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2. MOLYBDENUM AND TUNGSTEN[†]

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CONTENTS

INTRODUCTION

The review on molybdenum and tungsten chemistry this year deals with the inorganic and coordination chemistry of the elements which was cited in Chemical Abstracts, Volumes 102 and 103. Thus most of the work published in 1985 and some published towards the end of 1984 will be reviewed. Organometallic chemistry, including carbonyl chemistry, is not formally included in the review, but reference is made to some papers of general

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interest.

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

2.1 MOLYBDENUM(VI) AND TUNGSTEN(VI)

2.1.1 Halides and halo complexes

Force fields and mean amplitudes of vibration have been calculated for MF_6 and MO_2F_2 (M = Cr,Mo,W). The agreement between calculated and experimental data was good [1]. WF_6 reacts with F^-, Cl^-, Br^-, I^-, NO_3^-, NO_2^-, SF_5^- and SF_6^- in the gas phase and rate coefficients and branching ratios have been determined. The measurements indicated that the electron affinity of WF_6 is 3.3(+0.04,-0.2)eV [2].

High yields of pure MOF_4 are obtained by the interaction of MF_6 and SiO_2 at 120°C. The advantage of the method is the volatility of SiF_4 [3]. Compounds containing the $[NTeF_5]^{2-}$ group have been prepared by the reaction

$$2Me_3SiN(H)TeF_5 + MF_6 \longrightarrow 2Me_3SiF + H_2NTeF_5 + F_4M{=}NTeF_5$$

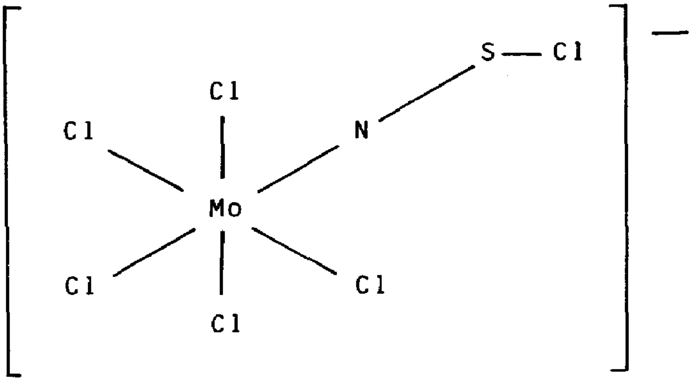
With the molybdenum compound, reaction with BCl_3 gave $Cl_4Mo{=}NTeF_5$. The compounds were characterized by IR, mass spectral and ^{19}F NMR studies [4].

$Ba_2[MO_3F_4]$ compounds have been prepared as single crystals (W) or as a powder (Mo). Crystallographic studies showed the compounds to be $Ba_2[MO_{2/2}O_2F_2]F_2$ with the structure containing chains of the linked anion units. IR and Raman spectra were reported [5].

Fluoro complex formation by tungsten(VI) in solutions containing H_2O_2 and F^- have been studied using a fluoride selective electrode. All the tungsten complexes contained a single peroxo group and the predominant species observed were the mono- and trifluoro derivatives. The formation constants lie in the ranges $4.84 \times 10^4 \leqslant \beta_1 \leqslant 7.15 \times 10^4$ and $1.96 \times 10^{12} \leqslant \beta_3 \leqslant 3.52 \times 10^{12}$ with β_2 and β_4 being negligibly small [6].

The chlorination of WO_3 and tungstates gives mixtures of $WOCl_4$ and WO_2Cl_2 which are difficult to separate. It has now been found that they can be easily separated by extraction with Et_2O since $WOCl_4$ is very soluble and WO_2Cl_2 is almost insoluble. After filtration, evaporation of the solvent gave pure $WOCl_4$ [7].

Interaction of either $MoCl_5$ or $MoCl_4$ with $(NSCl)_3$ in dichloromethane solution gave a mixture of $MoCl_3(N_3S_2)$ and $[N(SCl)_2][MoCl_5(NSCl)]$. Black crystals of the latter complex were characterized by X-ray diffraction and the structure of the anion is shown in (1).



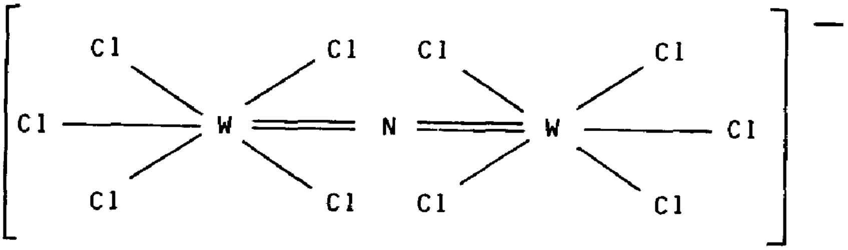
(1)

Bond distances are

Mo-N = 1.75
Mo-Cl(*trans* N) = 2.47   Mo-Cl = 2.32-2.37
N-S = 1.59   S-Cl = 2.03Å

The Mo-N-S unit is linear and the bond lengths suggested double bonding [8].

WCl_6 and $(Me_3Si)_3N$ react to give W_2NCl_9 which on the basis of IR data is dimeric with chloro bridges. However, on reaction with $(PPh_4)Cl$ it gives $(PPh_4)[W_2NCl_{10}]$ which was shown by X-ray diffraction to have the structure (2).



(2)

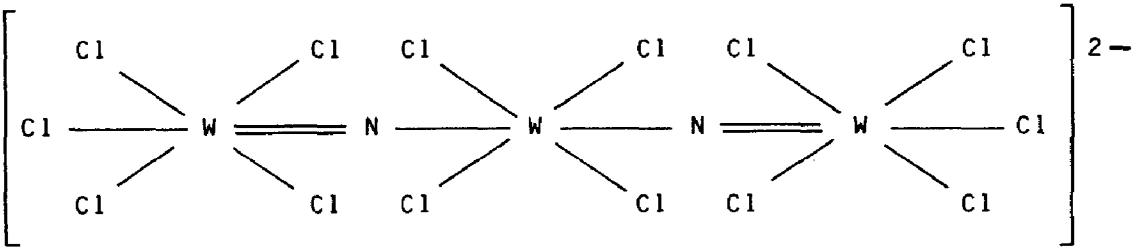
Bond distances are

$$\mathrm{W{=}N} = 1.79(2),\ 1.88(2)$$
$$\mathrm{W{-}Cl}(\textit{trans}\ \mathrm{N}) = 2.367(6),\ 2.399(6)$$
$$\mathrm{W{-}Cl}(\textit{cis}\ \mathrm{N}) = 2.276(6){-}2.316(6)\,\text{Å}$$

The W-N-W unit is linear and the bond lengths suggest double bonding [9]. A solution of $(PPh_4)[W_2NCl_{10}]$ in CH_2Cl_2 and CCl_4 slowly forms crystals of $(PPh_4)_2[W_3N_2Cl_{14}].CH_2Cl_2.CCl_4$ by the reaction

$$2[W_2NCl_{10}]^- \longrightarrow [W_3N_2Cl_{14}]^{2-} + WCl_6$$

The remarkable structure of the anion in this compound is shown in (3). There are almost linear but highly asymmetric nitrido bridges with W-N bond lengths corresponding to single and double bonds. The equatorial WCl_4 units are in the eclipsed configuration [10].



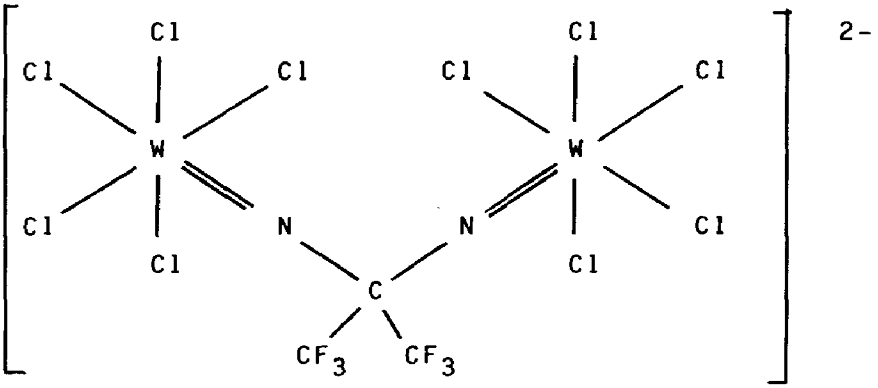
(3)

Average bond distances are

$\mathrm{W{=}N} = 1.835$ $\quad$ $\mathrm{W{-}N} = 2.065$

$\mathrm{W{-}Cl}(\textit{trans}\ \mathrm{N}) = 2.40$ $\quad$ $\mathrm{W{-}Cl}(\textit{cis}\ \mathrm{N}) = 2.31\,\text{Å}$

The interaction of WCl_3N and $(CF_3)_2CO$ in MeCN in the presence of catalytic quantities of NEt_3 led to the formation of $[(WCl_5)_2\ \mu\text{-}NC(CF_3)_2N\ ]^{2-}$ which was isolated as its $(AsPh_4)^+$ salt. The structure of the anion is shown in (4). The W-N-C unit is almost linear and there may be triple bond character in the W-N linkage [11].



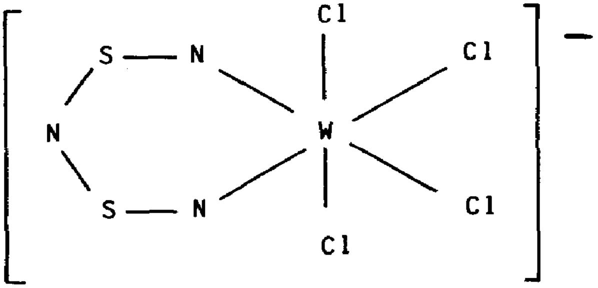
(4)

Bond distances are

W=N = 1.743(15) C-N = 1.415(22)

W-Cl(*trans* N) = 2.437(7) W-Cl(*cis* N) = 2.304(9)-2.326(8)Å

Two groups [12,13] have reported that dark brown cyclothiazen, $[N_3S_2]^-$, complexes $[MCl_3(N_3S_2)]_2$ are made by the interactions of $MoNCl_3$ and $WOCl_4$ with $(NSCl)_3$. According to IR data, the molybdenum compound is bridged by chloro groups and the tungsten complex is associated through the γ-nitrogens of the ligand. Both compounds react with $(AsPh_4)Cl$ to give $(AsPh_4)[MCl_4(N_3S_2)]$ and the structure of the tungsten compound was determined [12] by X-ray diffraction and is shown in (5). The WN_3S_2 unit is planar and the W-N distances correspond to double bonds.



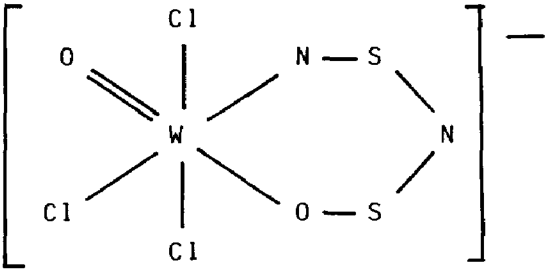
(5)

Bond distances are

W-N = 1.85(av) N-S = 1.54-1.61

W-Cl(*trans* N) = 2.44 W-Cl(*cis* N) = 2.39Å(av)

Reaction between (AsPh$_4$)[Cl$_4$W C Bu] and S$_4$N$_4$ in dichloromethane gave brown crystals of (AsPh$_4$)[WCl$_4$(N$_3$S$_2$)] described above and red crystals of (AsPh$_4$[WOCl$_3$(OS$_2$N$_2$)] which could be separated by hand picking. A structure determination on the latter compound revealed the stereochemistry shown in (6). The WNSNSO ring is planar and the W-N bond length corresponds to a double bond [14].

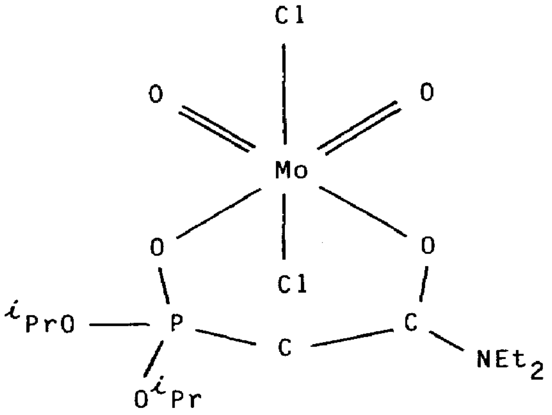


(6)

Bond distances are

W-N = 1.833(4)
W=O = 1.699(3)   W-O = 2.288(3)
W-Cl(*trans* N) = 2.406(1)   W-Cl(*cis* N) = 2.381(1)Å

MoO$_2$Cl$_2$ reacts with diisopropyl(N,N-diethylcarbamyl)methylenephosphate, (^{i}PrO)$_2$P(O)CH$_2$C(O)NEt$_2$, to give the 1:1 adduct whose structure is shown in (7) [15].



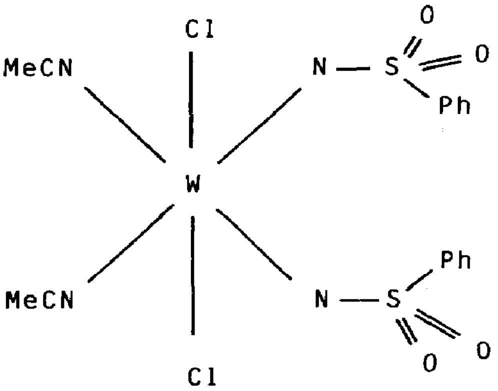
(7)

Average bond distances are

Mo=O = 1.682 Mo-O = 2.233

Mo-Cl = 2.380Å

N,N-dichlorophenylsulphonamide reacts with $W(CO)_6$ in refluxing CCl_4 to give polymeric $[(PhSO_2N)_2WCl_2]_x$ which on dissolution in MeCN gave crystals of monomeric $(PhSO_2N)_2WCl_2(MeCN)_2$ the structure of which is shown in (8) [16].



(8)

Average bond distances are

W-N(nitrene) = 1.775 W-N(MeCN) = 2.226

W-Cl = 2.335Å

The W-N(nitrene) bond distance is surprisingly long.

2.1.2 *Oxides, molybdates and tungstates*

The standard molar enthalpies of $WO_3.2H_2O$ and $WO_3.H_2O$ have been determined by solution calorimetry to be -(1430.1±1.0) and $-(1133.0\pm1.0)kJmol^{-1}$ respectively at 298.15K [17]. The sublimation of WO_3 has been investigated by the Knudsen effusion technique with mass spectral analysis. The vapour consists mainly of W_3O_9 and W_4O_{12} with W_2O_6 and W_3O_8 present as minor species [18]. The laser Raman spectrum of WO_3 has been reported and assigned on the basis of C_{3v} symmetry [19].

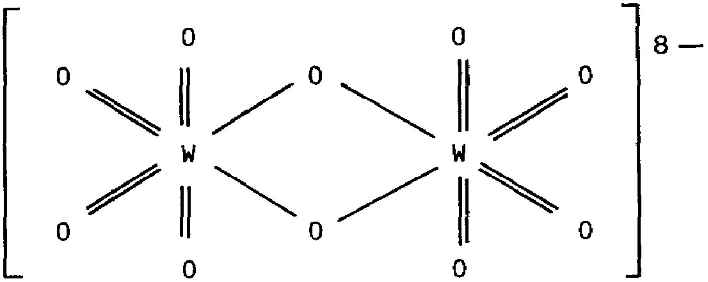
Co-condensation of MoO_3 vapour with MeOH at -196°C gives $Mo_2O_5(OMe)_2.2MeOH$ and photolysis of the slurry of the condensate in MeOH under O_2 gave $(MeO)_2CH_2$

in a slow catalytic conversion. Similar co-condensation of MoO_3 with H_2O gave a new form of $MoO_3.2H_2O$ [20].

It has been shown that ^{95}Mo NMR spectroscopy may be a viable probe for biochemical systems by examining the ^{95}Mo NMR spectra of $[MoO_4]^{2-}$ and $[MoS_4]^{2-}$ bound to bovine serum albumin [21].

Manganese molybdates were prepared by precipitation from aqueous solution. The yellow precipitate was transformed at 60-100°C into other more crystalline products depending upon the pH of the solution. At pH 7-8 the product obtained was $MnMoO_4.H_2O$ and its structure consists of tetrahedral molybdate and octahedral Mn(II) units in which the tetrahedra share corners with four different octahedra with water coordinated to manganese. At higher temperatures all the hydrates transform to α-$MnMoO_4$ [22].

Single crystals of $Na_6Li_2[W_2O_{10}]$ have been prepared by annealing mixtures of WO_3, Na_2O and Li_2O (W:Na:Li = 1:3:1) at 840°C for 60 days. An X-ray diffraction study revealed discrete $[W_2O_{10}]^{8-}$ anions with the structure shown in (9) with slight asymmetry in the oxo bridges [23].



(9)

Bond distances are

$$W{=}O = 1.809\text{-}1.916 \qquad W\text{-}\mu O = 2.024,\ 2.164\text{Å}$$

The correlation between bond length and valence has been applied to phosphate tungsten bronzes and other mixed valence tungsten oxides and led to estimates intermediate between 5 and 6 for the valences. This is in accord with physical measurements which indicate *d*-electron delocalization [24].

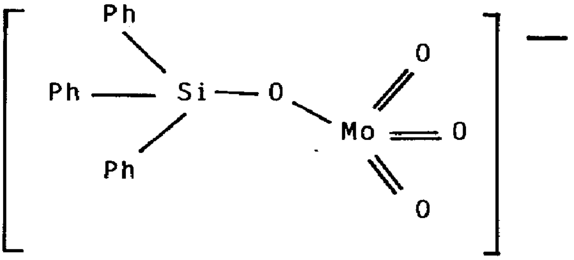
A new reddish brown diphosphate tungsten bronze $Cs[P_8W_8O_{40}]$ has been synthesized. The structural framework can be described as 2 x 2 WO_6 octahedral columns of the ReO_3 type extending indefinitely along [001] connected by P_2O_7 groups. Relationships with the mono phosphate bronzes are discussed [25].

Potassium vapour has been reacted directly with WO_3 crystals in an attempt to prepare tungsten bronzes by this method. Attack on the oxide was extensive, but only limited compound formation was observed under the conditions employed (200-900°C for 0.25-168h) [26].

The interaction of R_3SiOH (R = Ph, ^{t}Bu) with the $[Mo_2O_7]^{2-}$ ion gave the following reaction

$$2R_3SiOH + (NBu_4)_2[Mo_2O_7] \longrightarrow 2(NBu_4)[R_3SiOMoO_3] + H_2O$$

A structural study of the salt with R = Ph confirmed the structure of the anion as in (10) [27].



(10)

Bond distances are

$$Mo{=}O = 1.699(av) \qquad Mo{-}\mu O = 1.884(4)Å$$

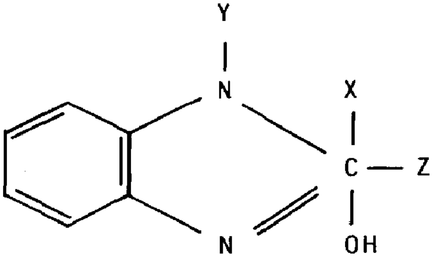
$[Mo_2O_7]^{2-}$ also reacts with $(Me_3Si)_2S$ in MeCN to give progressively $[MoO_{3-x}S_x(OSiMe_3)]^-$. The reaction sequence was followed by visible absorption, ^{95}Mo and ^{17}O NMR spectroscopies. The structure of the final product $[MoS_3(OSiMe_3)]^-$ was determined and is very similar to that of its analogue shown in (10). Bond distances are Mo=S = 2.154(6), Mo-μO = 1.881(7)Å [28].

2.1.3 Monomeric oxo complexes

A general review of seven coordinate structures in molybdenum chemistry has appeared [29]. It covers all oxidation states of the metal and includes the structures of a number of oxo complexes of Mo(VI).

Complex formation between tungstate and *l*(-)malic acid has been investigated by polarimetric, cryoscopic and ^1H NMR methods. All the species observed are thought to be oxo complexes. At high pH (>7) the stable complex is monomeric, but at lower pH's dimeric species predominate [30]. Similar reactions between tungstate and thiomalic acid at pH 2-7 have been conducted by a different group using ^1H and ^{13}C NMR spectroscopies. A number of oxo complexes containing two thiomalate ligands were identified [31].

Reaction of $MoO_2(acac)_2$ with a series of 2α-hydroxybenzimidazoles (L) **(11)**



(11)

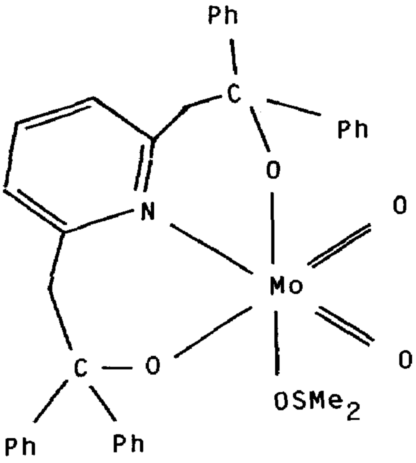
gave MoO_2L_2. A crystal structure determination on the compound with X = H, Y = H and Z = Ph showed the ligand to be chelating through the imino nitrogen and the alkoxy oxygen. The stereochemistry about molybdenum is octahedral with the imino nitrogens *trans* to the *cis* oxo groups. Bond distances were not given. The ^{95}Mo NMR spectra were recorded for all the complexes and they fall within the previously established range for *cis* dioxo complexes of Mo(VI) with two nitrogen and two oxygen donor atoms [32]. Similar studies with 2-*o*-hydroxyphenylbenzimidazoles revealed a different structure. In this case one oxygen and one nitrogen from different ligands in MoO_2L_2 are *trans* to the two *cis* oxo groups. Bond distances are Mo=O = 1.70(av), Mo-O = 1.938(5) and 2.059(4), Mo-N = 2.142(5) and 2.325(5)Å with the longer distances in each case *trans* to the oxo group. It was suggested that steric effects force the different structural arrangement in this case [33].

The compounds *cis*-$WO_2(R_2NO)_2$ (R = Et,bz) were prepared from WO_2Cl_2 and the appropriate N,N-dialkylhydroxylamine in dichloromethane in the presence of NEt_3

$$WO_2Cl_2 + 2R_2NOH + 2NEt_3 \longrightarrow WO_2(R_2NO)_2 + 2(Et_3NH)Cl$$

The corresponding dithio (mixed with monooxomonothio) complexes were prepared by reaction with B_2S_3 and separation was achieved by chromatography and recrystallization. The complexes gave IR spectra very similar to those of their molybdenum analogues and their ^{183}W chemical shifts were recorded [34].

The sterically demanding ligands 2,6-bis(2,2'-diphenyl-2-hydroxyethyl)-pyridine, $LN(OH)_2$ and its sulphur analogue $LN(SH)_2$ have been prepared and reacted with $MoO_2(acac)_2$ in dmso to give $MoO_2(LNO_2)(dmso)$ and $MoO_2(LNS_2)$ respectively. The structures of both compounds were determined and are shown in **(12)** and **(13)**.



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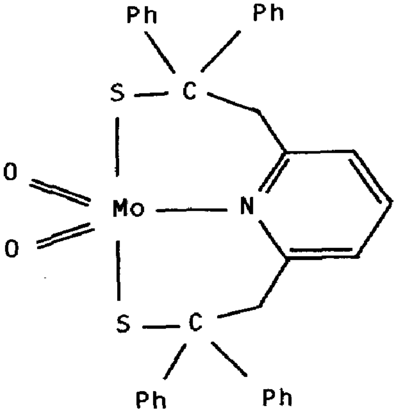


(13)

Bond distances are

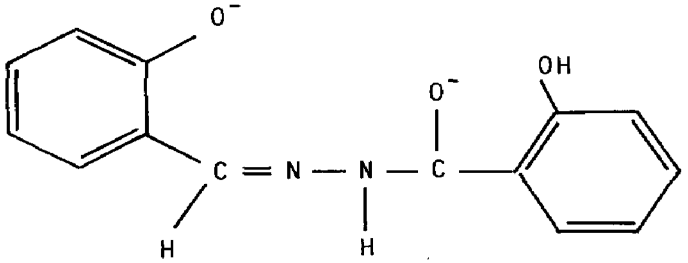
	MoO$_2$(LNO$_2$)(dmso)	MoO$_2$(LNS$_2$)
Mo=O	1.705(4)	1.694(6)
Mo-O	1.902(3)	
Mo-S		2.415(2)
Mo-N	2.417(4)	2.244(7)
Mo-O(dmso)	2.382(7)Å	

The bond to dmso in MoO$_2$(LNO$_2$)(dmso) is long, implying lability. MoO$_2$(LNS$_2$) is the first five coordinate Mo(VI) complex and the geometry is approximately trigonal bipyramidal. Electrochemical properties of both compounds are also reported [35].

The complexes $MoO_2(LNS_2)$ and $MoO(LNS_2)$ are useful models for oxo transfer molybdoenzymes [36]. $MoO_2(LNS_2)$ reacts with PPh_3 to yield $MoO(LNS_2)$ and PPh_3O. Oxo transfers to and from substrates have been coupled to produce a catalytic system which turns over the reaction

$$Me_2SO + PPh_3 \longrightarrow Me_2S + PPh_3O$$

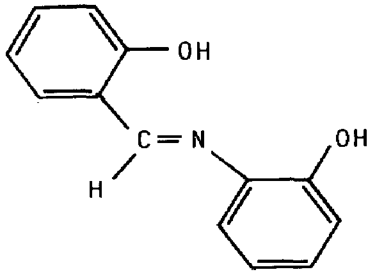
The Schiff base (sal-shz) (14)derived from salicylaldehyde and



(14)

salicylhydrazide is known to form $MoO_2(sal\text{-}shz)(H_2O)$ with the ligand coordinating through *O-N-O*. This compound reacts with bidentate nitrogen ligands AA (AA = phen, bipy, en etc) to give $MoO_2(sal\text{-}shz)(AA)$ which are thought to be seven coordinate on the basis of IR studies [37]. Very similar compounds have been reported containing the Schiff base derived from salicylaldehyde and benzoylhydrazide [38].

