4)^+$ salt is shown in (39).

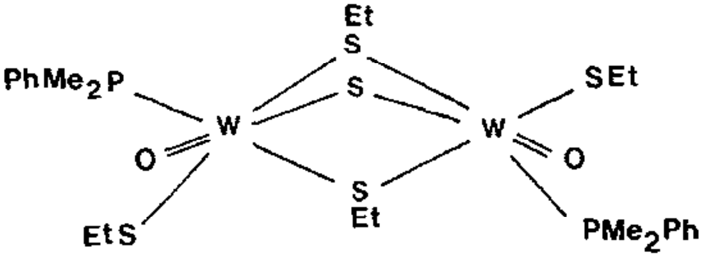
Treatment of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with excess EtSH followed by exposure of the solution to air gave brown diamagnetic $[W(SEt)O(PMe_2Ph)]_2(\mu\text{-}S)(\mu\text{-}SEt)_2$ whose structure is basically two octahedra sharing an edge as shown in (40) [129].



(39)

Bond distances are

Mo-Mo = 2.821(1)
Mo=S = 2.108(1),2.128(1)   Mo-μS = 2.306(1)-2.314(1)
Mo-S_2 = 2.375(2)-2.405(2)   S-S = 2.051(2),2.072(3)Å

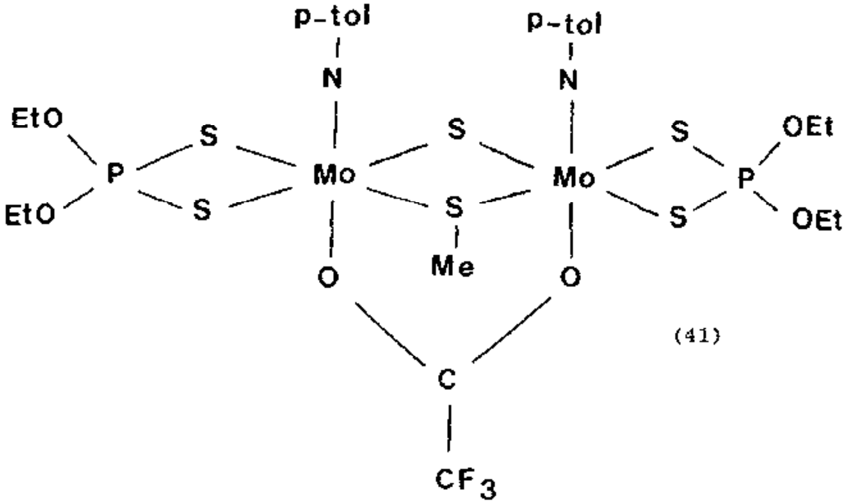


(40)

Bond distances are

W-W = 2.801(1)   W=O = 1.675(9)
W-μS = 2.340(5)   W-μSEt = 2.465(4)-2.675(4)
W-SEt = 2.402(5)   W-P = 2.595Å(av)

Reaction of [Mo(N-*p*-tol)(μ_3-S)(S_2P{OEt}$_2$]$_4$ with CF_3COOH, NEt_3 and MeBr gave orange crystals of [Mo(N-*p*-tol)(S_2P{OEt}$_2$]$_2$(μ-S)(μ-SMe)(μ-O_2CCF_3) whose structure is shown in (41) [130].



(41)

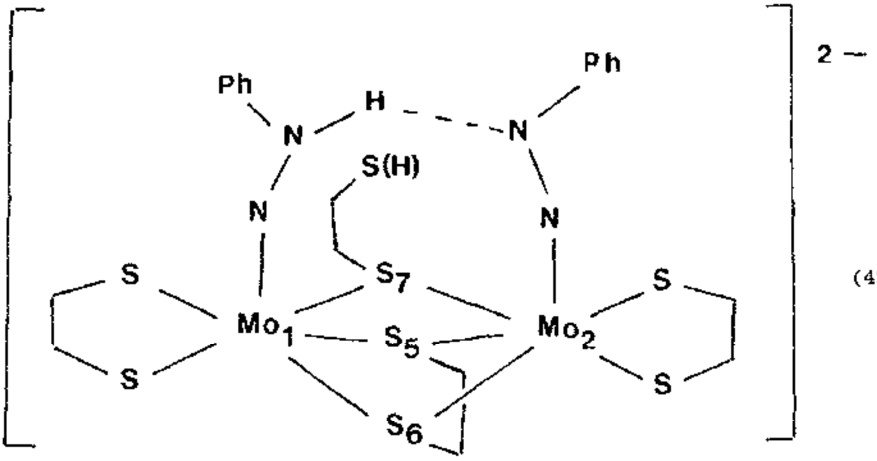
Bond distances are

Mo-Mo = 2.844(1)   Mo-N = 1.726(5)

Mo-μS = 2.35(av)   Mo-μSMe = 2.39(av)

Mo-O = 2.273(4)   Mo-S = 2.493(2)-2.548(2)Å

The crystal structure of $(NEt_3H)_2[Mo_2(NNPh)(NNHPh)(SCH_2CH_2S)_3(SCH_2CH_2SH)]$ revealed the remarkable molecular geometry shown in (42)



(42)

Bond distances are

$\mathrm{Mo_1{-}Mo_2} = 2.837(2)$

$\mathrm{Mo_1{-}S_5} = 2.426(5)$ $\mathrm{Mo_2{-}S_5} = 2.422(5)$

$\mathrm{Mo_1{-}S_6} = 2.582(5)$ $\mathrm{Mo_1{-}S_6} = 2.572(6)$

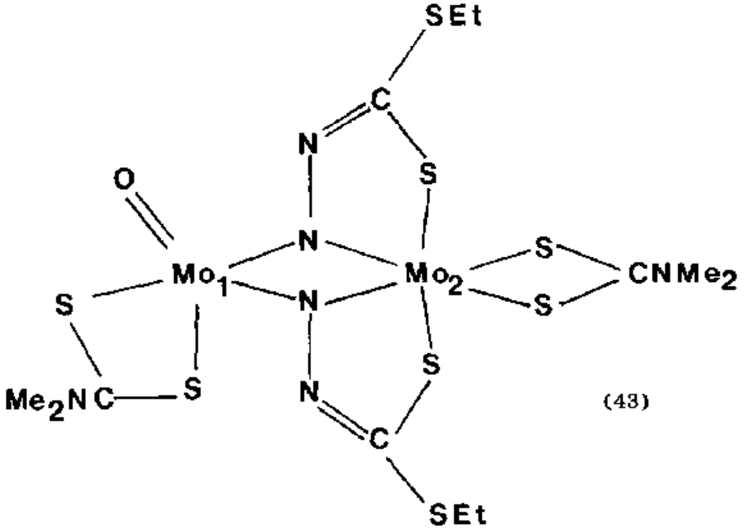
$\mathrm{Mo_1{-}S_7} = 2.44(6)$ $\mathrm{Mo_2{-}S_7} = 2.436(5)$

$\mathrm{Mo_1{-}N} = 1.793(6)$ $\mathrm{Mo_2{-}N} = 1.740(7)\text{Å}$

A unique feature of the structure is the occupancy of the sterochemical position *trans* to the hydrazido ligands, although the Mo-S bonds in these positions are significantly longer than the others. There is significant H-bonding between the hydrazido(2-) and hydrazido(3-) ligands [131].

2.2.4 *Complexes with nitrogen donor ligands*

An unusual complex containing two μ-hydrazido(3-) ligands has been prepared and its structure shown to be that given in (43).



(43)

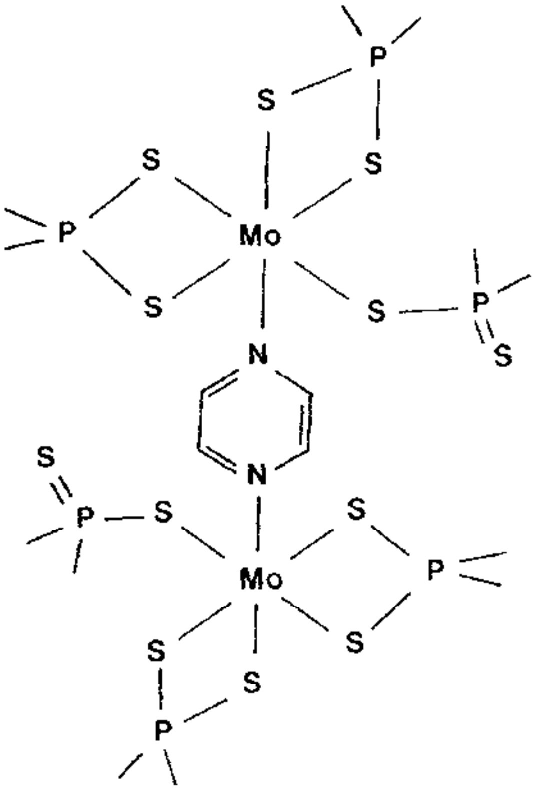
Bond distances are

$\mathrm{Mo_1{-}Mo_2} = 2.672(1)$ $\mathrm{N{-}N} = 1.350(\mathrm{av})$

$\mathrm{Mo_1{-}\mu N} = 1.935(\mathrm{av})$ $\mathrm{Mo_2{-}\mu N} = 1.983\text{Å}(\mathrm{av})$

The N-N distance is indicative of a close to single bond between the nitrogen atoms, thus favouring formulation of the ligands as hydrazido(3-). The molybdenum atoms are not equivalent and Mo_2 has approximately trigonal prismatic stereochemistry [132].

The reaction between $MoCl_3(thf)_3$ and *p*-$C_6H_4(NO_2)(N_3)$ in thf at room temperature in the presence of $[S_2P(OEt)_2]^-$ gave, after workup, the product $[Mo(S_2P\{OEt\}_2)_3]_2(\mu\text{-}p\text{-}NC_6H_4N)$ which has the structure shown in (44) with the bridging ligand formed by oxygen abstraction from the starting material [133].



(44)

Bond distances are

$$\text{Mo-N} = 1.729(8) \qquad \text{Mo-S(mono dtc)} = 2.460(3)$$

$$\text{Mo-S}(\textit{cis}\ \text{N}) = 2.471(3)\text{-}2.544(3) \qquad \text{Mo-S}(\textit{trans}\ \text{N}) = 2.630(3)\text{Å}$$

2.2.5 Complexes with metal-carbon bonds

The kinetics of the reaction

$$2[M(CN)_8]^{3-} + [SO_3]^{2-} \longrightarrow 2[M(CN)_8]^{4-} + [SO_4]^{2-}$$

in alkaline solution have been investigated over a wide pH range. The rate law was found to be of the form

$$R = (a[A^+ + b[H^+])/(c + [H^+])[M(CN)_8{}^{3-}][SO_3{}^{2-}]$$

The third order rate constants at $[OH^-] = 0.05M$ are 6.2×10^3 $dm^6m^{-2}s^{-1}$ and 22.3 $dm^6m^{-1}s^{-1}$ for molybdenum and tungsten respectively for $A^+ = Na^+$. It was established that the reaction is catalyzed by alkali metal ions and proceeds via an outer sphere mechanism [134].

2.3 MOLYBDENUM(IV) AND TUNGSTEN(IV)

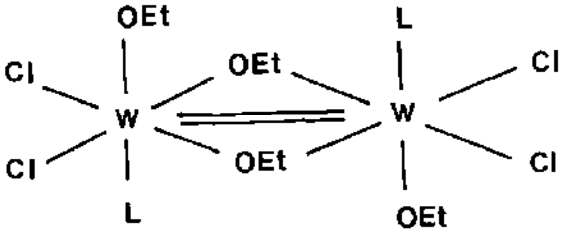
2.3.1 Halides and halocomplexes

The structure of WCl_4 in the gas phase has been determined by electron diffraction. It has a trigonal bipyramidal configuration of C_{2v} symmetry and two different (but unspecified) bond lengths [135].

The crystal structure of $[WI(CH_2)(PMe_3)_4](CF_3SO_3)$ has been determined. The methylene and iodo ligands are *trans* with W-C = 1.83(2)Å, indicating a bond order between 2 and 3, W-I = 2.881(2)Å and W-P = 2.513Å(av) [136].

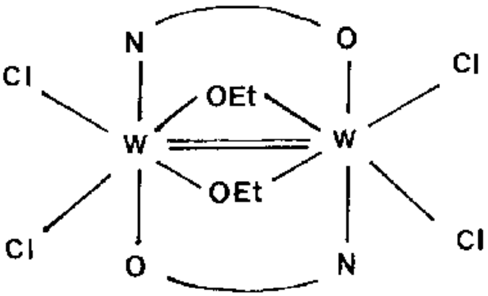
$MoCl_4(PhCCPh)$ reacted with Ph_4AsCl in dichloromethane to give brown crystals of $(Ph_4As)_2[Mo_2Cl_{10}]$. A crystal structure determination showed the anion to have the same structure as Mo_2Cl_{10}, that is, two octahedra sharing an edge. Bond distances are Mo...Mo = 3.797, Mo-μCl = 2.51(av), Mo-Cl = 2.307(2)-2.326(2)Å [137].

$W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(EtOH)_2$ reacted with L (= py,4-Mepy,4-Phpy) to give $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2L_2$. All spectroscopic evidence was in accord with the structure shown in (45). Electrochemical reduction of all the complexes was



(45)

irreversible, but oxidation gave two reversible one-electron couples under cyclic voltammetric conditions, to be compared with the behaviour of the parent compound which gave a single irreversible two-electron oxidation followed by deprotonation of the dication to give $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_4$. This follow up reaction is not available to the pyridine substituted compounds and so this system provides a nice example of the effect that available follow up reactions may have on the observed electrochemistry. Controlled potential electrolysis at potentials between the two oxidations gave yellow solutions of the monocations. The ligand 2-OHpy gave a different type of complex which, on the basis of spectroscopic evidence, was thought to have the structure (46).

