7.   MOLYBDENUM AND TUNGSTEN

C. D. GARNER

CONTENTS

INTRODUCTION

The material included in this review was obtained from the reports published in primary research journals during 1980 and/or volumes 92 and 93 of Chemical Abstracts. As has become the practice with this series, the emphasis for this article is the *co-ordination* chemistry of molybdenum and tungsten. Thus, although the organometallic chemistry of these elements is undergoing significant developments, this area is not covered comprehensively here and the reader is referred to specialist reviews in organometallic chemistry for further information. The material follows on from the corresponding reviews [1,2] of the 1979 literature and has been organised with the intention of producing a reasonably comprehensive account, with the major classification being by the oxidation state of molybdenum and/or tungsten. The review is concluded with several sections which summarise developments in this area which cut across a simple oxidation state classification.

Important new texts have been published concerned with the biochemistry and related chemistry of molybdenum [3,4] and the chemistry and uses of this element [5]. Each of these contains a considerable amount of interesting and relatively new information, as well as providing a good documentation of earlier advances. [95]Mo NMR spectroscopy has come of age and clearly has much to offer as a technique for characterising diamagnetic molybdenum complexes [6]. The ratio of the quadrupole moments of [95]Mo and [97]Mo, $[Q(^{97}Mo)/Q(^{95}Mo)]$, has been determined as 11.4 ± 0.3, from relaxation time for K_2MoO_4 (*aq.*) [7]. Bond-strength, bond-length relationships have been presented for Mo-N [8] and Mo-S [9] bonds.

The characterisation and understanding of the electronic structure of simple molecular species containing molybdenum or tungsten continues to attract attention. The dissociation energy of MoO has been estimated as 580 ± 25 kJ mol^{-1} [10]. MoO and MoN molecules produced in a hollow cathode discharge have been trapped in Ne, Ar, and Kr matrices at 4.2 and 13 K and investigated by optical absorption spectroscopy; vibronic coupling to the electronic transitions were identified and the ground state vibrational frequencies for $Mo^{14}N$ and $Mo^{16}O$ were 1040 and 894 cm^{-1}, respectively. Absorptions attributed to Mo_2 were also observed in this study [11]. The bonding within Mo_2 and the potential energy curve for its $^1\Sigma_g^+$ ground state have been discussed with the aid of detailed molecular orbital calculations

[12,13]. Several other studies, reporting the isolation and characterisation of small metal clusters containing molybdenum or tungsten atoms, have also been published [14 - 19].

7.1 MOLYBDENUM(VI) AND TUNGSTEN(VI)

7.1.1 Halide complexes

Reviews concerned with [WF$_6$], [MoF$_6$] and other molybdenum flourides have been published [20]. The ν_3 bond (740 - 750 cm^{-1}) of [MoF$_6$] has been observed for molybdenum of natural abundance and isotopically pure samples of [^{95}MoF$_6$], [^{96}MoF$_6$], and [^{100}MoF$_6$] [21]. SCF-Xα calculations, including estimations of the ionization potentials, for [MoF$_6$] and [WF$_6$] have been reported [22] and the extent of electron attachment to these molecules has been measured [23]. The photolysis of [MoF$_6$], isolated in an Ar matrix, has been investigated and the first step shown to lead to the formation of [MoF$_5$] [24]; the thermodynamic properties of these two molecules have been compared [25].

[Fe(NCMe)$_6$]$^{2+}$ is formed when iron metal reacts with [MoF$_6$] or [WF$_6$] in MeCN [26]. Me$_3$Si(N$_3$), azidotrimethylsilane, reacts with an excess of [WF$_6$] to form (the potentially explosive) material [WF$_5$(N$_3$)], the corresponding reaction with [MoF$_6$] yields a yellow solid, assumed to be [MoF$_5$(N$_3$)], which decomposes at -10 °C. The [WF$_5$(N$_3$)] molecule has an essentially octahedral coordination about the metal, with $\overline{W—F}$ = 1.84(4) Å, W—N = 1.58(2) Å, and the W—N(1)—N(2) angle is 157(2) ° [27].

Monothiolate derivatives of tunsten(VI) chloride, [WCl$_5$(SR)] (R = Me, Et, cych, ^{t}Bu, ^{t}Bu, Ch$_2$Ph, or Ph) have been found to be unstable, with at least two modes of degradation. If R$^+$ is relatively stable, the preferred pathway is heterolytic cleavage of the C—S bond to generate a carbonium iron, which abstracts Cl$^-$, to give WSCl$_4$ and RCl. The intermolecular elimination of R$_2$S$_2$ is the alternative route and is the exclusive degradative pathway for R = Ph. Thus, the isolation of [WCl$_5$(SR)] compounds is difficult and only those for which R = Me or Ph have been isolated in a pure form [28].

