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5. MOLYBDENUM AND TUNGSTEN

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CONTENTS

INTRODUCTION

The review on molybdenum and tungsten chemistry this year deals mainly with the inorganic and coordination chemistry of the elements which was cited in Chemical Abstracts, Volumes 98 and 99. Thus most of the work published in 1983 and some published towards the end of 1982 will be reviewed. Organometallic chemistry is not formally included in the review, but reference is made to some

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papers of general interest.

A change of author inevitably leads to a change of style and different emphasis on various aspects of the chemistry of the elements. However, if this and future reviews serve the needs of readers as well as did those of my predecessor, Prof. C.D. Garner, then they will serve their purpose.

The material is organized mainly by oxidation state of the elements and within each oxidation state by the type of donor atoms. Obviously overlap will occur with mixed ligand complexes and in those cases 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.

5.1 MOLYBDENUM(VI) AND TUNGSTEN(VI)

5.1.1 Halides and halo complexes

Ultrasonic attenuation has been measured for MoF_6 and WF_6 and in both cases a single relaxation process was observed with isothermal relaxation times of 2.8×10^{-8} and 2.3×10^{-8} s atm respectively [1]. When this data is converted to the number of collisions required for relaxation there is good correlation with the energies of the lowest vibrational mode for MF_6 (and also SeF_6 and ReF_6). The crystal structures of MoF_6 and WF_6 have been determined at 77 K by powder neutron diffraction to complete the study of the structures of these molecules as a function of temperature [2]. At this low temperature there are no significant changes in bond length (Mo-F = 1.824(7), W-F = 1.834(5)Å) but the octahedra do pack more efficiently.

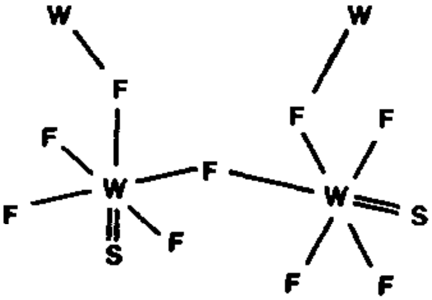
As part of an elegant study of the electrochemical behaviour of hexafluoro complexes of the second and third row transition elements, the reversible MF_6/MF_6^-, MF_6^-/MF_6^{2-} and MoF_6^{2-}/MoF_6^{3-} couples have been observed in acetonitrile solution [3]. A systematic pattern of electrode potentials has emerged for these systems which exhibit stepwise changes in E^o with core charge and *d* electron configuration.

Reaction of $AsPh_4[Cl_5Mo{\equiv}NCCl_3]$ with AgF in CH_3CN gave *cis*-$AsPh_4[MoF_2Cl_4]$ while the analogous reaction with $AsPh_4[Cl_5W{\equiv}NCCl_3]$ gave the perfluorinated complex $AsPh_4[F_5W{\equiv}NCF_3]$. Addition of a small amount of water to either reaction mixture gave $AsPh_4[MOF_5]$. The crystal structure of $AsPh_4[WOF_5]$ has been determined, but the structure solution was complicated by disorder between oxygen and the fluorine *trans* to it. Bond distances are W-(O,F) = 1.822(13) and W-F(equitorial) = 1.852(7)Å [4].

Prolonged heating in an autoclave (40-45h, 190-210°C) of nicotinic, *iso*-nicotinic or 2,6-pyridinedicarboxylic acids with excess MoF_6 gave the corresponding trifluoromethyl derivative of pyridine in 60-80% yield [5]

$$RCOOH + 2MoF_6 \longrightarrow RCF_3 + 2MoOF_4 + HF$$

WF_4S and WF_4Se were prepared by the interaction of WF_6 and S or Se. A crystal structure determination on WF_4S revealed a chain structure linked by *cis* fluorine bridges (1)



(1)

Bond distances are

$$W{=}S = 2.07$$
$$W\text{-}\mu F(\textit{trans}\ S) = 2.34(3)$$
$$W\text{-}\mu F(\textit{cis}\ S) = 1.92(3)$$
$$W\text{-}F = 1.85(3)$$

The angles at the bridging fluorines range from 146.8° to 160.5° [6].

The IR and electronic spectra of monomeric WYX_4 ($Y = S,Se$; $X = F,Cl,Br$) isolated in nitrogen matrices have been reported [7]. The W-S stretching modes ($\simeq 570cm^{-1}$) in the IR were unambiguously identified by means of the ^{34}S satellites, but the assignment of the W-Se stretches ($\simeq 370cm^{-1}$) is tentative. The principle features of the electronic spectra were assigned on the basis of vibrational fine structure.

Some reactions of WOF_4 have been followed using ^{19}F NMR spectroscopy [8]

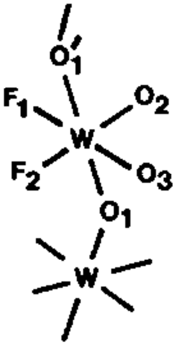
$$WOF_4/MeCN + \text{op. act. tartaric acid } (H_2L) \longrightarrow \begin{array}{l} WOF_4.MeCN \\ [W_2O_2F_9]^- \\ (WOF_3)\text{-}\mu L\text{-}(WOF_3) \\ WOF_3.HL \end{array}$$

$$WOF_4 + \textit{meso}\text{-tartaric acid } (H_2L) \longrightarrow \begin{array}{l} (WOF_3)\text{-}\mu L\text{-}(WOF_3) \\ WOF_3.HL \end{array}$$

Some new oxide fluorides of tungsten have been produced by heating the constituent mixtures [9]

$BaWO_3F_4$	monoclinic, a new structural type
PbW_3F_2	tetragonal, $SrAlF_5$ type
$Pb_3W_2O_6F_6$	tetragonal, $Sr_3Fe_2F_{12}$ type

Crystals of $Cs_2[WO_3F_2]$ were obtained from a melt of the constituents (2CsF + WO_3). The structure was found to be polymeric with *cis*-WO_4F_2 units linked by unsymmetrical *trans* oxygen bridges [10] as shown in (2)



(2)

Bond distances are

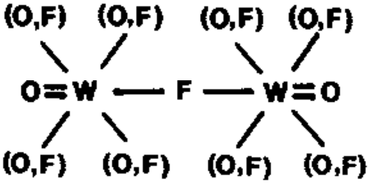
$W\text{-}F = 1.99(4)\text{Å}$ $W\text{-}O_2 = 1.78(3)$

$W\text{-}O_1 = 1.88(4)$ $W\text{-}O_3 = 1.90(3)$

$W\text{-}O_1' = 2.02(4)$

In the same paper [10] the crystal structure of $Cs_3[W_2O_4F_7]$ is also reported. The unit cell contains two independent dimeric anions in which the tungsten atoms are almost linearly bridged by a single fluorine atom with oxygen *trans* to the bridge (3). The positions of the remaining oxygen and fluorine atoms are disordered, but the IR spectrum shows that they always form a *cis*-WO_2F_2 unit. Bond distances are

$$W\text{-}\mu F = 1.95(7) - 2.32(7)\text{Å}$$
$$W{=}O = 1.74(6) - 1.86(8)$$
$$W\text{-}(O,F) = 1.77(6) - 2.05(9)$$



(3)

Raman measurements show that WCl_6 retains its octahedral structure in $AlCl_3$-NaCl melts of various compositions [11]. WCl_6 undergoes three reversible one-electron reductions in dichloromethane solution corresponding to

$$WCl_6 \rightleftarrows WCl_6^{-} \rightleftarrows WCl_6^{2-} \rightleftarrows WCl_6^{3-}$$

Both WCl_6 and $MoCl_5$ on reduction in dichloromethane solution with an Al electrode produce species which are active catalysts for olefin metathesis. Evidence suggests that the catalysts are carbene complexes with the metal in a high oxidation state [12]. The sequence WCl_6, $WOCl_4$, WO_2Cl_2 and WO_3 provides a series in which the metal oxidation state is constant and in which (using long range interactions) the metal coordination remains essentially six coordinate. A theoretical study of the vibrational spectra was used to assess the influence of successive replacement of 2 Cl's by O [13].

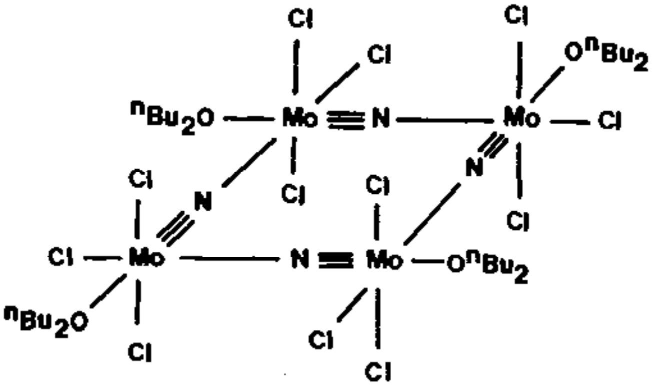
Reaction of $WOCl_4$ with RNCO (R = Et, Ph) gives tungsten(VI) imido complexes

$$WOCl_4 + RNCO \rightarrow W(NR)Cl_4 + CO_2$$

It is thought the compounds are dimeric with chloro bridges; with thf they give the adducts $W(NR)Cl_4(thf)$ [14].

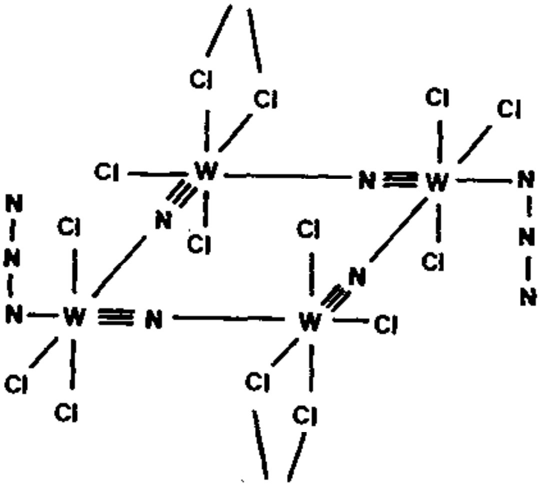
$[MoNCl_3(O^{n}Bu_2)]$ may be obtained directly from $MoNCl_3$ and di-*n*-butyl ether or by decomposition of $(C_6H_5N_2)[MoNCl_4]$ in the boiling ether [15]. A crystal structure determination showed the complex to be tetrameric with an approximate square of molybdenum atoms each pair of which is almost linearly bridged by a nitrogen atom. The Mo-N distances alternate between long and short, corresponding to single and triple bonds. The ether is coordinated *trans* to the short Mo-N bond and chlorines complete the octahedral arrangement about the metal atoms as shown in (4). Bond distances are

Mo=N = 1.65Å (av)   Mo-O = 2.396(6)
Mo-N = 2.16 (av)   Mo-Cl = 2.281(3) - 2.311(3)



(4)

Reaction of WCl_6 with iodine azide in dichloromethane yields dark red $WNCl_3.0.5HN_3$ which has a similar tetrameric core as shown in (5).



(5)

In this case two opposite tungsten atoms complete their octahedral coordination with three terminal chlorines and the α-N of a HN_3 ligand; the other two tungstens complete their coordination by two terminal chlorines and two (*cis*) chlorines which bridge to the corresponding tungsten in an adjacent tetranuclear unit [16]. Bond distances are

$W_1{\equiv}N = 1.69(3)\text{Å}$ $\quad W_2{\equiv}N = 1.68(3)$
$W_1{-}N = 2.11(3)$ $\quad W_2{-}N = 2.08(3)$
$W_1{-}N\ (HN_3) = 2.44(3)$ $\quad W_2{-}Cl = 2.38(1),\ 2.80(2)$
$W_1{-}Cl = 2.28\ (av)$ $\quad W_2{-}Cl = 2.28\ (av)$

5.1.2 Oxides, molybdates and tungstates

The matrix condensed vapours of MoO_3 and WO_3 are considerably more reactive than the solid oxides. On co-condensation, they react readily with organic substrates such as acacH, acetone, HCOOH and with inorganic compounds such as BCl_3, HCl etc. [17].

It has been found that irradiation of platinized WO_3 particles in the presence of water and an organic substrate such as HCOOH leads to marked colour changes without application of a bias voltage, indicating photoelectric chroism. During the reaction, CO_2 is evolved and hydrogen is incorporated into the lattice [18].

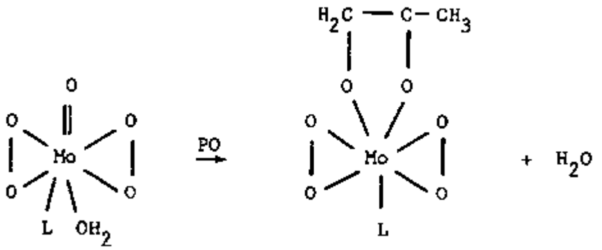
A monoclinic Mo(VI) hemihydrate $MoO_3.0.5H_2O$ has been isolated by precipitation of molybdenum containing solutions with nitric acid. It was characterized by thermal analysis and X-ray powder diffraction [19]. A single crystal study of $Th(MoO_4)_2$ has shown it to be a true molybdate [20]. Molybdenum is surrounded by an almost regular tetrahedron of oxygens (Mo-O = 1.743(4) - 1.778(4)Å) and each oxygen is shared between molybdenum and thorium which has almost regular square antiprismatic stereochemistry (Th-O = 2.403 (av)). $NiMoO_4$ and $CoMoO_4$ crystallize in the defect rock salt phase and may be transformed to the wolframite structure under conditions of high temperature and pressure. The magnetic properties of both phases were measured and the different θ values are consistent with an analysis of the magnetic interaction pathways in the two polymorphs [21]. X-ray photoelectron, IR and Raman spectra have been measured for $Ce_2(MoO_4)_3$ and several cerium molybdenum oxides. $Ce_2(MoO_4)_3$ contains tetrahedral molybdenum, but the other oxides contain highly irregular or mixed polyhedral arrangements of Mo-O bond lengths [22].

The ν_1 Raman modes of $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ in aqueous solution have been studied with great precision [23] and the effect of concentration and the identity of the counter-ion have been investigated for a number of alkali metal salts. As the concentration increases, ν_1 increases in the presence of Li^+ and Na^+ but decreases in the presence of K^+, Rb^+ and Cs^+. Extrapolation to infinite dilution yields $\nu_1 = 986.1 \pm 0.1 cm^{-1}$ (molybdate) and $931 \pm 0.1 cm^{-1}$ (tungstate).

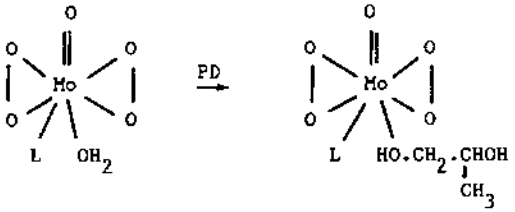
5.1.3 Monomeric oxo complexes

The first ^{17}O NMR signals for any peroxo complex have been observed for $[MoO(O_2)(CN)_4]^{2-}$, and it was shown that exchange between oxo and peroxo groups does not occur. It is believed that the failure of previous attempts to observe peroxo signals was due to reversible release of paramagnetic dioxygen [24].

It is known that the diperoxo complex $MoO(O_2)_2L(H_2O)$ (L = hmpa) acts as a selective stoichiometric reagent for olefin epoxidation under mild conditions. As a result of an investigation of the reactions between this reagent and propylene, two new complexes were isolated [25]. Reaction with propylene oxide (PO) leads to insertion in the Mo=O bond resulting in the formation of a (propane-1,2-diolato)diperoxo complex which is more active than the original complex



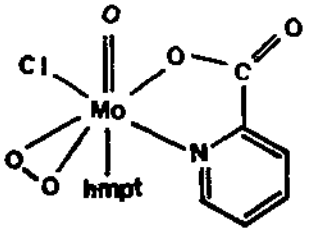
Propane 1,2-diol (PD) also reacts with the original complex by displacing the water molecule



Reaction of $MoO_2Cl(pic)(hmpa)$ (pic = pyridine-2-carboxylic acid) with Ph_3COOH and H_2O_2 gave $MoO(O_2)Cl(pic)(hmpa)$. ^{18}O labelling experiments showed that both atoms of the peroxo group originate from the alkylhydroperoxide [26]. The crystal structure (6) shows a distorted pentagonal bipyramid, the axial positions being occupied by the oxo group and the oxygen of hmpa. Bond distances are

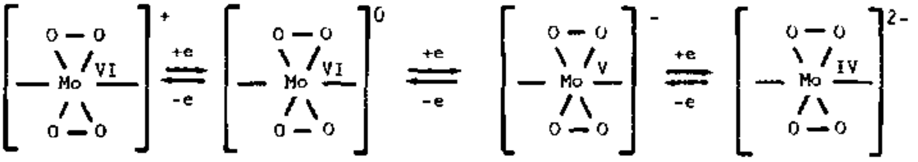
Mo-Cl = 2.383(1)Å
Mo-N = 2.207(3)
Mo-O(pic) = 2.051(3)

$Mo-O(O_2)$ = 1.916(3),1.927(3)
Mo-O(hmpa) = 2.130(3)
O-O = 1.414(5)



(6)

The electrochemical properties of $(O_2)_2Mo(TMTP)$ (TMTP = tetra-*m*-tolylporphyrin) have been investigated. In dichloromethane solution the complex shows one reversible oxidation and two reversible reductions (all one-electron processes) on the cyclic voltametric time scale. The oxidation and the first reduction steps are also reversible on the electrolytic time scale so the products could be investigated [27]. The oxidation product has an EPR spectrum typical of an organic radical, but the reduction product shows molybdenum satellites in its EPR spectrum suggesting a metal based reduction. The second reduction product could not be identified as it rapidly decomposed to Mo(IV) and free porphyrin. The proposed mechanism is shown in (7).



(7)

It has been confirmed that the complexes formed between molybdate and alizarin red S (ars), which are used for the analysis of molybdenum, are of 1:1 stoichiometry and that they are stable over the pH range 2-6 [28]. At 25°C and ionic strength 0.1

$$MoO_4^{2-} + ars^{3-} + 2H^+ \longrightarrow [MoO_3(ars)]^{3-} + H_2O$$

$$\log(\beta_1/mol^{-3}L^3) = 20.18 \pm 0.01$$

$$MoO_4^{2-} + ars^{3-} + 3H^+ \longrightarrow [MoO_3(arsH)]^{2-} + H_2O$$

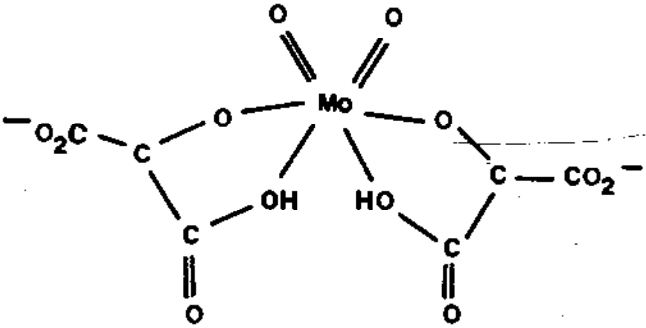
$$\log(\beta_1/mol^{-3}L^3) = 24.93 \pm 0.01$$

Alkaline hydrolysis of $CH_2{=}CHMoO_2Br(bipy)$ gave vinyl molybdate $[CH_2{=}CHMoO_3]^-$ as a colourless ion which slowly hydrolyses with evolution of ethylene [29]. The Mo-C bond hydrolysis is pH dependent. Vinyl molybdate has also been detected as an intermediate in the molybdothiol catalyzed reduction of acetylene to ethylene.

Two 1:1 complexes between molybdate and malonic acid have been identified at pH <1.75 and between pH 3.65-5.75; between these ranges the complexes are in equilibrium [30]. The interaction between $[WO_4]^{2-}$ and l(+)-sorbitol over a range of pH has been studied by polarimetry. At higher pH (9.5-11.5) the predominant species is monomeric $[WO(OH)(C_6H_{12}O_6)_2]^-$. At pH 7-9.5 it is in equilibrium with $[W_2O_3(OH)_4(C_6H_{10}O_6)]^{2-}$ and $[W_2O_3(OH)(C_6H_{11}O_6)_2]^-$ is believed to be present in solution in the pH range 1.25-4.0 [31].

Reaction of MoO_2Cl_2 with dme gives $MoO_2Cl_2(dme)$ with dme coordinated through both oxygens [32]. A crystal structure determination showed the oxo groups to be *cis* and the chlorines *trans*. Bond lengths are Mo-Cl = 2.344(4), Mo=O = 1.670(10) and Mo-O = 2.285(7)Å.

The crystal structure of $Cs_2[MoO_2(Hmal)_2]$ has been determined and is typical of MoO_2L_2 complexes [33]. The structure of the anion (8) reveals that the ligand is coordinated through the deprotonated hydroxo group and the vicinal carboxylate. The second carboxylate is not coordinated but it does H-bond to the next anion unit.

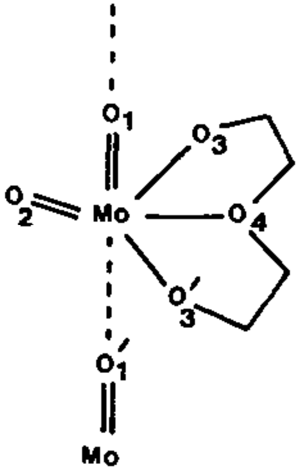


(8)

Bond distances are

$$\mathrm{Mo{=}O} = 1.708(9)\,\text{Å}$$
$$\mathrm{Mo{-}O^-} = 1.939(8)$$
$$\mathrm{Mo{-}O(CO)} = 2.243(9)$$

MoO_3 reacts with 2,2'-oxydiethanol (digol) to give $MoO_2(C_4H_8O_3)$. X-ray diffraction revealed an unusual structure with five oxygen atoms linked to molybdenum and the sixth position occupied by a long range interaction from a terminal oxo group on the next molybdenum atom, thus giving a linear unsymmetrical bridge as shown in (9) [34].

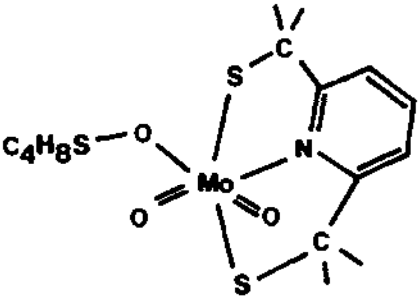


(9)

Bond distances are

$\mathrm{Mo{=}O_1} = 1.73(2)\,\text{Å}$ $\quad$ $\mathrm{Mo\ldots O_1'} = 2.38(2)$
$\mathrm{Mo{=}O_2} = 1.63(4)$
$\mathrm{Mo{-}O_3} = 1.82(2)$ $\quad$ $\mathrm{Mo{-}O_4} = 2.23(3)$

On irradiation, the complex $MoO_2(dbzm)_2$ loses a dbzm ligand radical in the primary photoprocess and this extracts a proton from the solvent. An EPR active Mo(V) species persists in solution and this is assigned a four coordinate structure [35]. Reaction of $MoO_2(acac)_2$ with pyridine-2,6-dimethanethiol, $L\text{-}N(SH)_2$, and recrystallization from tmso gave $MoO_2(L\text{-}NS_2)(tmso)$ [36] which a crystal structure showed to have a distorted octahedral stereochemistry with a *cis*-MoO_2 unit (O-Mo-O = 106.0(2)°) with tmso rather weakly bonded through oxygen as shown in (10).

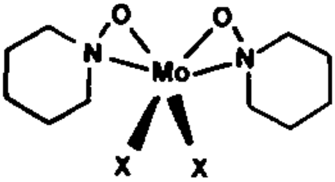


(10)

Bond distances are

Mo=O(*trans* N) = 1.723(3)Å Mo-S = 2.438(1), 2.402(1)
Mo=O(*trans* O) = 1.694(3) Mo-O = 2.357(3)

The complexes *cis*-$MoO_2(ONR)_2$ (where ONR is a substituted hydroxylamido ligand) react with H_2S to give *cis*-oxothio and *cis*-dithio complexes while H_2Se gave only the *cis*-oxoseleno compound [37]. The crystal structures of the dioxo and dithio compounds with R = C_5H_{10} have been determined. Although the compounds are not isomorphous, the molecular structures are similar with very distorted coordination about molybdenum as shown in (11).



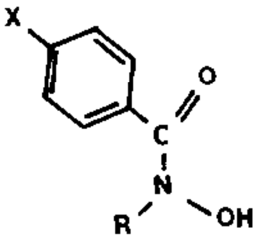
X = O or S

(11)

Bond distances are

	X = O	X = S
Mo=X	1.701(5), 1.879(5)Å	2.145(2) x2
Mo-O	1.971(7), 1.949(6)	1.956(4) x2
Mo-N	2.146(7), 2.137(7)	2.151(4) x2

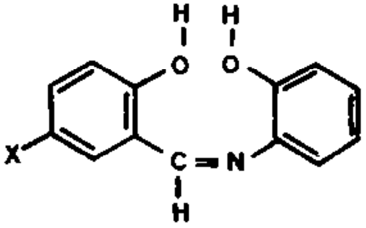
A series of $MoO_2(RX)$ complexes (RX = substituted hydroxamate,(12) , R = H,Me, Ph; X = OMe,Me,H,Cl,NO_2) have been prepared. They are believed to exist as



(12)

only one isomer with a *cis*-MoO_2 unit and the central carbonyl oxygen of the ligand *trans* to Mo=O. All show irreversible electrochemical reduction to Mo(V) although the reduction potential varies considerably with R and X [38].

The ^{95}Mo NMR spectra have been observed for a series of complexes $MoO_2L(dmso)$ where L is a bidentate Schiff base ligand based on (13) or (14) with X = NO_2,Br,Cl,H,OMe)



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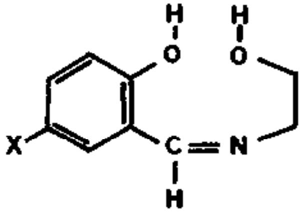
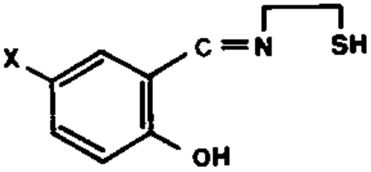


(14)

The ^{95}Mo chemical shifts vary significantly, reflecting small changes in the ligand structures [39]. Reaction of $MoO_2(NSH)$ (NSH = tridentate anion derived from (15), X = Cl,Br,H,OMe) with PPh_2Et resulted in oxygen transfer to the



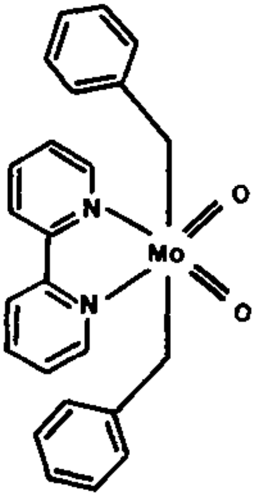
X = Cl, Br, H, CH_3O

(15)

phosphine yielding MoO(NSH) and $OPPh_2Et$ [40]. There was no evidence for formation of a dimeric Mo(V) species (from Mo(IV) and Mo(VI)) as occurs in the analogous reaction between $MoO_2(S_2CNR_2)_2$ and PPh_3.

Electrochemical oxidation, controlled potential electrolysis and spectroscopic measurements show that oxidation of MoO_2(TPP) (that is, extraction of an electron from the TPP π-system) is followed by a very rapid loss of an oxygen atom to give (ClO_4)MoO(TPP) which was recognized by its characteristic electrochemical behaviour and UV-visible spectrum [41]. This mechanism is similar to that proposed for the iron compound cytochrome P_{450}.

Dibenzyl(bipy)dioxomolybdenum(VI) has been synthesized by the reaction of the benzyl Grignard reagent and MoO_2Br_2(bipy) [42]. A crystal structure determination shows a planar MoO_2(bipy) unit and an approximately octahedral arrangement is completed by the benzyl groups as shown in (16).



(16)

Bond distances are

Mo=O = 1.70(1)Å (av)
Mo-N = 2.28(1) (av)
Mo-C = 2.25(2)

An interesting feature of the structure is the orientation of the benzyl phenyl rings indicating a π-interaction with the bipy rings. A similar reaction between MoO_2Br_2(bipy) and the *neo*-pentyl Grignard reagent yields

$MoO_2(CH_2.CMe_3)_2(bipy)$ which is remarkably stable due to the lack of hydrogen in the β-position of the alkyl ligand [43]. The structure is similar to (16) with an almost planar $MoO_2(bipy)$ unit with *neo*-pentyl groups completing a very distorted octahedral arrangement. An alternative view of the structure could be to regard the $MoO_2(alkyl)_2$ group as tetrahedral with a weak interaction with the bipy ligand. Bond distances are Mo=O = 1.708(3), Mo-C = 2.236(5), Mo-N = 2.317(4), 2.348(4)Å.

The known cations $[MoO(S_2CNR_2)_3]^+$ are readily prepared from $MoO_2(S_2CNR_2)_2$ and acid ($HBPh_4$, H_2PF_6, $HClO_4$) in acetone solution [44]. ^1H and ^{13}C NMR spectra show the molecules are rigid in solution and retain the pentagonal bipyramidal structure known in the solid state. The cations readily transfer oxygen to PPh_3 and give $Mo(NPh)(S_2CNR_2)_3$ with PhNCO.

$MoO_2(S_2CNEt_2)_2$ reacts with p-X-C_6H_4NO (X = Me,H,Cl) to give $MoO(S_2CNEt_2)_2(ONC_6H_4$-$p$-X) in which the ligand is bonded η^2 through *N* and *O*. These complexes undergo an irreversible one-electron reduction [45].

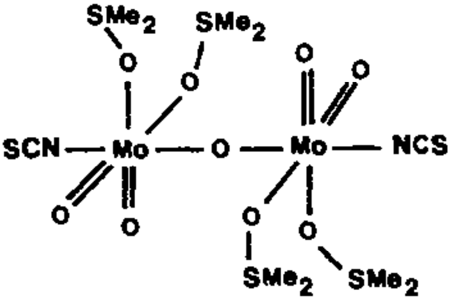
5.1.4 *Dimeric and polymeric oxo complexes*

The complex formed between molybdate and nitrilotriacetic acid $N(CH_2CO_2H)_3$ (H_3nta) at pH 2 has an IR spectrum which suggests that it contains a bridging oxygen atom. This has now been confirmed by a crystal structure determination [46] which showed the compound to be $Na_2[Mo_2O_5(Hnta)_2]8H_2O$. The bridge is linear with two terminal *cis*-oxo groups *cis* to the bridge. Completing the octahedron about the molybdenum atoms is nitrogen and two carboxylate oxygens, the protonated carboxylate being non-bonding. Bond distances are Mo-μO = 1.880(1), Mo=O = 1,695(6) (av), Mo-O = 2.069(5), 2.134(5), Mo-N = 2.410(6)Å.

The reaction

$$(pyH)_4[Mo_2O_4(NCS)_6].4H_2O \;+\; dmso \xrightarrow{MeOH,reflux} [\{MoO_2(NCS)(dmso)_2\}_2O]$$

gave pale yellow crystals which have the structure shown in (17)



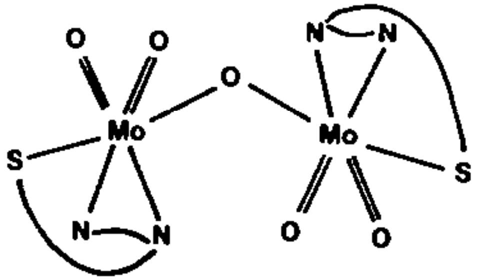
(17)

The Mo-O-Mo bridge is linear and bond distances are

Mo=O = 1.688(5)Å   Mo-μO = 1.864(1)
Mo-N = 2.094(5)   Mo-O = 2.214(5)

The compound is light sensitive and in sunlight its solutions rapidly change from pale yellow to orange; this process is reversible in the dark ($t_{\frac{1}{2}} \simeq 10$ days). The photoreaction is thought to be due to an intramolecular electron transfer from one thiocyanate to Mo(VI) to give a mixed Mo(VI)/Mo(V) complex [47].

A series of Mo(VI) complexes of the type $Mo_2O_5L_2$ (where L is a tridentate anion giving *NNS* coordination) has been prepared by interaction of $MoO_2(acac)_2$ and LH in acetone solution. IR and ^{17}O NMR spectra are consistent with a mono oxo bridged dinuclear unit and this was confirmed by the crystal determination for $[Mo_2O_5(Me_2NCH_2CH_2NHCH_2C(S)Me_2)]$. Each molybdenum is approximately octahedrally coordinated with the oxygens in *fac* stereochemistry and the tridentate ligand has sulphur *trans* to the bridgiug oxygen as shown in (18).