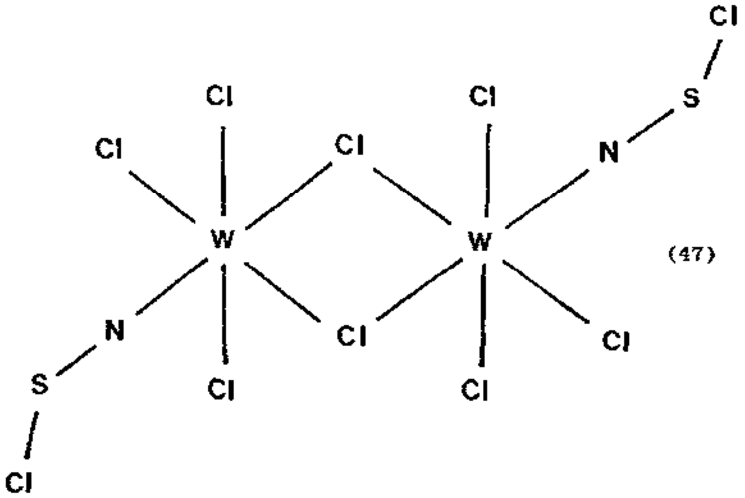


(46)

Its electrochemical behaviour is different and it gave a single reversible one-electron oxidation and two reversible one-electron reductions under conditions of cyclic voltammetry. Controlled potential electrolysis at the first reduction gave the intense blue monoanion which could be oxidized back to the starting material, thus demonstrating its stability on the longer coulometric timescale. The cation, however, was not stable on the longer timescale in contrast to those with monodentate pyridines described above [138].

Green and blue isomers of $MoOCl_2(PMe_3)_3$ have been obtained by interaction of $MoCl_4(thf)_2$ with an equimolar amount of water in the presence of PMe_3. The green isomer was the more soluble and ^1H NMR spectroscopy suggested it had the *mer-cis* stereochemistry. Reaction with KCNO and KCNS gave $MoOX_2(PMe_3)_3$ whilst $Na[Et_2dtc]$ gave $MoO(Et_2dtc)_2(PMe_3)$ which readily lost phosphine to give $MoO(Et_2dtc)_2$ [139].

WCl_6 reacted with trithiazyl chloride, $(NSCl)_3$, to give $[WCl_4(NSCl)]_2$ which upon addition of Ph_4AsCl gave $(Ph_4As)[WCl_5(NSCl)]$. A crystal structure determination of the former complex showed it to have the structure (47). The almost linear W-N-S linkages and very short W-N distances suggested the formulation $W{=}\overset{+}{N}{=}\overset{-}{S}\text{-}Cl$ [140].

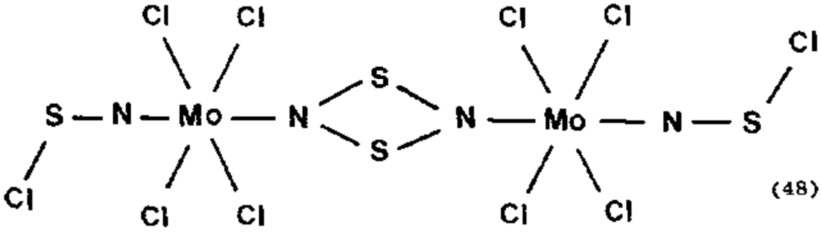


(47)

Bond distances are

W...W = 3.918(1)
W-Cl = 2.275(5)-2.288(6)
W-μCl(*trans* N) = 2.650(4)
W-μCl(*cis* N) = 2.441(4)
W-N = 1.76(2)Å

A similar reaction between $MoCl_5$ and $(NSCl)_3$ in dichloromethane gave several products among which was $[MoCl_4(NSCl)]_2(\mu\text{-}N_2S_2)$ isolated as black crystals. The structure was shown to be (48) in which the N_2S_2 unit is planar.

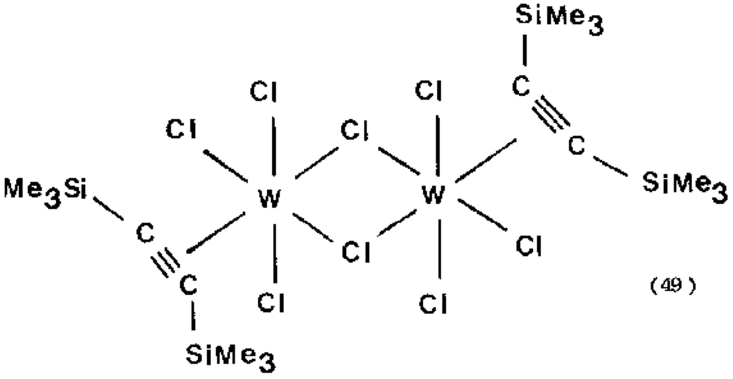


(48)

Bond distances are

Mo-N(NSCl) = 1.745(2)
Mo-N(N_2S_2) = 2.276(2)
Mo-Cl = 2.299(1)-2.357(1)
N-S(NSCl) = 1.586(2)
N-S(N_2S_2) = 1.643Å

Reaction of WCl_6 with bis(trimethylsilyl)acetylene and C_2Cl_4 in dichloromethane gave green $[WCl_4(Me_3SiCCSiMe_3)]_2$ which was shown to have the structure (49).



(49)

Bond distances are

$$\begin{aligned} W\text{-}Cl &= 2.307(2)\text{-}2.331(3) \\ W\text{-}\mu Cl &= 2.44(3),\ 2.724(3) \\ W\text{-}C &= 2.026(11)\text{Å} \end{aligned}$$

The chloro bridges were asymmetric with the long one *trans* to the acetylene ligand [142].

2.3.2 Complexes with oxygen donor ligands

The molar heat capacity of MoO_2 has been determined over a wide temperature range. An anomaly at 865K with an enthalpy change of $(178 \pm 24) KJmol^{-1}$ was observed which was associated with slight structural changes [11].

Trans-$MoO_2(CO)_4$ has been prepared at 10K by photolysis of $Mo(CO)_6$ in oxygen doped argon or methane matrices [143]. The complex was identified by extensive IR and Raman spectroscopic studies using natural abundance molybdenum isotopes and enriched ^{13}C and ^{18}O substitution.

Two new comproportionation reactions have been devised for the preparation of $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(H_2O)_9]^{4+}$. The reaction of $[MoO_4]^{2-}$ and $[Mo_2(H_2O)_8]^{4+}$ proceeded according to

$$3Mo_2{}^{4+}(aq) + 6[MoO_4]^{2-} + 16H_3O^+ \longrightarrow 4[Mo_3O_4(H_2O)_9]^{4+}$$

and the reaction of the Mo(III) dimer (produced by Zn/Hg reduction of $[MoO_4]^{2-}$) with further $[MoO_4]^{2-}$ gave

$$Mo_2^{6+}(aq) + [MoO_4]^{2-} + 6H_2O \longrightarrow [Mo_3O_4(H_2O)_9]^{4+}$$

The authenticity of the products was confirmed by their optical spectra together with the preparation of derivatives which were identified by comparing crystallographic unit cell parameters with known values [144].

A crystal structure determination for $Ba[Mo_3O_3S(Hnta)_3]$ (H_3nta = nitrilotriacetic acid) revealed that the anion contains a Mo_3O_3S core (sulphur capped) similar to that found in $[Mo_3O_4]^{4+}$ clusters. The tridentate Hnta ligand completed an approximately octahedral coordination about each molybdenum atom via two carboxylates and nitrogen, with one carboxylate remaining non-coordinated. Average bond distances are Mo-Mo = 2.589, Mo-μ_3S = 2.360, Mo-μ_2O = 1.917, Mo-O = 2.097 and Mo-N = 2.264Å [145].

Reduction of $Na_2[MoO_4]$ with zinc dust in refluxing acetic anhydride and recrystallization from methanol led to the isolation of red $[Zn_2(O_2CMe)_3][Mo_3O_2(O_2CMe)_6(OMe)_3].2H_2O$. The anion has a bicapped (oxo) triangular arrangement with two bridging acetates spanning an edge with the alkoxides axial. The cation contains two zinc atoms linked by three bridging acetates, but there are also Zn-O contacts to the alkoxide ligands of the anion [146]. Important bond distances are Mo-Mo = 2.763(3)-2.817(3), Mo-μ_3O = 1.99(1)-2.03(1), Mo-O(OMe) = 1.95(1)-2.06(1), Mo-O(acetate) = 1.95(1)-2.14(1)Å.

$[Mo_3O_2(O_2CPh)_6(H_2O)_3]^{2+}$ has been prepared by the oxidation of $Mo_2(O_2CPh)_4$ with dibenzyl peroxide. The corresponding tungsten complex was prepared from $W(CO)_6$ and HO_2CPh at 160°C. The crystal structure determination of the molybdenum compound showed a structure similar to that described for the acetate above, with water molecules axial [147]. Bond distances are Mo-Mo = 2.762(av), Mo-μ_3O = 1.98(av), Mo-O = 2.067(6)-2.093(6) and Mo-H_2O = 2.12Å(av).

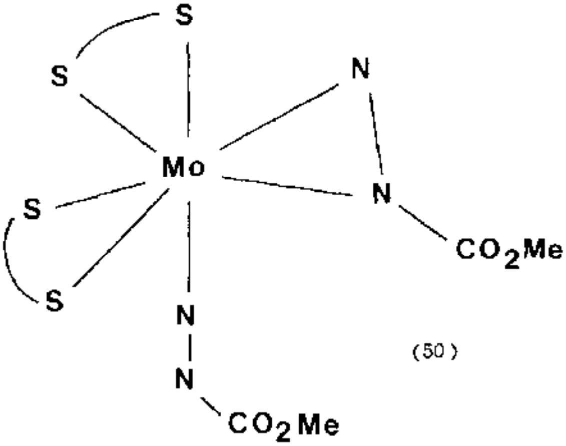
A detailed study has been made of the electronic structure of $Mo_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu_2\text{-}OR)_3(OR)_6$ for R = H by the Hall-Fenske MO method which may serve as a model for real compounds where R = CH_2CMe_3, $CHMe_2$. The HOMO is an *e* orbital that is predominantly Mo-Mo bonding in character and the LUMO is also an *e* type orbital with the HOMO-LUMO separation small [148]. Electrochemical experiments in thf on $Mo_3O(OCH_2CMe_3)_{10}$ revealed a quasi-reversible one-electron reduction to give an anion which appeared to be stable on the coulometric timescale. There was a further partially reversible one-electron reduction close to the solvent limit, but the product of this process was not characterized. There was also an irreversible oxidation in CH_2Cl_2 solution. It is apparent from the MO calculations and the electrochemical results that there is likely to be a rich redox chemistry of these clusters [148].

2.3.3 Complexes with sulphur donor ligands

Aluminium oxide supported sulphided Co/Mo hydrodesulphurization catalysts (and their oxide precursors) have been examined by both X-ray absorption near edge structure (XANES) and EXAFS techniques. The oxide precursors showed the presence of Co(III) and Mo(VI), but after sulphurization they contained octahedral Co(II) and Mo(IV) together with S-S linkages. The Co-S and Mo-S bond distances were close to those found in CoS_2 and MoS_2 [149].

Reactions between $Mo(CO)_6$ and K[dtc] in anhydrous solvents at high temperature gave diamagnetic $Mo(dtc)_4$ which are thought to have a dodecahedral structure [150].

The crystal structure of the previously reported $[Mo(NHNHCO_2Me)(N_2CO_2Me)(S_2CNMe_2)]$ has been determined. The molybdenum atom adopts a pentagonal bipyramidal structure as shown in (50) with a sulphur and the N_2CO_2Me ligand in the axial positions. The hydrazido(1-) ligand is η^2-N-N bonded, similar to the mode observed previously.



(50)

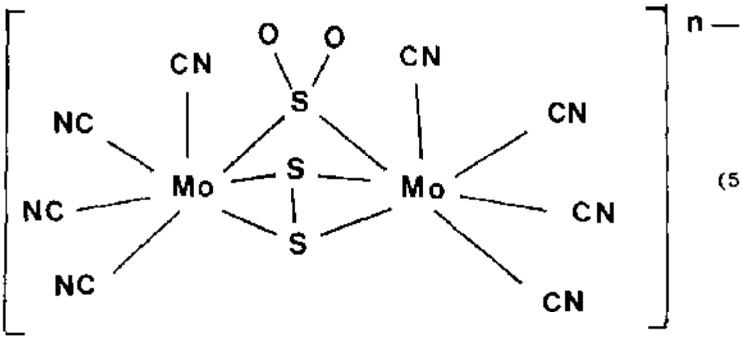
Bond distances are

Mo-N(ax) = 1.71(1) Mo-S(ax) = 2.597(5)

Mo-N(eq) = 2.12(1) Mo-S(eq) = 2.482(5)-2.519(4)Å

Interaction of $Mo(CO)_2(Et_2dtc)_2$ and $cp_4Fe_4S_6$ gave $cp_4Fe_4S_4$, a product thought to be $Mo_2S_2(Et_2dtc)_3$ and, after recrystallization from MeCN/thf, the complex $[Mo(SH)(Et_2dtc)_3]$.thf. The crystal structure determination showed a pentagonal bipyramidal arrangement with SH axial [152]. Bond distances are Mo-SH = 2.398(4), Mo-S(ax) = 2.467(4), Mo-S(eq) = 2.487(4)-2.524(4) and S-H = 0.72Å.