A series of octahedral complexes $MoO_2(sap)(imid)$ have been synthesized where H_2sap is the tridentate Schiff base (15).

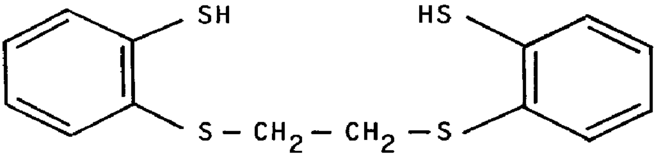


(15)

The compounds were prepared from $MoO_2(acac)_2$ and H_2sap in EtOH to give $MoO_2(sap)(EtOH)$ followed by reaction with imidazole [39].

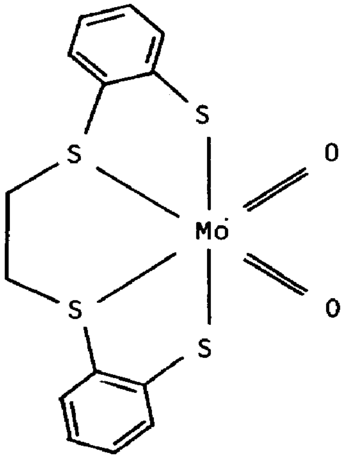
It has been shown that both $MoO_2(Et_2dtc)_2$ and $MoO(Et_2dtc)_2$ catalyze the reduction of NO_2^- to N_2O by HCOOH in dmf. The reaction of $MoO(dtc)_2$ with NO_2^- rapidly gives $MoO_2(dtc)_2$ and $[N_2O_2]^-$. Both products react with HCOOH to give $MoO(dtc)_2$ and N_2O respectively. The rate determining step in the cycle is the reduction of $MoO_2(dtc)_2$ by HCOOH [40].

Two reports have appeared on the preparation of $MoO_2(dttd)$ where $dttdH_2$ is 2,3,8,9-dibenzo-1,4,7,10-tetrathiadacane (16).



(16)

Reaction of $MoO_2(acac)_2$ with $dttdH_2$ in thf at room temperature gave $MoO_2(dttd)$ [41] while reaction of $dttdH_2$ with $(NBu_4)_4[Mo_8O_{26}]$ in MeOH gave a mixture of $MoO_2(dttd)$ and $Mo_2O_3(dttd)_2$ [42]. However, oxidation of this mixture yielded the pure Mo(VI) complex. An X-ray diffraction study on poor quality crystals revealed the structure shown in (17) with the thiolates *trans* to one another (Mo-S = 2.402(7)Å(av)) and the thioethers *trans* to each of the *cis* oxo groups with much longer Mo-S distances of 2.687(6)Å [42]. In the presence of NH_4Cl the complex shows a reversible one-electron reduction on the voltammetric time scale, but on the coulometric time scale a two-electron reduction was observed and the product was $[MoO(dttd)Cl]^-$ which could be oxidized to the EPR active species MoO(dttd)Cl. The electrochemical properties of these and related

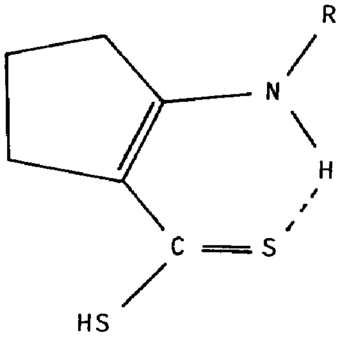


(17)

complexes were described and related to the behaviour of the molybdenum binding site of the molybdenum cofactor [42].

Catalytic air oxidation of benzil in dmf occurs in the presence of $MoO_2(L\text{-}L)_2$ or $Mo_2O_3(L\text{-}L)_4$ complexes (L-L = Et_2dtc, S-deprotonated cysteine alkyl ester, S-deprotonated cysteine-*n*-decylamide) but in most cases a slow deactivation of the catalyst occurred due to formation of $[Mo_2O_4]^{2+}$ species [43].

Compounds of the type $MoO_2(L\text{-}R)_2$ (where L-R = 2-(alkylamino)cyclopent-ene-1-dithiocarboxylic acids **(18)** were prepared by reacting HL-R with $MoO_2(acac)_2$.



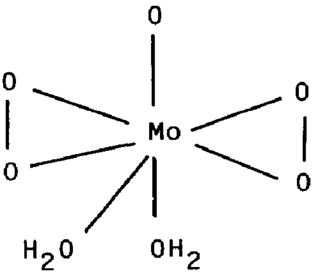
(18)

$MoO_2(L\text{-}R)_2$ complexes react with HCl to give $MoOCl_2(L\text{-}R)_2$. The ligand is thought to coordinate through both sulphur atoms, so the chloro derivatives are seven coordinate. With excess HCl reduction occurs to give $Mo(L\text{-}R)_4$ which are examples of the very rare paramagnetic (μ = 2.35-2.77BM) eight coordinate Mo(IV) systems [44].

'Molybdenum peroxide', prepared by the action of H_2O_2 on the metal or on MoO_3, has been shown to be $MoO_2(O_2).H_2O$ on the basis of IR, UV and thermal studies. On heating, it loses a mole of water and half a mole of O_2 to give MoO_3 [45].

MoO_3 and thf were co-condensed at 77K and the resulting solid stirred with excess thf exposed to air and light. Addition of water and 18-crown-6 gave crystals of $[MoO(O_2)_2(H_2O)_2](18\text{-crown-6}).H_2O$. The formation of peroxo groups in the absence of any strong oxidizing agent is surprising, but the structure was confirmed by X-ray diffraction which showed the molybdenum atom to be in a pentagonal bipyramidal environment as shown in **(19)** [46]. The peroxo groups are bonded asymmetrically, which is usual for Mo(VI) peroxo linkages.

After addition of malonic acid to a colourless solution of MoO_3 in KOH solution in the presence of excess H_2O_2, the complex $K_2[MoO(O_2)_2(ox)]$ gradually crystallized out at pH 3. Malic acid also gave the oxalato complex and the



(19)

Bond distances are

Mo=O = 1.647(4) Mo-O(O_2) = 1.900(4), 1.920(4)

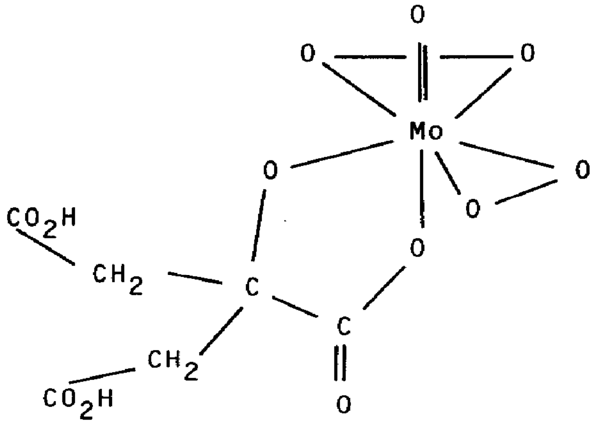
Mo-H_2O(ax) = 2.325 Mo(H_2O)(eq) = 2.084Å

mechanism of the reaction is not understood. An X-ray diffraction study confirmed the identification of the complex; the structure has been determined before but this new determination is more accurate. The structure of the anion is similar to (19) with the oxalato group replacing the aquo ligands, so the stereochemistry is pentagonal bipyramidal with the oxo and one carboxylate oxygen donor axial. The peroxo groups are again slightly asymmetric [47]. The structure of the isostructural $K_2[WO(O_2)_2(ox)]$ has also been determined [48] and data for both compounds are given below.

	$K_2[MoO(O_2)_2(ox)]$	$K_2[WO(O_2)_2(ox)]$
M=O	1.676(1)	1.716(7)
M-O(O_2)	1.940(1),1.960(1)	1.935(6),1.966(6)(av)
M-O(ax)	2.269(1)	2.245(6)
M-O(eq)	2.051(1)	2.033(6)Å

The complex $K_2[MoO(O_2)_2(C_6H_6O_7)].1/2H_2O_2.3H_2O$ has been isolated from the interaction of $K_2[MoO_4]$ and citric acid in the presence of excess H_2O_2. The stereochemistry of the anion shown in (20) is similar to the oxalato complexes but the interesting feature is the coordination of the deprotonated hydroxy group [49].

The interaction of MoO_3 and amino acids HAA (= glycine, α-alanine, valine, proline etc) in the presence of H_2O_2 gave complexes of the type $MoO(O_2)_2(HAA)(H_2O)$. Crystal structure determinations on the glycine and proline derivatives revealed very similar structures which are closely related to those discussed above. The amino acids are coordinated in a monodentate fashion in the form of their Zwitterions as shown in (21) for the glycine complex.

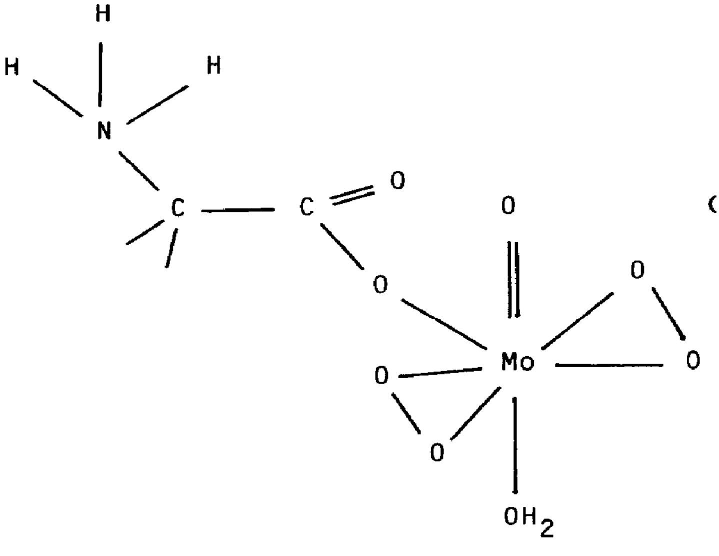


(20)

Bond distances are

Mo=O = 1.655(8)   Mo-O(O_2) = 1.926(9), 1.975(8)

Mo-O(ax) = 2.220(8)   Mo-O(eq) = 2.011(7)Å



(21)

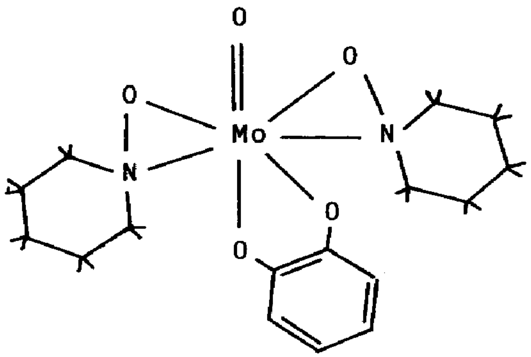
Bond distances are

Mo=O = 1.680(1)   Mo-O(O_2) = 1.932(1)-1.962(1)

Mo-O(H_2O) = 2.346(1)Å

The peroxo groups are only slightly asymmetric and the molybdenum atom is 0.36Å above the pentagonal plane towards the oxo group [50].

Cis-$[MoO_2(pip\text{-}NO)_2]$ reacts with 1,2-dihydroxybenzene (catechol, H_2cat) and its substituted derivatives to give $MoO(pip\text{-}NO)_2(cat)$ compounds. They are rigid in solution and their structures have been investigated using ^1H and ^{13}C NMR methods. The results inferred C_s symmetry with the chelated catechol lying in the mirror plane and this was confirmed by a structural determination which showed the molybdenum atom to be in a pentagonal bipyramidal environment as shown in (22).



(22)

Bond distances are

$Mo{=}O = 1.688(6)$ $Mo\text{-}O(cat) = 2.014(5)$

$Mo\text{-}O = 1.971(7)$ $Mo\text{-}N = 2.123(8)$Å(av)

The Mo-O(cat) bond distances are the same, so there is no apparent lengthening *trans* to the oxo group [51].

A series of compounds of the type $WO(OR)_2X_2$ (R = Me,Et,^{i}Pr,^{n}Bu; X = NCS,NCO,N_3) have been prepared [52] by the reaction

$$WO(OR)_2Cl_2 + 2KX \longrightarrow WO(OR)_2X_2 + 2KCl$$

The ^{95}Mo NMR spectra of a large number of seven coordinate complexes of the types $[MoL(dtc)_3]^{n+}$ and $MoLX_2(dtc)_2$ (L = O,N,NPh; X = Cl,Br) have been observed in dichloromethane solution. The $[MoO(dtc)_3]^+$ and $MoOX_2(dtc)_2$ complexes span a range of about 130ppm with the $MoOX_2(dtc)_2$ compounds showing an inverse halogen dependence. The nitrido complexes $MoN(dtc)_3$ have ^{95}Mo chemicals shifts about 180ppm to low frequency of their oxo analogues [53].

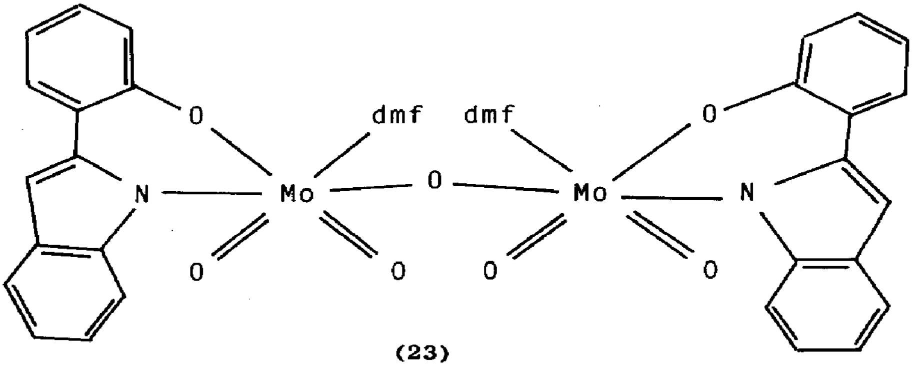
2.1.4 Dimeric and polymeric oxo complexes

There has been a Raman and FTIR study of the Mo(VI) oxalates in solution and on absorption onto alumina. As the pH increases dimeric oxo bridged species with chelated oxalato groups change to monomeric species with two monodentate oxalato groups. Both types retain their identities on absorption onto alumina, the dimers interact with the surface via their oxo groups while the monomeric species interact with the surface via their monodentate oxalato groups [54].

It has been suggested that a ^{95}Mo NMR signal at about 120ppm for Mo(VI) oxo complexes is diagnostic of a mono oxo bridged $[Mo_2O_5]^{2+}$ core [55].

The crystal structure of $Mo_2O_5(Me_2NCH_2CH_2N(H)CH_2CH_2S)_2$ has been determined. It is very similar to that of $Mo_2O_5(Me_2CH_2CH_2N(H)CH_2C(Me)_2S)_2$ described in the review for 1983. The tridentate ligand adopts a *facial* configuration and the angle at the bridging oxygen is 147.0(5)° [56].

Reaction of $MoO_2(acac)_2$ with 2-*o*-hydroxyphenylbenzimidazole (HL) followed by recrystallization from dmf/H_2O gave the compound $Mo_2O_5L_2(dmf)_2 1.5H_2O$. A crystal structure determination showed the stereochemistry shown in **(23)**.



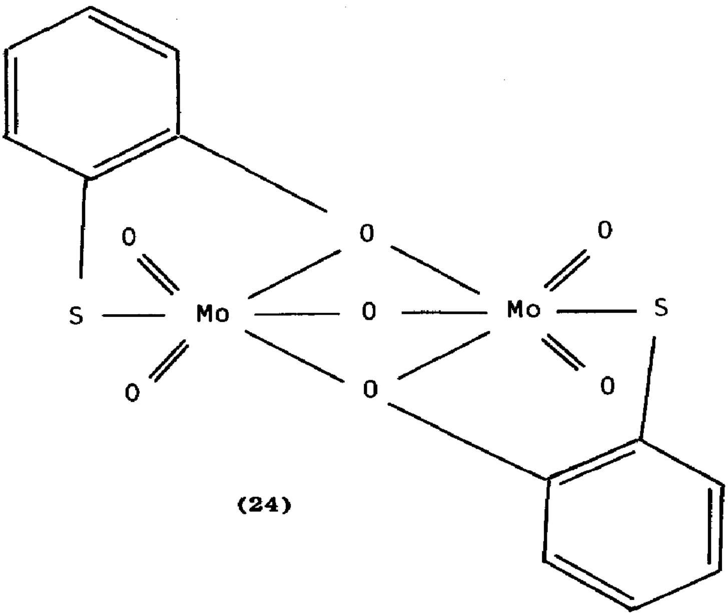
(23)

Bond distances are

Mo=O = 1.713(8)
Mo-O = 2.018(6)
Mo-O(dmf) = 2.353(7), 2.390(7)Å
Mo-μO = 1.855(8), 1.906(8)
Mo-N = 2.204(av)

The angle at the bridging oxygen is 165.4° and the bridge is distinctly asymmetric in the solid state [57].

The interaction of $(PPh_4)_2[MoOS_3(CuCl)_3]$ with KSPh in MeCN gave a complex sequence of reactions but the only product so far characterized is $(PPh_4)_2[Mo_2O_5(SC_6H_4O)_2]$ whose structure is shown in **(24)**.



(24)

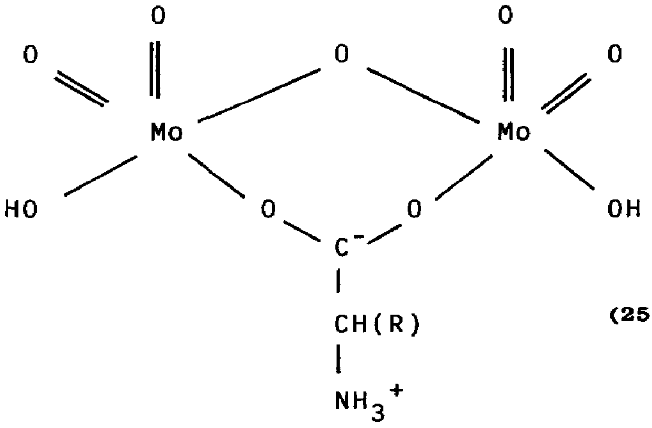
Bond distances are

$$Mo{=}O = 1.705(2)(av)$$

$$Mo\text{-}\mu O(ligand) = 2.117(2),\ 2.482(2) \qquad Mo\text{-}\mu O = 1.929(2)Å$$

The µ-O(ligand) bridges are asymmetric. It is thought that the formation of this highly oxygenated species is copper catalyzed [58].

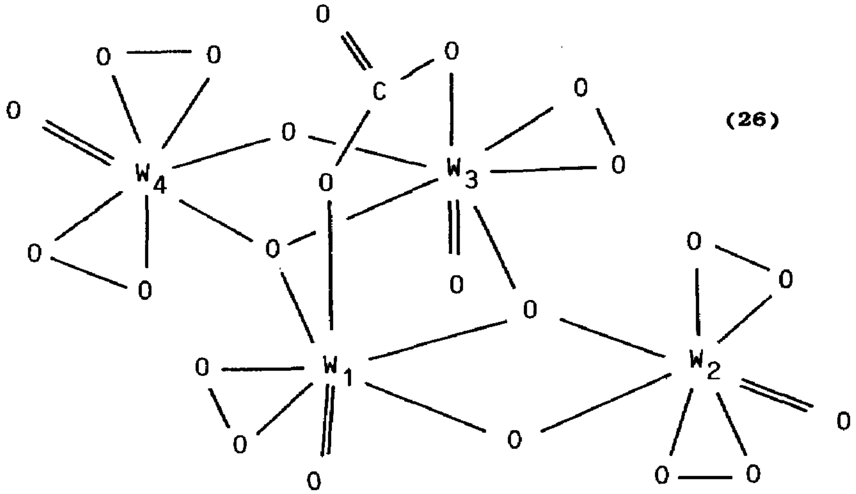
Interaction of $Na_2[MoO_4]$ with amino acids (LH) (LH = glycine, L-alanine, L-valine, DL-valine etc) in H_2O at pH 2 at 80°C gave the complexes $Mo_2O_5(LH)(OH)_2$ which are thought to have the structure **(25)** in which the amino



(25)

acid in the Zwitterion form bridges the metal atoms [59].

The compound $K_6[W_4O_8(O_2)_6(CO_3)].6H_2O$ was first obtained as a by-product from the mother liquor in the preparation of $K_2[WO(O_2)_2(ox)]$, but it can also be made more rationally from $[WO_4]^{2-}$, K_2CO_3 and H_2O_2 in water. X-ray crystallography showed a new type tetratungstate(VI) as shown in **(26)**.



(26)

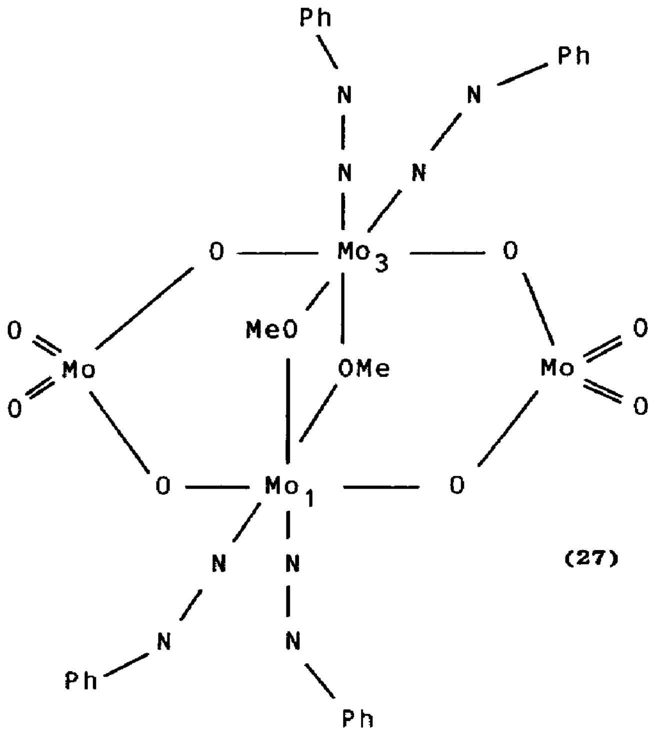
Average bond distances are

W=O = 1.70(4) $\qquad$ $W{-}O(O_2) = 1.95(5)$

W-O(ax) = 2.21(3) $\qquad$ W-O(eq) = 1.98(3)Å

The structure consists of a parallelogram of tungsten atoms with two opposite tungsten atoms bridged by the carbonato ligand. All the tungsten atoms are seven coordinate; tungsten atoms 1 and 3 which are bridged by the carbonate have only one peroxo group each. Atoms W2 and W4 have two peroxo groups each and all tungsten atoms have an oxo group axial together with another (not peroxo) oxygen as shown [60].

Reaction of $MoO_2(\text{butane-2,3-diolate})_2$ with excess phenylhydrazine and NEt_3 in acidified MeOH yielded black crystals of empirical formula $(NHEt_3)_2[Mo_2O_4(OMe)(NNPh)_2]$. X-ray diffraction showed the anion to have the tetranuclear structure shown in **(27)**.The overall geometry may be viewed as two *cis*-$Mo(NNPh)_2$ units bridged by methoxy groups and two $[MoO_4]^{2-}$ units acting as bidentate bridging groups. The Mo1-Mo3 distance suggests no Mo-Mo bonding. The short Mo-N distance, the N-N distance and the linear nature of the Mo-N-N unit all suggest multiple bond order in the Mo-N and N-N linkages. The electron



(27)

Bond distances are

Mo1...Mo3 = 3.465

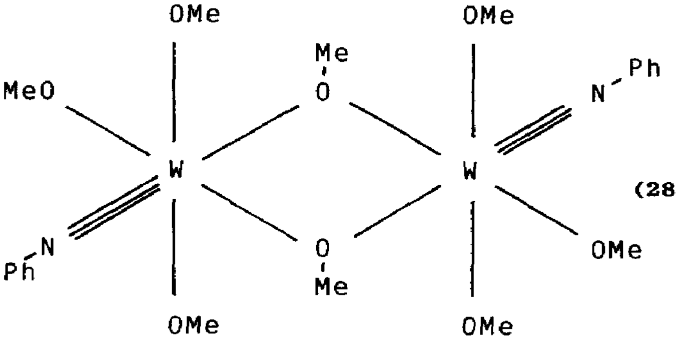
Mo-N = 1.823(9)(av)   N-N = 1.227(12)Å(av)

count is consistent with the diazenido ligands acting as three electron donors and therefore the octahedrally coordinated molybdenum atoms are formally in oxidation state (0) [61].

2.1.5 Complexes with oxygen donor ligands

The interaction of $W(NPh)Cl_4$ with various alcohols in the presence of base gave various products depending upon the steric requirements of the alkoxides. Thus, with MeOH in the presence of $(^{t}Bu)NH_2$ the dimeric species $[W(NPh)(\mu\text{-}OMe)(OMe)_3]_2$ and $[W(NPh)(\mu\text{-}OMe)(OMe)_2Cl_2]_2$ were formed. The structure of the former was shown to be as in **(28)**. The W-N-Ph group is linear and the W-N bond distance is suggestive of a triple bond [62].

$W(NPh)Cl_4$ reacts in the presence of $N(^{t}Bu)_3$ with two moles of 2,3-dimethyl-2,3-butanediol (pinacol-H_2, L-H_2) to give three products, WL_3,



(28)

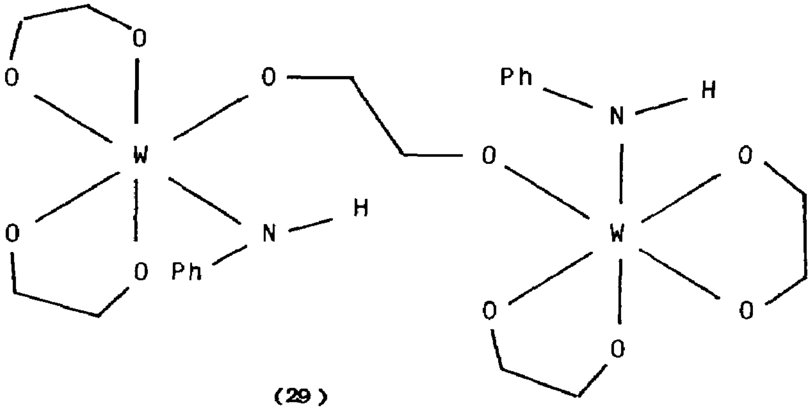
Bond distances are

W...W = 3.467(4)   W-N = 1.61(4)

W(μ-O)(*trans* NPh) = 2.16(2)   W(μ-O)(*cis* NPh) = 2.05(2)

W-O = 1.90(2)Å(av)

$W_2(NHPh)L_5$ and $W_2(NPh)_2OL_2(L-H)_2$, whilst a larger amount of pinacol gave only WL_3. The crystal structures of the latter two compounds were determined and that of $W_2(NHPh)L_5$ is shown in (29).