7.1.2 Oxo complexes

The crystal and molecular structure of [MoOCl$_4$] has been determined by neutron and X-ray diffraction at 293 and 77 K [29]. The Mo atoms occur in adjacent octahedral holes in the lattice but there is no dimer formation as exists in MoCl$_5$. The configuration around the Mo is a square pyramid, with four basal chlorine atoms ($\overline{Mo—Cl}$ = 2.32 Å), an apical oxygen atom (Mo—O =

1.7 Å), and the Mo atom is 0.41 Å above the basal plane. This structure is in agreement with a gas-phase electron diffraction study [30] (Mo—Cl = 2.279(3) Å, Mo—O = 1.658(5) Å) and with structures found for the related molecules [WOCl₄], [WSCl₄], and [WSBr₄]. Electronic absorption spectra, in the visible and near UV regions, have been measured for the vapours over MoOCl₄ and WOCl₄ and the results interpreted with the aid of SCF-Xα calculations [31]. The formation of WOCl₄, and other oxychlorides has been studied in the system WO₂—WCl₆ [32].

XeF₂ forms adducts with the weak fluoride acceptor species, [MoOF₄] and [WOF₄], of composition XeF₂.nMOF₄ (n = 1 or 2; M = Mo or W); ^{19}F NMR spectroscopic studies have indicated the occurrence of equilibria involving higher chain length species (n = 1 - 4) in SO₂ClF solution. These structures involve XeF...M bridges which, at low temperature, are non-labile on the ^{19}F NMR time scale and it has been concluded that [WOF₄] and its polymers are stronger F⁻ acceptors, relative to XeF₂, than their MoOF₄ analogues [33]. The formation of salts containing [WO₂F₄]²⁻, [W₂O₄F₇]³⁻, and [H₂W₂O₄F₇]²⁻ ions has been described for reactions involving WO₃.xH₂O and an organic base, in 40% HF solution [34]. ^{1}H NMR spectroscopy has been used to monitor the products of the reactions of [WAF₄] (A = O or S) with 2,3-butanediol (H₂L) in MeCN [35] and [WOX₄] (X = F or Cl) with aliphatic amides and monooximes [36]. In the former study, two diastereoisomers of composition WAF₃(HL) were obtained and their reactions investigated; in the latter study 1:1 adducts were obtained. The state of molybdenum(VI) (0.2 - 2.1 moles l⁻¹) in aqueous HF have been monitored spectroscopically [37] and the crystal structure of [NEt₄] [{MoO(O₂)(pydca)}₂F] (pydca = pyridine-2,6-dicarboxylate) has been described [38]. [WOCl₄(py)₂] has been reported [39] and the crystal structure of [MoO₂Cl₂(phen)] determined by X-ray crystallography [40].

Extended Hückel calculations have been accomplished [41] for the MoO₂²⁺ moiety (and for comparison, UO₂²⁺), and the conclusion that the maximum utilisation of the vacant 4d orbitals for π bonding with oxygen lone pairs, as suggested previously, has been confirmed. The calculated potential energy cure for dsp bonding, has a minimum for O—M̂o—O for ca. 100°, in good agreement with structural data obtained for the majority of cis-dioxomolybdenum(VI) complexes. Similar conclusions have been reached for the hypothetical complex cis-[MoO₂(PPh₃)₄] [42].

Molybdenum(VI) and tungsten(VI) diperoxo complexes are of interest because some of them are reagents for the oxidation of various organic substrates such as sulphides, aliphatic amines, ketones, and olefins. Furthermore, peroxo complexes of molybdenum are claimed to be involved as key intermediates in the hydroperoxide oxidation of olefins catalyzed by salts of this metal. New
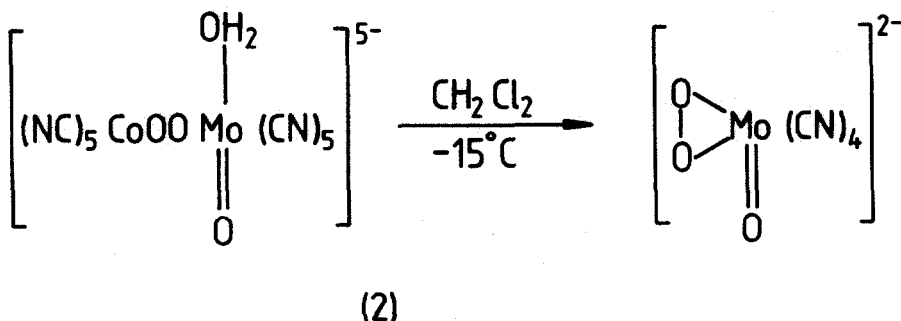
examples of this type of catalysis include asymmetric epoxidations of olefins
[43,44] and oxidation of organic sulphides [45] by *tert*-butyl hydroperoxide.
Asymmetric oxidation of simple prochiral olefins (*e.g.* propene, 1-butene,
trans-2-butene) can be achieved with stoicheiometric quantities of (1), in
which L represents the chiral bidentate ligand (*S*)-*N*,*N*-dimethyllactamide. A
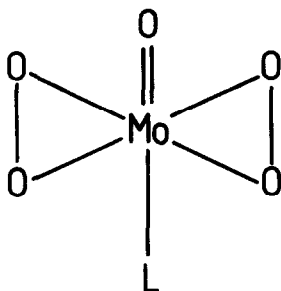
(1)