Oxygen reacted with an aqueous solution of the trivalent complex $[Mo_2S_2(CN)_8]^{6-}$ to give two isostructural anions $[Mo^{III}Mo^{IV}(SO_2)(S_2)(CN)_8]^{5-}$ (paramagnetic) and $[Mo^{IV}_2(SO_2)(S_2)(CN)_8]^{4-}$ (diamagnetic) which occur together in a mixed crystal. The two anions reside at crystallographically different positions in the lattice. They both have the same general structure **(51)** with



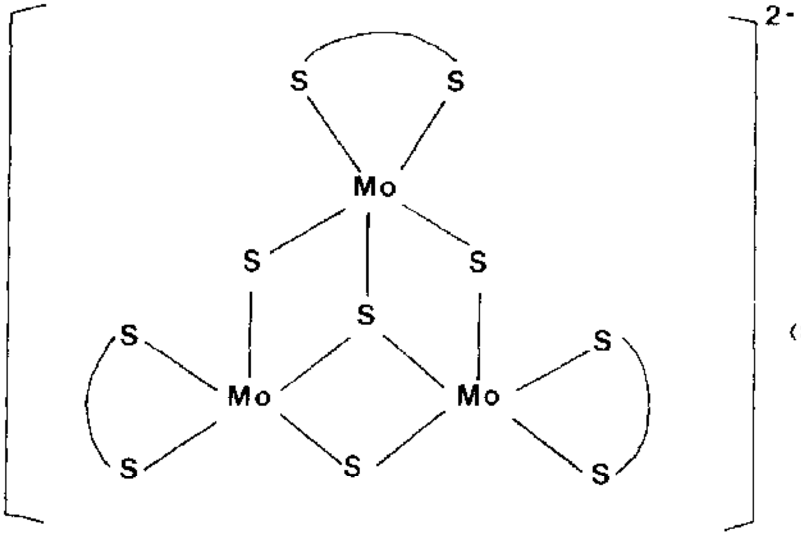
(51)

Bond distances are

	$[Mo_2(SO_2)(S_2(CN)_8]^{5-}$	$[Mo_2(SO_2)(S_2(CN)_8]^{4-}$
Mo-Mo	2.790(1)	2.684(1)
$Mo-S_2$	2.448(3),2.436(3)	2.427(3)
$Mo-SO_2$	2.346(3)	2.367(3)
Mo-CN(ax)	2.132(10)	2.182(11)
Mo-CN(eq)	2.129(10)-2.145(10)	2.147(9)-2.170(10)Å

pentagonal bipyramidal stereochemistry ($[SO_2]^{2-}$] axial) and the only substantial difference between the bond distances in the two anions is the Mo-Mo distance. EPR spectroscopy showed that the odd electron in the paramagnetic anion was delocalized over both molybdenum atoms [153].

Reaction of $(NH_4)_2[Mo_3S(S_2)_6]$ with NEt_4Br and an excess of $Na_2[SCH_2CH_2S]$ led to the isolation of $(NEt_4)_2[Mo_3S_4(SCH_2CH_2S)_3]$, the anion of which has the structure shown in **(52)** [154]. Interestingly, reaction of the complex with three equivalents of sulphur gave the complex $(NEt_4)_2[Mo_3S_7(SCH_2CH_2S)_3]$ in which the μ_2-sulphides of **(52)** are replaced by $[\mu_2-S_2]^{2-}$ groups with retention of the trimer unit and preservation of the metal oxidation state.



(52)

Average bond distances are

$\text{Mo-Mo} = 2.78$ $\qquad$ $\text{Mo-S} = 2.48$

$\text{Mo-}\mu_3\text{S} = 2.35$ $\qquad$ $\text{Mo-}\mu_2\text{S} = 2.316\text{A}$

The reaction was reversible by treatment with cyanide and other reagents. It was suggested that facile interchange between S^{2-} and $S_2{}^{2-}$ may be a basis of sulphide catalytic systems.

The cluster $[\text{Mo}^{\text{IV}}{}_3\text{S}_4(\text{CN})_9]^{5-}$ undergoes both a reversible one-electron oxidation and reduction in water [155]

$$[\text{Mo}_3\text{S}_4(\text{CN})_9]^{4-} \rightleftharpoons [\text{Mo}_3\text{S}_4(\text{CN})_9]^{5-} \rightleftharpoons [\text{Mo}_3\text{S}_4(\text{CN})_9]^{6-}$$

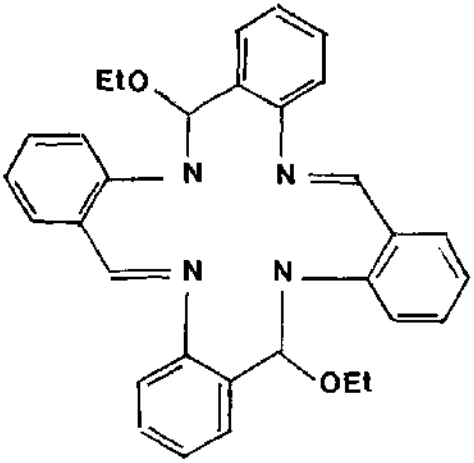
Reaction between $K_2[\text{MoOCl}_5]$ and P_2S_5 in EtOH saturated with HCl gas gave $\text{Mo}_3(\mu_3\text{-S})(\mu_2\text{-S}_2)_3\text{Cl}(\text{dtp})_3$ (dtp = $[S_2P(OEt)_2]^-$). A crystal structure determination showed a distorted cubane type of structure with the Mo_3, μ_3-S and one atom of each $\mu_2\text{-S}_2$ contributing to the cube with the final position being occupied by the chlorine atom. The chlorine is bonded to three sulphur atoms, one from each of the $[\mu\text{-S}_2]^{2-}$ groups, but is not bonded to any molybdenum atom. Each molybdenum is chelated by a dtp group. Bond distances are Mo-Mo = 2.725(3)(av), Mo-S = 2.360(2)-2.549(2)Å [156].

The complex $Ca_3[Mo_4S_4(edta)_2]_2$ has been isolated and its crystal structure determined [157]. The anion has a cubane type structure with each edta ligand bonding in a *facial* configuration to two molybdenum atoms. Bond distances are Mo-Mo = 2.755(2)-2.880(2), Mo-S = 2.351(3)-2.369(4)Å. The anion is a mixed oxidation state complex $Mo^{III}{}_3Mo^{IV}$ and although it was paramagnetic no EPR signal could be observed. The complex showed both a single one-electron oxidation and reduction.

2.3.4 Complexes with nitrogen donor ligands

The reduction of N_2 to N_2H_4 by coprecipitated Mo(III-V) hydroxide/Ti(III) hydroxide has been studied at the optimum ratio of Mo/Ti of about 0.1-0.2. In separate experiments with molybdenum alone, it was established that Mo(IV) is the active oxidation state. The mechanism involves initial formation of diazene, N_2H_2, which disproportionates at high concentration to N_2 and N_2H_4 and at low concentration to N_2 and H_2. The function of the titanium was to separate the molybdenum atoms to keep Mo(IV) mononuclear [158].

Binuclear $[Mo_2Cl_8]^{4-}$ acted as a template for the self-condensation of 2-aminobenzaldehyde in EtOH. The dimolybdenum unit was retained in the Mo(IV) product $[Mo_2(A)_2(H_2O)_2Cl_2]Cl_2$ where A is the macrocyclic ligand shown in (53).



(53)

Details of the structure of the complex are not known, but it was suggested that a double bond was retained between the molybdenum atoms with two bridging chlorines and that the macrocyclic ligands were orientated at right angles to the metal-metal axis [159].

2.3.5 Complexes with metal-carbon bonds

The thermal behaviour of $K_4[W(CN)_8].2H_2O$ has been investigated [160]. Dehydration occurred at 100-160°; formation of $K_3[W(CN)_7]$ at 200-300° was followed by further decomposition to $K_3[W(CN)_6]$ at 320-530° and finally total decomposition to WC, KCN and C occured at 540-730°C.

It has been shown previously that $[Mo(CN)_8]^{4-}$ reacts with phen according to

$$[Mo(CN)_8]^{4-} + 2phen \xrightarrow[MeOH/H_2O]{h\nu/\Delta} Mo(CN)_4(phen)_2 + 4CN^-$$

but it has now been discovered that the corresponding tungsten complex reacts quite differently, giving complete substitution of the cyanide ligands [161]

$$2[W(CN)_8]^{4-} + 2phen \xrightarrow[MeOH/H_2O]{h\nu/\Delta} W(OMe)_4(phen)_2$$

Treatment of an ice cold solution of $K_5[Mo(CN)_7]$ with acid (HOAc,HCl,H_2S) under strictly anaerobic conditions gave dark green diamagnetic $K_4[MoH(CN)_7]$, analogous to the known tungsten compound. The ^{13}C NMR spectrum showed only a doublet (J = 11.3Hz) suggesting a fluctional molecule [162]. A solution of $K_5[Mo(CN)_7]$ itself showed the same doublet (as well as resonances due to CN^- and $[Mo(CN)_7]^-$) which disappeared on addition of KOH. It was suggested that the equlibrium

$$[Mo(CN)_7]^{5-} + H_2O \rightleftharpoons [MoH(CN)_7]^{4-} + OH^-$$

is established in solution.

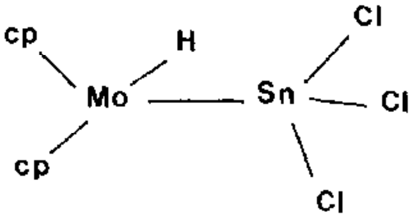
Two studies have been made on the effects of irradiation on octacyano complexes of tungsten. Irradiation of a mixture of $H_4[W(CN)_8]$ and $K_4[W(CN)_8]$ at 0.5°C gave a red stable compound identified as $[W(CN)_7(H_2O)]^{3-}$ and the aquation was reversible if the solution was allowed to stand in the dark [163]. The compound reacts with hydroxide according to

$$[W(CN)_7(H_2O)]^{3-} + OH^- \longrightarrow [W(CN)_7(OH)]^{4-} + H_2O$$

In the second study it was found that irradiation of the tungsten(V) complex $[W(CN)_8]^{3-}$ in H_2O/MeOH also gave a red complex which was thought to be $[W(CN)_7(O_2)]^{3-}$, although the compound could not be isolated [164]. Raman spectroscopy suggested that the red compound was a dioxygen complex of W(IV) which in the dark gradually decomposed to give $[W(CN)_7(H_2O)]^{3-}$.

In two separate publications, the structures of $Na[MoO(CN)_3(phen)].2phen$ and $Na[MoO(CN)_3(phen)].2phen.MeOH.H_2O$ have been reported [165,166]. They contain almost identical *mer* octahedral arrangements about the molybdenum atoms. Bond distances are Mo=O = 1.659(7), Mo-N = 2.174(7), 2.363(7) and Mo-C = 2.092(9)-2.179(10)Å. The long Mo-N bond is *trans* to the oxo group. In each compound the remaining phen ligands are coordinated to sodium.

The crystal structure of $(C_5H_5)_2MoH(SnCl_3)$ has been determined and the geometry is as shown in (54) [167].



(54)

Bond distances are

Mo-Sn = 2.652(1) Mo-H = 1.74(7)Å

2.4 MOLYBDENUM(III) AND TUNGSTEN(III)

The crystal structure of $(NMe_4)_3[Mo_2Cl_8H]$ has been examined by both X-ray (room temperature) and neutron diffraction (18K) to obtain a clear indication of the position of the hydrogen [168]. Although it is not a crystallographic requirement, the hydrogen atom is symmetrically bonded to both molybdenum atoms with Mo-H = 1.823(7)Å and the angle at H is 80.6(2)° (neutron). Other bond distances (neutron diffraction) in the biconfacial octahedral anion are Mo-Mo = 2.357(3), Mo-μCl = 2.486(6), Mo-Cl(*trans* H) = 2.490(8) and Mo-Cl(*trans* Cl) = 2.398(8)Å.

The iodo complex $[Mo_2I_8H]^{3-}$, analogous to the chloro anion described above, has been prepared and characterized by X-ray diffraction. The hydrogen atom was not detected in the analysis but the structure is similar to that of the chloro analogue. The Mo-Mo separation of 2.408Å is very similar to that of the chloro compound, suggesting that it is the strong Mo-H-Mo interaction which determines the metal-metal distance [169].

The kinetics of the 1:1 stoichiometric equilibration between $[Mo(H_2O)_6]^{3+}$ with oxalate were investigated in aqueous *p*-toluenesulphonic acid (Hpts) at 25°C [170]. In the pH range studied, the major form of oxalate is $[HC_2O_4]^-$

(dissociation constant = K_a) and

$$k_{eq} = k_1 K_a[Mo^{3+}]/([H^+] + K_a) + k_{-1}[H^+]$$

where k_1 and k_{-1} are defined by

$$Mo^{3+} + [HC_2O_4]^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Mo(C_2O_4)]^+ + H^+$$

The oxidation of monomeric $[Mo(H_2O)_6]^{3+}$ by the one-electron oxidants $[IrCl_6]^{3-}$, $[Co(ox)_3]^{3-}$ and $[VO]^{2+}$ have been examined. In all cases the dimeric molybdenum(V) species, $[Mo_2O_4]^{2+}$, was the only product. Kinetic studies indicated that an outer sphere mechanism for oxidation by Ir(IV) with a rate determining first step thought to be

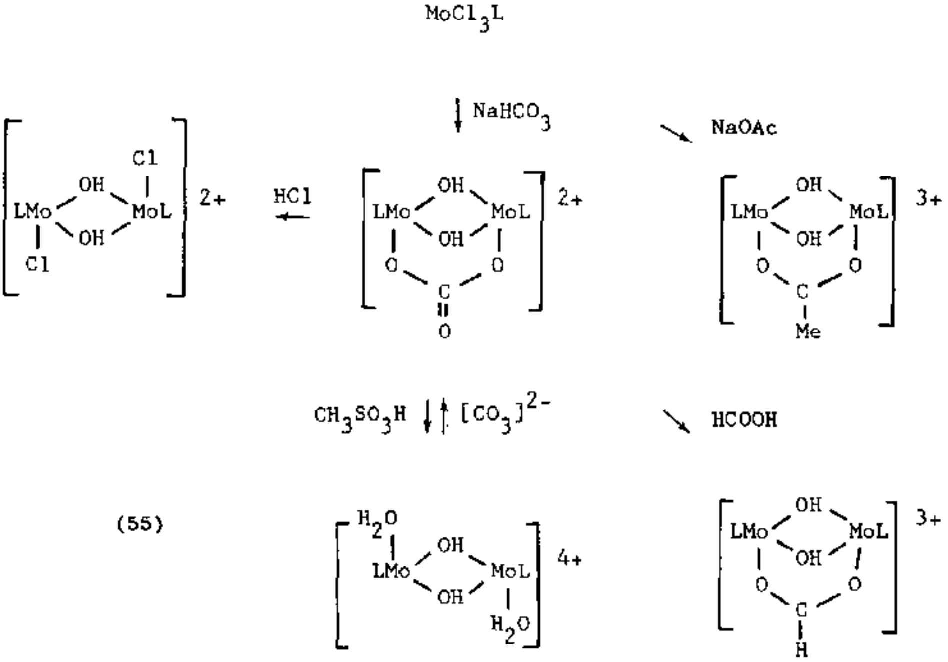
$$Mo(III) + Ir(IV) \longrightarrow Mo(IV) + Ir(III)$$

although build-up of Mo(IV) was not observed. A first order rate constant k_{obs} (stopped flow) gave the rate law at 25°C

$$k_{obs}/2[Mo(III)] = k_a + k_b[H^+]$$

at I = 0.2M (Lipts); $k_a = 3.44 \times 10^4 M^{-1}s^{-1}$ and $k_b = 2.9 \times 10^4 s^{-1}$. The Co(III) oxidation was acid independent and exhibited behaviour consistent with an inner sphere substitution controlled process [171].