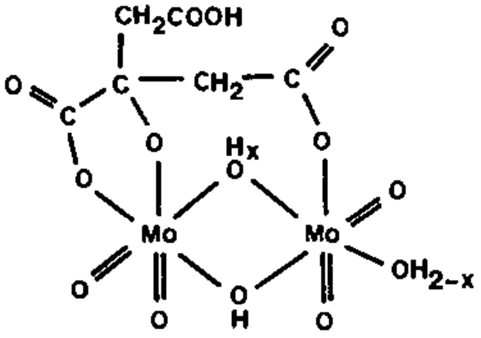
(18)

The angle at the bridging oxygen is 143.8(3)° and bond distances are

Mo=O = 1.71Å (av)   Mo-μO = 1.92 (av)
Mo-S = 2.42 (av)   Mo-N = 2.310(6) - 2.516(7)

There is weak H-bonding between a proton on the terminal nitrogen of each ligand and the oxo group of the other molybdenum atom [48].

Bridged dimeric Mo(VI) complexes $M'[Mo_2O_5(OH)(H_2O)(citH)]$ ($M' = K, NH_4$) have been isolated and on the basis of ^{13}C NMR and IR studies are thought to have the structure (19). The complexes undergo irreversible photochemical reduction in the solid state with release of CO_2 to give a paramagnetic Mo(V) species [49].

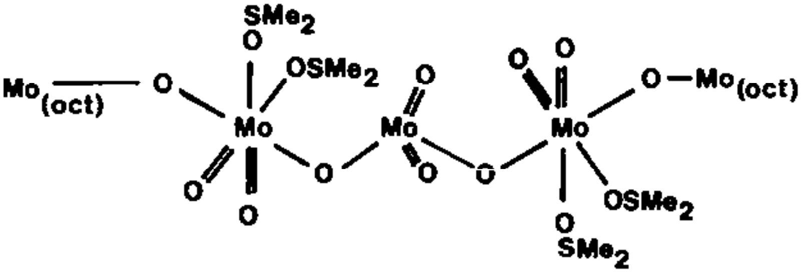


x = 0,1

(19)

Hydrolysis of $W(CCMe_3)(CH_2CMe_3)_3$ gives $W_2O_3(CH_2CMe_3)_6$ which preliminary X-ray data shows to have a linear O=W-O-W=O unit with a trigonal arrangement of *neo*-pentyl ligands about each tungsten [50]. The compound is remarkably stable in air and to hydrolysis. Reaction with HCl in dichloromethane (in presence of Me_3SiCl to remove water) gives $WOCl(CH_2CMe_3)_3$. The anion $[WO_3(CH_2CMe_3)]^-$ can be prepared by hydrolysis of $W(CCMe_3)(OCMe_3)_3$ by aq. NEt_4OH in thf solution.

Dissolving $MoO_3.2H_2O$ in dmso has led to the isolation of a number of adducts and the crystal structure of one of them, $Mo_3O_9(dmso)_4$, has been determined [51]. The structure consists of infinite chains in which the repeating unit has three molybdenum atoms, one tetrahedral and two octahedral, linked by oxygen atoms to give a molybdenum atom sequence of tet, oct, oct, tet, oct, oct, tet etc. as shown in (20).

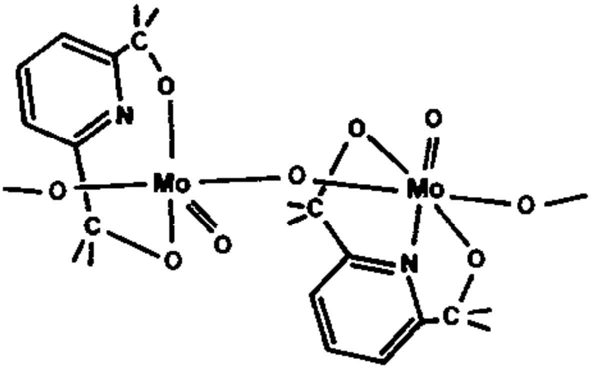


(20)

The oxygen bridges between octahedral molybdenums are close to linear, but those between octahedral and tetrahedral molybdenums have angles which vary between 137° and 169°. Average bond distances are

Mo(tet)=O = 1.703Å Mo(oct)=O = 1.702
Mo(tet)-μO = 1.806 Mo-O(dmso) = 2.245
Mo(oct)-μO(to Mo(tet)) = 1.994
Mo(oct)-μO(to Mo(oct)) = 1.879

Reaction of $MoO_2(acac)_2$ with pyridine-2,6-dimethanol ($L-N(OH)_2$) and recrystallization from tmso gave $[MoO_2(L-NO_2)]_n$ [36] which has a chain structure with asymmetric *trans* oxygen bridges as shown in (21).



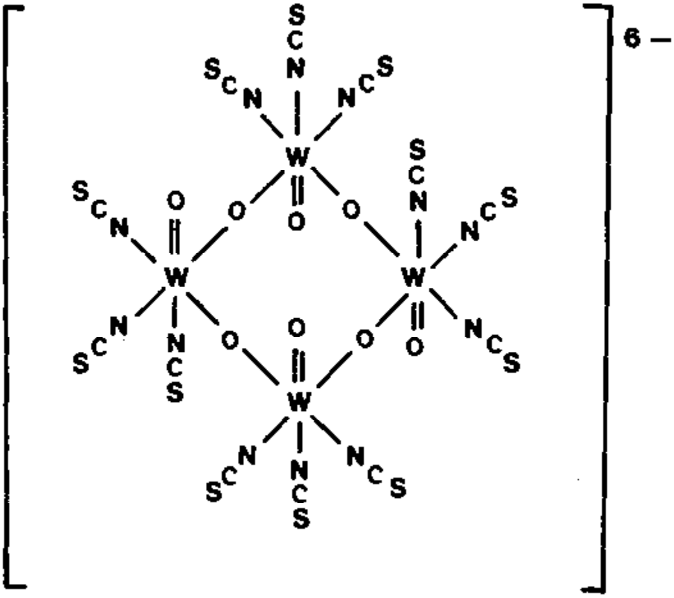
(21)

The angle at the bridge is 151.7(2)° and bond distances are

Mo=O = 1.710(3)Å Mo-μO = 1.719(3), 2.518(3)
Mo-O = 1.920(3) Mo-N = 2.190(3)

The contrast between this structure and that found for the complex with the similar ligand $L-NS_2$ (structure (10)) is noteworthy.

Finally in this section two mixed oxidation state oxo complexes will be described. The mixed valence complex $[W_4O_8Cl_8(H_2O)_4]^{2-}$, which contains W(VI) and W(V), has been used to prepare other derivatives such as $[W_4O_8Cl_6(dmf)_6]$, $[W_4O_8(NCS)_{12}]^{6-}$ and $[W_4O_8(NCS)_4(C_2O_4)_4]^{6-}$. The mixed salt $Cs_5(NH_4)[W_4O_8(NCS)_{12}].6H_2O$ has been shown by X-ray diffraction to have the structure (22). The W_4O_4 unit is planar and angles at the bridging oxygens range from 167(2) to 176(2)°.



(22)

Bond distances are

W=O = 1.53(4) - 1.83(4)Å

W-μO = 1.82(3) - 1.93(3)

W-N(*trans*=O) = 2.21(7) - 2.41(7)

W-N(*trans*-μO) = 2.01(4) - 2.11(6)

The disposition of the terminal oxo groups is different from that of the parent $[W_4O_8Cl_8(H_2O)_4]^{2-}$ in which the oxo groups alternate above and below the W_4O_4 plane. All the complexes have very high optical absorption which is consistent with intervalence transitions [52].

Reaction of $MoCl_5$ with 2-(2'-thienyl)benzimidazole gave a complex containing the 2-(2'-thienyl)-1-(2'-thienylmethyl)benzimidazolium cation and the $[Mo_4Cl_4O_8(OEt)_4]^{2-}$ anion [53]. The course of the reaction is obviously very complicated and the mechanism for formation of the anion is unknown. A crystal structure determination showed the anion to contain two Mo(VI) and two Mo(V) atoms linked by two μ_3 oxygens, two μ_2 oxygens and two μ_2 OEt groups.

5.1.5 Complexes with oxygen donor ligands

In a series of papers the identity of monomeric Mo(VI) species present at very low concentrations of molybdenum in acid solutions have been studied [54-56]. In H_2SO_4 the species present are thought to be $Mo(OH)_6$, $[Mo(OH)_5H_2O]^+$ and $[Mo(OH)_4(SO_4)_2]^{2-}$ while in HCl solution the first two species exist at low acid concentration, but increasing chloride concentration leads to the formation of $Mo(OH)_4Cl_2$ and $Mo(OH)_3Cl_3$.

The reaction

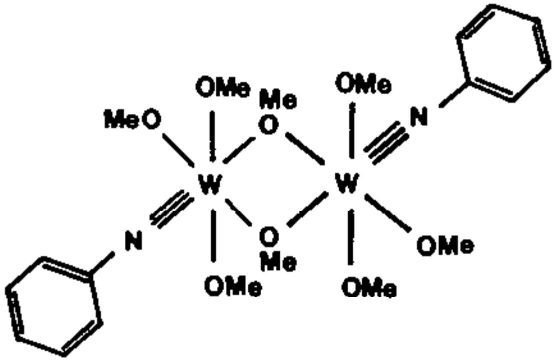
$$MoF_6 + 6Si(OMe)_4 \rightleftharpoons Mo(OMe)_6 + 6SiF(OMe)_3$$

is an equilibrium at -196°C, but it proceeds to completion if the $SiF(OMe)_3$ is removed under vacuum. WF_6 reacts only partially

$$WF_6 + 5Si(OMe)_4 \rightarrow WF(OMe)_5 + 5SiF(OMe)_3$$

but reaction of the product with NaOMe/MeOH gives $W(OMe)_6$. ^1H NMR suggests that the volatile liquid $M(OMe)_6$ compounds have all methoxy groups equivalent [57].

Reaction of WCl_4NPh with methanol in the presence of $^tBuNH_2$ gave the yellow complex $PhNW(OMe)_4$ which was shown to have the structure (23).

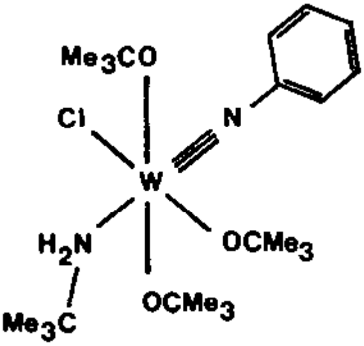


(23)

Bond distances are

W≡N = 1.65(2)Å
W-OMe = 1.92(1) - 2.02(1)
W-μOMe = 2.04(1) - 2.14(1)

Replacement of MeOH by ^{i}PrOH or *neo*-pentyl alcohol gave complexes identified as *trans*-$W(OR)_4(NPh)(^{t}BuNH_2)$ on the basis of ^1H and ^{13}C NMR measurements [58]. Reaction of WCl_4NPh and $^{t}BuOH$ gave $W(O^{t}Bu)_3Cl(NPh)(^{t}BuNH_2)$ which has the structure (24).



(24)

Bond distances are

$W{\equiv}N = 1.70(1)Å$

$W\text{-}O(trans\ Cl) = 1.82(1)$

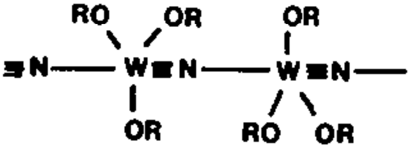
$W\text{-}Cl = 2.500(4)$

$W\text{-}N = 2.40(1)$

$W\text{-}O = 1.87(1)$

It is thought that steric interactions between Me_3CO groups cause the chlorine to be retained.

$W_2(O^{t}Bu)_6$ is known to react with MeCN to give $(^{t}BuO)_3W{\equiv}N$ polymer. A crystal structure determination [59] reveals a linear polymer based on alternate long and short W-N bonds with the alkoxide groups completing a trigonal bipyramidal geometry about tungsten (25)



(25)

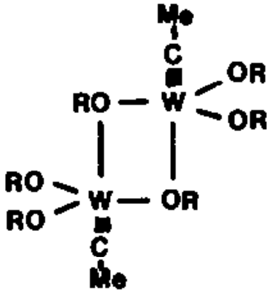
Bond distances are

$W{\equiv}N = 1.740(15)Å$

$W\text{-}N = 2.661(15)$

$W\text{-}O = 1.872(7)$

In contrast, the isoelectronic $(^{t}BuO)_3W\equiv CMe$, formed by the interaction of $W_2(^{t}BuO)_6$ with $MeC\equiv CMe$, consists of weakly linked dimer units, also based on trigonal bipyramidal coordination about tungsten, as shown in (26) [59].

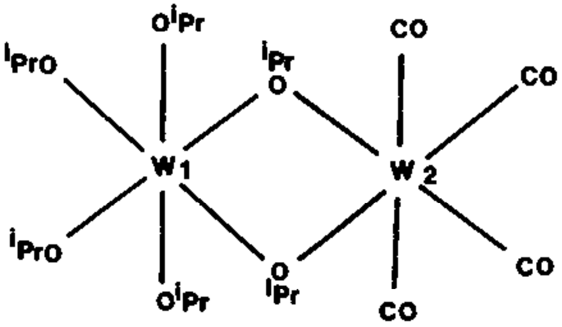


(26)

Also, the compound $(^{t}BuO)_3W\equiv CNMe_2$ [60] has a very similar structure to (26). Bond distances are

	$(^{t}BuO)_3W\equiv CMe$	$(^{t}BuO)_3W\equiv CNMe_2$
$W\equiv C$	= 1.759(6)Å	1.76 (av)
W-O(*trans* ≡C)	= 2.484(4)	2.42(1)
W-O(eq)	= 1.89 (av)	1.89(1)
W-μO(eq)	= 1.934(4)	1.95(1)

Exposure of $W_2(^{i}PrO)_6py_2$ to approximately 2 moles of CO led to the isolation of $W_2(^{i}PrO)_6(CO)_4$ [61]. A crystal structure determination shows two octahedra joined by unsymmetrical $O^{i}Pr$ bridges in which the short bonds are to W_1 (27).

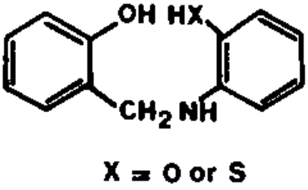


(27)

W_2 shows all the spectroscopic properties of a typical $W(CO)_4L_2$ compound, so the compound is best formulated as a W(VI)/W(0) complex, an unprecedented oxidation state difference in any compound. The large W-W distance of 3.410(1)Å suggests repulsion between the metal centres. Bond distances are

$$W_1\text{-}O = 1.826(15) - 1.876(12)\text{Å}$$
$$W_1\text{-}\mu O = 1.96\ (\text{av})$$
$$W_2\text{-}\mu O = 2.23\ (\text{av})$$

Reaction of $MoO_2(acac)_2$ or MoO_2Cl_2 with ligands LH_3 (28) gave MoL_2 with the



(28)

nitrogen atom deprotonated in the complexes [62]. These complexes show reversible reduction to MoL_2^- and MoL_2^{2-} and a crystal structure determination of the Mo(V) compound $NEt_4[MoL_2]$ (X = S) revealed a distorted octahedral arrangement with equivalent donor atoms of each ligand all *trans*. Bond distances are Mo-O = 2.023(8) (av), Mo-N = 2.050(8) (av) and Mo-S = 2.362(4)Å. In contrast, similar ligands with two NH_2 groups in the ligand backbone ($L'H_4$) react with $MoO_2(acac)_2$ to give $MoO_2(L'H_2)$ in which both nitrogens remain protonated. These complexes undergo irreversible reduction to Mo(V), a process which may involve nitrogen deprotonation [62].

5.1.6 Sulphides, thiomolybdates and thiotungstates

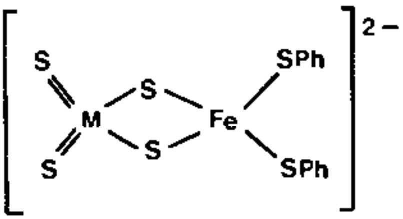
A molybdenum edge EXAFS analysis has been made of the thermal decomposition of amorphous MoS_3 to MoS_2 [63]. Improved syntheses have been reported for the preparations of $(NH_4)_2[MS_4]$, $(NH_4)_2[MOS_3]$ and $(NH_4)_2[MO_2S_2]$ together with a facile preparation of the NEt_4 salts. The purity of the various complexes may be monitored by a combination of IR and UV-visible spectroscopy [64]. The crystal structure of $(NEt_4)_2[MoS_4]$ reveals tetrahedral anions with Mo=S = 2.175(5)Å [65]. The low temperature UV-visible and resonance Raman spectra of $[WS]^{2-}$ have been observed. It is deduced that on excitation from the ground ($^1A_1$) state to the resonant excited state ($^1T_2$), the W-S bond length increases by 0.058Å [66].

There have been a large number of studies using MS_4^{2-} as ligands towards other transition metals with some emphasis on iron in attempts to produce model compounds for the Mo/Fe/S centre in nitrogenase. Reaction of $(NEt_4)_2[MS_4]$ with $Fe(S_2CNR_2)_2$ in dichloromethane gave $(NEt_4)_3[Fe(MS_4)_2]$ in which the bidentate MS_4 units replace dithiocarbamate [67]. Electrochemical studies show that for molybdenum only the couple $[Fe(MoS_4)_2]^{3-}/[Fe(MoS_4)_2]^{4-}$ is reversible, but for tungsten the couples

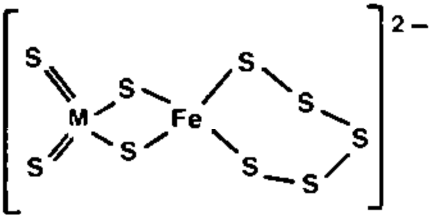
$$[Fe(WS_4)_2]^- \rightleftharpoons [Fe(WS_4)_2]^{2-} \rightleftharpoons [Fe(WS_4)_2]^{3-} \rightleftharpoons [Fe(WS_4)_2]^{4-}$$

are all reversible. The EPR spectra of $[Fe(MS_4)_2]^{3-}$ are consistent with a $S = 3/2$ spin state (similar to nitrogenase).

Reaction of $[Fe(SPh)_4]^{2-}$ with $[MS_4]^{2-}$ gave excellent yields of $[(PhS)_2FeS_2MS_2]^{2-}$ and the corresponding $[(S_5)FeS_2MS_2]^{2-}$ complexes were readily isolated by reacting $[(PhS)_2FeMS_4]^{2-}$ with $(C_7H_7)_2S_3$ in dmf [68]. Several crystal structures were done and all the complexes contain an essentially planar FeS_2M unit with structures as shown in (29) and (30).



(29)



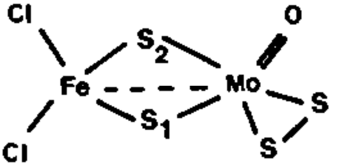
(30)

Bond distances are

	$[(PhS)_2FeMoS_4]^{2-}$	$[(PhS)_2FeWS_4]^{2-}$	$[(S_5)FeMoS_4]^{2-}$	$[(S_5)FeWS_4]^{2-}$
M-Fe	2.740(1)	2.775(1)	2.737(3)	2.752(3)
M=S (av)	2.15	2.16	2.15	2.16
M-μS (av)	2.26	2.25	2.26	2.26
Fe-μS (av)	2.26	2.29	2.25	2.27
Fe-S (av)	2.30	2.31	2.33	2.34

^{57}Fe Moessbauer and magnetic measurements were also made [68]. The complex $(NEt_4)_2[(PhS)_2FeMoS_4]$ has also been studied using IR, resonance Raman and UV-visible spectroscopy [69]. The Fe-S, M-S and M-μS fundamentals were assigned and Raman band excitation profiles indicate that the Fe(II) valence electrons are extensively delocalized. Reaction of $Fe(OAc)_2$ with $(NEt_4)_2[MS_4]$ in MeCN gave $[(OAc)_2FeMS_4]^{2-}$ which were characterized by IR and UV-visible spectra. In contrast, Fe(OAc)$_2$ reacts with $[MO_2S_2]^{2-}$ to give complexes not completely characterized but which do not contain acetate [70].

Molybdenum EXAFS studies have been carried out on $[MoS_4]^{2-}$, $[L_2FeS_2MoS_2]^{2-}$ (L = PhS,Cl,OPh), $[L_2FeS_2MoS_2]^{3-}$ (L = S-*p*-C$_6$H$_4$Me) and the di-iron complex $[S_2FeS_2MoS_2FeS_2]^{3-}$. The data was analysed to give Mo-S and Mo-Fe distances to better than 1% and 2% respectively. A new technique for fine adjustment based on models (FABM) was developed [71]. Similar Mo, W and Fe EXAFS studies on $[Cl_2FeS_2MS_2FeCl_2]^{2-}$ have been reported which give M-S, M-Fe and Fe(S,Cl) distances which agree well with crystallographic determinations. However, it was found that the Fourier transform of the Mo EXAFS of these model compounds did not compare well for peak intensities with those of the MoFe protein of nitrogenase [72]. Reaction of $[MoOS_3]^{2-}$ with FeCl$_2$ and S$_8$ in dmf led to the isolation of $(PPh_4)_2[Cl_2FeS_2MoO(S_2)]$.dmf. A crystal structure determination showed that the thiomolybdate had undergone substitution of S^{2-} by $(S_2)^{2-}$, the first substitution of a thiomolybdate, as shown in structure (31) [73].

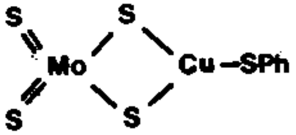


(31)

Bond distances are

Mo...Fe = 2.752(2)Å   Mo-S = 2.30 (av)
Mo=O = 1.660(8)   Fe-S = 2.24 (av)
Mo-S(S$_2$) = 2.40 (av)   Fe-Cl = 2.26 (av)

$[MoS_4]^{2-}$ also acts as a bidentate ligand towards Cu(I) and in a series of papers complexes of $[MoS_4]^{2-}$ with 1-4 coordinated copper groups have been reported. The anions $[(PhSCu)MoS_4]^{2-}$ and $[(PhSCu)_2MoS_4]^{2-}$ were prepared by the action of KSPh in MeCN on the corresponding coordinated copper cyanide complexes [74]. Crystal structure determinations showed them to have the structures shown in (32) and (33).



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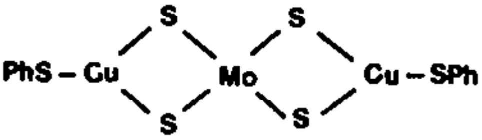
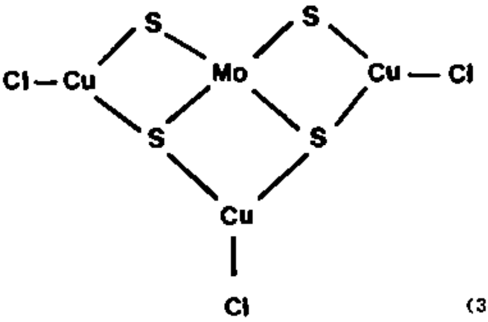


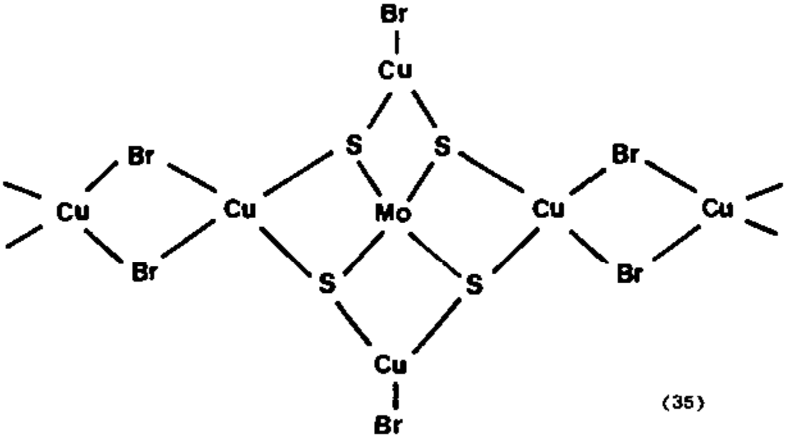
(33)

In each case the molybdenum is tetrahedral and the copper trigonal planar. The different symmetries of the MoS_4 unit are clearly reflected in the IR and Raman spectra; some ^{95}Mo NMR spectra are also reported. The interaction between $(PPh_4)_2[MoS_4]$ and CuCl (1:3) in MeCN gave $[(CuCl)_3MoS_4]^{2-}$ which has the structure shown in (34) [75].



(34)

The reaction between $[MoS_4]^{2-}$ and excess CuX (X = Cl,Br) in acetone gave $[(CuX)_4MoS_4]^{2-}$ and the structure of the anion for the $[PPh_4]^+$ salt of $[(CuBr)_4MoS_4]^{2-}$ is shown in (35). It is a one dimensional polymeric anion in

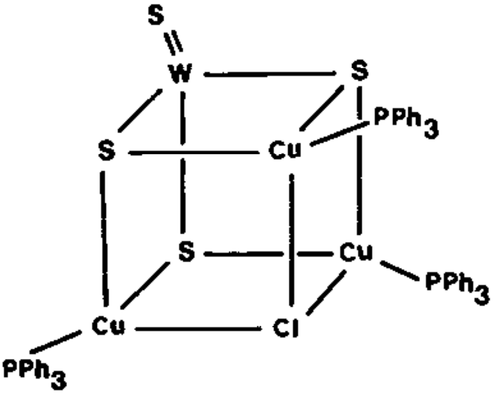


(35)

which four edges of the MoS_4 tetrahedron are bridged by copper atoms. Two *trans* copper atoms complete their trigonal stereochemistry with terminal bromines while the other two coppers are tetrahedral with two bromines involved in inter-aggregate bridging to a copper of the next MoS_4 based unit [76]. Bond distances in all these derivatives are

	(32)	(33)	(34)	(35)
Cu-Mo	2.636(1)	2.632(6)	2.618	2.618(3) - 2.685(3)
Mo=S (av)	2.16			
Mo-μ_2S (av)	2.22	2.21	2.20	
Cu-μ_2S (av)	2.21	2.21	2.23	
Mo-μ_3S (av)			2.26	2.23
Cu-μ_3S (av)			2.24	2.25

Compounds of the type $[\{Cu_3MS_3Cl\}(PPh_3)_3Y]$ (Y = O,S) have been prepared from $[MS_4]^{2-}$ or $[MOS_3]^{2-}$, $CuCl_2$ and PPh_3 in dichloromethane [77]. The structures of all four are similar and that of [Cu_3WS_3Cl $(PPh_3)_3S$] is shown in diagram (36).

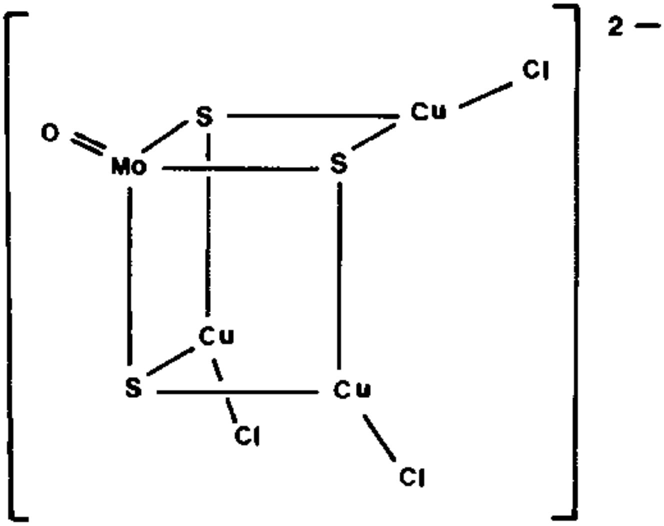


(36)

The Cu_3WS_3Cl core is a highly distorted cube. Bond distances in all the complexes (M and Y only specified) are

	W,S	W,O	Mo,S	Mo,O
M-Cu (av)	2.72	2.74	2.70	2.72
Cu-Cu (av)	3.18	3.18	3.18	3.20
M=Y	2.131	1.754	2.118	1.769
M-S (av)	2.25	2.24	2.25	2.26

Reaction of $(PPh_4)_2[MoOS_3]$ with three equivalents of CuCl in organic solvents in the presence of sulphur gave $(PPh_4)_2[(CuCl)_3MoOS_3]$ in which the three copper atoms bridge S-S edges to generate a $MoOS_3Cu_3$ core which has the geometry of a distorted cube with one position vacant as shown in (37) [78].



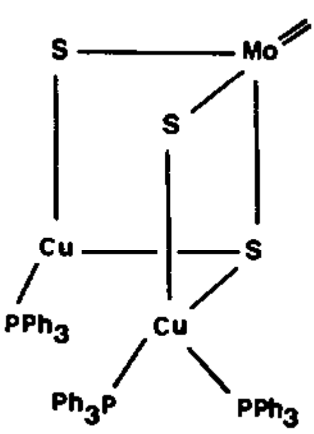
(37)

Bond distances are

Mo-μS = 2.26Å(av) Cu-S = 2.222(4) - 2.251(4)
Mo=O = 1.693(10) Cu-Cl = 2.15 (av)

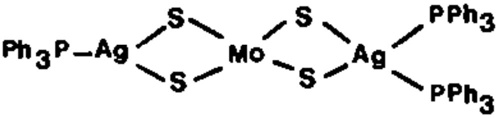
The same anion was found (and characterized by X-ray diffraction) in one of the products of the reaction of CuCl and $[MoS_4]^{2-}$, with the oxygen presumably being derived from the atmosphere [79]. Following extraction of compound (37) with a dichloromethane solution of CuCN and PPh_3, the complex $[(CuPPh_3)\{Cu(PPh_3)_2\}MoOS_3]$ was isolated [78]. It was shown to have the structure (38) which is basically a cube with two vacancies. Bond distances are

$Mo-\mu_3S$ = 2.277(3)Å $Cu_1-\mu_3S$ = 2.230(4)
$Mo-\mu_2S$ = 2.207(3), 2.230(3) $Cu_2-\mu_3S$ = 2.343(3)
Mo=O = 1.700(8) $Cu-\mu_2S$ = 2.218(4)
Cu_1-P = 2.220(4) $Cu_2-\mu_2S$ = 2.321(3)
Cu_2-P = 2.31 (av)



(38)

The interaction of $[MS_4]^{2-}$ with $AgNO_3$ and PPh_3 in dichloromethane gives $[(PPh_3)_2Ag_2MS_4]$ [77] and the structure of the Mo complex is shown in (39). The silver atoms are not equivalent, one being tetrahedral and the other trigonal.



(39)

Bond distances are

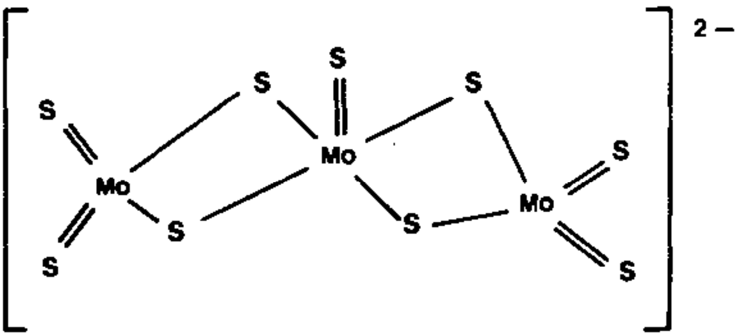
Mo-S = 2.21Å (av)

Ag(tet)-S = 2.572(5)   Ag(trig)-S = 2.458(5)

Heating $(NH_4)_2[MS_4]$ in dmf gives $[M_3S_9]^{2-}$, although the complexes were obtained pure only by heating in the presence of benzene thiol [80]. The crystal structure of the molybdenum compound reveals a central square pyramidal Mo(IV) atom and two tetrahedral Mo(VI) units as shown in (40). The Mo..Mo..Mo angle is 155.0(1)° and bond distances are

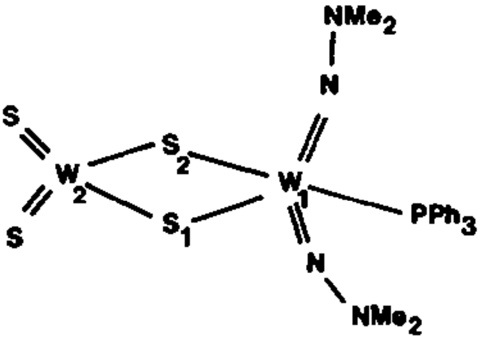
Mo(IV)=S = 2.086(4)Å   Mo(IV)-μS = 2.369(3) - 2.429(3)

Mo(VI)=S = 2.134(4) - 2.148(3)   Mo(VI)-μS = 2.231(3) - 2.251(3)



(40)

$(NBu_4)_2[WS_4]$ reacts with $[WCl(NNMe_2)_2(PPh_3)_2]Cl$ to give $[S_2WS_2W(NNMe_2)_2PPh_3]$ [81] which contains two non-equivalent tungsten atoms and provides a rare example of an MS_4 unit spanning axial and equatorial positions of a trigonal bipyramid as shown in (41).



