

8. Molybdenum 1994

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INTRODUCTION

This review surveys the coordination chemistry of molybdenum reported in 1994, and follows the same format as the ones which covered 1992 and 1993 [1, 2]. The references have been located by a search of volumes 120, 121 and 122 of *Chemical Abstracts*, together with use of the Current Contents and BIDS databases; in addition all the major inorganic chemistry journals have been examined individually. Where appropriate, late references from 1993 have also been included. The review is restricted to coordination complexes, including carbonyls but excluding organometallic compounds and solid-state chemistry. Synthetic models of Mo centres and clusters in biological systems are covered, but biochemical studies of the enzymes themselves are not.

A number of relevant review articles have appeared, including two on the role of metals in nitrogenase [3, 4], one on the bioinorganic chemistry of pterin-containing Mo and W enzymes [5], and a collection of proceedings dealing with molybdenum enzymes and their model systems [6]. A thematic issue of *Chemical Reviews* on metal-dioxygen complexes included an article covering peroxo and superoxo complexes of Cr, Mo and W [7], and an issue of *J. Cluster Sci.* was given over to metal-metal multiple bonds with an introduction by Cotton [8]. Reviews on organoimido complexes [9] and octacyano and oxo- or nitrido-tetracyano complexes [10] also contain large sections on molybdenum chemistry, while relevant material can also be found in articles about complexes of sterically hindered thiolate ligands [11], of diazoalkanes [12], of heavier polychalcogenide ligands [13], and of amidines [14]. A review of the EPR spectroscopic properties of low spin d^5 systems also contains a small section on Mo(I) complexes [15]. Shorter accounts have appeared dealing with electron transfer reactions of species such as $[\text{Mo}_6\text{Cl}_{14}]^{2-}$ [16], the reactions of SO_2 in metal complexes [17], the relevance of allyloxo and allyimido complexes to the industrial SOHIO process [18], and metal-catalysed epoxidation chemistry [19]. Two thought-provoking articles by Gibson discuss the way in which the orientation of π -donor ligands in tetrahedral complexes is determined by competition for the available metal orbitals [20, 21]. Books dealing with the chemistry and uses of molybdenum [22] and the solubility of its compounds [23] have been published. The first in the current series of reviews on the coordination chemistry of Mo, covering 1991, has appeared [24], as has the corresponding review of the organometallic chemistry of Cr, Mo and W during 1992 [25].

8.1 MOLYBDENUM(VI)

8.1.1 Complexes with halide ligands

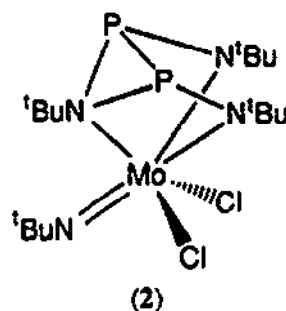
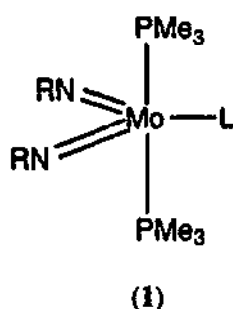
The caesium salt of the $[\text{MoF}_7]^-$ ion was made by the reaction of CsF with MoF_6 . The X-ray structures of this and the corresponding NO_2^+ and NMe_4^+ salts all show a capped octahedral structure. In solution the compound is fluxional and a single sharp ^{19}F NMR peak is observed in MeCN [26]. A thermodynamic study of the possibility of employing MoF_6 or MoCl_5 as precursors for the chemical vapour deposition of MoS_2 has appeared [27]. *Ab initio* calculations on

various metal oxo- or nitrido-halides, including MoOX_4 , MoNX_3 , $[\text{MoNX}_4]^-$ and $[\text{MoNX}_4]^{2-}$ where $\text{X} = \text{Cl}$ or F have concluded that the $\text{M}-\text{O}$ and $\text{M}-\text{N}$ bonds are strongly covalent whereas the metal halide bonds are largely ionic in character [28].

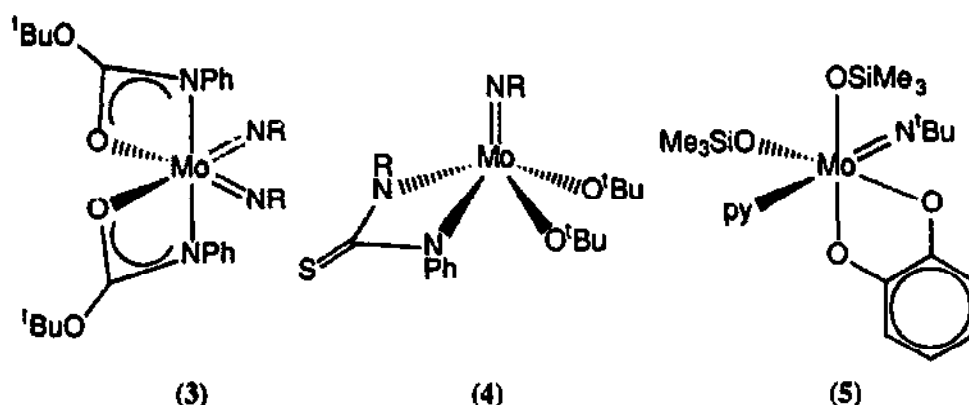
8.1.2 Complexes with nitrogen donor ligands

Alkylation of the nitrido species $[\text{Mo}(\text{N})(\text{O}^i\text{Bu})_3]$ with NpMgBr ($\text{Np} = \text{CH}_2\text{CMe}_3$) affords $[\text{Mo}(\text{N})\text{Np}_3]$, which adds HX ($\text{X} = \text{halide}$) to form trigonal bipyramidal $[\text{Mo}(\text{NH})(\text{X})\text{Np}_3]$ in which the three alkyl groups are equatorial. A similar compound, $[(\text{Mo}(\text{NH})\text{Np}_3)_2(\mu-\text{O})]$, is formed by addition of water [29]. Electrochemical studies of $[\text{MCl}_3(\text{NPPH}_2\text{NPPH}_2\text{N})]$, in which the metal (Mo or W) forms part of a phosphorus-nitrogen ring, confirm that this ligand is capable of stabilising high oxidation states [30].

Gibson and coworkers have explored two routes to unsymmetrical bis-imido species $[\text{Mo}(\text{NR}^1)(\text{NR}^2)\text{Cl}_2(\text{dme})]$. The first approach involves using a mixture of two amines in the preparation from Na_2MoO_4 , Me_3SiCl and NEt_3 in dme ; alternatively, for $\text{R}^1 = ^i\text{Bu}$, imido exchange in $[\text{Mo}(\text{N}^i\text{Bu})_2\text{Cl}_2(\text{dme})]$ can be effected by R^2NH_2 [31]. The resulting complexes can then be used to prepare new metathesis catalysts [32]. The reaction of $[\text{Mo}(\text{N}^i\text{Bu})_2\text{Cl}_2]$ with KHBpz^*_3 affords $[(\text{HBpz}^*_3)\text{Mo}(\text{N}^i\text{Bu})_2\text{Cl}]$; one of the imido groups can be protonated with HBF_4 [33]. Displacement of the chloride ligands in $[\text{Mo}(\text{N}^i\text{Bu})_2\text{Cl}_2]$ with two equivalents of carbonylmetallate anions such as $[\text{Co}(\text{CO})_4]^-$, $[\text{Mn}(\text{CO})_5]^-$, $[\text{CpM}(\text{CO})_3]^-$ ($\text{M} = \text{Mo}, \text{W}$) or $[\text{CpFe}(\text{CO})_2]^-$ gave average to excellent yields of the trinuclear species $[\text{Mo}(\text{N}^i\text{Bu})_2(\text{ML}_n)_2]$ containing direct bonds between high valent and low valent metals [34]. Reduction of $[\text{Mo}(\text{NR})_2\text{Cl}_2(\text{dme})]$ or $[\text{Mo}(\text{NR})_2(\text{PMe}_3)_2\text{Cl}_2]$ ($\text{R} = \text{Mes}$) with potassium-graphite in the presence of more PMe_3 affords $[\text{Mo}(\text{NR})_2(\text{PMe}_3)_3]$; one of the phosphine ligands is readily replaced by $\text{P}(\text{OEt})_3$, ethylene or alkynes to give $[\text{Mo}(\text{NR})_2(\text{PMe}_3)_2\text{L}]$ (1) in which the phosphines occupy the axial positions of a trigonal bipyramid. In the cases where $\text{L} = \text{an alkene or alkyne}$, the C_2 unit is oriented perpendicular to the equatorial plane [35]. Interaction of $[\text{Mo}(\text{N}^i\text{Bu})_2\text{Cl}_2(\text{dme})]$ with py gave $[\text{Mo}(\text{N}^i\text{Bu})_2\text{Cl}_2(\text{py})_2]$, while with excess $^i\text{BuNH}_2$, the dimer $[\text{Mo}(\text{N}^i\text{Bu})(\text{NH}_2^i\text{Bu})\text{Cl}(\mu-\text{Cl})]_2$ was isolated; the same group has also explored these compounds as precursors to molybdenum carbonitride films by CVD at 650°C [36, 37]. As part of a wider study of $[\text{Cp}^*\text{Mo}(\text{N}^i\text{Bu})\text{Cl}_2]$, its reaction with Cl_2 was found to give a 35% yield of $[\text{MoCl}_3(\mu-\text{N}^i\text{Bu})(\mu-\text{Cl})]_2$ which was structurally characterised [38].



The homoleptic imido dianion $\text{Li}_2[\text{Mo}(\text{N}^t\text{Bu})_4]$ reacts with PCl_3 to give the unusual species (2) in which three of the imido groups are joined by a P_2 unit [39]. Insertion of PhNCO occurs at the $\text{Mo}-\text{O}$ bonds of $[\text{Mo}(\text{NR})_2(\text{O}^t\text{Bu})_2]$ ($\text{R} = 2,6\text{-C}_6\text{H}_3\text{Pr}_2$) to give the bis(carbamate) complex $[\text{Mo}(\text{NR})_2[\text{NPhC}(\text{O}^t\text{Bu})\text{O}]_2]$ (3), whereas PhNCS adds reversibly at the imido groups to give the pyramidal thioureate species $[\text{Mo}(\text{NR})\{\text{NRC}(=\text{S})\text{NPh}\}(\text{O}^t\text{Bu})_2]$ (4) [40]. Treatment of $[\text{Mo}(\text{N}^t\text{Bu})_2(\text{OSiMe}_3)_2]$ with catechol (H_2cat) in the presence of py affords $[\text{Mo}(\text{N}^t\text{Bu})(\text{cat})(\text{OSiMe}_3)_2(\text{py})]$ (5), whereas 8-hydroxyquinoline (HL) gave $[\text{Mo}(\text{N}^t\text{Bu})(\text{O})\text{L}_2]$. The related $[\text{Mo}(\text{N}^t\text{Bu})_2(\text{Mes})_2]$ also reacted with HL to afford $[\text{Mo}(\text{N}^t\text{Bu})_2(\text{Mes})\text{L}]$ and a similar compound was produced with 8-hydroxyquinoline [41].



The *trans* influence of the imido group in $[\text{Mo}(\text{NH})\text{Cl}_3(\text{PR}_3)_2]^{0, \pm 1}$ ($\text{R} = \text{H}, \text{Me}, \text{F}$) has been studied by approximate density functional theory calculations. As the occupation of the Mo d -orbitals increases on going from d^0 to d^2 , the extent of lengthening of the $\text{Mo}-\text{Cl}$ bond *trans* to the imido group lessens, and the degree of bending of the *cis* ligands away from the imido group also decreases. This is due to backbonding from Mo to the phosphine σ^* orbitals, which is maximised by decreasing distortion [42].

8.1.3 Complexes with oxygen donor ligands

The X-ray structure of $[\text{NBu}_4]_2[\text{MoO}_4]$ has been determined [43]. A multinuclear NMR spectroscopic study of the interaction of aqueous molybdate with D-xylono-5-hexulosonic acid has shown that all three forms of the acid (α , β and keto form) can bind to form 1:1 complexes [44]. Four types of complex were detected in a similar study with D-galactaric acid and D-mannaric acid: a 4:2 complex and a 2:1 species, both involving $\text{Mo}_2\text{O}_5^{2+}$ units, and 2:2 and 1:1 complexes involving MoO_2^{2+} centres [45]. The binding properties of molybdate with glucuronic acid have been studied by polarography; complexes of the $\text{Mo}_2\text{O}_5^{2+}$ moiety were again proposed [46]. The interaction of molybdate with nitrilotriacetate (H_3nta) has been studied by potentiometric, spectrophotometric and enthalpimetric titrations and analysed with the Superquad program. Species involved include $[\text{MoO}_3(\text{nta})]^{3-}$, $[\text{MoO}_3(\text{Hnta})]^{2-}$ and $[\text{Mo}_2\text{O}_5(\text{Hnta})_2]^{2-}$, with $[\text{Mo}_2\text{O}_5(\text{nta})(\text{OH})]^{2-}$ and $[\text{Mo}_2\text{O}_5(\text{nta})(\text{H}_2\text{O})]^-$ also identified [47]. Adducts of BiCl_3 , MnCl_2 and

CoCl_2 with molybdate have been isolated [48]. New reagents for the extraction and determination of Mo(VI) have been developed based on hydrazones [49], naphthoic acids [50], and chromenones [51, 52], and sodium dithionite has been used to reduce Mo(VI) to Mo(V) for colorimetric analysis [53].

Further details on the reaction of $[\text{MoO}_2\text{Cl}_2]$, BuLi and $\text{O}(\text{Si}^t\text{Bu}_2\text{OH})_2$, which gives the 12-membered ring species $[\text{MoO}_2(\text{OSi}^t\text{Bu}_2\text{OSi}^t\text{Bu}_2\text{O})]_2$, have appeared; unfortunately the X-ray structure of the product could not be obtained [54]. The interaction of $[\text{MoOCl}_5]^{2-}$ with *cis*- $[\text{Cr}(\text{cyclam})(\text{OH})(\text{H}_2\text{O})][\text{ClO}_4]_2$ and NaOH afforded $[\text{MoO}_4\text{Cr}(\text{cyclam})]_2[\text{ClO}_4]_2$, which contains an 8-membered ring: two MoO_4 units bridge the Cr(III) centres [55].

Numerous publications have appeared on the synthesis and application of molybdenum peroxo complexes. A study of the kinetics of the oxidative bleaching of phenolphthalein by H_2O_2 catalysed by transition metal ions found that Mo(VI) was the most active; the active species is thought to be $[\text{Mo}(\text{O}_2)_4]^{2-}$. At higher concentrations of Mo, a second mechanism, involving the production of singlet oxygen, becomes predominant [56]. The oxidation of bromide by H_2O_2 is catalysed by Mo(VI) complexes such as $[\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})_2]$ and the system acts as a model for the vanadium bromoperoxidase enzyme [57]. Oxidation of bromide by H_2O_2 and $[\text{MoO}(\text{O}_2)_2(\text{ox})]^{2-}$ has also been examined; it is thought to involve production of $[\text{MoO}_2(\text{O}_2)(\text{ox})]^{2-}$ initially, though the final product is $[\text{MoO}_3(\text{ox})]^{2-}$ [58]. This product was also obtained on treating either of the two oxalate anions with NO ; NO_2 was produced too [59]. The oxidation of the Fe(II) complex $[\text{Fe}(\text{CN})_5(\text{mpyz})]^{2-}$ (mpyz = *N*-methylpyrazinium) by H_2O_2 is however not catalysed by Mo(VI); the absence of catalysis is thought to rule out oxygen atom transfer and inner sphere electron transfer mechanisms [60].

Several papers deal with the immobilisation of Mo complexes on polymer supports, usually by treatment with $[\text{MoO}_2(\text{acac})_2]$. A polybenzimidazole Mo(VI) complex prepared in this way was found to be a highly active and long-lived catalyst for the epoxidation of propene with $t\text{BuOOH}$, giving propylene oxide with excellent selectivity. Moreover, the activity of recycled catalyst actually increased [61]. The imidazole catalysts retained the Mo loading better than similar ones derived from 2-aminomethyl pyridine [62].

A theoretical study of alkene epoxidation by neutral six- and seven-coordinate Mo(VI) peroxo complexes found that the six-coordinate species display similarities to peracids whereas the seven-coordinate ones are more similar to hydroperoxides; these latter display lower reactivity due to the extra donation to the metal centre by the additional ligand [63]. A number of complexes of the type $[\text{MoO}(\text{O}_2)_2(\text{L})(\text{L}')]^{2-}$ have been prepared and characterised. The oxidation of pyridine by H_2O_2 in the presence of $[\text{MoO}_4]^{2-}$ gave the pyridine-*N*-oxide complex $[\text{MoO}(\text{O}_2)_2(\text{pyO})_2]$, which itself is a catalyst for H_2O_2 oxidations. The X-ray structure of the W analogue showed the familiar pentagonal bipyramidal coordination with the peroxo ligands in the equatorial plane [64]. A similar species, $[\text{MoO}(\text{O}_2)_2(\text{HIm})(\text{H}_2\text{O})]$ (HIm = imidazole), was made by treating $[\text{H}_2\text{Im}]_4[\text{Mo}_8\text{O}_{26}(\text{HIm})_2]$ with H_2O_2 [65]. The complex $[\text{MoO}(\text{O}_2)_2(\text{hmpa})(\text{H}_2\text{O})]$ was treated with various substituted pyridines; in most cases the hmpa ligand was replaced except for 3,5-dibromopyridine which displaced the water molecule. Compounds of the type

[MoO₃(O₂)₄L₂(H₂O)₂] were also made [66]. The dipole moments of some Mo(VI) peroxo complexes were measured by the same group [67]. In an attempt to increase the solubility of such complexes in organic solvents, 2-(3-pyrazolyl)-pyridines bearing long alkyl chains were also employed as didentate ligands in [MoO(O₂)₂(L)] [68]. Similar compounds with bpy, 2,2'-pyridylbenzimidazole and 8-aminoquinoline were made, but with 8-hydroxyquinoline (HL), the mono-peroxo species [MoO(O₂)L₂] was isolated [69].

The formation constants of [MoO(O₂)(dipic)] (H₂dipic = pyridine-2,6-dicarboxylic acid) and [MoO(O₂)(nta)][−] have been determined by potentiometry and the X-ray structure of the nta complex was determined [70]. The complexes [MoO(O₂)(L)(L')₂], where H₂L is diphenic acid and L' = various pyridines have also been prepared and used to oxidise PPh₃ to its oxide [71]. The oxidation of alcohols to aldehydes and ketones catalysed by anionic Mo(VI) peroxo complexes such as [MoO(O₂)₂(pic)][−], [Mo(O)(O₂)₂(pic-O)][−] and [MoO(O₂)₂(O₂CR)][−] (R = various aryls) has been explored. A common mechanism involving an alkoxy intermediate is proposed for all these catalysts even though they show widely differing activation parameters [72]. The mechanistic pathway of the reaction of 3-phenyl-2-methylbenzofuran epoxide with dimethyl dioxirane in the presence of [MoO(O₂)₂(hmpa)] has been elucidated and appears to involve a 1,2-dioxetane intermediate [73]. Molybdenum peroxo complexes have also been investigated as sources of singlet oxygen and as calibrants in thermal analysis [74, 75]. A detailed study of allylic amination promoted by [MoO₂(dtc)₂] or [MoO₂(dipic)(hmpa)] concluded that four stages were involved in the reaction, namely:

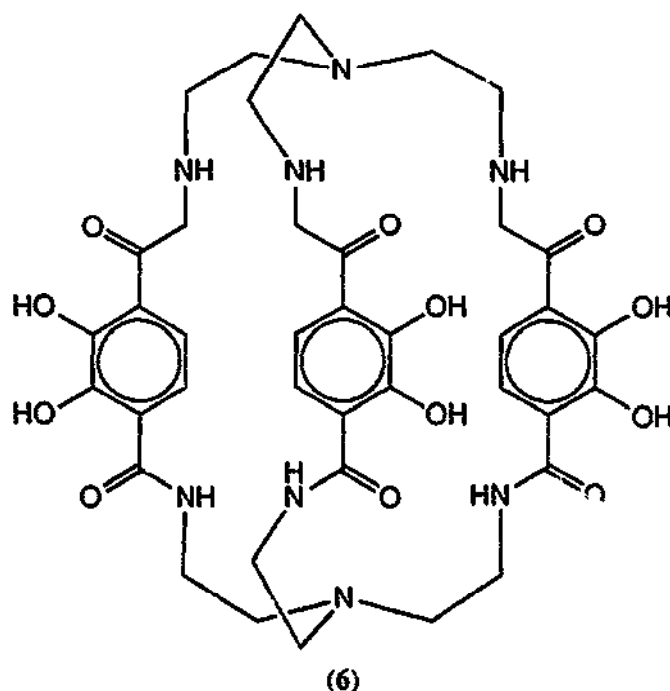
- i) reaction of [MoO₂(L)(L')] with RNHOH to give the side bound nitrosoarene complexes [MoO(η²-RNO)(L)(L')];
- ii) dissociation of RNO, leaving the Mo(IV) species [MoO(L)(L')];
- iii) reaction of RNO with the alkene to give an *N*-allyl hydroxylamine, and
- iv) reduction of this to an allylamine with concomitant oxidation of the Mo(IV) centre back to [MoO₂(L)(L')] [76].