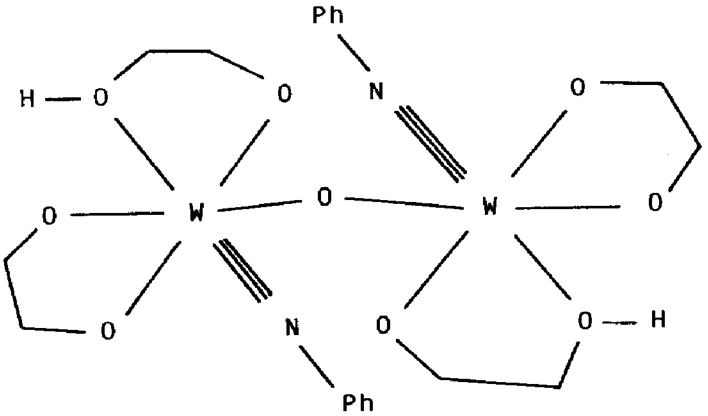
(29)

Bond distances are

W-N = 2.02(2)   W-O = 1.80(2)-2.00(2)Å

The W-N distance is not consistent with a triply bonded NPh group and although the protons of the proposed NHPh ligands were not resolved in the structure determination they were observed in solution by ^1H NMR spectroscopy [63].

The compound $W_2(NPh)_2OL_2(L-H)_2$ has the structure shown in (30).



(30)

Bond distances are

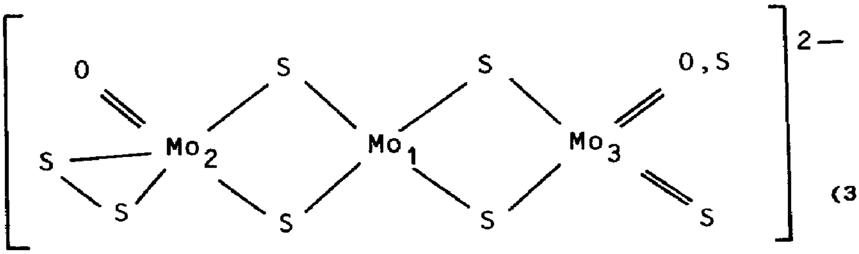
W-N = 1.75(5)
W-O(*trans* N) = 2.30(3)
W-μO = 1.89(4)
W-O = 1.82(4)-2.00(5)Å

The W-N distance is very short and typical for a triply bonded NPh ligand. The oxygen *trans* to the NPh group with the very long W-O bond distance is assumed to be the protonated oxygen [63].

2.1.6 *Thiomolybdates, thiotungstates and sulphur donor complexes*

Self consistent calculations have been performed using the local density theory (LDT) method for the $[MoS_4]^{2-}$ and $[Mo_3S_9]^{2-}$ anions. For $[MoS_4]^{2-}$ the calculations are in accord with earlier calculations, but the energies of the levels require re-assignment of the high absorption bands. For $[Mo_3S_9]^{2-}$, the terminal molybdenums are found to be Mo(VI) and the central one Mo(IV). In both systems the lowest levels are Mo-S bonding, weakly bonding S-S, weakly antibonding S-S and non-bonding Mo *d*-orbitals. The LUMO is Mo-Sπ* [64].

Reaction of an isomeric mixture (α:β_7:1) of $[Mo_8O_{26}]^{4-}$ with $(Me_3Si)_2S$ in MeCN resulted in cleavage of the cage and partial reduction of Mo(VI). With eight mole equivalents of $(Me_3Si)_2S$, a compound with empirical formula $(NBu_4)_2[Mo_3S_{7.45}O_{2.55}]$ was isolated which X-ray crystallography showed to consist of almost equal amounts of $[Mo_3S_8O_2]^{2-}$ and $[Mo_3S_7O_3]^{2-}$ which differ only in the identity of one terminal ligand. The structures are shown in (31).



(31)

Bond distances are

Mo1-Mo2 = 2.896(1)

Mo2=O = 1.677(5)

$Mo2-S(S_2)$ = 2.395(3)

S-S = 2.051(4)Å

Mo1-Mo3 = 3.047(1)

Mo3=O,S = 1.646(14) or 2.098(6)

Mo-μS = 2.287(3)-2.458(2)

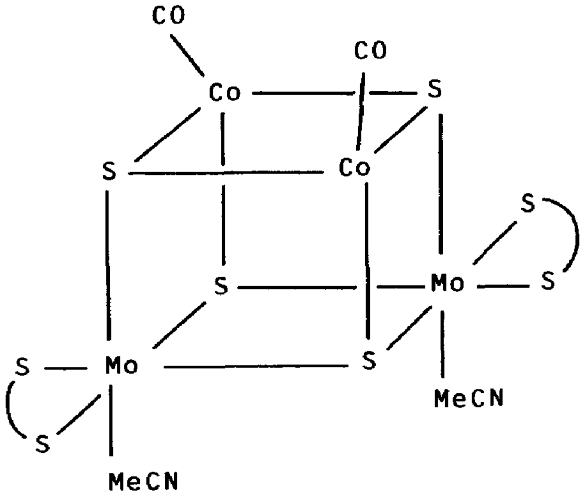
The central atom is oxidation state (IV) and the outer ones oxidation state (VI). ^{95}Mo and ^{17}O NMR studies were also reported [65].

The reactions of $(PPh_4)_2[MoS_4]$ with $MoBr_4$ and $Mo(NO)_2Br_2$ in SMe_2 solution led to dinuclear complexes $(PPh_4)_2[S_2MoS_2MoBr_3(SMe_2)]$ and $(PPh_4)_2[S_2MoS_2Mo(NO)_2Br_2]$ respectively [66].

The resonance Raman spectra of a number of iron complexes with the $[MS_4]^{2-}$ ions (e.g. $[Fe(H_2O)_2(WS_4)_2]^{2-}$, $[Fe_3S_2(WS_4)_3]^{4-}$) have been measured and discussed in terms of electron delocalization in the complexes [67].

The dark green compound $(NEt_4)_3[Co(MoS_4)_2]$ was prepared by the interaction of a solution of $CoCl_2$ and $(NEt_3H)SPh$ in MeCN with a solution of $(NEt_4)_2[MoS_4]$ in MeCN. This is the first cobalt derivative in the extensive series of heterometallic compounds of this type. Its X-ray powder pattern was almost identical to that of the fully characterized corresponding iron compound which has tetrahedral iron surrounded by two chelating MoS_4 ligands. Electrochemical studies revealed a reversible one-electron oxidation and a reversible one-electron reduction to give the corresponding 2- and 4- anions [68].

Interaction of $Mo_2S_4(Et_2dtc)_2$ and $Co_2(CO)_8$ in thf gave a dark brown product. Recrystallization from MeCN gave $Mo_2Co_2S_4(Et_2dtc)_2(CO)_2(MeCN)_2$ which X-ray crystallography showed has the distorted cubane structure (32).



(32)

Bond distances are

Mo-Mo = 2.788(1)
Mo-μS(Mo) = 2.360(1)(av)
Co-Co = 2.533(1)Å
Mo-Co = 2.680(1)
Mo-μS(Co) = 2.316(1)

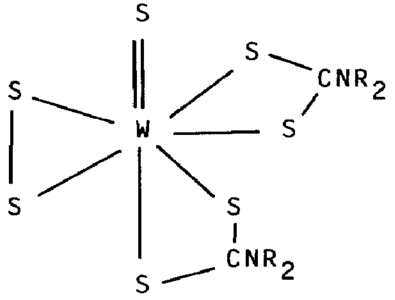
The original $Mo_2S_4(dtc)_2$ unit is recognisable and the Mo-Mo and Mo-μS(Mo) bond lengths are very similar to those in the starting material. The original Mo=S bond length is increased as it becomes the Mo-μS(Co) linkage [69].

Reaction of $[WS_4]^{2-}$ with tetraalkylthiuramdisulphides (tmds) causes a ligand based redox reaction

$$[W^{VI}S_4]^{2-} + \text{tmds} \longrightarrow W^{VI}S(S_2)(S_2CNR_2)_2$$

to give the green seven coordinate molecule whose structure is shown in **(33)**. Similar reaction of $[MoS_4]^{2-}$ with tmds gives reduction to Mo(V) (see later), but reaction with $[MoO_2S_2]^{2-}$ gives $MoS(S_2)(S_2CNR_2)_2$ which is known to have a structure similar to **(33)** [70].

Compounds of the type $Mo(L\text{-}L)_2(deaz)_n$ (L-L = dtc, dtp; deaz = diethyldiazenedicarboxylate) are readily prepared from $Mo(CO)_2(L\text{-}L)_2$ and deaz. These complexes readily react stoichiometrically with water and so provide a useful route to ^{18}O complexes $^{18}OMo(L\text{-}L)_2$ and $^{18}O_2Mo(L\text{-}L)_2$ [71].



(33)

Bond distances are

$W{=}S = 2.136(1)$

$W{-}S(S_2) = 2.366(3),\ 2.403(2)$

$S{-}S = 2.208(2)\text{Å}$

$W{-}S(ax) = 2.588(1)$

$W{-}S(dtc) = 2.454(1){-}2.528(2)$

2.1.7 Homonuclear polyanions

Anilinium-β-octamolybdate dihydrate has been isolated through the interaction of aniline with an aqueous solution of MoO_3 in water (pH 2.5). The crystals were characterized by X-ray crystallography which confirmed the presence of the well known β-$[Mo_8O_{26}]^{4-}$ anion [72].

Reaction between α-$(NBu_4)_4[Mo_8O_{26}]$ with excess phenylhydrazine and NEt_3 in EtOH gave a purple solution from which crystals of $(NBu_4)_2[Mo_8O_{20}(NNPh)_6]$ slowly separated. X-ray crystallography showed a crown of six oxo-bridged Mo centres which are alternating oxomolybdate $[MoO_4]^{2-}$ and *cis*-$[Mo(NNPh)_2]^{2+}$ moities with the crown capped by two more $[MoO_4]^{2-}$ units acting as tridentates to the three $Mo(NNPh)_2$ centres, thus giving three types of molybdenum environment. The structure bears a close resemblance to that of the precursor $[Mo_8O_{26}]^{4-}$ (whose structure is also reported) by replacement of three *cis*-MoO_2 units by *cis*-$Mo(NNPh)_2$ units [73].

Single crystal EPR spectra of UV irradiated $(NH_3Me)_8[Mo_8O_{26}(MoO_4)_2].2H_2O$ show the formation of two distinct localized $Mo^{V}O_5(OH)$ sites resulting from a hydrogen bonding proton transfer from the cation to a bridging oxygen atom in the anion. It is suggested that $[Mo_8O_{26}(MoO_4)_2]^{8-}$ undergoes a four-electron photochemical reduction [74].

^{17}O and ^{183}W NMR spectra have been obtained for acidified solutions of $Na_{10}[H_2W_{12}O_{42}].27H_2O$ and $Na_6[W_7O_{24}].14H_2O$. The spectra of $[W_7O_{24}]^{6-}$ do not change with pH and are fully consistent with the known solid state structure.

'Paratungstate A' formed during condensation of $[WO_4]^{2-}$ has spectra identical to those of $[W_7O_{24}]^{6-}$, so it is not a hexatungstate as previously thought [75].

2.1.8. Heteronuclear polyanions

A ^{31}P NMR study has been carried out on the equilibria in the $H^+/[MoO_4]^{2-}/[HPO_4]^{2-}$ system. At pH>5.5 and Mo/P<2.5 a single pentamolybdodiphosphate series of complexes exists whose members differ only by their degree of protonation as the pH varies [76].

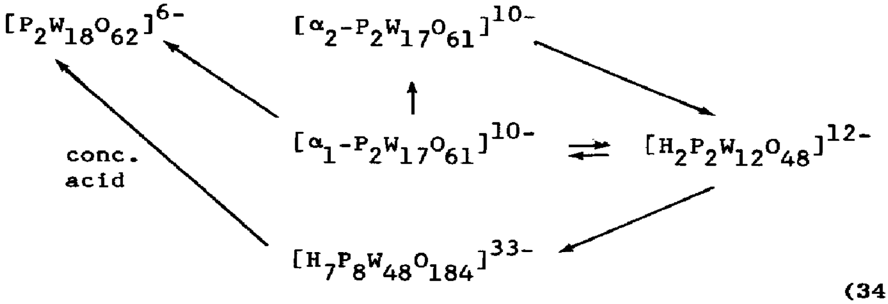
The dynamic behaviour of the α-$[Mo_8O_{26}]^{4-}$, $[(PhAs)Mo_7O_{25}]^{4-}$ and $[(PhAs)_2Mo_6O_{24}]^{4-}$ anions have been investigated using ^{17}O NMR spectroscopy. The three anions are structurally related by a common Mo_6O_{18} ring capped by tridentate $[MoO_4]^{2-}$ or $[PhAsO_3]^{2-}$ groups on either side of the ring. $[(PhAs)Mo_7O_{25}]^{4-}$ shows two dynamic processes, the low temperature one features Mo_6O_{18} ring inversion involving the breaking and making of relatively long Mo-O bonds whilst the second higher temperature process, although not fully defined, involves cleavage of strong Mo-O bonds. Similar processes occur for the other anions [77].

A new 8-tungsto-2-arsenate anion has been isolated in the compound $K_7[AsW_8O_{30}As(OH)].12H_2O$. A crystal structure determination revealed the first example of a β-type structure for the As^{III}/W family of polyanions. The structure is composed of two edge sharing groups of three WO_6 octahedra and one of two WO_6 octahedra which are linked by sharing corners. One As is the central atom of the heteropolyanion while the other is linked to three outer oxygen atoms and its coordination sphere is completed by a hydroxy group [78].

A four-electron reduced heteropolyblue $Ca_{0.5}[H_6Mo_{12}O_{40}].18H_2O$ has been isolated and its structure determined by X-ray diffraction. It has the same general structure as the β-$[SiW_{12})_{40}]^{4-}$ anion [79].

The anion $[NaP_5W_{30}O_{110}]^{14-}$ is formed as a by-product in the synthesis of $[P_2W_{18}O_{62}]^{6-}$ and has been characterized by X-ray crystallography. It has approximately D_{5h} symmetry and consists of a cyclic array of five PW_6O_{22} units with the Na^+ ion located within the polyanion on the fivefold axis, but above the plane containing the five phosphorus atoms. This asymmetry gives rise to a four line (2:2:1:1) ^{183}W NMR spectrum in solution. The sodium ion is tightly encapsulated and does not exchange readily with free Na^+ and its presence appears to be necessary for the formation of the anion. Reduced forms of this interesting anion and some vanadium substitution products were also described [80].

What is thought to be the largest known phosphotungstate, $K_{28}Li_5[H_7P_8W_{48}O_{184}].92H_2O$, has been prepared and characterized by X-ray crystallography. It crystallizes spontaneously from LiOAc/HOAc buffer solutions of $K_{12}[H_2P_2W_{12}O_{48}]$ which is itself obtained from $[P_2W_{18}O_{62}]^{6-}$ by alkali degradation in the presence of amine according to the scheme (34).



(34)

The structure of $[H_7P_8W_{48}O_{184}]^{33-}$ is in the form of a crown formed by the linkage of four $P_2W_{12}O_{48}$ subunits each derived from the well known structure of $[P_2W_{18}O_{62}]^{6-}$ by the loss of six adjacent WO_6 octahedra, two from the cap and four from the belt polyhedra [81].

The ions formed in a series of solutions of sodium phosphate, vanadate and tungstate in the P:V:W ratios of 1:6:6, 1:8:4 and 1:10:12 have been studied by ^{31}P and ^{51}V NMR spectroscopies. The compositions of the vanadophosphotungstates in each solution are dependent upon pH, but no solution ever contains just one species [82].

In dichloromethane the reaction

$$5[Mo_2O_7]^{2-} + 2cp_2TiCl_2 + H_2O \longrightarrow 2[cpTi(Mo_5O_{18})]^{3-} + 2C_5H_6 + 4Cl^-$$

led to the formation of the yellow heteropolymolybdate and the corresponding tungstate was prepared from $[WO_4]^{2-}$ and cp_2TiCl_2 in acidified CH_2Cl_2. The IR and ^{17}O NMR spectra of the two compounds are very similar, with the NMR spectra being particularly simple. A crystallographic study on the molybdenum compound confirmed the structure to based on that of $[Mo_6O_{19}]^{2-}$ with replacement of one Mo=O unit by cpTi. The resultant changes in the bond lengths were discussed in terms of surface activation and charge delocalization in these and similar species [83].

Reaction of $Na_2[WO_4]$ and $ZrOCl_2$ followed by addition of NMe_4Cl gave $(NMe_4)_2[H_2ZrW_5O_{19}]$. Various physical measurements including IR, UV and ^{183}W NMR spectroscopies were all consistent with a structure analogous to that of $[W_6O_{19}]^{2-}$ [84].

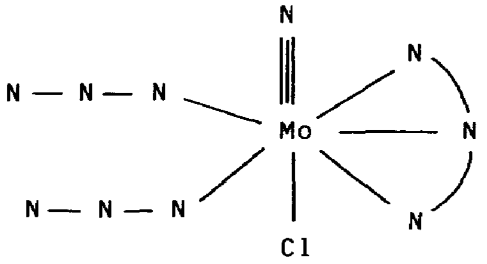
Addition of $(Me_3Si)_2S$ to $(NBu_4)_3[M'W_5O_{19}]$ (M' = Nb,Ta) in dry MeCN gave

$(NBu_4)_3[M'W_5O_{18}S]$ in which the terminal oxygen at Nb or Ta in the original complexes is replaced by sulphur. This was confirmed by X-ray crystallography. The ^{17}O NMR spectrum was fully consistent with retention of the same structure in solution as no M'=O resonance was observed. This is the first d^0 polyoxothioanion to be isolated for an early transition metal [85].

$(NBu_4)_4[$*cis*-$Nb_2W_4O_{19}]$ reacts with *fac*-$[M'(CO)_3(MeCN)_3]Cl$ (M' = Mn,Re) to give $[(CO)_3M'[Nb_2W_4O_{19}]^{3-}$. A crystal structure determination on the Mn compound showed the heteropolytungstate coordinated to Mn by three contiguous bridging oxygen atoms, but the heavy metals in the cluster were disordered in the solid state structure. Three distereoisomers are possible with $M'(CO)_3$ coordinated to an ONb_2 oxygen and two ONbW oxygens (isomer I), two ONbW oxygens and one OW_2 oxygen (isomer II) or three OW_2 oxygens (isomer III). ^{17}O NMR spectroscopy shows isomer II to predominate, but both other isomers are also present in solution [86].

2.1.9 Complexes with nitrogen and phosphorus donor ligands

The unusual complex $MoN(Cl)(N_3)_2$(terpy) was formed either by reacting $MoCl_4(MeCN)_2$ with Me_3SiN_3 and subsequent addition of terpy or alternatively by the interaction of $MoCl_3$(terpy) with Me_3SiN_3. A crystal structure determination showed it to have a seven coordinate pentagonal bipyramidal stereochemistry as shown in (35) with the nitrido and chloro ligands axial [87].



(35)

Bond distances are

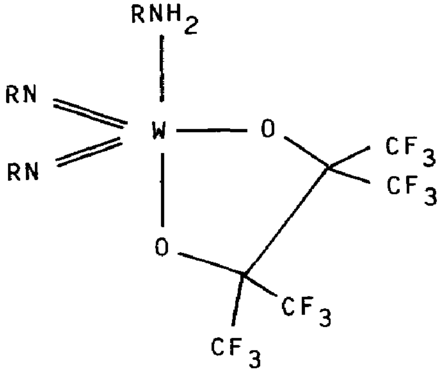
Mo-N(nitride) = 1.662(7)   Mo-Cl = 2.719(2)

$Mo-N(N_3)$ = 2.076(7), 2.114(6)

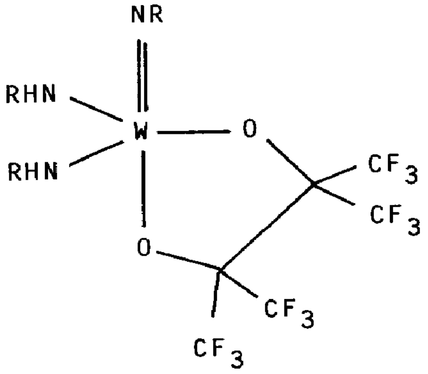
MO-N(terpy) = 2.235(5)-2.285(6)Å

The strong *trans* effect of the triply bonded nitride causes the long Mo-Cl bond distance.

Various pinacols were reacted with $(RN)_2W(HNR)_2$ (R = ${}^tBu$) to give a mixture of $(pinacol)W(NR_2)_2(NH_2R)$ and $(pinacol)W(NR)(NHR)_2$ as shown by ^1H and ^{13}C NMR studies. However, in the solid state each pinacol gave only one isomer, although not the same isomer for each pinacol as shown in **(36)** and **(37)**.



(36)



(37)

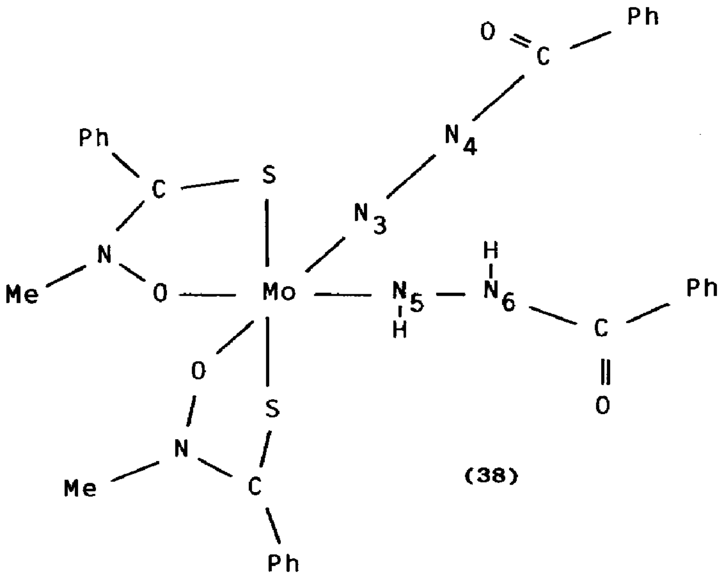
R = ${}^tBu$

Bond distances are

	(36)	(37)
W=NR	1.742(3)	1.753(4)
W-N	2.201(4)	1.927(4)Å

The tungsten atom in each case has a trigonal bipyramidal stereochemistry, in **(36)** the imino groups are equatorial, but axial in **(37)**. These molecules are considered to be homogeneous models for the molybdenum heterogeneous catalysts used for ammoxidation of propylene to acrylonitrile [88].

The reactions between $MoO_2(PhC(X)NMeO)_2$ (X = O,S) and $PhC(X)NHNH_2$ have been investigated and the structures of two of the products have been determined by X-ray crystallography. The interaction of $MoO_2(PhC(S)NMeO)_2$ and $PhC(O)NHNH_2$ provides the first structurally characterized 'end-on' bonded NHNHR hydrazido(1-) group for molybdenum as shown in **(38)**. It contains a $N_2C(O)Ph$ diazenido(2-) together with the NHNHC(O)Ph hydrazido (1-) group (for which the hydrogen atoms were located) [89]. The bond distances for the two hydrazido moities are quite different with the diazenido group bond distances being quite short, showing significant double bond character and electron delocalization.



(38)

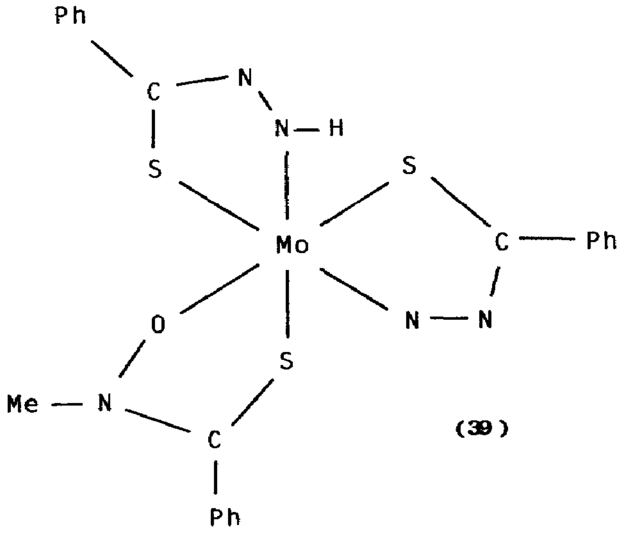
Bond distances are

Mo-N3 = 1.758(5)
N3-N4 = 1.292(4)
Mo-N5 = 1.938(4)
N5-N6 = 1.361(7)
Mo-O = 2.106(av)
Mo-S = 2.445Å(av)

Reaction between $MoO_2(PhC(S)NMeO)_2$ and $PhC(S)NHNH_2$ gave $Mo(NHNC(S)Ph)(N_2C(S)Ph)(PhC(S)NMeO)$ which was shown to have the octahedral structure shown in (39) [89].

The complexes $[MCl(NNMe_2)_2(PPh_3)_2]Cl$ react with $PhP(CH_2CH_2SH)_2$ in MeOH to give $M(NNMe_2)\{PhP(CH_2CH_2S)_2\}_2$ and a structural determination on the molybdenum compound showed it to have the pentagonal bipyramidal structure (40). The molecule is rigid in solution as shown by two non-equivalent ^{31}P and ^{1}H NMR signals [90].