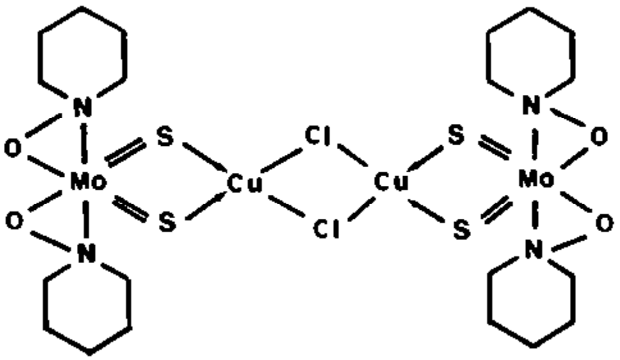
(41)

Bond distances are

$W \ldots W = 3.024(1)$ Å $W_2{=}S = 2.15$ (av)
$W_2\text{-}\mu S_1 = 2.281(6)$ $W_1\text{-}\mu S_1 = 2.405(6)$
$W_2\text{-}\mu S_2 = 2.233(8)$ $W_1\text{-}\mu S_2 = 2.528(8)$
$W_1\text{-}P = 2.482(6)$ $W_1\text{-}N = 1.78$ (av)

The angles at the α-N of the dimethylhydrazido(2-) ligands average 170°.

Reaction of *cis*-[MoO$_2$(pipNO)$_2$] (pipNO = piperidine-N-oxide) with B_2S_3 yields the *cis*-MoOS and subsequently *cis*-MoS$_2$ complexes. IR, Raman and NMR (^{95}Mo, ^{13}C) confirm the identities of the componnds [82]. The structure of *cis*-[MoOS(pipNO)$_2$] has been determined and is analogous to the corresponding MoO$_2$ and MoS$_2$ compounds. The coordination about the molybdenum may be described as a roughly tetrahedral MoO$_3$S core with the angle between the oxygens of the two N-oxide ligands closed down to about 84° to accommodate the extra Mo-N bonds. These are co-linear and in the same plane as the metal atom and the N-oxide oxygens. Bond distances are Mo=O = 1.711(4), Mo=S = 2.101(2), Mo-O = 1.97 (av), Mo-N = 2.14Å (av). CuCl reacts with *cis*-[MoS$_2$(pipNO)$_2$] to give green crystals of [(pipNO)$_2$MoS$_2$(CuCL)] which has the structure shown in (42). Interestingly, the copper in this complex is tetrahedral, but in most of the copper complexes of [MS$_4$]$^{2-}$ it is trigonal [83].



(42)

Bond distances are

Mo=S = 2.18Å (av)   Cu-S = 2.266(1)
Mo-O = 1.96 (av)   Cu-Cl = 2.35 (av)
Mo-N = 2.16 (av)   O-N = 1.43 (av)

^{95}Mo NMR spectra have been recorded for a series of [MoXY(ONHR)$_2$] and [MoXY(ONR$_2$)$_2$] species (X = O,S; Y = O,S,Se; R = Me,Et, Bu) which contain chelated substituted hydroxylamine anions. The dioxo complexes show a ^{95}Mo resonance at approx. δ -200, substitution by one sulphur shifts the resonance to approx. δ 540 and two sulphurs shift the resonance to δ 1200. The effect of one selenium is similar to, but greater, than the effect of one sulphur. The thiolation of MoO$_2$ complexes to MoOS and MoS$_2$ was followed by ^{95}Mo NMR [84].

5.1.7 Homonuclear polyanions

A detailed theoretical analysis of the bonding in systems with chains of condensed molybdenum octahedra has been presented. A one dimensional model proved to be applicable over the range of molybdates yet synthesized [85]. The structure of the complex of composition $(Na_2MoO_4)_3(MoO_3)_7$, i.e. $Na_6Mo_{10}O_{33}$, has been shown to have a structure containing two types of chains of molybdenum-oxygen polyhedra linked to each other approximately at right angles. One chain contains distorted edge and corner shared MoO_6 octahedra, while the other consists of corner shared pairs of octahedra edge shared to pairs of edge shared MoO_5 square pyramids [86]. The crystal structure of melaminium β-octamolybdate has been determined and the structure of the β-$[Mo_8O_{26}]^{4-}$ anion is similar to that in the NH_4 and 3-EtPyH salts although there are some significant differences in bond lengths and bond angles due to a very extensive network of H-bonding [87]. Reaction of $MoO_3.2H_2O$ with excess MeOH gave a precipitate of $Mo_2O_5(OMe)_2$, but after filtering, crystals of $Na_4[Mo_8O_{28}(OMe)_4].8MeOH$ slowly formed. A structure determination showed the anion to be very similar to those of a number of other substituted octamolybdates [88].

Polymolybdates(VI) are photochemically reduced to Mo(V) in solutions containing HOAc giving rise to blue mixed valence compounds. The main pathway is the photoredox reaction of polymolybdate(VI) with water to give $OH^\bullet$ and Mo(V), but in addition, CO_2, CH_4 and succinic acid are formed [89]. On irradiation at 254nm, solutions of $(N^{i}Pr_4)_5[W_6O_{20}(OH)]$ evolved H_2 without the presence of a platinum catalyst. The reaction is thought to proceed according to the scheme

$$W^{VI}{=}O \; + \; H_2O \;\xrightarrow{h\nu}\; W^{V}\text{-}OH \; + \; OH^\bullet$$

$$W^{V}\text{-}OH \;\longrightarrow\; W^{VI} \; + \; H_2$$

The $OH^\bullet$ radical and two different W(V) species were detected by EPR [90].

5.1.8 Heteronuclear polyanions

A potentiometric study has been made of the equilibrium between methyl arsenate, $[MeAsO_3]^{2-}$, $[MoO_4]^{2-}$ and H^+ in 1M NaCl at 25°C; a number of heteropolymolybdates were detected [91]. $Na_5[H_3PtW_6O_{24}].2H_2O$ has been found to have a structure of the Anderson type. The central platinum and all the tungstens are coplanar. Each tungsten is octahedrally coordinated by oxygen with a mean distance of 2.01Å [92]. Crystals of a compound shown by X-ray diffraction to be $Na_{12}[P_4W_8O_{40}].20H_2O$ were isolated during an attempted preparation of the previously reported $Na_3[PW_3O_{13}]$. The anion consists of a shell of WO_6 octahedra and PO_4 tetrahedra made up to form $[PW_2O_{13}]$ units linked by corner sharing, thus closely resembling the shell of the Keggin anions [93].

The complex $K_2(NBu_4)_4[MnMo_9O_{32}]$, which contains a D_3 symmetry MnO_6 octahedron, is soluble in MeCN and shows a Pfeiffer effect in the presence of *l*-brucine sulphate. This is reported to be only the third example of a heteropolyanion showing optical activity [94].

Reaction of $TiCl_4$ or $cpFe(CO)_2SnCl_3$ with aqueous $Na_2[WO_4]$ and $NaH_2[PO_4]$ at pH 8-8.6 gave $[Ti_2W_{10}PO_{40}]^{7-}$ and $[\{cpFe(CO)_2Sn\}_2W_{10}PO_{38}]^{5-}$ respectively. The ^{31}P NMR spectra of both compounds showed only a single line suggesting only one isomer of each compound was present. ^{183}W NMR shows in both cases five lines of equal intensity which unambiguously demonstrates the formation of the C_2 isomer (1,4 substitution of the Keggin structure) [95]. Similarly, the interaction of $TiCl_4$ and $SnCl_4$ with $(NBu_4)_4[H_3W_{11}PO_{39}]$ gave $(NBu_4)_4[ClM'W_{11}PO_{39}]$ (M' = Ti,Sn) whilst $AlCl_3$ gave $(NBu_4)_4H[ClAlW_{11}PO_{39}]$. The ^{183}W NMR spectra of all these complexes gave five resonances of intensity two and one resonance of intensity one confirming C_s substitution of the Keggin structure. An unambiguous assignment of the individual resonances was made on the basis of ^{183}W-^{183}W coupling in the satellite spectrum [96]. A different approach to ^{183}W resonance assignment was made for several other similar C_s substituted Keggin compounds using two dimensional ^{183}W NMR techniques (COSY and 2D INADEQUATE) on the satellite spectra, which gives a completely unambiguous assignment without any assumptions on the magnitude of edge versus corner sharing coupling constants [97]. The ^{183}W NMR spectra have been observed for diamagnetic $[Ce^{IV}(W_{11}PO_{39}]^{10-}$ and paramagnetic $[Ce^{III}(W_{11}PO_{39}]^{11-}$. The NMR results suggest different structures for the anions, which is also known to be the case in the solid state. The ^{183}W chemical shifts for the Ce(III) complex suggest electron delocalization to four adjacent tungsten atoms [98].

New mixed heteropolyanions $[XPbW_{11}O_{39}]^{n-}$ (X = Si,Ge,B,Ga), $[YPbW_{11}O_{40}]^{7-}$ and $[Y_2PbW_{17}O_{61}]^{8-}$ (Y = P,As) have been prepared and studied by conductimetric, polarographic, spectroscopic and crystallographic methods [99]. The structures are distorted due to the large size of Pb(II). Keggin and Dawson type heteropolyanions can be regarded as pentadentate ligands for many transition and Group III metals whose octahedral coordination is completed by a water molecule. Exchange of the sixth ligand has been studied for a number of Fe(III) heteropolyanion complexes, and in general the rates of exchange are similar to rates of substitution of a single ligand in $[Fe(H_2O)_6]^{3+}$ [100].

The anions $[ZnW_{12}O_{40}]^{6-}$ and $[AlW_{12}O_{40}]^{5-}$ have been isolated as NBu_4 salts. IR and UV-visible spectra indicate that the Zn resides in a site of tetrahedral symmetry, but the symmetry of the AlO_4 group is highly distorted [101].

The kinetics of the formation and decomposition of 12-molybdophosphates in acid solution have been investigated using stopped flow techniques [102]. Although the maximum rate of formation of the complex is first order with respect to phosphate, it varies with concentration of Mo(VI) and H^+ in a complex manner. The kinetics of the decomposition of $[PW_{12}O_{40}]^{3-}$ to give $[WO_4]^{2-}$ and $[PO_4]^{3-}$ have also been studied, in this case in the pH range 7-9. The reaction proceeds through two intermediates which were identified by their UV-visible spectra and polarographic behaviour [103]

$$[PW_{12}O_{40}]^{3-} \xrightarrow[\text{v. fast}]{OH^-} [PW_{11}O_{39}]^{7-} \xrightarrow[\text{fast}]{OH^-} [PW_9O_{34}]^{9-} \xrightarrow[\text{slow}]{OH^-} [PO_4]^{3-} + [WO_4]^{2-}$$

The first step is extremely fast and occurs at rates approximating to diffusion controlled while the second step is complete in a few seconds. The final hydrolysis is complicated and probably involves protonated forms of $[PW_9O_{34}]^{9-}$. The molybdophosphates have been investigated by Raman spectroscopy. Two forms of the yellow molybdophosphate have been identified in weakly acid solution, which are the 12-molybdophosphate and the 11-molybdophosphate. At pH 1-4 with excess phosphate the colourless $[P_2Mo_5O_{23}]^{6-}$ is formed [104].

A systematic study has been made of the effect of cation size on the vibrational spectra of α- and β-$[XM_{12}O_{40}]^{n-}$ anions (X = Bi,Si,Ge,P,As). The $Mo\text{-}O_d$ stretching frequency decreases as the cation size increases which is attributed to a weakening of the anion-anion interactions [105].

An IR study has been made of the reduction of 12-molybdophosphates by H_2 at 350-400°C and with $SnCl_2$ in acid solution. With H_2 reduction the IR bands due to P=O and $Mo\text{-}O_b\text{-}Mo$ decrease uniformly until the limit of four electrons has been introduced (i.e. two bridges removed from the Keggin structure) and thereafter terminal Mo=O bands decrease [106]. It is known that both 12-molybdosilicates and 12-molybdophosphates undergo three two-electron reductions in 50% dioxan/water mixtures. However, controlled potential electrolysis followed by cyclic voltammetry showed that the six electron reduction product of the molybdosilicate is stable on the longer time scale of electrolysis, but that of the molybdophosphate is not, indicating that the heteroatom has some influence on redox properties [107].

Paramagnetic polytungstates and heteropolytungstates were prepared by electrochemical reduction of the corresponding W(VI) W_6O_{19}, $XW_{12}O_{40}$, $As_2W_{18}O_{62}$ and $AsH_2W_{18}O_{60}$ structural types and studied by EPR and optical spectroscopy. At very low temperatures the unpaired electron is confined to one tungsten atom, but a the temperature increases it hops between different sites, although the ease of electron transfer depends upon the nature of the junction between adjacent WO_6 octahedra. Substitution by a foreign ion leads to a stronger delocalization of the electron [108].

The structure of hexaguanidinium octadecamolybdatediarsenate, $(CH_6N_3)_6[As_2Mo_{18}O_{69}].9H_2O$, has been determined [109]. The polyanion consists of 18 MoO_6 octahedra, composed of two Mo_3O_{13} and six Mo_2O_{10} units, and two AsO_4 tetrahedra. The Mo-O bond distances range from 1.69-2.34Å. Heteropolytungstates α-$[P_2(W,V)_{18}O_{62}]^{2-}$, containing one, two or three V atoms in one of the W_3O_{13} caps of the α-$[P_2W_{18}O_{62}]$ structure, have been synthesized and characterized by ^{31}P and ^{51}V NMR studies. EPR and UV-visible spectra of reduced species show electron delocalization between adjacent vanadium sites [110].

The compound 20-tungsto-2-arsenate has been prepared and used as a rigid tetradentate oxygen donor ligand to give five coordinate (sq. pyramidal) complexes of a number of divalent first row transition metal ions including Mn(II),Co(II),Ni(II),Cu(II),Zn(II) and VO^{2+} [111]. A rational synthesis of $[P_4W_{30}M'_4(H_2O)_2O_{112}]^{16-}$ (previously reported as $[P_2W_{16}M'_2(H_2)_2O_{60}]^{10-}$) (where M' = Co,Cu,Zn) is reported and ^{31}P and ^{183}W NMR spectra reveal only one isomer of C_{2h} symmetry is present in solution. There are four possible isomers of this symmetry, but detailed examination of the spectral data allowed identification of the αββα isomer [112].

5.1.9 *Ternary oxides*

It has been found that three compounds exist in the SrO/WO_3 system; they are $SrWO_4$ (scheelite structure), Sr_3WO_6 (Perovskite) and Sr_2WO_5 (orthorhombic). In this paper [113] investigations were made of the kinetics and mechanisms of formation of these species. The results can be represented by

$$WO_3 \xrightarrow[SrO]{873\text{-}923K} SrWO_4 \xrightarrow[SrO]{1073\text{-}1123K} Sr_2WO_5 \xrightarrow[SrO]{1223K} Sr_3WO_6$$

The general reaction

$$3LnOCl + WO_3 \longrightarrow Ln_3WO_6Cl_3$$

$$(Ln = La,Ce,Pr,Nd,Sm,Eu,Gd)$$

has been investigated and X-ray powder diffraction data for the La salt suggested trigonal prismatic WO_6 coordination for tungsten and 10 coordination for La [114]. This interesting result was subsequently confirmed by neutron powder diffraction [115]. Studies of the luminescence of $La_3WO_6Cl_3$ have also been reported (WO_4^{2-} and octahedral WO_6 are known to be efficient luminescent centres). $La_3WO_6Cl_3$ shows a weak blue emmission under UV irradiation at room temperature which is much stronger at low temperatures [116].

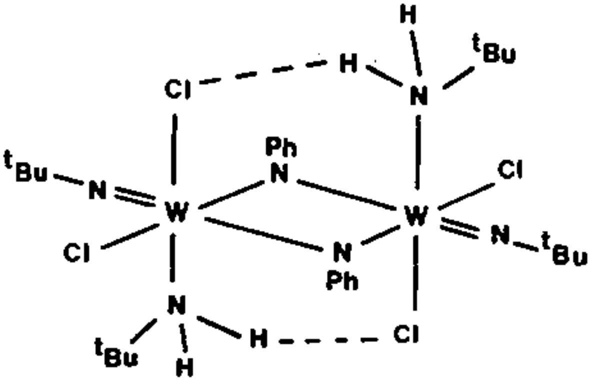
A single crystal X-ray diffraction study has been reported for UMo_2O_8 [117]. It consists of layers of oxide bridged U and Mo atoms connected by infinite interlayer U-O-U and Mo-O-Mo chains. The molybdenum atoms have highly distorted octahedral coordination with Mo-O distances in the range 1.684(7)-2.432(7)Å. $W_3Nb_{14}O_{44}$, made by the interaction of WO_3 and Nb_2O_5, has been examined by time-of-flight powder diffraction in a pulsed neutron source. The distribution of cations is different from that assigned from X-ray diffraction studies, but is consistent with site potentials calculated using an electrostatic model [118].

A number of reduced oxidation state mixed oxides have been prepared by fused salt electrolysis of the corresponding Mo(VI) compounds. The products, which were all highly crystalline, include new compounds and others, such as $M'_2Mo_3O_8$ (M' = Mg,Co,Ni,Zn), $La_5Mo_4O_{16}$, which had previously only been obtained as powders [119].

5.1.10 Complexes with nitrogen donor ligands

The Raman and resonance Raman spectra of $W(NMe_2)_6$ have been measured in solution at room temperature and in a KBr disc at 80 K. All bands moved to lower frequencies on deuteration showing that the vibrational modes associated with the $W(NC_2)_6$ framework are extensively coupled with the C-H vibrational modes - hence only a limited vibrational analysis was possible [120].

Reaction of $[W(NPh)Cl_4]$ with ${}^{t}Bu(SiMe_3)NH$ gave the dimeric $[W(N{}^{t}Bu)(NPh)Cl_2({}^{t}BuNH_2]_2$ which X-ray diffraction showed contains bridging phenylimido and terminal butylimido groups as shown in (43) [121].



(43)

Bond distances are

$W{\equiv}N = 1.729(4)\text{Å}$ $\quad$ $W\text{-}\mu N = 1.895(3),\ 2.324(3)$

$W\text{-}N = 2.223(3)$ $\quad$ $W\text{-}Cl = 2.398(1),\ 2.462(1)$

The bridges are highly asymmetrical with a long bond *trans* to the almost linear $N^{t}Bu$ groups, which suggests the bridging group π-bonds to only one metal atom. One proton of the $^{t}BuNH_2$ ligand is strongly H-bonded to the chlorine (this effect is also observable in solution by ^{1}H NMR).

As part of a wider survey of organoimido complexes [122], molybdenum complexes of *tert*-alkylimido ligands have been prepared by the reaction

$$MoO_2Cl_2 + 4RNH(SiMe_3) \longrightarrow (Me_3SiO)_2Mo(NR)_2 + 2[RNH_2(SiMe_3]Cl$$

$$(R = {}^{t}Bu,\ 1\text{-norbornyl})$$

The reaction did not proceed with WO_2Cl_2, but WCl_6 reacted smoothly with $^{t}BuNH_2$ in hexane

$$\begin{tikzcd}
WCl_6 + 10\,{}^{t}BuNH_2 \arrow[r] & ({}^{t}BuN)_2W(NH{}^{t}Bu)_2 \arrow[d, "ROH"] & + 6[{}^{t}BuNH_3]Cl \\
{[({}^{t}BuN)_2WMe_2]} & ({}^{t}BuN)_2W(OR)_2 \arrow[l, "ZnMe_2"'] &
\end{tikzcd}$$

5.2 MOLYBDENUM(V) AND TUNGSTEN(V)

5.2.1 Halides and halo complexes

The doping of polyacetylene $(CH)_n$ films with several pentafluorides, including MoF_5 and WF_5, has been investigated [123]. It seems that the resulting conductivities vary inversely with the fluoride affinity of the pentafluoride. Reaction of I_2 with MoF_6 in MeCN gives $[I(MeCN)_2][MoF_6]$ [124].

The magnetic moment of $[MoOF_5]^{2-}$ varies with HF concentration from 1.85BM in 40% acid to zero in 2% acid (similar to the corresponding chloro system). A series of salts of apparently binuclear oxofluoromolybdates have been isolated from this system which show both Mo=O and Mo-O-Mo vibrations in their IR spectra [125].

Reaction of $MoCl_5$ with $S(CN)_2$ and $Se(CN)_2$ in CS_2 solution gave the complexes $MoCl_5.X(CN)_2$ in which the ligands are coordinated by S or Se. The ompounds were characterized by their IR and EPR spectra [126]. The reactions f $OP(NCS)_3$ (=L) with halo compounds of Mo and W have been investigated. Some f the products obtained were $MoOCl_3.2L$ (from $MoCl_5$ or $MoOCl_4$ in CCl_4), $MoO(NCS)_5]^{2-}$ (from $MoCl_5$ in MeCN) whilst WCl_5 gave $[WCl_5L]_2$ at room emperature and $WOCl_3.2L$ at 60°C [127].

$K_2[MoOBr_5]$ has been isolated for the first time and the X-ray powder iffraction patterns for a number of alkali metal salts of $[MOX_5]^{2-}$ (X = Cl,Br) re reported together with a single crystal structure for $Cs_2[MoOBr_5]$. tatistical disorder in the lattice prevented accurate determination of bond engths, but they are approximately Mo=O = 1.64 and Mo-Br = 2.492(6)Å [128]. he crystal structure of $(PPh_4)[MoOBr_4]$ has been determined; the anion has the xpected square pyramidal stereochemistry with Mo=O = 1.73(1) and Mo-Br = .47(1)Å [129].

5.2.2 *Monomeric oxo complexes*

It has been found that Mo(V) EPR spectra fall into two types according to the *g*-anisotropy which apparently depends upon whether the complex is square pyramidal or octahedral. A survey of compounds with known stereochemistry confirms this relationship. Molybdenum enzymes are square pyramidal based on this criterion [130]. Complexes $MoOClL_2$ (L = β-diketonate) were prepared by the interaction of $MoCl_5$ and the diketone [131]. The complexes were investigated by EPR spectroscopy and unsymmetrical ligands were found to give a mixture of isomers. The interaction between acacH and Mo(V) salts has been investigated [132].

$$(pyH)_2[MoOX_5] + acacH \longrightarrow (pyH)[MoOX_3(acac)] \xrightarrow{heat} [MoOX_2(acac)py]$$

$$(X = Cl,Br)$$

The electrochemistry of MoOL(NCS) in dmso has been investigated (where L = *p*-X-TPP; X = OMe,Me,H,F,Cl,Br). In all cases three one-electron reversible reductions were observed, the first of which was assigned to be metal-based and the others due to reduction of TPP [133].

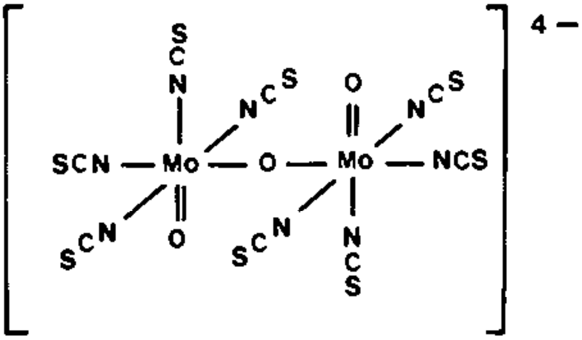
$$[OMo^{V}L(NCS)] \rightleftharpoons [OMo^{IV}L(NCS)]^{-} \rightleftharpoons [OMo^{IV}(L^{-})(NCS]^{2-} \rightleftharpoons [OMo^{IV}(L^{2-})(NCS)]^{3-}$$

MoO(TPP)Br is reduced by the superoxide ion at 25°C to give MoO(TPP). Two intermediates were observed; one is stable at low temperatures and is thought to be $[Mo^{IV}O(TPP)(O_2^{-})]^{-}$ on the basis of its diamagnetism and the stoichiometry of the reaction. Between -72°C and 0°C this complex undergoes a reversible change to the paramagnetic Mo(V) species [MoO(TPP)(O_2^{2-})]$^-$. Above 0°C the final product is [MoO(TPP)] [134].

5.2.3 μ-*oxo and* μ-*sulphido complexes*

The complex $Mo_2O_3Cl_4(dme)_2$ was prepared by refluxing $MoCl_5$ with dme in HCOOH or CH_3COOH [32]. It has a single oxo bridge with a terminal oxo group on each metal *cis* to the bridge and an oxygen of dme *trans* to the bridge. Polymer supported [$Mo_2O_3(S_2CNEt_2)_4$] has been used as a catalyst in the conversion of Me_2SO to Me_2SO_2 and of cyclohexene to cyclohexene oxide with $^{t}BuO_2H$ [135]. Reduction of W(VI) by dithionite at pH 5 in the presence of dialkyldithiocarbamates (dtc) gave [$W_2O_3(dtc)_4$] which are thought to have a single oxo bridge, analogous to the molybdenum compounds. However, at pH 2 the product is $W_2O_4(dtc)_2$ which contains square pyramidal W(V) with an apical terminal oxo group and two oxo bridges [136]. Treatment of this complex with H_2S gives the μ-oxo-μ-sulphido and di-μ-sulphido analogues. IR spectroscopy is useful to distinguish between the complexes using the bridge vibrations.

Absorption of the cation $[Mo_3O_2(O_2CMe_3)_6(H_2O)_3]^{2+}$ on a cation exchanger, followed by elution with KCNS solution and subsequent evaporation in air, led to the formation of $K_4[Mo_2O_3(NCS)_6]\cdot4H_2O$ in which the anion has the structure shown in (44).



(44)

The Mo-O-Mo bridge is linear and bond distances are

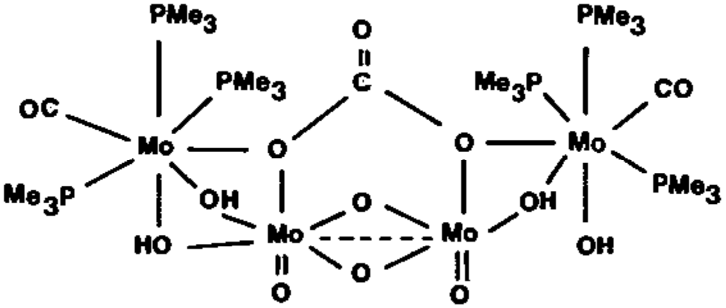
$$\text{Mo=O} = 1.661(5)\text{Å} \qquad \text{Mo-N}(\textit{trans}\text{=O}) = 2.262(6)$$
$$\text{Mo-}\mu\text{O} = 1.8490(6) \qquad \text{Mo-N}(\textit{cis}\text{=O}) = 2.10\ (\text{av})$$

The *trans* influence of the terminal oxo group is clearly evident from the bond length data [137].

The ^{95}Mo NMR spectra have been measured for a number of oxo bridged spin-paired Mo(V) complexes. The resonances fall within the narrow range of δ 434-982ppm [138]. X-ray absorption edge and EXAFS spectra have been obtained for aqueous Mo(V) solutions and the predominant species was shown to have the O=Mo(μ-O)$_2$Mo=O core with the oxo groups *cis* to the bridges. Bond distances are estimated to be Mo-Mo = 2.56, Mo=O = 1.67 and Mo-μO = 1.92Å [139].

The binuclear compound [Mo$_2$O$_4$(gly)$_2$(H$_2$O)$_2$] has been prepared and characterized [140]. It has a di-μ-oxo bridge system and chelated gly ligands. Below pH 5.5 it undergoes a proton assisted oxidation to a dimeric Mo(VI)/Mo(V) species which could not be isolated.

When an acetone/toluene solution of *cis*-[Mo(N$_2$)$_2$(PMe$_3$)$_4$] reacts with CO$_2$ at room temperature, the first product is a Mo(II) dimer described later in Section 5, but after 2-3 weeks red orange crystals of another complex separate out and these have been shown to have the most unusual tetrameric structure (45) [141]. It contains two central Mo(V) atoms and two outer Mo(II) atoms with a carbonato group bridging all four. The Mo(II) atoms are seven coordinate while the Mo(V) dimer has the characteristic Mo$_2$O$_4$ unit.



(45)

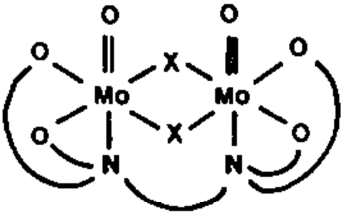
Bond distances are

Mo(V)-Mo(V) = 2.5522(9)Å Mo(II)-CO$_2$ = 2.221(3)

Mo=O = 1.672(4) Mo(V)-CO$_2$ = 2.419(4)

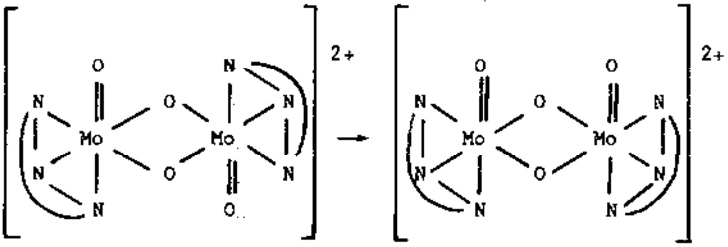
The magnetic properties and EPR spectra of [Mo$_2$O$_2$S$_2$(edta)]$^{2-}$ and [Mo$_2$O$_4$(edta)]$^{2-}$ (46) have been investigated. Each has a low magnetic moment of approx. 0.5BM indicating some interaction between the molybdenum atoms [142].

The first known binuclear Mo(V) compound with a *trans*-Mo$_2$O$_4$ unit has been isolated, although it does undergo acid catalysed isomerism to the *cis* form as shown in (47). Although in the *trans* form the Mo$_2$O$_2$ unit is planar, but



X = O or S

(46)



(47)

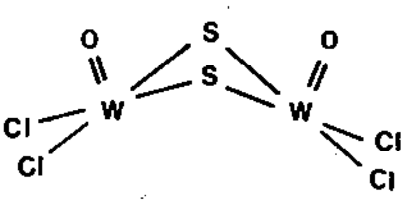
N-N-N = 1,4,7-triazacyclononane

puckered in the *cis* form, the environment of the molybdenum atoms is almost identical in the two isomers, both of which are diamagnetic [143]. Bond distances are

Mo-Mo = 2.555(1)Å   Mo=O = 1.695(3)

Mo-μO = 1.94 (av)   Mo-N = 2.219(5) - 2.341(3)

Treatment of $WOSCl_2$ with $[AsPh_4]Cl$ in dichloromethane gives $(AsPh_4)_2[Cl_2W(O)S_2W(O)Cl_2]$ which has the structure shown in (48).



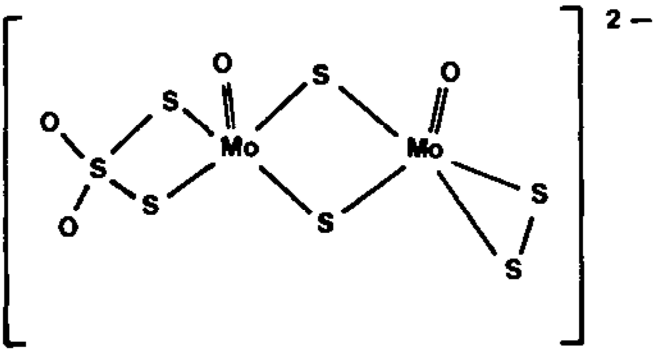
(48)

Bond distances are

$W-W = 2.844(1)Å$ $W-\mu S = 2.274(5) - 2.324(5)$
$W=O = 1.73$ (av) $W-Cl = 2.400(7) - 2.409(7)$

It is interesting that this anion is sulphur bridged as IR studies indicate that $WOSCl_2$ has terminal sulphur and bridging oxygen [144].

The previously unknown dithiosulphate ion, $S_3O_2^{2-}$, has been stabilized as a bidentate ligand by the oxidation of S_x^{2-} ligands in a metal complex [145]. Thus, the action of sulphur on $(PPh_4)_2[MoOS_3]$ in MeCN, or the action of oxygen on $(PPh_4)[MoS_4]$ in *dmf* both gave brown crystalline $(PPh_4)_2[(S_2)OMoS_2MoO(S_3O_2)]$ and the geometry of the anion is as shown in (49).

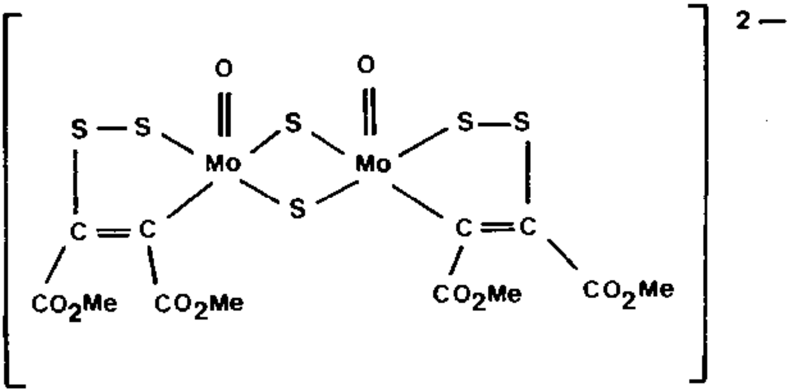


(49)

Bond distances are

$Mo=O = 1.69Å$ (av) $Mo-\mu S = 2.342(5) - 2.421(9)$
$Mo-S(S_2) = 2.377(5), 2.403(5)$ $Mo-S(S_3O_2) = 2.421(5) - 2.413(5)$
$S-S(S_2) = 2.063(7)$ $S-S(S_3O_2) = 2.021(7), 2.073(7)$
$S-O = 1.373(15), 1.429(15)$

Reaction of two equivalents of dimethylacetylenedicarboxylate (dmac) with a MeCN solution of $(NEt_4)_2[Mo_2O_2(\mu-S)_2(S_2)_2]$ at room temperature led to the isolation of $(NEt_4)_2[Mo_2O_2(\mu-S)_2(S_2)_2(dmac)_2]$, but spectroscopic evidence suggested asymmetric coordination of the acetylene fragment [146]. A crystal structure determination showed that insertion into a $Mo-(S_2)$ bond had occurred to give the complex shown in (50).