· determination of the crystal structure of this complex has identified a slightly
distorted pentagonal-bipyramidal coordination sphere about the molybdenum,
with the two peroxo groups located in equatorial positions; the chiral
lactamide ligand is bidentate, being coordinated through the carbonyl oxygen
at the fifth equatorial position and through the hydroxylic oxygen on the axial
position opposite to the oxo groups [46]. Several diperoxo complexes [$MO(O_2)_2$
LL'] (where M = Mo or W; L = amine oxide, tertiary phosphine oxide, or tertiary
arsine oxide, L' = L or H_2O) have been prepared. The frequency of the ν_1 mode
of the $M(O_2)$ moiety, which is essentially an O—O stretch, varies somewhat with
the nature of L. The energy of activation for loss of dioxygen from the dry
or dissolved complex is independent of whether L is a phosphine or arsine
oxide but is lower for a pyridine oxide complex. The complexes stoicheiometric-
ally oxidize olefins to epoxides and catalyze the epoxidation of olefins by
tert-butyl hydroperoxide [47]. Formation constants for diperoxymolybdate and
diperoxytungstate complexes have been obtained [48], the IR and electronic
spectra of $K_2[MoO(O_2)_2C_2O_4]$ have been recorded and interpreted [49], and the
crystal structure of [NEt_4] [{$MoO(O_2)$ (pydca)}$_2$F] (pydca = pyridine-2,6-
dicarboxylate) determined [38]. Photolysis of bisperoxo-molybdenum(VI)
porphyrins has been shown [50] to produce the related *cis*-dioxo-molybdenum(IV)
complex which, in the case of *tetra*-4-tolylporphyrin, has been characterised by
X-ray crystallography. The Mo—O bond lengths are 1.709(9) and 1.744(9) Å,
two sets of Mo—N distances are observed, 2.246(9) and 2.157(10) Å, and the
Mo lies 1.095(9) Å out of the mean plane of the carbon atoms of the porphyrin

ring which shows a significant "horse-saddle" deformation [51].   Dioxygen
has been transferred from cobalt to molybdenum according to the reaction (2);
$[MoO(O_2)(CN)_2]^{2-}$ may also be prepared by treatment of $[\{(NC)_5ClMoO\}_2O]^{8-}$, in
CH_2Cl_2 at −40 °C with Na_2O_2 [52].

$$\left[\begin{array}{c} \overset{\displaystyle OH_2}{\underset{\displaystyle \underset{O}{\|}}{(NC)_5\,CoOO\,\overset{|}{Mo}\,(CN)_5}} \end{array}\right]^{5-} \xrightarrow[-15°C]{CH_2Cl_2} \left[\begin{array}{c} \overset{\displaystyle O}{\underset{\displaystyle O}{\Big\rangle}}Mo\,(CN)_4 \\ \underset{O}{\|} \end{array}\right]^{2-}$$

(2)

Spectrophotometric studies have identified the formation of 1:1 complexes
between molybdenum(VI) and $MePO(OH)_2$, $(EtO)PO(OH)_2$ and $H_2PO_4^-$ and the
stability constants at pH 3.06 have been determined [53].   The formation of
$[MoO_2(tta)_2]$, during solvent extraction of molybdenum(VI) from halide solutions
by tta in CCl_4, has been reported [54] and $[MoO_2(MeCOCH_2CO_2Et)_2]$ has been
isolated [55]. ^1H NMR spectroscopy has been used to monitor complex formation
between lactic acid and molybdenum(VI) or tungsten(VI) [56], between L-malic
acid and tungsten(VI) [57], and partially deuterated thiamalic acid and
molybdenum(VI) [58].   Eperimerization of aldohexoses and −pentoses, to the
corresponding C-2 epimers, proceeds more rapidly when catalysed by $[MoO_2(acac)_2]$
in DMF than by aqueous molybdic acid [59].

The extraction of molybdenum(VI) from acidic media by diethyl phthalate
has been reported [60] and stability constants for the complexes formed when
$[MoO_4]^{2-}$ or $[WO_4]^{2-}$ react with 2-hydroxyaromatic ligands [61] and 2,5-
dihydroxy-1,4-benzoquinone [62] have been obtained.   The complexes involving
this dihydroxyquinone are suggested to be structurally related to those formed
by catechols (see [1] p. 119).   Electrochemical reduction of $[MoO_2(cat)_2]^{2-}$,
in aqueous buffers pH 3.5-7, occurs by sequential one- and two-electron
transfers to yield transiently stable molybdenum(V) and molybdenum(III) species.
Uptake of two protons accompanies each electron transfer step and converts
an oxo group to a coordinated H_2O molecule [63].   Such coupled proton/electron
transfer to $Mo^{VI} = O$ groups has gained general acceptance as the probable
mechanism for reduction of molybdenum(VI) centres in enzymes such as xanthine,
sulphite and aldehyde oxidase and nitrate reductase.   An interesting
development in the modelling of the redox behaviour of these enzymes has been

accomplished with the complexes **(3)**, $[Mo^VOL]^-$, for which one-electron
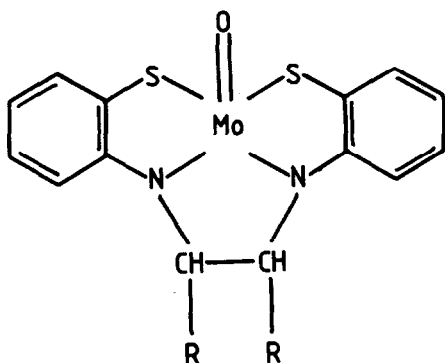
R=H or Me