The red purple complex $W(TPP)(O)(O_2)$ has been isolated and its ^{1}H NMR spectrum indicated an unsymmetrical porphyrin coordination and a structural study confirmed this. The tungsten atom is 1.49Å to one side of the N_4 plane of the porphyrin and, as a result, the oxo and peroxo groups are *cis* to each other. They eclipse the *trans* nitrogens of the porphyrin and this leads to very different W-N distances of 2.298 and 2.878Å for the eclipsed nitrogens and 2.086 and 2.092Å for the others. The W=O and $W-O(O_2)$ distances of 1.752(13) and 1.909(15)Å(av) are normal [91].



(39)

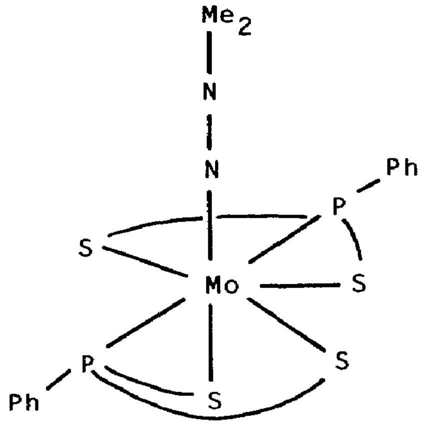
Bond distances are

Mo-N(NN) = 1.789(4)

Mo-O = 2.051(3)

Mo-N(NHN) = 1.972(3)

Mo-S = 2.436(1)-2.504(1)Å



(40)

Bond distances are

Mo-N = 1.775(6)

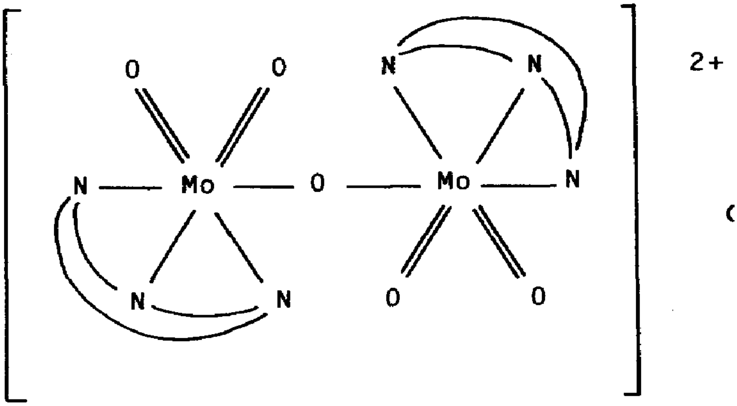
Mo-S(ax) = 2.499(3)

Mo-P = 2.517(2)Å(av)

N-N = 1.265(9)

Mo-S(eq) = 2.498(3)-2.548(2)

Oxidation of $LW(CO)_3$ (L = 1,4,7-triazacyclononane) with excess bromine in $CHCl_3$ gave WO_2Br_2L whose structure is unknown. In solution it transforms to $[W_2O_5L_2]^{2+}$ which contains a monoxo bridge [92]. Somewhat different chemistry is observed in the oxidation of $L'M(CO)_3$ (where L' = N,N',N''-trimethyl-1,4,7-triazacyclononane). Oxidation with bromine gave first $[L'M(CO)_3Br]Br$ which on further oxidation with conc. nitric acid yielded $[L'MO_2Br]^+$. In the case of tungsten this slowly hydrolyses to $[W_2O_5L'_2]^{2+}$ [93,94] while $[Mo_2O_5L'_2]^{2+}$ was made by direct oxidation of $L'Mo(CO)_3$ with more dilute HNO_3 [95]. The crystal structure of $[Mo_2O_5L'_2]^{2+}$ was determined and is shown in (41).



(41)

Bond distances are

Mo=O = 1.695(7) Mo-μO = 1.898(1)

Mo-N(*trans* μO) = 2.290(9) Mo-N(*trans* O) = 2.325(8), 2.355(8)A

The compound can be reduced chemically to the deep blue +1 cation which has a magnetic moment of 1.73BM per molecule. Electrochemically, two reversible one-electron reductions are seen [95]

$$[L'_2Mo^{VI}{}_2O_5]^{2+} \rightleftharpoons [L'_2Mo^{VI}Mo^{V}O_5]^{+} \rightleftharpoons [L'_2Mo^{V}{}_2O_5]$$

In the tungsten system both $[L'WO_2X]^+$ and $[L'_2W_2O_5]^{2+}$ show single reversible one-electron reductions [94].

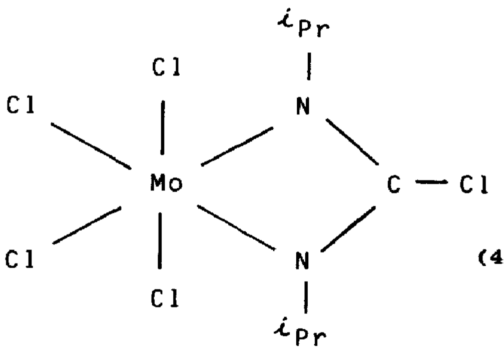
Reaction of $WCl_4(PMe_3)_4$ with $LiAlH_4$ in ether at -78°C led to the isolation of colourless $WH_6(PMe_3)_3$. The structure in solution could not be determined unambiguously as the molecule is fluxional and crystals suitable for X-ray diffraction could not be obtained. Reaction with CO_2 gave $WH_2(\eta^1\text{-}O_2CH)(\eta^2\text{-}O_2CH)(PMe_3)_3$ whose ^1H and ^{31}P NMR spectra were studied over a wide temperature range. The spectra indicated exchange between monodentate and bidentate formato groups and also phosphine/hydride site exchange [96].

2.2 MOLYBDENUM(V) AND TUNGSTEN(V)

2.2.1 *Halides and halo complexes*

Chlorination of MoF_3 in a long sealed tube at 120-150°C gave MoF_3Cl_2 with the product condensing in the cooler region of the tube. The IR spectrum showed bands due to Mo-F_t at 720 and 680cm^{-1} and Mo-F_b at 494 and 446cm^{-1}. A polymeric chain structure with fluoro bridging was suggested. The magnetic moment at room temperature is 1.29BM per molybdenum and decreases with temperature. This is consistent with magnetic exchange in a polymeric chain structure [97].

Interaction of $MoCl_5$ and diisopropylcarbodiimide in CCl_4 suspension gave monomeric $MoCl_4(^iPrNC(Cl)N^iPr)$ and X-ray diffraction showed it to have the structure **(42)** [98].



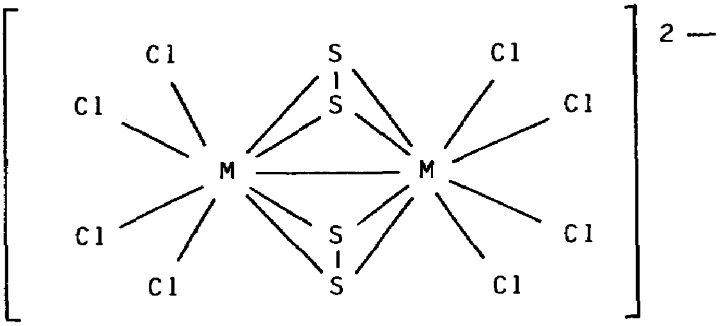
(42)

Bond distances are

Mo-N = 2.079(4)

Mo-Cl(*trans* N) = 2.266(1)   Mo-Cl(*cis* N) = 2.343(1)Å

$Mo(S_2)Cl_3$ in dichloromethane reacts with $(PMePh_3)Cl$ to give $(PMePh_3)_2[Cl_4Mo(\mu\text{-}S_2)_2MoCl_4].2CH_2Cl_2$. The corresponding bromo complex was made from $MoBr_4$ and S_7NH and subsequent addition of $(PMePh_3)Br$ in CH_2Br_2 solution. The crystal structures of both were determined, they are very similar and are shown in **(43)**. The Mo-Mo distance suggests a single bond [99].



(43)

Bond distances are

	$[Mo_2(S_2)_2Cl_8]^{2-}$	$[Mo_2(S_2)_2Br_8]^{2-}$
Mo-Mo	2.875(1)	2.855(4)
Mo-S	2.422(1)-2.429(2)	2.412(6)-2.424(6)
Mo-X	2.407(1)-2.518(1)	2.566(4)-2.688(3)
S-S	1.981(1)	1.969(9)Å

Trimethylsilyldialkylamines, Me_3SiNR_2, (R_2 = Et_2,pip,pyroll) react with $MoOCl_4$ (1:1) in dichloromethane or ether to give a Mo(V) compound

$$MoOCl_4 + Me_3SiNR_2 \xrightarrow{+H} MoOCl_3(NHR_2) + Me_3SiCl$$

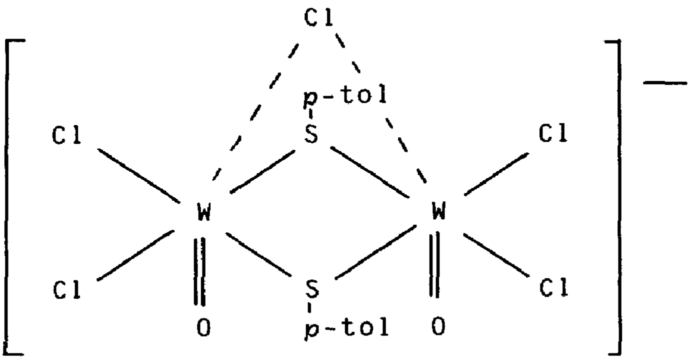
In aprotic solvents such as CCl_4, Me_3SiNEt_2 gives the tetraethylhydrazine complex $MoOCl_3(N_2Et_4)$ while in CS_2 the product is $(MoOCl_3)_2$tds [100,101]. At 2:1 proportions in dichloromethane the reaction is

$$MoOCl_4 + 2\ Me_3SiNR_2 \xrightarrow{+H} MoOCl_2((NR_2)(NHR_2) + 2\ Me_3SiCl$$

but excess Me_3SiNR_2 causes oxygen transfer to occur to give Mo(IV) [101].

$$MoOCl_4 + 3Me_3SiNR_2 \xrightarrow{+2H} MoCl_3(NR_2)(NHR_2)_2 + Me_3SiCl + (Me_3Si)_2O$$

Interaction of PPh_4Cl or $AsPh_4Cl$ with $(Me_2S)Cl_3W(SR)_2WCl_3(SMe_2)$ gave crystals of salts of the anion $[Cl_2OW(SR)_2WOCl_2]^-$ with the oxygen coming from moisture. X-ray crystallography of the compound with R = 4-tolyl confirmed the structure (44). The structure may be regarded either as a grossly distorted



(44)

Bond distances are

$W-W = 2.878(2)$ $W-S = 2.427(3), 2.450(3)$

$W-Cl = 2.378(9)$ $W-\mu Cl = 2.604(7)Å$

confacial bioctahedral or as two square pyramids sharing an edge with two long W-Cl interactions filling the octahedral positions [102].

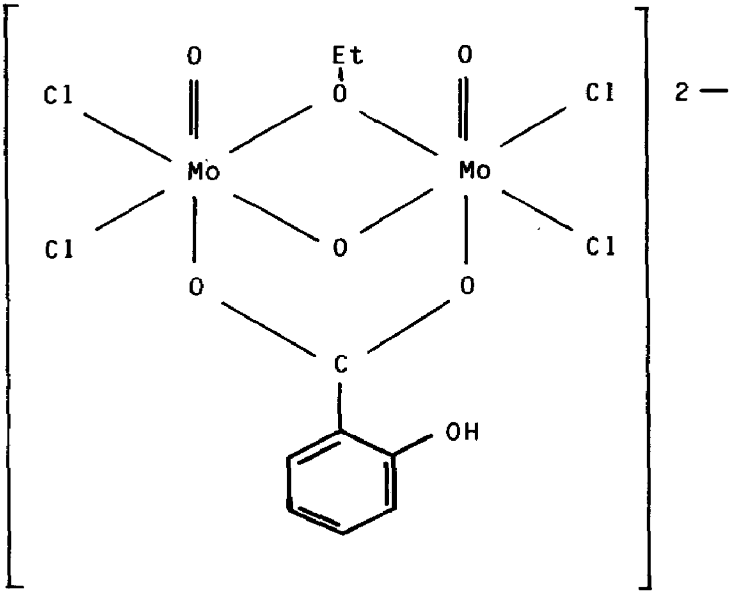
The crystal structure of the known salicylate complex $(pyH)_2[Mo_2O_3Cl_4(OEt)(HOC_6H_4CO_2)]$ has been determined and is as in (45) [103].

Oxidative addition of H_2 at 60°C to $WCl_2(PMe_3)_4$ gave $WH_2Cl_2(PMe_3)_4$. Interaction of the latter with $Tl[BF_4]$ or $AlCl_3$ gave $[WH_2Cl(PMe_3)_4]^+$ and in MeCN this formed $[WH_2Cl(PMe_3)_4(MeCN)]^+$. In MeCN the square reaction scheme (46) is set up by electrochemical oxidation.

$$\begin{tikzcd}
WH_2Cl_2P_4 \arrow[r, shift left, "\pm e^-"] \arrow[d, shift left, "MeCN"] & {[WH_2Cl_2P_4]^+} \arrow[l, shift left] \arrow[d, shift left, "MeCN"] \\
{[WH_2ClP_4(MeCN)]^+} \arrow[u, shift left] \arrow[r, shift left, "\pm e^-"] & {[WH_2ClP_4(MeCN)]^{2+}} \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd} \qquad (46)$$

The crystal structure of $[WH_2Cl_2(PMe_3)_4](BF_4)$ was determined and the cation may be described as dodecahedral but the hydride ligands were not detected in the analysis. Bond distances are $W-Cl = 2.438(6)$ and $W-P = 2.482(6)-2.595(5)Å$ [104].

Tridentate Schiff bases with *O-N-O* and *N-N-O* donor sets have been used to prepare Mo(V) complexes. The *O-N-O* donor ligands (L) gave monomeric species $MoOCl_2L$ with magnetic moments of approximately 1.7BM. The *N-N-O* donor set ligands gave dinuclear complexes $Mo_2O_3Cl_2L_2$ thought to be oxo bridged and which have severely depressed magnetic moments [105].



(45)

Bond distances are

Mo-Mo = 2.646(2)   Mo=O = 1.670(14)
Mo-μO = 1.912(av)   Mo-μOEt = 1.964(10)
Mo-O(sal) = 2.306(14)(av)   Mo-Cl = 2.399(5)-2.432(6)Å

A series of complexes of the type MoOClL (L = tridentate *O-N-O* donor Schiff bases from various substituted salicylaldehydes and ethanolamine) were prepared by reacting $(NH_4)_2[MoOCl_5]$ and H_2L in EtOH. The complexes are thought to be dimeric with the alkoxide oxygens acting as bridges as well as chelating [106].

2.2.2 Monomeric oxo complexes

The visible absorption spectra of MoO(TPP)X compounds (X = F,Cl,Br,NCS) in organic solvents have been investigated. The compounds were shown to be monomeric in dichloromethane solution. The axial ligand is substituted by dmso to give [MoO(TPP)(dmso]X in CH_2Cl_2/dmso mixtures [107]. In 2-Methf MoO(TPP)X compounds are photosensitive when irradiated in the Soret region and the changes in the absorption spectra suggest reduction to MoO(TPP). The EPR signal of MoO(TPP)X disappears as the EPR silent MoO(TPP) is generated [108].

2.2.3 μ-*oxo*, μ-*sulphido complexes*

The kinetics of the oxidation of $[Mo_2O_4]^{2+}$ by $[Fe(H_2O)_6]^{3+}$ and $[Fe(phen)_3]^{3+}$ in aqueous solution have been examined at 25°C. In both systems the rate of reaction is first order in reductant and oxidant and indicates that the first electron transfer step is rate determining for the overall process. With the aquo complex, the predominant pathway involves a hydroxy species, probably $[Fe(OH)]^{2+}$, which reacts with a second order rate constant $k = 1.3 \times 10^{-3} M^{-1} s^{-1}$, probably by an inner sphere mechanism. The oxidation with $[Fe(phen)_3]^{3+}$ is expected to be outer sphere and the rate constant is $13 M^{-1} s^{-1}$. Oxidations of $[Mo_2O_2S_2]^{2+}$ and $[Mo_3O_4]^{4+}$ were also investigated [109].

The compounds $Mo_2O_3(L\text{-}L)_2F_4$ (L-L = bipy, phen) were prepared by the interaction of the ligand dissolved in 40% HF and a solution of $MoO(OH)_3$ in the same solvent. On digestion with water these compounds were converted to the known $Mo_2O_4(L\text{-}L)_2F_2$ [110]. Similarly, reaction of $(pyH)_4[Mo_2O_4(NCS)_6]$ with L-L in EtOH gave $Mo_2O_3(L\text{-}L)_2(NCS)_4$, which on reaction with water yielded $Mo_2O_4(L\text{-}L)_2(NCS)_2$ [111].

The oxo-imido Mo(VI) complex *cis*-MoO(N-*p*-tolyl)$(S_2CNEt_2)_2$ reacts with 0.5 mole equivalent of PPh_3 to give $[Mo(N\text{-}p\text{-tolyl})(S_2CNEt_2)_2]_2O$ and PPh_3O. The electronic spectrum of the dimer in solution does not obey Beers Law and it is proposed that it undergoes an equilibrium dissociation

$$[Mo(N\text{-}p\text{-tolyl})(dtc)_2]_2O \rightleftharpoons Mo(N\text{-}p\text{-tolyl})(dtc)_2 + MoO(N\text{-}p\text{-tolyl})(dtc)_2$$

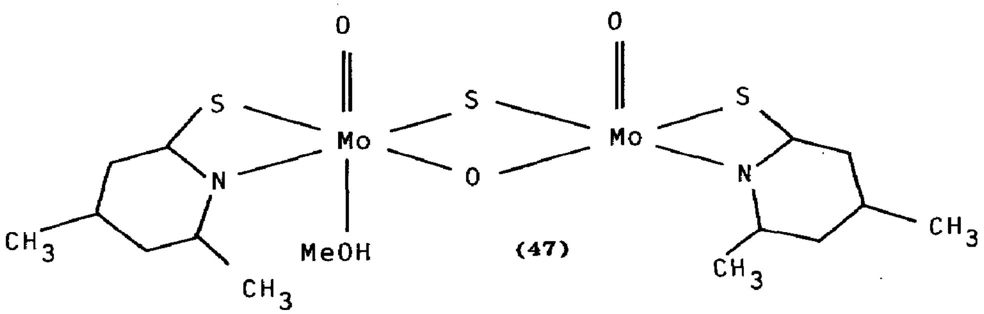
Support for this scheme is given by the reaction with further PPh_3 which gave the Mo(IV) complex Mo(N-*p*-tolyl)$(dtc)_2$. This compound is reactive and could not be isolated, but it was trapped as its dimethylacetylenedicarboxylate adduct. Solutions of Mo(N-*p*-tolyl)$(dtc)_2$ react with oxygen to reform MoO(N-*p*-tolyl)$(dtc)_2$, thus completing a catalytic cycle for the oxidation of PPh_3 [112].

The mixed Mo(V)/Mo(IV) complexes $[Mo_2O_4L_n]^{2-}$ (L = edta,(L-cyst)$_2$, $(ox)_2(H_2O)_2$) were obtained by reduction of the Mo(V) dimers with hydrated electrons which were generated by pulse radiolysis. In the absence of oxygen the mixed oxidation state dimers decay slowly ($t_{1/2} \simeq 5$ -10s) but in the presence of oxygen they rapidly reform the Mo(V) dimers [113].

A series of Mo(V) species with carboxylates $R_2CO_2^-$ (R_2 = Me,*c*-hexyl and (*c*-hexyl)$_2$) have been prepared. They are of the general formulae $Mo_2O_3(R_2CO_2)_4$ (monooxo bridged), $Mo_2O_4(R_2CO_2)_2$ (dioxo bridged), $Mo_2O_2S_2(R_2CO_2)_2$ (disulphido bridged) and $Mo_2O_3S(R_2CO_2)_2$ (monooxo,monosulphido bridged) [114].

The complex (dmmp)OMo(μ-O)(μ-S)MoO(MeOH)(dmmp) (dmmpH = 4,6-dimethylpyrimidine-2-thione) has been prepared by the interaction of

$MoO_2(acac)_2$ with excess dmmpH in refluxing MeOH. A crystal structure determination revealed the stereochemistry shown in (47) with one molybdenum atom octahedral and the other five coordinate.



(47)

Bond distances are

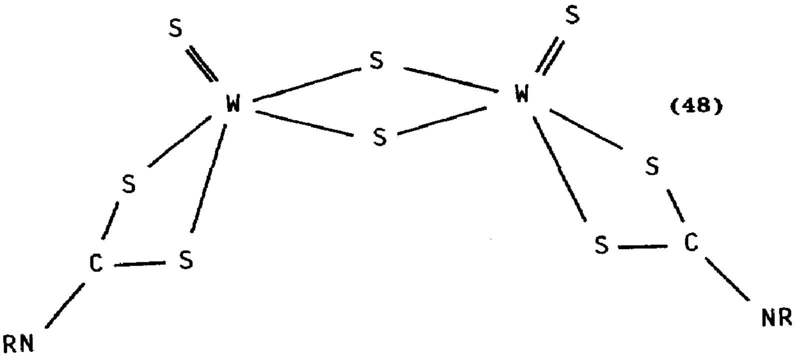
Mo-Mo = 2.660(1)
Mo-μS = 2.320(3)
Mo-S = 2.435(3), 2.489(2)
Mo-N = 2.180(7), 2.209(7)
Mo-MeOH = 2.535(6)Å

Mo=O = 1.667(6)
Mo-μO = 1.911(5), 1.933(5)

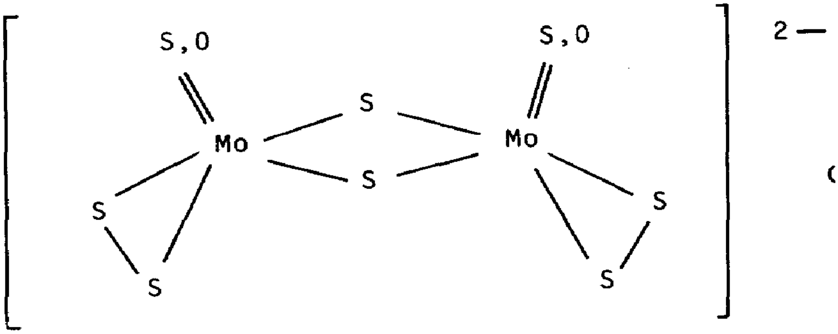
The Mo-Mo bond distance is suggestive of a single bond and the compound is diamagnetic. The shorter bond lengths refer to the five coordinate molybdenum atom. Previous examples of this type of structure have been discussed in terms of 'crevice coordination' with the extra ligand interacting with both metal atoms. This structure shows it is possible to form simple adducts of dimeric Mo(V) compounds [115].

Compounds of the known type $Mo_2S_4(R_2dtc)_2$ (R = Me,Et,bz; R_2 = pyrr,pip, 4-Memorph) have been prepared from $[MoS_4]^{2-}$ and they show two reversible one-electron reductions on the timescale of cyclic voltammetry [116]. Interaction of $W_2O_2S_2(R_2dtc)_2$ with P_2S_5 (R_2 = morph,pip) gave the corresponding $W_2S_4(dtc)_2$ compounds. They are thought to have the structure (48) with five coordinate tungsten atoms [117].

Dissolving $(NH_4)_2[MoS_4]$ in dilute HCl solution gave a dark red solution and subsequent addition of $(NBu_4)Br$ gave $(NBu_4)_2[Mo_2S_7O]$. A crystal structure determination revealed a stereochemistry very similar to the known $Mo_2(S_2)(\mu\text{-}S)_2O_2$ and $Mo_2(S_2)(\mu\text{-}S)_2S_2$ structures with disorder between oxygen and sulphur in the apical positions as shown in (49).



(48)



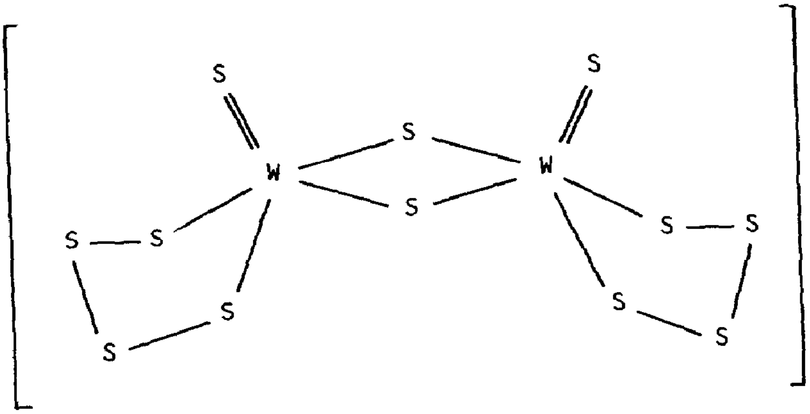
(49)

Bond distances are

Mo-Mo = 2.811(1)	Mo=O,S = 1.945(6), 1.986(6)
Mo-μS = 2.307(3)-2.320(4)	Mo-S_2 = 2.376(4)-2.398(4)Å

The Mo-Mo distance is indicative of a single bond. Spectroscopic evidence suggests, but does not unequivocally prove, the existence of the unsymmetric dimer rather than a solid state mixture of $[Mo_2S_6O_2]^{2-}$ and $[Mo_2S_8]^{2-}$ anions [118].

Interaction of $[MS_4]^{2-}$ with S in hot thf yielded the $[M_2S_{12}]^{2-}$ anions. Spectroscopic evidence suggested that they have similar structures and that of the tungsten complex was determined and is shown in (50). The structure is similar to those of other M(V) dimers containing the *syn*-M_2S_2 unit. These compounds are useful precursors for the preparation of other species containing this core unit, for example $M_2S_4(dtc)_2$ [119].