(50)

Bond distances are

Mo-Mo = 2.882(1)Å   Mo-μS = 2.33 (av)

Mo=O = 1.676(6)   Mo-S = 2.382(3)

Mo-C = 2.215(8)

Treatment of $MoO_2(S_2CNR_2)_2$ with Al_2Se_3 in refluxing xylene gave red complexes $Mo_2Se_4(S_2CNR_2)_2$ which are thought to contain two terminal and two bridging Se atoms. IR spectra gave bands assigned to Mo=Se (350cm^{-1}) and Mo-Se-Mo (245cm^{-1}) [147].

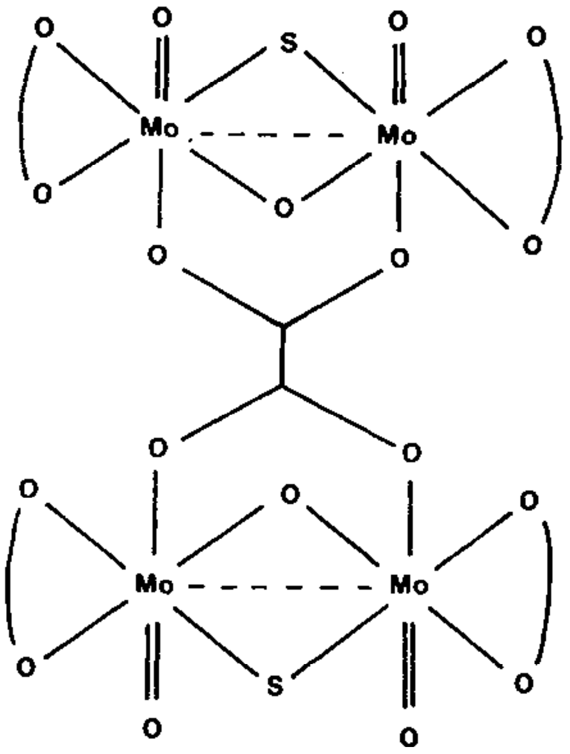
The crystal structure of the complex $K_6[\{Mo_2O_3S(ox)_2\}_2(ox)].10H_2O$ has been determined [148]. The tetrameric anion consists of two $Mo_2O_3S(ox)$ units bridged by a tetradentate ox group as shown in **(51)**. Bond distances are

Mo-Mo = 2.667(1)Å   Mo=O = 1.685(5)

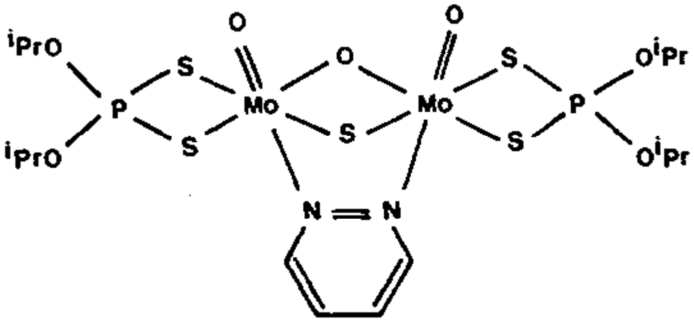
Mo-μO = 1.93 (av)   Mo-μS = 2.325(2)

Mo-O($\mu_4$ox) = 2.30 (av)   Mo-O(ox) = 2.093(4) - 2.120(4)

The structure of the 1:1 adduct between $[\{(C_3H_7O)_2PS_2\}_2Mo_2O_3S]$ (containing O,S bridging ligands) and pyramidine has been determined. The adduct retains the structure of the parent compound with only slight distortions and the pyramidine is weakly coordinated to one metal atom [149]. Similarly, reaction of pyridazine with $[\{(O^iPr)_2PS_2\}_2Mo_2O_3S]$ gave a 1:1 adduct whose structure is shown in **(52)**.



(51)



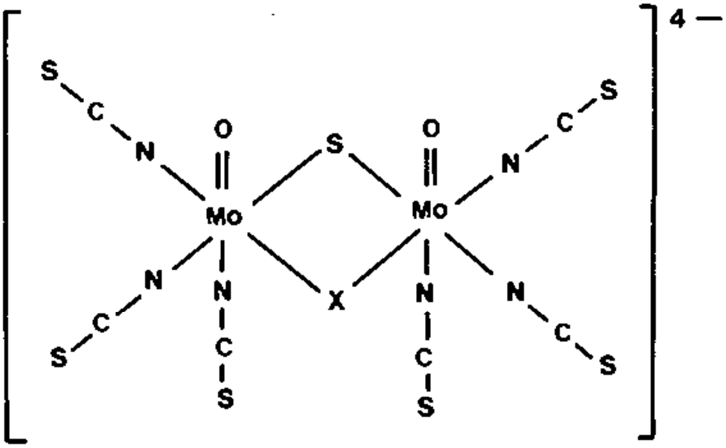
(52)

Bond distances are

Mo-Mo = 2.671(2)Å Mo-N = 2.59 (av)
Mo=O = 1.66 (av) Mo-μO = 2.16 (av)
Mo-μS = 2.32 (av) Mo-S = 2.058(6) - 2.524(7)

The structure of the 1:1 adduct with py containing a single py loosely shared between both molybdenum atoms is also described in this paper [150], but details were reported last year in a preliminary communication.

Reaction of NaCNS on $[Mo_2O_2S_2(H_2O)_6]^{2+}$ or $[Mo_2O_3S(H_2)_6]^{2+}$ in HCl, followed by addition of py gave $(pyH)_4[Mo_2O_2S_2(NCS)_6]$ and $(pyH)_4[Mo_2O_3S(NCS)_6]$ respectively [151]. The complexes are isostructural and the anions are of the form shown in (53).



X = O or S

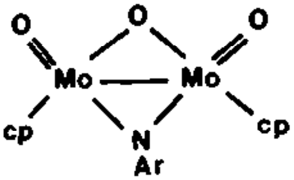
(53)

Bond distances are

	$[Mo_2O_2S_2(NCS)_6]^{4-}$	$[Mo_2O_3S(NCS)_6]^{4-}$
Mo-Mo	2.827(2)Å	2.688(2)
Mo=O	1.683(6)	1.669(6)
Mo-N(*cis*=O)	2.180(6)	2.17(2)
Mo-N(*trans*=O)	2.269(6)	2.27(2)

Reaction of $[cpMo(CO)_2]_2$ with *p*-nitrotoluene rapidly gives

$\{cpMoO\}_2O(NAr)]$ (Ar = p-C_6H_4Me) and the reaction is general for other nitro ompounds [152]. The crystal structure determination shows a molecule with a wo-fold axis of symmetry with bridging oxo and NAr groups (54).



(54)

The Mo-Mo separation is consistent with a single bond. Bond distances are

Mo-Mo = 2.6497(5)Å Mo-N = 1.958(2)
Mo=O = 1.708(2) Mo-μO = 1.933(2)

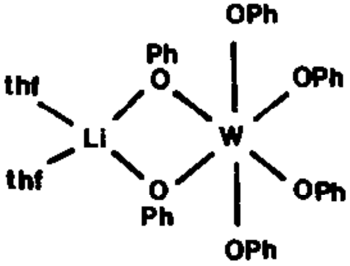
It was later shown [153] that the same reaction occurs with nitrosoarenes to give the same products.

A new molybdenum(V) phosphate $K_4[Mo_8P_{12}O_{52}]$ has been isolated and its structure determined. The anion framework consists of corner sharing PO_4 tetrahedra, P_2O_7 groups and MoO_6 octahedra, but in these the Mo(V) atom is displaced from the centre so much it can best be regarded as pyramidal. Mo-O bond distances are 1.660(2), four in the range 1.983(1) - 2.048(1) and the sixth at 2.275(1)Å [154].

Reduction of $W(OPh)_6$ by Li, Na, K in thf leads to salts of $[W(OPh)_6]^-$. The anion in the NEt_4 salt has almost perfect octahedral symmetry with a W-O distance of 1.943(5)Å, with the angle at oxygen being 139.0° (av). In contrast, the Li salt which crystallizes as $Li[W(OPh)_6]$.2thf has two *cis* phenoxide groups coordinated to lithium to give a distorted octahedral array about tungsten as shown in (55) [155]. Bond distances are

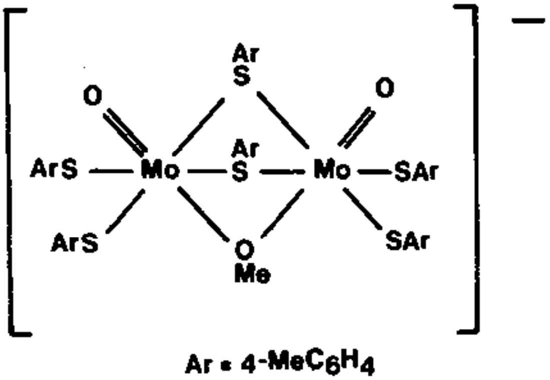
W-O = 1.918(6)Å W-μO = 2.012(6)

Reaction of $MoOCl_3(thf)_2$ with aromatic thiols HSAr (Ar = Ph, p-C_6H_4Me) and NaOMe/MeOH yields the anions $[Mo_2O_2(SAr)_6(OMe)]^-$ which were isolated as the NEt_4 salts [156]. The crystal structure of the p-C_6H_4Me salt was determined; there are three independent anions in the unit cell, although they have very similar bond lengths and bond angles, and their structure is shown in (56). The arrangement is approximately octahedral with the terminal oxo groups *trans* to



(55)

the OMe bridge. The compound is diamagnetic and its ^{95}Mo NMR chemical shift is significantly to higher frequency compared with Mo(VI) oxothiolates [156].



(56)

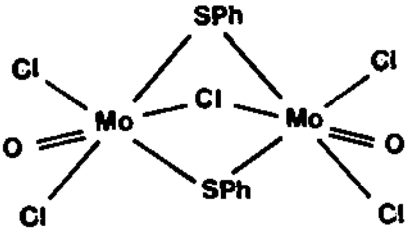
Bond distances are

Mo-Mo = 2.916(4)Å   M=O = 1.673(20)

Mo-μO = 2.11 (av)   Mo-S = 2.430(7) - 2.501(8)

Mo-μS = 2.446(8) - 2.480(7)

The stoichiometric reaction between HCl and $(NBu_4)[MoO(SPh)_4]$ gives $(NBu_4)[Mo_2O_2Cl_5(SPh)_2]$ in which the molybdenum atoms are approximately octahedrally coordinated as shown in (57) with the oxo groups *trans* to the μ-Cl [157].

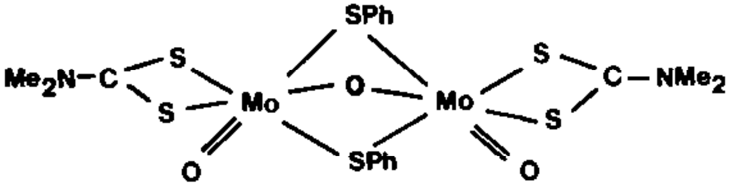


(57)

Bond distances are

Mo-Mo = 2.915(1)Å M=O = 1.66 (av)
Mo-μCl = 2.65 (av) Mo-μS = 2.45 (av)
Mo-Cl = 2.369(30 - 2.389(3)

The previously known complex [$Mo_2O_3(SPh)_2(S_2CNMe_2)_2$] (prepared by the reduction of $MoO_2(S_2CNMe_2)_2$ with PhSH in MeOH) has the structure (58) with both oxo groups *trans* to one μ-SPh group [157].



(58)

Bond distances are

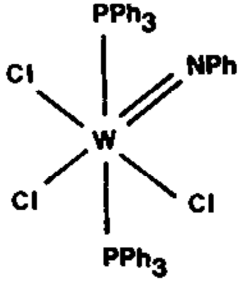
Mo-Mo = 2.649(1)Å Mo-μS(*trans* O) = 2.637(3), 2.691(3)
Mo=O = 1.683(3), 1.955(9) Mo-μS(*trans* S) = 2.493(3), 2.475(3)
Mo-S = 2.447(4) - 2.475(3)

5.2.4 Complexes with multiple metal-nitrogen bonds

$(PPh_3Me)_2[MoNCl_4]$ was prepared by reduction of $(PPh_3Me)[MoNCl_4]$ or by reaction of $MoNCl_3$ with $[PPh_3Me]I$ in dichloromethane solution [158]. The IR spectrum indicates C_{4v} symmetry and the Mo-N stretching frequency of 1050cm^{-1}

suggested a Mo-N triple bond. This was confirmed by a crystal structure determination which showed a monomeric square pyramidal stereochemistry with $Mo{\equiv}N = 1.634(6)$ and Mo-Cl bond distances in the range $2.358(1) - 2.471(1)$ Å.

Reduction of $W(NR)Cl_4$ with phosphine in boiling benzene gives paramagnetic $W(NR)Cl_3L_2$ ($L = PPh_3, PMe_2Ph$, L_2 = dppe) which are the first alkylimido complexes of W(V) [14]. A crystal structure detrmination of the PPh_3 compound showed it to have octahedral stereochemistry with *mer* chlorines as in (59).



(59)

Bond distances are

$W{=}N \equiv 1.742(8)$ Å $\quad$ W-Cl(*trans* N) = 2.443(3)

$W{-}P = 2.590(3)$ $\quad$ W-Cl(*cis* N) = 2.38 (av)

indicating a slight *trans* effect for the NPh group.

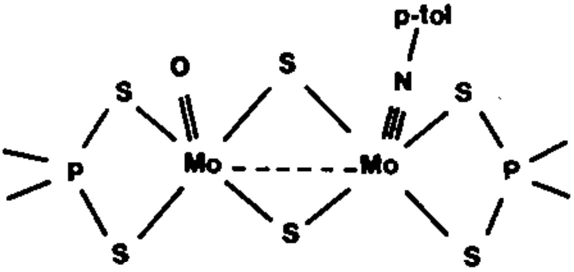
The acid assisted hydrolysis of $[Mo(NR)(\mu_3\text{-}S)(S_2P\{OR'\}_2)]_4$ (which contains a cubane like Mo_4S_4 core) proceeds through an intermediate $[Mo_2O(NR)(\mu\text{-}S)_2(S_2P\{OR'\}_2)_2]_n$ (n = 1 or 2) and finally to $[MoO(\mu\text{-}S)(S_2P\{OR'\}_2)_2]$. The kinetics of the reaction have been followed using ^{31}P NMR and the structure of the binuclear and tetranuclear intermediates have been determined (although for different R and R' groups) [159]. The binuclear complex $[Mo_2O(N\text{-}p\text{-}tol)(\mu\text{-}S)_2(S_2P\{OMe\}_2)_2]$ has the structure shown in (60). It is best described as two square pyramids joined at one edge. Bond distances are

Mo-Mo = 2.812(1) Å $\quad$ $Mo{-}\mu S = 2.309(3) - 2.327(3)$

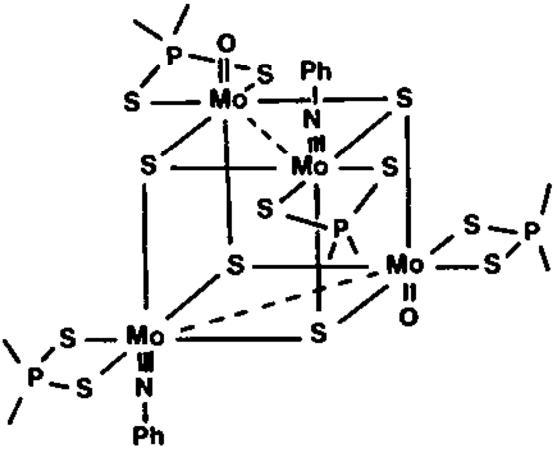
$Mo{=}O = 1.675(7)$ $\quad$ $Mo{-}S = 2.490(3) - 2.527(3)$

$Mo{\equiv}N = 1.724(9)$

The tetranuclear complex $[Mo_2(NPh)(\mu_3\text{-}S)_2(S_2P\{OEt\}_2)_2]_2$ has the structure shown in (61).



(60)



(61)

Bond distances are

Mo-Mo = 2.843(1)

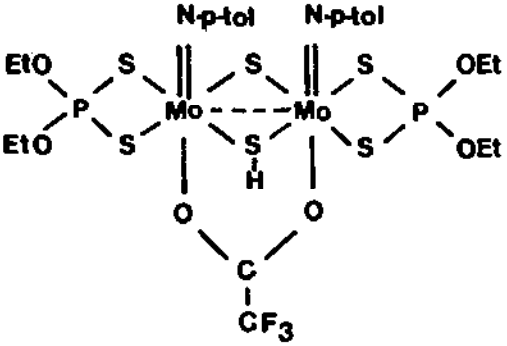
Mo=O = 1.671(6), 1.697(7)

Mo≡N = 1.695(7), 1.727(8)

Mo-μS = 2.351(3) - 2.898(3)

Mo-S = 2.523(3) - 2.545(3)

In the dinuclear form, the Mo-μS bonds are shorter than the Mo-S(dtp) bonds, but in the tetranuclear complex this is reversed [159]. Addition of CF_3COOH to solutions of $[Mo(N\text{-}p\text{-}tol)(\mu\text{-}S)(S_2P\{OEt\}_2)]_4$ in dichloromethane leads to the formation of a complex with the structure shown in (62).



(62)

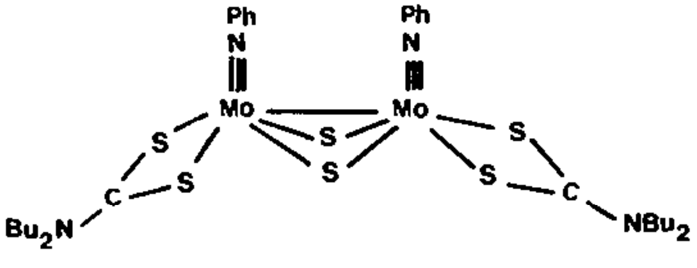
Bond distances are

$$\text{Mo-Mo} = 2.839(2) \qquad \text{Mo-}\mu\text{S} = 2.342(5),\ 2.354(5)$$

$$\text{Mo-O} = 2.26(1) \qquad \text{Mo-}\mu\text{SH} = 2.44(5)$$

$$\text{Mo}\equiv\text{N} = 1.74(1)$$

In solution two conformers were detected by ^{1}H NMR at low temperature which are thought to be due to different orientations of the S-H bond. Other carboxylic acids also induce protonation of the bridging sulphur to varying degrees in the order $CF_3COOH \simeq CCl_3COOH > CHCl_2COOH > CH_2ClCOOH \gg CH_3COOH$, for which no reaction could be detected. This order is the same as the aqueous acidities of the acids [160]. Reaction of $[Mo(N\text{-}p\text{-tol})(\mu\text{-}S)(S_2P\{OEt\}_2)]_4$ with $(S_2CN^{i}Bu_2)^-$ produced either yellow or red crystals (of the same constitution) depending upon the crystallization conditions [161]. Solutions of the different crystals gave identical ^{1}H NMR spectra suggesting that a facile equilibrium occurs in solution. The crystal structures of both forms were determined; the yellow complex contained square pyramidal Mo(V) as shown in (63).



(63)

Bond distances are

$$\text{Mo-Mo} = 2.807(2)\text{Å} \qquad \text{Mo-}\mu\text{S} = 2.321(3) - 2.345(3)$$
$$\text{Mo}\equiv\text{N} = 1.720(8) \qquad \text{Mo-S} = 2.471(3) - 2.499(3)$$

The red crystals have a structure very similar to (61) except that each molybdenum carries a (N-*p*-tolyl) group. Bond distances are Mo-Mo = 2.881(3), Mo-S = 2.52 (av), Mo-μS(*trans* NAr) = 2.69 (av) and Mo-μS = 2.38(2)Å. It would appear that the dimer ⇌ tetramer equilibrium in solution occurs through the making and breaking of the long bond *trans* to the N-*p*-tolyl groups.

5.2.6 Complexes with metal-carbon bonds

$(NBu_4)_3[W(CN)_8]$ has been found to undergo phase changes at 273-283 K and 333-343 K. Evidence for the changes comes from IR and X-ray powder diffraction measurements [162]. The catalytic oxidation of Fe^{2+} by $[Mo(CN)_8]^{3-}$ and the catalytic reduction of Fe^{3+} by $[Mo(CN)_8]^{4-}$ were investigated at a pyrolytic graphite rotating disc electrode [163]. The rate constants for the redox cross reaction

$$\text{Fe(II)} + \text{Mo(V)} \rightleftharpoons \text{Fe(III)} + \text{Mo(IV)}$$

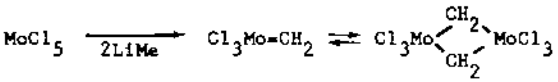
were determined to be $(7.0\pm0.5) \times 10^6$ (forward) and $(6.6\pm0.5) \times 10^6 \text{cm}^3\text{mol}^{-1}\text{s}^{-1}$.

Some preliminary results on the alkylation of $[WLCl_4]_2$ ($L = \eta^5\text{-}C_5Me_4{}^tBu$) and subsequent hydrogenation have been reported [164] and are summarized in the scheme

$$[WLCl_4]_2 \xrightarrow[ZnMe_2]{} WLMe_2Cl_2 \xrightarrow[LiMe]{} WLMe_4 \xrightarrow[H_2]{} [WLH_4]_2 + [WLH_3]_3$$

Field desorption mass spectrometry confirms the formulation of the complexes, but the structures of the hydrides are still unknown. At room temperature all protons in each compound are equivalent and the low temperature limiting spectra have not yet been obtained.

Mo(V) chloro species appear to react with LiMe in thf at -70°C to give carbene complexes [165].

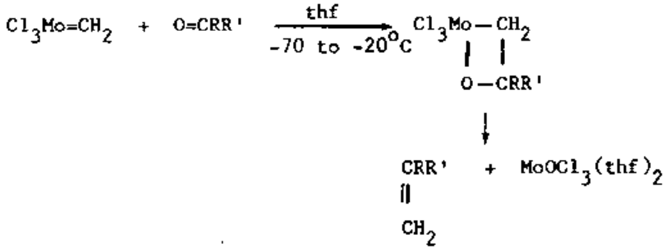


$$MoCl_5 \xrightarrow[2LiMe]{} Cl_3Mo{=}CH_2 \rightleftharpoons Cl_3Mo(\mu\text{-}CH_2)_2MoCl_3$$

$$MoOCl_3(thf)_2 \xrightarrow[LiMe]{} Cl(O)Mo{=}CH_2$$

$$(OEt)_3MoCl_2 \xrightarrow{LiMe} (OEt)_3Mo{=}CH_2$$

These compounds are all carbonyl olefination reagents



5.3 MOLYBDENUM(IV) AND TUNGSTEN(IV)

5.3.1 Halides and halo complexes

Reaction of MoH_4L_4 (L =$PMePh_2$) with HBF_4 in thf gives $[(H_2L_3Mo)_2F_3]BF_4$. A crystal structure determination revealed the unusual arrangement of three bridging fluoro atoms (derived from BF_4^-). Only one hydride per metal was revealed directly by the crystallographic analysis, but the presence of the second hydride was confirmed by IR and NMR studies. The ligands adopt a dodecahedral arrangement about the metal centres [166].

The reaction

$$WCl_6 + WO_2 \longrightarrow WCl_4 + WOCl_4$$

proceeds in a sealed tube at 250-300°C. The thermal decomposition of WCl_4 involves dissociation and redox reactions to give WCl_2, WCl_3 and WCl_5 [167]. $MoCl_5$ or $(NEt_4)[MoCl_6]$ dissolved in either of the room temperature ionic liquids $AlCl_3$/N-*n*-butylpyridinium chloride or $AlCl_3$/1-methyl-3-ethylimidazolium chloride gave $[MoCl_6]^{2-}$ in solution as a stable entity, which was identified by its UV-visible spectrum. A reversible one-electron reduction was observed and controlled potential electrolysis gave a solution containing $[MoCl_6]^{3-}$ [168].

Reduction of WCl_4 by Na/Hg in thf in the presence of $(Ph_3PNPPh_3)Cl$ gave $(Ph_3PNPPh_3)_2[W_2Cl_9]$ in which the metals have an average oxidation state of 3.5. A crystal structure determination showed a biconfacial octahedral anion similar in structure to the well known $[W_2Cl_9]^{3-}$, but in this case the W-W bond length of 2.540(1)Å is 0.122(9)Å longer. This is attributed to a poorer σ-bond because of contracted *d* orbitals due to the increased charge. Bond distances are W-Cl = 2.36 (av) and W-μCl = 2.45Å (av) [169]. Reaction of $WCl_4(SMe_2)_2$ with $SiMe_3(SPh)$ gives $[(Me_2S)Cl_2W(\mu\text{-}Cl)(\mu\text{-}SPh)_2WCl_2(SMe_2)]$ which when reacted with

$(AsPh_4)Cl$ led to the isolation of $(AsPh_4)_2[Cl_3W(\mu\text{-}Cl)(\mu\text{-}SPh)_2WCl_3]$; the anion has a similar structure to $[W_2Cl_9]^{2-}$ described above. The tungsten atoms are in equivalent positions imposed by a crystallographic two-fold axis. The W-W distance of 2.519(2)Å is interpreted as indicating a bond order of 2.5. Other bond distances are W-Cl = 2.39, W-μCl = 2.44 and W-μS = 2.43Å (av) [170].

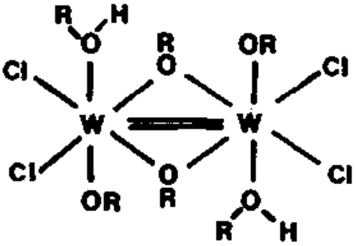
Excess PPh_3 reacts with WCl_4Y (Y = O,S,Se) to give $WCl_4(PPh_3)_2$ which has a centrosymmetric structure with W-Cl = 2.320(5), 2.344(6) and W-P = 2.629(6)Å. The rather long W-P bond distance is attributed to steric interactions [171]. Similarly, reduction of WCl_6 with PMe_3 in toluene at 120°C in a sealed tube gives $WCl_4(PMe_3)_2$ or $WCl_4(PMe_3)_3$ which are easily interconverted by addition of PMe_3 or by heating a solution to drive off excess PMe_3. Both complexes react with water (wet acetone) to give $WOCl_2(PMe_3)_3$ and this is a general reaction. The halide may be replaced by X = NCO, NCS to give $WOX_2(PMe_3)_3$ and the structures of these complexes in solution were determined by IR and NMR studies [172]. In a separate paper the crystal structure of $WOCl_2(PMe_3)_3$ has been reported [173] and it has the *mer-cis* configuration with W-P = 2.473(3) - 2.517(4); W-Cl = 2.479(6) and W=O = 1.67(1)Å. $WCl_4(PMe_3)_3$ reacts with Na/Hg in the presence of PMe_3 in thf under H_2 to give $WH_2Cl_2(PMe_3)_3$, whilst the reaction of $WCl_2(PMe_3)_4$ with MeOH in thf gave a mixture of $WH_2Cl_2(PMe_3)_4$ and $WOCl_2(PMe_3)_3$ [173].

The electronic and vibrational spectra of the complex $[\{Cl(PMe_2Ph)_4ReN_2\}_2MoCl_4]$ have been recorded. The complex, which has previously been shown to contain a linear Cl-Re-N-N-Mo-N-N-Re-Cl backbone, shows resonance enhancement of bands at 1818 (ν_1 $(a_{1g})\nu_{NN}$); 689 ($\nu_2(a_{1g})\nu_{M\text{-}N}$) and 290cm^{-1} ($\nu_5(a_{1g})\nu_{Re\text{-}Cl}$). An MO scheme is proposed which is consistent with the spectra and the observed bond lengths [174].

The alcohol/alkoxide exchange between $[W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(EtOH)_2]$ and R'OH has been studied. When R' is a primary alkyl group complete exchange occurs to give $[W_2Cl_4(\mu\text{-}OR')_2(OR')_2(R'OH)_2]$ as evidenced by both ^{1}H NMR in solution and crystallographic studies in the solid state. However, when R' is a secondary alkyl group incomplete exchange occurs with retention of the μ-OEt groups, although $[W_2Cl_4(\mu\text{-}O^iPr)_2(O^iPr)_2(^iPrOH)_2]$ can be prepared by the alternative reaction of WCl_4 and ^{i}PrOH [175]. Three complexes were studied by crystallographic methods and they all have the general structure (64).

5.3.2 Complexes with oxygen donor ligands

The cation $[Mo_3O_2(O_2CMe)_6(H_2O)_3]^{2+}$ has been made by the reaction between $Mo_2(O_2CMe)_4$ and $Na_2MoO_4.2H_2O$ (1:2) and isolated as the $(CF_3SO_3)^-$ salt [176]. The cation has previously been structurally characterized and the salt isolated here is isostructural with the tungsten analogue. These well known triangular



(64)

Bond distances are (only bridging groups and alcohol/alkoxide specified)

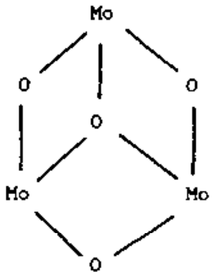
	(μ-OEt)(O^{i}Pr)	(μ-O^{i}Pr)(O^{i}Pr)	(μ-OEt)(OC$_5$H$_{11}$)
W-W	2.488(1)Å	2.514(1)	2.489(1)
W-Cl	2.395(3)	2.398(13)	2.384(3)
Wμ-O	2.023(8)	2.022(7)	2.027(6)
W-OR	1.987(6)	1.967(7), 1.999(7)	1.983(4), 2.010(4)

bi-oxo-capped molybdenum acetate clusters have also been prepared by reducing Na_2MoO_4 in acetic anhydride with Zn dust or $W(CO)_6$. The initial product is $Na[Mo_3O_2(O_2CMe)_9]$ which is presumed to have three monodentate acetate groups in the equatorial positions. This compound is catalytically hydrolyzed in acid solution to give the aquo compound. However, hydrolysis in neutral water is slow and the intermediate $[Mo_3O_2(O_2CMe)_6(H_2O)(OH)_2].16H_2O$ was isolated and characterized by X-ray diffraction. It has the usual type structure with the metal triangle slightly distorted because of the differing ligands [177]. Bond distances are Mo-Mo = 2.773(1), 2.796(1); Mo-μ_3O = 1.989(5) - 2.112(5); Mo-μO = 2.104(6) - 2.125(5); Mo-OH = 1.979(7); Mo-OH,H_2O = 2.049(5)Å.

Molybdenum EXAFS spectra show that aqueous Mo(IV) is predominantly trinuclear with the core (65) [139]. Bond distances are

Mo-Mo = 2.49Å
Mo-μ_2O = 1.88   Mo-μ_3O = 2.04

The ^{95}Mo NMR spectra of a series of Mo(IV) species all containing the same Mo_3O_4 core have been reported [138]. The resonances fall in the narrow range δ 990 - 1162ppm, including the Mo(IV) aquo ion which is formulated as in (65). The crystal structure of $[Mo_3O_4\{(O_2CCH_2)_2NMe\}_3]^{2-}$ was determined and is as shown in (66).



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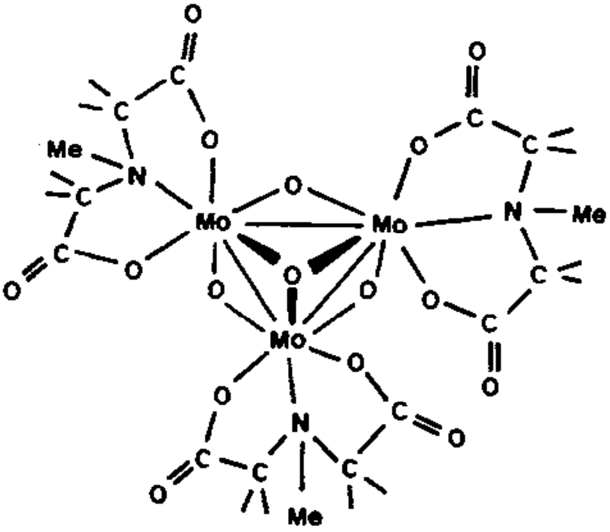


(66)

Bond distances are

$$\text{Mo-Mo} = 2.484(1),\ \ 2.520(1)\text{Å}$$
$$\text{Mo-}\mu_3\text{O} = 2.024(4) - 2.073(4)$$
$$\text{Mo-}\mu_2\text{O} = 1.900(4) - 1.924(4)$$
$$\text{Mo-O} = 2.081(4) - 2.114(4)$$
$$\text{Mo-N} = 2.227(4) - 2.238(5)$$

The electrochemical reductions of $[Mo_3O_4(H_2O)_9]^{4+}$ and $Mo_3O_4(ox)_3(H_2O)_3]^{2-}$ have been examined [178]. The oxalate derivative gives two reversible waves of two electrons and one electron, but the aquo complex gives a single three-electron reduction. The reductions are thought to be accompanied by protonation of the bridging and capping oxo groups. The new trinuclear Mo(III) species produced by controlled potential electrolysis are stable and give characteristic EPR spectra, but the intermediate $Mo^{III}{}_2Mo^{IV}$ species are diamagnetic [178].