Columnar liquid crystals based on the [MoO₂(dipic)] motif have been prepared using a derivative of the dipic ligand which has a OCH₂C₆H₂-3,4,5-(OR)₃ substituent, where R = a long alkyl chain. The degree of association between molecules can be monitored by variable temperature IR spectra of the MoO₂ unit [77].

The salt [PPh₄]₂[MoO₂(NCS)₄] has been prepared from Na₂MoO₄ and KSCN followed by cation exchange. It transfers an oxygen atom to PPh₃ over 20 times more efficiently than the well known [MoO₂(dtc)₂] complexes [78]. The X-ray structure of a second form of another thiocyanate complex, [Mo₂O₂(NCS)₆(μ-O)(μ-SO₄)] has been determined [79]. Fluorination of molybdate with pyridinium poly(hydrogen fluoride) gave [pyH]₂[MoO₂F₄] [80].

The X-ray structure of [NEt₄]₂[MoO₂(cat)₂] has been determined [81]. An unusual example of this type of complex, K₂[MoO₂(cat)₂-bicapped-TRENCAM], has been isolated and structurally characterised; the ligand is N{CH₂CH₂NHCOC₆H₂(OH)₂CONHCH₂CH₂}₃N (6) which is coordinated as a bis-catecholate [82]. The thiobenzilate complex [MoO₂(O₂CCPh₂S)₂]^{2−} undergoes a proton-assisted electrochemical reduction to two Mo(IV) species,

$[\text{MoO}(\text{O}_2\text{CCPh}_2\text{S})_2]^{2-}$ and $[\text{MoO}(\text{O}_2\text{CCPh}_2\text{S})(\text{solv})_2]$. These in turn can be reoxidised to Mo(V) species [83]. The same Mo(VI) thiobenzilate complex can be intercalated into a layered Zn(II)/Al(III) double hydroxide to produce a heterogeneous catalyst for the oxidation of aliphatic and aromatic thiols by air or O_2 . Intercalation is thought to prevent the formation of the inactive Mo(V) species which occurs with the free complex in solution [84, 85].



Complexes of the type $[\text{MoO}_2(\text{L})]$ where $\text{H}_2\text{L} = \text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$, $\text{HN}(\text{CH}_2\text{CH}_2\text{SH})_2$, or $\text{HOCH}_2\text{CH}_2\text{NMeCH}_2\text{CH}_2\text{NMeCH}_2\text{CH}_2\text{OH}$ have been prepared from $[\text{MoO}_2(\text{acac})_2]$. The second of these is trigonal bipyramidal and transfers an oxo ligand to PPh_3 to afford the Mo(V) dimer $[\text{Mo}_2\text{O}_3(\text{L})_2]$ [86]. The electrochemistry of $[\text{MoO}_2\text{L}_2]$, $[\text{Mo}(\text{O})(\text{S})\text{L}_2]$ and $[\text{MoS}_2\text{L}_2]$ where HL is piperidine-*N*-oxide has been studied and shows a one-electron reduction to Mo(V) but on a longer timescale replacement of S by O and release of HL also occurs [87].

Further details of the interaction of solutions of MoO_3 in HCl with various solvents have appeared; in this way, adducts $[\text{MoO}_2\text{Cl}_2(\text{solv})_2]$ where solv = dmf, hmpa, dmsO or diglyme have been isolated. The complex where solv = H_2O can also be made and stabilised with polyethers, and the structure of $[\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2] \cdot 2,5,8\text{-trioxanonane}$ shows that the ether is hydrogen bonded to the coordinated water molecules [88]. The catalytic activity of $[\text{MoO}_2\text{X}_2(\text{dmsO})_2]$ in oxygen atom transfer to PPh_3 and deoxygenation of azoxybenzene was examined; the complex with $\text{X} = \text{Cl}$ was most effective. Oxygen atom transfer from $[\text{MoO}_2\text{Cl}_2(\text{dmf})_2]$ to PPh_3 and from dmsO to $[\text{MoOCl}_2(\text{dmf})_2]$ are both second order reactions [89]. The synthesis and vibrational spectra of a number of adducts of *O*- and *N*-donors such as dme, tmeda, bpy, thf and 2,5,8-trioxanonane with $[\text{MoO}_2\text{Cl}_2]$ and other halides such as MoCl_4 and MoOCl_3 have been reported [90]. Adducts of $[\text{MoO}_2\text{Cl}_2]$ with Schiff's bases derived from salicylaldehyde and various hydrazones have been

characterised [91], and an adduct with 2-mercapto-3-phenylquinazolin-4-one has been prepared [92]. The interaction of $[\text{MoO}_2\text{Cl}_2]$ with tetrahydropterin affords $[\text{MoOCl}_3(\text{L})]$ in which a dihydropterin is coordinated in a quinonoid form [93].

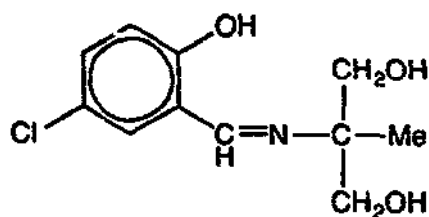
Numerous complexes of the MoO_2^{2+} unit containing Schiff's base ligands have been prepared and studied. For uninegative ligands (from H_2L) they usually take the form $[\text{MoO}_2\text{L}_2]$ or $[\text{Mo}_2\text{O}_5\text{L}_2]$, and for dianionic ones (from H_2L) they tend to be $[\text{MoO}_2\text{L}(\text{S})]$ where S = solvent. Molybdate units can also be anchored to polymer supports through didentate Schiff's base linkages [94]. Further details of the complexes prepared are given below in Table 1.

Table 1. Dioxomolybdenum (VI) complexes with Schiff's base ligands

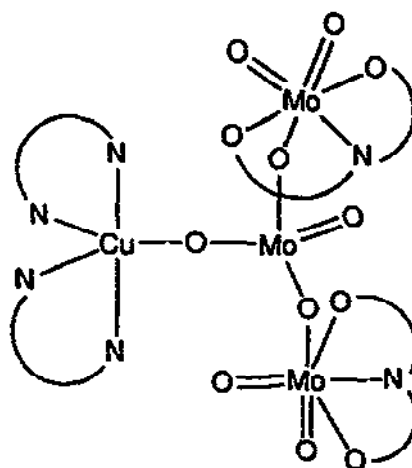
Carbonyl compound	Amine	Complex type	Reference
Salicylaldehyde	$\text{H}_2\text{NNHC}(\text{S})\text{SMe}$	$[\text{MoO}_2\text{L}(\text{S})]$ $\text{S} = \text{MeOH, dmf, py, dmsO}$	[95]
Salicylaldehyde	Girard's reagent P $[\text{C}_5\text{H}_5\text{NCH}_2\text{CONHNH}_2]\text{Cl}$	$[\text{MoO}_2(\text{L})(\text{MeOH})]\text{Cl}$	[96]
Salicylaldehyde	Girard's reagent T $[\text{Me}_3\text{NCH}_2\text{CONHNH}_2]\text{Cl}$	$[\text{MoO}_2(\text{L})(\text{MeOH})]\text{I}$	[97]
Salicylaldehyde	Malonyl dihydrazone	$[\{\text{MoO}_2(\text{dmsO})\}_2(\text{L})]$	[98, 99]
Salicylaldehyde <i>o</i> -hydroxyacetophenone	Thiosemicarbazide	$[\text{MoO}_2(\text{L})(\text{MeOH})]$	[100]
Isonicotinic acid	Hydrazine	$[\text{MoO}_2(\text{L})(\text{S})]$	[101]

The complex $[\text{MoO}_2(\text{L})(\text{MeOH})]$, where H_2L (7), is the Schiff's base derived from 5-chlorosalicylaldehyde and the amine $\text{H}_2\text{NCMe}(\text{CH}_2\text{OH})_2$, reacts with cupric acetate in MeOH/MeCN to give a complex formulated as $[\text{Cu}_2\text{Mo}_2\text{O}_4(\text{L})_2(\text{OMe})_2]$, which on heating in MeCN with bpy afforded $[\text{CuMo}_3\text{O}_8(\text{L})_2(\text{bpy})_2]$. This compound, (8), contains a $\text{Mo}_3\text{O}_8^{2-}$ unit bound to a $\text{Cu}(\text{bpy})_2^{2+}$ fragment [102].

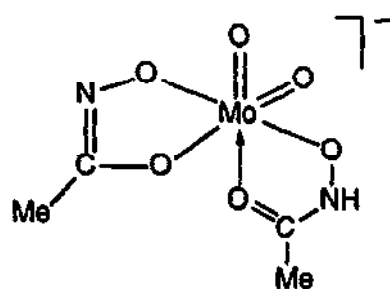
The reaction of $[\text{MoO}_2(\text{acac})_2]$ with two equivalents of $[\text{R}^1\text{R}^2\text{NNH}_3]\text{X}$ ($\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Ph}$ or Me ; $\text{X} = \text{Cl, Br, I}$) in MeCN affords $[\text{MoX}_2(\text{acac})(\text{NHNHR}^1\text{R}^2)(\text{NNR}^1\text{R}^2)]$ which contains two different types of hydrazido ligand [103]. Subsequent reaction with phosphines ($\text{L} = \text{PPh}_3$, PPh_2Me , PMe_2Ph) gives $[\text{Mo}(\text{NNR}^1\text{R}^2)_2\text{Cl}_2\text{L}_2]$ with elimination of acacH . On heating the complex with $\text{L} = \text{PPh}_3$, one phosphine ligand dissociates to afford $[\text{Mo}(\text{NNR}^1\text{R}^2)_2\text{Cl}_2\text{L}]$ [104]. The reaction of $[\text{MoO}_2(\text{dtc})_2]$ with Me_2NNH_2 gave $[\text{MoO}(\text{NNMe}_2)(\text{dtc})_2]$, with *cis* oxo and hydrazido ligands confirmed by an X-ray structure of the complex with $\text{dtc} = \text{S}_2\text{CN}^i\text{Bu}_2$. Treatment of the dioxo complex with HCl gave seven-coordinate $[\text{MoOCl}_2(\text{dtc})_2]$ [105].



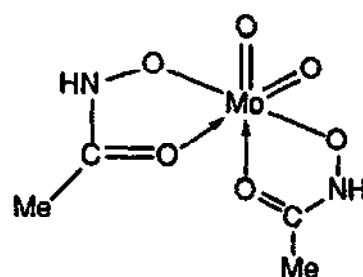
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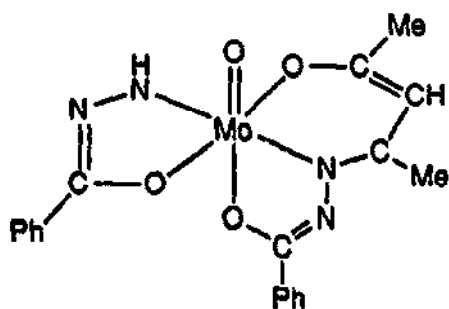
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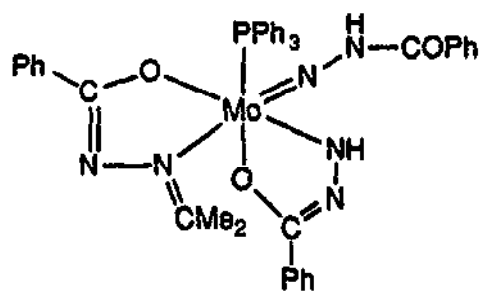
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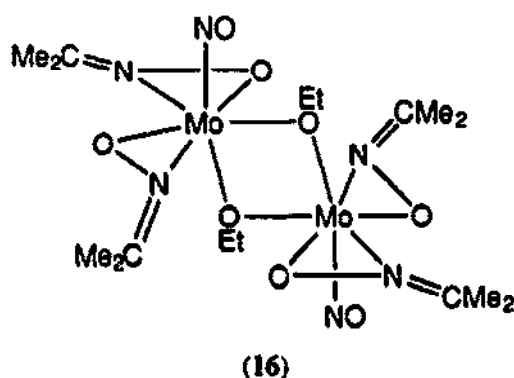
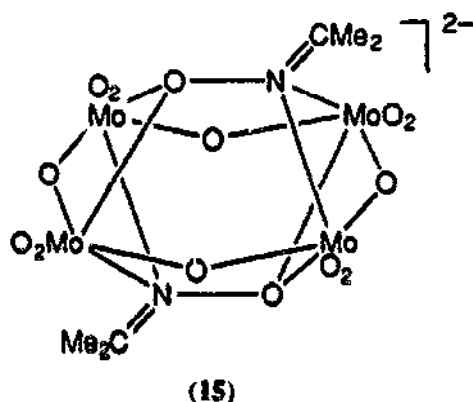
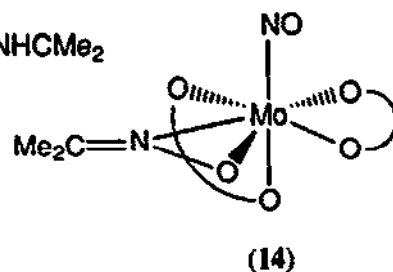
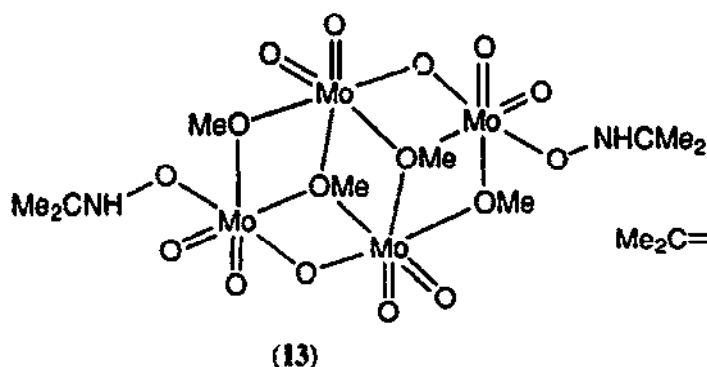
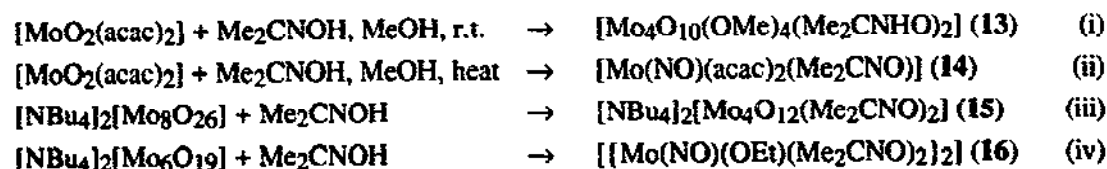
(11)



(12)

The interaction of $[\text{MoO}_2(\text{dtc})_2]$ ($\text{dtc} = \text{S}_2\text{CNEt}_2$) with acetohydroxamic acid, MeCONHOH , gave $[\text{NH}_2\text{Et}_2][\text{MoO}_2(\text{MeCONHO})(\text{MeCONO})]$ (9), in which the hydroxamate and hydroximate ligands are both O,O-bonded. Protonation gave neutral $[\text{MoO}_2(\text{MeCONHO})_2]$ (10) [106]. The reaction of $[\text{MoO}_2(\text{acac})_2]$, PPh_3 and PhCONHNH_2 in refluxing MeOH produced (11) as the major product by a template condensation of the hydrazone with acac ligand [107]. A second product from the reaction, isolated in 5% yield, is the Mo(V) species (12) [108]. A selection of unusual complexes, (13)–(16), have been made by reaction of Mo(VI) species with acetone

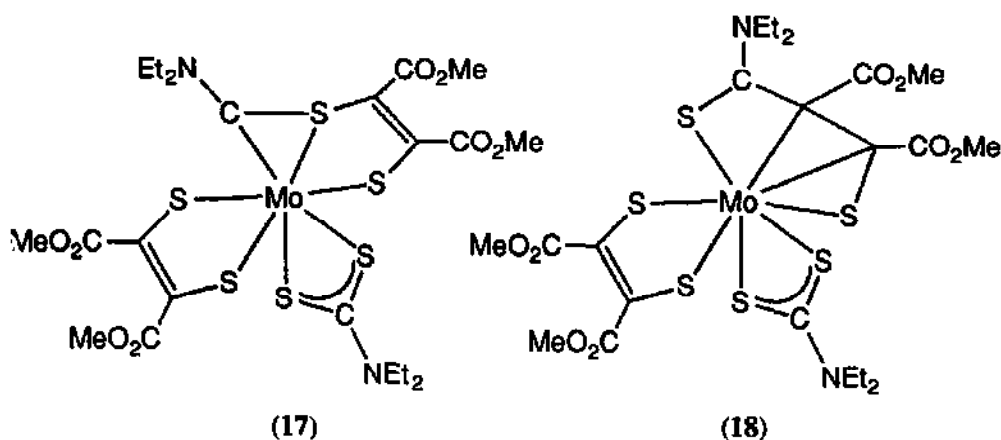
oxime, $\text{Me}_2\text{C}=\text{NOH}$, as detailed in equations (i)–(iv) [109, 110]. Further reaction of compound (16) with $[\text{NBu}_4]_2[\text{Mo}_2\text{O}_7]$ gave $[\text{NBu}_4]_2[\text{Mo}_4\text{O}_{10}(\text{NO})(\text{OMe})(\text{Me}_2\text{CNO})_2]$.



8.1.4 Complexes with sulfur donor ligands

The salt $[\text{PhCH}_2\text{NMe}_3]_2[\text{MoS}_4]$ has been used as a sulfur transfer reagent in the solid phase synthesis of phosphorothioate oligonucleotides [111]. The reaction of $[\text{MoS}_4]^{2-}$ with $[\text{NEt}_4][\text{Mo}(\text{CO})_4(\text{dtc})]$ in MeOH gave the complex $[\text{NEt}_4]_2[(\text{OC})_4\text{Mo}(\mu\text{-S})_2\text{Mo}(\mu\text{-S})_2\text{Mo}(\text{CO})_4]$; the ^{95}Mo NMR spectrum confirms the presence of two different oxidation states [112]. A similar compound, $[\text{R}_2\text{Ni}(\mu\text{-S})_2\text{Mo}(\mu\text{-S})_2\text{NiR}_2]^{2-}$ ($\text{R} = \text{C}_6\text{F}_5$) was prepared from a 1:1 ratio of $[\text{MoS}_4]^{2-}$ and $[\text{Ni}_2\text{R}_4(\mu\text{-OH})_2]^{2-}$; if a 2:1 ratio was used in the presence of additional NBu_4^+ , the dinuclear complex $[\text{R}_2\text{Ni}(\mu\text{-S})_2\text{MoS}_2]^{2-}$ was produced [113]. Similarly $[\text{MoSe}_4]^{2-}$ reacts with two equivalents of CuCN in MeCN to give $[\text{PPh}_4][(\text{NC})\text{Cu}(\mu\text{-Se})_2\text{Mo}(\mu\text{-$

$\text{Se}_2\text{Cu}(\text{CN})$. Addition of PMe_2Ph to this compound gave $[\text{PPh}_4]_2[(\text{NC})\text{Cu}(\mu\text{-Se})_2\text{MoSe}_2]$ [114]. The reaction of $[\text{Mo}_2(\mu\text{-S}_2)_2(\text{dtc})_4][\text{BF}_4]_2$ or $[\text{MoO}(\text{S}_2)(\text{dtc})_2]$ ($\text{dtc} = \text{S}_2\text{CNEt}_2$ or S_2CNMe_2) with the electron-deficient alkyne DMAD ($\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$) gives the two unusual isomeric complexes, orange (17) and green (18), by coupling of the alkyne with the sulfur and dtc ligands. Heating (17) causes it to rearrange to (18) [115].



8.2 MOLYBDENUM(V)

8.2.1 Complexes with halide ligands

Iodine and molybdenum EXAFS spectra have been recorded for $[\text{I}(\text{MeCN})_2][\text{MoF}_6]$ and $[\text{I}(\text{py})_2][\text{MoF}_6]$, as well as $[\text{I}(\text{py})_2][\text{NO}_3]$ and $[\text{Ag}(\text{py})_4][\text{MoF}_6]$; they provide good evidence for discrete linear IL_2 molecules both in the solid state and in MeCN solution [116]. Infra-red spectra of the vapour above MoCl_5 showed the presence of two species; one was MoCl_5 monomer, which shows four fundamental IR-active vibrations consistent with D_{3h} symmetry, and the other was an impurity of MoOCl_3 [117]. The addition of two equivalents of AlMe_3 to various Mo halides, including MoCl_5 , $[\text{MoOCl}_3]$, $[\text{MoCl}_3(\text{OMe})_2]$ and $[\text{MoCl}(\text{OMe})_4]$, affords carbonyl methylenating agents which are thought to be binuclear, with structures related to the Tebbe reagent. Similar results were obtained with ZnMe_2 or MeMgBr in some cases [118]. The solid state polymerisation of $[\text{HC}\equiv\text{CCH}_2\text{PPh}_3]\text{Br}$ by MoCl_5 and $\text{Sn}^{\text{IV}}\text{H}_4$ or EtAlCl_2 gives a quantitative yield of high molecular weight material [119], and MoCl_5 has also been used as a Lewis acid to effect a ring expansion rearrangement of a steroidal organomercury compound [120].