(50)

Bond distances are

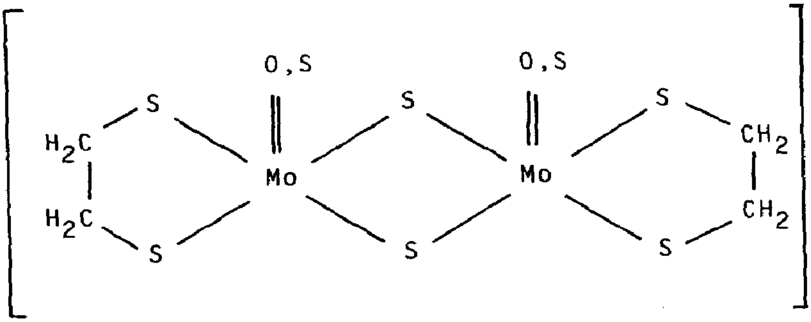
W-W = 2.836(2)

W=S = 2.116(5)

W-μS = 2.320(6)

W-S = 2.387Å(av)

The reaction between phenylhydrazine and $MoO(SCH_2CH_2S)_2$ gave the $[Mo_2O_2S_2(SCH_2CH_2S)_2]^{2-}$ anion and the analogous $[Mo_2S_4(SCH_2CH_2S)_2]^{2-}$ anion was also isolated. The crystal structures of salts of both anions were determined; they are very similar to each other and shown in (51) [120].



(51)

Bond distances are

	O_2S_2	S_4
Mo-Mo	2.866(3)	2.855(1)
Mo=O,S	1.659(30)	2.103(av)
Mo-μS	2.334(14)	2.313(2)
Mo-S	2.404(13)-2.418(11)	2.381(2)-2.412(2)Å

The interaction of arsenite with oxidized, partially reduced and fully reduced forms of xanthine oxidase have been studied by Mo and As EXAFS. A Mo-As distance of 3.02Å was found for the Mo(V) complex, but no interaction was observed in the oxidized form from either Mo or As EXAFS and the Mo=O and Mo=S distances were unaltered. In the reduced form the Mo=S interaction disappeared and a Mo-S-As interaction was suggested [121].

$[Mo(Et_2dtc)_4]I_3$ has been prepared by the iodine oxidation of $Mo_2(Et_2dtc)_6$ in toluene. A structural determination showed an eight coordinate cation with Mo-S distances in two sets, one set of S_4 forming a flattened tetrahedron with Mo-S = 2.545(2)Å and the other S_4 set forming an elongated tetrahedron with Mo-S = 2.500(2)Å [122].

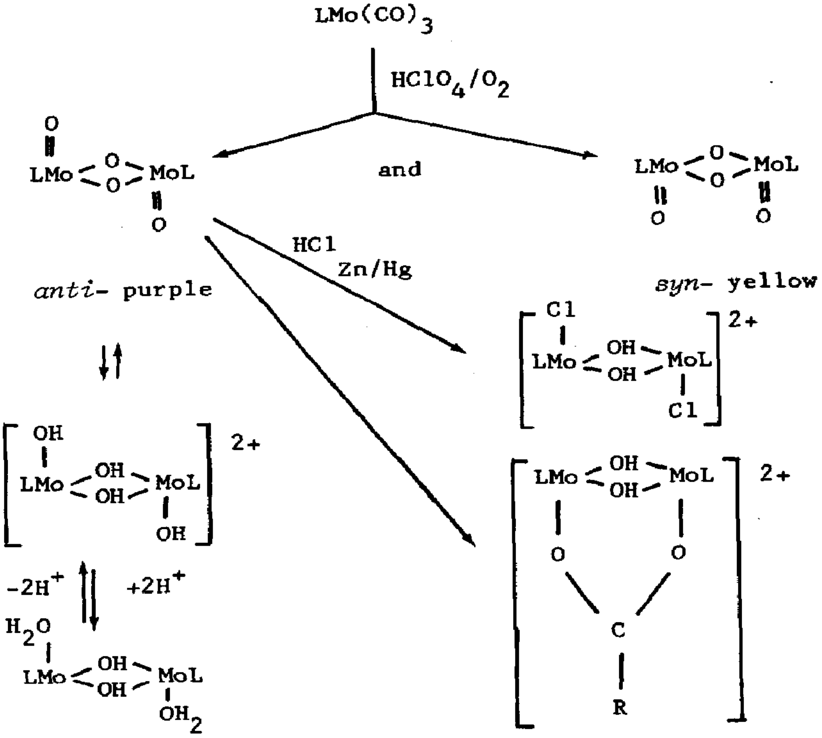
$[MoS_4]^{2-}$ reacts with tetramethylthiuramdisulphide to give $Mo^V(S_2)(dtc)_3$ in contrast to the W(VI) product (shown in **(33)**) in the corresponding $[WS_4]^{2-}$ reaction. $Mo(S_2)(dtc)_3$ is eight coordinate although a detailed description of the stereochemistry was not given. Bond distances are Mo-S(dtc) = 2.496(2)-2.553(2), Mo-S_2 = 2.418(2), 2.445(2), S-S = 2.022(3)Å [70].

2.2.4 Complexes with nitrogen donor ligands

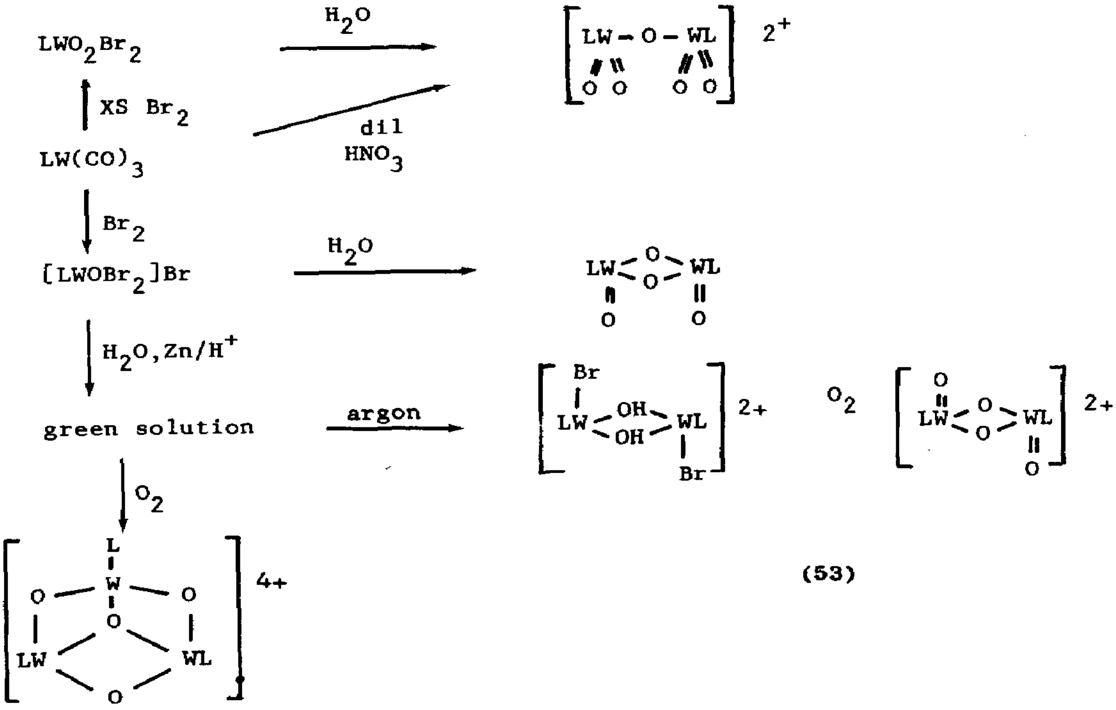
A series of complexes of Mo containing 1,5,9-triazacyclododecane (L) have been prepared with the metal in a number of oxidation states. The ligand always assumes a *facial* geometry and the reaction scheme is shown in **(52)**. A crystal structure determination of *anti*-$[L_2Mo_2O_4](ClO_4)_2 \cdot 2H_2O$ confirmed the structure shown in the scheme. Bond distances are Mo-Mo = 2.586(1), Mo=O = 1.706(6), Mo-μO = 1.952(3)(av) and Mo-N = 2.265(4)-2.346(4)A. The compound is diamagnetic and the bond distance is consistent with a single bond between the metal atoms.

Rather different chemistry is observed by oxidizing $LW(CO)_3$ (where L = 1,4,7-triazacyclononane) and the overall reaction scheme is shown in **(53)** [92].

The more highly substituted N,N',N''-trimethyl-1,4,7-triazacyclononane (L') gives different chemistry to L and seems to favour M(III) complexes. However, the pentavalent compounds $[L'MOX_2]^+$ have been prepared by oxidation of $L'MX_3$ compounds [93,94,124]. Two isomers, blue and green, have been isolated for $[L'WOCl_2]^+$. Their IR spectra differ only in their W=O stretching frequencies (980cm^{-1} blue, 960cm^{-1} green) and crystal structure determinations showed almost identical *facial* geometry about tungsten. The only differences are in the W=O bond distances (1.719(18) blue, 1.893(20)Å green) and with less certainty in the W-N distances *trans* to the oxo group [124]. Interestingly, the isomers dissolve in dry MeCN to give stable blue and green solutions which do not interconvert, in contrast to the similar $MoOCl_2P_3$ complexes (P = PMe_2Ph, PMe_3) in which one form predominates in solution. This example adds to the small number of such isomers which are not yet well understood [124].


LMo(CO)3
HClO4/O2
and
anti- purple
syn- yellow
HCl
Zn/Hg
2+
-2H+
+2H+
H2O
OH2
LMo
MoL
OH
Cl
C
R
O

(52)


LWO2Br2
XS Br2
LW(CO)3
Br2
[LWOBr2]Br
H2O,Zn/H+
green solution
O2
H2O
dil
HNO3
H2O
argon
2+
4+
O2
LW
WL
Br
OH
O
L
W

(53)

Reaction of $Mo(CO)_6$ with phthalodinitrile in toluene in a sealed tube at 180°C gave oxophthalocyanato Mo(V). A crystal structure determination showed a square pyramidal geometry with the Mo atom 0.69Å out of the N_4 plane towards the oxo group. Bond distances are Mo=O = 1.668(6) and Mo-N = 2.068(6)-2.112(7)Å [125].

2.3 MOLYBDENUM(IV) AND TUNGSTEN(IV)

2.3.1 Halides and halo complexes

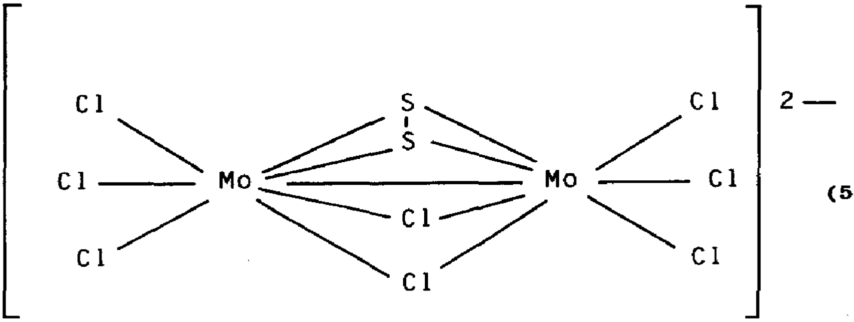
Interaction of $MoCl_5$ or WCl_6 with Et_2O in the presence of an olefin (norbornene, cyclooctadiene) gave crystals of $MCl_4(Et_2O)_2$ [126].

A theoretical study of the trinuclear 8-electron $(Mo^{III})_2Mo^{IV}$ cluster $[Mo_3S_2Cl_9]^{3-}$ has been carried out and it explains the distortion from idealized D_{3h} symmetry in terms of a Jahn-Teller distortion. The treatment leads to some general conclusions on the role of bridging and capping ligands in clusters of the early transition metals [127].

The interaction of NEt_4SH and $MoCl_5$ in dichloromethane gave the reaction

$$(MoCl_5)_2 + 2SH^- \longrightarrow [Cl_3Mo(S_2)Cl_2MoCl_3]^{2-} + 2HCl$$

The disulphide bridge was identified by IR spectroscopy (ν_{S-S} = 609cm^{-1}) and confirmed by a crystallographic study and the structure is shown in (54).



(54)

Bond distances are

Mo-Mo = 2.763(2)
Mo-Cl = 2.393(3)-2.416(3)
Mo-S = 2.435(4)
Mo-μCl = 2.468(3)Å

If $(S_2)^{2-}$ is regarded as a single ligand the geometry of the molecule is almost ideal for two face sharing octahedra. The Mo-Mo distance is consistent with a single bond and interestingly the magnetic properties are consistent with one electron localized on each metal atom [128].

2.3.2 Complexes with oxygen donor ligands

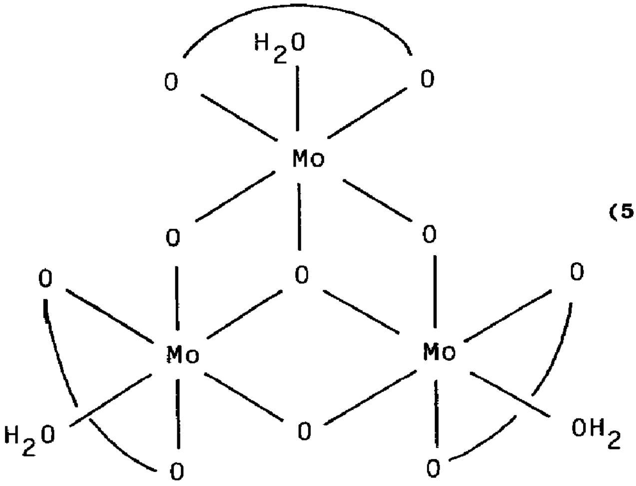
The ^{95}Mo NMR spectra of a large number of Mo(IV) complexes have been recorded. They cover a very wide range of chemical shift (δ1035 to δ3180) and some of the signals are extremely broad. The effects of stereochemistry and the nature of the donor ligands on the linewidths and chemical shifts are discussed [129].

Blue diamagnetic $W(OR)_4$ ($R = 2,6\text{-}C_6H_3({}^{i}Pr)_2$) is the first monomeric W(IV) compound to be reported and it was prepared by treating $WCl_4(SEt_2)_2$ with four mole equivalents of LiOR in toluene/ether. An X-ray structure determination showed it to almost square planar with W-O = 1.86Å(av) and *trans*-O-W-O angles of 168°. The compound is unreactive towards acetylenes due to the arrangement of the phenoxides which block potential coordination sites with their ^{i}Pr groups. The analogous $W(OR)_4$ ($R = 2,6\text{-}C_6H_3Me_2$) was prepared similarly and it is more reactive towards acetylenes [130].

The kinetics of the anation of $[Mo_3O_4]^{4+}$ by $[NCS]^-$ have been studied. With a large excess of $[NCS]^-$, the product is $[Mo_3O_4(NCS)_9]^{5-}$ and a statistically corrected rate constant was used assuming three equivalent sites to give the equilibrium constant $k_{eq} = (k_1/3)[NCS^-] + k_1$. With a small amount of $[NCS]^-$, the product is $[Mo_3O_4(NCS)]^{3+}$ and $k_{eq} = k_1[Mo_3O_4{}^{4+}] + k_1$. The aquation of the thiocyante complexes was also studied [131].

The rate of exchange of oxygen in $[Mo_3O_4]^{4+}$ with solvent water molecules has been studied at 25°C using ^{18}O isotopic tracer techniques. It was found that the four types of oxygen exchange at very different rates with half lives as follows: μ_3 oxygen about 5 days, μ_2O > 3yrs, H_2O(*trans* μ_3O) about 1.1h and H_2O(*trans* μ_2O) about 20min. Reaction with oxalate gave $[Mo_3O_4(ox)_3(H_2O)_3]^{2-}$ and a crystal structure determination of the $[Pt(en)_2]^{2+}$ salt confirmed that the remaining water molecule was *trans* to μ_3-O [132]. Others have prepared two complexes containing the same anion, $Cs_3[Mo_3O_4(ox)_3(H_2O)_3].CF_3SO_3.3H_2O$ and $Cs_2[Mo_3O_4(ox)_3(H_2O)_3].4H_2O.0.5H_2C_2O_4$. In all cases the structure of the anion is the same as is shown in (55) [133].

Orange $[W_3(\mu_3\text{-}O)(\mu_2\text{-}O)_3(H_2O)_9]^{4+}$ has been prepared by the hydrolysis of $K_2[WCl_6]$ in 2M HCl at 90°C followed by ion exchange separation. It reacts with $[NCS]^-$ to give $[W_3O_4(NCS)_9]^{5-}$ which was shown to have the same structure as its molybdenum analogue with bond distances W-W = 2.534, W-μ_3O = 2.039, W-μ_2O = 1.911 and W-N = 2.110Å. $[W_3O_4(H_2O)_9]^{4+}$ can be reduced to the corresponding $(W^{III})_2W^{IV}$ cluster like its molybdenum analogue [134].



(55)

Bond distances for the triflate complex are

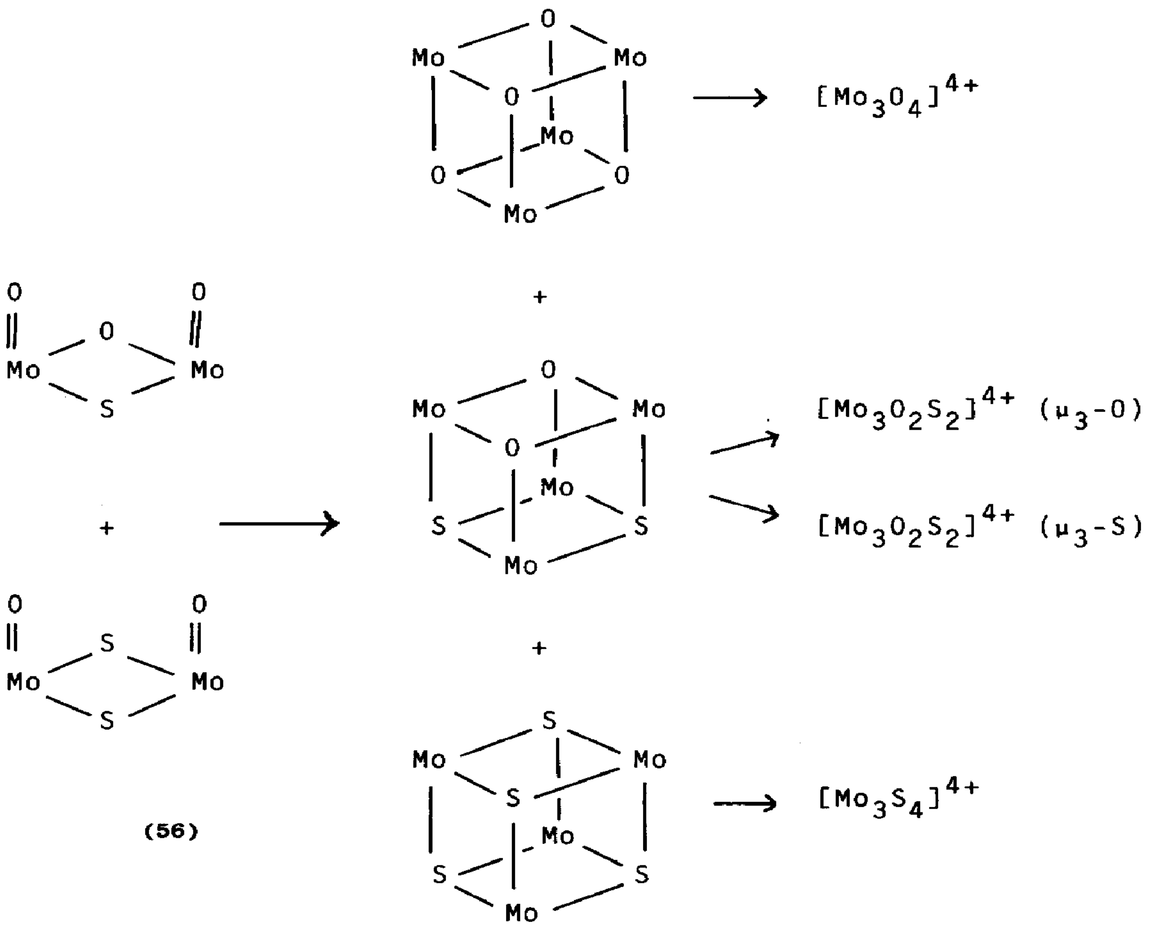
Mo-Mo = 2.491(1)
Mo-O(H_2O) = 2.15(1)
Mo-O(ox) = 2.102(8)Å
Mo-μ_3O = 2.01(1)
Mo-μ_2O = 1.908(2)

The compound $[W_3O_2(OAc)_6(H_2O)(OH)_2].16H_2O$ has been prepared and found to be isostructural with its molybdenum analogue. There is disorder in the crystal between water and hydroxy groups. However in the presence of KBr, the double salt $[W_3O_2(OAc)_6(H_2O)(OH)_2].KBr.15H_2O$ crystallizes and X-ray diffraction detected no disorder in this crystal so that H_2O and OH ligands could be distinguished. However, the W-H_2O bond distance is almost as short as the W-OH distance (and shorter than in the tris aquo cation) suggesting that this bond length is dependent upon H-bonding in the lattice [135].

$[W_3O_2(OAc)_6(H_2O)_3](CF_3SO_3)_2$ was dissolved in dilute KCNS solution and after evaporation the complex $[W_3O_2(OAc)_6(H_2O)(H_3O_2)](NCS).H_2O$ crystallized out and was characterized by X-ray diffraction. The structure is the usual trinuclear arrangement with two μ_3-O oxygen atoms and two acetates bridging each edge of the metal triangle. The H_3O_2 groups link the clusters at two corners and are formed by strong H-bonding between OH on one cluster and H_2O on the other [136].

Interaction of $W(CO)_4(pip)_2$ and HOAC/acetic anhydride mixture gave, after extensive workup, a low yield of the $[W_3O(CMe)(OAc)_6(H_2O)_3]^{2+}$ cluster. A crystal structure determination for the bromide showed a stereochemistry similar to those of other bicapped trinuclear species, but the capping groups were disordered. The W-W distance is 2.801(1)Å. The cluster is paramagnetic, but may be reduced to the diamagnetic +1 cluster. The +1 cation is slowly re-oxidized and there is a pH dependent equilibrium in solution. A reversible one-electron couple is observed electrochemically. The ^1H NMR spectrum of a fresh solution of the +1 cation is sharp, but slowly broadens due to formation of the +2 cation and subsequent fast electron exchange between them [137].

Electrochemical reduction at a mercury pool electrode at -0.95V vs NHE of pairs of $[Mo_2O_4(cys)_2]^{2-}$, $[Mo_2O_3S(cys)_2]^{2-}$ and $[Mo_2O_2S_2(cys)_2]^{2-}$ in equimolar amounts led to the formation of all eight possible triangulo $[Mo_3O_xS_{4-x}]^{4+}$. Individual complexes could be separated by ion exchange techniques. The distribution of products is consistent only with initial formation of the cubic compounds $[Mo_4O_xS_{4-x}]^{5+}$ and the general scheme envisaged is shown in (56) for one pair of reactants [138].



(56)

2.3.3 Complexes with sulphur donor ligands

Addition of $MoCl_4$ to two mole equivalents of $Me_3Si(SR)$ (SR = 2,4,6-triisopropylbenzenethiolate) gave, surprisingly, $Mo(SR)_4Cl$. It is rapidly reduced to $Mo(SR)_4$ which is very sensitive to moisture and oxygen. X-ray crystallography on $Mo(SR)_4$ showed the stereochemistry about molybdenum to be a slightly flattened tetrahedron with Mo-S = 2.262(2)Å. The compound forms a number of acetylene adducts which could be isolated, but a carbonyl adduct was too unstable to be isolated [139]. $W(SCMe_3)_4$ was prepared by the interaction of $WCl_4(SEt_2)_2$ with the thiol in the presence of NEt_3. X-ray crystallography showed it to be isomorphous with the corresponding molybdenum compound with geometry between tetrahedral and square planar [130].

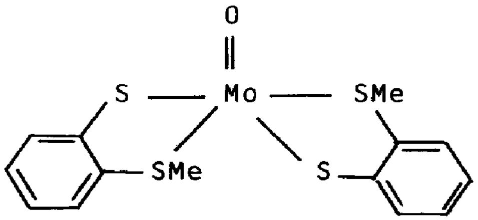
The Mo(VI) compound $MoO_2(dttd)$ (17) (dttd = 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane) is reduced by PPh_3

$$MoO_2(dttd) + PPh_3 \longrightarrow MoO(dttd) + PPh_3O$$

and an analogous complex was formed by the reaction

$$MoCl_4(thf)_2 + 2\textit{o}\text{-}MeSC_6H_4SH + H_2O \longrightarrow MoO(MeSC_6H_4S)_2$$

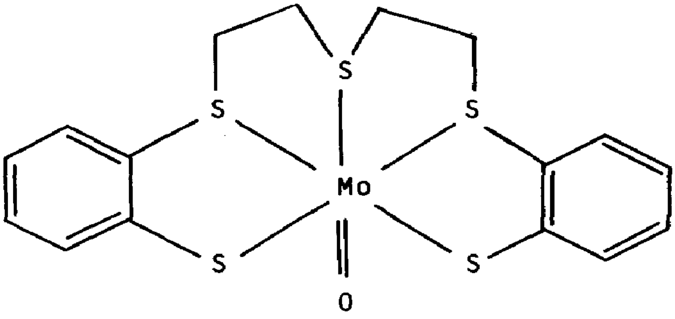
and the structure of the latter compound was determined and is shown in (57).



(57)

Similarly the pentadentate ligand 2,3,11,12-dibenzo-1,4,7,10,13-pentathiatridecane (H_2L) reacted with $MoCl_4(thf)_2$ in the presence of water to give the compound MoOL, whose structure is shown in (58) [41].