The compounds MoL_3Cl (where L = anion of picolinic acid or 8-quinolinol derivative) have been prepared by prolonged reaction between MoO_2Cl_2 and HL. Their magnetic moments are slightly below the spin-only value for two unpaired electrons [179].

Reaction between $MoCl_2(TTP)$ and N-phenylhydroxylamine in toluene/pyridine gave $[MoCl(TTP)]_2O$. The angle at the bridging oxygen is 177.5(3)° and the molybdenum atoms are displaced 0.08Å from the N_4 plane towards oxygen. Bond distances are Mo-μO = 1.851(6); Mo-N = 2.080(6); Mo-Cl = 2.407(3)Å. The compound obeys the Curie Law between 4.2 and 293 K (μ = 2.82BM per Mo) with no magnetic interaction between the metal centres [180].

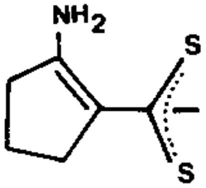
5.3.3 Chalcogenides and complexes with sulphur donor ligands

A review has appeared which surveys the preparation, properties, structures and uses of molybdenum dichalcogenides [181]. The heat of formation of WSe_2 from the elements has been determined calorimetrically as $-154.2\pm2 KJmol^{-1}$ [182]. The Helium-I UV-photoelectron spectrum of $Mo(S^tBu)_4$ has been reported. It exhibits a low ionization potential band (IP = 6.43ev) which corresponds to ionization of mainly Mo $4d_{z^2}$ electrons [183].

IR, UV-visible and ^{13}C NMR data all suggest that substantial back π-bonding occurs in 8-coordinate $Mo(S-S)_4$ type complexes when S-S is a dithiobenzoic acid, but dithiocarbamates do not show evidence of this effect [184]. MO calculations at the CNDO/INDO level have been performed for a series of $[Mo(S-S)_4]^+/Mo(S-S)_4$ complexes (where S-S is a bidentate uni-negative sulphur ligand) of idealized dodecahedral geometry [185]. It emerges that the HOMO in Mo(IV) in this symmetry is metal based with over 90% d_{xy} character. Good correlations with electrochemical, EPR and X-ray photoelectron binding energies are obtained. The reaction between $MoCl_5$ and pyrroledithiocarbamate (dtc) led, rather surprisingly, to $Mo(dtc)_4$ rather than a complex containing the Mo_2O_3 core which occurs for dialkyldithiocarbamates. A crystal structure determination revealed a dodecahedral arrangement with average Mo-S distances of 2.51 and 2.54Å [186].

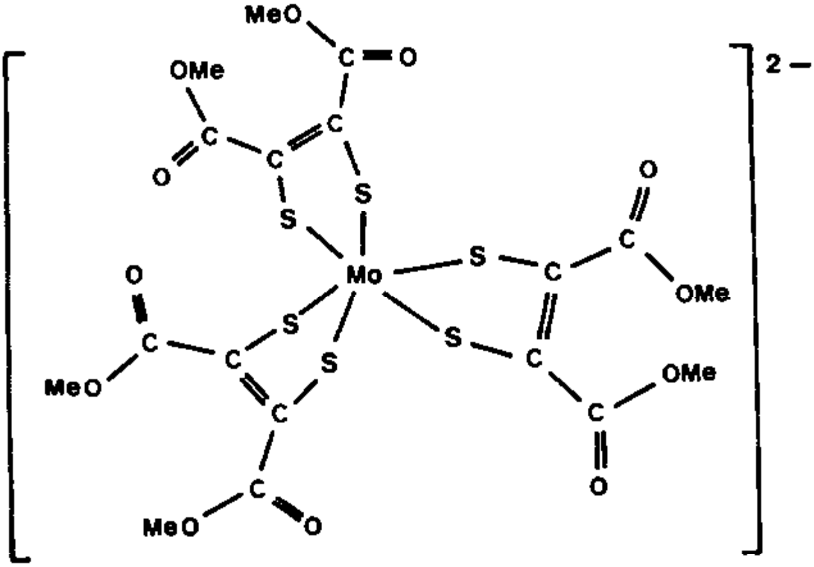
The ligand 2-amino-1-cyclopentenedithiocarboxylate (L) (87) could potentially coordinate through *SS* or *NS*. The product MoL_4, obtained by the reaction of $MoCl_4py_2$ and L, has a UV-visible spectrum similar to those of other complexes with the MoS_8 chromophore [187].

Reaction of dmac with solutions of the $[(S_4)_2MoS]^{2-}$ anion leads to the isolation of $(PPh_4)_2[Mo\{S_2C_2(COOMe)_2\}_3].dmf.C_6H_6$. The structure of the anion reveals that the dmac adds across the S-S bond (rather than insertion into the



(67)

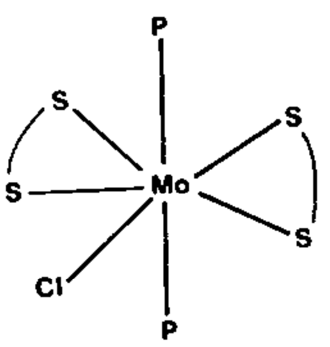
Mo-S bond as occurs for Mo(V), structure (50). The stereochemistry about the molybdenum is almost perfect trigonal prismatic (68) with Mo-S distances in the range 2.385(6) - 2.399(5)Å.



(68)

The complex undergoes two reversible one-electron oxidations at low potentials which suggests that the oxidation products may be readily isolated [188].

Reaction of $MoOX_2(S_2CNR_2)_2$ (X = Cl,Br; R = Me,Et) with two equivalents of PMe_2Ph in refluxing thf gives $[MoX_2(S_2CNR_2)_2(PMe_2Ph)]$. However, the reactions of phosphines P (P = PMe_2Ph,$PMePh_2$,½ dppe) with $MoOX_2(S_2CNR_2)_2$ in MeOH gave $[MoX(S_2CNR_2)_2P_2]X$. The derivatives of the monodentate phosphines were orange and that of dppe was olive green. Crystal structure determinations showed that both cations have pentagonal bipyramidal stereochemistry, but the distribution of ligands is different with the monodentate phosphines axial and dppe spanning axial and equatorial positions as shown in (69) and (70) [189].



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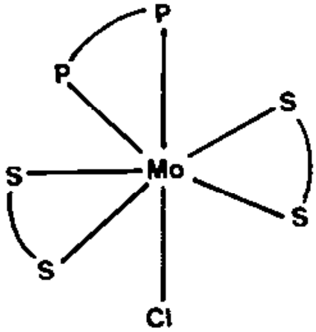


(70)

Bond distances are

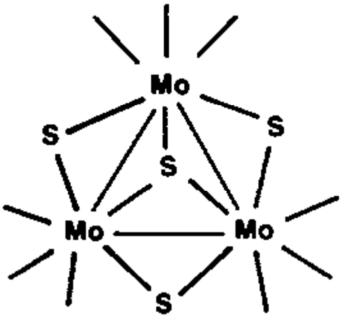
	$[MoCl(S_2CNEt_2)_2(PMePh_2)_2]^+$	$[MoCl(S_2CNEt_2)_2dppe]^+$
Mo-P(axial)	2.584(9), 2.608(9)Å	2.564(2)
Mo-P(equatorial)		2.604(2)
Mo-Cl	2.431(9)	2.404(2)
Mo-S	2.477(9) - 2.496(8)	2.482(9) - 2.492(2)

Chemical and electrochemical reduction of $[MoCl(S_2CNEt_2)_2dppe]^+$ under CO gives $[Mo(CO)_2(S_2CNEt_2)_2dppe]$, but under N_2/Ar dimeric $[Mo(S_2CNEt_2)_2dppe]_2$ is formed [189].

Reaction of $WCl_4(SMe_2)_2$ and $SiMe_3(SEt)$ in CH_2Cl_2 gives $[(Me_2S)Cl_2W(\mu\text{-}S)(\mu\text{-}SEt)_2WCl_2(SMe_2)]$ which has been shown to have a biconfacial octahedral structure with the terminal thiolates *trans* to a thiolate bridge. Reaction with 2 moles of $(PPh_4)Cl$ gave $[Cl_3W(\mu\text{-}S)(\mu\text{-}SEt)_2WCl_3]^{2-}$ which has a very similar structure [190]. Bond distances are

	$[(SMe_2)_2W_2Cl_4(\mu\text{-}S)(\mu\text{-}SEt)_2]$	$[W_2Cl_6(\mu\text{-}S)(\mu\text{-}SEt)_2]^{2-}$
W-W	2.526(2)Å	2.522(1)
W-Cl	2.355(8)	2.427(6)
W-μS	2.311(6)	2.308(5)
W-μSEt	2.403(7) - 2.477(7)	2.417(7)
$W\text{-}SMe_2$	2.59 (av)	

The crystal structure of $K_5[Mo_3S_4(CN)_9].7H_2O$ has been determined [191] and is shown in (71).



(71)

Bond distances are

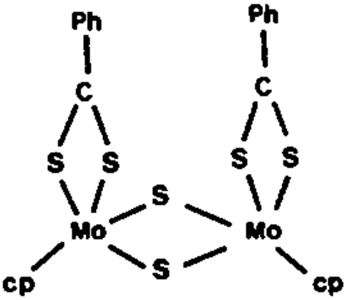
Mo-Mo = 2.765(7)Å

Mo-μ_2S = 2.312(5)   Mo-C(*trans* μ_2S) = 2.194(17)

Mo-μ_3S = 2.363(4)   Mo-C(*trans* μ_3S) = 2.159(13)

The Mo-Mo bond distance is significantly longer than that in the analogous Mo_3O_4 core (2.50Å). On the cyclic voltammetric time scale a pseudo reversible one-electron oxidation is observed, but on the longer coulometric time scale the products of oxidation are monomeric Mo(V) species [191].

Reaction of $[cpMo(CO)_3]_2$ and $Zn(S_3CPh)_2$ leads to the formation of monomeric $[cpMo(CO)_2(S_2CPh)]$ and a new type of diamagnetic Mo(IV) dimer, $[cpMo(S)(S_2CPh)]_2$, which has the structure shown in (72) [192]. The phenyl rings are almost parallel and the Mo_2S_2 unit is non-planar.

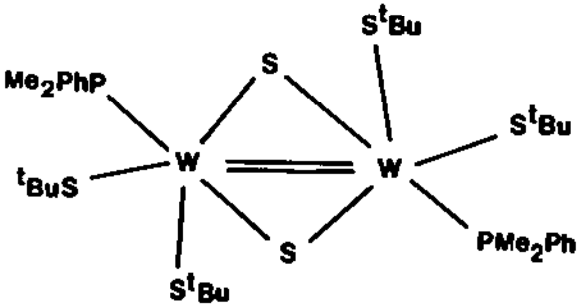


(72)

Bond distances are

Mo...Mo = 3.073(1)Å
Mo-μS = 2.319(2), 2.331(2)
Mo-S = 2.489(2), 2.530(2)

The reaction between *cis*-[$W(N_2)_2(PMe_2Ph)_4$] and ^tBuSH gives the diamagnetic binuclear complex [{$W(^tBuS)_2(PMe_2Ph)$}$_2(\mu\text{-}S)_2$] in which each tungsten has trigonal bipyramidal stereochemistry as shown in (73) [81].



(73)

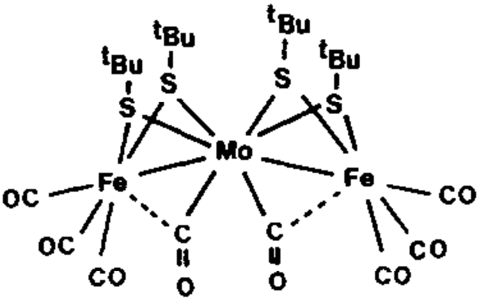
Bond distances are

W-W = 2.736(2)Å
W-P = 2.571(7)
W-S = 2.32 (av)
W-μS(*trans* P) = 2.345(7)
W-μS = 2.254(6)

$Mo(^tBuS)_4$ reacts with $Fe_2(CO)_9$ in toluene to give $MoFe_2(^tBuS)_4(CO)_8$ as the main product [193]. A crystal structure determination showed that two carbonyls had been transferred to the molybdenum which has an irregular stereochemistry best described as distorted trigonal prismatic (74). The angle Fe-Mo-Fe is 160.43(3)° and bond distances are

Mo-Fe = 2.756(11) (av)
Mo-S = 2.441(1) - 2.537(1)Å

The ^1H NMR spectrum shows two ^tBuS signals at room temperature which coalesce at higher temperatures.



(74)

5.3.4 *Complexes with multiple metal-nitrogen bonds*

$[Mo(N)(N_3)(dppe)_2]$ is octahedral with the nitride and a highly unusual linear azide (which suggests strong π-bonding with this ligand) *trans* to each other. Bond distances are Mo≡N = 1.79(2) (rather long), $Mo\text{-}N_3$ = 2.20(2) and Mo-P = 2.50Å (av). $[Mo(NH)Br(dppe)_2]$ is also octahedral with the monodentate ligands *trans*; Mo≡N = 1.73(2), Mo-Br = 2.612(4), Mo-P = 2.53Å (av) [194].

By reduction of $MoO_2(S_2CNR_2)_2$ with alkyldithiocarbazates, $NH_2.NHC(S)SR'$, the mixed ligand complex $[Mo(N_2C\{S\}SR')(NH_2NC\{S\}SR')(S_2CNR_2)_2]$ was isolated and X-ray diffraction revealed a pentagonal bipyramid with a chelated (*N,S*) hydrazido(1-) and one dithiocarbamate in the equatorial plane and the other spanning axial and equatorial positions as shown in (75)[195]. The hydrazido (2-) ligand is almost linear. Bond distances are

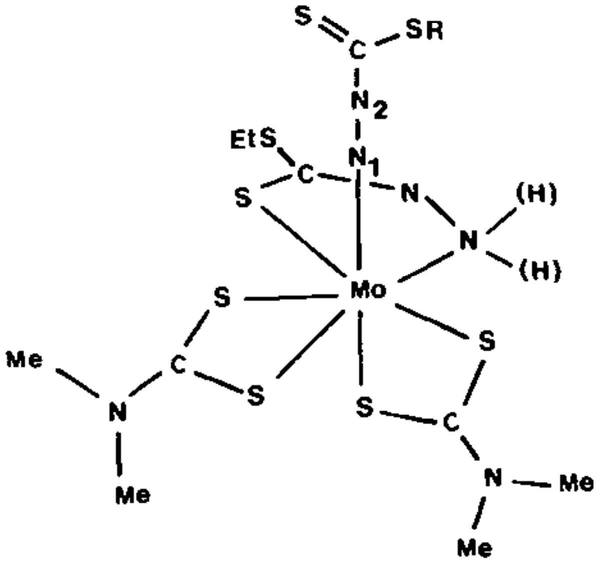
$$
\begin{array}{ll}
Mo\text{-}N_1 = 1.77(1)\text{Å} & Mo\text{-}S(eq) = 2.464(4) - 2.526(4) \\
Mo\text{-}NH_2 = 2.250(8) & Mo\text{-}S(ax) = 2.562(4) \\
N_1\text{-}N_2 = 1.21(1) &
\end{array}
$$

The kinetics of the reactions

$$trans\text{-}[W(NH)X(dppe)2]^+ \xrightarrow[NEt_3 \text{ or } LiOMe]{MeOH} trans\text{-}[W(NH)(OMe)(dppe)_2]^+$$

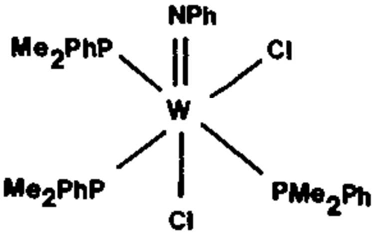
have been investigated. Both reactions are thought to proceed via initial deprotonation to yield *trans*-$[WN(X)(dppe)_2]$ followed by loss of halogen. Rate limiting attack by OMe^- gives $[WN(OMe)(dppe)_2]$ which rapidly extracts a proton from the solvent to yield the observed product [196].

Reduction of $W(NR)Cl_4$ with Na/Hg in the presence of L (L = PMe_2Ph, PMe_3,



(75)

CNBu; R = Et,Ph) gives diamagnetic $W(NR)Cl_2L_3$. A crystal structure determination for $[W(NPh)Cl_2(PMe_2Ph)_3]$ showed an octahedral stereochemistry with the phosphines *mer* as shown in (76) [14].



(76)

Bond distances are

W=N = 1.755(3)Å

W-Cl(*trans* N) = 2.501(1)

W-Cl(*trans* P) = 2.491(1)

W-P(*trans* Cl) = 2.453(1)

W-P(*trans* P) = 2.483(1), 2.497(1)

5.3.5 *Complexes with metal-carbon bonds*

It has been shown that photolysis of an aqueous solution of $K_4[Mo(CN)_8]$ in the presence of oxygen gives the known mixed oxidation state complex $K_6[Mo^{IV}{}_2Mo^{VI}(CN)_8O_6].2H_2O$ [197]. The kinetics of the rapid reaction between $[Mo(CN)_8]^{4-}$ and $VO_2{}^+$ have been studied spectrophotometrically by stopped flow techniques in acidic perchlorate medium. The overall reaction is

$$[Mo(CN)_8]^{4-} + VO_2{}^+ + 2H^+ \longrightarrow [Mo(CN)_8]^{3-} + VO^{2+} + H_2O$$

which proceeds by two reaction pathways [198].

Reduction of $Na_2[MoO_4]$ with CN^- solution gave $[MoO(CN)_5]^{3-}$ which was isolated as blue or green salts. The structure of $(PPh_4)_3[MoO(CN)_5]$ was shown to be octahedral with bond distances Mo=O = 1.705(4), Mo-C(*trans* O) = 2.373(6), Mo-C(*cis* O) = 2.161(8) - 2.190(5)Å. Also isolated were salts of *trans*-$[MoO(H_2O)(CN)_4]^{2-}$ which are blue or green depending on the cation. Two crystal structures were determined and although the anion had basically the same structure in each salt, there were marked differences in bond lengths and the salts are considered to be distortional isomers. Bond distances are

	yellow green	blue
	$(PPh_4)_2[MoO(H_2O)(CN)_4]$	$(AsPh_4)_2[MoO(H_2O)(CN)_4]$
Mo=O	1.72(2)Å	1.60(2)
$Mo-H_2O$	2.96(6)	2.48(3)
Mo-C	2.08(3) - 2.19(5)	2.14(3) - 2.23(3)
$\nu_{Mo=O}$	920cm^{-1}	980cm^{-1}

The complex $K_6[\{Mo(CN)_6\}_2S].4H_2O$ has been prepared and a crystal structure determination revealed pentagonal stereochemistry about each molybdenum with the bridging sulphur in the axial position. The molecular geometry is D_{5d} (staggered) whereas D_{5h} (eclipsed) has been observed previously for a different salt of this anion. The entire axial N≡C-Mo-S-Mo-C≡N unit is linear with very short Mo-S distances (2.1716(2)Å). Other bond distances are Mo-C(axial) = 2.200(3), Mo-C(equatorial) = 2.165 Å (av) [200]. The electrochemical properties of this complex have been investigated [201]. In dmso it shows a quasi-reversible two-electron reduction, but in water it undergoes an irreversible two-electron reduction, apparently producing monomeric Mo(III) species. A quasi-reversible two-electron oxidation is observed in both solvents (two distinguishable steps in water) but the oxidation products are not stable on the coulometric time scale.

The compounds cp_2MX_2 (X = halogen) all show quasi-reversible oxidations in MeCN solution together with another peak due to the solvolysis product of the

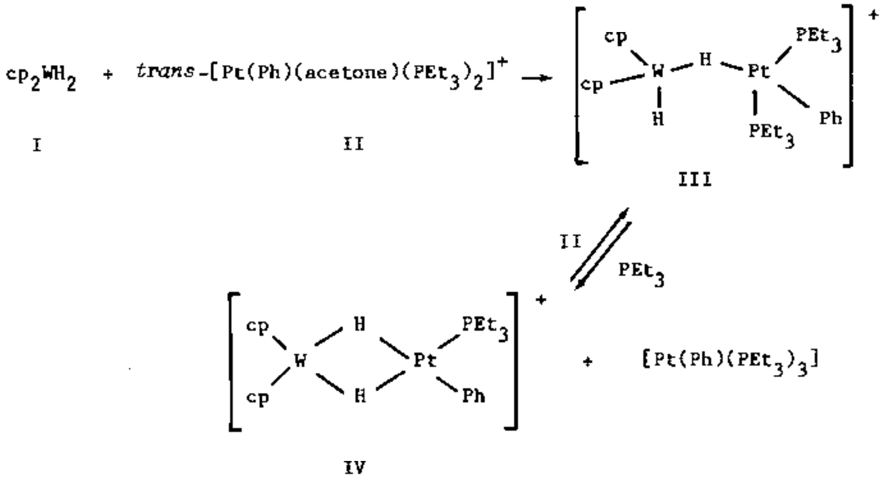
17-electron cation

$$cp_2MX_2 \rightleftharpoons [cp_2MX_2]^+ \xrightarrow{MeCN} [cp_2M(MeCN)X] + \tfrac{1}{2}X_2$$

$$[cp_2M(MeCN)X]^+ \rightleftharpoons [cp_2M(MeCN)X]^{2+}$$

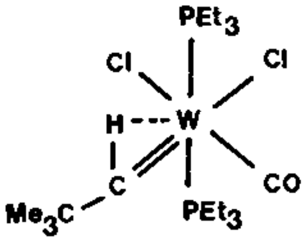
This assignment was confirmed by an authentic preparation of $[cp_2M(MeCN)X]^+$ by the slow (c.f. reaction of the 17 electron cation) reaction of cp_2MX_2 with MeCN [202].

The interaction between cp_2MoH_2 and $SnCl_4.5H_2O$ or $SnCl_4(Et_2O)_2$ in ether gives $[cp_2MoH(SnCl_3)]$ which is thought to contain a hydride bridge as well as a direct Mo-Sn bond. Reaction between cp_2MoH_2 and $SnCl_4$ in benzene is more complex, and the product $[cp_2MoH(SnCl_3)]_2SnCl_4$ is thought to contain hydride bridges between the central $SnCl_4$ unit and the two molybdenum fragments. The structure was determined using IR, ^1H NMR and ^{119}Sn Moessbauer spectroscopy [203]. Reaction between cp_2WH_2 and the cation *trans*-$[Pt(Ph(acetone)(PEt_3)_2]^+$ gave two products as shown in the scheme



The crystal structures of the cations III and IV were determined although the hydrides were not observed. However, the ^1H NMR spectrum of IV unambiguously supported the structure as it showed two non-equivalent hydrides coupled to ^{31}P, ^{183}W and ^{195}Pt. Compound III is fluctional (exchange of hydrides) to the lowest attainable temperatures [204].

A crystal structure determination for the previously reported $[W(CHCMe_3)(CO)(PMe_3)_2Cl_2]$ shows a highly distorted octahedral geometry, although an alternative description is a seven coordinate capped octahedron with H in the capping position as shown in (77)[205].



(77)

The *neo*-pentylidene ligand is highly distorted with W-C-C =168.7°. Bond distances are

W=C = 1.859(4)Å W-Cl = 2.458(1), 2.478(1)
W-C(CO) = 1.968(4) W-P = 2.506(1), 2.522(1)
W-H = 1.835(36)

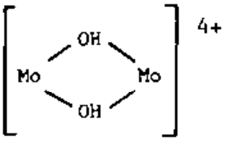
One of the products of the attempted addition of *trans*-$[WBr(CO)_4(CPh)]$ across the triple bond of $Mo_2(O^iPr)_6$ in the presence of py was found to be $[WBr(CO)_2py_2(CPh)]$ [206]. A crystal structure determination showed an octahedral array with *cis* carbonyls and bromine *trans* to the carbyne. Bond distances are W≡C = 1.84(2), W-CO = 2.00 (av), W-N = 2.27(av) and W-Br = 2.696(2)Å.

5.4 MOLYBDENUM(III) AND TUNGSTEN(III)

WCl_3 has been prepared by the reaction of WCl_2 or WO_2 with WCl_4, WCl_5 or WCl_6. It is stable below 470°C and melts with disproportionation to WCl_2 and WCl_5 [207]. The stoichiometric reaction between $SnCl_2$ in HCl solution and $[MoOCl_5]^{2-}$ in the presence of M'Cl (M' = Na,K) gives good yields of $M'_3[MoCl_6]$ [208]. Single crystal X-ray studies on $(NH_4)_2[MoCl_5(H_2O)]$ and $(NH_4)_2[MoBr_5(H_2O)]$ have been carried out [209]. The bond distances in these octahedral complexes are

	$[MoCl_5(H_2O)]^{2-}$	$[MoBr_5(H_2O)]^{2-}$
Mo-X(*trans* O)	2.415(1)Å	2.560(1)
Mo-X	2.428(1) - 2.437(1)	2.573(1) - 2.597(1)
$Mo-OH_2$	2.155(3)	2.185(3)

Mo EXAFS studies show that the predominant species in aqueous Mo(III) is



with Mo-Mo = 2.54 and Mo-μOH = 2.06Å [139]. The kinetics of the oxidation of aqueous Mo(III) (formulated as $[Mo(H_2O)_6]^{3+}$) by three substrates, $[IrCl_6]^{3-}$, $[Co(C_2O_4)_3]^{3-}$ and VO^{2+} have been investigated. In all cases the final product is the Mo(V) dimer $[Mo_2O_4]^{3+}$ but interesting variations in the reaction pathways were identified [210].

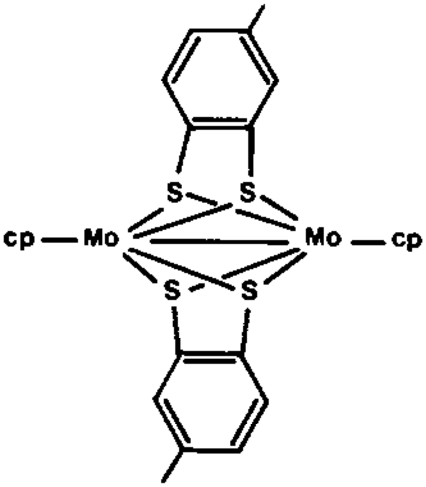
$[Mo(S_2P\{OMe\}_2)_3]$ was prepared by the action of MeOH solutions of $(NH_4)[S_2P(OMe)_2]$ on $MoCl_3(thf)_3$, which was itself prepared by an improved method using tin reduction of $MoCl_4(thf)_2$. The dithiophosphate complex has octahedral stereochemistry with Mo-S = 2.51Å (av) [211].

The reaction between MoS_3 and aqueous cyanide solution generated the cluster complex $K_8[Mo_4S_4(CN)_{12}].4H_2O$. A crystal structure determination revealed a cubane type Mo_4S_4 core with three cyano groups completing the octahedral arrangement about each metal atom. The complex is diamagnetic and single Mo-Mo bonds are proposed [212]. Bond distances are Mo-Mo = 2.854(1), Mo-C = 2.190(10) and Mo-S = 2.382(2)Å.

Reaction of $[cpMo(CO)_3]_2$ with 3,4-dimercaptotoluene yields a purple dimer containing carbonyls and the anion of the ligand, but it was not structurally characterized. On irradiation it decomposes to a green compound $[cpMo(S_2C_6H_3Me)]_2$ which has the structure (78) in which the core is similar to that of the previously reported $[cpMo(SC_2H_2S)]_2$ whose structure is also reported in this paper [192]. Bond distances are

	$[cpMo(S_2C_6H_3Me)]_2$	$[cpMo(S_2C_2H_2)]_2$
Mo-Mo	2.580(2)Å	2.576(1)
Mo-S	2.449(4) - 2.460(2)	2.460(4)

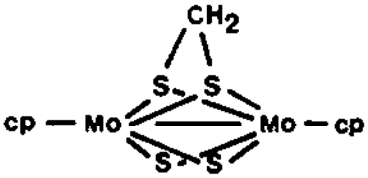
The interaction between $[(C_5H_4{}^{i}Pr)MoCl_2]_2$ and LiSH yields $[(C_5H_4{}^{i}Pr)MoS]_4$ which can readily be oxidized both chemically and electrochemically (reversibly) to the corresponding +1 and +2 cations. The structures of all three complexes have been determined and all are based on a Mo_4S_4 cubane type structure. The bond distances show that the removal of one or two electrons has little effect on the structure of the clusters [213].



(78)

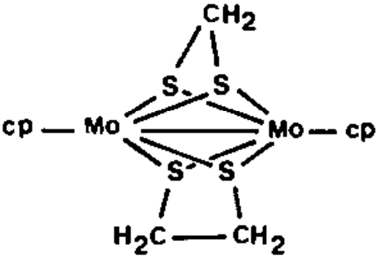
	$[^{i}\mathrm{PrcpMoS}]_4$	$[^{i}\mathrm{PrcpMoS}]_4^{+}$	$[^{i}\mathrm{PrcpMoS}]_4^{2+}$
Mo-Mo	2.904(3)Å	2.894(8)	2.858(18)
Mo-S	2.344(2)	2.343(3)	2.343(2)

Deprotonation of $[\mathrm{cpMo(S)SH}]_2$ with 2 equivalents of NaOMe in the presence of CH_2Br_2 gave $(\mathrm{cpMoS})_2S_2CH_2$ which spectroscopic evidence suggests has the structure (79).

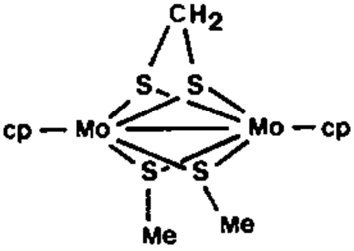


(79)

Alkenes, alkynes and other unsaturated systems add (often reversibly) across the two bridging sulphido groups The ethylene adduct has the structure (80) with Mo-Mo = 2.601(1)Å, but disorder in the positions of the dithiolate bridges prevented accurate determination of other bond lengths. Reaction of (79) with MeI and then LiMe gives $(\mathrm{cpMo})_2(S_2CH_2)(\mathrm{SMe})_2$ with the structure (81) [214].



(80)



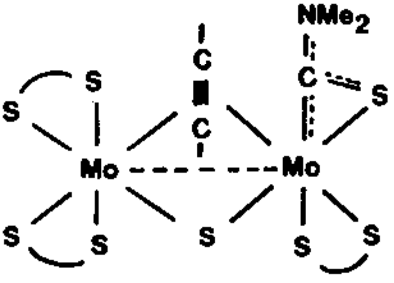
(81)

Bond distances are

Mo-Mo = 2.596(1)Å

Mo-S(SMe) = 2.453(1) Mo-S($S_2C_2H_4$) = 2.448(1)

Reaction of [Mo(R'C=CR'')$_2$(S_2CNR_2)$_2$] with tertiary phosphines PR_3 yields derivatives [Mo_2(μ-S)(μ-R'C≡CR'')(S_2CNR_2)$_3$($SCNR_2$)] containing a η^2-CS bonded thiocarboxamide ligand as in (82) which shows the structure of [Mo_2(μ-S)(μ-EtC≡CEt)(S_2CNMe_2)$_3$($SCNMe_2$)].



(82)

Bond distances are

Mo-Mo = 2.647(1)Å Mo-C(C≡C) = 2.111(8) - 2.255(5)

Mo-μS = 2.27 (av) Mo-C(CS) = 2.056(6)

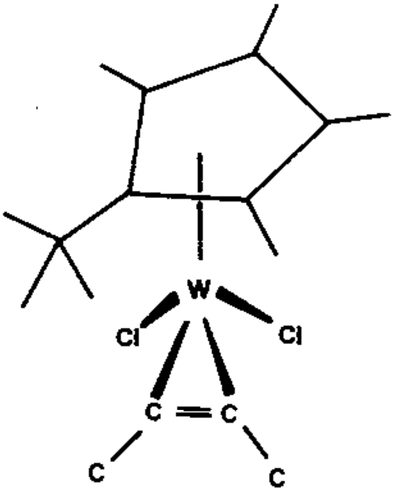
Mo-S(CS) = 2.573(2) Mo-S(dtc) = 2.431(2) - 2.590(1)

The diamagnetism and the Mo-Mo distance suggest the presence of a single Mo-Mo bond. The short Mo-C(η^2-CS) distance suggests some carbene character for this ligand. The ^1H NMR spectrum suggests the presence of several isomers of the complexes in solution [215].

Reaction of the tridentate ligand tri-(2-pyridyl)amine (TPAm) with $Mo(CO)_6$ gives $(TPAm)Mo(CO)_3$ and further reaction with $SOCl_2$ or Br_2 in CH_2Cl_2 gives $Mo(TPAm)X_3$ (X = Cl,Br) [216].