A series of binuclear Mo(III) complexes have been prepared by the hydrolysis of $MoCl_3L$ (L = 1,4,7-triazacyclononane) in aqueous solution as shown in the scheme (55) [172]. The aquo complex was easily oxidized to dimeric Mo(V), $[Mo_2O_4L_2]^{2+}$. Crystal structure determinations were performed on two compounds; the $[Mo_2(OH)_2Cl_2L_2]^{2+}$ cation has the structure shown in the scheme with the nitrogen atoms of the ligand adopting a *facial* configuration. Bond distances are Mo-Mo = 2.501(3), Mo- OH = 2.130(av), Mo-Cl = 2.438(5) and Mo-N = 2.215Å(av). The crystal structure of the acetato/hydroxo bridged complex has also been determined. It also contains octahedral Mo(IV) with the octahedra sharing an edge. The Mo-Mo bond distance is 2.471(2)Å and the Mo-O and Mo-N distances are very similar to those of the previous compound. It was suggested that a triple bond exists between the metal atoms in these compounds.


(55)

Reaction of $K_4[Mo_2Cl_8]$ with 3,6-dithiaoctane (dto) is known to give $Mo_2(\mu\text{-}SEt)_2(dto)_2$, but it has now been reported that better yields result when the reaction is carried out in the presence of EtSSEt. Also, the reaction of $\beta\text{-}Mo_2Cl_4(dmpe)_2$ with EtSSEt gave $Mo_2Cl_4(\mu\text{-}SEt)_2(dmpe)_2$. The structures of the two compounds are similar and consist of two octahedra sharing an edge. The chelating ligands are *trans* to the bridging SEt groups. Bond distances are

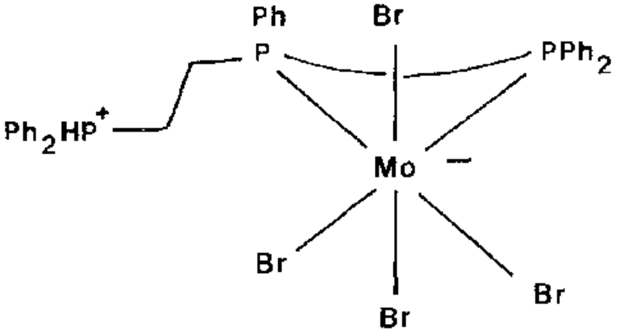
	$Mo_2Cl_4(SEt)_2(dto)_2$	$Mo_2Cl_4(SEt)_2(dmpe)_2$
Mo-Mo	2.682(1)	2.712(3)
Mo-μSEt	2.402(2)	2.411(4)
Mo-S(or P)	2.579(av)	2.541(3)
Mo-Cl	2.403(av)	2.417(3)Å

The Mo-Mo bond lengths indicated a bond order of at least one and the compounds were diamagnetic [173].

$[MoCl_3(NO)(PPh_3)_2]$ reacted with excess aryl thiols in MeOH/NEt_3 to give $(NEt_3H)[Mo(NO)(SR)_4]$, although ^tBuS gave only $[MoCl(^tSBu)_3(NO)]^-$. The analogous reactions with $WCl_3(NO)(PPh_3)_2$ gave $[W(SR)_4(NO)]^-$ with all thiols. ^1H NMR spectra for $[Mo(SR)_4(NO)]^-$ showed two SR signals (1:3) suggesting a trigonal bipyramidal structure and this was confirmed by X-ray diffraction for $[Mo(SPh)_4(NO)]^-$. The NO and one SPh were axial. Bond distances are Mo-N = 1.766(6), Mo-S(ax) = 2.574(2) and Mo-S(eq) = 2.33Å(av). The complex

$[WCl(SPh)_3(NO)]^-$ has a similar structure with NO and Cl axial. Bond distances are W-N = 1.755(13), W-Cl = 2.490(4), W-S = 2.32Å(av). In both cases the W-N-O unit is linear [174].

In the review last year the reaction of *trans*-$[Mo(N_2)_2(triphos)(PPh_3)]$ with anhydrous HBr in C_6H_6 to give N_2 and hydrazine was described. These reactions proceed via a pair of isomeric hydrazido(1-) complexes, but careful work-up gave only a single Mo(III) complex (56)



(56)

It is believed that the two separate reactions giving N_2 and N_2H_4 coincidently give the same molybdenum containing product [175].

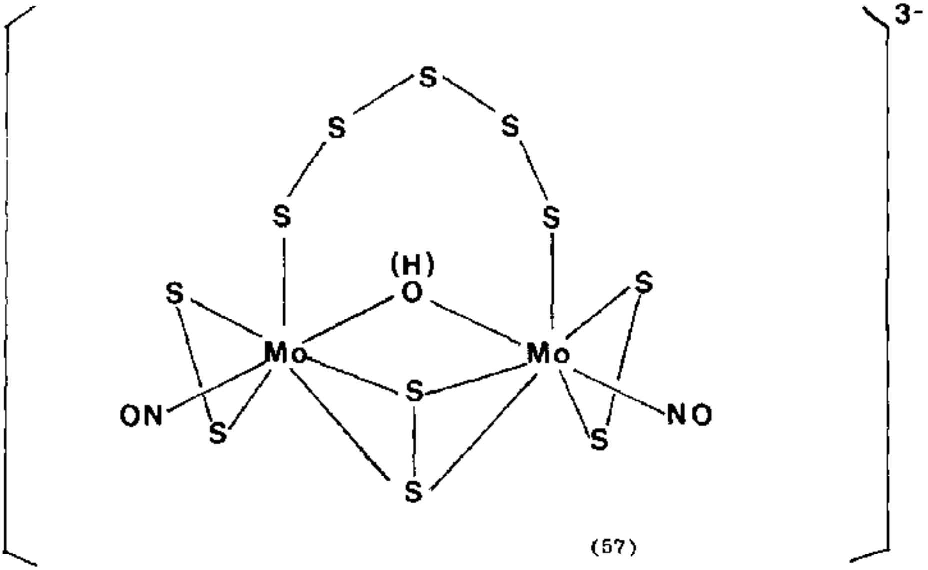
The cluster $[Mo_4S_4(CN)_{12}]^{8-}$ undergoes two reversible one-electron oxidations [155]

$$[Mo_4S_4(CN)_{12}]^{8-} \rightleftharpoons [Mo_4S_4(CN)_{12}]^{7-} \rightleftharpoons [Mo_4S_4(CN)_{12}]^{6-}$$

2.5 MOLYBDENUM(II) AND TUNGSTEN(II)

The structure of a remarkable complex $(NH_4)_3[Mo_2(NO)_2(S_2)_3(S_5)(OH)]$ has been determined and is shown in (57). The geometry about each molybdenum is pentagonal bipyramidal with all the atoms in the equatorial plane being sulphur. The geometry of the $Mo_2S_5(\mu\text{-}S_2)$ unit is very similar to that of S_8 [176].

The compound $MoL(NO)I_2$ (L = $HB(3,5\text{-}Me_2pz)_3$) reacted with nitrogen heterocycles to give $[MoL(NO)Z_2]^+$ (Z = py, imidH, pzlH etc) and with organoamido anions to give $MoL(NO)Y_2$ (Y = $NHEt^-$, $NHPh^-$, pyrollide etc). The crystal structure of the pyrollide compound was determined. It showed octahedral molybdenum with Mo-NO = 1.163 and Mo-N(pyr) = 2.01Å(av) [177].



(57)

Bond distances are

Mo-N = 1.709(10)   Mo-O = 2.15(av)

Mo-μS_2 = 2.50(av)   Mo-S_2 = 2.46(av)

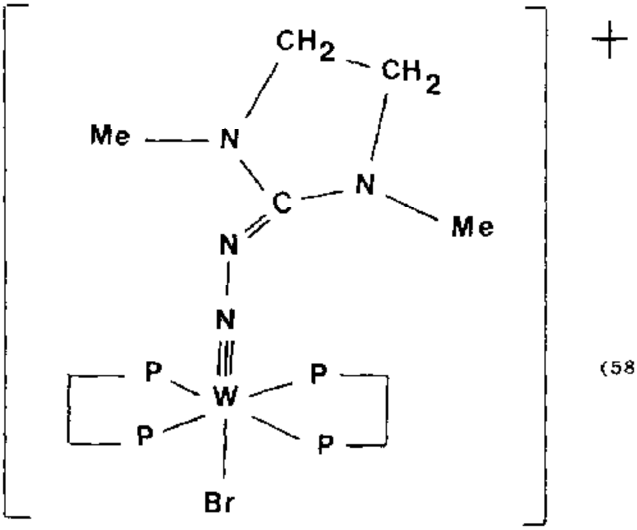
Mo-S = 2.48Å(av)

Reduction of $MoCl_2$(TTP) with zinc amalgam under CO yielded $Mo(CO)_2$(TTP) with the carbonyls *cis* in an approximately trigonal prismatic arrangement, whilst reaction with pyridine gave *trans*-$Mo(py)_2$(TTP). Crystal structure determinations were carried out for both complexes and theoretical calculations were performed for the model compounds $Mo(CO)_2(NH_2)_4$ and $Mo(py)_2(NH_2)_4$ in order to account for the different stereochemistries of the real compounds in terms of the σ and π properties of the ligands [178].

^{95}Mo NMR spectra have been examined for a range of complexes containing the *cis*-$[Mo(NO)_2]^{2+}$ group, such as $Mo(NO)_2(Et_2dtc)_2$, $[Mo(NO)_2Cl_4]^{2-}$, $Mo(NO)_2Cl_2$(bipy) etc. Molybdenum chemical shifts ranged from -985 to +201ppm, but the ordering with respect to ligands was different to that previously observed for MoO_2 complexes. No correlations were found between ^{95}Mo chemical shifts and either electronic spectra or nitrosyl stretching frequencies [179].

Two isomers of $Mo(NO)(NCS)_2$(phen) were obtained by either heating $Mo(NO)(NH_2O)(NCS)_2$(phen) in refluxing acetophenone or be photolysis in the same solvent. It was suggested that they were trigonal bipyramidal (refluxing) and square pyramidal; both isomers were paramagnetic and gave EPR signals. The corresponding bipy complex, $Mo(NO)(NH_2O)(NCS)_2(bipy)$, reacted similarly upon photolysis to give square pyramidal $Mo(NO)(NCS)_2(bipy)$, but refluxing in acetophenone gave $Mo_2(NCS)_4(bipy)_2$ which was thought to be a quadruple bonded dimer [180].

The compound $[WBr(dppe)_2\{NN{=}\overline{CN(Me)(CH_2)_2N}(Me)\}](PF_6)$ has been prepared and the structure of the cation shown to be as in (58)



(58)

Bond distances are

$W{\equiv}N = 1.776(7)$

$W{-}Br = 2.611(1)$ $\qquad$ $W{-}P = 2.511(2){-}2.539(2)$Å

There was considerable distortion in the structure due to steric interactions between the methyl group and one dppe ligand. In solution, the methyl groups gave only a single resonance at room temperature but at -60°C they became non-equivalent. In contrast, the corresponding $NNCMe_2$ complex is rigid and it was suggested that in the present case it is steric effects which make the fluctional behaviour (rotation about the C-N bond) possible [181].

Reduction of $MoCl_4(thf)_2$ in the presence of PMe_3 produced $MoH_2(PMe_3)_5$. An X-ray structural determination showed pentagonal bipyramidal geometry about the metal atom with the hydrides and three phosphines in the equatorial plane. Two phosphines which are almost *trans* to the hydrides have the longest bonds to molybdenum. Bond distances are Mo-H = 1.68(4), Mo-P(*trans* H) = 2.474(av), Mo-P(eq) = 2.403(3), Mo-P(ax) = 2.425(3)Å. The dihydride reacted with CO_2 which inserted into one of the Mo-H bonds to give a formato complex $MoH(O_2CH)(PMe_3)_4$ which also has a pentagonal bipyramidal structure with H *trans* to the symmetrically bidentate formate group in the equatorial plane. Bond distances are Mo-H = 1.68(3), Mo-O = 2.318(4), Mo-P(eq) = 2.369(3) and Mo-P(ax) = 2.426(3)Å. A similar insertion into the dihydride with phenylisocyanate gave $MoH(PhNC\{H\}O)(PMe_3)_4$ whilst reaction with trifluoroacetic acid gave $MoH(O_2CCF_3)(PMe_3)_4$ [182].