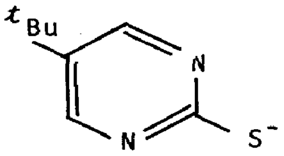
Reaction of MCl_4L_2 (L = PPh_3, MeCN) with $PPh(CH_2CH_2SH)_2$ gave $M[PhP(CH_2CH_2S)_2]_2$ compounds and the structure of the molybdenum compound was shown to be octahedral with the phosphorus atoms *cis* to each other. Bond distances are Mo-P = 2.472(10)(av) and Mo-S = 2.348(12)Å(av). The compound is an interesting contrast with $Mo[S(CH_2CH_2S)_2]_2$ which is trigonal prismatic. It is thought that S-S interactions tend to favour the latter and the introduction



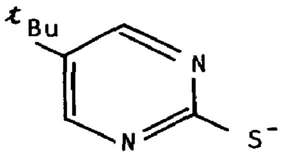
(58)

of the two phosphorus atoms into the coordination sphere tips the balance in favour of octahedral geometry [90].

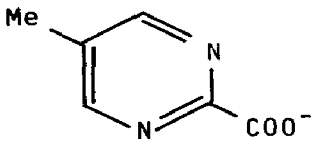
Two new series of mixed chelate ligand complexes of W(IV) of the types $W(bmpd)_x(mpd)_{4-x}$ and $W(bmpd)_x(mpic)_{4-x}$ have been prepared and isolated and the structures of the ligands are shown in (59 -61) .



bmpd⁻ (59)



mpd⁻ (60)

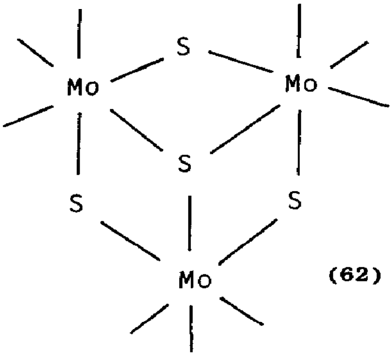


mpic⁻ (61)

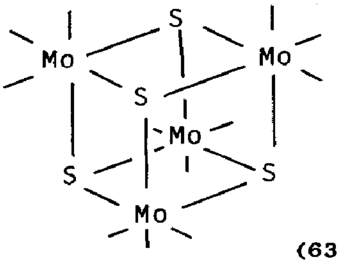
The former series gave six compounds (two stereoisomers for the stoichiometry with n = 2) while the second series gave only five compounds. In the first series both ligands give 4 membered rings on chelation while in the second series there are 4 and 5 membered rings. All the compounds were isolated and their structures determined on the basis of their 360MHz ^1H NMR spectra [140].

Reaction of $(NH_4)_2[Mo_3S_{13}].2H_2O$ with excess nitrilotriacetic acid (H_3nta) in refluxing dmf afforded (after protracted workup) crystals of $(NH_4)_3[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(nta)(ntaH)_2]$. The structure consists of the Mo_3S_4 core with each of the tridentate nta ligands coordinated to one molybdenum through nitrogen and two carboxylate oxygens. For the purposes of charge balance one of the nta ligands is assumed to be present in the trianion form. The interesting feature of this reaction is the conversion of the original μ_2-(S_2) group to μ_2-S [141].

Electrochemical reduction of $Na_2[Mo_2O_2S_2(cys)_2]$ in 2M HCl under H_2 at -0.85V vs NHE at a mercury pool electrode gave a green solution which, after ion exchange separation procedures, gave $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_4S_4(H_2O)_{12}]^{5+}$. On addition of $[NCS]^-$ they gave the known $[Mo_3S_4(NCS)_9]^{5-}$ and $[Mo_4S_4(NCS)_{12}]^{7-}$. The structures of the cations are given in (62) and (63) [142].



(62)



(63)

Reaction of $Mo(CO)_6$, Na_2S and acetic anhydride under reflux followed by hydrolysis and ion exchange separation yielded green bands due to $[Mo_3S_4]^{4+}$ (I) and a second product (II) whose visible and UV spectra were similar to, but not identical with, that of (I). Confirmation of the identity of $[Mo_3S_4]^{4+}$ was provided by the isolation of the oxolato complex $Cs_2[Mo_3S_4(ox)_3(H_2O)_3].3H_2O$ whose structure was determined [143]. In a subsequent publication, band (II) was shown to be due to $[Mo_4S_4]^{6+}$ and the isolation and structure of the derivative $(NH_4)_6[Mo_4S_4(NCS)_{12}].10H_2O$ was reported [144]. The structure is a grossly distorted cubane type with Mo-Mo = 2.791(1) and 2.869(1)Å. It was observed that $[Mo_4S_4]^{6+}$ is slowly converted to the $[Mo_3S_4]^{4+}$ by air oxidation and the change is accelerated in the presence of coordinating ligands (such as oxalate) which stabilize the trimer [144].

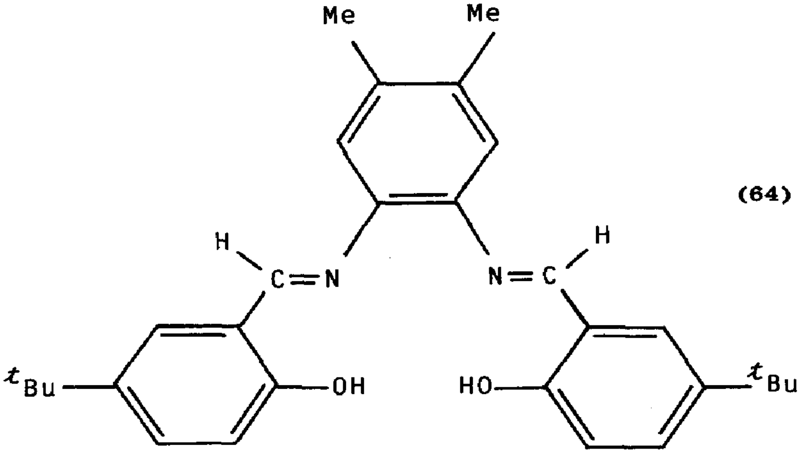
2.3.4 Complexes with nitrogen and phosphorus donor ligands

Reactions of $Mo(NMe_2)_4$ with a series of alkylated phenols have been investigated. All the products were paramagnetic (μ = 1.10-1.79BM) but the stoichiometry of the products depended upon the steric demands of the alkoxide. With $4\text{-}MeC_6H_4OH$ and $3,5\text{-}Me_2C_6H_3OH$ the products were $Mo(OAr)_4(NMe_2)_2$ which were presumed to be *trans*. $Mo(OAr)_4(HNMe_2)$ was obtained with $2,6\text{-}Me_2C_6H_3OH$ but the geometry of this five coordinate species is not known. The sterically demanding $2,6\text{-}{}^iPr_2C_6H_3OH$ and $2\text{-}{}^tBu,6\text{-}MeC_6H_3OH$ gave $Mo(OAr)_3(NMe_2)(HNMe_2)$ [145].

$[W_3O_4L_3]^{4+}$ (L = 1,4,7-triazacyclononane) was isolated as indicated earlier in scheme (53). A crystal structure determination confirmed the structure indicated in the scheme with the tridentate coordinated in a *facial* manner. Bond distances are W-W = 2.52(av), W-μ_3O = 2.10(av), W-μ_2O = 1.94 and W-N = 2.14(3)-2.26(3)Å [92].

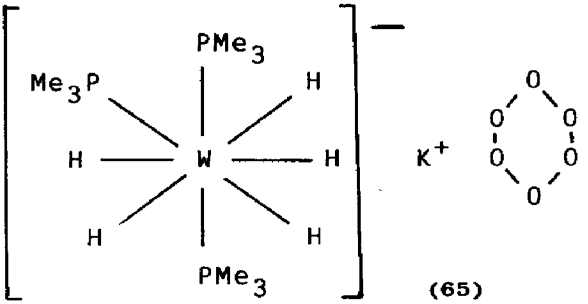
The ligand N,N',N''-trimethyl-1,4,7-triazacyclononane (L') gave Mo(IV) compounds of the type $[L'MoBr_3]^+$ by mild oxidation of $L'MoBr_3$. A crystallographic study confirmed the *facial* coordination of the ligand. Bond distances are Mo-N = 2.237(13), Mo-Br = 2.365(4)-2.458(3)Å [93]. Similar tungsten complexes were also prepared [94].

The reaction of $W(CO)_6$ with N,N-bis(5-^{t}Bu-2-hydroxybenzylidene)-1,2-diaminobenzene (H_2-L_2-L'_2) (64) in dry mesitylene at 170°C gave a very complex mixture of more than 15 species. Partial separation was achieved by TLC and four species have been characterized as stereoisomers of the neutral eight coordinate $W(L_2\text{-}L'_2)_2$. Visible and IR spectra of the four isomers are almost identical, but their 360MHz ^{1}H NMR spectra are different. All showed four ^{t}Bu signals indicating a set of complexes with no inherent symmetry and possible stereochemistries were discussed [146].

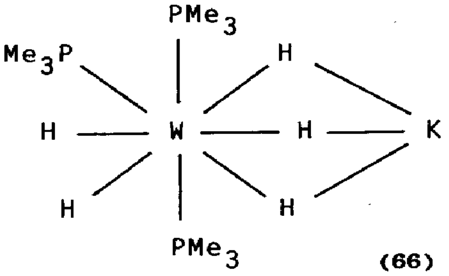


(64)

Reaction of $WH_6(PMe_3)_3$ with NaH or KH in thf gave yellow compounds $WH_5(PMe_3)_3M'$. Crystals suitable for X-ray diffraction were prepared for the crown ether adducts $WH_5(PMe_3)_3M'$(crown) and the structures of both adducts were determined. In the case of the sodium salt, the hydrides were not detected in the analysis, but the geometry of the $W(PMe_3)_3$ fragment was identical to that of the potassium salt for which all the hydride ligands were observed. Three of the hydrides are directed towards potassium and two away from potassium. There are two extreme views of the bonding as shown in (65) and (66) [147].



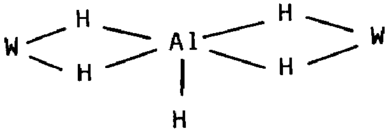
(65)



(66)

Reaction between $WH_6(PMe_3)_3$ and ^nBuLi gave $[WH_5(PMe_3)_3Li]_4$ which X-ray crystallography showed contains a square of tungsten atoms having lithium atoms along the edges with alternating long and short Li-W distances. Although the analysis did not reveal the hydride ligands, it is possible that some bridge between lithium and tungsten and the arrangement of the $W(PMe_3)_3$ fragments is similar to that in the Na and K salts [147].

Reaction between $WCl_4(PMe_3)_3$ and $LiAlH_4$ in Et_2O at -80°C followed by addition of excess $Me_2NCH_2CH_2NMe_2$ yielded insoluble $Me_2NCH_2CH_2NMe_2AlH_3$ and a yellow solution from which was isolated $(PMe_3)_3H_3W(\mu\text{-}H)_2Al(H)(\mu\text{-}H)_2WH_3(PMe_3)_3$. A crystal structure determination resolved the hydrides attached to Al, but the terminal tungsten hydrides were not clearly resolved. The most interesting feature of the structure is the bridging section shown in (67). The complex



(67)

can be considered as a bis-$WH_4(PMe_3)_3$ adduct of AlH_3, but it is equally valid to describe it as $[AlH_5]^{2-}$ bridging two $[WH_3(PMe_3)_3]^+$ units. The compound is fluxional in solution at room temperature but rigid on the NMR timescale at -80°C and at this temperature the ^1H and ^{31}P NMR spectra are consistent with the solid state structure [148].

2.3.5 Complexes with metal-carbon bonds

Reaction between $NaK_3[MoO_2(CN)_4].6H_2O$ and NaN_3 at pH 9.5-10 followed by addition of CsCl gave $Cs_2Na[MoO(N_3)(CN)_4]$. A crystallographic study showed a *trans* configuration for the distorted octahedral anion with the Mo atom displaced 0.28Å out of the plane of the four cyano groups towards the oxo group. Bond distances are Mo=O = 1.70(1), Mo-N = 2.29(2), Mo-C = 2.17(1)Å. The N_3 ligand is linear, but the angle at the nitrogen bound to molybdenum is 121(6)° [149].

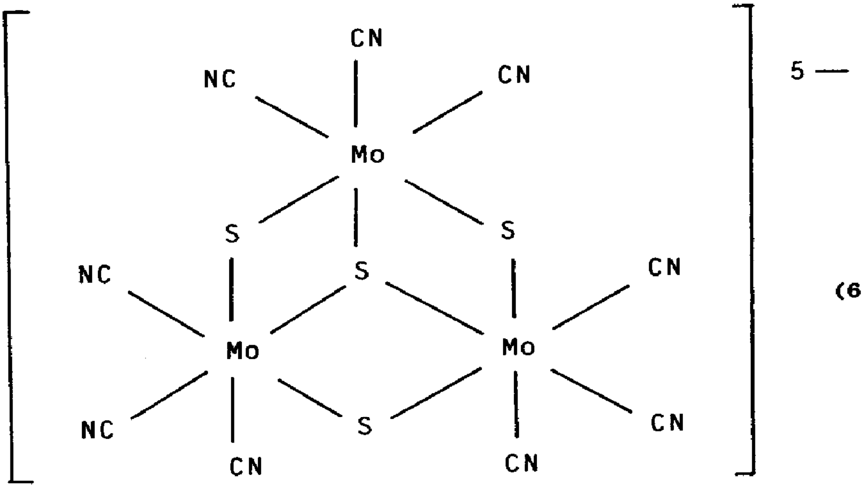
Ligand field photolysis of aqueous alkaline solutions of $K_4[M(CN)_8]$ containg KCN gave $[MO(CN)_5]^{2-}$ species. For Mo, the pentacyano complex was also formed by the interaction of $[MoO(OH)(CN)_4]^{2-}$ and cyanide, but not for the tungsten complex [150].

Further details have been given on $K_4[MoH(CN)_7]$. The molecule is fluxional with the ^{13}C NMR spectrum appearing as a doublet and the hydride signal appears at δ2.3. The ^{13}C NMR spectra of solutions of $K_5[Mo(CN)_7]$ also showed the presence of the signal due to the hydride, but addition of base reduced its intensity. It is suggested that the equilibrium

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

occurs in solution [151].

Reaction of MoS_3 with KCN gives $K_5[Mo_3S_4(CN)_9].3KCN.4H_2O$ and a crystal structure determination showed a typical Mo(IV) trimer core as shown in (68).



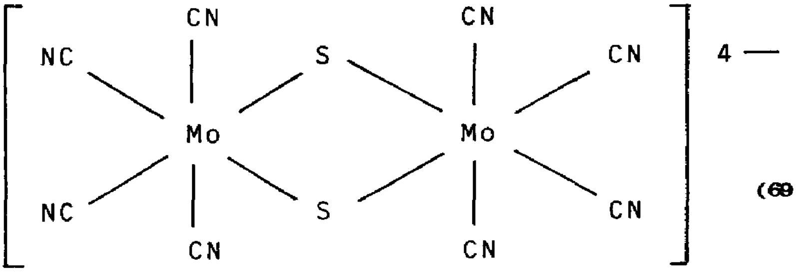
(68)

Bond distances are

Mo-Mo = 2.775(11)(av) Mo-C = 2.182(13)-2.222(10)

$Mo-\mu_3S$ = 2.363(3) $Mo-\mu_2S$ = 2.312(2)-2.324(2)Å

The crystal structure of $(PPh_4)_2[Mo_2S_2(CN)_8].nH_2O$ was also reported in the same paper and the stereochemistry of the anion is shown in (69).



(69)

Bond distances are

Mo-Mo = 2.758(7)　　Mo-S = 2.295(14)
Mo-C = 2.06(5)-2.22(5)Å

IR, Raman and resonance Raman spectra were presented together with a detailed vibrational analysis for $[Mo_4S_4(CN)_{12}]^{8-}$ [152].

2.4 MOLYBDENUM(III) AND TUNGSTEN(III)

The preparations of $(dppeH_2)_3[MoCl_6]_2$ and $(dppeH_2)_3[Mo_2Cl_9]_2$ have been reported and the former proved to be active in olefin epoxidation. A crystal structure determination of this complex confirmed the octahedral stereochemistry with Mo-Cl = 2.439(2)-2.469(2)A [153].

The anion $[Mo_2Br_8H]^{3-}$ in $(H_7O_3)(NMe_4)[Mo_2Br_8H]$ does not show disorder in the solid state as has been the case in previous structural studies on salts of this anion. Bond distances are Mo-Mo = 2.384(4), Mo-μBr = 2.630(av), Mo-Br(*trans* H) = 2.635(5) and other Mo-Br = 2.546Å(av) [154].

The reactions of $(NBu_4)_2[Mo_2Br_6]$ with monodentate and bidentate phosphines have been investigated and the course of the reactions is as in scheme (70).

$$\begin{tikzcd}
(NBu_4)_2[Mo_2Br_6] + 2L \arrow[r] & (NBu)[Mo_2Br_5L_2] \arrow[d, "2L"] \\
Mo_2Br_4L_4 & (NBu_4)[Mo_2Br_5L_4] \arrow[l]
\end{tikzcd}$$

(70)

where L = $PEtPh_2$, PEt_2Ph, PEt_3 or 1/2dppe. In addition, the reaction

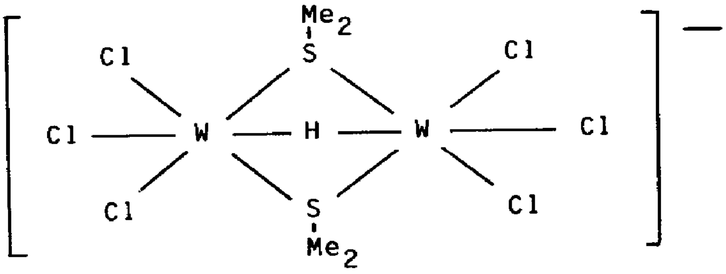
$$(NBu_4)[Mo_2Br_5(dppe)_2] + 2NBu_4Br \longrightarrow (NBu_4)[MoBr_4(dppe)] + (NBu_4)[MoBr_3(dppe)(Me_2CO)]$$

was reported in acetone solution. The crystal structure of $(NBu_4)[MoBr_4(dppe)]$ was determined and the anion has a distorted octahedral geometry. Bond distances are Mo-Br(*trans* P) = 2.586(4)(av), Mo-Br(*cis* P) = 2.565(4), Mo-P = 2.532(8)Å [155].

Trans -$[MoCl_4(thf)_2]^-$ has been prepared and will probably prove to be a very useful starting material for the preparation of other Mo(III) complexes. A crystal structure determination confirmed the stereochemistry with Mo-Cl = 2.421(9)-2.442(8) and Mo-O = 2.154(12)Å. It is more stable in solution than $MoCl_3(thf)_3$. It reacts readily to give $[MoCl_4(dppe)]^-$, $[MoCl_4(PMe_2Ph)_2]^-$ and $[MoCl_4py_2]^-$ [156].

A series of complexes of Mo(III) have been prepared by the interaction of $MoCl_3(thf)_3$ or $MoCl_3(PrCN)_3$ with the polythiaethers 1,4,8,11-tetrathiacyclotetradecane (ttt) and 1,4,7,10,13,16-hexathiacyclooctadecane (hto). Among the complexes isolated were $MoCl_3(hto)$, $(MoCl_3)_2(hto)(thf)$, $MoCl_3(ttt)(thf)$ and $MoCl_3(ttt)$. The complexes are insoluble and polymeric structures were proposed on the basis of IR studies. In addition, some mixed oxidation state compounds were formed in reactions which involved cleavage of the macrocyclic ring [157].

The reaction between $WCl_4(SMe_2)_2$ and excess Et_3SiH gave diamagnetic $Cl_3W(\mu\text{-}H)(\mu\text{-}SMe_2)_2WCl_2(SMe_2)$. Addition of PPh_4Cl gave the chloro derivative whose structure was determined by X-ray diffraction and is shown in (71).



(71)

Bond distances are

W-W = 2.419(1)

W-Cl(*trans* H) = 2.407(5), 2.435(5)

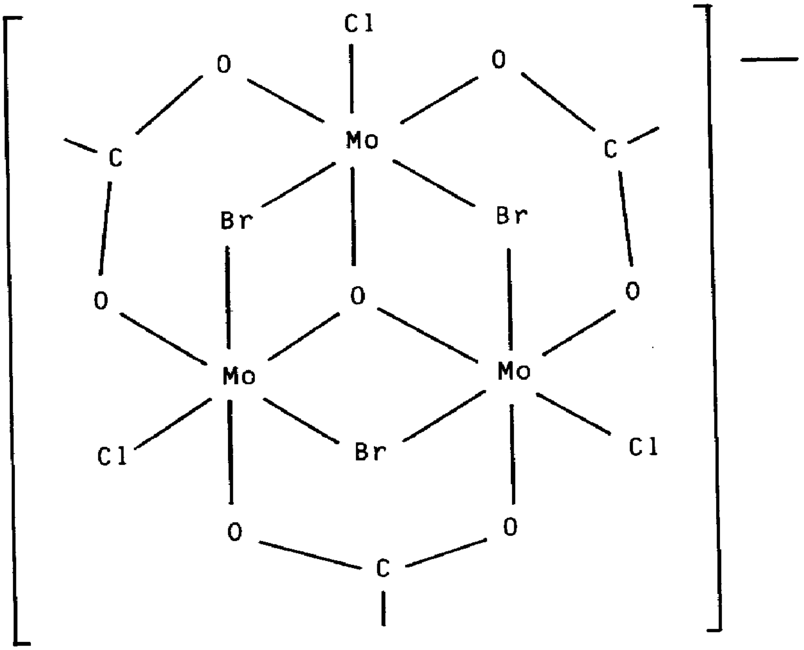
W-S = 2.372(5)-2.389(4)Å

W-H = 1.48

W-Cl = 2.375(5)-2.394(4)

The W-W bond length is consistent with a triple bond and the *trans* effect of the hydride is noticable in the W-Cl bond distances. The hydride NMR signal occurs at the very high frequency of 63.71 at room temperature and shows interesting variation with temperature which is discussed in terms of various rotomeric forms of the anion [158].

Crystals of $(NMe_4)[\{MoClBr(O_2CH)\}_3O]$ were isolated from the reaction mixture of $MoBr_3$, NMe_4Br and HCOOH in EtOH saturated with HCl. The structure of the anion is shown in (72).



(72)

Bond distances are

Mo-Mo = 2.596(1)

Mo-Cl = 2.420(av)

Mo-Br = 2.531Å(av)

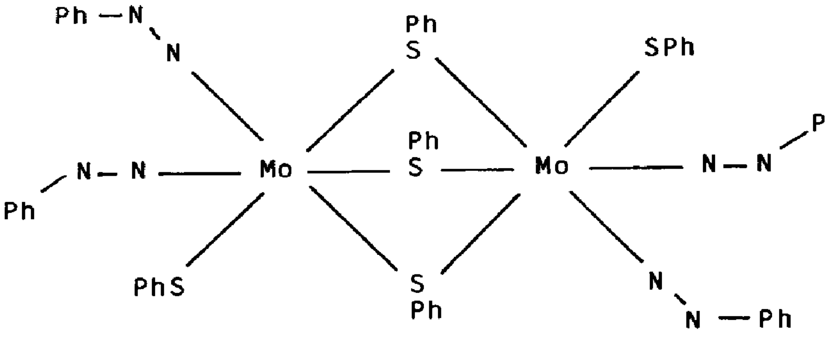
Mo-μ_3O = 1.976(3)

Mo-O = 2.080(4)-2.098(4)

The structure is similar to that of the Mo(IV) trimers with a μ_3-O capping the metal triangle, but the formal oxidation state is 3.33, so there are eight electrons available for metal-metal bonding. This suggests a bond order of 1.33 and the internuclear distance is consistent with this [159].

A Raman study has been made of $(Mo^{IV})_3$, $(Mo^{III})_3$ and $(Mo^{III})_2$ in aqueous solution. The spectra suggested that the latter species has a μ_2-oxo bridge and the spectra of the first two were almost identical suggesting that the trimeric structure is retained on reduction of $(Mo^{IV})_3$ [160].

Interaction of $Mo(NNHPh)_2(butane\text{-}2,3\text{-}diolate)_2.H_2NNHPh$ with excess HSPh in MeOH in the presence of NEt_3 gave a deep purple solution from which were isolated black crystals of $(NHEt_3)[Mo_2(NNPh)_4(SPh)_5]$. A crystal structure determination revealed the arrangement shown in (73).



(73)

Bond distances are

Mo-Mo = 3.527(1)

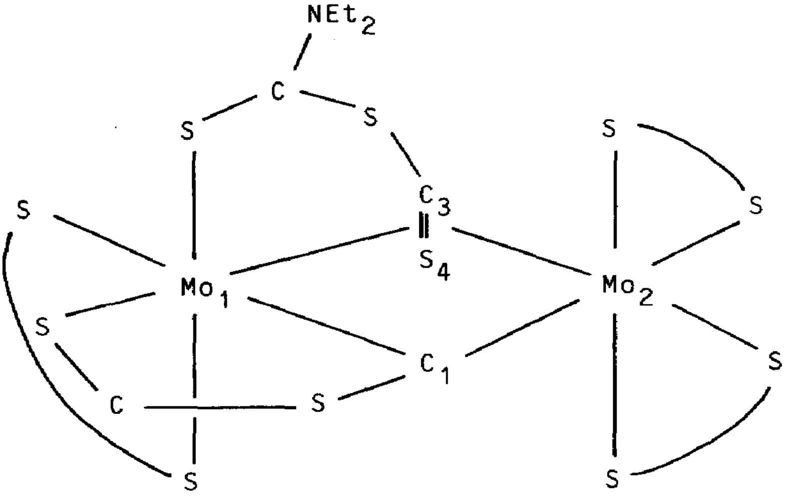
Mo-μSPh = 2.533(5)-2.653(5)   Mo-SPh = 2.449(7), 2.525(5)

Mo-N = 1.73(1)-1.83(1)   N-N = 1.26(2)-1.37(2)Å

The very long Mo-Mo distance precludes a metal-metal bond and this is probably due to the electron withdrawing NNPh groups. The $Mo_2(SPh)_3$ unit is distorted as a consequence of the lengthening of the Mo-Mo distance [161].