(3)

oxidation results in the binding of another oxo-group and the protonation of
ligand L to form the previously isolated complexes $[MoO_2LH_2]$. These
molybdenum(VI) complexes undergo a two-electron irreversible reduction to a
molybdenum(IV) complex [64].

EXAFS studies of the molybdenum centres in the oxidised forms of sulphite
oxidase and active and desulpho xanthine oxidase (see [1] p. 149, with the
latter studies being reported in more detail [65]) give stimulation and scope
for the preparation of chemical analogues for these centres. Two complexes
worthy of special mention in this respect are [MoO_2(*N*-methyl-4-tolylthio-
hydroxamate)_2] (= $[MoO_2(4-MeC_6H_4C(S)N(Me)O)_2])$ [66] and $[MoO_2(SC(Me)_2CH_2NHMe)_2]$
[67]. The former represents the first example of a $Mo^{VI}O_2^{2+}$ complex involving
two *S,O* chelates and has an unexceptional structure at the metal (within the
$Mo^{VI}O_2^{2+}$ group, Mo—O = 1.71 Å, O—$\widehat{Mo}$—O = 104°; for the chelates Mo—O,
each of which is essentially *trans* to an oxo group, = 2.14 Å, Mo—S = 2.46 Å)
whereas the latter, representing another example of a $Mo^{VI}O_2^{2+}$ complex
involving two *S,N* chelates, has an unusual structure. The donor atoms are *not*
arranged in the customary octahedral manner and there are no atoms *trans* to
any Mo—O bond; the largest angle for any O_t—Mo—X group is only 122 ° and
that is for X = O. The geometry is best described as a skew-trapezoidal
bipyramid, with the N_2S_2 donor atoms forming a plane and the O atoms 1.49 Å
above and 1.52 Å below this plane. Further unusual features of this structure
are the S—$\widehat{Mo}$—S angle of 69.8 ° and the 2.76 Å separation of the sulphur atoms,
the approach being sufficiently close for the existence of a significant

S....S bonding interaction to be postulated. This unique geometry apparently arises as a consequence of the unfavourable steric repulsions between the two N-Me groups which would occur in the normal *cis*-dioxo octahedral structure. $[MoO_2(S_2CNEt_2)_2]$, originally reported as involving abnormally short Mo—O bonds has been shown to have normal dimensions for the MoO_2^{2+} moiety (Mo—O = 1.703(2) $\overset{\circ}{A}$ and O—$\hat{Mo}$—O = 105.6(1)°) [68].

Tripeptides, Gly-Gly-Met or Gly-Gly-His, immobilized *via* the terminal glycine to a polystyrene matrix have been reacted with MoO_2Cl_2 to obtain peptide complexes of molybdenum(VI). The tripeptides seem to function as tridentate ligands and the molybdenum(VI) is reduced by Ph_3P to molybdenum(IV); the original complex can be regenerated by oxidation with $NaNO_3$. Thus the molybdenum(VI) complex behaves as a model of an oxidase enzyme [69]. A series of complexes containing amino acids (β–alanine, glycine, cysteine, serine, or lysine) or edta coordinated to the $W_2O_4^{4+}$ core have been reported [70] and the electrochemical reduction characteristics of $[(MoO_3)_2$ edta$]^{4-}$ have been investigated [71].

The coordination behaviour of molybdenum(VI) towards diols and aminoalcohols has been discussed, with particular reference to new and previously reported structural data. The compounds may be classified as follows: (i) $[MoO_2(HL)_2]$, containing the *cis*–dioxo-MoO_2 core and two monodeprotonated ligands. (ii) Yellow vicinal diol derivatives, $[Mo_2O_3(HL)_2L_2]$, with an $O_tMoO_bMoO_t$ core; the generic structure having been established for H_2L = pinacol, and an IR absorption at *ca.* 750 cm^{-1} is characteristic of this core. (iii) A class having an $(O_t)_2MoO_b Mo(O_t)_2$ core, as typified by the nitrilotriacetate complex in $Na_2[Mo_2O_5(Hnta)_2].8H_2O$. (iv) Compounds such as $[\{MoO_2(npg)(OH_2)\}_2]$ (H_2npg = neopentyl glycol), with a *cis*-MoO_2^{2+} group and six-coordination being achieved by bridging by a ligand oxygen atom [72].