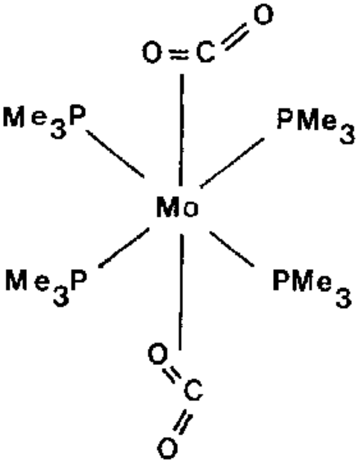
The known compound $WH(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)$, which was prepared by the co-condensation of tungsten atoms and PMe_3, is remarkably reactive as shown in the scheme (59)

$$\begin{tikzcd}
\mathit{fac}\text{-}W(CO)_3(PMe_3)_3 & & W(N_2)(PMe_3)_5 & \\
{[W(PMe_3)_4H_2(H_2O)F]F} \arrow[d, shift left, "\text{KH in thf}"] & WH(PMe_3)_4(\eta^2\text{-}CH_2PMe_2) \arrow[l, "\text{aq HF}", "Et_2O"'] \arrow[ul, "CO"] \arrow[ur, "N_2"'] \arrow[r, "H_2"] \arrow[d, "SiH_4"] & W(PMe_3)_5 \arrow[r] & W(PMe_3)_4H_4 \\
W(PMe_3)_4H_2F_2 \arrow[u, shift left, "\text{wet } Et_2O"] & W(PMe_3)_4H_2(SiH_3)_2 & &
\end{tikzcd} \tag{59}$$

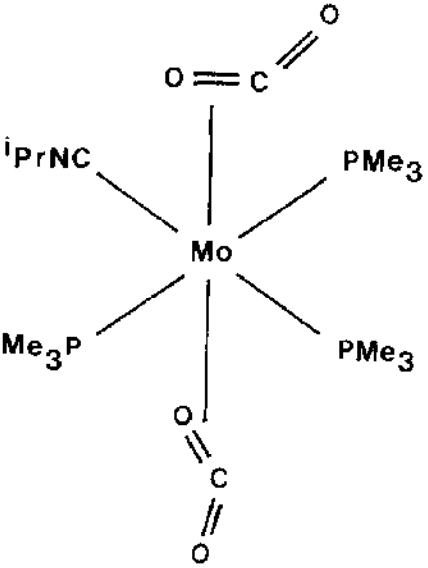
The crystal structure of $[W(PMe_3)_4H_2(H_2O)F]F$ was determined and although the hydride atoms were not detected, their positions were implied by the dodecahedral arrangement of the ligands about the metal atom (their presence was confirmed by NMR spectroscopy). Bond distances are W-F = 2.08(1), W-P = 2.451(4)-2.473(3), W-O = 2.084(9)Å [183].

2.6 MOLYBDENUM(0) AND TUNGSTEN(0)

It has been reported that under irradiation *trans*-$Mo(N_2)_2(dppe)_2$ reacted with CO_2 at room temperature. IR and ^{31}P NMR studies suggested that the material was a bis(CO_2) adduct, but the head-to-tail arrangemnt of C_2O_4 could not be excluded [184]. The very similar reaction of CO_2 at 5atm pressure with *trans*-$Mo(N_2)_2(PMe_3)_4$ has been investigated and the structure of the product was suggested by ^{31}P and ^{13}C NMR studies to be as shown in (60) with CO_2 η^2-bonded to the metal [185]. *Trans*-$Mo(CO_2)_2(PMe_3)_4$ reacted with isocyanates to give *trans,mer*-$Mo(CO_2)_2(CNR)(PMe_3)_3$ and a crystal structure determination was carried out on the CN^iPr complex. The geometry is octahedral about the metal atom as shown in (61) and the staggered configuration of the two η^2-bonded CO_2 ligands was confirmed [186].



(60)



(61)

Bond distances are

$Mo-C(CO_2) = 2.105(av)$ $Mo-C = 2.07(2)$

$Mo-O(CO_2) = 2.147(av)$ $Mo-P = 2.489(4)-2.548(5)Å$

The angle O-C-O is 133.5(10)°

The orientation of the double bonds is similar to that of the analogous bis(ethylene) complex.

Carbon dioxide also reacted with $[W(CO)_5R]^-$ anions (R = Me,Ph) but in these cases insertion occurred to give carboxylate anions $[W(CO)_5(O_2CR)]^-$. A significant acceleration of the rate of reaction was noted in the presence of alkali metal ions, although subsequent side reactions such as

$$[W(CO)_5(O_2CR)]^- + LiCl \longrightarrow [W(CO)_5Cl]^- + Li(O_2CR)$$

occurred. The compounds *cis*-$[MeW(CO)_4(PR_3)]^-$ reacted even more quickly with CO_2 to give carboxylate species. The crystal structure of one salt of the *cis*-$[MeW(CO)_4(PMe_3)]^-$ anion was determined. Bond distances in the octahedral anion are W-Me = 2.18(3), W-P = 2.532(3), W-C(*trans* P) = 1.941(13), W-C(*trans* Me) = 2.09(2), other W-C = 2.006(15)Å [187].

$Mo(CO)_6$ reacted with $(NEt_4)SR$ in MeCN to give dinuclear $[Mo_2(CO)_8(SR)_2]^{2-}$ which contain SR bridges. They show reversible two-electron oxidations in toluene to give dinuclear Mo(I) species $Mo_2(CO)_8(SR)_2$ which contain a Mo-Mo bond and for which the R = ^{t}Bu complex was previously known. In MeCN, oxidation of the zerovalent anion gave $Mo_2(CO)_6(SR)_2(MeCN)_2$ [188].

A detailed electrochemical and spectroscopic study of the redox couple $[Mo(CO)_3P_3]^{+/o}$ (P = monodentate phosphorus ligand) has shown that the electrode processes can be explained interms of the square reaction scheme

$$\begin{tikzcd} fac^{\circ} \arrow[r, shift left] & fac^{+} + e^{-} \arrow[l, shift left] \arrow[d] \\ mer^{\circ} \arrow[r, shift left] & mer^{+} + e^{-} \arrow[l, shift left] \end{tikzcd}$$

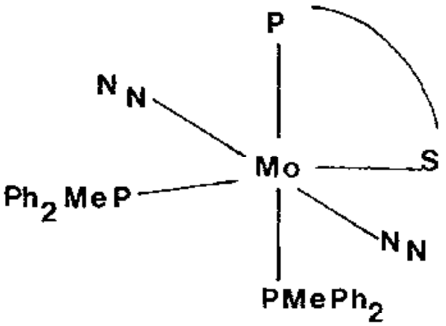
and the cross redox reaction

$$fac^{+} + mer^{\circ} \overset{K}{\rightleftharpoons} fac^{\circ} + mer^{+}$$

At low temperatures it was possible to measure $E^{\circ}(fac^{+/o})$ and $E^{\circ}(mer^{+/o})$ and hence the equilibrium constant K. For *fac*-$Mo(CO)_3P_3$ a satisfactory linear correlation between $\delta(^{13}C)$ (carbonyl) and $E^{\circ}(fac^{+/o})$ was observed, but such correlations with $\delta(^{31}P)$ and $\delta(^{95}Mo)$ did not exist [189].

Purple $M(CO)_3(Pcy_3)_2$ complexes reacted with hydrogen to give *mer,trans*-$M(CO)_3(Pcy_3)_2H_2$, the first isolable H_2 adduct (not a dihydride). X-ray and neutron diffraction studies on the tungsten compound showed the hydrogen to be η^2 bonded to give an approximately octahedral geometry about the metal. The H-H distance is 0.84Å, slightly greater than in free H_2 and the W-H distance is 1.75Å. N.M.R. and I.R studies (including ^{2}D labelling) confirmed the bonding between the hydrogen atoms and that the complex is not a dihydride [190].

Reaction of $Mo(N_2)_2(PMePh_2)_4$ with $Ph_2P(CH_2)_2SMe$ in ether/benzene gave crystals of *trans,cis*-$Mo(N_2)_2(PMePh_2)_2(Ph_2PCH_2CH_2SMe)$ with the structure shown in (62).



(62)

Bond distances are

Mo-P(*cis* S) = 2.500(8) Mo-P(*trans* S) = 2.443(9)

Mo-P(P-S) = 2.457(9) Mo-S = 2.483(8)

Mo-N = 1.99Å(av)

The complex reacted with H_2SO_4 in MeOH to give some NH_3, but the yield was lower than with $Mo(N_2)_2(PMePh_2)_4$ itself [191].

The kinetics of the reaction between *trans*-$Mo(N_2)_2(depe)_2$ and HCl in thf have been studied. The initial reaction produced $[MoH(N_2)_2(depe)_2]^+$ which, on the basis of spectrscopic studies could be either pentagonal bipyramidal or capped octahedral. In solutions of low acid concentration (<0.3M) loss of N_2 led to the formation of $MoH_2Cl_2(depe)_2$, but at higher acidities, protonation of dinitrogen occurred to give *trans*-$[Mo(NNH_2)Cl(depe)_2]^+$ [192].

Electrochemical studies have been carried out on a series of complexes *trans*-$M(N_2)_2(R_2PCH_2CH_2PR_2)_2$ (R = *p*-$CF_3C_6H_4$,*p*-ClC_6H_4,*p*-MeC_6H_4, C_6H_{11}). All displayed reversible one-electron oxidations and the variations of E^o with the phosphine substituents suggested through-metal conjugation between phosphorus and the dinitrogen ligands [193].

The ^{15}N N.M.R. spectra of a number of complexes of the type *trans*-$M(N_2)(NCR)(P\text{-}P)_2$ and *trans*-$M(N_2)_2(P\text{-}P)_2$ (P-P = dppe,depe) have been observed. Linear correlations of nitrogen chemical shift with $E_{1/2}{}^{ox}$ and Hammet σ_p parameters were found [194].

Although *trans*-$Mo(N_2)_2(PPh^nPr_2)_4$ is stable in the solid state, in solution it reacts with N_2 to give the first tris(dinitrogen) complex, $Mo(N_2)_3(PPh^nPr_2)_3$. ^{31}P N.M.R. and I.R. studies indicated a *mer* configuration and this was confirmed by an X-ray crystallographic investigation which showed all the N_2 groups to be linear. Bond distances are Mo-N(*trans* P) = 1.984(9), Mo-N(*trans* N) = 2.050(9), 2.015(8), Mo-P(*trans* N) = 2.512(2) Mo-P(*trans* P) = 2.483(2),2.497(2)Å [195].

Reaction between $Mo(CO)_6$ and $NOPF_6$ gave *cis*-$Mo(NO)_2(PF_6)_2$ from which complexes of the types $[Mo(NO)_2L_4]^{2+}$ and $[Mo(NO)_2(L\text{-}L)_2]^{2+}$ (L = monodentate ligand, L-L = bidentate ligand) have been prepared [196].

$Mo(PMePh_2)_4$ which contains an arene bound η^6 Ph-PMePh ligand, reacted with many small molecules L ($CO, N_2, P(OMe)_3$) to give $Mo(\eta^6PhPMePh)L(PMePh_2)_2$ [197].

2.7 METAL-METAL BONDED SPECIES

2.7.1 Triple bonded species of molybdenum(II) and tungsten(II)

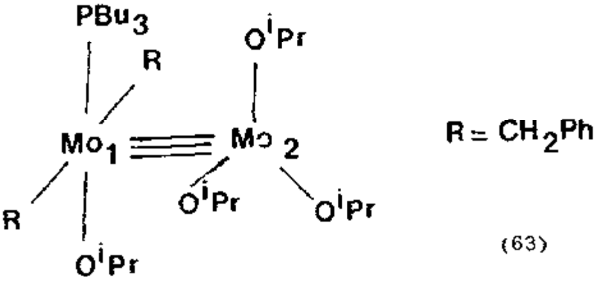
Single determinant STO-3G calculations on Mo_2H_6 and Mo_2F_6 show a favouring of the staggered over the eclipsed equilibrium geometry. The rotational barrier is higher for the hydride reflecting the increased repulsions between the polar Mo-H bonds in the eclipsed configuration. The Mo-F bonds are lower in energy and more localized than the Mo-H bonds. $Mo_2(OH)_6$ is predicted to be eclipsed with a low rotational energy barrier [198].

Mesitylenethiol reacted with $Mo_2(NMe_2)_6$ and $Mo_2(OR)_6$ (R = ^tBu, ^iPr, $CH_2{}^tBu$) to give $Mo_2(NMe_2)_2(SR)_4$ and $Mo_2(OR)_2(SR)_4$ respectively [199]. The ^1H N.M.R. spectra of the NMe_2 derivatives were consistent with a mixture of *gauche* and *anti* rotomers. but those of the alkoxides were relatively simple and were consistent with the presence of only the *anti* rotomer (or rapidly interconverting *anti* and *gauche* rotomers). The crystal structure of $Mo_2(O^iPr)_2(SC_6H_2Me_3)_4$ confirmed the *anti* rotomer in the solid state. The structure is typical of Mo_2L_6 complexes with bond distances Mo-Mo = 2.230(1), Mo-S = 2.320(av), Mo-O = 1.878(2)Å.

Reaction of 1,2-$Mo_2(CH_2Ph)_2(O^iPr)_4$ with PMe_3 (2 equivalents) gave $(O^iPr)_3Mo{\equiv}Mo(CH_2Ph)_2(O^iPr)(PMe_3)$ which X-ray diffraction showed to be the first example of a triply bonded Mo_2 species with different coordination around the two metal atoms as shown in **(63)**. The rather long Mo-P bond length is reflected in solution behaviour since at slightly above room temperature ^1H N.M.R. spectroscopy shows dissociation of the PMe_3 occurs according to the equation

$$(O^iPr)_3Mo{\equiv}Mo(CH_2Ph)_2(O^iPr)(PMe_3) \rightleftharpoons (O^iPr)_2(CH_2Ph)Mo{\equiv}Mo(CH_2Ph)(O^iPr)_2 + PMe_3$$

This system also provides the first example of exchange between atoms of alkyl



(63)

Bond distances are

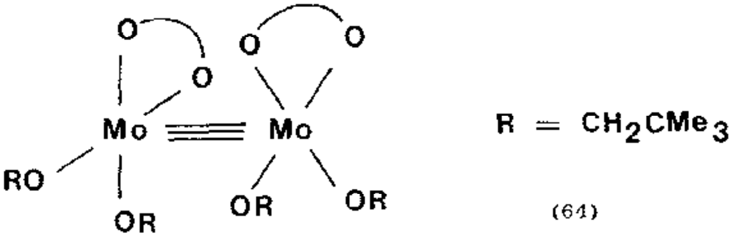
Mo-Mo = 2.235(1)   Mo-C = 2.22(1)

Mo(1)-O = 1.920(4)   Mo(2)-O = 1.89(2)

Mo-P = 2.581(2)Å

and alkoxy groups in Mo_2 systems [200].

Reaction of $M_2(OR)_6$ compounds with β-diketones $R'COCH_2COR''$ gave mixed alkoxide/β-diketonate complexes of the type $M_2(OR)_4(R'COCHCOR'')_2$. The structure of $Mo_2(OCH_2{}^tBu)_4(acac)_2$ is almost exactly staggered as shown in (64).