$Mo(CO)_2(Et_2dtc)_2$ undergoes an extraordinary reaction with CS_2 in the presence of PPh_3 to give $Mo_2(dtc)_3(\mu\text{-}CSC(S)S)(\mu\text{-}S_3C_2NEt_2)$ which has the structure shown in (74). Three dtc ligands remain intact and are chelating in the usual manner while the fourth of the original dtc ligands is modified by addition of a CS unit which is bound $\mu\text{-}\eta^2$ between the metals. The C_2S_3 ligand is presumably formed by the interaction of CS_2 and CS (formed by S abstraction from CS_2 by PPh_3). This ligand contains a free C=S unit which was methylated to yield the corresponding cation [162].

The kinetics and mechanism of the reaction of green diamagnetic $[L(H_2O)Mo(OH)_2Mo(H_2O)L]^{4+}$ (L = 1,4,7-triazacyclononane) with nitrate ion in acidic aqueous solution have been investigated. The reaction yields *anti*-$[L_2Mo_2O_4]^{2+}$ quantitatively. By use of ^{18}O enriched NO_3^- it was shown that the terminal oxygen atoms in the product are derived from the nitrate, thus confirming oxygen atom transfer [163]. With the same ligand, oxidation of $LMo(CO)_3$ with Br_2 in $CHCl_3$ gave monomeric $[LMoOBr_2]Br$. Reduction of this in

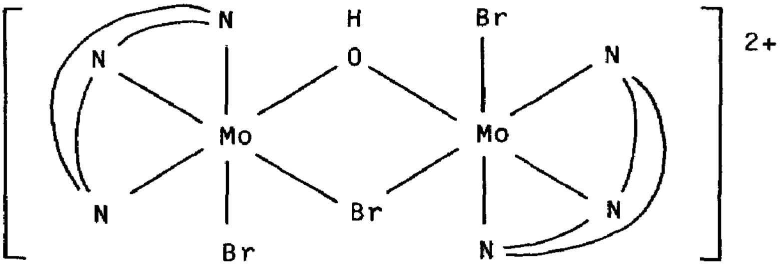


(74)

Bond distances are

Mo-Mo = 2.616(1)
Mol-C3 = 2.026(8)
Mol-S4 = 2.449(3)
Mo-Cl = 1.920(9)
Mo2-C3 = 2.086(9)
Mo2-S4 = 2.406(3)Å

aqueous solution by Zn under N_2 followed by addition of NaBr gave $[Mo_2L_2(\mu\text{-}OH)(\mu\text{-}Br)Br_2]Br_2.4H_2O$ whilst reduction at elevated temperatures gave $[Mo_2L_2(\mu\text{-}OH)_2Br_2].2H_2O$. The structure of the former was determined and is shown in (75).



(75)

Bond distances are

Mo-Mo = 2.558(3)
Mo-Br = 2.547(7)
Mo-μOH = 1.84(2)Å
Mo-N = 2.19(3)(av)
Mo-μBr = 2.558(5)

The short Mo-Mo separation indicates strong bonding and a triple bond is suggested [164]. The structure of $[W_2L_2(\mu\text{-}OH)_2Br_2]^{2+}$ was found to be very similar with bond distances W-W = 2.477(3), W-μOH = 2.095(20), W-Br = 2.545(5) and W-N = 2.20Å(av) [92].

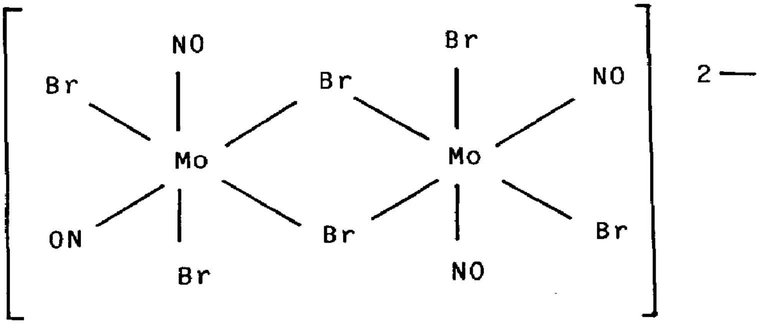
Reactions of $W(N_2)_2(dppe)_2$ with $HFeCo_3(CO)_{12}$ in H_2O/thf solution gave $[W(OH)(NNH_2)(dppe)_2][FeCo_3(CO)_{12}]$. In acetone, a condensation product $[W(OH)(NNCMe_2)(dppe)_2]PF_6$ was isolated. Reactions of $W(N_2)_2(dppe)_2$ with $HFeCo_3(CO)_{12}$ in dichloromethane gave $[WCl_2(dppe)_2]^+$ and a crystallographic study on the $[BF]^-$ salt showed the cation to have *trans* geometry with W-Cl = 2.312(5) and W-P = 2.522(5), 2.563(5)Å [165].

2.5 MOLYBDENUM(II) AND TUNGSTEN(II)

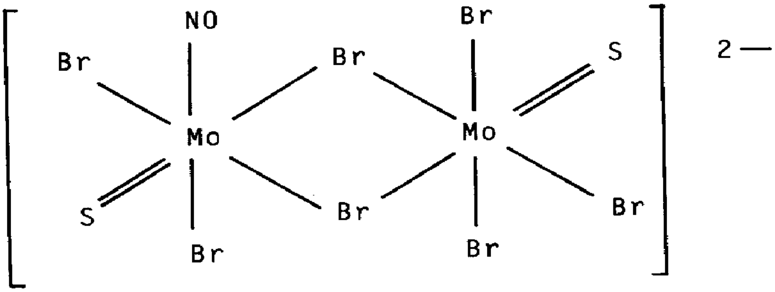
Reactions of the tetrameric clusters $Mo_4Cl_8(PR_3)_4$ (PR_3 = PEt_3,$P(^{n}Pr)_3$, $P(^{n}BU)_3$,PMe_2Ph) with $Mo(CO)_4Cl_2$ or $Mo(CO)_6$ in refluxing ClC_6H_5 gave the products $[Mo_4Cl_8(PR_3)_2]_n$. On the basis of spectroscopic studies these appear to retain the rectangular cluster arrangement of their precursors and reaction with phosphine re-generates $Mo_4Cl_8(PR_3)_4$. Prolonged reaction with $Mo(CO)_6$ gave a different product which appeared to be β-$MoCl_2$ [166]. $Mo_2(OAc)_4$ and $AlCl_3$ reacted in refluxing ClC_6H_5 to give a reactive form of β-$MoCl_2$. A spectroscopic comparison of this product with the rectangular clusters $Mo_4Cl_8(PR_3)_4$ suggested that β-$MoCl_2$ also contains tetrameric clusters. Direct reaction with PR_3 at room temperature to give $Mo_4Cl_8(PR_3)_4$ supports this view [167].

$[Mo_2Br_6]^{2-}$ has been prepared by the interaction of $Mo(CO)_6$ and NEt_4Br in 1,2-dibromoethane. The anion shows two electrochemical oxidations. The first is reversible on faster scan rates but the second is irreversible under all scan conditions at room temperature [168].

The interaction of $Mo(NO)_2Br_2$ and $(PPh_3Me)_2S_6$ gave mixed single crystals of containing 2/3 $(PPh_3Me)_2[Mo_2Br_6(NO)_4]$ and 1/3 $(PPh_3Me)_2[Mo_2Br_6S_2(NO)_2]$ whose structures are shown in (76) and (77) [66].



(76)



(77)

Bond distances are

Mo...Mo = 3.978
Mo=S = 2.396(15)
Mo-Br = 2.590(av)
Mo-μBr) = 2.662(av)
Mo-N = 1.837(12)Å

Electrochemical studies on Mo(HB{Me$_2$pz}$_3$)(NO)I$_2$ showed the formation of [Mo(HB{Me$_2$pz}$_3$(NO)I$_2$]$^-$ which slowly loses I$^-$ to form Mo(HB{Me$_2$pz}$_3$(NO)I(solv) which itself undergoes a reversible one-electron oxidation [169].

Reaction between M(CO)$_4$Br$_2$ and Htipt (Htipt = 2,4,6-^{i}Pr$_3$C$_6$H$_2$SH) gave [M(CO)$_2$(tipt)$_3$]$^-$ and other sterically demanding thiols gave similar products. X-ray diffraction of the PPh$_4^+$ salt of the molybdenum complex showed a trigonal bipyramidal structure with the carbonyls axial. Bond distances are Mo-C = 1.96(av), Mo-S = 2.317(5)-2.342(5)Å. As expected for a formally 14-electron species, it is reactive to substitution and addition. Addition of CO gave the corresponding tricarbonyl anion, but the extra carbonyl could be easily removed. NCR and PMe$_2$Ph replace one carbonyl ligand whilst [NNPh]$^+$ in MeCN gave [Mo(MeCN)(NNPh)(tipt)$_3$]$^-$ whose structure was also determined, confirming the MeCN and NNPh ligands to be axial. Bond distances are Mo-N(NNPh) = 1.782(12), Mo-N(MeCN) = 2.227(14), Mo-S = 2.32(av) and N-N = 1.211Å [170].

2.6 MOLYBDENUM(0) AND TUNGSTEN(0)

A series of mono(dinitrogen) complexes Mo(N$_2$)(P-P-P)(PMe$_2$Ph)$_2$ or Mo(N$_2$)(P-P-P)(L-L) have been prepared by Na/Hg reduction of MoCl$_3$(P-P-P) (P-P-P = PhP(CH$_2$CH$_2$PPh$_2$)$_2$) under limited amounts of nitrogen in the presence of two mole equivalents of PMe$_2$Ph or one mole of L-L (L-L = dmpm,dppm,dppe,diars). The structures of the compounds were determined by ^{31}P NMR studies and the tridentate ligand was usually bound in a *facial* manner. Reaction with acids HX gave either NH$_3$ or N$_2$H$_4$ [171].

Reaction of $WCl_4(PMe_3)_3$ with a Na dispersion in thf under N_2 gave *cis*-$W(N_2)_2(PMe_3)_4$ which reacted with further PMe_3 under Ar at 40-50°C to give $W(N_2)(PMe_3)_5$. X-ray diffraction of the latter gave bond distances W-N = 2.04(2), W-P(*trans* N) = 2.473(4), other W-P = 2.444(7)Å(av). Various reactions by both complexes to give carbonyl and acetylene derivatives were described [172].

The complexes *cis*-$W(N_2)_2(dppm)_2$ and *trans*-$W(N_2)_2(Ph_2PCH{=}CHPPh_2)_2$ were prepared by reduction of WCl_6 or $WCl_4(Ph_2PCH{=}CHPPh_2)_2$ by Mg in thf in the presence of the phosphine. The crystal structure of *cis*-$W(N_2)_2(PMe_2Ph)_4$ was also reported. Bond distances are W-N = 1.983(3), 2.015(3), W-P = 2.444(1)-2.481(1), N-N = 1.123(4)Å(av) [173].

Photoluminescence data have been recorded over a wide temperature range for *trans*-$M(N_2)_2(dppe)_2$ and assignments made for the lowest lying excited states [1774].

The single diastereoisomer *trans*-$M(N_2)_2$(S,S-chiraphos)$_2$ (S,S-chiraphos = (-)(2S,3S)-bis(diphenylphosphino)butane) reacted with racemic 2-bromooctane to form $MoBr(NNCH(Me)C_6H_{13})$(S,S-chiraphos) in which there was a 10% excess of one enantiomer over the other. Several 1,4-dihaloalkanes all reacted with *trans*-$Mo(N_2)_2(dppe)_2$ to form corresponding cyclic dihydrazido(2-) complexes [175].

2.7 METAL-METAL BONDED SPECIES

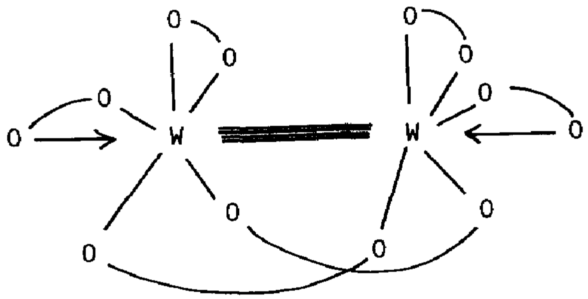
2.7.1 *Triple bonded species of molybdenum(III) and tungsten(III)*

Two reviews on aspects of this area of chemistry have appeared in the last year. One [176] is a general review of triply bonded dimeric alkoxide compounds and compares their structures with those of metal oxides. The other is review of the reactions of the triple bond in $M_2(OR)_6$ compounds with C≡C, C≡N and C≡O triple bonds [177].

The photoelectric spectrum of a number of $M_2(OR)_6$ complexes have been reported. As noticed before, two bands are observed due to the σ and π metal-based ionizations. The σ band is sharp suggesting that the bond distance changes only slightly on ionization, which in turn implies only a weak interaction. The origins of this unexpected result lie in the close contact of the two metal atoms which causes substantial overlap and repulsion between the valence nd_{z^2} orbital of one metal and the outer core ns and np_z orbitals of the other metal. The ionization of a valence σ electron reduces this repulsion and as a result the M-M distance does not increase as might be expected. This effect also seems to destabilize the valence σ level so that its ionization occurs in close proximity to the π ionization and not much higher as previously predicted. Thus the 'extra' sharp ionization in the quadruply bonded dimeric species may also be assigned to the σ ionization [178].

A disagreement in the literature on the existence of $W_2(O^iPr)_6py_2(\mu\text{-CO})$ has been resolved. It appears the compound does exist, but in solution it is rapidly and irreversibly converted to $[W_2(O^iPr)_6py(\mu\text{-CO})]_2$ and py. The structures of both compounds have been reported before and are now confirmed. Also, $W_2(O^tBu)_6(\mu\text{-CO})$ is formed from $W_2(O^tBu)_6$ and CO with or without the presence of py. It is isomorphous and isostructural with the previously described molybdenum analogue [179].

Reaction of $W_2(O^tBu)_6$ with pivalic acid (^tBuCOOH) gave $W_2(O_2C^tBu)_6$ and ^tBuOH. X-ray diffraction showed the structure in (78) with five oxygens in



(78)

Bond distances are

W-W = 2.2922(8)   W-O(chelate piv) = 2.138(7)-2.164(7)

W...O = 2.53(av)   W-O(monod. piv) = 2.072(7)Å

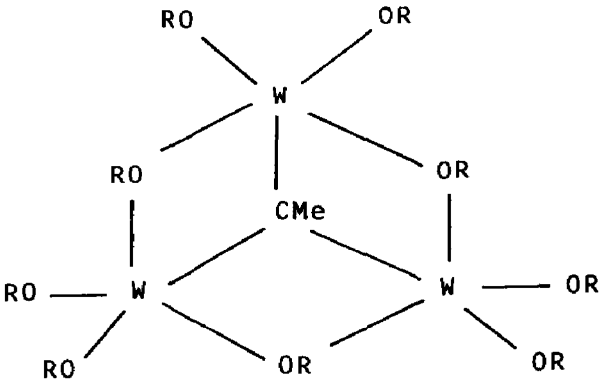
eclipsed pentagons about the tungsten atoms. Two pivalates bridge between the metals and two are chelated to one metal each. On each metal the final pivalate is essentially monodentate, but there is a long weak interaction between the second oxygen of this ligand and the metal in the axial position. The structure is similar to that of $W_2(O_2CNMe_2)_6$ except that in this compound the bridging ligands are *trans* across the W-W bond. In solution $W_2(O_2C^tBu)_6$ exists at room temperature as an equilibrium mixture of isomers, most likely corresponding to the solid state structures of $W_2(O_2C^tBu)_6$ and $W_2(O_2CNMe_2)_6$. At low temperatures both isomers are rigid but as the temperature increases exchange occurs betyween monodentate and bridging ligands on each metal. At higher temperature, complete ligand exchange occurs for each isomer, but interconversion between the isomers is not rapid on the NMR timescale even at 80°C [180].

The comproportionation reaction

$$(OR)_3M{\equiv}M(OR)_3 + (OR)_4MO \longrightarrow M_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu_2\text{-}O)_3(OR)_6$$

has been used to prepare W_3 and W_2Mo clusters. A crystallographic study of the W_3 compound showed its structure to be very similar to that previously reported for its molybdenum analogue [181].

Reaction of $W_2(O^iPr)_6py_2$ and $(^tBuO)_3W{\equiv}CMe$ in hexane/^{i}PrOH solution gave $W_3(CMe)(O^iPr)_9$. The isomorphous mixed metal complex $Mo_2W(CMe)(O^iPr)_9$ was synthesized from $(^tBuO)_3W{\equiv}CMe$ and $Mo_2(O^iPr)_6$. The structure of the W_3 complex is shown in (79) [182].



(79)

Bond distances are

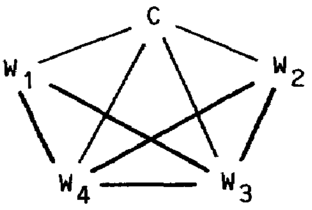
W-W = 2.74(1)(av) W-C = 2.06(1)
W-O = 1.90-1.93 W-μO = 2.02-2.06Å

Interaction of $4\text{-}MeC_6H_4OH$ or $3,5\text{-}Me_2C_6H_3OH$ with $Mo_2(NMe_2)_6$ gave $(NH_2Me_2)[Mo_2(OAr)_7(HNMe_2)_2]$ and the structure of the $4\text{-}MeC_6H_4OH$ derivative was shown to be a confacial bioctahedral arrangement with the alkoxides acting as bridging groups. The Mo-Mo bond distance of 2.601(2)Å is very similar to that in $[Mo_2Cl_9]^{3-}$ (2.66Å). The Mo-N distance of 2.24Å confirms the ligand is an amine and not amido NMe_2^-. There is a small temperature dependent paramagnetism, but despite this the ^{1}H NMR spectrum showed four different Me signals, although they were contact shifted. The reaction of $3,5\text{-}Me_2C_6H_3OH$ with $Mo_2(NMe_2)_6$ in the presence of $NHMe_2$ gave mainly blue $Mo_2(OAr)_4(HNMe_2)_4$ but its structure was not determined. However, a few crystals of another product were also obtained and this was $Mo_2(OAr)_6(NMe_2)(HNMe_2)_2$ whose structure was determined. It also has the confacial bioctahedral arrangement with two alkoxides and the NMe_2 groups acting as the bridges. The terminal amine groups are *trans* to the NMe_2 bridge. The bridging Mo-NMe_2 bond length of 2.11Å is longer than typical terminal bond lengths (1.90-2.00Å), but shorter than the Mo-$HNMe_2$ bond length of 2.26Å. The Mo-Mo bond distance is 2.4139(6)Å corresponding to a bond order of 2.5 [183].

2,6-$Ph_2C_6H_3OH$ reacts with $Mo_2(NMe_2)_6$ in hexane to give 1,2-$Mo_2(OAr)_2(NMe_2)_4$, but in benzene the product is 1,1,2-$Mo_2(OAr)_3(NMe_2)_3$. The ^1H NMR spectrum of $Mo_2(OAr)_2(NMe_2)_4$ is as expected for the usual ethane-type structure in the *gauche* rotomeric form whilst that of $Mo_2(OAr)_3(NMe_2)_3$ shows three types of Me signal and is consistent with the unique groups on each metal being *gauche* to each other. Activation energies of rotation about the Mo-NMe_2 bond were determined both from coalescence temperatures and spin-magnetization transfer techniques [184].

Addition of 2-^{t}Bu,6-Me-C_6H_3OH to $M_2(NMe_2)_6$ compounds gave $M_2(OAr)_2(NMe_2)_4$. A single crystal study on the molybdenum compound showed the typical ethane type staggered *gauche* structure. The Mo-Mo bond length of 2.2198(14)Å is similar to that of the starting material and typical for triple bonds in this type of complex. ^1H NMR studies showed the compound to be rigid at -20°C, but at higher temperatures exchange between proxima and distal Me groups occurred, but not exchange between different types of NMe_2 groups [185].

The major product of the reaction between $W_2(NMe_2)_6$ and ^{i}PrOH (>>6 equivs) is known to be $W_4(H)_2(O^iPr)_{14}$, but in addition, small amounts of a black crystalline material were isolated from the reaction. This is $W_4(C)(NMe)(O^iPr)_{12}$ which has been characterized in solution by NMR spectroscopy (12 different O^iPr groups and carbido carbon δ366.8ppm) and by X-ray crystallography in the solid state. The skeleton of the butterfly type structure is shown in **(80)**.



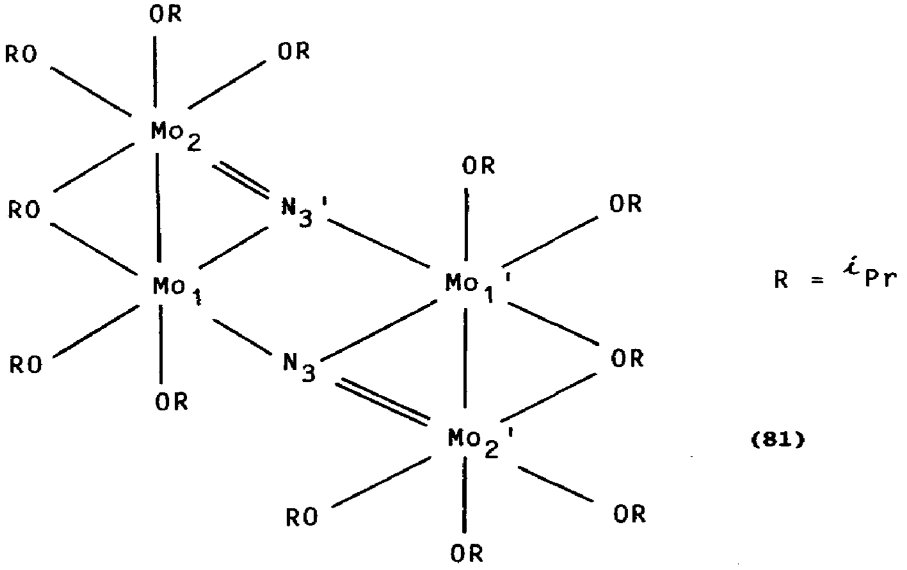
(80)

Bond distances are

W1-W3 = 2.799(2)
W1-W4 = 2.814(2)
W2-W3 = 2.822(1)
W2-W4 = 2.747(2)
W3-W4 = 2.795(2)
W1-C = 1.914(14)
W2-C = 1.956(15)
W3-C = 2.251(4)
W4-C = 2.241(14)Å

All five edges of the butterfly are bridged by a μ_2 group, four of them $O^{i}Pr$ and the other (spanning W2-W4) is the NMe group. There are three terminal $O^{i}Pr$ groups per tungsten atom [186].

The compound $Mo_4(\mu_3\text{-}N)_2(\mu_2\text{-}O^{i}Pr)_2(O^{i}Pr)_{10}$ was isolated from the reaction between $(^{t}BuO)_3Mo{\equiv}N$ and $Mo_2(O^{i}Pr)_6$ and its structure is as shown in (81).



(81)

Bond distances are

Mo1-Mo1' = 2.552(1) Mo1-Mo2 = 2.918(1)

Mo1-N3 = 2.034(2) Mo1-N3' = 1.996(2)

Mo2-N3' = 1.841(2)

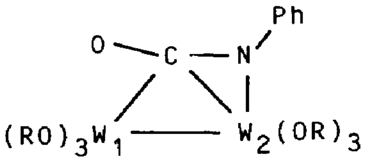
Mo1-μOR = 2.139(2) Mo2-μOR = 2.058(2)Å

The molybdenum, nitride and oxygen atoms of the bridging alkoxides are all coplanar and the stereochemistry about nitrogen is T shaped. The geometry about molybdenum is trigonal bipyramidal (excluding any Mo-Mo bonds) with two short and two long Mo-N distances corresponding to single and double bonds respectively [186].

The analogous reaction between $(^{t}BuO)_3W{\equiv}N$ and $W_2(O^{i}Pr)_6py_2$ gave the imido species $W_3(NH)(O^{i}Pr)_{10}$. X-ray diffraction showed the usual bicapped triangular structure with the imido and one $O^{i}Pr$ groups being the caps. The compound is isomorphous with $W_3O(O^{i}Pr)_{10}$ but the W-W distances are longer at 2.556(2)Å(av) compared with 2.541(3)Å(av) for the oxo complex. Although the imido proton was not detected in the crystallographic analysis, IR and ^1H NMR spectra confirmed its presence [187].

It was reported in the review for 1984 that PhNCO reacts with $M_2(OR)_6$ to give $(OR)_2M(PhNC(OR)O)_2M(OR)_2$ with the anion of the carbamatoester bridging through nitrogen and oxygen. The intermediate with only one bridging PhNCO has now been isolated by working at low temperature. It has been characterized by X-ray crystallography and it has the central core shown in **(82)**.

(82)

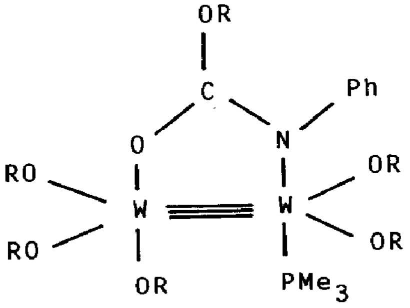


R = CMe_3

Bond distances are

W-W = 2.488(1)
W1-C = 2.17(1)
W1-O = 2.255(9)
W2-C = 2.24(1)
W2-N = 2.15(1)Å

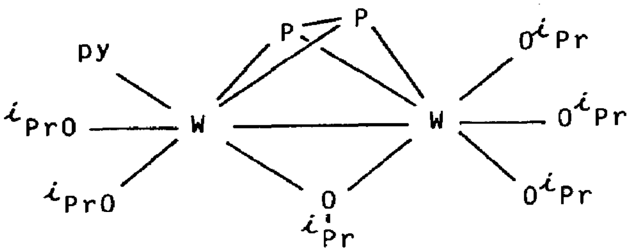
Reaction with PMe_3 gave very unstable $W_2(O^tBu)_5(PMe_3)[\mu\text{-}PhNC(OR)O]$ which has the structure shown in **(83)**.



(83)

The data set was not good, but W-W = 2.358(2)Å. The isolation of this product suggests that the formation of the product shown in **(82)** may proceed through an intermediate of the same type with monodentate PhNCO instead of PMe_3 [188].

Interaction of $W_2(O^iPr)_6py_2$ with $Co_2(CO)_6(\mu\text{-}P_2)$ in hexane at room temperature gave $W_2(O^iPr)_6(py)(\mu\text{-}P_2)$ which was characterized by X-ray diffraction. The central pseudotetrahedral W_2P_2 unit is shown in (84).