Some dienes react with $[cpMoX(CF_3C{\equiv}CCF_3)_2]$ (X = Cl,Br,I,SAr) to give, via an oxidative disproportionation reaction, monomeric paramagnetic $[cpMoX_2(diene)]$. Unexpectedly, further reaction with $Tl(C_6F_5S)$ gives diamagnetic $[cpMoTl(SC_6F_5)_4]$ which ^{19}F NMR shows to have four non-equivalent SC_6F_5 groups at low temperature, although scrambling of the SC_6F_5 groups occurs at higher temperatures [217].

The reaction of $[W(CCMe_3)(dme)Cl_3]$ and excess 2-butyne yields a complex of empirical formula $[W(CCMe_3)(2\text{-butyne})_3Cl_2]$, but which X-ray diffraction showed to be $[W(\eta^5\text{-}C_5Me_4{}^tBu)(\eta^2\text{-}MeC{\equiv}CMe)Cl_2]$ with the highly substituted cp ligand being generated in the reaction. The 2-butyne is strongly η^2 coordinated and the metal atom may be regarded as pseudo-tetrahedral as shown in (83).



(83)

Bond distances are

W-Cl = 2.364(2), 2.382(2)Å

W-C(C≡C) = 2.007(7), 2.021(6)

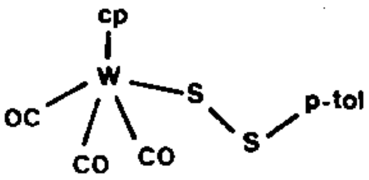
C≡C = 1.312(10)

This compound has the shortest tungsten-acetylene bond distance known [218].

5.5 MOLYBDENUM(II) AND TUNGSTEN(II)

Reaction of $[MoCl_4(thf)_2]$ and the sodium salt of 2,4,6-tri-*iso*propylbenzene thiol (its bulk prevents bridge formation) under CO gives $[Mo(CO)_2(SC_6H_2{}^iPr_3)_3]^-$. The complex shows only one carbonyl stretch and a crystal structure determination revealed a trigonal bipyramidal structure with the carbonyls axial. Bond distances are Mo-S = 2.317(5) - 2.3442(5) and Mo-C = 1.91Å (av). This formally 14-electron system reacts reversibly with CO to give the corresponding tricarbonyl, but the equilibrium favours the five coordinate complex [219].

Treatment of $[cpW(CO)_3SH]$ with RSNpht, RSSNpht and RS(O)Npht (Npht = N-phthalimide, R = Bz,*p*-tol) gives novel catenated sulphur ligand complexes $[cpW(CO)_3S_xR]$ (x = 2,3) and $[cpW(CO)_3SS(O)R]$ respectively. The structure of $[cpW(CO)_3SS\text{-}p\text{-}tol]$ was determined to be as shown in (84) [220].



(84)

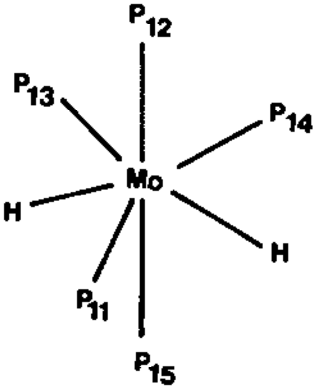
Bond distances are

W-S = 2.506(2)Å   S-S = 2.053(4)

Reaction of $[MoCl(\eta^2\text{-}COCH_2SiMe_3)(CO)(PMe_3)_2]$ with $(S_2CNMe_2)^-$ in aqueous acetone gives $[Mo(CH_3CO)(CO)(S_2CNMe_2)(PMe_3)_2]$. However, instead of the metal attaining an eighteen electron configuration via η^2 coordination of the acetyl group, this ligand is bonded through carbon and there is interaction with the Me group. The Mo-βC distance is 2.60(1) and Mo-H = 2.06(9)Å [221].

Reduction of $MoCl_4(thf)_2$ by Mg under H_2 in the presence of PMe_3 gives $MoH_2(PMe_3)_5$ which a structure determination shows to be a distorted pentagonal bipyramidal stereochemistry as shown in (85) with both hydrides in the equatorial plane, but angular distortions make two of the phosphines *trans* to the hydrides. Bond distances are

Mo-H = 1.67Å (av)   Mo-P(*trans* H) = 2.47 (av)
Mo-P(ax) = 2.43 (av)   Mo-P(eq) = 2.403(3)



(85)

Both ^1H and ^{31}P NMR spectroscopy show the molecule to be fluxional even at low temperature [222].

The kinetics and equilibrium position of the reaction

$$[HMo(CO)_2(dppe)_2]BF_4 \ + \ \text{base} \ \rightleftharpoons \ \textit{cis}\text{-}[Mo(CO)_2(dppe)_2] \ + \ \text{baseH}^+BF_4^-$$

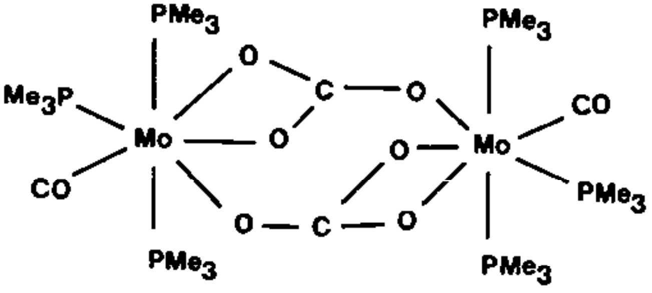
have been determined for a number of different bases and it was found that the rates did not correlate with the thermodynamic base strengths. Further experiments implied an anion assisted transfer of the proton [223]. In addition, the structure of $[HMo(CO)_2(dppe)_2]AlCl_4$ was determined and described as pentagonal bipyramidal, although the hydride was not detected and its position was inferred from the angular displacement of the phosphine ligands. Bond lengths are Mo-Co = 1.900(8) - 2.021(8), Mo-P = 2.466(1) - 2.583(2)Å [223].

Reaction of $WCl_4(PMe_3)_2$ with $MgCl(CH_2SiMe_3)$ gives paramagnetic five coordinate $[ClW(CH_2SiMe_3)_3(PMe_3)]$ which reacts with CO to give a η^2-acyl dimeric complex $[ClW(COCH_2SiMe_3)(CO)_2(PMe_3)]_2$ which is isostructural with the known molybdenum complex [224].

Treatment of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ with CO_2 (50-60 psi) at room temperature in petroleum ether gives $[Mo(CO_2)_2(PMe_3)_4]$, which may contain a head-to-tail dimer of CO_2, and also orange $[Mo(CO_3)(CO)(PMe_3)_3]_2$ and small amounts of blue $[Mo(CO_3)(CO)(PMe_3)_4]$. An equilibrium exists between these latter two complexes

$$2[Mo(CO_3)(CO)(PMe_3)_4] \ \underset{PMe_3}{\overset{thf}{\rightleftharpoons}} \ [Mo(CO_3)(CO)(PMe_3)_3]_2$$

The dimer has an interesting structure (86), but bond distances were not reported [141].



(86)

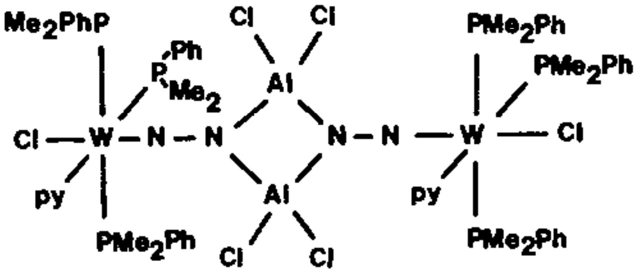
Reduction of $MCl_3(PMe_3)_3$ in thf by Na/Hg under N_2 yields a complex of composition $[MCl(N_2)(PMe_3)_4]$, but spectroscopic evidence suggests it should be formulated as a mixture of *trans*-$[M(N_2)_2(PMe_3)_4]$ and *trans*-$[MCl_2(PMe_3)_4]$, even though pure $[M(N_2)_2(PMe_3)_4]$ can only be isolated as the *cis* isomer. Crystal structure determinations of "*trans*-$[MCl(N_2)(PMe_3)_4]$" showed them to be isostructural with *trans*-$[MoCl_2(PMe_3)_4]$ although chlorine and dinitrogen are disordered in the mixed complex [225]. Bond distances are

	t-$[MoCl(N_2)(PMe_3)_4]$	*t*-$[WCl(N_2)(PMe_3)_4]$	*t*-$[MoCl_2(PMe_3)_4]$
M-Cl	2.415(8)Å	2.46(1)	2.420(6)
M-P	2.461(1)	2.458(2)	2.496(3)
M-N	2.08(1)	2.04(2)	

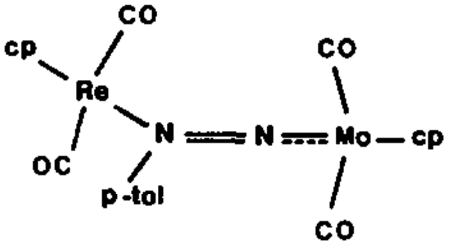
Reaction of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with two moles of $AlCl_3$ and two moles of py in benzene gave $[W(N_2)(py)(PMe_2Ph)(AlCl_2)]_2$ which a crystal structure determination shows to contain octahedral tungsten with a planar $W(N_2)Al_2(N_2)W$ unit containing an unusual μ_3-dinitrogen ligand as shown in (87), but unusual thermal parameters made the actual positions of the nitrogen atoms ambiguous [226].

Reaction of $[cpMo(CO)_2(N_2$-*p*-tol)] and $[cpRe(CO)_2(thf)]$ gave $[cp(CO)_2Mo(\mu$-NN-*p*-tol)$Re(CO)_2cp]$ which X-ray diffraction shows to contain a μ-aryldiazamido-NN' bridge which is regarded as a three electron donor to molybdenum and a two electron donor to rhenium [227]. The Mo-N-N unit is linear as shown in (88). Bond distances are

Mo-N = 1.822(4)Å Re-N = 2.152(4)
N=N = 1.256(6)

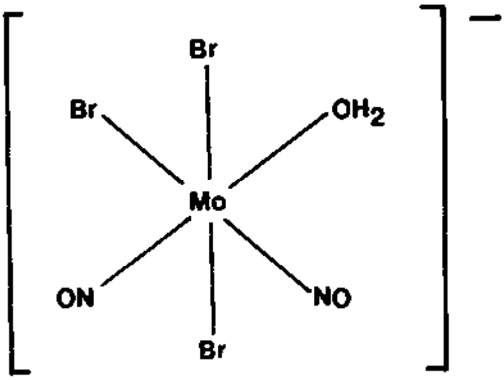


(87)



(88)

In aqueous aerobic solution $[MoO_4]^{2-}$ can be reduced with $NH_2OH.HCl$ and SCN^-, the products depending critically on the pH. In the pH range 4-4.5 mono nitrosyls are produced exclusively and complexes such as $[Mo(NO)(NH_2O)(NCS)_4]^{2-}$ and $[Mo(NO)(NH_2O)(S_2CNR_2)_2]$ have been isolated. At pH 5.2-5.4 the dinitrosyl entity is produced as evidenced by the isolation of $[Mo(NO)_2(NHO)(NCS)_4]$ and $[Mo(NO)_2(NHO)(NCS)_2(bipy)]$. At pH 5.7-6 an initially formed $[Mo(NO)]^{2+}$ species undergoes disproportionation to give $[Mo(NO)_2(NCS)_4]^{2-}$ and an oxo molybdenum(V) complex $[Mo_2O_4(NCS)_6]^{4-}$ [228]. *Cis*-$[Mo(NO)_2(CN)_4]^{2-}$ was prepared in a one pot synthesis from $[MoO_4]^{2-}$ and excess NH_2OH in alkali solution [229]. A different research group has also found that reduction of Mo(VI) with hydroxylamine gives yellow solutions from which may be isolated a solid (probably polymeric) nitrosyl complex with one coordinated hydroxylamido(1-) ligand. Reaction with other monodentate ligands gives complexes such as $[Mo(NO)(NH_2O)Cl_4]^{2-}$, $[Mo(NO)(CN)_5]^{2-}$ and $[Mo(NO)(NH_2O)(N_3)_4]^{2-}$. A crystal structure determination of the latter complex showed the formally Mo(II) centre to have pentagonal bipyramidal stereochemistry with a η^2-bonded NH_2O ligand and three azide ligands in the equatorial plane [230]. Bond distances are Mo-NO = 1.761(8), Mo-N = 2.125(5), Mo-O = 2.048(5), Mo-N_3(*trans* NO) = 2.24(10) and Mo-N_3(equatorial) = 2.17(5)Å. The crystal structure of $(PPh_4)_2[Mo(NO)_2Br_3(H_2O)]$ has been determined [129] and is shown in (89).



(89)

Bond distances are

Mo-O = 2.186(6)Å   Mo-Br = 2.586(11) - 2.626(1)
Mo-N = 1.793(9) - 1.821(7)

The crystal structure of $[Mo(NO)_2(bipy)Cl_2]$ has been determined and shows the metal to be coordinated to *cis* linear nitrosyl groups and *trans* chlorine ligands [231]. Bond distances are Mo-NO = 1.826(6), 1.875(4); Mo-Cl = 2.408(3), 2.428(2); Mo-N = 2.195(9)Å. Reaction of $[Mo(NO)_2L_2Cl_2]$ (L = MeCN,py,PPh_3 etc) with silver salts in dme leads to the formation of $[Mo(NO)_2L_2Cl(dme)]^+$ and $[Mo(NO)_2L_2(dme)_2]^{2+}$. Some of the dicationic species catalyze the polymerization of norbornadiene [232].

A number of papers have been published on Mo(II) nitrosyl complexes containing the $HB(Me_2pz)_3$ ligand (L) where Me_2pz is 3,5-dimethylpyrazole. Thus, reaction of $[MoL(NO)I_2]$ with amines and phenols gave [MoL(NO)I(NHR)] and [MoL(NO)I(OR)]. Crystal structure determinations for two arylamide complexes (R = *p*-tolyl, *p*-C_6H_4Me) showed the molybdenum atom to be coordinated in a *facial* geometry with short Mo-NHR bond lengths [233]. Bond distances are

	R = C_6H_4Me	R = C_6H_4OMe
Mo-NO	1.78Å	1.754(11)
Mo-N(L)	2.140(2) - 2.255(22)	2.169(9) - 2.263(10)
Mo-NHR	1.99(2)	1.945(10)
Mo-I	2.790(3)	2.785(2)

Reaction of $[MoL(NO)I_2]$ with various hydrazine ligands leads to the formation of $[MoL(NO)I(NHRR')]$ (R and R' are H,Me,Ph). Crystal structures have been determined for the complexes with R = Me,R' = Ph and R = R' = Me and both contain monodentate hydrazido(1-) ligands. The Mo-N distances seem to be intermediate between single and double bond lengths [234]. Bond distances are

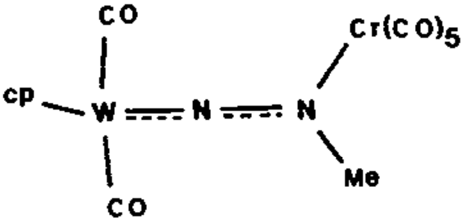
	$[MoL(NO)I(HNN\{Me\}Ph)]$	$[MoL(NO)(HNNMe_2)]$
Mo-NO	1.70(3)Å	1.80(2)
Mo-N(HNRR')	1.88(3)	1.980(17)
Mo-N(L)	2.17(3) - 2.30(2)	2.178(18) - 2.261(18)

Similarly reaction of $[MoL(NO)I_2]$ with RSH gives $[MoL(NO)I(SR)]$ and with silver acetate and RSH the complex $[MoL(NO)(SR)_2]$ is obtained. A crystal structure determination on $[MoL(NO)I(SC_6H_{11})]$ showed *fac*-octahedral coordination about molybdenum with Mo-S = 2.31Å [235]. Reaction of $[MoL(NO)I_2]$ with HX (HX = *o*-$C_6H_4(NH_2)_2$, *o*-$C_6H_4(NH_2)(OH)$ and *o*-$C_6H_4(NH_2)SH$) afforded the complexes $[MoL(NO)IX]$. However, reaction with *o*-$C_6H_4(OH)_2$ gave $[Mo(NO)(C_3HMe_2N_2H)_3(O_2C_6H_4)]I_3$ in which the dimethylpyrazole ligand has been removed from boron. A crystal structure determination showed the cation to have the *mer* configuration with all the Mo-N distances similar (2.140(4)-2.169(11)Å. However, the catechol ligand has different Mo-O bond lengths (1.933(8), 2.093(8)Å) due to the *trans* effect of NO; Mo-No = 1.771(13)Å [236]. Examples of compounds of the type $[MoL(NO)XY]$ (X = Y = F,Cl,Br and X = OEt, NHMe, SR etc) have been prepared [237]. Finally, a series of homo and heterobimetallic complexes of molybdenum and tungsten have been prepared in which the metals are bridged by a variety of *para*-disubstituted bifunctional aromatic groups and the coordination of the metal is completed by NO and L [238]. Their electrochemical reductions were studied and, depending on the nature of the bridging groups, they revealed strong, intermediate and weak interactions between the two metal centres.

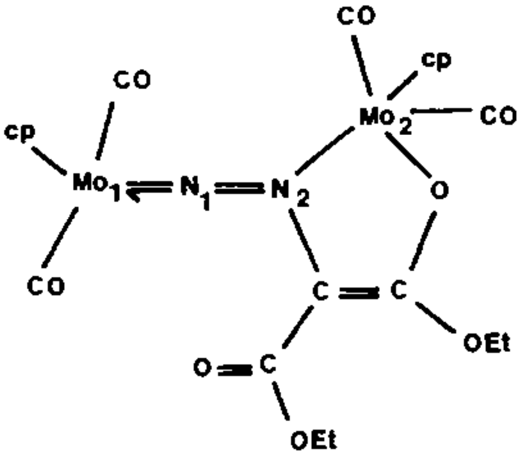
Reaction of $[cpW(CO)_2(N_2Me)]$ with $Cr(CO)_5(thf)$ gave a dinuclear complex with a new mode of bridging for organodiazo ligands as shown in (90) [239]. The W-N-N unit is almost linear (174.4(3)°) and bond distances are

W-N = 1.830(3)Å   N-N = 1.247(4)

The triple bond in $[cpMo(CO)_2]_2$ reacts with diethyldiazomalonate to give a complex in which the Mo-Mo bond is completely disrupted to give a system similar to the previous example as shown in (91) [240].



(90)



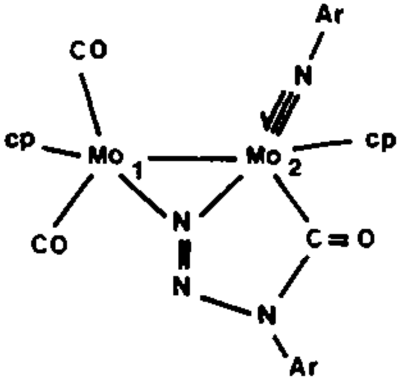
(91)

Bond distances are

Mo_1-N_1 = 1.851Å Mo_2-N_2 = 2.218
N_1-N_2 = 1.255

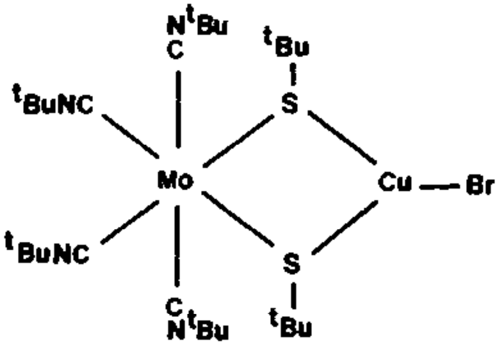
Aryl azides react with $[cpMo(CO)_2]_2$ to give 1:1 adducts which then rapidly give 1:2 adducts which have the structure shown in (92) [240]. Bond distances are

Mo-Mo = 2.904(3)Å
Mo_1-μN = 1.99(1) Mo_2-μN = 2.04(2)
Mo_2-C = 2.19(1)



(92)

Mo(^{t}BuS)$_4$ or *cis*-[Mo(^{t}BuS)$_2$(^{t}BuNC)$_4$] react with CuBr(^{t}BuNC)$_3$ in acetone to give [(^{t}BuNC)$_4$Mo(μ-^{t}BuS)$_2$CuBr]. Two isomers have been isolated in the solid state which differ only in the orientation of the ^{t}Bu groups at the bridging ligands. The *anti*-upright isomer (93) is produced when the complex is co-crystallized with diphenylacetylene; the *syn*-upright configuration is produced on crystallization alone from acetone [241].



(93)

Bond distances are

Mo-μS = 2.41Å	Cu-μS = 2.24 (av)
Mo-C = 2.07(1) - 2.12(1)	Cu-Br = 2.317(2)

The two isomers gave identical ^{1}H NMR spectra consistent with the presence of both isomers in solution and at higher temperatures *anti*-*syn* exchange occurs.

The crystal structure of [Mo(dppm)(CNC$_6$H$_{11}$)$_5$](PF$_6$)$_2$ has been determined.

The cation adopts a distorted pentagonal bipyramidal stereochemistry with dppm in the equatorial plane. Bond distances are Mo-P = 2.54 (av), Mo-C = 2.109(2) - 2.132(11)Å [242].

Two monoclinic forms of $[W(CO)_2I_2(^{t}BuNC)_3]$ have been isolated and both have been shown to have the 4:3 piano stool geometry about the metal atom, with two iodine atoms and one isocyanide constituting the triangular cap. Previously another 4:3 isomer of this complex had been reported with two iodines and a carbonyl in the triangular cap. The different forms of the complex are consistent with the fluctional nature of the complex in solution and the dominant effect of crystal packing forces on crystallization from different solvents. In contrast, $W(CO)I_2(^{t}BuNC)_4$ adopts a capped octahedral structure with CO capping a triangular face of three ^{t}BuNC groups [243].

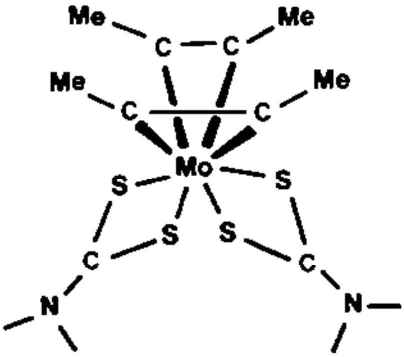
$[Mo(CN\text{-}c\text{-}C_6H_{11})_7](PF_6)_2$ reacts with bidentate nitrogen donor ligands (N-N = bipy,phen,Me_2bipy) to give monomeric $[Mo(CN\text{-}c\text{-}C_6H_{11})_5(N\text{-}N)]^{2+}$. However, under the same conditions $[Mo(CN^{t}Bu)_7]^{2+}$ reacts to give a de-alkylated cyano bridged species $[\{Mo(CN^{t}Bu)_4(N\text{-}N)\}_2(\mu\text{-}CN)](PF_6)_3$. In the bipy compound each molybdenum has a capped trigonal prismatic stereochemistry with the bridging CN occupying the capping position, thus giving non-equivalent metal atoms, which is also detected electrochemically. This interesting dimer reacts with ^{t}BuCl to give $[Mo(CN^{t}Bu)_4(bipy)Cl]^{+}$ which on further reaction with ^{t}BuNC gives $[Mo(CN^{t}Bu)_5(bipy)]^{2+}$ [244].

The kinetics of the reaction

$$Mo(CO)(RC{\equiv}CR')(S_2CNMe_2)_2 \;+\; RC{\equiv}R' \;\rightleftharpoons\; [Mo(RC{\equiv}CR')_2(S_2CNMe_2)_2 \;+\; CO$$

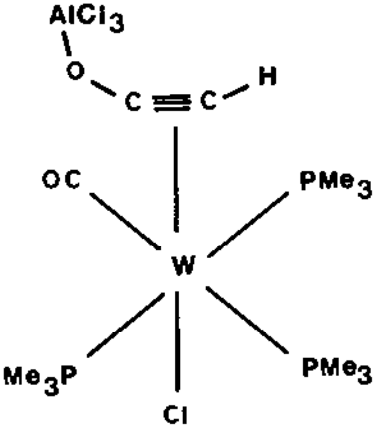
have been studied and the rate law indicates a dissociation pathway to a formally 14-electron intermediate before addition of the second alkyne, rather than an associative mechanism through an 18-electron intermediate. In contrast, replacement of acetylene by ligands L = CO,PR_3,$P(OR)_3$ does appear to proceed through an 18-electron intermediate [245]. A series of complexes $[Mo(RC{\equiv}CR)_2(S_2CNC_4H_4)]$ containing the pyrroledithiocarbamate ligand have been prepared by the reaction of alkyne with $[Mo(CO)_3(S_2CNC_4H_4)_2]$. The molecules are fluctional in solution and the crystal structure of $[Mo(MeC{\equiv}CMe)_2(S_2CNC_4H_4)_2]$ shows an octahedral arrangement about the metal atom as shown in (94) [246]. Bond distances are

Mo-S(*trans* S) = 2.51Å (av)
Mo-S(*trans* C) = 2.61 (av)
Mo-C = 2.02(1) - 2.09(1)



(94)

The complex [W(HC≡COAl)CO(PMe$_3$)$_3$Cl] has previously been reported to be formed by an AlCl$_3$ promoted coupling of [W(CH)(PMe$_3$)$_4$Cl] and CO. X-ray diffraction revealed the structure (95) [247].

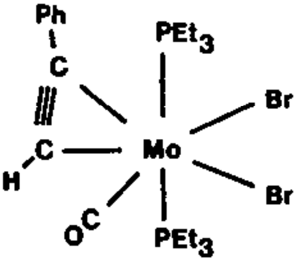


(95)

Bond distances are

Al-O = 1.751(3)Å W-P(*trans* CO) = 2.571(1)
W-CO = 1.984(4) W-P(*trans* P) = 2.521(1)
W-C = 2.009(5), 2.034(4)

Reaction of $[Mo(CO)_2(PEt_3)_2Br_2]$ with $RC{\equiv}CR'$ ($R = H$; $R' = H, Ph$) gives $[Mo(CO)(RC{\equiv}CR')(PEt_3)_2Br_2]$ which have the structure (96) in the solid state, which may be regarded as either a distorted octahedron or a pentagonal bipyramid with the phosphines axial [248].



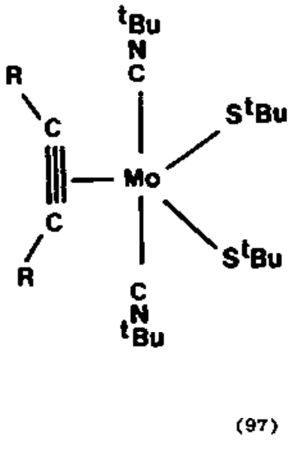
(96)

Bond distances are

$\text{Mo-CO} = 1.939(10)\,\text{Å}$ $\quad$ $\text{Mo-P} = 2.543(3)$

$\text{Mo-C} = 1.985(14)$ $\quad$ $\text{Mo-Br} = 2.673(1),\ 2.700(1)$

Cis-$[Mo(^tBuS)_2(^tBuCN)_4]$ reacts readily with acetylenes to give $[Mo(^tBuS)_2(^tBuCN)_2(RC{\equiv}CR')]$. The crystal structures of two such complexes ($R = R' = H$ or Ph) have been determined [249]. In both cases the metal shows trigonal bipyramidal geometry (counting the acetylene to occupy one position) with the acetylene axis parallel to the axial isocyanides as shown in (97).



(97)

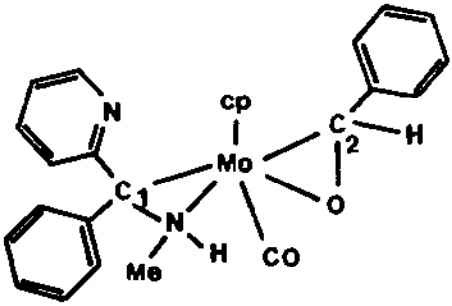
Bond distances are

	R=R'=H	R=R'=Ph
Mo-*S*	2.33Å (av)	2.337(3)
Mo-C(C≡C)	2.04(2)	2.05(1)
Mo-C	2.10 (av)	2.13 (av)

An extended Huckel MO calculation shows that the theoretically most stable configuration is in fact the observed structure.

Near UV irradiation of [(η^5-C_5R_5)W(CO)$_3$(CH_2SiMe_2H)] (R = H,Me) at 77 and 196K give loss of CO and cleavage of the Si-H bond resulting in the formation of [(η_5-C_5R_5)W(CO)$_2$(CH_2SiMe_2)] in which the silyl ligand is thought to be bonded to tungsten through *C* and *Si* [250].

The crystal structure of the previously reported [cpMo(CO){NH(Me)CN(C_5H_4)C_6H_5}OCC_6H_5] has been determined [251]. The structure is best described as a capped trigonal pyramid, with cp as the capping ligand, with the basal ligands being CO and two η^2 ligands - benzaldehyde and a modified Schiff base, as shown in (98).



(98)

Bond distances are

Mo-C_1 = 2.223(12)Å Mo-N = 2.178(8)
Mo-C_2 = 2.261(17) Mo-O = 2.070(8)
Mo-CO = 1.932(13)

The crystal structure of [cpMo(CO)$_2${CPh$_2$N(Me)C(Ph)NMe}] is based on a distorted square pyramidal coordination about molybdenum with cp apical and the complex ligand bonded through *C* and *N* . Bond distances are Mo-CO = 1.941(11), Mo-C = 2.353(8) and Mo-N = 2.160(7)Å [252].

5.6 MOLYBDENUM(0) AND TUNGSTEN(0)

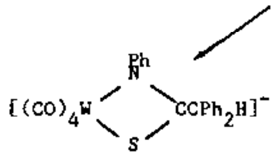
It has been found that Group VI hexacarbonyls may be adsorbed into a porous Vycor glass without change of electronic and IR spectra. On irradiation at 312nm the pentacarbonyl species $M(CO)_5(ads)$ are formed which have electronic spectra almost identical to those of $M(CO)_5$ in a methane matrix. However, the lifetimes of the pentacarbonyls adsorbed in glass are much longer, although there appears to be little reduction in their reactivities. $M(CO)_5(ads)$ show no indication of unpaired electrons, so they are thought to have singlet C_{4v} symmetry [253].

The anion $[W(CO)_5SH]^-$ is reactive to organic electrophiles [254]. For example, it reacts with RNCO to give a monodentate thiocarbamate complex

$$[W(CO)_5SH]^- + RNCO \longrightarrow [(CO)_5WSC(O)NHR]$$

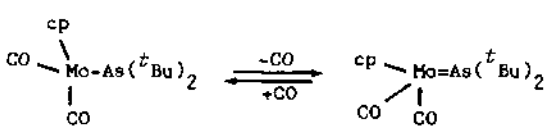
with ketene, $Ph_2C{=}C{=}O$, it gives a monodentate (*S*-bonded) thioacetate and with ketenimines it reacts as follows

$$[W(CO)_5SH]^- + Ph_2C{=}C{=}NPh \longrightarrow [(CO)_5WSC(NPh)(CPh_2H)]$$



(not observed)

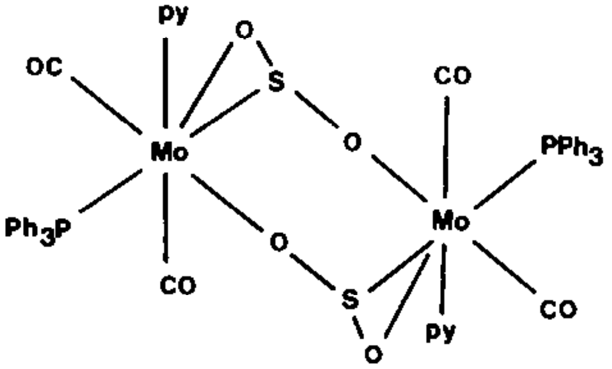
Compounds of the type $[cp(CO)_3M{-}AsMe_2]$ usually lose CO and dimerize to give complexes with dimethylarsine bridges. However, with the sterically hindered $({}^tBu)_2As$ group, loss of CO occurs without dimerization to give a metal-arsenic double bond



$$cp(CO)_2(CO)Mo{-}As({}^tBu)_2 \underset{+CO}{\overset{-CO}{\rightleftharpoons}} cp(CO)_2Mo{=}As({}^tBu)_2$$

Two ${}^tBu$ signals are seen in the ${}^1H$ NMR spectrum at -50°C, although exchange occurs at higher temperatures. The reaction is reversible and also ligands such as $L = PMe_3, {}^tBuNC$ give $[cp(CO)_2ML(As({}^tBu)_2]$. The tungsten complex reacts with other ligands such as CS_2, S, CH_2 (derived from CH_2N_2) which bridge between tungsten and arsenic with retention of a single W-As bond [255].