Stability constants and the thermodynamics of formation of molybdenum(VI) complexes with DL–α–aminobutyric acid have been reported [73] and some new molybdenum(VI) complexes with triazene 1-oxides (HL), of composition $[MoO_2L_2]$, have been isolated and their vibrational spectra recorded [74]. Spectrophometric and analytical information has been obtained for the 1:2 complexes formed between molybdenum(VI) and 2-hydroxy-5-chloro- and 2-hydroxy-5-bromoacetophenone oximes [75]. The ^{13}C NMR spectra of 8-quinolinol, 4-methyl-8-quinolinol (Hmq) and $[MoO_2(mq)_2]$ have been recorded and have provided new insights into the solution structure and bonding of this and the $[Zn(mq)_2]$ complex; thus both ligands are equivalent and the molybdenum-ligand oxygen interaction has significant covalent character [76]. Several complexes of some *N,O* donor ligands, including MoO_2LCl_2 (L = $PhCONHNH_2$, 2- or 4- $H_2NC_6H_4CONHNH_2$) and $MoO_2L'Cl$ (HL' = $2-HOC_6H_4CONHNH_2$, $2-(H_2NNHCO)C_6H_4N:CHC_6H_4OH-2$,$4-xC_6H_4CONHN:$

CHC$_6$H$_4$OH-2, X = H, NH$_2$, or MeC(:NOH)CMe:NNHCOC$_6$H$_4$R-2, R = H, OH, or NH$_2$)
have been prepared and characterised by IR and UV spectroscopy [77].

The complex of *N,N*-diethylhydroxylamine (HL) [MoO$_2$L$_2$] has been
structurally characterised [78] as have the hydroxylamino complexes
[MoO(H(Me)NO)$_2$(HNC(S)N(Me)O)] and [MoO(H(Me)NO)(HNC(S)N(Me)O)(H$_2$NC(S)N(Me)O].
H$_2$O. These latter complexes were prepared in the course of the
reactions of [MoO$_4$]$^{2-}$ in aqueous solution (pH ~6) with *N,N*-substituted
hydroxylamines, the colourless complexes [MoO$_2$(RR'NO)$_2$] (RR' = H(Me), Me$_2$,
Et$_2$, Bz$_2$) are formed, in which the ligands are *N,O*-bonded. The deprotonated
N-methyl-*N*-hydroxylthiourea complexes were obtained from related reactions
in the presence of NCS$^-$ and both complexes involve a pentagonal bipyramidal
coordination geometry at the metal [79].

The complexes *cis*-MoO$_2$LL' (L = EtOH or dmso), of the potentially
tridentate Schiff bases (4) (= H$_2$L', X = H, NO$_2$, Br, or MeO) have been
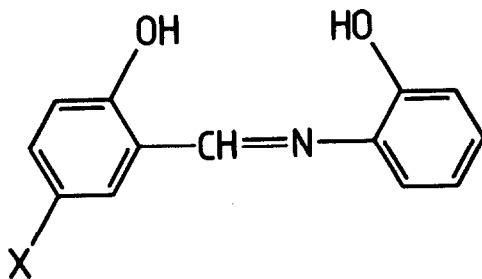
(4)

prepared and their electronic spectra and redox potentials measured [80]. A
large number of bidentate, tridentate, and tetradentate Schiff base ligands
containing *O,N*, and *S* donor atoms have been employed as ligands for the *cis*-
MoO$_2$$^{2+}$ centre and the structures of the resultant complexes discussed with
reference to their IR and ^{1}H NMR spectroscopic properties [81]. The
preparation of MoO$_2$L$_2$.*n*H$_2$O (HL = isonicotinic acid hydrazide or one of its
derivatives) [82] and WOCl$_4$L$_2$ (L = nicotinamide, isonicotinamide acid
hydrazide or one of its derivatives) [83] have been reported. The thiocyanate
ligands in [MoO$_2$(NCS)$_2$(hmpa)$_2$] have been shown to be *N*-bonded by X-ray
crystallography [84] and molybdenum(VI) thiocyanate complexes shown to be more
stable in HOAc, as compared to aqueous solution [85].

Although a metallo-carbene seems to be the reactive intermediate for
metal-catalysed olefin metathesis, it has been established that the presence
of oxo-ligands has a dramatic effect on catalytic activity. Thus WOCl$_4$, in
combination with main group metal alkyls, provides a consistent source of an

exceedingly active catalyst precursor for olefin metathesis. The character of the Me_2Mg – $WOCl_4$ reaction has been investigated further and an active catalyst precursor $MeWOCl_4.OEt_2$ characterized [86]. The complexes MoCl-(neopentyl)$_3$ (M = Mo or W) have been isolated from solutions which are active in olefin metathesis and, although inactive alone, these species can be converted into very active catalysts; MO(neopentyl)$_4$ complexes have also been reported [87]. The oxo alkylidene complexes, $[WO(CHCMe_3)(PEt_3)Cl_2]$ **(5)** and analogous benzylidene, ethylidene, propylidene and methylene derivatives, have been isolated and shown to be olefin metathesis catalysis. The structure of **(5)** has been determined and the geometry about the tungsten shown to be a distorted
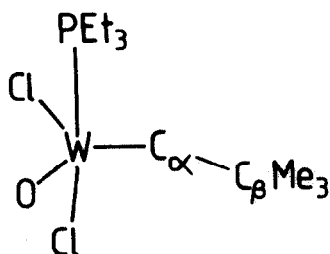
(5)