Template condensation of acetone with en occurred in the presence of $[\text{MoOX}_5]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$) to give $[\text{MoO}(\text{L})\text{X}]^{2+}$ where $\text{L} = 5,7,7,12,14,14$ -hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. The macrocycle could be decomplexed with perchloric acid [121]. A complex product, $[\text{H}_4\text{L}][\text{Mo}(\text{OH})\text{Cl}_4(\text{H}_2\text{O})][\text{Cl}]_3[\text{OH}]$, has been isolated from the reaction of $[\text{MoOCl}_5]^{2-}$ with the related macrocycle 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L) [122]. Interaction of Mo(V) oxo species with Cl^- and ox^{2-} in the presence of 2-(2-pyridyl)-benzothiazole (L) produced species such as $[\text{H}_2\text{L}][\text{MoOCl}_5]$, $[\text{MoOCl}_3(\text{L})]$, $[\text{MoO}(\text{Cl})(\text{ox})\text{L}]$, and

[Mo₂O₃Cl₄L₄] [123]. Similar compounds were obtained from bis-(2-benzimidazolyl)alkanes [124].

The magnetic circular dichroism spectra of [MoOCl₄][−] and its Cr and W analogues have been analysed in two papers. The temperature and field dependence are consistent with a paramagnetic ground state, and the lowest energy bands are assigned to $d_{xy} \rightarrow d_{xz}$, d_{yz} and $d_{xy} \rightarrow d_{x^2-y^2}$ ligand field transitions; the first of these displays vibronic coupling to the symmetric Mo=O vibration. The low energy of the $b_1(Cl) \rightarrow b_2(d_{xy})$ charge transfer band is advanced as an explanation of the inverted EPR spectroscopic parameters of these compounds and molybdenum hydroxylase enzymes [125]. The high resolution single crystal absorption spectra of [PPh₄][MoOCl₄] and its H₂O adduct were also recorded and assigned, and used to interpret the spectra of lower symmetry complexes of the type [(HBpz*₃)MoOX₂] [126].

8.2.2 Complexes with nitrogen donor ligands

The nitrido porphyrin complexes [Mo(≡N)(P)] (H₂P = tetraphenyl, -tolyl or -mesityl porphyrin) have been prepared by reaction of the dimers [Mo(P)]₂ with Me₃SiN₃ [127]. The synthesis of a Mo(V) tetrasulfophthalocyanine complex has been reported; photolysis in ⁱPrOH leads to hydrogenation of the ligand, with reoxidation being effected by O₂ [128]. The electrochemistry of [MoO(OH)(Pc)] shows oxidation to Mo(VI) and reduction to Mo(IV) as well as other ligand-centred redox processes; the complex is readily photo-oxidised [129].

Several papers deal with Mo(V) complexes of the hydridotris(3,5-dimethylpyrazolyl)borate ligand, HBpz*₃ (also known as Tp* and denoted for the next two paragraphs by L). The single crystal, room temperature Q-band EPR spectra of [LMo(E)Cl₂] (E = O or S) and [LMoO(NCS)₂] doped into the tin compound [LSnCl₃] have been recorded and analysed [130]. The X-band frozen EPR spectra of [LMo(O)(SC₆H₄S)] (a rare example of a mono-oxo Mo(V) dithiolene complex) and [LMo(O)(SCH₂CH₂S)] both show an unusual coupling pattern which is evidently a feature of the sulfur ligation. This pattern is different to that observed for the low pH form of sulfite oxidase, though the g values for the two systems are similar [131]. The reaction of [LMoO₂Br] with [NBu₄][SH] affords the Mo(V) dimer [(LMoO)₂(μ-O)(μ-S₂)], and oxygen atom transfer from [LMoO₂(SPh)] to PPh₃ affords [(LMo(SPh))₂(μ-O)] by a comproportionation reaction. The mixed valence species [LMoO₂(μ-O)Mo(O)(X)L] (X = SPh, Br) can be made by treating [LMoO₂Br] with PhSH and NEt₃ [132].

A study of the rates of heterogeneous electron transfer and E° values for compounds of the type [LMoO(X-X)] where X-X is a chelating ligand with O[−] or S[−] donors has shown that the rates are about 1.5 times faster when X = S and the E° value changes by about 1 V, i.e. sulfur ligation favours electron transfer [133]. Enemark and coworkers have shown that a Mo(VI)O₂ → Mo(IV)O oxygen atom transfer can be coupled to the reoxidation of the Mo(IV) species to Mo(V) by an iron porphyrin. Thus, reaction of [LMoO₂Cl] with PPh₃ gives [LMoOCl], which in turn reacts with [Fe(TPP)Cl] to give [LMoOCl₂] and [Fe(TPP)]. The kinetics of the oxidation step

indicate an inner-sphere halide transfer mechanism [134]. Taking this a step further, they have prepared a modified porphyrin ligand with a pendant catechol functionality which can be coordinated in the complex $[\text{LMoO}(\text{cat-PFe}(\text{B})_2)]\text{Cl}$ where $\text{B} = N$ -methyl imidazole. The Mo(V) and Fe(III) centres are essentially independent electrochemically, but a weak interaction was observed in the EPR spectrum [135].

The related hydridotris(3,5-dimethyl-1,2,4-triazolyl)borate complex $[(\text{HBtz}^*)_3\text{MoO}_2(\text{SPh})]$ undergoes reduction with $[\text{CoCp}_2]$ to give the first example of a structurally characterised Mo(V) radical anion, $[\text{CoCp}_2][(\text{HBtz}^*)_3\text{MoO}_2(\text{SPh})]$. The structure differs from that of the Mo(VI) starting material in that the Mo–O bonds are longer and the O–Mo–O angle has opened up slightly [136].

The geometries of several Mo(V) and Mo(VI) complexes with N_2S_2 and N_2O_2 donor ligands have been optimised by ab initio and INDO methods, and, where appropriate, their EPR g values have been calculated. The ligands involved are $\text{HXC}_6\text{H}_4\text{NMeCH}_2\text{CH}_2\text{NMeC}_6\text{H}_4\text{XH}$ where $\text{X} = \text{O}$ or S , and $\text{HSCH}_2\text{CH}_2\text{NMeCH}_2\text{CH}_2\text{NMeCH}_2\text{CH}_2\text{SH}$, and the complexes modelled were of the type $[\text{MoO}_2\text{L}]$, $[\text{MoO}_2\text{L}]^-$ and $[\text{MoO}(\text{OH})\text{L}]$ [137].

The reaction of $[\text{MoCl}_4(\text{thf})_2]$ with allyl azide followed by $\text{Ph}_3\text{P}=\text{O}$ gave the imido complex *cis,mer*- $[\text{MoCl}_3(\text{OPPh}_3)_2(=\text{NCH}_2\text{CH}=\text{CH}_2)]$; in moist air it hydrolyses to $[\text{MoOCl}_3(\text{OPPh}_3)_2]$ [138].

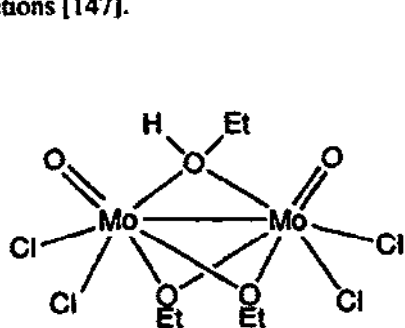
8.2.3 Complexes with oxygen and sulfur donor ligands

A spectrophotometric and EPR spectroscopic study of aqueous Mo(V), made by reducing Mo(VI) with Hg, in 2–9M H_2SO_4 noted a concentration dependence in the most acid solutions, attributed to a tetrameric species [139]. A method of determining Mo(V) as a chromone complex has been developed [140]. The structure of the Mo(V) hydroxide formed by reduction of molybdate with hydrazine hydrate has been established as $[\text{Mo}_2\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_2]^{2-}$, which reacts with oxalate to give $[\text{Mo}_2\text{O}_4(\text{ox})_2(\text{H}_2\text{O})_2]^{2-}$. Reducing molybdate with NaBH_4 or hydrolysing $[\text{MoOCl}_5]^{2-}$ gives related species [141]. A solid state reaction between ammonium molybdate, sodium oxalate, $\text{NH}_2\text{OH}\cdot\text{HCl}$ and NBu_4Br afforded $[\text{NBu}_4]_2[\{\text{MoO}(\text{OH})\text{Cl}_2\}_2(\mu\text{-ox})]$ [142]. Extended Hückel calculations have been carried out which support the proposed mechanism for the photolabilisation of $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_m\text{L}_{6-m}]^{n+}$ ($\text{L} = \text{H}_2\text{O}$, Cl^- , NCS^-) in aqueous acid, involving intermediates with a singly-bridged $\text{Mo}_2\text{O}_3^{4+}$ core [143].

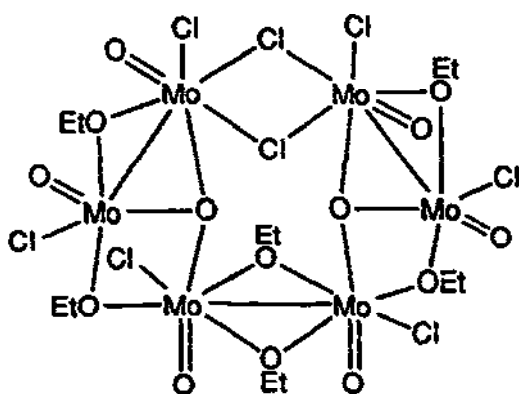
The reaction of MoCl_5 with EtOH in CHCl_3 affords a quantitative yield of the diamagnetic $[\text{Cl}_2(\text{O})\text{Mo}(\mu\text{-OEt})_2(\mu\text{-EtOH})\text{Mo}(\text{O})\text{Cl}_2]$ (19); the unsolvated species and its CHCl_3 solvate were both structurally characterised [144]. Reaction of this compound with $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ results in the elimination of propene and formation of $[\text{Mo}_6\text{O}_6\text{Cl}_6(\mu\text{-Cl})_2(\mu_3\text{-O})_2(\mu\text{-OEt})_6]$ (20) [145].

The reaction of $[\text{MoO}_2(\text{acac})_2]$ with H_3hidpa $[\text{HON}(\text{CHMeCO}_2\text{H})_2]$ yields $[\text{Mo}(\text{hidpa})_2]^-$, which is the molybdenum analogue of amavadin. Interestingly one of the hidpa ligands has the *R,R* configuration and the other the *R,S* [146]. The synthesis of $[\text{MoO}(\text{L})\text{NCS}]$ where H_2L are the pentadentate Schiff's bases *N,N'*-bis(salicylidene)diethylene triamine and *N,N'*-bis(salicylidene)

dipropylene triamine, has been reported; they undergo a series of one electron electrochemical reductions [147].

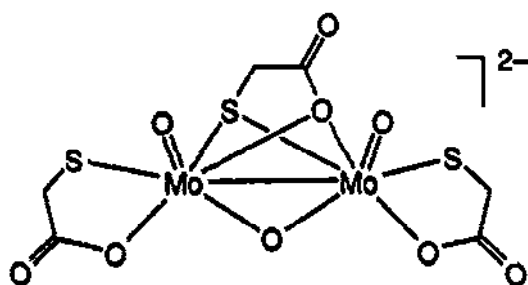


(19)



(20)

The interaction of $[\text{MoO}_4]^{2-}$ with thioglycolic acid, $\text{HSCH}_2\text{CO}_2\text{H}$, has been studied in detail. Initially $[\text{MoO}_2(\text{SCH}_2\text{COO})_2]^{2-}$ is formed, which is reduced by more acid to give two Mo(V) species in equilibrium; the major one of these is $[\text{NBu}_4]_2[\text{Mo}_2\text{O}_3(\text{SCH}_2\text{COO})_3] \cdot 2\text{H}_2\text{O}$ (21), which was isolated and structurally characterised. The Mo(V) dimer is probably formed by comproportionation since reduction of these compounds further gives the Mo(IV) species $[\text{MoO}(\text{SCH}_2\text{COO})_2]^{2-}$ and $[\text{MoO}(\text{SCH}_2\text{COO})(\text{solv})_2]$ [148].



(21)

Oxidation of $[\text{Mo}(\text{S}_2)(\text{dtc})_3]$ ($\text{dtc} = \text{S}_2\text{CNEt}_2$) with one equivalent of *m*-CPBA gave the S_2O complex $[\text{Mo}(\text{S}_2\text{O})(\text{dtc})_3]$ in 70% yield. The structures and electronic properties of the two complexes are very similar but EHMO calculations indicate that S_2O is a worse π -acid and π -base than S_2 [149]. Treatment of $[\text{MoO}(\text{dtc})_3][\text{BF}_4]$ ($\text{dtc} = \text{S}_2\text{CNR}_2$ where $\text{R} = \text{Et}, \text{iPr}, \text{iBu}$) with B_2S_3 produced the dinuclear complex $[\text{Mo}_2(\mu\text{-S}_2)_2(\text{dtc})_4][\text{BF}_4]_2$ as well as $[\text{Mo}(\text{dtc})_4][\text{BF}_4]$ [150]. The crystal structure of the salt $[\text{Mo}(\text{dtc})_4][\text{Sm}(\text{dtc})_4]$ has been determined [151, 152], and the oxidative decarbonylation of $[\text{Mo}(\text{CO})_5\text{I}]^-$ with dtc^- ($\text{dtc} = \text{S}_2\text{CNC}_4\text{H}_8$) gave $[\text{Mo}(\text{dtc})_4][\text{I}_3]$ and $[\text{Mo}_2\text{O}_2\text{S}_2(\text{dtc})_2]$ [153]. The electrochemistry of compounds of the type $[\text{Mo}_2\text{O}_4\text{-nS}_n(\text{dtc})_2]$ has been studied for a number of dtc ligands and $n = 0\text{--}2$; with the exception of the complex with $n = 2$ and $\text{dtc} = \text{S}_2\text{CNPh}_2$, all showed a quasi-reversible one electron reduction [154]. A molecular orbital study of $[\text{Mo}_2\text{S}_4(\text{SCH}_2\text{CH}_2\text{S})_2]^{2-}$ and its mono- and bis-adducts with $\text{Cu}(\text{PPh}_3)^+$ fragments has

appeared [155]. Complexes $[\text{Mo}_2\text{O}_4\text{L}_2]$ and $[\text{Mo}_2\text{O}_2\text{S}_2\text{L}_2]$ where HL is 5-phenylazo-8-hydroxyquinoline have been prepared [156].

8.3 MOLYBDENUM(IV)

8.3.1 Complexes with halide and cyanide ligands

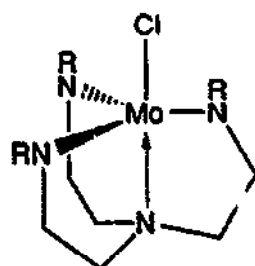
The reactions of $[\text{MoCl}_4(\text{MeCN})_2]$ with ligands such as PPh_3 , dppe or phen have given the complexes $[\text{MoCl}_4\text{L}_2]$ and $[\text{MoCl}_4(\text{L-L})]$ [157]. The reaction of $[\text{MoCl}_4(\text{thf})_2]$ with allyl azide gives $[\text{MoCl}_4(\text{thf})(=\text{NCH}_2\text{CH}=\text{CH}_2)]$; dissolving this in pyridine produced a 5% yield of the unusual nitrido species $[\text{Cl}_3(\text{py})_2\text{Mo}(\mu\text{-N})\text{Mo}(\text{py})_2\text{Cl}_3]^-$ as its *N*-allylpyridinium salt. The two Mo–N distances are 1.887(10) Å and 1.793(10) Å, neither identical nor yet sufficiently different to warrant a description as a $\text{Mo}\equiv\text{N}\rightarrow\text{Mo}$ bonding arrangement [158]. Oxidative decarbonylation of $[\text{Mo}(\text{CO})_6]$ with S_2Cl_2 produced a green material of empirical formula $\text{Mo}_2\text{S}_2\text{Cl}_6\cdot\text{CH}_2\text{Cl}_2$ which on further reaction with thf, tht or PhCH_2SMe gave the dimeric Mo(IV) species $\{[\text{MoCl}_3\text{L}]_2(\mu\text{-S}_2)(\mu\text{-L})\}$ or the Mo(IV)/Mo(V) mixed valence complex $[(\text{Me}_2\text{S})_2\text{Cl}_2\text{Mo}(\mu\text{-S}_2)(\mu\text{-S})\text{MoCl}_3(\text{SMe}_2)]$ in the case of SMe_2 [159].

Outer sphere charge transfer absorptions have been observed in the visible and near-IR region for various cyanometallates, including $[\text{Mo}(\text{CN})_8]^{4-}$, in the presence of $[\text{Fe}(\text{CN})_6]^{3-}$ as acceptor [160]. The kinetics of the electron transfer reaction between $[\text{Mo}(\text{CN})_8]^{4-}$ and the Mn(III) complex of *trans*-1,2-diaminocyclohexane *N,N,N',N'*-tetraacetate have been studied by stopped flow methods [161]. The interaction of $[\text{Mo}(\text{CN})_8]^{4-}$ with $[\text{Os}(\text{en})_2(\eta\text{-H}_2)(\text{H}_2\text{O})]^{2+}$ initially forms a Os(II)-Mo(IV) species, $[\text{Os}(\text{en})_2(\eta\text{-H}_2)\text{Mo}(\text{CN})_8]^{2-}$, which can be oxidised to a Os(IV)-Mo(IV) one [162]. The isolation of $[(\text{NC})_7\text{Mo}(\mu\text{-CN})\text{Os}(\text{NH}_3)_5]^-$ has also been achieved; it exhibits a moderately intense intervalent charge transfer band at 638 nm, and shows an irreversible electrochemical oxidation to Mo(V) [163]. A multinuclear NMR spectroscopic study of the protonation of aqueous solutions of $[\text{MoO}_2(\text{CN})_4]^{2-}$ has been undertaken; and a value of 9.88 was determined for the pK_a of $[\text{MoO}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ compared with 7.87 for its tungsten analogue [164].

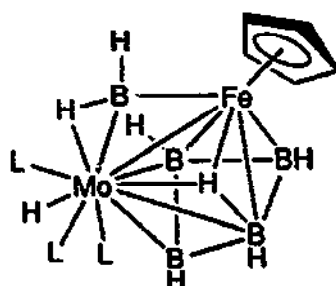
8.3.2 Complexes with nitrogen and phosphorus donor ligands

As part of a general study of the synthesis of early transition metal porphyrin complexes, $[\text{Mo}(\text{TPP})\text{Cl}_2]$ was prepared from $[\text{MoCl}_4(\text{MeCN})_2]$ and $[\text{Li}_2(\text{thf})_2][\text{TPP}]$ [165]. The reaction of $[\text{MoCl}_4(\text{thf})_2]$ with $\text{Li}_3[\text{N}(\text{CH}_2\text{CH}_2\text{NR})_3]$ produced the trigonal bipyramidal molybdenatranes complex $[\text{MoCl}[\text{N}(\text{CH}_2\text{CH}_2\text{NR})_3]]$ (22) where R = SiMe₃, SiMe₂Ph, or SiMePh₂. The chloride ligand could be replaced with organic groups from MeLi or $\text{LiC}\equiv\text{CR}'$ (R' = Me, Ph, SiMe₃). When $\text{LiC}\equiv\text{CH}$ was used, coupling of the acetylide occurred to give $[\text{LMo}\equiv\text{CCH}=\text{CHC}\equiv\text{MoL}]$ [166]. The reaction of $[\text{Mo}(\text{NMe}_2)_4]$ with the related amine $\text{N}(\text{CH}_2\text{CH}_2\text{NHA}r)$ (Ar = C₆F₅) afforded a similar compound $[\text{Mo}(\text{NMe}_2)[\text{N}(\text{CH}_2\text{CH}_2\text{NAr})_3]]$. From this a range of other derivatives were

prepared including $[\text{LMoCl}]$, $[\text{LMo}(\text{OTf})]$, $[\text{LMo}(\equiv\text{N})]$ and $[\text{LMo}(\equiv\text{NMe})][\text{OTf}]$. Reduction of $[\text{LMo}(\text{OTf})]$ under N_2 gave $[\text{LMo}(\mu\text{-N}_2)\text{MoL}]$; the same species could be made for the silylated triamine by reacting the lithiated ligand directly with $[\text{MoCl}_3(\text{thf})_3]$ under N_2 [167].