It has been shown that in a series of complexes of the type *cis*,*trans*-[Mo(CO)$_2$(PPh$_3$)$_2$(SO$_2$)L] (L = MeCN,py,CN^{t}Bu) the coordination of SO$_2$ may vary between *S*-bonded (planar η^1) and η^2-*S,O*-bonded geometries. Similarly, *fac*-[Mo(CO)$_3$(dppe)(η^2-SO$_2$)] can be isomerized to *mer*-[Mo(CO)$_3$(dppe)(SO$_2$)] containing *S*-bonded SO$_2$. The crystal structure determination for *mer*,*trans*-[Mo(CO)$_3$(P^{i}Pr$_3$)$_2$(SO$_2$)] confirmed the first example of planar η^1-SO$_2$ with the longest Mo-S bond distance yet reported (2.239(3)Å) [256]. The complex [Mo(CO)$_2$(py)(PPh$_3$)(μ-SO$_2$)]$_2$ shows a novel SO$_2$ bridging mode in which all the atoms of the ligand are coordinated (99).



(99)

Bond distances are

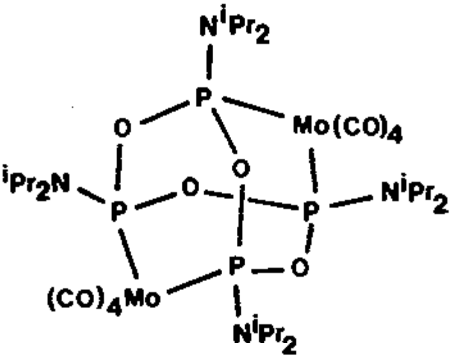
Mo-S = 2.419(2)Å Mo-O(η^2-SO$_2$) = 2.188(4)
Mo-P = 2.531(2) Mo-O = 2.243(3)
Mo-N = 2.283(4) Mo-C = 1.889(6), 1.991(3)

Reaction of Mo(CO)$_6$ with bis(N,N-di-*iso*-propylamino)phosphine oxide caused de-amination to give a molybdenum complex of the tetradentate ligand 2,4,6,8-tetrakis(N,N-di-*iso*-propylamino)cyclotetraphosphoxane

$$2Mo(CO)_6 + 4(^iPr_2N)_2P(O)H \longrightarrow (^iPrNPO)_4Mo_2(CO)_8 + 4CO + 4^iPr_2NH$$

The structure is similar to that of adamantane containing a central core similar to that in P$_4$O$_6$ with two oxygens replaced by μ-Mo(CO)$_4$ units as shown in (100) [257]. Bond distances are

Mo-P = 2.50(1)Å
Mo-C(*cis* P) = 2.039(6) Mo-C(*trans* P) = 1.986(6)



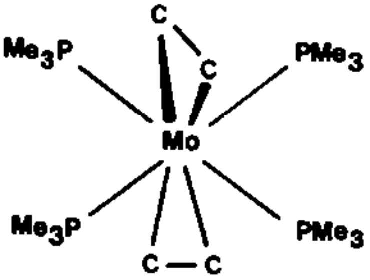
(100)

The electrochemistry of $[Mo(CO)_2(CNR)_2(PR'_3)_2]$ and *cis*-$[Mo(CO)_2(CNR)_4]$ has been investigated at room temperature [258]. In all cases a one-electron oxidation is followed by rapid isomerization to the all *trans* cation, and reduction back to Mo(0) leads to reformation of the starting materials. Thus a square reaction scheme summarizes the behaviour of these systems

$$\begin{tikzcd}
\mathit{c,c,t}\text{-}[Mo(CO)_2(CNR)_2(PR'_3)_2] \arrow[r, phantom, "\rightleftharpoons"] & \mathit{c,c,t}\text{-}[Mo(CO)_2(CNR)_2(PR'_3)_2]^+ \arrow[d, "k_1"] \\
\mathit{t,t,t}\text{-}[Mo(C)_2(CNR)_2(PR'_3)_2] \arrow[u, "k_2"] \arrow[r, phantom, "\rightleftharpoons"] & \mathit{t,t,t}\text{-}[Mo(CO)_2(CNR)_2(PR'_3)_2]^+
\end{tikzcd}$$

The ^{95}Mo NMR spectra of a number of complexes of the types $Mo(CO)_5L$, *cis*-$[Mo(CO)_4L_2]$ and *fac*-$[Mo(CO)_3L_3]$ (L = phosphine or phosphite) have been observed and chemical shifts range from δ -1090 to -1870ppm. The first example of Mo-H coupling (J = 15Hz) has been observed for the complex $[Mo_2(CO)_{10}(\mu\text{-}H)]^-$ [259]. For the complexes $[Mo(CO)_4(PPh_2R)_2]$ and $[Mo(CO)_4(Ph_2P.Y.PPh_2)]$ a good correlation is found between the ^{95}Mo chemical shifts and the wavelength of the lowest energy optical absorbtion band, but no correlation with ^{13}C chemical shifts [260]. The first examples of ^{95}Mo-^{14}N coupling have been observed for $[cpMo(CO)_2(NO)]$ (J = 46Hz) and $[(C_5Me_5)Mo(CO)_2(NO)]$ (J = 44Hz); observations were made in both the ^{95}Mo and ^{14}N NMR spectra [261].

$[Mo(N_2)_2(PMe_3)_4]$ was prepared by the reduction of $[MoCl_3(PMe_3)_3]$ with dispersed sodium under N_2. A crystal structure determination confirmed the *cis*-octahedral arrangement with Mo-N = 1.97(1)Å (rather short) and Mo-P = 2.45Å (av). The complex reacts with alkyl halides (RX),CO and PMe_3 to give respectively *trans*-$[MoX_2(PMe_3)_4]$, *cis*-$[Mo(CO)_2(PMe_3)_4]$ and $[Mo(N_2)(PMe_3)_5]$. Also reaction of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ with C_2H_4 gives *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$ for which a crystal structure determination showed the C_2H_4 molecules symmetrically bonded to molybdenum, but in a staggered configuration as shown in (101) [262].



(101)

Bond distances are

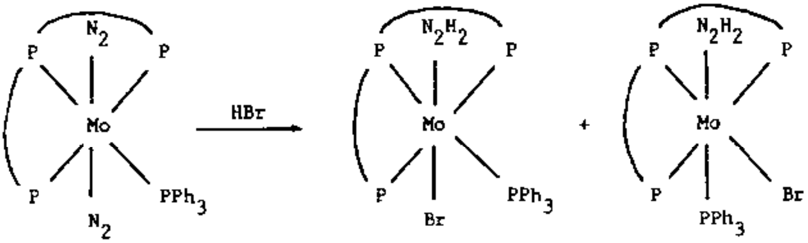
Mo-C = 2.27Å (av)   Mo-P = 2.49 (av) (rather long)
C≡C = 1.40

Two papers [263, 264] have appeared on the reaction

$$2\ trans\text{-}[Mo(N_2)_2L(PPh_3)] \xrightarrow[thf]{HBr} 2[MoBr_3(L)] + 2PPh_3 + 3N_2 + 2NH_4Br$$

(where L = triphos)

which proceeds slowly (⩾ 60h) with no production of N_2H_4. However, if the reaction is stopped early and water added to the reaction mixture then large amounts of N_2H_4 are produced. One mole of nitrogen is evolved early in the reaction and evaporation of the solvent gives a mixture of two isomeric hydrazido(2-) complexes (102) and (103).



(102) (103)

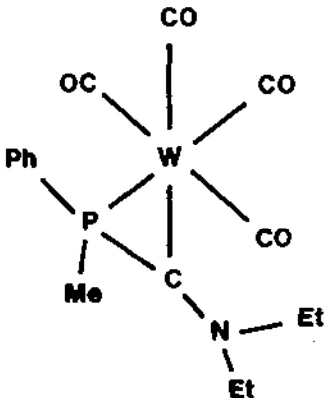
The production of N_2H_4 corresponds to decomposition of (102) but no further intermediates were detected; this behaviour mimics nitrogenase. The PPh_3 in (102) exchanges with PMe_2Ph and dissociation of PPh_3 from (102) preceeds ammonia evolution [264].

The complexes *trans,mer*-$[Mo(N_2)_2(PMe_2Ph)_3L]$ (L = py,4-Mepy) are formed in solution by the reaction

$$\textit{trans}\text{-}[Mo(N_2)_2(PMe_2Ph)_4] \ + \ L \ \rightleftharpoons \ \textit{trans,mer}\text{-}[Mo(N_2)_2(PMe_2Ph)_3)L]$$

On heating they lose N_2 to give $[Mo(\eta^6\text{-py})(PMe_2Ph)_3]$, the first stable η^6-py compounds [265].

The crystal structure of the unusual carbene complex $[(CO)_4W\{Me(Ph)P\text{-}CNEt_2\}]$ has been determined and shown to be as in (104)[266]. The geometry about phosphorus is unusual, the three P-C bonds retain close to tetrahedral stereochemistry, but the Me, α-Ph groups and the W atom are coplanar.



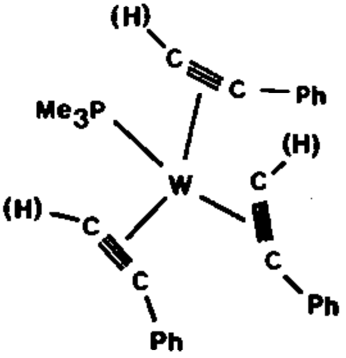
(104)

Bond distances are

$W\text{-}P = 2.465(3)\text{Å}$

$W\text{-}C = 2.108\ (av) \qquad P\text{-}C = 1.807(10)$

Reduction of $[WCl_4(PMe_3)_3]$ by Na/Hg in the presence of PhC≡CH gives $[W(PMe_3)(PhC{\equiv}CH)_3]$. The hydrogens of the acetylenes were not observed directly in the crystal structure determination, but the phenyl groups bend back as expected and all the phenyl rings are parallel to the W-P axis as shown in (105) [173].



(105)

Bond distances are

$W\text{-}C = 2.07\text{Å}\ (av) \qquad W\text{-}P = 2.455(4)$

5.7 METAL-METAL BONDED SPECIES

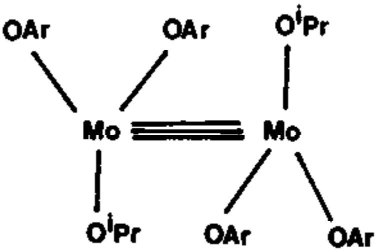
5.7.1 Triple bonded species of molybdenum(III) and tungsten(III)

Hartree-Fock-Slater calculations have been reported for MoL_3 fragments ($L = H, Me, Cl, NH_2, OH$) all of which are trigonal. Extension to binuclear Mo_2L_6 species show that the staggered geometry is preferred in all cases. Optimized metal-metal bond lengths are in the range 2.22-2.25Å and the Mo≡Mo bond strength is calculated to be in the range 414-468KJmol^{-1} [267]. Generalized molecular orbital (GMO) and configuration interaction (CI) calculations are reported for Mo_2H_6 in a large Gaussian set and for Mo_2H_6 and $Mo_2(NH_2)_6$ on a smaller basis set. For Mo_2H_6, the larger basis set increases the calculated dissociation energy by 40KJmol^{-1} and the calculated bond length of 2.194Å agrees well with the experimental values for similar compounds. On changing to

$Mo_2(NH_2)_6$ the dissociation energy increases due to the π-donating ability of this ligand which expands the Mo orbitals, and this behaviour may be responsible for much of the variation in Mo-Mo triple bond lengths [268].

A review has appeared on metal-metal bonded alkoxide derivatives of molybdenum and tungsten, including discussions of exchange reactions, oxidative additions and reactions with organic substrates [269].

Addition of excess 2,6-dimethylphenol (ArOH) to a solution of $Mo_2(O^iPr)_6$ at 25°C leads to the initial formation of 1,2-$[Mo_2(O^iPr)_2(OAr)_4]$ and melting this isolated solid with ArOH gave $Mo_2(OAr)_6$. The crystal structure of $[Mo_2(O^iPr)_2(OAr)_4]$ contains two similar but crystallographically independent molecules in which each molybdenum is coordinated to three oxygens in a staggered ethane-like configuration with the Mo-O bonds perpendicular to the Mo-Mo axis as shown in (106). This structure allows a direct comparison of alkoxide and aryl oxide groups; bond distances suggest the alkoxide is the better π-donor, and this is supported by the fact that the angle at oxygen is larger for the OAr groups [270].

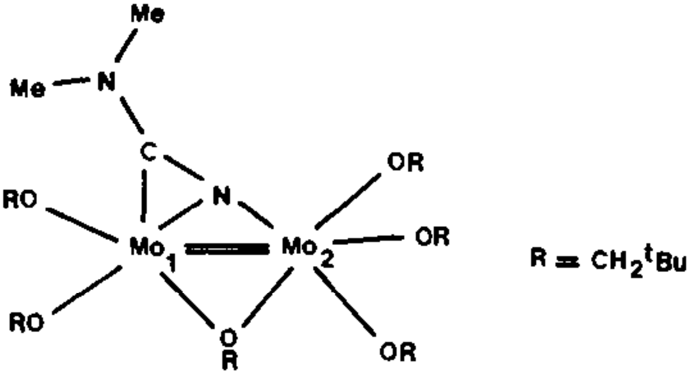


(106)

Bond distances are

$$Mo{\equiv}Mo = 2.249(1)Å$$
$$Mo\text{-}^iOPr = 1.883(4) \qquad Mo\text{-}OAr = 1.900(4)$$

As noted earlier, $W_2(O^iBu)_6$ reacts with $Me_2NC{\equiv}N$ to give $[(^tBuO)_3W{\equiv}N]_x$ (25) and $[(^tBuO)_3W{\equiv}CNMe_2]$ (similar to (26)), but under similar conditions $Mo_2(OR)_6$ (R = $^tBu, ^iPr, CH_2{}^tBu$) gives 1:1 adducts $[Mo_2(OR)_6(NCNMe_2)]$. The crystal structure of the *neo*-pentyl complex contains molecules with the dimethylcyanamide bridging through *N* and acting as a η^2 ligand to the other metal as shown in (107) [60]. The Mo_2NCNMe_2 unit is planar and bond distances are



(107)

Mo=Mo = 2.449(1)Å

Mo_1-μOR = 2.146(2)

Mo_1-N = 1.908(3)

Mo_1-C = 2.014(4)

Mo-OR = 1.92 (av)

Mo_2-μOR = 1.999(2)

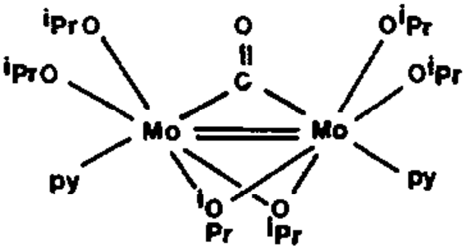
Mo_2-N = 2.134(2)

The reaction between *trans*-$[W(CO)_4Br(CPh)]$ and $Mo_2(O^iPr)_6$ in the presence of py is thought to follow the reaction scheme

$$[W(CO)_4Br(CPh)] + py \longrightarrow [W(CO)_2Br(py)_2(CPh)] + 2CO$$

$$Mo_2(O^iPr)_6 \xrightarrow[py]{} [Mo_2(O^iPr)_6py_2] \xrightarrow[CO]{} [Mo_2(O^iPr)_6py_2CO]$$

The structure of $[W(CO)_2Br(py)_2(CPh)]$ has already been described (Section 5.3.5) and that of $[Mo_2(O^iPr)_6py_2(CO)]$ is a biconfacial octahedral structure as shown in (108).

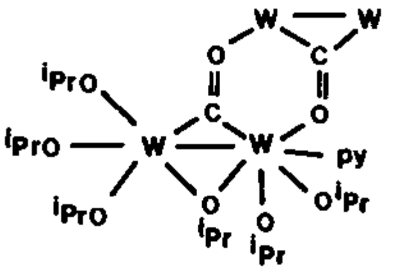


(108)

Bond distances are

$Mo{=}Mo = 2.487(1)$Å $Mo\text{-}O = 1.91$ (av)
$Mo\text{-}\mu CO = 2.045(5)$ $Mo\text{-}\mu O = 2.10$ (av)
$Mo\text{-}N = 2.341(4)$

It was a surprise therefore, that one of the products of the reaction between $[W_2(O^{i}Pr)_6py_2]$ and CO is $[W_2(O^{i}Pr)_6py(CO)]_2$, which X-ray crystallography shows to be a tetranuclear complex with a unique bridging mode for CO linking two dimeric units [272]. Each pair of tungsten atoms is bridged by both CO and $O^{i}Pr$, but the oxygen of CO links to the second tungsten dimer unit to give discrete tetranuclear molecules. There are two types of tungsten atom, one five coordinate and the other octahedral as shown in (109) which emphasizes the linkage between the dimer units.

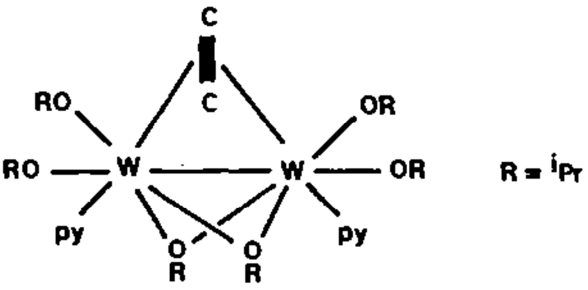


(109)

Bond distances are

$W\text{-}W = 2.654(1)$Å
$W_1\text{-}\mu C = 2.00(3)$ $W_2\text{-}\mu C = 1.91(3)$
$W_1\text{-}O^{i}Pr = 2.075(14)$ $W_2\text{-}\mu O^{i}Pr = 2.012(14)$
$W_1\text{-}O^{i}Pr = 1.915(14)$ $W_2\text{-}O^{i}Pr = 1.910(5)$
$C\text{-}O = 1.33(3)$ $W_2\text{-}O(CO) = 2.012(14)$

Acetylene reacts with $[W_2(O^{i}Pr)_6py_2]$ to give $[W_2(O^{i}Pr)_6py_2(C_2H_2)]$ which has the structure shown in (110) [273]. In solution at room temperature the ^1H NMR spectrum shows that there is rapid bridge-terminal $O^{i}Pr$ exchange, but the low temperature limiting spectrum is consistent with the solid state structure.

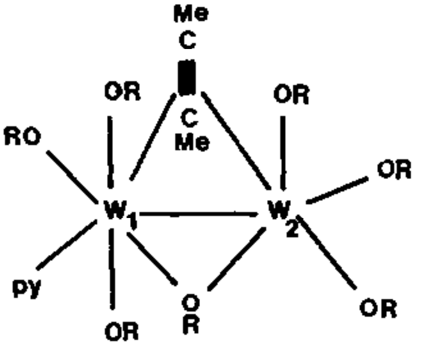


(110)

Bond distances are

W-W = 2.567(1)Å W-O = 1.94 (av)
W-N = 2.31 (av) W- O = 2.12 (av)
W-C = 2.10 (av)

It is known that $W_2(O^tBu)_6$ reacts with MeC≡CMe to give $[(^tBuO)_3W\equiv CMe]$, but in contrast $[W_2(OCH_2{}^tBu)_6py_2]$ gives blue $[W_2(OCH_2{}^tBu)_6py_2(C_2Me_2)]$ which contains one octahedral and one trigonal bipyramidal tungsten atom bridged asymmetrically by the acetylene as shown in (111) [273].



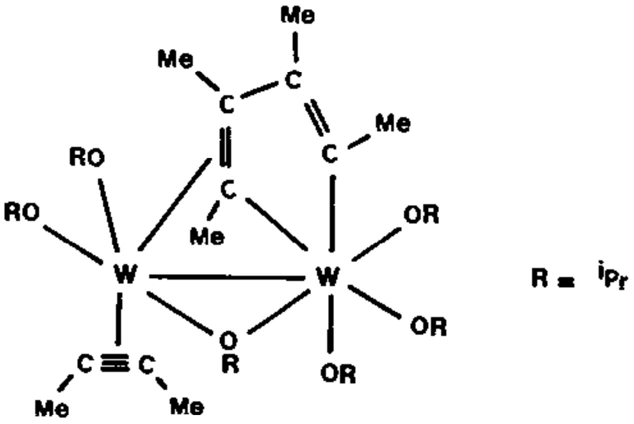
$R = CH_2{}^tBu$

(111)

The W-W separation is 2.602(1)Å and other bond distances are

	W_1	W_2
W-O	1.95Å (av)	1.95 (av)
W-μO	2.12(1)	2.025(7)
W-C	2.18 (av)	2.07 (av)
W-N	2.32(1)	2.24(1)

Reaction of $[W_2(O^{i}Pr)_6py_2(\mu\text{-}C_2R_2)]$ with two moles of C_2R_2 (R = H,Me) gives $[W_2(O^{i}Pr)_6(\mu\text{-}C_4R_4)(C_2R_2)]$. A crystal structure determination shows two completely non-equivalent tungsten atoms (W-W = 2.852(1)Å), one formally W(II) and the other W(VI), and a dimerized acetylene unit acting as a bidentate through carbon to one metal atom and as an olefin to the other as shown in (112) [273].



(112)

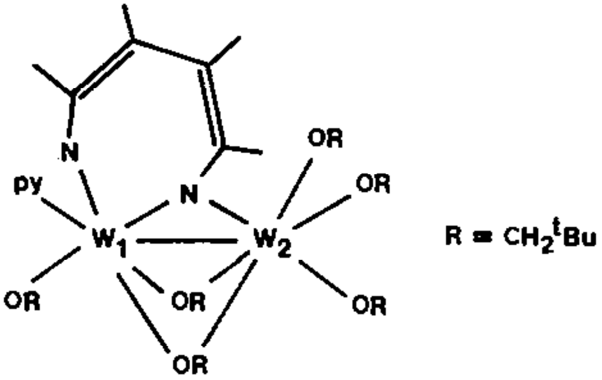
Bond distances are

	W_1	W_2
W-μOR	2.11(1)Å	1.99(1)
W-OR	1.93 (av)	1.93 (av)
$W\text{-}C(C_4Me_4)$	2.40(2) - 2.51(2)	2.15(2)
$W\text{-}C(C_2Me_2)$	2.08(2)	

An even more extraordinary example of metal oxidation and ligand synthesis is given by the reaction sequence

$$\begin{tikzcd}
{[W_2(OCH_2{}^{t}Bu)_6py_2]} + MeC{\equiv}CMe \arrow[r] & {[W_2(OCH_2{}^{t}Bu)_6py_2(\mu\text{-}C_2Me_2)]} \arrow[d, "\text{excess MeCN}"] \\
 & {[W_2(OCH_2{}^{t}Bu)_6(py)(\mu\text{-}NC_4Me_4N)]}
\end{tikzcd}$$

X-ray diffraction revealed the structure (113); if the ligand is considered to be the (4-) anion of 1,4-diamino-1,2,3,4-tetramethylbuta-1,3-diene, then each tungsten is formally W(V). The W-W separation suggests a single bond between the metal centres [274].



(113)

Bond distances are

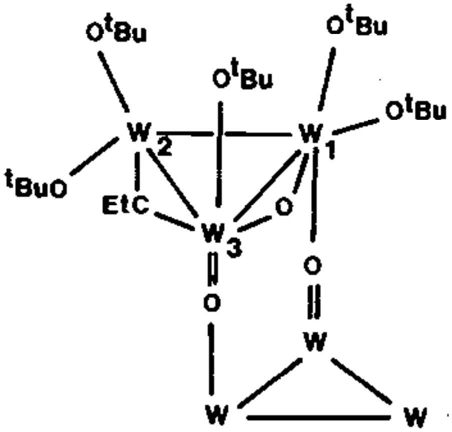
W_1-N = 1.78(1)Å
W_1-N(py) = 2,20(1)
W_1-μN = 2.09(1)
W_2-μN = 1.90(1)
W-O = 1.93 (av)
W-μO = 2.10 (av)

The W-N distances are very short, similar to those for bridging and terminal imido ligands.

Reaction between $W_2(O^tBu)_6$ and EtC≡CEt at 75-80°C gives a remarkable hexameric product $[W_3(\mu\text{-}O)(\mu\text{-}CEt)(O^tBu)_5O]_2$. The molecule consists of two trimeric units joined by two highly asymmetric oxo bridges (which are regarded as W=O⟶W bridges) and within each trimer unit the metal atoms are non-equivalent. An approximately isosceles triangle has two long edges symmetrically bridged by oxygen and CEt groups with the short edge unbridged. The geometry about each tungsten is irregular and oxidation states are not easily assigned, although the average is four. The detailed structure of one trimer and the bridges to the second trimer are shown in (114) [275]. Bond distances are

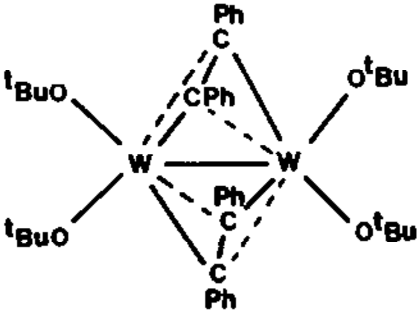
W_1-W_2 = 2.420(1)Å
W-μO = 1.896(1)
W_1-W_3 = 2.895(1)
W-μCEt = 1.95 (av)
W_2-W_3 = 2.899(1)
W-O^tBu = 1.838(8) - 1.932(8)
W-μO(intercluster) = 2.119(8)
W=O = 1.755(8)

The interaction between $W_2(O^tBu)_6$ and PhC≡CPh at 70°C in a non-polar



(114)

solvent gives two products, one of which is $[W_2(O^tBu)_4(\mu\text{-}CPh)_2]$ the structure of which consists of two tetrahedra joined centrosymmetrically on a common edge by the two μ-CPh groups. Bond distances are W-W = 2.665(1), W-O = 1.831(6) - 1.855(7) and W-C = 1.94Å (av). The second product is $[W_2(O^tBu)_4(PhC_2Ph)_2]$ in which the acetylene remains intact as shown in (115). The bridging alkynes define a plane which is not perpendicular to the O_2WWO_2 plane, so that each carbon forms one long and one short bond to tungsten [276].



(115)

Bond distances are

W≡W = 2.677(1)Å   W-C = 1.99(3), 2.34(10)

W-O = 1.86 (av)

Reaction of [$Mo_2Cl_2(NMe_2)_4$] with LiSR gives [$Mo_2(SR)_2(NMe_2)_4$] and a crystal structure determination for [$Mo_2(S^tBu)_2(NMe_2)_4$] confirmed the unbridged *anti*-rotomeric form for the $Mo_2S_2N_4$ skeleton. Bond distances are $Mo\equiv Mo$ = 2.217(1), Mo-N = 1.95 (av) and Mo-S = 2.36Å (av) [277]. Attempts to prepare $Mo_2(SR)_6$ complexes failed with simple thiols due to the formation of SR bridges, C=S bond cleavage etc., but reactions with the bulky aromatic thiol 2,4,6-trimethylbenzene thiol were succesful. Reaction of the thiol with $Mo_2(NMe_2)_6$ or $Mo_2(OR)_6$ gave replacement of only four of the original ligands, but reaction with [$Mo_2(S^tBu)_2(NMe_2)_4$] did give [$Mo_2(SC_6H_2Me_3)_6$]. A crystallographic analysis confirmed it to be a typical member of the $L_3Mo\equiv MoL_3$ class of complexes with $Mo\equiv Mo$ = 2.228(1) and Mo-S = 2.325(2)Å [278].

$W_2(NMe_2)_6$ reacts with EtOH or MeOH to give complete replacement of NMe_2 by OR^- to give [$W_4(OR)_{16}$]. However, it reacts with EtOH in the presence of Me(H)N.CH_2.CH_2N(H)Me (= L) in hexane to give [$W_2(OEt)_6L$], that is, no oxidative addition occurs. A crystal structure determination showed the complex ligand to span the W-W bond. Bond distances are $W\equiv W$ = 2.296(2), W-N = 2.28 (av), W-O = 1.88(2) - 1.97(2)Å [279].

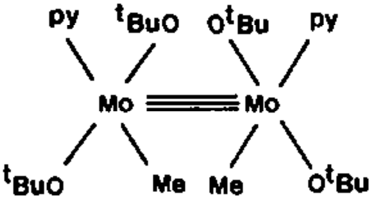
A series of complexes 1,2-[$M_2R_2(NMe_2)_4$] (R = bz,*p*-tol, *o*-tol,*neo*-pentyl) have been prepared from [$MCl_2(NMe_2)_4$] and RMgCl or LiR. These new complexes are diamagnetic, air sensitive and similar to the $M_2(NMe_2)_6$ species. The crystal structures of three examples have been determined; they all show the staggered configuration but two have the *gauche* configuration while the third has the *anti* configuration. In all these compounds the $MoNC_2$ units are planar and the NC_2 blades are aligned along the Mo-Mo axis as a result of NMe_2 π-bonding to molybdenum [281]. Bond distances are

	[$Mo_2(bz)_2(NMe_2)_4$]	[$Mo_2(p\text{-tol})_2(NMe_2)_4$]	[$Mo_2(o\text{-tol})_2(NMe_2)_4$]
config.	*gauche*	*anti*	*gauche*
$Mo\equiv Mo$	2.200(1)Å	2.196(1)	2.226(1)
Mo-N	1.95(1)	1.95(1)	1.944(4)
Mo-C	2,19(1)	2.156(1)	2.169(4)

These compounds react with alcohols according to the scheme

$$Mo_2R_2(NMe_2)_4 \; + \; R'OH \longrightarrow Mo_2R_2(OR')_4 \longrightarrow Mo_2R(OR')_5 \xrightarrow{\text{slow}} Mo_2(OR')_6$$

with the rates depending on the steric bulk of R and R'. [$Mo_2(Me)_2(O^tBu)_4$] reacts with py and the structure of the resulting adduct is shown in (116).



(116)

Bond distances are

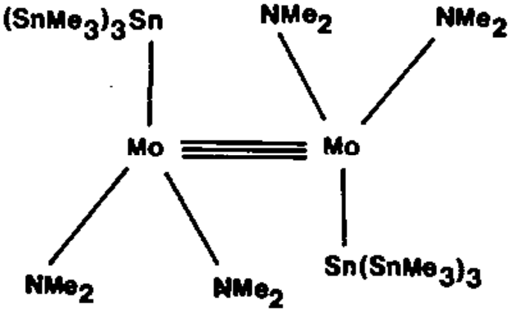
$Mo{\equiv}Mo = 2.256(1)$ Å $Mo{-}C = 2.167(7)$

$Mo{-}O = 1.92$ (av) $Mo{-}N = 2{,}349(6)$

The product of the reaction

$$[M_2Cl_2(NMe_2)_4] + 2Li[Sn(SnMe_3)_3] \longrightarrow [M_2\{Sn(SnMe_3)_3\}_2(NMe_2)_4] + 2LiCl$$

has been shown to have the usual *anti* configuration as shown in (117).



(117)

Bond distances are

$Mo{\equiv}Mo = 2.201(2)$ Å $Mo{-}Sn = 2.78$ (av)

$Mo{-}N = 1.95$ (av) $Sn{-}Sn = 2.78$ (av)

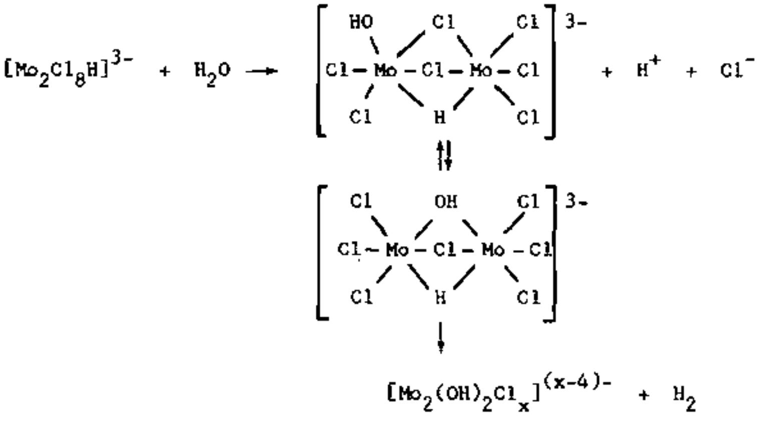
Spectroscopic measurements indicate formation of the analogous silicon derivatives [282].

Addition of 4-Mephenol (HOAr) to $Mo_2(NMe_2)_6$ surprisingly gave

$(NH_2Me_2)[Mo_2(OAr)_7(NHMe_2)_2]$ which was shown to have a biconfacial octahedral structure with the neutral $NHMe_2$ groups terminal and arranged to give overall C_2 symmetry. The Mo-Mo bond distance is similar to that in $[Mo_2Cl_9]^{3-}$ and, like that anion, this complex is slightly paramagnetic at room temperature. Bond distances are Mo-Mo = 2.601(2), Mo-O = 2.04 (av), Mo-μO = 2.11 (av) and Mo-N = 2.25Å (av) [283].