trigonal bipyramid, in which the oxo ligand (W—O = 1.661(11) Å) C_α and C_β of the neopentyl ligand (W—C_α = 1.882(14) Å) and the chloride ligand (W—Cl = 2.389(5) Å) all lie in the equatorial plane [88]. Potential energy profiles, for olefin metathesis and epoxidation involving oxo-complexes of chromium and molybdenum, have been produced using accurate *ab initio* molecular orbital methods. The results obtained suggest that, for activity, metal chlorides should have at least one "spectator" metal-oxo bond [89].

7.1.3   Oxides and homonuclear polyanions

A new determination of the vibrational molecular constants for the WO_3 molecule has been presented, on the basis of a structure with C_{3v} symmetry [90] and a mass spectrometric study of the vapour over WO_3 has indicated the presence of W_3O_9, W_4O_{12}, and W_5O_{15} [91]. An electron diffraction study of these vapours has suggested that the trimer and tetrameric species are predominant, at *ca.* 80% and 20% levels, respectively; W_3O_9 is composed of WO_4 tetrahedra linked by μ-oxo atoms to form a puckered ring [92]. Spectral sensitization by metal-free phthalocyanine films has been observed on various semiconductor electrodes, including single crystals of *n*-WO_3, and the oxidation of several solutions species achieved [93].

The nature of water in $MO_3 \cdot nH_2O$ (M = Mo or W; n = 1 or 2) has been studied by ^1H NMR spectroscopy. For half of the H_2O molecules, the interproton separation is 1.58 Å and for the other half it is 1.38 Å; the latter was attributed to the interaction of the protons with bridging oxygen atoms [94]. A stable nickel(II)- rubeanic acid coordination polymer, prepared in the interlayer space of MoO_3, has been separated by dissolving the MoO_3 layers in boiling $[NH_4]Cl$ solution [95].

The results of SCF-Xα calculations of the one-electron cross section for K-shell photoabsorption of $[MoO_4]^{2-}$ have been used to explain the profile of the X-ray absorption spectrum above and below the molybdenum K-shell ionization threshold. The first fairly intense peak on the low energy side of the rising edge is attributed to a dipole allowed transition to a bound state of primarily metal d character, the transition being allowed because of mixing with oxygen p orbitals [96]. The identification of this and other transitions for $[MoO_4]^{2-}$, and related species, marks a significant improvement in the understanding of the processes responsible for X-ray absorption edge structure, information which can be a useful fingerprint of the chemical nature of a particular atom.

The kinetics of the substitution reaction between $[WO_4]^{2-}$ and $cis-$ $[Co(en)_2(H_2O)_2]^{3+}$, to form $[Co(en)_2(OH)(WO_4)]$, have been measured and interpreted [97]. The system $H^+/[MoO_4]^{2-}$ has been investigated by Raman spectroscopy. However, contrary to earlier reports, evidence for species intermediate between $[MoO_4]^{2-}$ and $[Mo_7O_{24}]^{6-}$ could not be obtained and the amount of any such species was estimated to be < 3% [98]. Nevertheless, the results of a potentiometric investigation of the equilibria between molybdenum(VI) species present in aqueous acidic media have implied the existence of a dimeric $HMo_2O_7^-$ species under certain conditions [99]. ^{95}Mo NMR spectra of α- and β-$[Mo_8O_{26}]^{4-}$ in MeCN exhibit the *same* single narrow resonance at room temperature, implying an exchange of *all* the molybdenum atoms. A new interconversion, consistent with this and other observations for these and related polyanions, has been proposed; the mechanism is based upon concerted translations of close-packed fragments along molecular mirror planes and is reminiscent of the concept of crystallographic shear [100]. $[W_6O_{19}]^{2-}$ has been characterised by X-ray crystallography, in the $[(^tBuNC)_7W]^{2+}$ salt obtained from the reaction of $K_3[W_2Cl_9]$ with excess ^tBuNC which is promoted by a small quantity of H_2O. The anion has near perfect octahedral symmetry with dimensions similar to those reported earlier for this moiety [101].

As an extension of previous elegant work defining polyoxomolybdate-carbonyl interactions, $[OHCCHMo_4O_{15}H]^{3-}$ has been shown to react with some

acids, HX, to yield $[HCCHMo_4O_{15}X]^{3-}$. The product (6) contains a polycentric anion binding site capable of accommodating anions, X^-, having a variety of
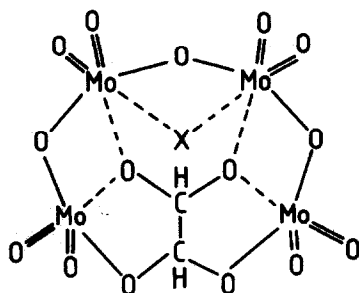
(6)

sizes and shapes; the systems for X = F and HCO_2 have been characterised by X-ray crystallography [102].