(22)



(23)

The low temperature electrochemistry of $[\text{MoCl}(\text{NMe})(\text{dppe})_2]^+$ in thf has been investigated by microelectrode techniques. One electron reduction is followed either by a further four-electron reduction to $[\text{Mo}(\text{N}_2)_2(\text{dppe})_2]$ and MeNH_2 , or deprotonation of further cationic starting material to form the methyleneimido complex $[\text{MoCl}(\text{N}=\text{CH}_2)(\text{dppe})_2]$ depending on the electrode material [168]. Electrochemical reduction of $[\text{MH}_2(\eta^2\text{-O}_2\text{CMe})(\text{dppe})_2]^+$ ($\text{M} = \text{Mo}, \text{W}$) affords initially $[\text{MH}_2(\eta^1\text{-O}_2\text{CMe})(\text{dppe})_2]$ and then an anionic species which is unstable for Mo but in the case of W can be trapped as $[\text{WH}_3(\eta^1\text{-O}_2\text{CMe})(\text{dppe})_2]$ [169]. Protonation of the 2-methallyl complex $[\text{MoH}(\eta^3\text{-H}_2\text{CCMeCH}_2)(\text{dppe})(\eta^1\text{-dppe})]$ with HCl occurred to give $[\text{MoH}_2\text{Cl}_2(\text{dppe})_2]$, with the organic fragment dimerising to $^i\text{BuCH}_2\text{CMe}=\text{CH}_2$ [170]. The reaction of $[\text{MoF}(\text{NNH}_2)(\text{dppe})_2][\text{BF}_4]$, made from $[\text{Mo}(\text{N}_2)_2(\text{dppe})_2]$ and HBF_4 , with 2,5-dimethoxy tetrahydrofuran gives the pyrrolyl imido complex $[\text{MoF}(\text{=NNC}_4\text{H}_4)(\text{dppe})_2][\text{BF}_4]$; pyrrole can be liberated on reduction with LiAlH_4 [171]. Alkylation of $[\text{MoF}(\text{NN}=\text{CHCH}=\text{CHMe})(\text{dppe})_2]^+$ with lithium dialkyl cuprates, LiCuR_2 ($\text{R} = \text{Me}, \text{Ph}$), occurred on the terminal β -carbon to produce $[\text{MoF}(\text{NNCH}=\text{CHCHMeR})(\text{dppe})_2]$, which could subsequently be protonated or alkylated on the α -carbon [172]. The complex $[\text{MoH}_4(\text{dippe})_2]$ ($\text{dippe} = ^i\text{Pr}_2\text{PCH}_2\text{CH}_2\text{P}^i\text{Pr}_2$) could be made either from $[\text{MoCl}_4(\text{thf})_2]$, dippe and NaBH_4 , or from $[\text{Mo}(\text{N}_2)_2(\text{dippe})_2]$, itself available in low but reproducible yield by Na/Hg reduction of $[\text{MoCl}_3(\text{thf})_3]$ with dippe under N_2 . Addition of HBF_4 to the dinitrogen complex gave the hydrazide $[\text{MoF}(\text{NNH}_2)(\text{dippe})_2][\text{BF}_4]$. Reducing $[\text{MoCl}_3(\text{thf})_3]$ and dippe under Ar gave $[\text{MoCl}_2(\text{dippe})_2]$ [173].

Treatment of $[\text{MoH}_4(\text{dppe})_2]$ with alkyl malonates $\text{CH}_2(\text{CO}_2\text{R})_2$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}$) gave the complexes $[\text{MoH}(\text{CH}(\text{CO}_2\text{R})_2)(\text{dppe})_2]$ in which the malonates act as O,O' -donors rather like an acac ligand [174]. The reaction of $[\text{MoH}_4(\text{PMe}_2\text{Ph})_4]$ with *nido*-[2-(FeCp) B_5H_{10}] affords the unusual compound *closo*-[1-(FeCp)-2- $[\text{MoH}(\text{PMe}_2\text{Ph})_3]\text{B}_5\text{H}_7]$ (23) [175].

8.3.3 Complexes with oxygen and sulfur donor ligands

The synthesis of $[\text{NEt}_4]_2[\text{MoO}(\text{tdt})_2]$, where tdt = toluenedithiolate, and the X-ray structure of its Et_2O adduct have been reported. This compound is inert to oxidation by Me_3NO , either because of the narrow SMoS angles preventing coordination or strong Mo-S bonds preventing rearrangement from a *trans*-dioxo to the more stable *cis*-dioxo structure [176]. Similar complexes have been prepared with the $[3\text{-SiPh}_3\text{-1,2-C}_6\text{H}_3\text{S}_2]^{2-}$ and $[5\text{-SiPh}_3\text{-3-Me-1,2-C}_6\text{H}_2\text{S}_2]^{2-}$ ligands; the first of these does react with Me_3NO to give $[\text{MoO}_2(\text{Ph}_3\text{Si-bdt})_2]^{2-}$ quantitatively with no evidence for the formation of dimeric Mo(V) species [177]. Two groups have reported complexes of the *mnt* ligand, $[\text{SC}(\text{CN})=\text{C}(\text{CN})\text{S}]^-$; square pyramidal $[\text{MoO}(\text{mnt})_2]^{2-}$ could be oxidised with Me_3NO to $[\text{MoO}_2(\text{mnt})_2]^{2-}$, which in turn oxidised $[\text{HSO}_3]^-$ to $[\text{HSO}_4]^-$ without forming a Mo(V) species. The Mo(IV) species will undergo a quasi-reversible 1-electron oxidation, but also disproportionates to $[\text{Mo}(\text{mnt})_3]^{2-}$ and MoO_3 . The corresponding $[\text{MoO}\{\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2\}_2]^{2-}$ reacts with Me_3NO to give a transient Mo(VI) species which decomposes to thiolate oxidation products, which indicates that the *mnt* ligand is able to provide some extra stabilisation for the Mo(VI) state [178, 179]. The reaction of $[\text{MoO}(\text{S}_2\text{P}^i\text{Pr}_2)_2]$ with $\text{K}[\text{H}_2\text{Bpz}^*]_2$ produced $[(\text{H}_2\text{Bpz}^*)_2\text{MoO}(\text{S}_2\text{P}^i\text{Pr}_2)]$, which can be reversibly oxidised to Mo(V) [180].

Further complexes of 2-aminocyclopentene-1-carbodithioate, $[\text{Mo}(\text{ox})(\text{acda})(\text{Racda})]$ ($\text{R} = \text{Et, Pr, Bu}$) have been prepared; they are weakly paramagnetic with a spin-paired d^2 ground state and undergo reversible 1-electron oxidation and reduction [181].

The complex *trans*- $[\text{Mo}(\text{NH})(\text{OTf})(\text{L})][\text{OTf}]$ ($\text{L} = \text{Meg}[16]\text{ane-S}_4$) is made by reaction of $[\text{Mo}(\text{N}_2)_2(\text{L})]$ with Me_3SiN_3 to give $[\text{Mo}(\equiv\text{N})(\text{N}_3)(\text{L})]$ followed by addition of 4 equivalents of HOTf . The α -hydroxyalkylimido complexes $[\text{Mo}\{\text{NC}(\text{OH})\text{R}^1\text{R}^2\}(\text{OTf})(\text{L})][\text{OTf}]$ were formed by reaction with Me_2CO or PhCHO , while NaBPh_4 afforded the adduct $[\text{Mo}(\text{NBPh}_3)(\text{OTf})(\text{L})][\text{OTf}]$ [182].

8.4 MOLYBDENUM(III)

8.4.1 Complexes with halide and phosphine ligands

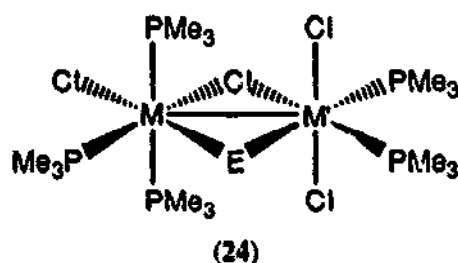
The deuterium NMR spectra of $[\text{MoX}_3(\text{py-d}^5)_3]$ ($\text{X} = \text{Cl, Br, NCS, F}$) have been used to assign *fac* or *mer* structures [183]. The complexes $[\text{MoCl}_3\text{L}_2(\text{MeCN})]$ where $\text{L} = \text{PPh}_3$ or $\text{L}_2 =$ phenylene diamine have been prepared from MoCl_5 ; the chloride ligands can be removed with AgClO_4 to form cationic solvento species [184]. Reaction of $[\text{MoCl}_3(\text{thf})_3]$ with the macrocycle [15]-ane N_4 (1,4,8,12-tetraazacyclopentadecane) gave *cis*- $[\text{MoCl}_2([\text{15-ane-N}_4])][\text{Cl}]$ [185].

The compound *cis*- $[\text{pyH}][\text{MoCl}_4(\text{py})_2]$ was prepared by reacting $[\text{pyH}]_3[\text{MoCl}_6]$ with py in MeCN , and the corresponding *trans* complex was obtained by its isomerisation above room temperature. A series of salts were made by cation exchange and the structure of *cis*- $\text{Rb}[\text{MoCl}_4(\text{py})_2]\cdot\text{H}_2\text{O}$ was determined, as was that of *cis*- $[\text{NH}_4][\text{MoCl}_4(\text{py})_2]\cdot 0.5\text{H}_2\text{O}\cdot\text{py}$ [186, 187]. The bromide $[\text{pyH}][\text{MoBr}_4(\text{py})_2]$ was made as a mixture of *cis* and *trans* isomers from

$[\text{MoBr}_5(\text{H}_2\text{O})]^-$ and py; the *cis* isomerises to *trans* in refluxing MeCN. The X-ray structure of *cis*- $[\text{NH}_4][\text{MoBr}_4(\text{py})_2]$ was determined [188].

Molecular orbital calculations on $[\text{C}]_3[\text{Mo}_2\text{X}_9]$ ($\text{C} = \text{K}, \text{Rb}, \text{Cs}, \text{NMe}_4$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) using SCF-X α -SW methods have shown that the Mo–Mo σ and π -bonding interactions are reduced for Br and I compared to Cl leading to longer metal-metal distances [189]. The synthesis of several salts of the $[\text{Mo}_2(\text{H})\text{Br}_8]^{3-}$ anion have been reported, together with the crystal structure of the piperidinium salt and studies of their thermal decomposition [190, 191].

Conproportionation of $[\text{MCl}_2(\text{PMe}_3)_4]$ with $[\text{M}'(\text{E})\text{Cl}_2(\text{PMe}_3)_3]$ ($\text{M} = \text{Mo}, \text{W}$; $\text{E} = \text{O}, \text{S}$) in what amount to incomplete E-atom transfer reactions afford the edge-sharing bioctahedral complexes $[(\text{Cl})(\text{PMe}_3)_3\text{M}(\mu\text{-E})(\mu\text{-Cl})\text{M}'\text{Cl}_2(\text{PMe}_3)_2]$ (24). Two different isomeric MoW complexes were obtained depending on the starting materials used. Treatment of $[\text{MoCl}_2(\text{PMe}_3)_4]$ with $\text{S}=\text{PMe}_3$, $^t\text{BuSH}$ or ethylene sulfide also gave $[\text{Mo}_2\text{Cl}_3(\mu\text{-Cl})(\mu\text{-S})(\text{PMe}_3)_5]$ [192]. The oxidative addition of S_2Pr_2 to $[\text{Mo}_2\text{Cl}_4(\text{PrSCH}_2\text{CH}_2\text{SPr})_2]$ produced $[\text{Mo}_2\text{Cl}_4(\mu\text{-SPr})_2(\text{PrSCH}_2\text{CH}_2\text{SPr})_2]$, and then ligand exchange yielded $[\text{Mo}_2\text{Cl}_4(\mu\text{-SPr})_2(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)_2]$. The two resulting edge-sharing bioctahedral compounds have Mo–Mo distances of 2.682(6) Å and 2.769(1) Å respectively, consistent with double bonds [193].



8.4.2 Complexes with oxygen and nitrogen donor ligands

Addition of $[\text{NBu}_4][\text{CN}]$ to $[\text{Mo}_2(\text{OR})_6]$ ($\text{R} = ^t\text{Bu}, ^i\text{Pr}, \text{CH}_2^t\text{Bu}$) affords initially $[\text{NBu}_4][\text{Mo}_2(\text{OR})_6(\text{CN})]$, with a bridging cyanide, and then $[\text{NBu}_4]_2[\text{Mo}_2(\text{OR})_6(\text{CN})_2]$; coordination of the second cyanide is less favourable [194]. Addition of KH and 18-crown-6 to $[\text{Mo}_2(\text{OCH}_2^t\text{Bu})_6]$ gave $[\text{K}(18\text{-C-6})][\text{Mo}_4(\mu_4\text{-H})(\text{OCH}_2^t\text{Bu})_{12}]$ in which the hydride bridges all four metals of a butterfly cluster [195].

8.5 MOLYBDENUM(II)

8.5.1 Complexes with halide and phosphine or carbonyl ligands

The reaction of $[\text{MoBr}_2(\text{CO})_2(\text{PPh}_3)_2]$ with aqueous NaBF_4 in CH_2Cl_2 gave initially $[\text{Mo}_2(\mu\text{-Br})(\mu\text{-F})_2(\text{CO})_4(\text{PPh}_3)_4]^+$, which was structurally characterised and showed rather long Mo–Br distances. The bromide ligand was gradually replaced under the reaction conditions by F or OH. Use of KPF_6 in the same reaction gave $[\text{Mo}_2(\mu\text{-Br})_n(\mu\text{-OH})_{3-n}(\text{CO})_4(\text{PPh}_3)_4]^+$ where $n = 1$

or 2 [196]. Treatment of the complex $[\text{MoBr}_2(\text{CO})_2(\text{PPh}_3)_2]$ with NaNO_2 in MeOH gave $[\text{Mo}(\text{NO}_2)_2(\text{CO})_2(\text{PPh}_3)_2]$ which contains chelating, equivalent nitrite groups [197]. A similar species, $[\text{MoX}(\text{NO}_3)(\text{CO})_2(\text{PPh}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}$) with a chelating nitrate was made from NH_4NO_3 [198].

Oxidation of $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ with Br_2 affords $[\text{MoBr}_2(\text{CO})_3(\text{MeCN})_2]$, which reacts with one equivalent of L ($\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3$) to give $[\text{MoBr}_2(\text{CO})_3(\text{MeCN})(\text{L})]$ [199]. The MeCN ligands in the analogous iodide $[\text{MoI}_2(\text{CO})_3(\text{MeCN})_2]$ can be replaced by the chelating thioether $\text{PhSCH}_2\text{CH}_2\text{SPh}$; with a tridentate ligand $[\text{MoI}_2(\text{CO})_2(\text{MeSCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SMe})]$ was prepared [200]. In a similar way, $[\text{MoI}_2(\text{CO})_2(\text{triphos})]$ ($\text{triphos} = \text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$) was also made [201]. Addition of 1–4 equivalents of pyrazole to $[\text{MoI}_2(\text{CO})_3(\text{MeCN})_2]$ gave $[\text{Mo}(\mu\text{-I})(\text{CO})_3(\text{Hpz})_2]$, $[\text{MoI}_2(\text{CO})_3(\text{Hpz})_2]$, $[\text{MoI}(\text{CO})_3(\text{Hpz})_3][\text{I}]$ and $[\text{MoI}(\text{CO})_2(\text{Hpz})_4][\text{I}]$ respectively [202]. The use of Polya's theorem to enumerate the possible geometrical isomers of these and other seven-coordinate species has been described [203].

Oxidative addition of GeCl_4 to $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ gave $[\text{MoCl}(\text{GeCl}_3)(\text{CO})_3(\text{MeCN})_2]$, the MeCN ligands were then replaced by various other ligands [204]. For example, with $\text{Ph}_3\text{P}=\text{E}$ ($\text{E} = \text{O}$ or S), $[\text{Mo}(\mu\text{-Cl})(\text{GeCl}_3)(\text{CO})_3\text{L}]_2$, $[\text{MoCl}(\text{GeCl}_3)(\text{CO})_3\text{L}_2]$ and $[\text{Mo}(\text{GeCl}_3)(\text{CO})_3\text{L}_3][\text{Cl}]$ were produced with 1–3 equivalents respectively [205]. Addition of phosphine ligands to $[\text{MoCl}(\text{SnRCl}_2)(\text{CO})_3(\text{MeCN})_2]$ ($\text{R} = \text{Ph}, \text{Me}$) gave $[\text{MoCl}(\text{SnRCl}_2)(\text{CO})_3\text{L}(\text{MeCN})]$ in CH_2Cl_2 , but in acetone a chloride-bridged dimer or an acetone complex was formed depending on the concentration [206]. Oxidative addition of RSnCl_3 (same R) to $[\text{Mo}(\text{CO})_3(\text{phen})(\text{PPh}_3)]$ gave $[\text{MoCl}(\text{SnRCl}_2)(\text{CO})_2(\text{phen})(\text{PPh}_3)]$ which has a five-coordinate tin atom with a chloride bridging the Mo–Sn bond [207]. Displacement of the MeCN ligand and one carbonyl group in $[\text{Mo}(\text{S}_2\text{PX}_2)(\text{SnRCl}_2)(\text{CO})_3(\text{MeCN})]$ by $\text{S}_2\text{CPR}'_3$ ($\text{R} = \text{Ph}, \text{Bu}$; $\text{R}' = \text{Cy}, \text{tPr}$; $\text{X} = \text{OEt}, \text{Ph}$) gave $[\text{Mo}(\text{S}_2\text{PX}_2)(\text{SnRCl}_2)(\text{S}_2\text{CPR}'_3)(\text{CO})_2]$ in which one of the sulfur atoms of the $\text{S}_2\text{CPR}'_3$ ligand is within bonding distance of the tin atom [208]. Oxidative addition of HgCl_2 to $[\text{Mo}(\text{CO})_4(\text{L}_2)]$ ($\text{L}_2 = 2,9\text{-dimethylphen}$) gave $[\text{MoCl}(\text{HgCl})(\text{CO})_3(\text{L}_2)]$ [209].

8.5.2 Complexes with nitrogen donor ligands

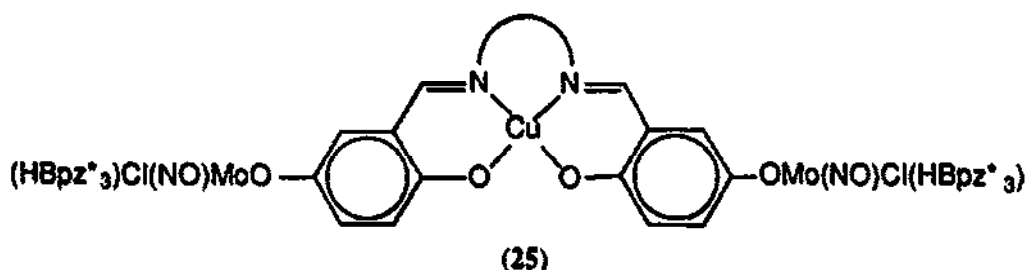
A short account of the synthesis of quadruply-bonded porphyrin dimers and the measurement of the barrier to rotation about the M–M bond has appeared [210]. The synthesis of the heterometallic examples $[(\text{OEP})\text{MoOs}(\text{OEP})]$ and $[(\text{OEP})\text{MoRu}(\text{TOEP})]$ ($\text{TOEP} = \text{dianion of } 5\text{-}p\text{-tolylactaethylporphyrin}$) has been achieved by co-thermolysis of $[(\text{OEP})\text{Mo}(\text{C}_2\text{Ph}_2)]$ with the appropriate metal porphyrin complex. The heterometallic complex was separated from the two homonuclear ones by redox titration. There is no barrier to rotation about the MoRu bond, which means that either there is a very weak δ -bond or the d_{xy} orbitals are non-bonding [211].

Further developments in the extensive chemistry of the tris(3,5-dimethylpyrazolyl)borate complex $[(\text{HBpz}^*_3)\text{Mo}(\text{NO})\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) have been reported. This redox-active 16-electron complex reacts with alcohols and amines with elimination of HX and formation of

$[(\text{HBpz}^*_3)\text{Mo}(\text{NO})(\text{X})(\text{OR})]$ or $[(\text{HBpz}^*_3)\text{Mo}(\text{NO})(\text{X})(\text{NHR})]$, or the corresponding disubstituted species. The complexes $[(\text{HBpz}^*_3)\text{Mo}(\text{NO})\text{X}(\text{EC}_6\text{H}_3\text{-3-R-4-Fc})]$ and their analogues with $\text{EC}_6\text{H}_3\text{-3-R-N=NC}_6\text{H}_3\text{-3-R'-4-Fc}$ ligands ($\text{E} = \text{O}, \text{NH}$; $\text{R}, \text{R}' = \text{H}, \text{Me}$; $\text{X} = \text{Cl}, \text{I}$; $\text{Fc} = \text{ferrocenyl}, \text{C}_5\text{H}_4\text{FeCp}$) have been prepared and tested for their non-linear optical properties by the Kurtz powder test [212, 213]. In order to introduce an element of chirality into such compounds, the ligand $(-)\text{-HOCH}_2\text{CHMeC}_{10}\text{H}_5\text{-6-OMe}$ was also used [214].