5.7.2 Quadruple bonded species of molybdenum(II) and tungsten(II)

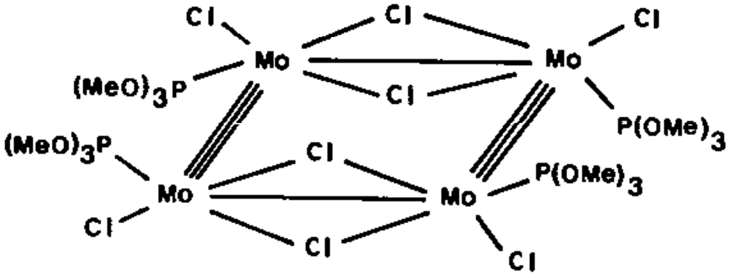
The kinetics of the reaction between $[Mo_2Cl_8]^{4-}$ and protons to produce the triply bridged species $[Cl_3MoCl_2HMoCl_3]^{3-}$ were studied as a function of concentration of HCl. The reaction is first order with respect to $[Mo_2Cl_8]^{4-}$. This reaction represents addition of a proton across the Mo-Mo quadruple bond, the breaking of metal-metal bonding and the formation of chlorine bridges. The hydride bridged complex then hydrolyzes through a series of observable steps [284].



$$\text{overall:- } [Mo_2Cl_8H]^{3-} + 2H_2O \longrightarrow [Mo_2(OH)_2Cl_x]^{(x-4)-} + H_2 + (8-x)Cl + H^+$$

The interaction of $K_4[Mo_2Cl_8]$ and $P(OMe)_3$ gives the tetranuclear complex $[Mo_4Cl_8\{P(OMe)_3\}_4]$. The four molybdenums form a rectangle whose larger sides are each bridged by two chlorines as shown in (118). The bond distances suggest triple bonds between the pairs of molybdenum atoms in the non-bridged sides of the rectangle and single bonds between the other pairs [285]. Bond distances are

Mo≡Mo = 2.26(1)Å   Mo-Mo = 2.878(1)
Mo-Cl = 2.392(2)   Mo-P = 2.506(1)
Mo-μCl(*trans* Cl) = 2.372(2)
Mo-μCl(*trans* P) = 2.441(2)



(118)

Na/Hg reduction of WCl_4 in thf in the presence of monodentate phosphines gives $[W_2Cl_4(PR_3)_4]$ which contain a quadruple metal-metal bond, and these react further with L-L = dppe and dmpe to give $[W_2Cl_4(L\text{-}L)_2]$. Also, the reduction of of $[W_2Cl_6(thf)_2]$ with Na/Hg gives deep blue, rather unstable, $Na_4[W_2Cl_8(thf)_x]$ [286].

The reaction of $[Mo_2Cl_4(PEt_3)_4]$ with dmpe in toluene gave the red-brown form of $[Mo_2Cl_4(dmpe)_2]$. A structural analysis shows two bridging dmpe groups with the usual type of coordination about each molybdenum, but the most significant feature of the structure is a twist of about 40° about the Mo-Mo quadruple bond to give an almost staggered configuration. The Mo-Mo distance of 2.183(3)Å is the longest known for a molybdenum compound in the $[Mo_2X_4(PR_3)_4]$ or $[Mo_2X_4(P\text{-}P)_2]$ series, and together with data (Mo-Mo bond lengths and twist angle χ) for $[Mo_2Cl_4(dppm)_2]$ and $[Mo_2Br_4(arphos)_2]$ gives a linear plot between Mo-Mo distance and cos 2χ (a measure of the δ overlap). A short extrapolation to $\chi = 45°$ (no δ bond) gives an estimate of the length of a true triple bond. It appears that a full δ bond decreases the Mo-Mo distance by 0.055(2)Å [287].

A series of arsine derivatives of Mo-Mo quadruple bonded species have been prepared, such as $[Mo_2X_4(AsEt_3)_4]$ (X = Cl,Br,NCS) and $[Mo_2(O_2CCF_3)_4(AsR_3)_2]$ (R = Et,Ph). ^{75}As NQR studies were carried out [288]. $[Mo_2Cl_4(AsEt_3)_4]$ and $[Mo_2Br_4(AsEt_3)_4]$ show reversible one-electron oxidations and controlled potential electrolyses at 0°C led to the formation of the corresponding cations. The thiocyanate complex $[Mo_2(NCS)_4(AsEt_3)_4]$ gave two one-electron oxidations, to give first the monocation and then the diamagnetic $[Mo_2(NCS)_4(AsEt_3)_4]^{2+}$ dication [288].

$[Mo_2(O_2CCF_3)_4]$ reacts with ($Bu_4N)X$ (X = Br,I) which leads to the isolation of $[Mo_2(O_2CCF_3)_4X_2]^{2-}$ and $[Mo_2(O_2CCF_3)_2Br_4]^{2-}$. The dihalo anions have two axial halides coordinated to the usual D_{4h} $[Mo_2(O_2CCF_3)_4]$ unit. The Mo-Mo bond distances (2.134(2) (Br) and 2.140(2)Å (I)) are significantly longer than in $[Mo_2(O_2CCF_3)_4]$ itself (2.090(4)Å. The tetrabromo adduct contains two *trans*

O_2CCF_3 groups and two *trans* bromo groups about each molybdenum to form a cubic arrangement about the Mo_2 core (Mo-Mo = 2.098(1)Å [289].

The kinetics of the reactions of $[Mo_2(H_2O)_8]^{4+}$, which contains a quadruple bond, with NCS^- and ox have been made to give comparisons with mononuclear aquo ions [290].

The gas phase core electron ionization energies of a series of Cr_2L_4 and Mo_2L_4 complexes are reported and there is a correlation between metal electron ionization energies and the large variation in metal-metal bond lengths. This conclusion is substantiated by *ab-initio* calculations [291]. An approach to multiple bonds, which regards them as single bonds intensified by screening of internuclear repulsions, has been applied successfully to multiply bonded Cr, Mo and W complexes [292].

The electronic spectra of $[Mo_2(O_2CCF_3)_4]$ and $[Mo_2(O_2CH)_4]$ have been measured at 10K in an inert matrix. Also, the Raman spectra of these compounds and $[Mo_2O_2CMe)_4]$ have been examined and, unlike the case for $[Mo_2Cl_8]^{4-}$, no resonance Raman enhancement was observed for the metal-metal vibration band. A theoretical treatment of the optical spectrum was also attempted [293]. Using the Raman spectrum of $[Mo_2(O_2CCF_3)_4]$, the fine details of the optical spectrum were calculated using a new time-dependent theory of electronic transitions. The agreement between theory and experiment is impressive. The excited state distortion of the Mo-Mo quadruple bond is much less than previously thought, being about 0.045Å [294].

$[W_2(O_2CCF_3)_4]$ has been obtained by the reaction of $[W_2Cl_4(thf)_2]$ with NaO_2CCF_3 in thf. It was not possible to obtain crystals suitable for a structural analysis, but the Raman spectrum (W-W stretch 310cm^{-1}) and the ^{183}W NMR chemical shift (δ 6760ppm) support the characterization. However, two adducts were examined by X-ray crystallography and both have the expected D_{4h} structure with axial coordination of the additional ligands. Bond distances are

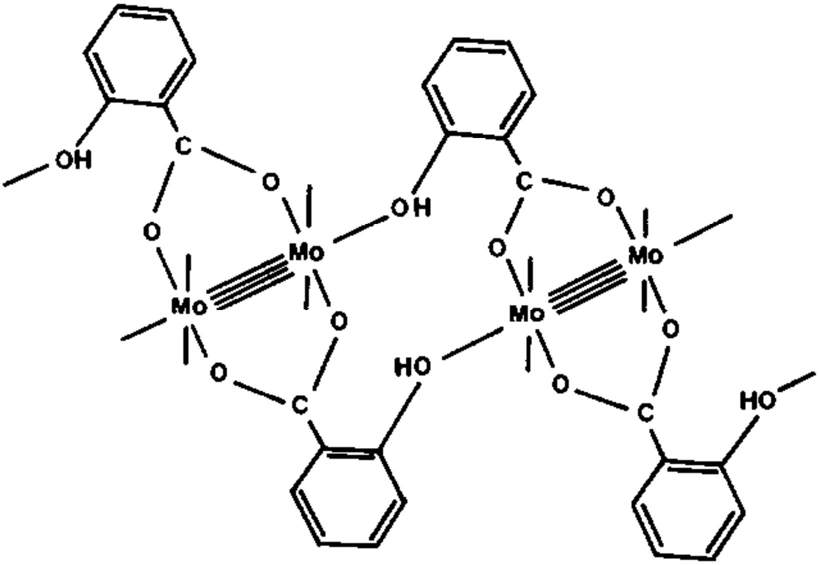
	$[W_2(O_2CCF_3)_4.\frac{1}{2}diglyme]$	$[W_2(O_2CCF_3)_4(PPh_3)_2]$
W≣W	2.209(2)Å	2.242(2)
W-O	2.087(4)	2.091(2)

The ^{95}Mo NMR spectra of $[Mo_2(O_2CCF_3)_4]$ (δ 4026ppm) and $[Mo_2(O_2C^nPr)_4]$ (δ 3730ppm) have been observed. They are the highest frequency molybdenum signals so far observed and very different to those of monomeric Mo(II) complexes [138].

Aqueous Mo_2^{4+} solutions react with D-mandelic acid to give yellow $[Mo_2(C_8H_7O_3)_4]$ which X-ray diffraction shows to have the usual eclipsed stereochemistry. The absolute configuration was determined and is in agreement with a previous conformation analysis by chemical methods. Mo-Mo = 2.103(2), and Mo-O = 2.119(4)Å [296].

$[Mo_2(O_2CMe)_4]$ reacts with concentrated solutions of arsenic acid in air and addition of pyH salts led to the isolation of $(PyH)_2[Mo_2(HAsO_4)_4].2H_2O$. A crystal structure determination showed the usual eclipsed configuration with the arsenate acting as a normal bridging ligand in the equatorial positions, but in addition, another oxygen of the arsenate acts as an axial ligand for a different dimer unit. Bond distances are Mo-Mo = 2.265(1), Mo-O(eq) = 2.00 (av) and Mo-O(axial) = 2.526(6)Å [297].

The structures of two adducts of binuclear molybdenum complexes containing salicylate ligands have been determined [298]. $[Mo_2(O_2CC_6H_4OH)_4.2diglyme]$ has a conventional structure with axial diglyme ligands. Bond distances are Mo-Mo = 2.101(1), Mo-O(eq) = 2.112(4) and Mo-O(axial) = 2.588(2)Å. However, the dichlorobenzene adduct $[Mo_2(O_2CC_6H_4OH)_4.o\text{-}C_6H_4Cl_2]$ shows a unique linkage between dimers through the OH group of the salicylate which acts as the axial group for the next dimer as shown in (119).



(119)

Bond distances are

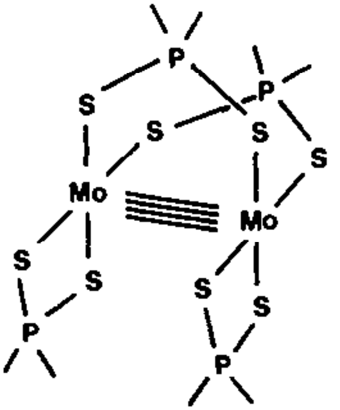
Mo≡Mo = 2.093(1)Å

Mo-O(eq) = 2.109(5)   Mo-O(ax) = 2.601(3), 2.645(3)

Aromatic dithiocarbamates, such as pyrrole dtc, react with $[Mo_2(O_2CMe)_4]$ to give $[Mo_2(dtc)_4.2thf]$ which are thought to retain the essential features of the $[Mo_2(O_2CMe)_4]$ structure [299]. Diorganophosphinodithiolates, $[S_2PR_2]^-$ (R = Et,Ph),form complexes of Mo(II) prepared by the reaction

$$K_4[Mo_2Cl_8] + 4S_2PR_2^- \longrightarrow [Mo_2(S_2PR_2)_4] + 4KCl + 4Cl^-$$

The structure of the complex (R = Et) has been determined and contains two bridging and two chelating ligands as shown in (120).



(120)

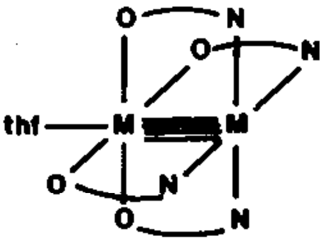
Bond distances

$Mo \equiv Mo = 2.137(1)$Å

$Mo-S(\mu-L) = 2.50$ (av) $Mo-S(chel) = 2.54$ (av)

Recrystallization of the complex from thf gives $[Mo_2(S_2PEt_2)_4.2thf]$ which has the usual quadruple bridged D_{4h} structure with a single axial thf ligand. This is an unusual isomerization and there appears to be an equilibrium dependent upon solvent [300].

Reaction of $[Mo_2(O_2CMe)_4]$ in thf with Li(fhp) (fhp = anion of 6-fluoro-2-hydroxy pyridine) or Na(thf) with WCl_4 in thf leads to the isolation of $[M_2(fhp)_4(thf)]$. The two compounds are isostructural and the structure is unprecedented in that all the asymmetric bridges are oriented the same way so that one metal is coordinated by four nitrogens and the other by four oxygens and an axial thf as shown in (121) [301].



(121)

Bond lengths are

	Mo	W
M≣M	2.092(1)	2.185(2)
M-O(fhp)	2.077(2)	2.06(1)
Mo-O(thf)	2.528(5)	2.49(2)
M-N	2.164(3)	2.15(1)

The reaction

$$\begin{tikzcd} {[Mo_2(O_2CH)_4] + 4TFMS} \arrow[r] & {[Mo_2(H_2O)_4(TFMS)_4](TFMS)_2} \arrow[d, "8\ MeCN"] \\ & {[Mo_2(MeCN)_8](TFMS)_4} \end{tikzcd}$$

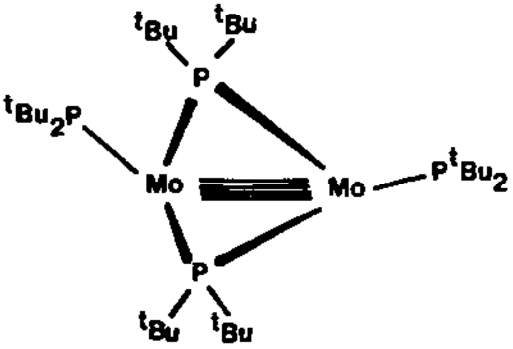
(HTFMS = trifluoromethane sulphonic acid)

leads to the first example of a quadruple bonded dimer in which all the ligands are non-charged [302].

Reaction of four equivalents of Li(^{t}Bu$_2$P) with [Mo$_2$(O$_2$CMe)$_4$] in ether at -78°C gives [Mo$_2$(^{t}Bu$_2$P)$_4$] as red crystals. A crystal structure analysis revealed the structure (122) in which two phosphides bridge to give a butterfly arrangement and two terminal phosphides complete a planar arrangement about each molybdenum atom. There is also a planar arrangement about the terminal phosphides, suggesting some involvement of π-bonding [303]. Bond distances are

Mo≣Mo = 2.209(1)

Mo-P(μ-L) = 2.434(1) Mo-P(terminal) = 2.382(1)



(122)

5.7.3 *Hexameric clusters*

The cluster ions $[Mo_6Cl_{14}]^{2-}$, $[Mo_6Br_{14}]^{2-}$ and $[W_6Cl_{14}]^{2-}$ are luminescent and life times and quantum yields have been measured. All these clusters undergo reversible one-electron oxidations and controlled potential electrolysis in CH_2Cl_2 gave the anions $[M_6X_{14}]^-$ which are paramagnetic [304]. The elctronic structures of the clusters $[Mo_5Cl_{13}]^{2-}$ and $[Mo_4I_{11}]^{2-}$ (derived from the $[(Mo_6X_8)X_6]$ structure) have been investigated by MO methods. There is a single bond between each pair of molybdenum atoms in $[Mo_5Cl_{13}]^{2-}$ (8 Mo-Mo bonds in total), but no bonding occurs between the wing tip molybdenums in the butterfly shaped Mo_4 core in $[Mo_4I_{11}]^{2-}$ [305].

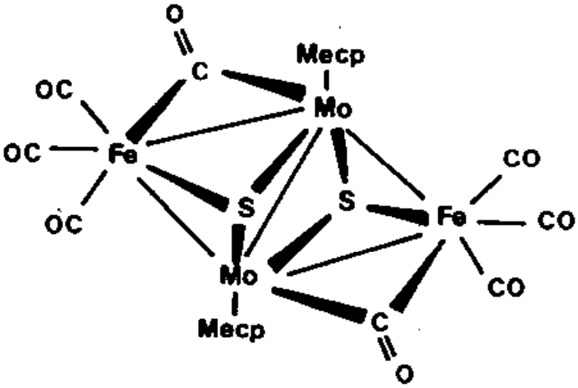
A heterogeneous reaction between $[(Mo_6Cl_8)Cl_4(H_2O)_2]$ (containing H_2O molecules in the *trans* positions) and $(AsPh_4)Br$ in HBr solution yields $(AsPh_4)_2[(Mo_6Cl_8)Cl_4Br_2]$. A crystallographic analysis confirmed *trans* bromine ligands, Mo-Mo = 2.600(1) - 2.614(1)Å [306].

A new type of Mo(II) complex $[Mo_6Br_8S_2]$ and $[Mo_6I_8Y_2]$ (Y = S,Se) has been characterized by an X-ray structural determination of $[Mo_6I_8Se_2]$. The structure contains chains of $[Mo_6(I_5Se)Se_{2/2}]$ units linked by Se bridges in *trans* positions across the clusters. The (I_5Se) atoms are disordered [307]. The structure of $[Mo_6Br_6S_3]$ has been determined. It contains octahedral clusters of molybdenum atoms of the form $[Mo_6Br_4S_2S_{2/2}]Br_{4/2}$ and can be regarded as a layer lattice. Bond distances are Mo-Mo = 2.66 (av), Mo-S = 2.396(8) - 2.496(8), Mo-Br = 2.61Å [308]. The compounds $M'[Mo_6X_8]$ (X = S,Se) contain (Mo_6X_8) clusters and the position of the ternary atom depends upon its size. The systems $Yb[Mo_6X_8]$ - $La[Mo_6X_8]$ have been investigated to determine the effects on the crystal structure parameters and superconducting properties by replacing Yb by La [309]. Similarly, the effect on crystallographic parameters by replacing S by Se have been examined in the series $M'[Mo_6(S_{(1-x)}Se_x)_8]$

(M' = La,Sm,Eu,Yb,Pb,Ag; $0 < x < 1$). The hexagonal ratio c/a shows a minimum when plotted against x due to a strong preference by Se for the general position chalcogen site, rather than the special site on the three fold axis preferred by S [310]. A molecular orbital and crystal orbital study of Mo_6X_8, Mo_9X_{11} and $Mo_{12}X_{14}$ (X = S,Se,Te) (the Chevrel phases) has been carried out and all the modes of packing of the clusters into crystals is rationalized in terms of cluster frontier orbitals [311].

5.7.4 Molybdenum-iron complexes

A review has appeared on EPR, XAS and EXAFS studies on the molybdenum hydroxylases and model compounds for these systems [312]. Reaction of $[RMo(CO)_2]_2$ (R = cp,Mecp) and $[FeS(CO)_3]_2$ generates two isomeric molybdenum-iron sulphur clusters with different $Mo_2Fe_2S_2$ skeletons. One product (80%) is the previously characterized $[R_2Mo_2Fe_2(\mu_3\text{-}S)_2(\mu_3\text{-}CO)_2(CO)_6]$ with the butterfly arrangement expected for a 62 electron cluster. The other product (20%) is a centrosymmetric cluster with a planar Mo_2Fe_2 skeleton shown in (123) which apparently violates electron counting rules [313].



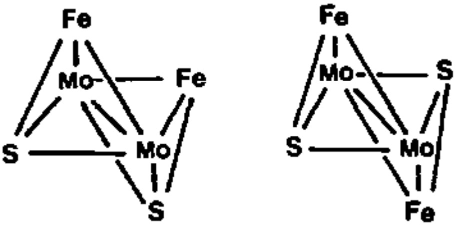
(123)

Bond distances are

Mo-Mo = 2.282(1)Å   Mo-Fe = 2.776(11), 2.805(1)

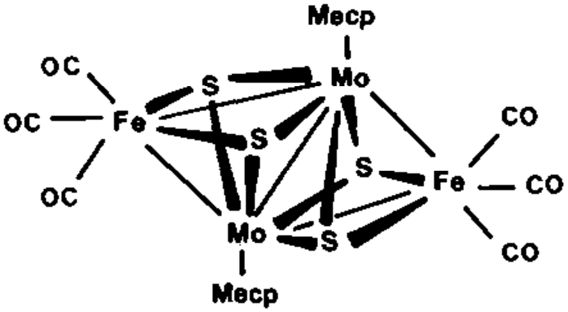
Mo-μCO = 2.025(6)   Mo-S = 2.344(1), 2.381(2)

It was noted that it is unusual to have two isomeric clusters with different metal skeletons and apparently different oxidation states. However, it was quickly pointed out [314] that if both isomers were considered as hexameric $Mo_2Fe_2S_2$ clusters as shown in (124) then both isomers are electron precise clusters.



(124)

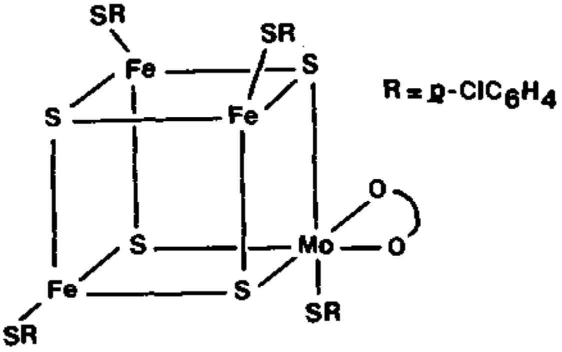
Reaction of $[(Mecp)Mo(\mu-S)(\mu-SH)]_2$ with $Fe(CO)_5$ in the presence of Me_3NO gives $[(Mecp)MoS_2Fe(CO)_3]$ which X-ray diffraction showed to have the structure (125). The structure is similar to (123), the main difference being the replacement of μ_2-CO by μ_3-S [315].



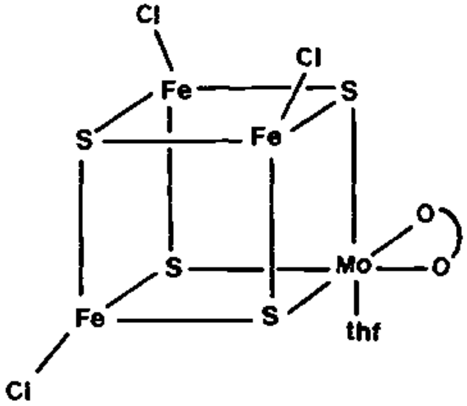
(125)

The interaction of $[cp'_2Mo_2S_4]$ ($cp' = C_5Me_5$) with $(Ph_3PNPPh_3)[Fe(NO)(CO)_3]$ yields $[cp'_2Mo_2Fe_2S_4(NO)_2]$ which is thought to contain a cubane type $Mo_2Fe_2S_4$ core. Although no crystallographic data was obtained, IR, mass spectral and analytical data all support this formulation. It is thought this may be a general way of preparing Mo to Fe, Co or Rh bonds [316].

The doubly bridged cubanes $[Mo_2Fe_6S_8(SR)_6(R'_{3,6}\text{-cat})_2]^{4-}$ ($R'_{3,6}$-cat = 3,6-disubstituted catechol) react with coordinating solvents to give solvated simple cubanes $[MoFe_3S_4(SR)_3(R_{3,6}\text{-cat})solv]^{2-}$ which themselves may undergo thiolate exchange or replacement with halide and solvent displacement with ligands L such as $p\text{-ClC}_6H_4S^-$, PhO^-, CN^-, PEt_3 etc. The crystal structures of two such clusters, $(NEt_4)_2[MoFe_3S_4(S\text{-}p\text{-}C_6H_4Cl)_4\{(C_3H_5)_2\text{-cat}\}]$ (126) and $(NEt_4)_2[MoFe_3S_4Cl_3\{(C_3H_5)_2\text{-cat}\}(thf)]$ (127) have been determined [317, 318].



(126)



(127)

Bond distances are

	(126)	(127)
Mo-Fe	2.76Å (av)	2.78 (av)
Mo-μ_3S	2.38 (av)	2.36 (av)
Fe-μ_3S	2.27 (av)	2.28 (av)
Mo-O(cat)	2.08	2.045
Mo-SR	2.600(3)	
Mo-O(thf)		2.352(6)

The solvated clusters are fluctional due to coordinated solvent exchange; they also undergo reversible one-electron reductions and the reduced clusters are readily isolated [317].

The electronic properties of $[MoFe_3S_4(SR)_3(R'_{3,6}\text{-cat})(solv)]^{2-,3-}$, $[MoFe_3S_4(SR)_4(R'_{3,6}\text{-cat})]^{3-}$ and the double cubane $[Mo_2Fe_6S_8(SR)_6(R'_{3,6}\text{-cat})]^{4-}$ have been investigated by Moessbauer, EPR and magnetic studies [319]. The oxidized single cubanes are electronically delocalized anti-parallel spin-coupled clusters ($S = 3/2$) and the reduced simple cubanes are similar with an $S = 2$ ground state. Moessbauer studies indicate that it is mainly the iron atom which is effected by the electronic changes. The double cubane exhibits sub-cluster spin pairing to give a singlet ground state [319].

The Mo and Fe EXAFS spectra of $(NBu_4)_3[Mo_2Fe_6S_8(SEt)_9]$, $(NEt_4)_3[Mo_2Fe_6S_9(SEt)_8]$ and $(Et_3NCH_2PPh_2)[Mo_2Fe_6S_8(SEt)_3(OPh)_6]$ have been examined. The important result is that in their Fe EXAFS spectra they show no back scattering due to neighbouring Mo and Fe atoms, which is explained in terms of cancellation of the Fe-Fe and Fe-Mo waves due to phase differences. However, this shows the complexes are not good models for the EXAFS of the Fe-Mo cofactor of nitrogenase [320].

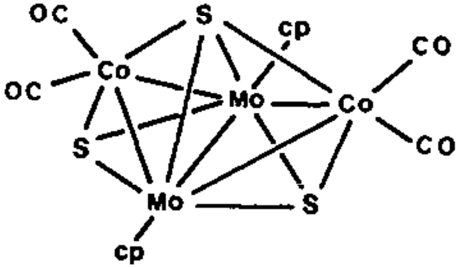
In the presence of the clusters $[Mo_2Fe_6S_8L_9]^{3-}$ ($L = SPh, SCH_2CH_2OH$) N_2H_4 can be catalytically reduced to NH_3 by controlled potential electrolysis at -1.30V vs SCE [321] and azide ion is reduced under similar conditions to NH_3, N_2 and H_2 with the formation of both N_2H_2 and N_2H_4 as intermediates [322]. The reduced clusters $[Mo_2Fe_6S_8(SPh)_9]^{4-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{5-}$ evolve H_2 from benzene thiol in NN'dma at room temperature [323].

5.7.5 Miscellaneous metal-metal bonded species

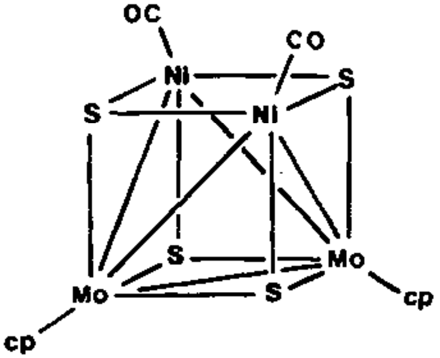
A facile synthesis of $[cp_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2]$ and its reactions with metal carbonyls to give heterobimetallic compounds has been reported. Reaction with $Fe(CO)_5$ gives $[cp_2Mo_2S_2Fe_2(CO)_6]$ whose structure (123) has already been described. $Co_2(CO)_8$ gives $[cp_2Mo_2S_3Co_2(CO)_4]$ which has the butterfly structure (128) containing a rare μ_4-S atom in the fold of the butterfly with the μ_3-S atoms capping the Mo_2Co faces [324]. Bond distances are

Mo-Mo = 2.646Å	Mo-Co = 2.64 (av)
Mo-μ_4S = 2.390	Co-μ_4S = 2.239
Mo-μ_3S = 2.362	Co-μ_3S = 2.199

With $Ni(CO)_4$, $[cp_2Mo_2S_2(SH)_2]$ reacts to give $[cp_2Mo_2(\mu_3\text{-}S)_4Ni_2(CO)_2]$ whose structure (129) may be regarded as a cubane type with five metal-metal bonds, or alternatively as a butterfly with Ni at the wing tips [324].



(128)



(129)

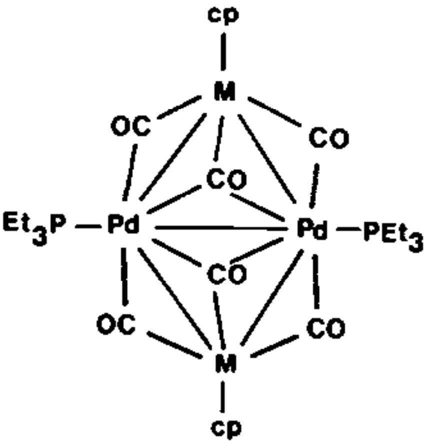
Bond distances are

Mo-Mo = 2.829(1)Å Mo-Ni = 2.722

Ni-S = 2.158 Mo-S = 2,28 (av)

Ni...Ni = 2.962(2)

A new class of M-Pd bonded clusters of the type $[cp_2M_2Pd_2(\mu_3\text{-}CO)_2(\mu_2CO)_4(PR_3)]$ have been synthesized by the action of the phosphine on $[cpM(CO)_3]_2Pd(PhCN)_2$. Crystal structure determinations on the PEt_3 complexes showed them to be isostructural as shown in (130). The metals form a triangulated parallelogram with two carbonyls on each Group VI metal semi-bridging to one palladium while the third is semi-bridging to both palladium atoms [325].

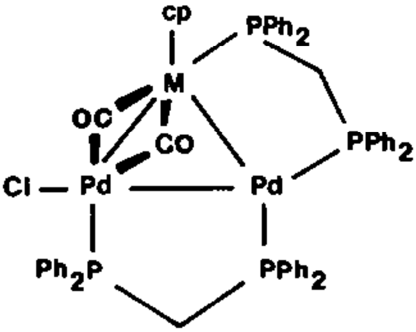


(130)

Bond distances are

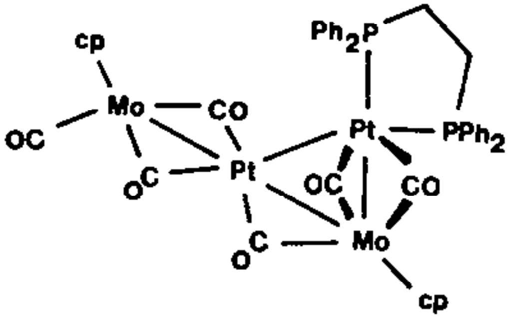
	M = Mo	M = W
Pd-Pd	2.582(1)Å	2.573(3)
Pd-M	2.827(1)	2.829(1)
M-μ_2CO	1.98(1)	1.97(1)
M-μ_3CO	2.04(2)	2.05(2)

The reaction between $[PdCl(dppm)]_2$ and $[cpM(CO)_3]^-$ yielded a complex which appears to have the structure shown in (131) that is, insertion of a $[cpM(CO)_3]$ fragment into a Pd-P bond has occurred [326].



(131)

In contrast, reaction of dppe with *trans*-$[Pt\{cpMo(CO)_3\}_2(PhCN)_2]$ gives a complex with the remarkable structure (132) in which Mo_1 has all its carbonyls semi-bridging while Mo_2 has one terminal carbonyl while the platinum atoms are also completely non-equivalent. The Pt-Mo distances are the shortest known [326].



(132)

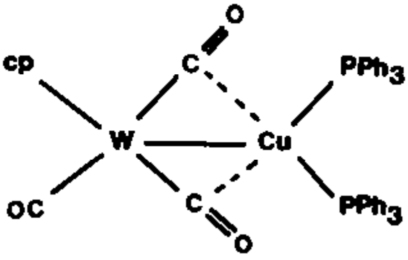
Bond distances are

Pt_1-Mo_1 = 2.721(2)Å
Pt_2-Mo_1 = 2.773(3)
Pt_2-Mo_2 = 2.651(4)

The structures of the compounds prepared by the reaction

$$[Cu(PPh_3Cl]_4 \ + \ Na[cpM(CO)_3] \ \longrightarrow \ [cpMCu(CO)_3(PPh_3)_2]$$

have been determined by X-ray diffraction. There are two forms of the tungsten complex which differ in the strengths of the interactions between the carbonyls and copper, but the basic structure is as shown in (133)[327].



(133)

In both forms the W-Cu bond lengths are rather long (2.721(1) and 2.771(1)Å). The crystal structure of [cpMo(CO)$_2$(AsMe$_2$Ph)(HgCN)] showed the molybdenum atoms to have square pyramidal stereochemistry (cp apical) and the carbonyls *trans* to each other. The Mo-Hg-C-N unit is linear with Mo-Hg = 2.654(11)Å, which is the shortest Mo-Hg bond length observed so far [328].

ACKNOWLEDGEMENTS

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