7.1.4 *Ternary oxides and heteronuclear polyanions*

The crystal structures of $Li_2WO_4(IV)$, the most dense phase amongst the four polymorphs, [103] and $CsLiWO_4$ [104] have been determined. The Raman spectrum of $Na_2W_2O_7$ has been assigned with reference to its crystal structure [105] and X-ray diffraction studies of $Na_4W_3O_{11}$ glass have been interpreted in terms of a chain structure consisting of WO_4 tetrahedra and WO_6 octahedra [106]. IR and mass spectra of Na_2MO_4 (M = Mo or W) have been examined [107]. Studies of the formation and structure of $[Mo_2O_7]^{2-}$, $[W_2O_7]^{2-}$, and $[CrMoO_7]^{2-}$ have been reported; force-field calculations for the mixed-metal anion suggest a value of 125 ° for the Cr—O—Mo angle [108]. The conditions for formation of $Mg_2Mo_3O_{11}$ have been investigated [109] and the state of H_2O in $K_2WO_6.2H_2O$, $MgWO_6.3H_2O$, and $M_2Mg(WO_6)_2.nH_2O$ (n = 3 or 4, M = K; n = 5, M = Rb or Cs) has been studied by ^1H NMR spectroscopy [110]. The structure of $Ba_3W_2O_9$ has been shown to be isomorphous with that of $Cs_3Tl_2Cl_9$ [111], the thermodynamic characteristics of Ba_3WO_6, Ba_2WO_5, and $BaWO_4$ have been determined [112] and Raman spectra have been obtained for Na_2MO_4 and $M'MO_4$ (M = Mo or W; M' = Ca, Sr, Ba, or Pb) at high pressure [113]. Revised crystallographic data have been presented for $Ca_8[Al_{12}O_{24}][WO_4]_2$ [114], the synthesis and some physical properties of $[pyH]^+$ salts of $[Ga(OH)_6Mo_6O_{18}]^{3-}$ have been reported [115], and a new heteropoly tungstate anion, tentatively formulated as $[(GaO_6)_2W_{10}O_{24}]^{6-}$, has been isolated as its guanadinium salt [116]. The crystal structure of $Tl_2W_4O_{13}$ consists of corner sharing chains of

WO_6 octahedra and the hexagonal and pentagonal tunnels bound by these chains are occupied by Tl atoms [117]. The X-ray amorphous compounds $MIn(MoO_4)_2.nH_2O$ (n = 3.5; M = Ag, Tl) and $MIn(WO_4)_2.4H_2O$ have been prepared from aqueous solutions of MNO_3, $In(NO_3)_3$, and Na_2MoO_4 or Na_2WO_4 [118].

The structure of the $[SiMo_{12}O_{40}]^{4-}$ ion has been determined in a lattice of its guanadium salt [119] and $H_4SiMo_{12}O_{40}.13H_2O$, in which the hydrate envelope contains $H_5O_2^+$ and $H_7O_3^+$ ions [120]. The structure of $K_4[\beta-SiMoW_{11}O_{40}]$.$9H_2O$ is isomorphous with that of $K_4[\beta-SiW_{12}O_{40}].9H_2O$, with the Mo atom statistically distributed on three equivalent sites [121]. These results have been discussed with respect to the $\alpha - \beta$ isomerisation of the heteropolyanions and the kinetics of this process have been reported for molybdosilicic acid [122].

Conditions and the mechanism for the solid phase synthesis of lead(II) molybdates, including the preparation of Pb_2MoO_5 crystals, have been described [123]. $Pb_3M_2MoO_9$ (M = Ni, Fe, Mn, or Sc), Pb_2MMoO_6 (M = Fe, Mn, Ca, or Hg), and Pb_2MWO_6 (M = Ca or Hg) have been prepared from their respective oxides at 35 – 50 kbar and < 700 °C [124].

[183]W NMR chemical shifts have been demonstrated to be extremely sensitive to environmental and structural perturbations therefore, interpretation of these data, in terms of charge distribution arguments, can only be made when a close structural analogy is maintained. This statement has been well illustrated for the ions $[W_6O_{19}]^{2-}$, $\alpha-$ and $\beta-$ $[SiW_{12}O_{40}]^{4-}$, $\alpha-$ $[PW_{12}O_{40}]^{3-}$, and $\alpha-$ $[(\eta5-C_5H_5)Ti(PW_{11}O_{39})]^{4-}$; a *trans* bond alternation mechanism for the charge transmissions in this last anion has been proposed to interpret the [183]W NMR chemical shifts observed [125]. $K_{11}M[PW_{11}O_{39}]_2.mH_2O$, $K_{17}M[P_2W_{17}O_{61}]_2.nH_2O$ (M = In, m = 31, n = 48; M = Rh, m = 35, n = 42) have been prepared and characterized by IR and UV spectroscopy and thermogravimetric analysis [126]. Heteropolymolybdate complexes of the type $[(ROPO_3)_2Mo_5O_{15}]^{4-}$ (where $ROPO_3H_2$ = riboflavin 5'-monophosphate, AMP, UMP, or β-glycerophosphoric acid) have been prepared as guanadinium or alkali metal salts and spectroscopically characterised. The anions are considered to have structures similar to that of $[P_2Mo_5O_{23}]^{6-}$ [127]. Ion, exchangers, which have a marked selectivity for alkali metal ions, have been prepared by precipitate formation between crown ethers and phosphomolybdic acid [128]. *In situ* IR measurements have shown that rapid and reversible [18]O exchange occurs between H_2O vapour and all of the bulk O atoms of 12-molybdophosphoric acid, with the exception of O atoms attached to phosphorus [129].