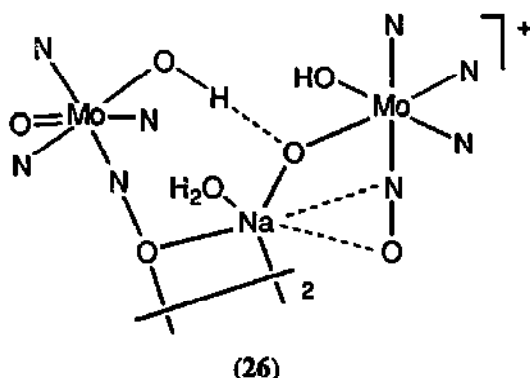
Attaching a $(\text{HBpz}^*_3)\text{Mo}(\text{NO})\text{X}$ unit to each end of the 4-(imidazol-1-yl)phenol ligand allows interaction between the metal centres to be probed. The starting $16e^-$, $17e^-$ system is valence trapped, but one-electron reduction yields a $17e^-$, $17e^-$ system which has a strong exchange interaction despite the fact that the ligand is unable to assume a planar structure easily [215]. The trinucleating ligands $\text{C}_6\text{H}_3\text{-1,3,5-(CH=CHC}_5\text{H}_4\text{N)}_3$ and $\text{C}_6\text{H}_3\text{-1,3,5-(CH=CHC}_6\text{H}_4\text{OH)}_3$ have been made; up to three Mo units can be attached to the three arms. For the first of these ligands, fast exchange was observed between two or three $17e^-$ Mo centres by EPR spectroscopy. Cobaltocene reduction of the tris-Mo complex of the second ligand produced a species with three $17e^-$ centres which showed an identical EPR spectrum [216].

Interaction between heterometallic redox centres has also been studied. Trinuclear MoCuMo complexes (**25**) were made from Cu(II) complexes of Schiff's base ligands derived from 2,5-dihydroxybenzaldehyde and various diamines, $\text{H}_2\text{N}(\text{Y})\text{NH}_2$, where the spacer group $\text{Y} = (\text{CH}_2)_n$ ($n = 2\text{--}5$) or $o\text{-C}_6\text{H}_4$. The compounds undergo two sequential reductions at the Mo centres with weak interaction between the metals [217]. Complexes of dipyriddy ligands such as 4,4'-bpy, bis-(2-pyridyl)ethylene and α,ω -bis(2-pyridyl)alkanes have been made which have one of the pyridyl groups coordinated to a $(\text{HBpz}^*_3)\text{Mo}(\text{NO})\text{Cl}$ unit. The remaining pendant pyridyl group was then attached to the ruthenium porphyrin complexes $[\text{Ru}(\text{CO})(\text{EtOH})(\text{TPP})]$ and $[\text{Ru}(\text{thf})_2(\text{TTP})]$ to give dinuclear and trinuclear systems. Weak electrochemical interactions between the metals could be detected, as well as a weak spin exchange interaction between the two Mo centres in the trinuclear $[\text{Ru}(\text{TTP})\{(\text{HBpz}^*_3)\text{Mo}(\text{NO})\text{Cl}\}_2]$ [218].



The complexes $[(\text{HBpz}^*_3)\text{Mo}(\text{NO})(\text{SR})_2]$ ($\text{R} = \text{Et}, \text{Bu}, \text{CH}_2\text{CONHMe}, \text{CH}_2\text{CONMe}_2$ etc) have been made and a correlation observed between the IR stretching frequency $\nu(\text{NO})$ and the redox potential. The presence of inter- and intra-ligand hydrogen bonds was also noted [219]. New types of pyrazolyborate ligands have also been investigated; these include hydridotris(3-p-methoxyphenylpyrazolyl)borate [220], hydridotris(4-benzyl-3,5-dimethylpyrazolyl)borate [221], hydridotris(3-phenyl-5-methylpyrazolyl)borate and hydridotris(2H-benz[G]indazol-2-yl)borate

[222, 223]. In general complexes of these ligands are very similar to their HBpz*₃ analogues, though adjusting the ligand does have subtle steric effects.



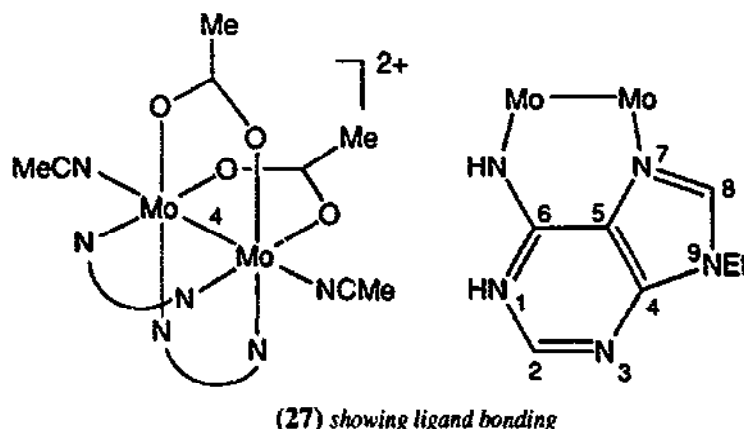
An unusual complex $[\{L\text{Mo}(\text{NO})(\text{O})(\text{OH})\}_2\text{Na}(\text{H}_2\text{O})][\text{PF}_6]$ (26) where $L = 1,4,7$ -triisopropyl-1,4,7-triazacyclononane has been prepared; it contains one nitrosyl ligand which bridges from Mo to two Na atoms, and another which is side-bonded to the sodium. The synthetic sequence involves bromination of $[\text{LMo}(\text{CO})_2(\text{NO})][\text{PF}_6]$ to $[\text{LMo}(\text{NO})\text{Br}_2][\text{Br}_3]$, followed by treatment with H_2O and KPF_6 to give $[\text{LMo}(\text{NO})(\text{OH})_2][\text{PF}_6]$. Dissolution of this species in acetone with NaOH gave the complex or $[\text{LMo}(\text{NO})(\text{O})(\text{OH})]$ depending on the conditions [224].

8.5.3 Complexes with oxygen donor ligands

The synthesis of a range of compounds of the type $[\text{M}_2(\text{O}_2\text{CR})_4]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) has been described where R is a long chain alkyl group, $(\text{CH}_2)_n\text{CH}_3$. In cases where $n = 3$ –9 they show liquid crystal phases. The transition temperature can be lowered to an extent by using branched chains as R [225]. The exchange reaction of $[\text{Mo}_2(\text{OAc})_4]$ with the carboranyl carboxylate $[1,2\text{-C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2]^-$ could only be persuaded to proceed as far as $[\text{Mo}_2(\text{OAc})(\text{O}_2\text{CR})_3]$, though a range of other metal carboxylates were successfully made with the same ligand [226]. A polymeric chain complex $[\text{Mo}_2(\text{O}_2\text{C}^i\text{Bu})_4(4,4'\text{-bpy})]_n$ was made from the pivalate complex and the bpy ligand; the Mo–Mo distance in the product is $2.092(1)\text{\AA}$ [227]. The incorporation of multiply metal-metal bonded dimers into ordered arrays has been reviewed [228], and an account of the calculation of transition energies in quadruply-bonded dimers using a model which only considers the δ and δ^* electrons has been published [229].

Protonolysis of $[\text{Mo}_2(\text{OAc})_4]$ with HOTf affords $[\text{Mo}_2(\text{OTf})_4]$, which on addition of MeCN yields $[\text{Mo}_2(\text{MeCN})_8][\text{OTf}]_4$. This serves as a useful precursor for other homoleptic species such as $[\text{Mo}_2(\text{NH}_3)_8][\text{OTf}]_4$ and $[\text{Mo}_2(\text{dmf})_8][\text{OTf}]_4$ [230]. In the presence of a cocatalyst of EtAlCl_2 , compounds such as $[\text{Mo}_2(\text{OAc})_2(\text{MeCN})_6]^{2+}$ will catalyse the ROMP polymerisation of norbornene; when supported on silica, $[\text{Mo}_2(\text{MeCN})_8][\text{BF}_4]_4$ was effective even without the cocatalyst [231]. The reaction of 9-ethyladenine with $[\text{Mo}_2(\text{O}_2\text{CR})_2(\text{MeCN})_4][\text{BF}_4]_2$

(R = Me, CHF₂) gave [Mo₂(O₂CR)₂(μ-L)₂(MeCN)₂][BF₄]₂ (27) in which the two adenines are arranged in a head-to-tail way, bonding in an unprecedented way through N(6) and N(7). Coordination is accompanied by a prototropic shift from N(6) to N(1) which allows this to happen. The Mo–Mo distance is 2.1436(17) Å, typical for the quadruple bond [232].



On irradiation with visible light, the diphenyl phosphate complex [Mo₂{O₂P(OPh)₂}]₄ reduces 1,2-dichloroalkanes and -alkenes. The inorganic product is the mixed valence Mo(II)/Mo(III) species [Mo₂{O₂P(OPh)₂}]₄⁺ which was structurally characterised as its BF₄[−] salt; the Mo–Mo distance of 2.191 Å is slightly longer than in the neutral compound [233]. The reaction of [Mo(CO)₆] with Hmonp (7-methyl-1,8-naphthyridin-2-one) or the corresponding thione (Hmsnp) gave [Mo₂(monp)₄] and [Mo₂(msnp)₄] where the ligands act as uninegative N,O- or N,S-donors. The Mo–Mo distances are 2.090(4) and 2.131(2) Å respectively [234].

8.5.4 Complexes with sulfur donor ligands

The reaction of [Mo(SPh)(NO)(S₄)], where the S₄ ligand is [−]SC₆H₄CH₂CH₂SC₆H₄S[−], with phosphines gave 17-electron paramagnetic complexes [Mo(L)(NO)(S₄)] (L = PMe₃, PEt₃, PMe₂Ph) which undergo reversible one-electron electrochemical oxidation and reduction. The dinitrosyl complex [Mo(NO)₂(S₄)] was also prepared [235].

8.6 MOLYBDENUM(I)

The electrochemistry of *trans*-[Mo(CO)₂(dppe)₂]⁺ and its Z-Ph₂PCH=CHPh₂ analogue has been studied by cyclic voltammetry and potential sweep voltammetry. They undergo one-electron oxidation and reduction by a well-defined EC_{irrev} mechanism [236].

8.7 MOLYBDENUM(0)

8.7.1 Complexes with carbonyl ligands

The geometries of $[M(CO)_6]$ and $M(CO)_5$ fragments ($M = Cr, Mo, W$) have been optimised by Hartree-Fock and MP2 calculations; for Mo and W the M–CO distances obtained are in excellent agreement with those observed experimentally. The carbonyl dissociation energy of $[Mo(CO)_6]$ was calculated to be $167 \pm 8 \text{ kJ mol}^{-1}$ [237]. The vapour pressure above mixtures of $[Cr(CO)_6]$ and $[Mo(CO)_6]$ has been measured, and the presence of a species $CrMo(CO)_{12}$ was postulated [238]. The decarbonylation of $[Mo(CO)_6]$ adsorbed on silica has been studied by DRIFTS spectroscopy which allowed the detection of subcarbonyl species which were not observable by normal IR methods [239]. The adsorption of $[Mo(CO)_6]$ on dehydroxylated active zirconia has been studied by IR. Attachment to a Lewis acid site on the surface labilises the CO ligands and reversible decarbonylation occurs on exposure to vacuum [240]. A further study of the substitution reaction of $[Mo(CO)_6]$ encapsulated in Na-Y zeolite with PMe_3 to give mainly $[Mo(CO)_5(PMe_3)]$ with small amounts of $[Mo(CO)_4(PMe_3)_2]$ has confirmed that an associative mechanism operates at lower temperatures and a dissociative one at higher temperatures, leading to a two-term rate law [241].

The reaction of $[M(CO)_6]$ ($M = Cr, Mo, W$) with NH_2OH proceeds by oxidation of a CO ligand to CO_2 and coordination of the amine; this mechanism was compared to that known for Me_3NO [242]. The mechanism of the dimerisation of 1,1,2,2-tetrafluoro-1,2-disilacyclobutenes to fluorosilyl trifluorosilylalkenes induced by $[Mo(CO)_6]$ has been studied, and some intermediate metallacycles have been isolated [243].

The reaction of $[M_2(CO)_{10}]^{2-}$ ($M = Cr, Mo, W$) with $SnCl_2$ afforded $[Cl_2Sn\{M(CO)_5\}_2]^{2-}$, all of which were crystallised as their $[Na(12-C-4)]_2$ salts and structurally characterised [244]. Addition of $[NO][BF_4]$ to $[NEt_4][Mo_2(\mu-H)(CO)_9L]$ ($L = PPh_3, Ptol_3$ etc.) afforded the complex $[Mo_2(\mu-H)(CO)_8(NO)L]$; similarly $[Mo_2(\mu-H)(CO)_7(NO)L_2]$ ($L = PMe_2Ph, P(OMe)_3$) and $[Mo_2(\mu-H)(\mu-L_2)(NO)(CO)_7]$ ($L_2 = dppe, dppe$, etc.) were obtained from suitable anionic precursors. The last of these undergoes an unusual reaction with $Ph_3P=NPr$ to give the isonitrile species $[Mo_2(\mu-H)(\mu-L_2)(CNPr)(NO)(CO)_6]$ [245]. The reaction of $[Mo(CO)_6]$ with OH^- under phase transfer conditions gave $[(OC)_3Mo(\mu-OH)_3Mo(CO)_3]^{3-}$; no reaction was observed under a variety of other conditions [246]. However the complex $[(OC)_3Mo(\mu-OPh)_3Mo(CO)_3]^{3-}$ was obtained by reaction of $[Mo(CO)_6]$ with $[NEt_4][OPh]$ and was structurally characterised [247].

The reaction of $[PPN]_2[Mo(CO)_3(\eta-7,9-C_2B_{10}H_{10}Me_2)]$ with allyl bromide gave $[PPN][MoBr(CO)_3(\eta-7,9-C_2B_{10}H_{10}Me_2)]$, together with small amounts of the corresponding bromide with a $7,9-C_2B_9H_9Me_2$ ligand, formed by ejection of a BH vertex. Protonation of $[PPN][Mo(CO)_2(\eta-allyl)(\eta-7,9-C_2B_{10}H_{10}Me_2)]$ gives the first bromide salt under CO, but the second one if CO is absent [248]. Protonation of $[NEt_4][Mo(CO)_2(\eta-allyl)(\eta-7,8-C_2B_9H_8Me_2-10-OEt)]$ under CO gave $[Mo(CO)_4(\eta-7,8-C_2B_9H_8Me_2-10-OEt)]$ which gradually underwent a

polytopal rearrangement to the 2,8-isomer [249]. The reaction of $[\text{Mo}(\text{CO})_2(\eta\text{-C}_2\text{Me}_2)(\eta\text{-7,8-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$ with CN^tBu gave $[\text{Mo}(\text{CO})_{4-n}(\text{CN}^t\text{Bu})_n(\eta\text{-7,8-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$ where $n = 3, 4$ [250].

The salt $[\text{NEt}_4][\text{Mo}(\text{CO})_5(\text{CN})]$ reacts with R_2BCl [$\text{R} = \text{CH}(\text{SiMe}_3)_2$] to give the thermally stable product $[\text{Mo}(\text{CO})_5(\text{CNBR}_2)]$ [251]. The complexes $[(\text{OC})_5\text{M}(\mu\text{-CN})\text{M}'(\text{NH}_3)_5][\text{OTf}]_2$ ($\text{M} = \text{Cr, Mo, W}$; $\text{M}' = \text{Ru, Os}$) have been prepared. They all show a reversible $\text{M}'(\text{II})/\text{M}'(\text{III})$ couple and an irreversible $\text{M}(\text{0})/\text{M}(\text{I})$ wave in their cyclic voltammograms, and behave as class II Robin-Day mixed-valence systems [252, 253].

A theoretical study of the substitution reactions of d^6 metal carbonyls $[\text{M}(\text{CO})_5\text{L}]$, which show a high degree of *cis* stereospecificity, has appeared; although it deals mainly with $[\text{Mn}(\text{CO})_5\text{Cl}]$, it includes calculations of the optimised geometry of $[\text{Mo}(\text{CO})_4(\text{NH}_3)]$ as a possible intermediate [254]. Further details on the cyclisation of 1-alkyn-4-ols to 2,3-dihydrofurans induced by photogenerated $[\text{Mo}(\text{CO})_5(\text{NEt}_3)]$ have appeared; carbene complexes are thought to be involved [255]. Photolysis of $[\text{M}(\text{CO})_6]$ ($\text{M} = \text{Cr, Mo, W}$) with fumaronitrile afforded $[\text{M}(\text{CO})_5\text{L}]$ in which the ligand is bonded through one nitrogen atom. In toluene the Mo complex dissociates into L and $[\text{Mo}(\text{CO})_5(\text{toluene})]$ in an equilibrium process [256]. A similar photolysis reaction with TCNE gave $[\text{Mo}(\text{CO})_5(\text{TCNE})]$, but in this case the ligand is bonded through the C=C bond [257].

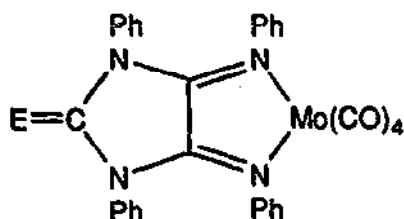
The reduction potentials of a range of molybdenum bpy complexes, including $[\text{Mo}(\text{CO})_4(\text{bpy})]$, $[\text{Mo}(\text{CO})_2(\text{bpy})_2]$ and $[\text{Mo}(\text{bpy})_3]$ have been measured and parameterised with an additive ligand contribution parameter [258]. The visible absorption spectra of $[\text{Mo}(\text{CO})_4(\text{bpz})]$ ($\text{bpz} = \text{bipyrazine}$) and $[\text{Mo}(\text{CO})_4(\text{bpy})]$ depend on the solvent, but their emission spectra less so. The compounds have large dipole moments in the ground state compared to the first MLCT excited state, suggesting less Mo–CO backbonding in the excited state [259]. Reduction of 2,2'-bpy with Sn and HCl gave 2-(2'-piperidiny)pyridine and 1,2,3,6-tetrahydro-2,2'-bpy, both of which form complexes $[\text{Mo}(\text{CO})_4\text{L}]$ that display solvatochromic behaviour similar to that of the bpy complex [260]. The complexes $[\text{M}(\text{CO})_4(\text{terpy})]$ have been made for $\text{M} = \text{Cr, Mo, W}$; in solution the terpy ligand is fluxional and oscillates between equivalent didentate bonding modes [261]. Heating the mono- or bis-Mo complexes of 2,3-bis(2-pyridyl)pyrazine, $[\text{Mo}(\text{CO})_4]_n(\text{dppz})$ ($n = 1, 2$) in MeCN produced $[\text{Mo}(\text{CO})_3(\text{MeCN})]_n(\text{dppz})$; the labile MeCN ligands can then be replaced by PPh_3 [262].

The pyrazolymethane ligand PhCHpz^*_2 forms a complex $[\text{Mo}(\text{CO})_4\text{L}]$, as do bis(3,5-dimethyl-4-benzylpyrazolyl)methane and bis(3-phenylpyrazolyl)methane. However the analogous ligand with 3- t -Bu-pyrazolyl groups was too sterically hindered [263]. Heterocycles with an exocyclic 1,4-diaza-1,3-diene unit form complexes $[\text{Mo}(\text{CO})_4\text{L}]$ (28) ($\text{E} = \text{O, S, NPh, NCO}_2\text{Et}$) which resemble the diazabutadiene complexes; the ligands are predominantly σ -donors with a small amount of backbonding [264].

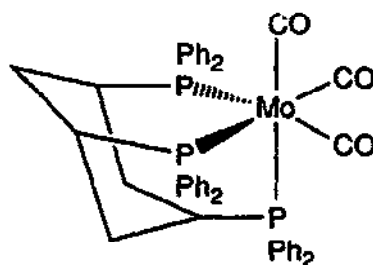
Aldimines $\text{RCH}=\text{N}(\text{CH}_2)_n\text{N}=\text{CHR}$ and $\text{RCH}=\text{NCH}_2\text{CHMeN}=\text{CHR}$ ($\text{R} = \text{various aryl}$; $n = 3, 4, 6$) react with $[\text{Mo}(\text{CO})_6]$ to give compounds of the type *cis*- $[\text{Mo}(\text{CO})_4\text{L}]$ and with $[\text{Mo}(\text{CO})_5(\text{PPh}_3)]$ to give $[(\text{Ph}_3\text{P})(\text{OC})_4\text{Mo}(\mu\text{-L})\text{Mo}(\text{CO})_4(\text{PPh}_3)]$. Halogenation of the first type gave $[\text{Mo}(\text{CO})_3\text{X}_2(\text{L})]$ or $[\text{LMoCl}_4]$ [265]. Diazines $\text{Y}=\text{NN}=\text{CHCH}=\text{NN}=\text{Y}$ and $\text{Y}=\text{NN}=\text{CH-2-}$

C_5H_4N , where the Y groups are camphor or fenchone, have also been made into complexes of the type $[Mo(CO)_4L]$ and $[Mo(CO)_3(L)(L')]$ ($L' = NCMe, PPh_3, AsPh_3$) [266]. The X-ray structure of the Schiff's base complex $[Mo(CO)_4(C_5H_4N-2-CH=NCHMePh)]$ has been determined [267].

The $Mo(CO)_3$ complex of the macrocycle cyclen (1,4,7,10-tetrazacyclododecane) undergoes alkylation with RBr to give the monoalkylated product exclusively, whereas if RI is used, the $N(1), N(7)$ dialkylated macrocycle is formed [268]. Liquid crystalline behaviour has been observed for metal tricarbonyl complexes of triazacyclononane macrocycles functionalised with $CH_2C_6H_3-3,4-(OC_{10}H_{21})_2$ groups [269].