(64)

Bond distances are

Mo-Mo = 2.237(1)   Mo-OR = 1.888(3)-1.919(3)

Mo-O = 2.064(3)-2.117(3)A

The significant shortening of the Mo-OR bond lengths compared with the Mo-O(acac) bonds suggests the presence of π-bonding in the former. The ^1H N.M.R. spectra suggest that rapid rotation about the Mo-Mo triple bond occurs in solution [201].

$Mo_2(OR)_6$ compounds are known to react with CO and alkynes whilst with RNC ligands they give $[M(RNC)_7]^{2+}$ species. In contrast, the closely related $M_2(OR)_4(R'COCHCOR'')$ complexes do not react with either CO or alkynes and only undergo simple addition with RNC to give $M_2(OR)_4(R'COCHCOR'')(RNC)_2$. The structure of $Mo_2(OCH_2{}^tBu)_4(acac)_2({}^tBuNC)_2$ was determined and shown to be two octahedral units linked by two OR bridges with the acac groups chelated in the $Mo_2(OR)_2$ plane. There was some disorder among the remaining ligands. The formal $\sigma^2\pi^4$ triple bond in the starting material is converted to a $\sigma^2\pi^2\delta^2$ triple bond in the product with a lengthening of about 0.3Å to 2.508(2)Å [202].

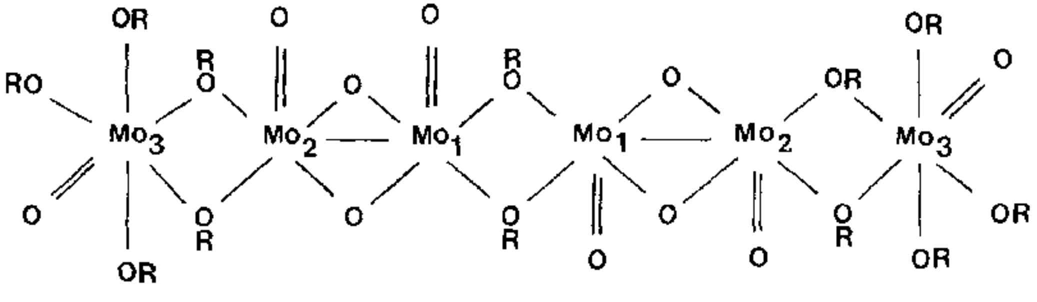
A number of papers have appeared in which $M_2(OR)_6$ complexes have been reacted with various substrates to give higher oxidation state complexes. $Mo_2(O^tBu)_6$ reacts with oxygen to give $MoO_2(O^tBu)_2$ quantitatively. Labelling experiments showed that the oxo ligands are derived from the molecular oxygen and not from the alkoxide groups. No intermediates were detected in this reaction. In contrast, although the corresponding reaction with $Mo_2(O^iPr)_6$ does give $MoO_2(O^iPr)_2$ (which is rather unstable but may be stabilized as $MoO_2(O^iPr)_2(bipy)$) the intermediates $Mo_3O(O^iPr)_{10}$ (green) and $Mo_6O_{10}(O^iPr)_{12}$ (brown) were isolated. With $Mo_2(OCH_2{}^tBu)_6$ oxygen gave mainly $MoO_2(OCH_2{}^tBu)_2$, but some $MoO(OCH_2{}^tBu)_4$ was produced together with some $Mo_3O(OCH_2{}^tBu)_{10}$ early in the reaction. The $Mo_3O(OR)_{10}$ compounds are best produced by the reaction

$$Mo_2(OR)_6 + MoO(OR)_4 \longrightarrow Mo_3O(OR)_{10}$$

and the best synthesis of $Mo_6O_{10}(O^iPr)_{12}$ is by the reaction

$$Mo_2(O^iPr)_8 + 6MoO_2(O^iPr)_2 \longrightarrow Mo_6O_{10}(O^iPr)_{12} + 2\ MoO(O^iPr)_4$$

and the products are easy to separate. The structure of $MoO_2(O^iPr)_2(bipy)$ is distorted octahedral with *cis* oxo and *trans* O^iPr ligands. Bond distances are Mo=O = 1.70(av), Mo-OR = 1.93(av) and Mo-N = 2.357(8)Å. The structures of $Mo_3O(OR)_{12}$ complexes with R = $CH_2{}^tBu$ and ${}^iPr$ were both determined and the central cores are almost identical consisting of a triangle of metal atoms capped by both an oxo and an alkoxide ligand. Each edge of the triangle is bridged by an OR group in the plane of the triangle and the remaining six OR groups are terminal, two per metal atom above and below the plane of the triangle. Average bond distances for the compound with R = $CH_2{}^tBu$ are Mo-Mo = 2.529, Mo-μ_3O = 2.034, Mo-μ_3OR = 2.212, Mo-μ_2OR = 2.018 and Mo-OR = 1.90Å. $Mo_6O_{10}(O^iPr)_{12}$ is a centrosymmetric molecule with six molybdenum atoms in a plane as shown in (65). The bond distance between Mo(1)-Mo(2) is indicative of a single bond whilst the distances between other pairs of metal atoms indicate no direct bonding. The average oxidation state of molybdenum in the complex is



R = ^{i}Pr (65)

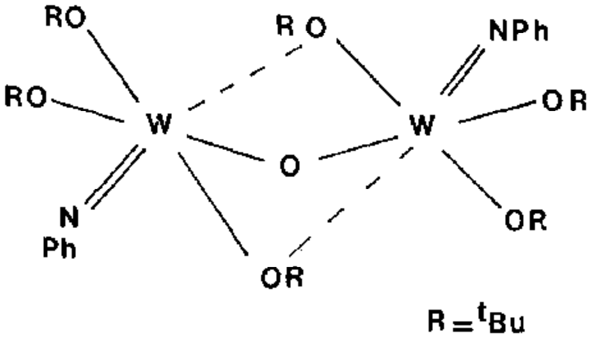
Bond distances are

Mo(1)-Mo(2) = 2.585(1)
Mo(1)-Mo(1)' = 3.353(1)
Mo(3)=O = 1.691(2)
Mo(3)-μOR = 2.128(2),2.197(2)
Mo(1)-μO = 1.925(2)
Mo(2)-Mo(3) = 3.285(1)
Mo(1),Mo(2)=O = 1.672(2)
Mo(2)-μOR = 2.057(2),2.044(2)
Mo(2)-μO = 1.939(2)Å

5.33, so if Mo(1) and Mo(2) are Mo(V) and Mo(3) is Mo(VI) the structure can be understood [203].

$Mo_2(O^tBu)_6$ reacted with HCCPh in pentane to give $Mo(CPh)(O^tBu)_3$. In the presence of quinolidine (quin) an inseparable mixture of $Mo(CPh)(O^tBu)_3(quin)$ and $Mo(CH)(O^tBu)_3(quin)$ was obtained [204]. A similar reaction between $W_2(O^tBu)_6$ with HCCPh gave $W(CPh)(O^tBu)_3$ which was shown to be a monomeric tetrahedral species with W-O = 1.865(4) and W-C = 1.758(5)Å [205].

The reaction of nitrosobenzene with $W_2(O^tBu)_6$ gave $[W(O^tBu)_2(NPh)]_2(\mu\text{-}O)(\mu\text{-}O^tBu)_2$, a W(VI) compound in which a remarkable double oxidation has occurred leading to formation of a W=N bond and loss of the W-W triple bond. The structure can be regarded as consisting of two similar, very distorted octahedra sharing a face. The oxygen forms a symmetrical bridge, but both O^tBu bridges are very unsymmetrical with the long bonds *trans* to the terminal NPh ligands as shown in (66). Alternatively, the sterochemistry about each tungsten atom may be regarded as square pyramidal (NPh apical) with a long sixth (bridging) contact. The NPh groups are close to linear (164.7°(av)) and there is thought to be considerable triple bond character in the W-N linkages. In addition, there is thought to be considerable π-bonding from O to W and these effects reduce the formal charge at tungsten. This helps to explain the comparatively close metal-metal contact even though there can be no formal W-W bond [206].



(66)

Bond distances are

W...W = 3.059(0)

W-OR(term) = 1.876(4)-1.901(4)

W-μOR(short) = 2.078(4),2.092(4)

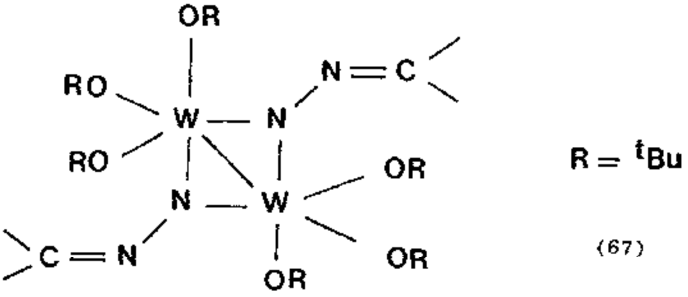
W-μOR(long) = 2.260(4),2.269(4)Å

W-N = 1.737(5)

W-μO = 1.937(4)

The complexes $M_2(OR)_6$ react with various aryl substituted diazomethanes in a variety of ways, but in no case was there formation of alkylidienes. The M-M triple bond acts as an electron source to reduce the diazomethane to the NNCRR'(2-) ligand. Reaction of $Mo_2(O^tBu)_6$ with Ph_2CN_2 causes cleavage of the Mo-Mo triple bond and formation of trigonal bipyramidal $Mo(O^tBu)_4(NNCPh_2)$ with a short Mo-N (1.797(3)Å) and a long Mo-O (1.944(3)Å) axial bonds; the other Mo-O bond lengths are 1.889Å(av). The ^1H N.M.R. spectrum at room temperature showed only one O^tBu signal, but at -40°C this split into two signals (1:3) as expected for trigonal bipyramidal geometry. Similar reactions with $W_2(OR)_6$ and Ar_2CN_2 gave dinuclear $W_2(OR)_6(NNCAr_2)_2$ complexes. The crystal structure of the p-tolyl derivative showed two trigonal bipyramidal tungsten atoms sharing an equatorial/axial edge as shown in (67). The W-W distance of 2.675(1)Å is indicative of a single bond which is consistent with the formulation of the bridging diazo alkane as a (2-) ligand [207].

Alkyne adducts of $W_2(OR)_6$ react with nitriles to form dinuclear complexes containing a seven membered heterocyclic ring. The structure of $W_2(O^tBu)_6(CHCHC\{Ph\}N)$ was determined and consists of two trigonal bipyramidally coordinated tungsten atoms joined along an equatorial/axial edge with a single W-W bond as shown in (68). It reacts with 2-propanol to give $W_2(O^iPr)_7(CH_2CHC\{Ph\}N)$ which is the product of both alcoholysis and addition of ROH across the tungsten-carbon double bond [208].



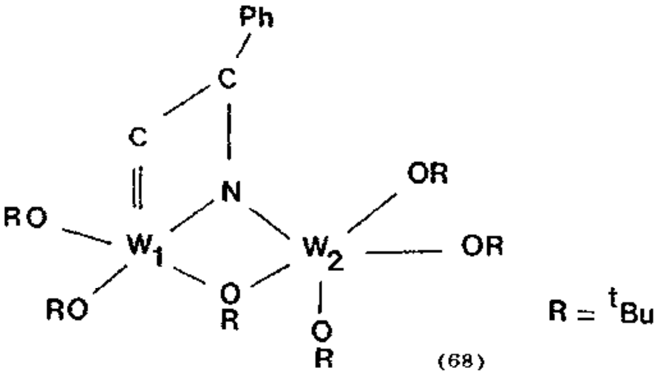
(67)

Bond distances are

W-W = 2.675(1)

W-N(ax) = 1.942(11)   W-N(eq) = 1.991(11)

W-O(ax) = 1.944(8)   W-O(eq) = 1.866Å(av)



(68)

Bond distances are

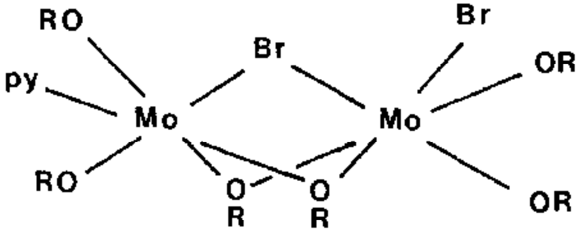
W(1)-W(2) = 2.674(1)

W(1)-N = 2.041(5)   W(2)-N = 1.903(5)

W(1)-μO = 2.058(4)   W(2)-μO = 2.107(4)

W(1)-C = 1.980(6)Å

$M_2(OR)_6$ compounds do not react with primary and secondary alkyl halides, but they do react with more labile halides such as CCl_4, CH_2Br_2 and allyl halides. When reaction does occur several inorganic products are often formed which usually include $M_2(OR)_6X_4$ (M-M). Reaction between $Mo_2(OCH_2{}^tBu)_6py_2$ and $PhCHBr_2$ gave the green complex $Mo_2(OCH_2{}^tBu)_6Br_2py$ which has the structure shown in (69) with two non-equivalent molybdenum atoms (one oxidation state 4.5 and the other 3.5) in a highly distorted confacial bisoctahedron arrangement [209].