(84)

Bond distances are

W-W = 2.695(1)

W-O = 1.892(7)-1.932(7)

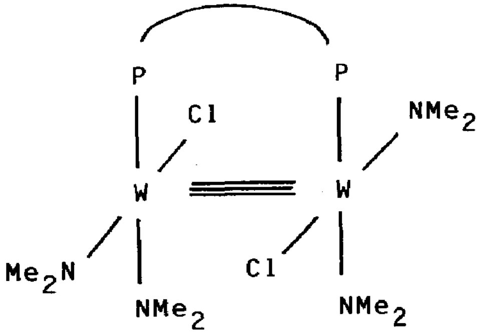
P-P = 2.154(4)Å

W-P = 2.45(2)(av)

W-μO = 1.989(6), 2.074(7)

The structure is analogous to that of $W_2(OR)_6(py)(C_2H_2)$ compounds which in turn are related to $Co_2(CO)_6(\mu-P_2)$ and $Co_2(CO)_6(\mu-C_2H_2)$ by isolobal relationships [189].

Bidentate phosphine ligands L-L (L-L = dmpm, dmpe) react with $M_2Cl_2(NMe_2)_4$ to form stable 1:1 adducts $M_2Cl_2(NMe_2)_4(L-L)$. ^1H and ^{31}P NMR studies suggest that they have the structure shown in (85).



(85)

In contrast, monodentate phosphines L (L = PMe_3, PMe_2Ph) cause dissociations of the types

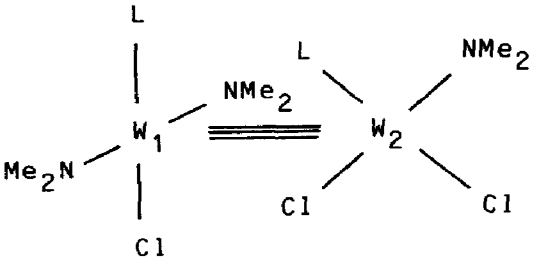
$$3M_2Cl_2(NMe_2)_4 + 4L \longrightarrow 2M_2Cl_3(NMe_2)_3L_2 + M_2(NMe_2)_6$$

$$2M_2Cl_2(NMe_2)_4 + 2L \longrightarrow M_2Cl_4(NMe_2)_2L_2 + M_2(NMe_2)_6$$

(the second reaction with PMe_2Ph only). The $M_2Cl_3(NMe_2)_3L_2$ compounds precipitate from the reaction mixture, but on redissolving in hydrocarbon solvents they disproportionate further

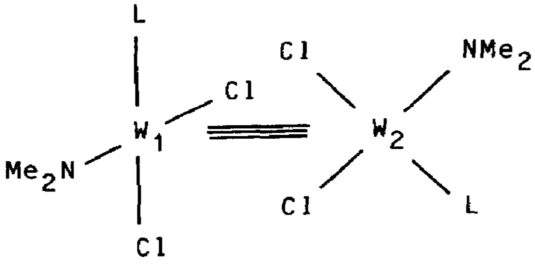
$$4M_2Cl_3(NMe_2)_3L_2 \xrightarrow[60^\circ]{\text{toluene}} 3M_2Cl_4(NMe_2)_2L_2 + M_2(NMe_2)_6 + 2L$$

Crystal structure determinations on $W_2Cl_3(NMe_2)_3L_2$ and $W_2Cl_4(NMe_2)_2L_2$ (L = PMe_2Ph) were carried out and the structures are shown in (86) and (87) [190].



L = PMe_2Ph

(86)



L = PMe_2Ph

(87)

Bond distances are

	$W_2Cl_3(NMe_2)_3L_2$	$W_2Cl_4(NMe_2)_2L_2$
W≡W	2.338(1)	2.322(1)
W1-N	1.987(7)	1.940(7)
W1-P	2.515(2)	2.534(2)
W1-Cl	2.457(2)	2.380(2), 2.424(2)
W2-N	1.932(7)	1.931(7)
W2-P	2.522(2)	2.526(2)
W2-Cl	2.411(2), 2.428(2)	2.415(2), 2.430(2)Å

Using the bulky mesitylene thiol, the compounds $M_2(SR)_6$ have been prepared from $M_2(NMe_2)_6$ in toluene at 80°C. X-ray diffraction revealed the usual M_2L_6 structure with Mo-Mo = 2.228(1), Mo-S = 2.325(2) and W≡W = 2.312(2) , W-S = 2.32(1)Å [191]. The same molybdenum compound was also prepared by reaction of $MoCl_4$ with NaSR in 1,2-dimethoxyethane. $Mo_2(SC_6H_2{}^{i}Pr_3)_6$ (together with some $MoO(SC_6H_2{}^{i}Pr_3)_4$) was similarly prepared. Separation of the products was easy due to the insolubility of the oxo derivative [192].

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

The ^{95}Mo NMR spectra of a large number of quadruply bonded Mo(II) dimers have been observed and confirm that this class of compound have the highest chemical shifts known for molybdenum, ranging from 3227 to 4148. Linewidths vary from 220 to 1440Hz [193].

A detailed study has been carried out of the electronic, IR, Raman and resonance Raman spectra of several $Mo_2X_4(H_2O)_2$ species containing Mo-Mo quadruple bonds. From the IR and Raman spectra the skeletal stretching modes were located and from the resonance Raman spectra the ground state harmonic frequencies, anharmonic constants, force constants and dissociation energies of the Mo-Mo bonds were estimated [194].

The two compounds β-$Mo_2Cl_4(depe)_2$ and β-$Re_2Cl_4(depe)_2$ have been prepared. They are isomorphous and have the bridging depe stereochemistry with torsion angles of 42.7(2)° and 43.7(3)° respectively. Using data from these compounds, the previously proposed correlation between Mo-Mo bond distance and *cos2x* has been revised. It is now estimated that the complete loss of the δ bond is associated with a bond length increase of 0.097Å [195].

β-$Mo_2Cl_4(dmpe)_2$ has a twist angle of 40° and it is paramagnetic compared with $Mo_2Cl_4(PMe_3)_4$ which is diamagnetic. The magnetic and spectral properties of β-$Mo_2Cl_4(PMe_3)_4$ have been examined over a wide temperature range and the former are consistent with an antiferromagnetically coupled system with the thermally populated triplet state 400-500cm^{-1} above the ground state. This is almost an order of magnitude lower than for the eclipsed rotamer. Together with spectral data, this leads to a value of about 5200cm^{-1} (15Kcalmol^{-1}) as an experimental measure of the δ bond component of the barrier to rotation about the quadruple bond [196].

There has been a re-investigation of the interaction of bidentate phosphines with $K_4[Mo_2Cl_8]$ in alcohols. Dppm gives only the bridging β-isomer in all solvents. In MeOH, dppe and arphos give the α-isomer with chelated ligands, but in 1-propanol the β-isomer is obtained [197].

Interaction of $(NH_4)_4[Mo_2Br_8]$ with dppe in alcohols gave three products according to the reaction conditions. The major products were α- and β-$Mo_2Br_4(dppe)_2$ containing two chelated and two bridging dppe ligands respectively. The structure of β-$Mo_2Br_4(dppe)_2$ was confirmed by a partial structural analysis. The isomerization of α to β-$Mo_2Br_4(dppe)_2$ is unimolecular and it is proposed that the mechanism involves internal rotation of the Mo_2 unit within the ligand cage. Prolonged reaction between $[Mo_2Br_8]^{4-}$ and dppe gave brown *trans*-$MoBr_2(dppe)_2$ which was characterized by X-ray crystallography. Bond distances are Mo-Br = 2.569(1), Mo-P = 2.520Å(av) [198].

Hartree-Fock-Slater calculations have been performed on $M_2(O_2CH)_4$ (M = Cr,Mo,W) to yield the metal-metal bond distances and the M-M force constants together with analogous calculations for $[M_2(O_2CH)_4]^+$. In the latter molecules, the three alternatives of the electron being removed from σ, π or δ orbitals were considered. It was shown that for $W_2(O_2CCF_3)_4$ the observed photoelectric spectrum is consistent with σ, π and δ all being at higher energies than the ligand orbitals [199].

The optical spectrum of $Mo_2(O_2CH)_4$ in the near UV has been calculated using the CAS SCF method and effective core potential techniques. The barrier to internal rotation in $[Mo_2Cl_8]^{4-}$ has been calculated and it is concluded that the barrier is very low (if it is present at all). This conclusion supports a previous assignment of the peak at 19,000cm^{-1} to a forbidden $\delta' \longrightarrow \delta''$ transition which becomes allowed following a twist [200].

$W_2(OC^tBu)_4$ has been prepared by the reduction of $(WCl_4)_n$ in thf by Na/Hg in the presence of $Na[O_2C^tBu]$. The corresponding acetate could not be prepared by this method, but it was isolated by metathesis of $W_2(O_2CCF_3)_4$ and NaOAc. Neither complex could be isolated in the form of crystals suitable for X-ray crystallography, but the axial adduct $W_2(O_2C^tBu)_4(PPh_3)_2$ was examined at -160°C. It was shown to have the usual quadruply bonded structure with W-W = 2.218(1)Å. The tungsten carboxylates undergo reversible one-electron oxidation at potentials considerably less positive than their molybdenum analogues, which probably explains why oxidative methods of preparation fail in the tungsten system. Iodine reacts with $W_2(O_2C^tBu)_4$ to give paramagnetic $W_2(O_2C^tBu)_4I$ [201].

$Mo_2(O_2CCF_3)_4$ reacts with PBu_3 to give the 1:2 adduct in which the phosphines are bonded equatorially with generation of two monodentate O_2CCF_3 ligands as in the corresponding tungsten system reported in the review for 1984. A crystal structure determination confirmed this and showed the Mo-P bond length to be quite long (2.542(2)Å). ^{31}P and ^{19}F NMR studies showed the presence of only one isomer in solution (the same one as in the solid state) in contrast to earlier studies which suggested that several isomers could be present. It is thought that the earlier samples of $Mo_2(O_2CCF_3)_4$ could have been contaminated with $Mo_2(O_2CCF_3)_3(O_2CCMe)$. A series of elegant ^{31}P NMR experiments showed that the phosphine liagnds in the molybdenum complex are much more labile than those in the tungsten analogues, which is consistent with the solid state structure [202].

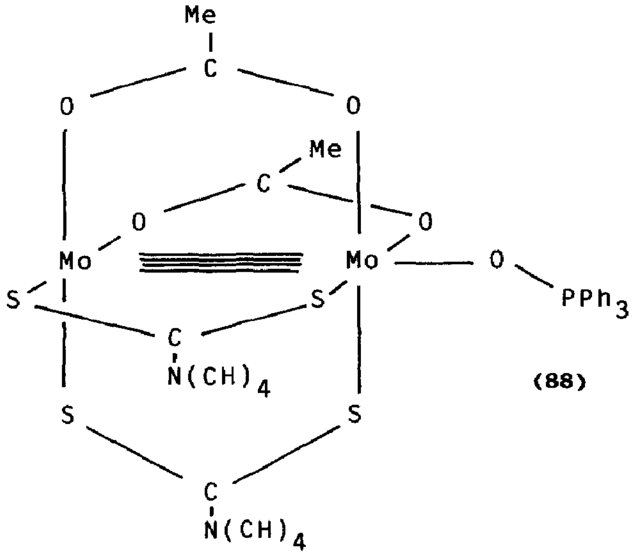
Reaction of $Mo_2(O_2CPh)_4$ with $(PPh_4)N_3$ in pyridine or PPh_4Br in CH_2Br_2 gave $[Mo_2(O_2CPh)_4X_2]^{2-}$ compounds. $[Mo_2(O_2CPh)_4(N_3)_2]^{2-}$ dissolves in CH_2Cl_2 with evolution of N_2 forming $[Mo_2(O_2CPh)_4Cl_2]^{2-}$. The crystal structure of $(PPh_4)_2[Mo_2(O_2CPh)_4Cl_2]$ was determined; it is as expected with long axial Mo-Cl bonds of 2.879(1)Å and Mo-Mo = 2.128(1) and Mo-O = 2.121(3)Å [203]. The axial adducts $(pyH)_2[Mo_2(OAc)_4X_2]$ (X = Cl,Br) have been isolated and their crystal structures determined. The Mo-Mo distance is almost identical in both cases at 2.114Å [204].

Two derivatives of $Mo_2(OAc)_4$ have been reported in which two acetate groups have been replaced by MeCN. In one, *cis*-$[Mo_2(OAc)_2(MeCN)_6]^{2+}$, two of the MeCN groups are axial with very long Mo-N distances of 2.64(2) and 2.77(2)Å while the equatorial Mo-N distances are 2.135Å(av). The other complex is *cis*-$Mo_2(OAc)_2(MeCN)_4(O_3SCF_3)_2$ which has axial triflate ligands with long Mo-O bonds of 2.576(5)Å. This compound is the first example of an axially coordinated triflate in a quadruply bonded system [205].

In an attempt to rationalize the observation that the W-W bond distance in $W_2(O_2CEt)_4(CH_2Ph)_2$ is almost the same as that in $W_2(O_2CEt)_4$ itself, despite the axial ligation, Xα-SW relativistic MO calculations have been performed on $W_2(O_2CH)_4$ and $W_2(O_2CH)_4(CH_3)_2$. It transpires that in the adduct the involvement of a *s,s* σ-bonding orbital makes a considerable contribution to the W-W bonding. Since this orbital is lower for 3rd row transition metals than 1st row ones, it may be the cause of the different behaviour of tungsten towards axial ligation compared with chromium [206].

Pyrrole dtc (pdtc) reacts with $Mo_2(OAc)_4$ and PPh_3O to give *cis*-$Mo_2(OAc)_2(pdtc)_2(PPh_3O)$ which has the structure shown in **(88)**. Pyrrole dtc appears to coordinate in the dithio acid form (with a single C-N linkage) rather than the more usual 1,1-dithiolate form with other dtc ligands, because the formation of multiple bond character in the C-N linkage would lead to loss of aromaticty of the pyrrole ring. The same paper also reported the preparation and characterization of $[Mo_2(OAc)_3(S_2PEt_3)(PEt_3O)](BF_4)$ from the reaction of $Mo_2(OAc)_4$, S_2PEt_3 and HBF_4. The structure is similar to that described above with Mo-Mo = 2.1384(8)Å. The S_2PEt_3 ligand coordinates in the dithio acid form [207].

$Mo_2(mhp)_4$ reacts with $SiClMe_3$ in the presence of PEt_3 to give *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$ which has the structure shown in **(89)**. The compound shows strong fluorescence even in ordinary laboratory illumination and has a fluorescence lifetime of 33.8ns [208].

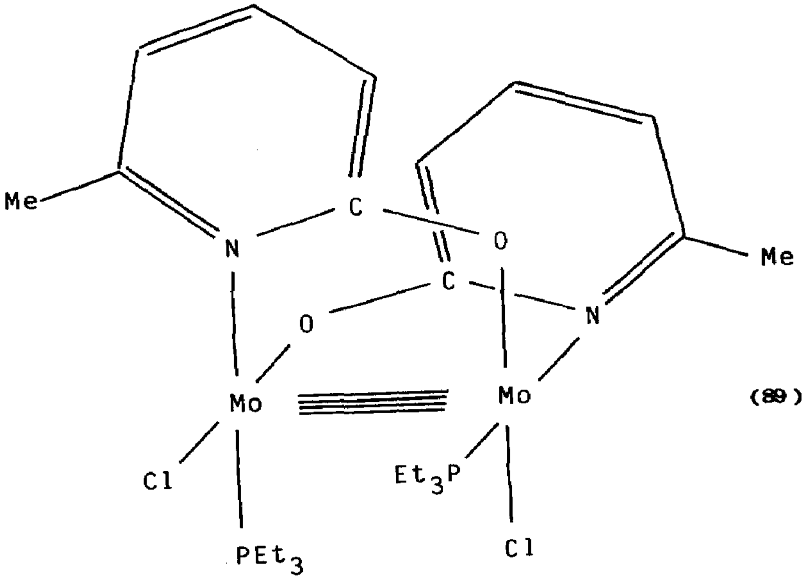


(88)

Bond distances are

Mo-Mo = 2.134(1) Mo-S = 2.444(3)

Mo-O(OAc) = 2.115(7) Mo-O(ax) = 2.370(7)Å



(89)

Bond distances are

Mo-Mo = 2.103(1) Mo-O = 2.052(6)

Mo-Cl = 2.435(av) Mo-P = 2.559Å(av)

$Mo_2(R\text{-}1,2\text{-}pn)_4$ has been prepared and its absorption and CD spectra have been recorded. After comparison with the α (chelated) and β (bridged) isomers of $Mo_2Cl_4(R\text{-}dppp)_2$ and $Mo_2Cl_4(S,S\text{-}dppb)_2$ it was concluded that only the staggered bridged isomer exists [209].

2.7.3 Hexameric species

A re-examination of the metal-metal bonding in $[M_6X_8]^{4+}$ clusters has been made using the methods of metal physics rather than the more familiar extended Huckel techniques. It emerges that the *d* band of orbitals resulting from the Huckel treatment is too narrow and that *d*-electrons have a strong influence on the bonding even though *d* orbital overlap appears to be small [210].

The temperature dependence of the luminescence lifetime of $(NEt_4)_2[Mo_6Cl_{14}]$ has been determined over the range 1.4-300K. The lifetime decreases as the temperature increases and this has been analyzed in terms of the emissions for several Boltzmann populated triplet energy levels [211].

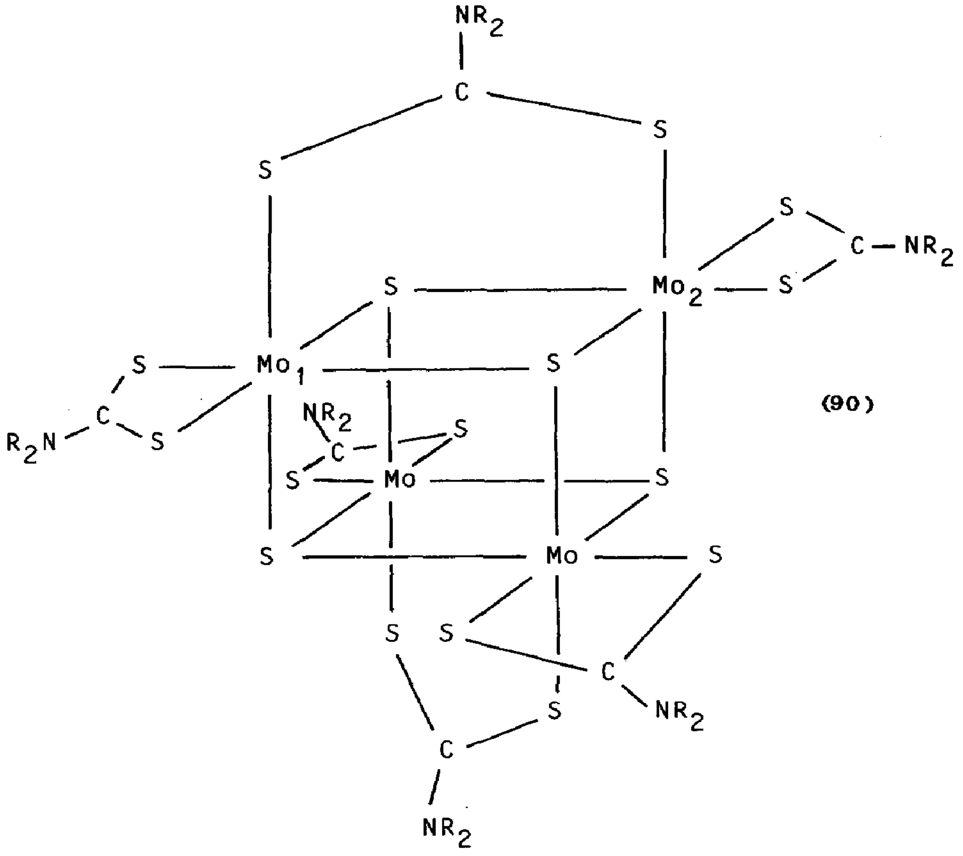
A number of tungsten iodo hexameric clusters have been prepared and their lattice constants determined. They include W_6I_{12}, W_6I_{14} and W_6I_{17} which are all based on the $[W_6I_8]^{4+}$ core. WI_3 has been prepared by interaction of the elements [212].

The physical properties of an isoelectronic series of Chevral phases $M'^{II}Mo_6S_8$ (M'^{II} = Ca,Sr,Ba,Yb,Eu,Sn,Pb) have been reviewed. All show electrical and structural anomalies at particular temperatures, the value of which correlate with the second ionization potentials of the ions, indicating that the ternary metal-sulphur interactions influence the stability of the high temperature rhombohedral phase [213].

2.7.4 Other cluster species

The new compounds $LiZn_2Mo_3O_8$ (I), $Zn_3Mo_3O_8$ (II) and $ScZnMo_3O_8$ (III) have been prepared and characterized by IR, magnetic and X-ray diffraction studies. They all contain the Mo_3O_{13} cluster containing within each unit one μ_3-O, three μ_2-O groups and three oxo ligands on each molybdenum which bridge to other clusters (two to one other cluster and one to two other clusters) to give a connectivity formula $Mo_3O_4O_{6/2}O_{3/3}$. (I) and (II) have one unpaired electron per cluster [214].

The black crystalline compound $Mo_4(\mu_3\text{-}S)_4(\mu\text{-}S_2CNEt_2)(S_2CNEt_2)_4$ was made by refluxing a toluene solution of $Mo_2(S_2CNEt_2)_6$ for 20hrs. Its structure is shown in (90) [215].



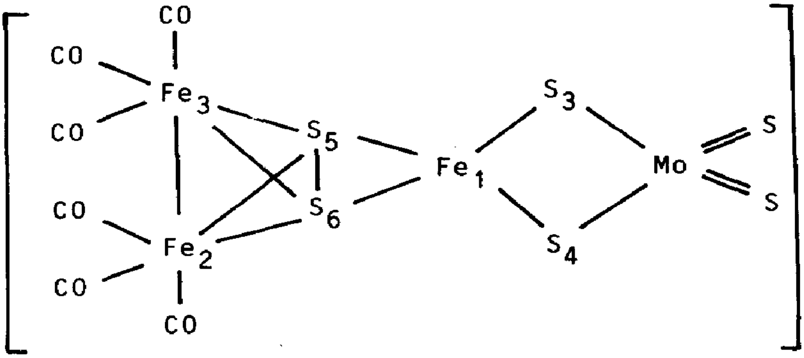
(90)

Bond distances are

$$\begin{array}{rlrl} \text{Mo1-Mo2} &= 2.732(5) & \text{other Mo-Mo} &= 2.861(6)(\text{av}) \\ \text{Mo-}\mu\text{S} &= 2.32(1)\text{-}2.40(1) & \text{Mo-S} &= 2.49(1)\text{-}2.54(1) \\ \text{Mo-S}(\mu\text{-dtc}) &= 2.51(1),\ 2.56(1)\text{Å} & & \end{array}$$

Reaction of $(NEt_4)_2[Cl_2FeMoS_4]$ and $Li_2[Fe_2S_2(CO)_6]$ at -78°C gave $(NEt_4)_2[MoFe_3S_6(CO)_6]$ which has the expected structure shown in **(91)**. The compound could be oxidatively decarbonylated with $(p\text{-}XC_6H_4S)_2$ (X = Cl,Br) to give $(NEt_4)_4[Mo_2Fe_6S_{12}(S\text{-}p\text{-}C_6H_4X)_6$ and a structural determination on the bromide compound showed it to consist of two $MoS_4(Fe\text{-}SR)_3$ cubanes linked through their molybdenum atoms and two $\mu_2\text{-}\eta^3$ persulphide groups as shown in **(92)** [216].

MS-Xα calculations have been carried out on the hypothetical cluster $[MoFe_3S_4(SH)_6]^{3-}$. The geometry selected was that found in the single cubane $MoFe_3S_4$ clusters. The results of the calculations were compared with those reported previously for the Fe_4S_4 clusters [217].

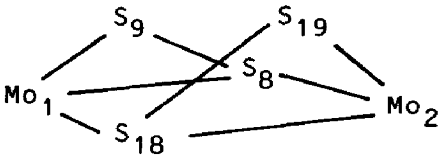


(91)

Average bond distances are

Mo-Fe = 2.762 Mo=S = 2.156

Mo-μS = 2.263 Fe-μS = 2.262Å



(92)

Bond distances are

Mo1-S8 = 2.47(4) Mo1-S9 = 2.40(1)

Mo1-S18 = 2.64(5) S8-S9 = 1.99(5)Å

It has been found that $(NBu_4)_3[Mo_2Fe_6S_8(SPh)_9]$ in MeOH/thf catalyzes the multi-electron electrochemical reduction of RN_3 to give NH_3, N_2H_4 and RNH_2. It was shown that it is the reduced form of the cluster which reacts with RN_3 [218].

The double cubane $[MoFe_3S_4(SEt_2)_3]_2(\mu\text{-}SEt)_3$ (which has three SEt groups bridging between Mo atoms in each cluster) reacts with PhOH to yield the corresponding phenoxide $[MoFe_3S_4(OPh)_3]_2(\mu\text{-}SEt)_3$ with the phenoxides coordinated to iron. The magnetic properties of the double cluster are not markedly changed by the substitution. The compound shows two quasi-reversible one-electron reductions similar to those of the parent compound, although the phenoxide is more difficult to reduce [219].

The molybdenum environment in the Mo/Fe/S cluster in nitrogenase has been examined by comparison of the Mo-K-edge X-ray absorption edge and near edge structure (collectively called XANES) of two natural isolated Mo/Fe cofactors and a variety of synthetic Mo/S and Mo/Fe/S complexes of known structures. The results show the Mo XANES of the nitrogenases are quite similar to each other and to those of the cubane type $MoFe_3S_4$ clusters containing the MoS_3O_3 coordination unit. This result complements and is consistent with the independent EXAFS information [220].

Two reversible one-electron reductions have been observed for isolated Mo/Fe/S cofactor for the molybdenum-iron protein of *Azotobacter vinelandii* nitrogenase in N-methylformamide [221].

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