(28)



(29)

A number of phosphine ligands have been synthesized and characterised as complexes of the type $[Mo(CO)_5L]$, $[Mo(CO)_4L_2]$, and $[Mo(CO)_3L_3]$. These include 1-phenylphosphirane, $PhPCH_2CH_2$, and 1-phenylphosphetane, $PhPCH_2CH_2CH_2$, which were made by reaction of $PhPLi_2$ with the appropriate dichloroalkane and both structurally characterised as their *fac*- $[Mo(CO)_3L_3]$ complexes [270], as were $HOCH_2C(CH_2PPh_2)_3$, derived from pentaerythritol [271], and *cis,cis*-1,3,5-tris(diphenylphosphino)cyclohexane (29) [272]. The reaction of $MeC(CH_2Cl)_3$ with Ar_2PH in *dms*o containing aqueous KOH provides a general route to tripod ligands of the type $MeC(CH_2PAR_2)_3$ ($Ar = Ph, C_6H_4-4-tBu, naphthyl$ etc.); some were then made into $[Mo(CO)_3L]$ complexes [273]. The complexes *cis*- $[Mo(CO)_4L_2]$ and *fac*- $[Mo(CO)_3L_3]$ were made from adamantylphosphine, $PAdH_2$ [274].

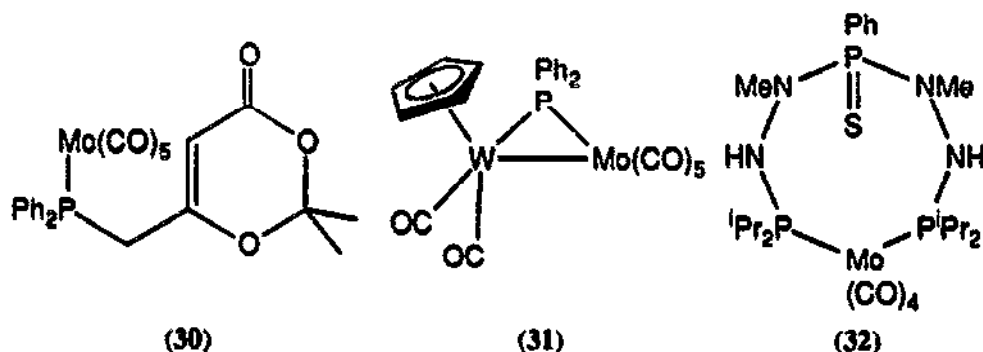
The phosphine ligand $P(C_6H_4-2-OMe)_3$ reacts with $[Mo(CO)_3(cht)]$ to give $[Mo(CO)_3L]$ in which the ligand bonds through P and two of the OMe groups. On reaction with CO the oxygen coordination can be released, allowing sequential isolation of $[Mo(CO)_4L]$ and $[Mo(CO)_5L]$ [275].

Studies of the dipole moments, electric birefringencies, IR spectra and bond distances in the complexes $[M(CO)_5\{P(OCH_2)CMe\}]$ ($M = Cr, Mo, W$) provide support for the idea of π -acid behaviour by the cage phosphite ligand [276]. A systematic structural investigation of $[M(CO)_5(AsPh_3)]$, $[M(CO)_5(SbPh_3)]$ ($M = Mo, W$) and $[W(CO)_5(PPh_3)]$ has been carried out, with trends in bond lengths and conformation of the ligands analysed; all have a very similar propeller conformation [277]. Tri- and tetranuclear complexes have been made by attaching $Mo(CO)_5$ units to each of the phosphorus atoms of the ligands $PhP(CH_2CH_2PPh_2)_2$ and $P(CH_2CH_2PPh_2)_3$ [278]. Similarly four $Mo(CO)_5$ units can be added to the functionalised cyclam macrocycle 1,4,8,11-tetrakis(diphenylphosphinomethyl)-1,4,8,11-tetrazacyclotetradecane [279]. Complexes of dppm monoxide and monosulfide of the type $[Mo(CO)_5L]$ and $[Mo(CO)_4L_2]$ have

been prepared [280]. Elaboration of $[\text{Mo}(\text{CO})_5(\text{PPh}_2\text{Cl})]$ with lithiated 2,2,5-trimethyl-4H-1,3-dioxin-4-one gave (30), which underwent ring opening with ROH ($\text{R} = \text{Cy}, \text{Me}$) or PrSH to produce $[\text{Mo}(\text{CO})_5(\text{PPh}_2\text{CH}_2\text{COCH}_2\text{COER})]$ ($\text{E} = \text{O}, \text{S}$) [281].

The X-ray structure of $[\text{Li}(\text{thf})_3]_2[\text{Mo}_2(\mu\text{-PPh}_2)_2(\text{CO})_8]$ has been determined; the lithium atoms are coordinated to one carbonyl ligand on each metal [282]. The mononuclear phosphido complex $[\text{CpW}(\text{CO})_3\text{PPh}_2]$ reacts with $[\text{Mo}(\text{CO})_4(\text{nbd})]$ to give the metal-metal bonded species $[\text{CpW}(\text{CO})_2(\mu\text{-PPh}_2)\text{Mo}(\text{CO})_5]$ (31), which can be opened up by addition of CO [283]. The complexes $[(\text{OC})_4\text{M}(\mu\text{-PPh}_2)(\mu\text{-CO})\text{PtH}(\text{PPh}_3)]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) have also been prepared [284]. The pendant phosphines of *fac*- $[\text{ReBr}(\text{CO})_3(\eta^1\text{-dmpm})_2]$ have been coordinated to $[\text{Mo}(\text{CO})_3(\text{cht})]$ to give $[(\text{OC})_3\text{Re}(\mu\text{-Br})(\mu\text{-dmpm})_2\text{Mo}(\text{CO})_3]$ [285].

Gas phase photoelectron spectroscopy has been used to study the effect of the bite angle of *cis*-phosphine ligands on electron distribution in *cis*- $[\text{Mo}(\text{CO})_4(\text{PMe}_3)_2]$, $[\text{Mo}(\text{CO})_4(\text{dmpm})]$ and $[\text{Mo}(\text{CO})_4(\text{dmpe})]$. They all gave simple spectra whereas the analogous W complexes had a complicating spin-orbit perturbation. In fact the results were very similar despite a difference of 15° in the bite angle, accounted for by a twisting in the phosphine ligand [286]. The compound *cis*- $[\text{Mo}(\text{CO})_4(\text{PCy}_3)_2]$ is readily prepared and stable, despite the large cone angle (170°) of the ligand; its X-ray structure showed that the principal means of relieving the steric congestion was by long Mo–P bonds [287]. As part of a systematic study of such compounds, the X-ray structures of *cis*- $[\text{Mo}(\text{CO})_4\text{L}_2]$ where $\text{L} = \text{P}(\text{C}_6\text{H}_4\text{-4-F})_3$ [288] or $\text{P}(\text{OPh})_3$ [289] and where $\text{L}_2 = \text{dppf}$ [290] have been determined.



The kinetics of the substitution reaction of $[\text{Mo}(\text{CO})_4(\text{cod})]$ with dppm have been studied; the reaction rate depends on the concentrations of complex, cod, and dppm, and an associative transition state is indicated by the entropy parameters. The breaking of one Mo–alkene bond is proposed to be the rate-determining step [291]. The Raman spectra of $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1\text{--}4$) have been recorded and the coordination shifts in the complexes $[\text{Mo}(\text{CO})_4\text{L}]$ examined for $n = 1$ or 2 [292]. The reaction of $[\text{Mo}(\text{CO})_4(\text{nbd})]$ with $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 5$ or 6) gave $[\text{Mo}(\text{CO})_4\text{L}]$ containing 8- or 9-membered chelate rings [293]. However when $n = 5$, the same group have isolated a complex of the type $[\text{Mo}_2(\text{CO})_8(\mu\text{-L})_2]$ [294]. The reaction of $\text{PhP}(=\text{S})(\text{NMe}_2\text{NH})_2$ with $\text{P}(\text{Pr}_2)_3$ afforded $\text{PhP}(=\text{S})(\text{NMe}_2\text{NHP}(\text{Pr}_2)_2)$ which coordinated to a $\text{Mo}(\text{CO})_4$ unit to form complex (32), which contains an eight-membered chelate ring [295]. Photolysis of *cis*-

$[\text{Mo}(\text{CO})_4(\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_2\text{CH}_2\text{PPh}_2)]$, which contains a 17-membered chelate ring, caused isomerisation to the *trans* form [296].

The complexes $[\text{M}(\text{CO})_4(\text{Ph}_2\text{P})_2\text{C}=\text{CHR}]$ ($\text{M} = \text{Mo}, \text{W}$; $\text{R} = \text{Me}, \text{Ph}$) have been prepared [297]. The pendant phosphine group in $[\text{M}(\text{CO})_4(\text{Ph}_2\text{P})_2\text{CHPPh}_2]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) can be coordinated to gold fragments such as AuX ($\text{X} = \text{Cl}, \text{C}_6\text{F}_5$) and $\text{Au}(\text{PPh}_3)^+$ [298]. The $\text{Mo}(\text{CO})_4$ complex of $^t\text{BuP}[\text{P}=\text{C}(\text{SiMe}_3)_2]_2$ has been structurally characterised [299].

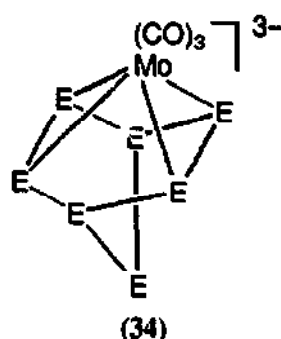
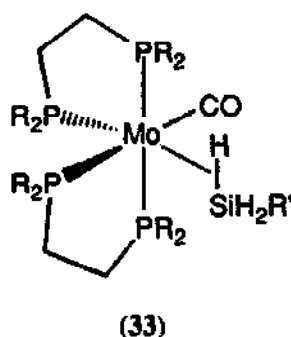
The complex $[\text{Mo}(\text{CO})_4(\text{L}_2)]$ ($\text{L}_2 = \text{bpy}, \text{dppm}, \text{dppe}$) reacts with the cyclic aminophosphine $\text{MeOPNMeCH}_2\text{CH}_2\text{NMe}$ to give *fac*- $[\text{Mo}(\text{CO})_3(\text{L}_2)(\text{L})]$. Subsequent abstraction of OMe^- with $\text{BF}_3 \cdot \text{OEt}_2$ gave the cationic species *fac*- $[\text{Mo}(\text{CO})_3(\text{L}_2)(\text{PNMeCH}_2\text{CH}_2\text{NMe})]$, which spontaneously change to the *mer*-isomers. [300]. The 3-arsolenes $\text{RAsCH}_2\text{CMe}=\text{CMeCH}_2$ ($\text{R} = \text{Ph}, \text{Me}$) have been synthesized and used to make the compounds $[\text{Mo}(\text{CO})_3(\text{L}_2)\text{L}]$ where $\text{L}_2 = \text{dppm}, \text{dppe}$ [301]. Full details of the excision of the $\text{Mo}(\text{II})$ vertex of the tetraphosphoxane cage compound $[(\text{CO})_4\text{Mo}\{\text{P}(\text{N}^i\text{Pr}_2)\text{O}\}_4\text{Mo}(\text{CO})_2\text{I}_2]$ with $\text{NaS}_2\text{CNEt}_2$ and subsequent coordination of the remaining $[\text{Mo}(\text{CO})_4\{\text{P}(\text{N}^i\text{Pr}_2)\text{O}\}_4]$ to a range of other metal fragments have been published [302].

The reaction of $[\text{Mo}(\text{CO})(\text{L}_2)_2]$, where $\text{L}_2 = \text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2$ ($\text{R} = \text{Et}$ or CH_2Ph) with silanes PhSiH_3 or $\text{C}_6\text{H}_{13}\text{SiH}_3$ gave η^2 -silane complexes $[\text{Mo}(\eta^2\text{-SiH}_3\text{R})(\text{L}_2)_2]$ (33). The silane ligand is coordinated through one of the Si–H bonds in a manner analogous to the H_2 complexes prepared previously [303]. The compounds $[\text{Mo}(\text{N}_2)_2(\text{L}_2)_2]$ and, by reaction with ethyl acetate, $[\text{Mo}(\text{CO})(\text{L}_2)_2]$ have been prepared for a range of similar diphosphine ligands ($\text{R} = \text{CH}_2\text{Ar}$ where $\text{Ar} = \text{Ph}, o-, m-$ and p -tolyl, $o-, m-, p\text{-C}_6\text{H}_4\text{F}$ etc.). Addition of H_2 , N_2 or SO_2 gave $[\text{Mo}(\text{CO})(\text{L})(\text{L}_2)_2]$, including further examples of dihydrogen complexes. Since the analogous complex with $\text{R} = \text{Et}$ gives a dihydride, the oxidative addition reaction of H_2 is under electronic control and depends on the basicity of the phosphine ligand [304].

A range of phosphorus-nitrogen ligands have been coordinated to Mo carbonyl fragments, sometimes simply through P atoms and sometimes as *P,N*-donors. The ligands $\text{Ph}_2\text{PN}^i\text{PrPPh}(\text{OR})$ ($\text{R} = \text{tolyl}, \text{Mes}, 2\text{-pyridyl}$) and $\text{Ph}_2\text{PN}^i\text{PrP}(\text{OC}_6\text{H}_4\text{O})$ react with $[\text{Mo}(\text{CO})_4(\text{pip})_2]$ to give $[\text{Mo}(\text{CO})_4\text{L}]$ [305]. The pendant phosphorus atom in $[\text{Mo}(\text{CO})_4\{\text{P}(\text{OMe})_3\}\text{L}]$ where $\text{L} = \text{P}(\text{Otoly})_2(\text{NPh})_2\text{P}(\text{Otoly})_2$ can be coordinated to additional metal fragments [306].

Reaction of fenchone with hydrazine, followed by pinacolone and then BuLi and PPh_2Cl gave $\text{Y}=\text{NN}=\text{C}(^t\text{Bu})\text{CH}_2\text{PPh}_2$ which coordinates as a *P,N* ligand in its $\text{Mo}(\text{CO})_4$ complex [307]. The ligand 1-(diphenylphosphino)-2-ethoxy 1-(2-pyridyl)ethane, $\text{C}_5\text{H}_4\text{NCH}(\text{PPh}_2)\text{CH}_2\text{OEt}$ reacts with $[\text{Mo}(\text{CO})_3(\text{cht})]$ to give the *P,N,O*-bonded complex $[\text{Mo}(\text{CO})_3\text{L}]$ initially, but this redistributes to the *P,N*-bonded $[\text{Mo}(\text{CO})_4\text{L}]$ [308]. The new ligands (*S*)- $\text{Ph}_2\text{POCH}_2\text{CH}(\text{NMe}_2)\text{CH}_2\text{CH}_2\text{SMe}$ and (*R*)- $\text{Ph}_2\text{POCH}_2\text{CH}(\text{NMe}_2)\text{CH}_2\text{SMe}$, derived from the amino acids methionine and cysteine, have been prepared; they form *fac*- $[\text{Mo}(\text{CO})_3\text{L}]$ complexes in which they act as *P,N,S*-donors [309]. Interaction of 2-vinylpyridine with pyridine-2-thiol gave $\text{C}_5\text{H}_4\text{N-2-SCH}_2\text{CH}_2\text{-2-C}_5\text{H}_4\text{N}$ which acts as an *N,N,S*-chelate in *fac*- $[\text{Mo}(\text{CO})_3\text{L}]$ [310].

Complexes of a number of 1,3,2-diazaphosphorinan-4-ones, $\text{RPN}(\text{Me})\text{C}(=\text{O})\text{C}_6\text{H}_4\text{NMe}$ ($\text{R} = \text{F}, \text{NMe}_2$ etc.) of the type $[\text{Mo}(\text{CO})_4\text{L}_2]$ have been made [311], while the similar ligand $\text{ClPN}(\text{PCl}_2)\text{C}(=\text{O})\text{C}_6\text{H}_4\text{NMe}$ coordinates through both P atoms to form $[\text{Mo}(\text{CO})_4\text{L}]$ [312]. Complexes of the related 1,3,2-oxazaphosphorinanones have also been prepared [313]. The reaction of MeNHNH_2 with RPNH_2 ($\text{R} = \text{Et}, \text{Ph}$) gave the 6-membered 1,2,4,5-tetraza-3,6-diphosphorinane ring $[\text{RPNMeNH}]_2$, which reacted with $[\text{Mo}(\text{CO})_4(\text{pip})_2]$ to give $[(\text{pip})(\text{OC})_4\text{Mo}(\mu\text{-L})\text{Mo}(\text{CO})_4(\text{pip})]$ [314]. The phosphadiazole $\text{PhP}(=\text{S})\text{NMeC}_6\text{H}_4\text{NH}$ reacts with PhPCl_2 to give $\text{PhP}(=\text{S})\text{NMeC}_6\text{H}_4\text{N}(\text{PPhCl})$ as a mixture of two isomers; it coordinates through P and S in its $\text{Mo}(\text{CO})_4$ complex [315].



The phosphazenes *gem*- $\text{N}_3\text{P}_3\text{Ph}_4(\text{pz}^*)_2$ and $\text{N}_3\text{P}_3(\text{OCH}_2\text{CH}_2\text{NMe})_2(\text{pz}^*)_2$ formed complexes $[\text{Mo}(\text{CO})_3\text{L}]$ in which they coordinate through one nitrogen of the ring and the two pyrazole nitrogen atoms [316]. The related $\text{N}_3\text{P}_3(\text{NMe}_2)_4\{\text{NH}(\text{CH}_2)_n\text{NH}\}$ ($n = 2, 3$) gave complexes $[\text{Mo}(\text{CO})_4\text{L}]$, coordinating through one N of the ring and one N of the diaminoalkane moiety [317].

Solutions of K_3E_7 ($\text{E} = \text{P}, \text{As}, \text{Sb}$) in *en* react with $[\text{Mo}(\text{CO})_3(\text{cht})]$ in the presence of 2,2,2-crypt to give $[\text{K}(\text{crypt})]_3[\text{Mo}(\text{CO})_3(\text{E}_7)]$ (34). The $\text{Mo}(\text{CO})_3$ group is η^4 -bonded to a square face of the E_7 unit, which resembles a norbornadiene ligand [318]. A second group have also reported the $[\text{Na}(\text{crypt})]$ salt of the Sb_7 complex, prepared in the same way [319].

The synthesis and X-ray structure of the pyridine-2-thiolate complex $[\text{NEt}_4][\text{Mo}(\text{CO})_4(\text{pyS})]$ has been reported [320]. The structure of $[\text{NEt}_4][\text{Mo}_2(\text{CO})_9(\mu\text{-pyS})]$, which has an additional $\text{Mo}(\text{CO})_5$ unit coordinated to the sulfur atom, has also been determined [321], as has that of $[\text{Mo}_3(\text{CO})_6(\mu\text{-pyS})_2(\mu_3\text{-pyS})_2]$ which is made by the reaction of $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ with pySH and PPh_3 [322]. The synthesis of the ethyl xanthate species $[\text{PPh}_4][\text{Mo}(\text{CO})_4(\text{S}_2\text{COEt})]$ has been developed as an undergraduate laboratory experiment [323].

Lithiated dimethyl sulfide, LiCH_2SMe , reacts with $\text{BF}_3\cdot\text{OEt}_2$ to give $[\text{B}(\text{CH}_2\text{SMe})_4]^-$; this tetrakis(methylthiomethyl)borate acts as a tridentate ligand on reaction with $[\text{Mo}(\text{CO})_3(\text{cht})]$, forming $[\text{Mo}(\text{CO})_3\{\text{B}(\text{CH}_2\text{SMe})_4\}]^-$ which can be protonated at the metal [324]. The complex $[\text{Mo}(\text{CO})_3(\text{16-ane-S}_4)]$ was made by treating $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ with the macrocycle [325]. The compound $[\text{Mo}(\text{CO})_3(\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{S})]^{2-}$, prepared from 3-thiapentane-1,5-dithiolate, reacts with substituted 1,2-dibromopropanes by ring closure to give complexes of functionalised

1,4,7-trithiacyclononanes, which can be displaced from the metal by addition of further dithiolate [326]. The X-ray structures of $[(\text{CO})_4\text{Mo}(\mu\text{-SPh})_2\text{Fe}(\mu\text{-SPh})_2\text{Mo}(\text{CO})_4]$ and its two electron reduction product have been determined; the neutral complex has Mo–Fe bonds (2.77 Å) whereas these are broken in the dianion (Mo...Fe 3.40 Å), and in both cases the trimetallic chain is bent, not linear [327]. The reaction of $[\text{Mo}_3(\text{CO})_7(\text{SC}_6\text{H}_4\text{O})_3]^{2-}$ with FeCl_2 gave $[\text{Mo}_2\text{Fe}(\text{CO})_4(\text{SC}_6\text{H}_4\text{O})_3\text{Cl}_2]$; the suggested structure has a central $\text{Mo}(\text{SC}_6\text{H}_4\text{O})_3$ unit with a $\text{Mo}(\text{CO})_4$ group coordinated to two of its sulfur atoms and FeCl_2 coordinated to the three oxygens [328].