R = $CH_2{}^tBu$

(69)

Bond lengths are

Mo(1)-Mo(2) = 2.534(1)

Mo(1)-μBr = 2.736(1)   Mo(2)-μBr = 2.720(1)

Mo(1)-μOR = 2.04(av)   Mo(2)-μOR = 2.08(av)

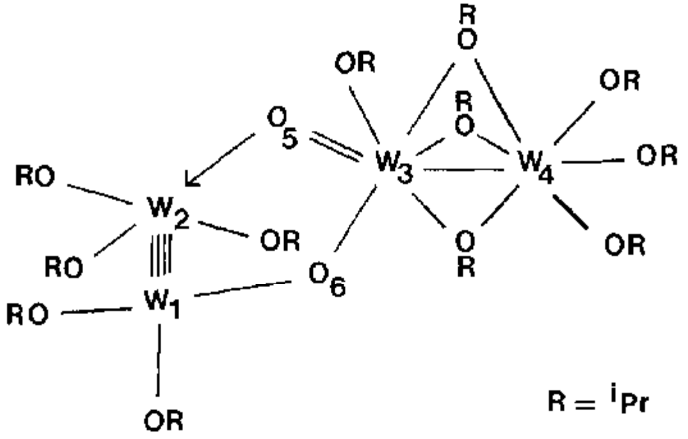
Mo-OR = 1.90(av)   Mo-Br = 2.584(1)Å

One of the products of the reaction between $W_2(O^iPr)_6$ and NBu_4Cl was $W_2(\mu\text{-}O^iPr)_2(O^iPr)_6Cl_2$. Its structure consists of two octahedra sharing an edge with a W-W bond distance of 2.784(1)Å. The chloro ligands are *trans* to each other across the molecule. Other bond distances are W-Cl = 2.449(3), W-μO^iPr = 2.013(7), 2.076(7), W-O^iPr = 1.837(6)-1.913(8)Å [210].

$W_2(O^iPr)_6py_2$ and acetone react according to the equation

$$2W_2(O^iPr)_6py_2 + 2Me_2CO \longrightarrow W_4O_2(O^iPr)12 + 4py + Me_2C{=}CMe_2$$

The structure of the tetranuclear complex is remarkable and is shown in (70). The distances W(1)-W(3) and W(2)-W(3) are approximately 2.95Å and are considered too long for significant bonding to be present. W(1)-W(2) and W(3)-W(4) are considered to be triply and singly bonded respectively on the basis of bond lengths and electron counting. O(6) is regarded as an O^- group, that is, similar to an alkoxide OR^- with the W(3) substituted for the R group. The structure therefore can be regarded as being composed of two separate dinuclear units [211].



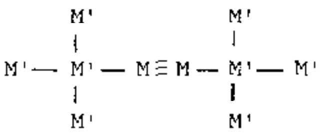
(70)

Bond distances are

W(1)-W(2) = 2.404(2)
W(3)-W(4) = 2.684(2)
W(3)=O(5) = 1.857(13)
W(2)-O(5) = 1.942(13)
W(1)-O(6) = 1.845(13)
W(3)-O(6) = 2.008(13)Å

Reaction between $W_2(O^{i}Pr)_6py_2$ and MeC≡CMe in excess py gave several products identified by proton NMR spectroscopy. A crystalline product $W_3(CMe)(O^{i}Pr)_9$ was isolated and its structure contains a triangle of tungsten atoms capped by the CMe group. Three alkoxides act as bridges along the edges of the triangle whilst the remaining two alkoxides per metal are terminal. The stereochemistry about each tungsten atom is square pyramidal with CMe axial. This is the first example of a triangular alkoxide cluster with only five ligands per metal atom. Average bond lengths are W-W = 2.75, W-O = 1.92, W- OR = 2.04, W-C = 2.06Å [212].

Reaction of $M_2Cl_2(NMe_2)_4$ with $[Li(thf)_3][M'(M'Me_3)_3]$ (M' = Si,Sn) in hydrocarbon solvents gave $M_2(NMe_2)_4[M'(M'Me_3)_3]_2$ which have the metal arrangement shown in (71).

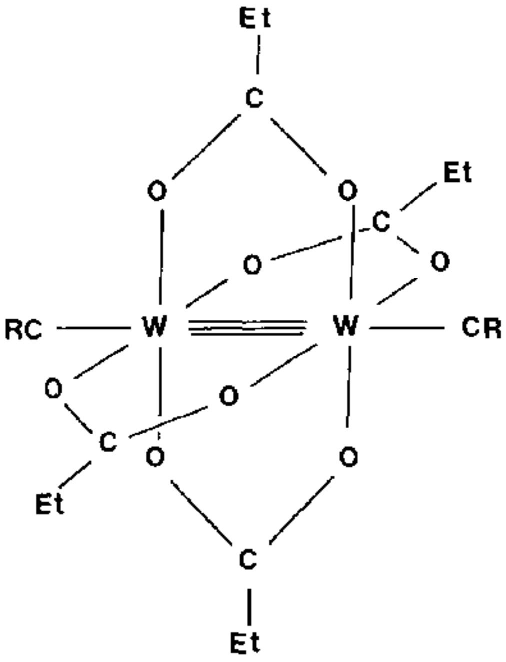


$$\begin{array}{ccccccc} & M' & & & & M' & \\ & | & & & & | & \\ M'- & M' & - & M\equiv M & - & M' & -M' \\ & | & & & & | & \\ & M' & & & & M' & \end{array}$$

(71)

Apart from the unusual nature of the substituents these compounds are typical $M_2L_2(NMe_2)_2$ compounds, although ^1H NMR studies did indicate an unusually high barrier to rotation about the Mo-N bond, presumably due to steric effects. The crystal structures of both molybdenum compounds (M' = Si,Sn) were determined and they both showed the expected *anti* rotomeric form with Mo-Mo = 2.216(11)Å (M' = Si) and 2.201(2)Å (M' = Sn) [213].

A new type of geometry for the disposition of ligands around d^3-d^3 dimers has been observed in the molecules $W_2(CH_2Ph)_2(O_2CEt)_4$ and $W_2(CH_2{}^tBu)_2(OCEt)_4$ which is shown in (72).



R Ph, $CH_2{}^tBu$

(72)

Bond distances are

	R = Ph	R = $CH_2{}^tBu$
W-W	2.186(1)	2.187(2)
W-C	2.18(1)	2.21(2)
W-O	2.084(9)	2.08Å(av)

These are the first complexes of this type to show axial ligation and the W-W bond distances are significantly decreased by about 0.1Å from the usual value for a triple bond. Possible reasons for this shortening are discussed [214].

Reaction of the sterically demanding 2,6-dimethylphenol (HOAc) with $Mo_2(NMe_2)_6$ gave 1,2-$Mo_2(NMe_2)_2(OAc)_4$. A crystal structure determination at -168°C showed the complex to have the usual staggered ethane type configuration with an Mo-Mo bond distance of 2.227(1)Å which is typical for the Mo_2^{6+} core. However, the Mo-N distance of 1.908(4)Å is very short which suggests strong π-bonding and this is reflected by the very high energy barrier to rotation about the Mo-N bond. Treatment of the complex with CO_2 yielded the dimethylcarbamato complex $Mo_2(O_2CNMe_2)_2(OAr)_4$ in which the Mo_2^{6+} core is retained, although each metal atom now has four attached ligands with the bridging carbamate groups *cis* to each other. The Mo-Mo bond distance is 2.220(1)Å [215].

2.7.2 Quadruple bonded molybdenum(II) and tungsten(II) species

A fully relativistic MO calculation has been performed for the $[W_2Cl_8]^{4-}$ ion. Except for some aspects of the W-W σ-bond, there are few changes from the MO energies obtained by simpler calculations [216]. The optical spectrum of $[Mo_2Cl_8]^{4-}$ has been calculated using the CAS SCF method with an effective core potential description of the inner states of molybdenum and chlorine. The results indicate that the first absorption at about 19,000cm^{-1} is not the δ δ^* transition, but rather that it is associated with a transition within the split δ orbital components [217].

Reaction of $(morph)_2[Mo_2Cl_6(H_2O)_2]$ with pipzH (pipzH = piperazine) in 1:1 HCl solution gave crystals of $(pipzH_2)_2[Mo_2Cl_8].4H_2O$ showing that substitution of chloride in $[Mo_2Cl_8]^{4-}$ is reversible. A crystal structure determination showed the usual eclipsed configuration, but the Mo-Mo distance of 2.129(3)Å is the shortest so far found for $[Mo_2X_8]^{4-}$ structures [218].

Hartree-Fock-Slater calculations have been made on $M_2Cl_4(PH_3)_4$ (M = Cr,Mo,W). The calculated bond energies for the quadruple bonds are 153(Cr), 524(Mo) and 428KJmol^{-1}(W). The analysis suggested that the bond is rather weak [219].

The absorption and emission spectra of $Mo_2X_4(PMe_3)_4$ (X = Cl,Br,I) have been measured at low temperature. Vibrational fine structure was observed (with spacing ≈ Mo-Mo stretch) for the iodide and there was a mirror image relationship between the two spectra which was distorted in the bromide and not resolved in the emission spectrum of the chloride. At 5K microcrystalline $Mo_2X_4(PMe_3)_4$ revealed progressions involving ν_{Mo-X} and it was suggested that the lack of a mirror image relationship for the chloride and bromide was due to coupling of the metal-metal and metal-halogen stretches [220].

The β (bridged) form of $Mo_2Cl_4(dppe)_2$ has been prepared in crystalline form by the interaction of $Mo_2(O_2CCF_3)_4$ and Me_3SiCl and dppe in toluene/thf according to the equation

$$Mo_2(O_2CCF_3)_4 + 4Me_3SiCl + dppe \longrightarrow Mo_2Cl_4(dppe)_2 + 4Me_3Si(O_2CCF_3)$$

A crystal structure determination revealed that the molecular shape is as expected, but in the crystal there are two forms of the molecule which differ in the configurations of the fused rings. In the major component, each ring has a nearly identical chair conformation and in the minor component both rings have a twist configuration. Bond distances for the major form are Mo-Mo = 2.183(3), Mo-Cl = 2.385(av), Mo-P = 2.588Å(av) [221].

The bridged form of $Mo_2Cl_4(P\text{-}P)_2$ (P-P = 2,3-diphenylphosphinobutane) has also been prepared and its structure determined by X-ray crystallography. It has the usual ligand arrangement but there is a 23° twist between the planes about molybdenum. The complex is chiral and shows strong Cotton effects under both the δ δ^* transition at $13{,}700 cm^{-1}$ and the next highest energy transition at $21{,}000 cm^{-1}$ [222].

Reaction of $K_4[Mo_2Cl_8]$ with racemic amino acids such as phenylalanine, tyrosine and C-phenylglycine, followed by addition of counter ions gave the products Mo_2L_4 with the usual carboxylate bridged dimeric structure. The chirality of the ligands was arranged in the order DDLL in each case and in all compounds studied the Mo-Mo distance was 2.114(2)Å [223].

Ab initio restricted Hartree-Fock calculations have been made on the ground state of $CrMo(O_2CH)_4$. Complete CI expansions were carried out and the resulting natural orbital analysis was similar to the correlated wave functions obtained for the homonuclear parent systems [224].

The molar enthalpies of sublimation of $Mo_2(O_2CMe)_4$ and $Mo_2(O_2CCF_3)_4$ have been determined to be $(170.5 \pm 6.5) KJmol^{-1}$ and $(113 \pm 1.7) KJmol^{-1}$ respectively. The relative magnitudes of these values are consistent with the shorter Mo...O contacts in the acetate derivative [225].

Metal-metal vibrational fine structure has been observed in a photoelectron band for $Mo_2(O_2CMe)_4$. The Mo-Mo frequency is lower than in the ground state indicating an appreciable reduction of the Mo-Mo bond strength upon loss of the δ-bonding electron. The change of metal oxidation state also has an important role in the resultant Mo-Mo interaction [226].

A new method of generating dimeric quadruple bonded species has been developed from the reduction of $MoCl_3(thf)_3$ with phosphines and zinc in thf to give $Mo_2Cl_4L_2$ (L = PPh_3, PEt_3, PMe_2Ph, 1/2dppm) while zinc and acetic acid gave $Mo_2(O_2CMe)_4$ [139].

The products of alcoholysis of 1,2-$Mo_2{}^tBu_2(NMe_2)_4$ appear to be determined by steric effects. With ${}^tBuOH$ the product is $Mo_2{}^tBu(O^tBu)_5$, but with ${}^tBuCH_2OH$ the purple complex $Mo_2(OCH_2{}^tBu)_4(NMe_2)_4$ ($M \overset{4}{—} M$) was isolated. With ${}^iPrOH$ a mixture of products, but containing $Mo(O^iPr)_4(NMe_2)_4$, was produced, but the final crystalline product is $Mo_2(O^iPr)_4(HO^iPr)_4$ ($M \overset{4}{—} M$). This reactive species reacted with CO_2 and acacH to give $Mo_2(O_2CO^iPr)_4$ and $Mo_2(acac)_4$ respectively [227].

A general method for the preparation of quadruple bonded tungsten dimeric complexes has been reported [228]. The interaction of $W_2Et_2(NMe_2)_4$ with acid anhydrides RCOOCOR (R = Me,Et,^{t}Bu) gave good yields of the required species according to the equation

$$W_2Et_2(NMe_2)_4 + 4RCOOCOR \longrightarrow W_2(O_2CR)_4 + 4RCONMe_2 + C_2H_4 + C_2H_6$$

which involves disproportionation of the ethyl group.

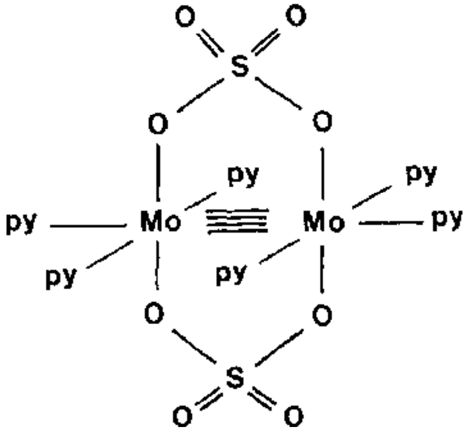
Three examples of the hitherto elusive $W_2(O_2CR)_4$ complexes have been produced by a second new method, namely reduction of WCl_4 in thf by Na/Hg in the presence of the appropriate sodium carboxylate. The complexes isolated were orange $W_2(O_2CPh)_4(thf)_2$, orange $W_2(O_2C\text{-}p\text{-}tol)_4(thf)_2$ and red $W_2(O_2Cmesit)_4.2Me_2C_6H_4$ and all were fully characterized by X-ray diffraction. All adopt the usual carboxylate structure, with the thf ligands axially bound, with W-W bond distances in the range 2.176(1)-2.203(1)Å [229].