The reaction of $[\text{MBr}(\eta\text{-allyl})(\text{CO})_2(\text{MeCN})_2]$ with S_2CPR_3 ($\text{R} = \text{Cy}, \text{iPr}$) afforded $[\text{MBr}(\eta\text{-allyl})(\text{CO})_2(\text{S}_2\text{CPR}_3)]$, which in turn reacted with $[\text{M}'(\text{CO})_3(\text{MeCN})_3]$ ($\text{M} = \text{Mo}, \text{W}$; the EtCN complex was used for W) to give $[(\text{OC})_2(\eta\text{-allyl})\text{M}(\mu\text{-Br})(\mu\text{-S}_2\text{CPR}_3)\text{M}'(\text{CO})_3]$; all four combinations were made [329]. Treatment of *fac*- $[\text{ReBr}(\text{CO})_3(\text{S}_2\text{CPR}_3)]$ with $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ gave $[(\text{OC})_3\text{Re}(\mu\text{-Br})(\mu\text{-S}_2\text{CPR}_3)\text{Mo}(\text{CO})_3]$ [330]. Further reactions of the anion $[(\text{OC})_3\text{Mn}(\mu\text{-S}_2\text{CPR}_3)\text{Mo}(\text{CO})_3]^-$ have been reported. With PPh_2Cl , the initial product is $[(\text{OC})_3\text{Mn}(\mu\text{-S}_2\text{CPR}_3)(\mu\text{-PPh}_2)\text{Mo}(\text{CO})_3]$ which on heating rearranges to the compound $[(\text{OC})_2\text{Mn}(\mu\text{-S}_2\text{CPR}_3)(\mu\text{-PPh}_2)\text{Mo}(\text{CO})_3]$ in which the coordination of the S_2CPR_3 ligand has changed around. The analogous $\mu\text{-SePh}$ complex does not rearrange in this way [331].

8.7.2 Complexes with nitrogen and phosphorus donor ligands

The geometries of *trans*- $[\text{Mo}(\text{N}_2)_2\text{L}_4]$ where $\text{L} = \text{PH}_3$ or SH_2 have been optimised by local density functional theory DVX $_{\alpha}$ calculations, which show good agreement with observed bond lengths, N_2 stretching frequencies, and sites of attack by electrophiles. Comparison with Hartree-Fock calculations shows that the current method provides a more accurate model [332].

The kinetics of the reaction of *trans*- $[\text{Mo}(\text{N}_2)_2(\text{PPh}_2\text{Me})_4]$ with the tripod ligands $\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ and $\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ are complex, involving four consecutive steps. The proposed mechanism is initiated by dissociation of one PPh_2Me ligand, to give an intermediate which then reacts by two parallel pathways [333]. The radiation yields of NH_3 and N_2H_4 and the catalytic efficiency of $[\text{Mo}(\text{N}_2)_2(\text{triphos})(\text{PPh}_3)]$ and $[\text{Mo}(\text{N}_2)_2(\text{dppe})_2]$ for N_2 reduction in neutral and acid solutions have been studied; the importance of Mo–H bonds in N_2 reduction has been pointed out as a result [334].

The reaction of $[\text{Mo}(\text{NO})_2(\text{CN})_4]^{2-}$ with various anilines produced complexes of the type $[\text{Mo}(\text{NO})_2(\text{CN})_2\text{L}_2] \cdot 2\text{H}_2\text{O}$ [335]. A number of Schiff's base ligands derived from 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone and various anilines have been coordinated to $[\text{Mo}(\text{NO})_2(\text{acac})_2]$; for didentate ligands HL, these take the form $[\text{Mo}(\text{NO})_2(\text{L})_2]$, whereas for tetradentate ones H_2L derived from phenylenediamines, they are $[\text{Mo}(\text{NO})_2\text{L}]$ [336]. Starting from $[\text{Mo}(\text{NO})_2\text{Cl}_2]_n$, symmetrical and unsymmetrical pyrazine complexes $[\text{Cl}(\text{dppp})(\text{NO})_2\text{M}(\mu\text{-pyz})\text{M}'(\text{NO})_2(\text{dppp})\text{Cl}]^{2+}$ and $[\text{Cl}(\text{phen})(\text{NO})_2\text{M}(\mu\text{-pyz})\text{M}'(\text{dppp})\text{Cl}]^{2+}$ ($\text{M}, \text{M}' = \text{Mo}, \text{W}$) were prepared [337]. The coordination of a range of carboxylic acids in complexes of the type $[\text{MoCl}_2(\text{NO})_2(\text{HL})_2]_n$ has been explored [338].

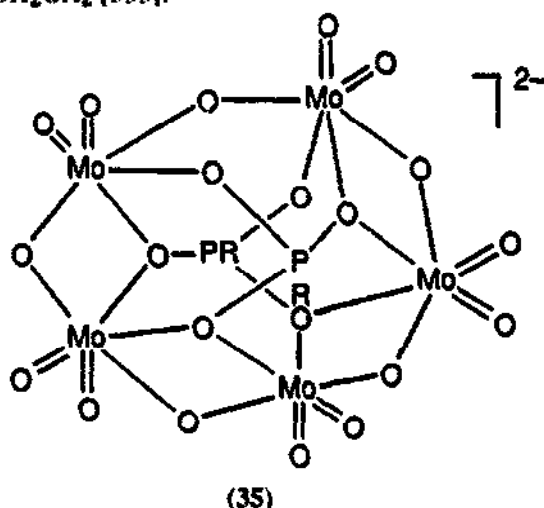
8.8 MOLYBDENUM CLUSTERS

8.8.1 Polyoxomolybdates

The following brief discussion deals first with homonuclear species and then with heteropolymolybdates. A book on the many and varied aspects of polyoxometallate chemistry has appeared [339] and reviews have been published on the role of heteropolyanions and heteropolyacids in catalysis [340, 341] and on supramolecular inorganic chemistry involving polyoxometallates [342]. A selection of shorter reviews appeared in a special issue of *Molecular Engineering*; after an introduction [343], others dealt with the topological analysis of polyoxometallate structures [344], the synthesis of novel heteropoly compounds [345], functionalisation of polyoxomolybdates with nitrosyl groups [346], and polyoxoalkoxide clusters of Mo and V [347].

The clusters $\text{Na}_2[\text{MMo}_3(\mu_3\text{-O})_3(\mu\text{-O})(\mu\text{-O}_2\text{CR})_5(\text{O}_2\text{CR})_3]_2$ ($\text{M} = \text{Cr}, \text{W}$; $\text{R} = \text{Me}, \text{Et}$) can be made by several routes, including reaction of $\text{Na}[\text{Mo}_3\text{O}_2(\text{O}_2\text{CR})_9]$ with $\text{M}(\text{CO})_6$, or refluxing $[\text{M}(\text{CO})_6]$ with Na_2MoO_4 in the appropriate acid; the structure consists of two $(\text{Mo}_3\text{O}_4)^{4+}$ units which are linked to the two M atoms by oxo and carboxylate bridges [348, 349]. The analogous vanadium complex $\text{Na}_2[\text{VMo}_3\text{O}_4(\text{O}_2\text{CEt})_8]_2$ was also prepared [350]. A similar reaction between $[\text{Mo}(\text{CO})_6]$ and Na_2WO_4 in propionic anhydride gave the trinuclear cluster cation $[\text{MoW}_2(\mu_3\text{-O})_2(\text{O}_2\text{CEt})_6(\text{H}_2\text{O})_3]$, isolated as its $[\text{ZnBr}_4]^{2-}$ salt [351].

The thermal analysis of a sample of a commercial molybdate containing $[\text{NH}_4]_2[\text{Mo}_4\text{O}_{13}]$, its β -isomer, and its dihydrate, has been examined [352]. The incorporation of crown ether macrocycles into a pentamolybdo-diphosphonate cage compound has been achieved by the reaction of $[\text{MoO}_4]^{2-}$ with RPO_3H in the presence of $[\text{C}(\text{NH}_2)_3]^+$, which gave the zwitterionic $[\text{C}(\text{NH}_2)_3]_2[\text{Mo}_5(\text{PR})_2\text{O}_{21}]$ (35) where the R groups are $\text{CH}_2\text{NH}^+(\text{CH}_2\text{CH}_2)_2\text{O}$ or $\text{CH}_2\text{NH}^+(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_2\text{CH}_2$ [353].



The reaction of $[\text{NBu}_4]_2[\text{Mo}_6\text{O}_{19}]$ with $\text{Ph}_3\text{P}=\text{NPh}$ gave mixtures of monosubstituted $[\text{Mo}_6\text{O}_{18}(\text{NPh})]^{2-}$ and disubstituted $[\text{Mo}_6\text{O}_{17}(\text{NPh})_2]^{2-}$; their presence was demonstrated by

^{95}Mo and ^{14}N NMR spectra, and a crystal structure showed that all three compounds could exist in the same crystal [354]. Treatment of the same starting material with RNCO ($\text{R} = \text{Bu}, \text{Cy}, \text{C}_6\text{H}_3\text{-2,6-}^i\text{Pr}_2$) gave $[\text{Mo}_6\text{O}_{18}(\text{NR})]^{2-}$, but for the aryl isocyanate increasing the amount of reagent led to the isolation of $[\text{Mo}_6\text{O}_{19-n}(\text{NR})_n]^{2-}$ where $n = 2, 4$ and 5 ; the X-ray structures of the compounds with $n = 2$ and 4 were reported [355]. The synthesis and structure of the diazenido-substituted complex $[\text{NBu}_4]_3[\text{Mo}_6\text{O}_{18}(\text{N}_2\text{C}_6\text{H}_4\text{-4-NO}_2)]$ has been reported [356]. The compound $[\text{NEt}_4]_2[\text{H}_4\text{Mo}_6\text{O}_{19}]$, containing four Mo(V) and two Mo(VI) centres, has been reported as the product of irradiation of MoCl_5 in a dmf/MeOH mixture [357]. The crystal structure of the 3,3'-dimethyl-4,4'-diphenyl-2,2',5,5'-tetrathiafulvalenium salt of $[\text{Mo}_6\text{O}_{19}]^{2-}$ has been determined [358].

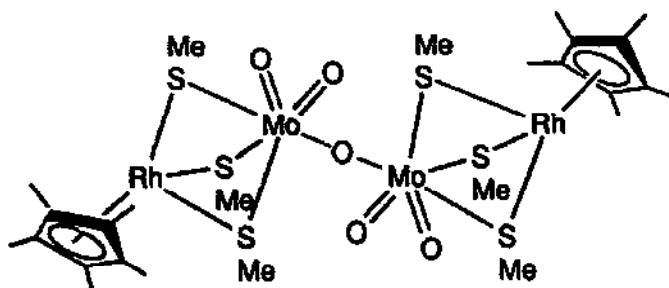
A kinetic study has shown that the rate of epimerisation of D-mannose to D-glucose, catalysed by aqueous ammonium molybdate, is greatly accelerated by the presence of MeCN [359]. The IR and polarised Raman spectra of the 2-aminopyridinium salt of $[\text{Mo}_7\text{O}_{24}]^{6-}$ have been recorded [360] and the synthesis and structure of $(\text{NH}_3)_3[\text{Pd}(\text{NH}_3)_4]_3[\text{Mo}_7\text{O}_{24}]$ were reported [361]. The crystal structure of $[\text{tBuNH}_3]_6[\text{Mo}_7\text{O}_{24}] \cdot 7\text{H}_2\text{O}$ has been published [362]. The synthesis of meso-structured oxide materials from ammonium molybdate involving the use of surfactants as templates gave rise to layered structures whereas tube-like forms were produced from tungstates [363]. A ^{183}W NMR spectroscopic study of the replacement of W(VI) by Mo(VI) in $[\text{W}_7\text{O}_{24}]^{6-}$ has shown that any or all of the W atoms can be replaced, leading to the identification of at least 19 different mixed-metal species. However in $\alpha\text{-}[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ and $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ only a single substitution was observed, at a site furthest away from the centre [364].

The reaction of NEt_3 with $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ or ammonium molybdate gave $[\text{NHEt}_3]_4[\text{Mo}_8\text{O}_{26}]$. If sodium molybdate was used, the salt $[\text{NHEt}_3]_3[\text{NaMo}_8\text{O}_{26}]$ resulted, and could also be made by treating the octamolybdate with NaCl . A similar potassium species could also be isolated [365]. The chiral amines $\text{R}^*\text{N} = (+)\text{-cinchonine}, (+)\text{-hydroquinidine}$ and $(-)\text{-quinine}$ reacted in the same way to give $[\text{R}^*\text{NH}]_4[\text{Mo}_8\text{O}_{26}]$ or in the case of coordinating bases, $[\text{R}^*\text{NH}]_4[\text{Mo}_8\text{O}_{26}(\text{NR}^*)_2]$. Refluxing these in ethanol with NaCl led to the formation of $[\text{R}^*\text{NH}]_2[\text{Mo}_6\text{O}_{19}]$ [366]. Mixing MoCl_5 , CoCl_2 , thiosemicarbazide and dmf under irradiation gave the double salt $[\text{NEt}_4][\text{Co}(\text{H}_2\text{NCSNHNH}_2)_3][\text{Mo}_8\text{O}_{26}] \cdot 4\text{dmf}$ which was structurally characterised [367]. The crystal structure of $[\text{tPrNH}_3]_4[\beta\text{-Mo}_8\text{O}_{26}]$ has also been determined [368], as has that of the photochromic piperidinium salt $[\text{C}_5\text{H}_{10}\text{NH}_2]_4[\beta\text{-Mo}_8\text{O}_{26}]$ [369].

The electronic and structural relationships between MoO_3 and ions with the Keggin structure such as $[\text{Mo}_{12}\text{O}_{40}]^{8-}$ have been explored [370]. The solid phase reaction of ammonium molybdate, NBu_4Br and $\text{NH}_2\text{OH} \cdot \text{HCl}$ gave $[\text{NBu}_4]_6[\text{H}_3\text{O}]_2[\text{Mo}_{13}\text{O}_{40}]_2$; the two $\text{Mo}_{13}\text{O}_{40}$ tetraanions have slightly different structures, though both are based on the Keggin structure with a Mo atom in the centre [371].

The reaction of $[(\text{Cp}^*\text{Rh})_4\text{Mo}_4\text{O}_{16}] \cdot 2\text{H}_2\text{O}$ with MeSH has given several different products depending on the conditions used. One of these is $[\text{Rh}_2(\mu\text{-SMe})_3\text{Cp}^*_2]_4[\text{Mo}_8\text{O}_{26}]$, in which the octamolybdate displays an intermediate structure described as $\alpha\text{-}\gamma$ or $\beta\text{-}\gamma$ [372]. The others are the

compounds $[(\text{Cp}^*\text{Rh}(\mu\text{-SMe})_3\text{MoO}_2)_2(\mu\text{-O})]$ (36) and $[(\text{Cp}^*\text{Rh}(\mu\text{-SMe})_3\text{MoO})_2(\mu\text{-O})(\mu\text{-E})]$ (E = O or S) which has a closely-related structure [373, 374].



(36)

The reaction of $[\text{NBu}_4]_2[\text{Mo}_2\text{O}_7]$ with $[\text{Cp}^*\text{TiCl}_3]$ in MeCN gave $[\text{Cp}^*\text{TiMo}_5\text{O}_{18}]^{3-}$; its monoprotonated form $[\text{Cp}^*\text{TiMo}_5\text{O}_{18}\text{H}]^{2-}$ was also isolated and its X-ray structure determined as the $[\text{NBu}_4]^+$ salt [375]. A theoretical study on the bonding of organometallic fragments to polyoxometallates included an analysis of these compounds [376].

The activity of cetylpyridinium salts of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ and $[\text{PO}_4\{\text{MoO}(\text{O}_2)_2\}_4]^{3-}$ in the oxidation of sulfides has been examined. They show the same product selectivity whereas the analogous tungsten species show a dramatic difference in selectivity [377]. A comparison of the spectroscopic properties of $[\text{PO}_4\{\text{MoO}(\text{O}_2)_2\}_4]^{3-}$ with those of mononuclear peroxo species has been made [378]. The synthesis and structure of $[\text{H}_3\text{O}][\text{Me}_2\text{NH}_2]_5[\text{P}_2\text{Mo}_5\text{O}_{23}]$ has been reported [379]. The hydrothermal reaction of MoO_3 , py, H_3AsO_4 and H_2O at 230°C for 4 d gave the new compound $[\text{pyH}]_4[(\text{Mo}_4\text{O}_{10})(\text{HAsO}_4)_4]$ [380].

A comparison of the thermal behaviour and catalytic activity in methanol oxidation of free and silica-supported $[\text{H}_3\text{PMo}_{12}\text{O}_{40}]$ has been made. The free acid converts methanol to Me_2O below 240°C and at higher temperatures gives formaldehyde. The silica-supported acid formed the unexpected $\beta\text{-MoO}_3$ phase at 500°C which changes to the α -form at higher temperatures, this accompanying a change from $\text{CH}_2(\text{OMe})_2$ to methyl formate as the product of MeOH oxidation [381]. The thermal behaviour of $[\text{H}_3\text{PMo}_{12}\text{O}_{40}]\cdot 13\text{H}_2\text{O}$ has also been examined by XRD and ^{31}P NMR spectroscopy [382]. Reduction of Keggin-type structures such as $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ by one electron causes little change in their IR spectra, whereas a two-electron reduction causes substantial changes [383].

The reaction of $[\text{PMo}_{11}\text{O}_{39}]^{7-}$, produced by NBu_4OH -induced degradation of the initial Keggin structure, reacts with sources of the $\text{Mo}(\text{NO})^{3+}$ fragment to give $[\text{NBu}_4]_4[\text{PMo}_{12}\text{O}_{39}(\text{NO})]$ [384]. The A-type trisubstituted isomer of $[\text{NBu}_4]_3[\text{PMo}_3\text{W}_9\text{O}_{40}]$ is deoxygenated with PPh_3 to give a reduced species $[\text{NBu}_4]_3[\text{PMo}_3\text{W}_9\text{O}_{39}]$ which contains two $\text{Mo}(\text{V})$ centres [385]. The reduction of $[\text{H}_3\text{PMo}_{12-n}\text{W}_n\text{O}_{40}]$ ($n = 0, 3, 6, 9, 11, 12$) has been studied by EPR methods [386]. The structure of $\text{K}_8[\text{P}_2\text{Mo}_2\text{Co}_2\text{W}_{18}\text{O}_{68}(\text{H}_2\text{O})_2][\text{MoO}_6]\cdot 15\text{H}_2\text{O}$, which consists of two fused Keggin structures, has been determined [387].

The zinc porphyrin complex $[\text{Zn}(\text{TPP})]$ formed weak charge transfer salts with various Keggin-type anions of the type $[\text{NEt}_4]_5[\{\text{Zn}(\text{TPP})\}_2\{\text{ZMo}_{12}\text{O}_{40}\}\text{X}_n]$ where $\text{Z} = \text{P}$ or Si , $\text{X} =$ halide, $n = 1$ or 2 [388]. Decamethyl ferrocenium salts of the anions $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ and $[\text{PMo}_{12}\text{O}_{40}]^{4-}$ and some corresponding tungstates have been isolated; their structures reveal linear chains of Cp^*Fe cations in most cases [389]. The cyclic voltammograms of $[\text{ZMo}_{12}\text{O}_{40}]^{n-}$ ($\text{Z} = \text{S}, \text{P}, \text{As}, \text{Si}, \text{V}$; $n = 2-4$) show one electron and two-electron reduction waves depending on the pH [390]. The interaction of some of these anions with $\text{Np}(\text{VI})$ and $\text{Pu}(\text{VI})$ ions has been studied [391].

The 11-molybdo germanate ion, $[\text{H}_4\text{GeMo}_{11}\text{O}_{39}]^{4-}$, was detected in solution by ion transfer voltammetry and isolated as its $[\text{NBu}_4]^+$ salt. Although its IR spectrum is similar to that of $\alpha\text{-}[\text{GeMo}_{12}\text{O}_{40}]^{4-}$, its electrochemistry is completely different [392]. The compounds $\text{K}_6[\text{Nd}(\text{GeMo}_3\text{W}_9\text{O}_{39})_2]$ and $[\text{H}_5\text{GeVMoW}_{10}\text{O}_{40}]$ have been isolated [393, 394]. The synthesis of the gallium derivatives $[\text{H}_5\text{GaMo}_{12-n}\text{W}_n\text{O}_{40}]$ ($n = 3, 6, 9$) has been described for the first time [395].