$Mo_2(O_2CH)_4.KCl$ was synthesized from $K_4[Mo_2Cl_8]$ and formic acid. The chloro ligands are axial and bridge between successive dimers to give a zig-zag structure with bond distances Mo-Mo = 2.109(2) and Mo-Cl = 2.86Å(av). In addition, two new polymorphs of $Mo_2(O_2CH)_4$ itself were also isolated which differ from each other and from the previously reported form by adopting alternative packing arrangements. Single crystal optical absorption spectra were measured at 6K and they showed relatively intense vibronic progressions [230].

$Mo_2(O_2CMe)_4$ was reacted with the non-complexing acids CF_3SO_3H and $HBF_4.Et_2O$ in MeCN and led to the isolation of $[Mo_2(O_2CMe)_2(MeCN)_4](CF_3SO_3)_2$ and $[Mo_2(O_2CMe)_2(MeCN)_5](BF_3OH)_2$ respectively. On the basis of UV-visible and IR spectra one acetate in $[Mo_2(O_2CMe)_2(MeCN)_5]^{2+}$ is thought to be monodentate. It was concluded that in both complexes the MeCN ligands occupy equatorial and not axial positions [231].

$Mo_2(O_2CMe)_4$ reacted with concentrated H_2SO_4 in py to give $[Mo_2(SO_4)_2(py)_6].2py$ which was shown to have the structure shown in (73). This is the first substituted sulphato complex and also the first with a planar Mo-O-S-O-Mo ring [232].

$W_2(O_2CCF_3)_4$ reacted with PR_3 (R = Me,Et,^{n}Bu) to give $W_2(O_2CCF_3)_4.2PR_3$. ^{19}F, ^{31}P NMR and IR spectra were similar for all the complexes and the solid state structure of $W_2(O_2CCF_3)_4.2P^nBu_3$ was shown to be as in (74) [233]. With PMe_3 only, further reaction gave $W_2(O_2CCF_3)_4.3PMe_3$. IR, ^{19}F and ^{31}P NMR spectroscopies all suggested substitution in the equatorial position with only one bridging carboxylate and this was confirmed by X-ray crystallography, with the structure being shown in (75).

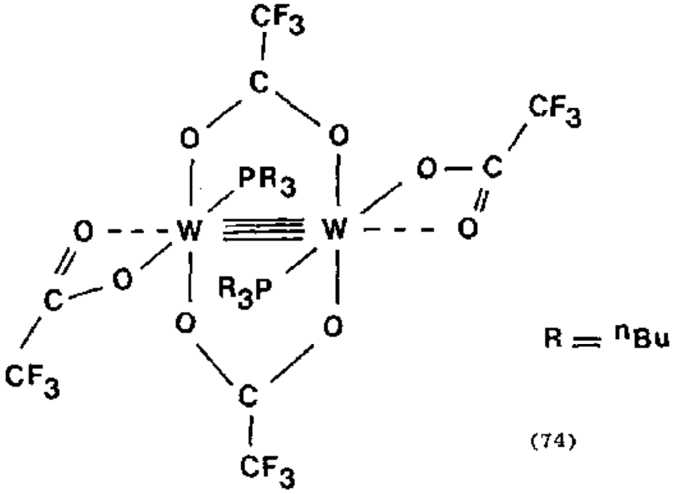


(73)

Bond distances are

Mo-Mo = 2.1341(1) Mo-O = 2.112(4)

Mo-N(eq) = 2.228(7) Mo-N(ax) = 2.712(8)Å(av)



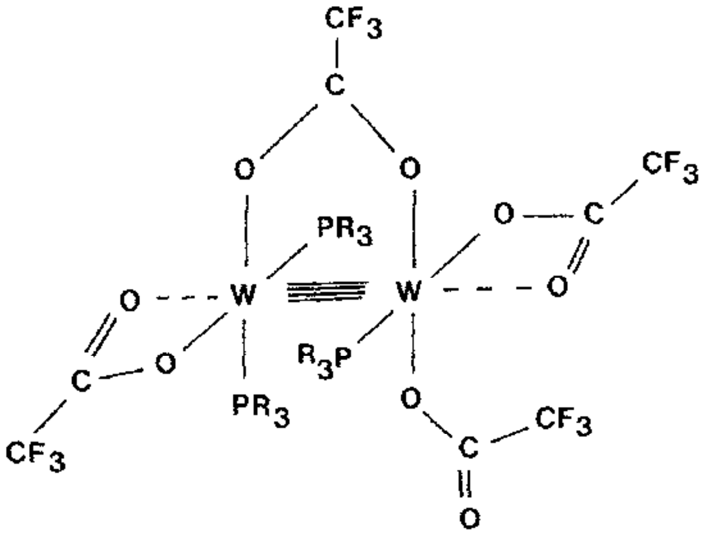
(74)

Bond distances are

W-W = 2.224(1) W-P = 2.489(3)

W-O(monodent) = 2.132(7) W-O(bident) = 2.107(av)

W-O(ax) = 2.845(8)Å



R = Me

(75)

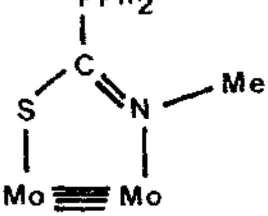
Bond distances are

W-W = 2.246(1) W-P = 2.462(5)-2.504(5)

W-O(*trans* O) = 2.06(1) W-O(*trans* P) = 2.122(13)

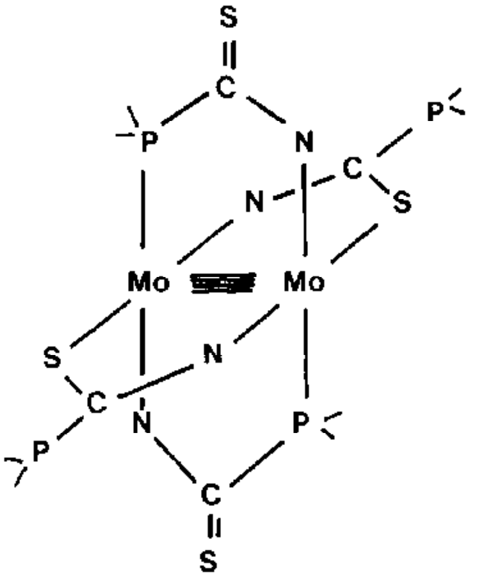
W-O(ax) = 2.84(1),3.10(1)Å

Reactions of $Mo_2(OCMe)_4$ with ligands of the types $[Ph_2PC(S)NR]^-$ (R = Ph,Me) and $[Me_2NC(S)NPh]^-$ gave Mo_2L_4. Various spectrscopic and electrochemical measurements suggested *N*,*S* coordination was operating in most cases, although for $Mo_2(Ph_2PC(S)NMe)_4$ two complexes were isolated for which IR and ^{31}P NMR spectroscopies suggested isomerism had occurred. This was confirmed by X-ray diffraction. One isomer (B) of $Mo_2(Ph_2C(S)NMe)_4$ has all four ligands equivalent (*N*,*S* coordination) in the usual quadruple bonded structure. Bond distances indicate that the ligand has the electronic structure indicated in (76) with considerable double bond character in the C-N bond and none in the P-C bond.



(76)

In the other isomer (A) there are two ligands with *N,S* coordination (dimensions very similar to isomer B) and the other two display *P,N* coordination as shown in (77) [234].

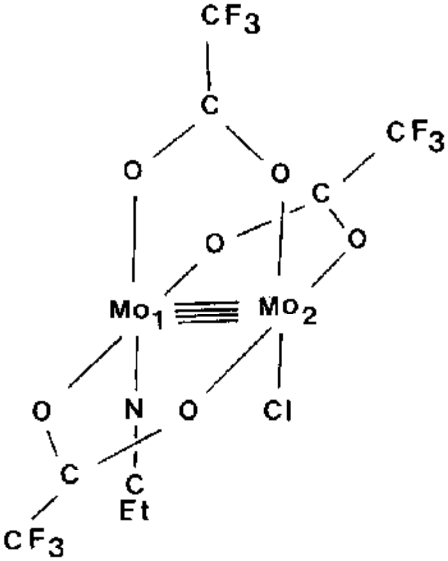


(77)

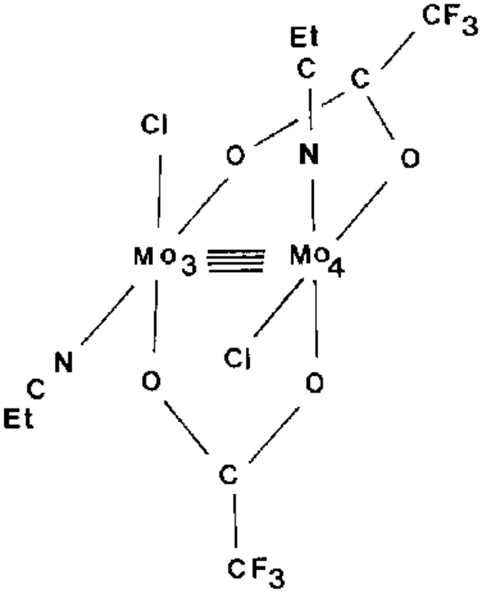
Bond distances are

	Isomer A	Isomer B
Mo-Mo	2.104(2)	2.083(1)
Mo-S	2.439(3)	2.466(8)
Mo-N	2.182(8)	2.124(5)
Mo-P	2.571(3)	
C-N	1.35(1)	1.304(9)Å

Reaction of $Mo_2(O_2CCF_3)_4$ with Me_3SiCl and EtCN at low temperature gave orange red crystals of $Mo_2(O_2CCF_3)_2(EtCN)_2Cl_2.Mo_2(O_2CCF_3)_3(EtCN)Cl$. The compound contains two different dinuclear molecules as shown in (78) and (79). The dimers are linked by one Mo...O and three Mo...Cl contacts to form chains of alternating dimers as shown in (80) [235].



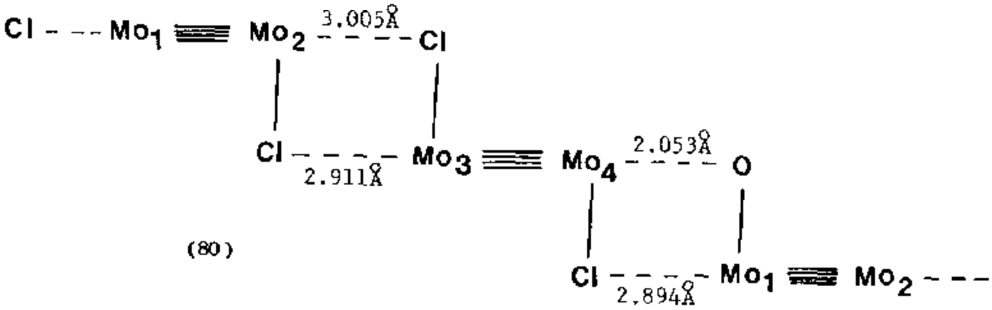
(78)



(79)

Bond distances are

	(78)	(79)
Mo-Mo	2.127(2)	2.134(2)
Mo-O	2.10(av)	2.13(av)
Mo-N	2.12(2)	2.10(4)
Mo-Cl	2.425(5)	2.394(5)Å



(80)

2.7.3 Hexameric species

The complexes $[M_6X_{14}]^{2-}$ (X = Cl,Br) show a reversible one-electron oxidation and a reversible one-electron reduction in MeCN at very positive and very negative potentials respectively with about 3.1V between the couples. Pulsing the potential between these extremes led to electrochemically generated chemical luminescence which is caused by the reaction

$$[M_6X_{14}]^{3-} + [M_6X_{14}]^{-} \longrightarrow 2[M_6X_{14}]^{2-}$$

with one of the product molecules being in an electronically excited state. The luminescence spectra are identical to the emission spectra observed by irradiating $[M_6X_{14}]^{2-}$ at 436nm [236].

The crystal structures of salts of the $[Mo_6(\mu_3\text{-}Cl)_8(OMe)_6]^{2-}$ and $[Mo_6(\mu_3\text{-}OMe)_8(OMe)_6]^{2-}$ anions have been determined [237]. The structures of the anions are based on the usual octahedral arrangement of metal atoms within a cube of triply bridging ligands with one terminal ligand bound axially to each metal. Average bond distances are

	$[Mo_6Cl_8(OMe)_6]^{2-}$	$[Mo_6(OMe)_{14}]^{2-}$
Mo-Mo	2.607	2.536
Mo-μ_3L	2.409	2.173
Mo-L	2.051	2.130Å

Two papers have appeared on the insertion of lithium into Mo_6X_8 (X = S,Se) structures to give ternary molybdenum chalcogenides $Li_xMo_6X_8$ [238.239] and similar insertion compounds with lead and tin were also described [238].

The superconducting critical temperatures for the Chevral phases $La_{1-x}Eu_xMo_6Se_8$ show similar behaviour to those of $La_{1-x}Yb_xMo_6Se_8$; there is a decrease in the critical temperatures as x increases [240].

2.7.4 Other cluster species

Hydrothermal reaction of KOH/$K_2[MoO_4]$ solution with molybdenum metal at 500-700°C and 3Kbar pressure gave black crystals of $K_2[Mo_8O_{16}]$. The tunnel like structure is closely related to that of hollandite, $Ba[Mn_8O_{16}]$, and contains two types of planar Mo_4O_{16} units joined via shared oxygen atoms. The Mo-Mo bond lengths indicate different electron populations in the two types of cluster [241].

Electrolytic reduction at 1100°C of a melt containing $Na_2[MoO_4]$, MoO_3 and La_2O_3 in a porcelain crucible gave black crystals of $La_3Mo_4SiO_{14}$ with the silica coming from the crucible. An X-ray structure determination revealed an interesting structure containing Mo_3O_{13} units and a chain of octahedrally coordinated molybdenum atoms (linked in pairs) with bridging oxygen atoms between the triangular clusters [242].

The synthesis of $Ag_{3.6}[Mo_9Se_{11}]$ has been reported. The structure can be described in terms of stacking of Mo_9Se_{11} units. Within each unit the metal atoms are arranged in three triangular layers resembling a portion of a hexagonally close packed lattice [243].

The substitution chemistry of $MoFe_3S_4$ cubane type clusters containing catechol ligands has been further investigated. These species undergo both iron and molybdenum site specific reactions which include catechol exchange at the molybdenum site [244].

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