The lanthanide hexamolybdotellurates $\text{Ln}_2[\text{TeMo}_6\text{O}_{24}]\cdot n\text{H}_2\text{O}$ where $n = 21$ or 31 have been prepared; the inclusion of extra water molecules stabilises the lattice for larger lanthanides [396]. The thermal decomposition of the Anderson-type compounds $[\text{NH}_4]_3[\text{H}_6\text{MMo}_6\text{O}_{24}]\cdot 7\text{H}_2\text{O}$ where $\text{M} = \text{Al}, \text{Co}$ or Fe has been studied; MoO_3 and $\text{M}_2(\text{MoO}_4)_3$ are the main products [397]. The compound with $\text{M} = \text{Co}$ has been used to grow thin films on a glassy carbon surface by electroreduction [398] and a spectroscopic study of the compound with $\text{M} = \text{Fe}$ has been carried out [399]; the vibrational spectra and thermal behaviour of $[\text{NH}_4]_4[\text{H}_6\text{CuMo}_6\text{O}_{24}]$ have also been studied [400]. The X-ray structures of $[\text{NH}_4]_x[\alpha\text{-H}_{8-x}\text{PtMo}_6\text{O}_{24}]$ have been determined for $x = 4.5, 4$ and 3.5 . The first and third of these contain the Anderson structure whereas the second has an isomeric arrangement, showing that the protonation plays some part in the geometry [401]. The structure of $\text{K}_2[\text{H}_6\text{PtMo}_6\text{O}_{24}]\cdot 5\text{H}_2\text{O}$ was also determined [402]. The preparation of the compounds $[\text{NH}_4]_4[\text{H}_6\text{NiMo}_{6-x}\text{W}_x\text{O}_{24}]$ ($x = 0, 2, 3, 4, 6$) has been described [403].

Phosphomolybdic acid catalyses the reduction of VO_2^+ to VO^{2+} in 1M aqueous H_2SO_4 . The dominant species in solution are $[\text{PVMo}_{11}\text{O}_{40}]^{4-}$ and $[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]^{5-}$, which lowers the reduction potential of $\text{V}(\text{V})$ from 0.8 V in the free state to about 0.55 V when bound in the polyoxoanion [404]. A potentiometric, ^{31}P and ^{51}V NMR study of $\alpha\text{-}[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]^{5-}$ in 0.6M aqueous NaCl has shown the presence of five positional isomers, which were all identified [405]. The oxidation of various thioethers (acting as model compounds for mustard gas) to the corresponding sulfoxides in the presence of polyoxoanions, including $[\text{H}_3\text{PMo}_{12}\text{O}_{40}]$ has been examined. Better selectivity for sulfoxide over sulfone was observed for $[\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}]$ in the case of tht as substrate [406]. The catalytic properties of $[\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}]$ supported on silica have been studied [407], and the activity of $[\text{H}_4\text{PVMo}_{11}\text{O}_{40}]$ for the oxidation of MeOH and hydrocarbons has been tested [408]. Mixing $\text{NH}_4[\text{VO}_3]$ with sodium molybdate in 2M HCl followed by addition of morpholine led to the isolation of $[\text{Hmorph}]_6[\text{Mo}_4\text{V}_5\text{O}_{27}][\text{Cl}]\cdot \text{H}_2\text{O}$ which consists of a hybrid of the decavanadate and octomolybdate structures [409]. The oxidation and coupling of 2,3,6-trimethylphenol by O_2 is catalysed by a phosphomolybdovanadate catalyst

supported on carbon [410]. The synthesis and characterisation of the $[\text{SiVMo}_{11}\text{O}_{40}]^{5-}$ ion has been reported [411], and the reactions of $[\text{EMMo}_{11}\text{O}_{39}]^{n-}$ ($\text{E} = \text{Si}, \text{P}; \text{M} = \text{Co}, \text{Ni}$) with NO under phase transfer conditions have been studied [412]. An improved method for making $[\text{PMMo}_{11}\text{O}_{40}(\text{H}_2\text{O})]^{5-}$ ($\text{M} = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) has been described [413].

The reaction of $[\text{NH}_4]_6[\text{Mo}_7\text{O}_{24}]$, NH_4VO_3 , As_2O_3 , NH_4SCN and $[\text{NMe}_4]\text{Cl}$ in a water/dmf mixture with hydrazinium sulfate gave $[\text{NMe}_4]_4[\text{As}_4\text{Mo}_6\text{V}_7\text{O}_{39}(\text{SO}_4)] \cdot \text{H}_2\text{O}$ which can be described as an inclusion compound with SO_4 trapped in the centre [414]. By similar routes the same group was able to prepare $[\text{NMe}_4]_5[\text{As}_3\text{Mo}_8\text{V}_4\text{O}_{40}] \cdot 3\text{H}_2\text{O}$, two salts involving the $[\text{Mo}_5\text{V}_6(\text{NO})_6\text{O}_{183}(\text{H}_2\text{O})_{18}]^{24-}$ anion, and $[\text{NH}_4]_{12}[\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}] \cdot 33\text{H}_2\text{O}$. Two of these had been previously reported incorrectly in the literature. The presence of the Mo_{17} motif was also commented on [415]. From an aqueous HCl solution of sodium molybdate, iron(III) nitrate and $\text{NH}_2\text{OH} \cdot \text{HCl}$, the same authors were able to isolate the salt $\text{Na}_3[\text{NH}_4]_{12}[\text{Mo}_5\text{Fe}_6(\text{NO})_6\text{O}_{174}(\text{OH})_3(\text{H}_2\text{O})_{24}] \cdot 76\text{H}_2\text{O}$, which contains a giant cluster anion with three such Mo_{17} units arranged as a doughnut-like core [416, 417]. The structure of the pyrophosphate polyoxometallate $[\text{NBu}_4]_4[(\text{P}_2\text{O}_7)\text{Mo}_{18}\text{O}_{54}]$ has been determined and shows that the POP linkage is constrained into a linear geometry. The compound can be reduced to a green penta-anion and then to a blue hexa-anion [418].

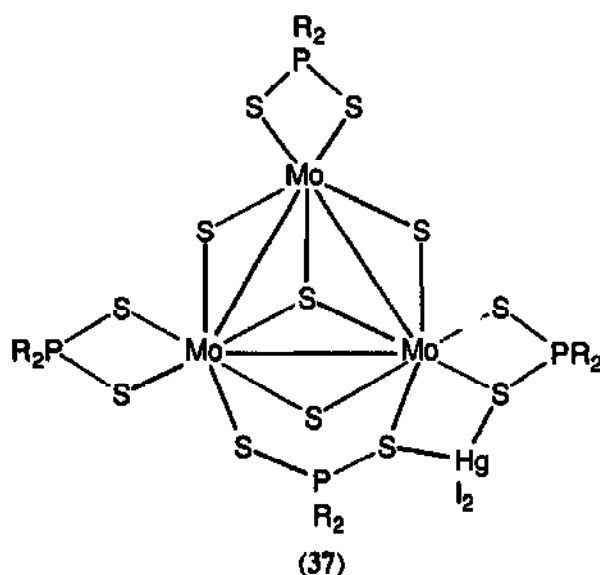
8.8.2 Halide clusters

The crystal structures of $[(\text{Mo}_6\text{Br}_8)\text{X}_6]^{2-}$ where X is varied along the series F, Cl, Br and I have been determined as their $[\text{NBu}_4]^+$, $[\text{PPh}_4]^+$ or $[\text{AsPh}_4]^+$ salts. Changing the halide causes a systematic lengthening of the Mo–Mo bonds and a slight compression of the Br_8 cube; the IR and Raman spectra at 10 K show the Mo_6Br_8 vibrations remaining constant whereas those involving X change. The ^{95}Mo NMR shift moves to lower field as the electronegativity of X increases [419]. The X-ray structure of $[\text{PPh}_4]_2[\text{Mo}_6\text{Cl}_{14}]$ has also been determined [420]. The complete system of mixed metal clusters $[(\text{Mo}_{6-n}\text{W}_n\text{Cl}_8)\text{F}_6]^{2-}$ ($n = 0-6$), ten in all (there are two isomers each for $n = 2-4$), have been prepared as a mixture and analysed by ^{19}F NMR spectroscopy; the assignments of the 24 signals were confirmed by a ^{19}F COSY spectrum [421]. The synthesis of $[\text{NBu}_4]_2[(\text{Mo}_6\text{Br}_7\text{S})\text{Cl}_5(\text{MeCN})]$ was carried out to judge the effect of a neutral ligand on the Mo_6^{12+} core; its structure is very similar to that of $[\text{NEt}_4]_3[(\text{Mo}_6\text{Br}_7\text{S})\text{Cl}_6]$ [422]. The reaction of $[\text{Mo}_6\text{Cl}_{12}]$ with NaSH and NaOBu in a mixture of BuOH and py gave materials which serve as precursors for the Chevrel phases $[\text{Mo}_6\text{S}_8\text{L}_6]$ where L = py, pip or pyrrolidine [423].

8.8.3 Other clusters, including cubanes

Further details of the synthesis of $[\text{MoFe}_4\text{S}_6(\text{PET}_3)_4\text{Cl}]$ from $[\text{MoCl}_3(\text{thf})_3]$, $\text{S}(\text{SiMe}_3)_2$ and $[\text{FeCl}_2(\text{PET}_3)_2]$ have appeared. The chloride ligand can be replaced by thiolates (SPh, SEt) [424].

Energy localised CNDO calculations have been carried out to investigate whether chalcogenide clusters of the type $[M_3(\mu_3-E)(\mu-E)_3]^{4+}$ ($M = Mo, W$; $E = O, S, Se, Te$) can be regarded as pseudo-aromatic because of $dp \pi$ -bonding around the triangle [425, 426]. The reaction of $[Mo_3S_4(dtp)_4]$ ($dtp = S_2PR_2$ where $R = Et, Pr$) with MI_2 ($M = Zn, Cd, Hg$) in the presence of py gave clusters of formula $[Mo_3S_4(dtp)_3(py)_3][M(py)_3I_3]$ or in the case of Hg , as the $[HgI_3]^-$ salt [427]. If the reaction is carried out in thf the adduct $[Mo_3S_4(dtp)_4(HgI_2)]$ (37) is formed in which the HgI_2 is bonded to two sulfur atoms; the variable temperature NMR spectra suggest dissociation in solution to $[Mo_3S_4(dtp)_3]^+[HgI_2(dtp)]^-$ [428]. The reaction of $[Mo_3S_4(dtp)_4] \cdot H_2O$ (R of $dtp = OEt$) with $[M(CO)_6]$ ($M = Mo, W$) in $EtCO_2H$ gave the cubane clusters $[Mo_3MS_4(\mu-O_2CEt)_2(dtp)_3(dtpH)]$ [429].

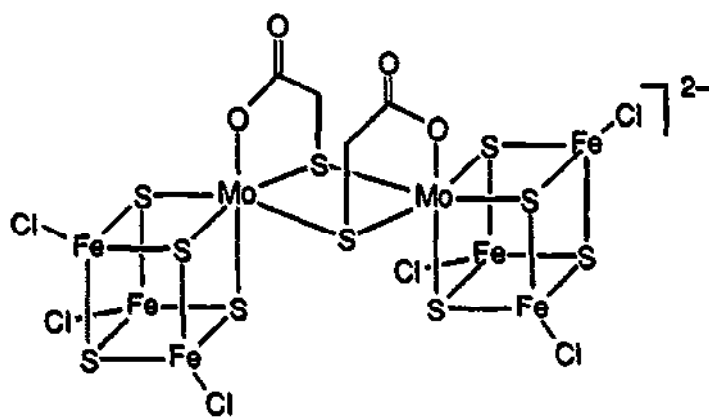


Reaction of $[Mo_3S_7Cl_4]$ with py and PPh_3 gave the molecular cluster $[Mo_3S_4Cl_4(py)_5]$ which was structurally characterised [430], while gamma irradiation of polymeric $[Mo_3S_7Br_4]$ in concentrated HBr caused extrusion of $[Mo_3S_7Br_6]^{2-}$, identified by structural characterisation of its $[H_9O_4][NEt_4]$ double salt. An unusual aggregation of the anions involving short $S \cdots Br$ contacts was observed [431]. The reaction of $[NEt_4]_2[Mo_3S_7Br_6]$ with $p-HSO_3C_6H_4Me$ gave the aqua species $[Mo_3S_7(H_2O)_6]^{4+}$; the analogous Se cluster was also made. Kinetic studies of the replacement of the H_2O ligands by Cl^- show that it is a two stage process, consistent with the two different types of water ligand on each Mo . Desulfurisation with the water-soluble phosphine $[P(C_6H_4SO_3)_3]^{3-}$ gave $[Mo_3S_4(H_2O)_9]^{4+}$ [432]. The complex $[Mo_3S_7(dtc)_3][Tl] \cdot 8.2CH_2Cl_2$ ($dtc = S_2CNC_4H_8$) has been prepared by a solid state reaction and structurally characterised [433], and the synthesis of $[NEt_4]_2[Mo_3S_7(tdt)_3]$ and $[NEt_4]_2[Mo_3S_3O_2(tdt)_3]$ where $tdt =$ tolene dithiolate, $^-[SC_6H_3MeS]^-$ has been reported [434]. The double cluster $Cs_4[Mo_3(\mu_3-S)(S_2)_6][Mo_3(\mu_3-S)(S_2)_5(S_4)]$ has been made from Mo powder, K_2S_5 and $CsCl$ solution at $150^\circ C$ for 72 hours; one of the clusters has a normal Mo_3S_{13} structure, but in the other, one of the terminal S_2 groups is replaced by an S_4 unit [435].

A number of papers have appeared on the use of $[\text{MoS}_4]^{2-}$ and $[\text{MoSe}_4]^{2-}$ in reactions with coinage metal compounds to form cubane clusters, especially in the solid state; several review articles deal with synthetic methods [436, 437] and cluster self-assembly [438, 439]. The synthesis of $[\text{MoS}_4\text{Cu}_6\text{X}_4(\text{py})_4]_n$ ($\text{X} = \text{Br}, \text{I}$) from $[\text{NH}_4]_2[\text{MoS}_4]$, CuX and NBu_4X in the solid state followed by treatment with py has been reported; the structure is linked into a polymer by CuXCu bridges [440]. The cluster $[\text{NEt}_4]_4[\{\text{Mo}(=\text{O})\text{Cu}_3\text{S}_3(\text{Br})(\text{I})(\mu\text{-I})\}_2]$ was obtained from $[\text{MoO}_2\text{S}_2]^{2-}$, CuI and NEt_4Br ; it consists of two nest-shaped incomplete cubane fragments linked through a $\text{Cu}(\mu\text{-I})_2\text{Cu}$ bridge [441]. The reaction of $[\text{NH}_4]_2[\text{MoOS}_3]$ with $[\text{Cu}(\text{S}_2\text{P}(\text{OEt})_2)(\text{PPh}_3)]$ in dmf gave $[\text{Mo}(=\text{O})\text{Cu}_3\text{S}_3\{\text{S}_2\text{P}(\text{OEt})_2\}(\text{PPh}_3)_3]$ [442]. The mixed-metal species $[\text{MS}_4\text{Cu}_3(\text{PPh}_3)_3\text{Cl}]$ where $\text{M} = \text{Mo}_{0.42}\text{W}_{0.56}$ was made by solid phase synthesis [443]. Starting from $[\text{MoS}_4]^{2-}$, CuCl_2 and a large cation such as $[\text{PPh}_4]^+$ or $[\text{NBu}_4]^+$, compounds of the formula $[\text{C}][\text{CuMoS}_4]$ were made; they are presumably polymeric in structure [444].

The cubane clusters $[\text{NBu}_4]_3[\text{Mo}(=\text{S})\text{Ag}_3(\text{Br})\text{S}_3\text{X}_3]$ have been made by a solid state reaction between $[\text{NH}_4]_2[\text{MoS}_4]$, AgX , and NBu_4Br , and their non-linear optical properties investigated [445]. Analogous reaction starting from $[\text{MoOS}_3]^{2-}$ also gave the appropriate clusters [446]. The reaction of $[\text{PPh}_4]_2[\text{MoSe}_4]$ with $[\text{Ag}(\text{PPh}_3)\text{I}]$ in CH_2Cl_2 and MeCN gave the cubane $[\text{Mo}(=\text{Se})\text{Ag}_3(\text{I})\text{Se}_3(\text{PPh}_3)_3]$; the W analogue was also made [447]. The X-ray structure of $[\text{Mo}(=\text{S})\text{Ag}_3\text{S}_3\{\text{S}_2\text{P}(\text{OEt})_2\}(\text{PPh}_3)_3]$ has been determined [448]. The reaction of $[\text{NMe}_4]_2[\text{Mo}_2\text{S}_4(\text{tdt})_2]$ ($\text{tdt} = \text{toluene dithiolate}$) with $[\text{Ag}(\text{NO}_3)(\text{PPh}_3)]$ or $[\text{Cu}(\text{S}_2\text{P}(\text{OEt})_2)(\text{PPh}_3)]$ gave $[\text{Mo}_2\text{M}_2\text{S}_4(\text{tdt})_2(\text{PPh}_3)_2]$ [449].

The double cubanes $[\text{NEt}_4]_4[\{\text{MoFe}_3\text{S}_4\text{Cl}_3(\mu\text{-SCHRCOO})\}_2]$ (38) ($\text{R} = \text{H}, \text{Me}, \text{CH}_2\text{CO}_2\text{H}$) have been prepared by reaction of $[\text{MoFe}_3\text{S}_4\text{Cl}_3(\text{OC}_6\text{Cl}_4\text{O})(\text{MeCN})]^{2-}$ with the appropriate acid; the X-ray structure of the thiolactate ($\text{R} = \text{Me}$) was determined. These compounds will reduce N_2H_4 to NH_3 in the presence of CoCp_2 and lutidine.HCl to provide electrons and protons respectively; this probably involves breakdown to a single cubane [450]. The reaction of $[\text{MoFe}_3\text{S}_4\text{Cl}_4(\text{ox})]^{3-}$ with NEt_4CN gave $[\text{MoFe}_3\text{S}_4\text{Cl}_3(\text{CN})(\text{ox})]^{3-}$, but if only 0.5 equivalents is used, the double cubane $[\{\text{MoFe}_3\text{S}_4\text{Cl}_2\}_2(\mu\text{-CN})(\mu\text{-S})]^{5-}$ results [451]. The conversion of $[\text{Fe}(\text{dmf})_6][\text{Cl}_2\text{Fe}(\mu\text{-S})_2\text{Mo}(\mu\text{-S})_2\text{FeCl}_2]$ to cubanes and double cubanes on reaction with dtc^- or SPh^- has been described [452].



(38)

The incomplete cubane $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ has been used to prepare a range of heterometallic cubane clusters. Full details of its reaction with Pd black to give $[\text{PdMo}_3\text{S}_4(\text{H}_2\text{O})_9\text{Cl}]^{3+}$ have appeared. In the presence of OTs^- this can be crystallised as the double cubane $[\text{Pd}_2\text{Mo}_6\text{S}_8(\text{H}_2\text{O})_{18}]^{8+}$. The preparation of $[\text{PdMo}_3\text{S}_4(\text{tacn})_3\text{Cl}]^{3+}$ and the subsequent displacement of its chloride ligand by CO, $^i\text{BuNC}$ and alkenes were also described; a further unusual feature is that this cluster catalyses the addition of alcohols to alkynes with high selectivity [453]. Addition of Cu metal to $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ gave $[\text{Mo}_3\text{CuS}_4(\text{H}_2\text{O})_{10}]^{4+}$ whereas the new oxidised form $[\text{Mo}_3\text{CuS}_4(\text{H}_2\text{O})_{10}]^{5+}$ was obtained from Cu^+ or solid CuCl . The EPR spectrum of the 4+ cubane shows the unpaired electron interacting with one Cu atom, and it therefore behaves in solution as a single cubane even though it previously crystallised out as a double cubane [454, 455]. Reaction of $[\text{Mo}_3\text{OS}_3(\text{H}_2\text{O})_9]^{4+}$ with indium metal gave $[\text{InMo}_6\text{O}_2\text{S}_6(\text{H}_2\text{O})_{18}]^{8+}$ which was structurally characterised as its tosylate salt [456].

The reaction of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ with $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ gave $[\text{Mo}_3\text{CrS}_4(\text{H}_2\text{O})_{12}]^{4+}$; the Cr(II) centre is labile and undergoes substitution of H_2O by NCS^- by a conjugate base mechanism, unlike the analogous Mo_4 cluster [457]. The rates of oxidation of the double cubane $[\text{Co}_2\text{Mo}_6\text{S}_8(\text{H}_2\text{O})_{18}]^{8+}$ by $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Co}(\text{dipic})_2]^-$ have been measured; the iron shows a two term rate law indicative of both outer sphere reaction of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and inner sphere reaction of its conjugate base $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ [458]. The reduction of $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ to the corresponding 4+ state has been examined for a range of one-electron reducing agents such as Ti(III), Cr(II), Eu(II), V(II), $[\text{Ru}(\text{NH}_3)_6]^{2+}$, and Co(II) among others. The self exchange rate for the two clusters was also calculated [459].

The reaction of $[\text{WS}_4]^{2-}$ with $[\text{Mo}_2\text{O}_2\text{S}_2(\text{cys})_2]^{2-}$ gave a mixture of clusters which was separated chromatographically into $[\text{MoW}_2\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ and $[\text{Mo}_2\text{WS}_4(\text{H}_2\text{O})_9]^{4+}$, which were both crystallised as the tosylate salts and as $\text{Na}_2[\text{M}_3\text{S}_4(\text{Hnta})_3]$; a statistical disorder of Mo and W was present in all four X-ray structures. Trends were observed in the IR spectra with the bands between $550\text{--}400\text{ cm}^{-1}$ shifting to lower wavenumber on going from Mo_3 to W_3 clusters [460].

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