The full details, including neutron diffraction data, of the crystal structure of $[CN_3H_6]_2[Me_2AsMo_4O_{15}H].H_2O$ have been published [130,131]. The anion comprises two face- and two edge-sharing MoO_6 octahedra, in an almost

flat rectangular array, capped by the tetrahedral Me_2AsO_2 group. The oxygen atom that is asymmetrically shared by all four molybdenum atoms is protonated (O—H = 0.991(5) Å) and this hydrogen atom participates in a hydrogen bond to a water molecule which is 1.779(5) Å away from the hydrogen. The anion of $[CN_3H_6]_2$ $[MeAsMo_6O_{21}(H_2O)_6].6H_2O$ is an assembly of six MoO_6 octahedra and a tetrahedral $MeAsO_3$ group. These six octahedra constitute a ring with alternate edge- and corner-sharing and the $MeAsO_3$ group shares its oxygen atoms with the ring. Each molybdenum atom has two terminal oxygen atoms mutually *cis* and is also coordinated by a water molecule [131]. The anions of $Na_3[NMe_4]_2$ $[HMo_6As_2O_{26}].7H_2O$ consist of six MoO_6 octahedra, joined in a hexagonal ring by edge-sharing, with one AsO_4 tetrahedron attached on each side of the ring [132].

No heteropolymolybdates containing tetrahedrally coordinated molybdenum(VI) are known. This is surprising since several isopolymolybdates have been shown to contain such atoms. Therefore, it is of interest to note the synthesis of $[Ph_3Bi(MoO_4)_2]^{2-}$ and $[Ph_3Bi(MoO_4)]_x$; the former probably involves a trigonal bipyramidal geometry at bismuth, with phenyl groups occupying equatorial sites and unidentate tetrahedral oxoanions occupying the axial sites, and the latter appears to contain Ph_3Bi^{2+} units linked together by bridging MoO_4^{2-} groups [133]. Crystallographic data have been reported for Bi_6MO_{12} (M = Mo or W) [134] and solid state syntheses have been described for Bi_2MoO_6 systems [135].

$Rb_2SMo_3O_{13}$ has been prepared and the anion shown to involve double chains of MoO_6 octahedra, with three neighbouring octahedra having common vertices with an SO_4 tetrahedron [136]. $MgTeMoO_6$ has been reported and the properties of the corresponding Fe^{2+} and Ni^{2+} materials have been examined [137].

A new fluorotungstate, $H_8[H_2W_{18}F_6O_{56}]$, has been synthesised and characterised by ^{19}F and ^{1}H NMR spectroscopy. Its NMR properties are consistent with a structure in which one or more non-exchangeable protons are bound to three identical fluorines. Unlike other fluorotungstates, this anion does not belong to the 1-12 series; its X-ray powder pattern and properties lead to its classification in the 2-18 series [138]. The crystal structure of $K_5[IMo_6O_{24}].5H_2O$ has been determined and the anion is a typical Anderson – type heteropolyanion [139].

Advances made by Klemperer *et al.* and Noth in preparing η^5-cyclopentadienyltitanium polyoxoanions of molybdenum and tungsten, omitted from this review last year, *were* included in the titanium review by Fay [140]. Ion exchange properties of zirconium(IV) molybdates and tungstates have been studied [141]. The preparation and some properties of $Rb_2M(MoO_4)_3$ and $Rb_8M(MoO_4)_6$ (M = Zr or Hf) have been described [142]; $Cs_2Hf(MoO_4)_3$ has been shown to involve three non-equivalent tetrahedrally coordinated Mo atoms [143].

Details of the preparation and the unit cell of $[NH_4]_5\ [MoV_6O_{19}].12H_2O$ have been given [144], procedures leading to the formation of $[Mo_4V_2O_{19}H_3]^{3-}$, $[Mo_3V_3O_{19}H_6]^{2-}$, and $[Mo_2V_4O_{19}H_7]^{3-}$ described [145], and the structures of $[Mo_4V_8O_{36}]^{3-}$ [146] and $[Mo_8V_5O_{40}]^{7-}$ determined [147]. Several studies of the properties of vanadium-molybdenum or - tungsten heteropoly blue anions have been published and all agree that the initial reduction(s) occur at the vanadium centre(s) [148-151]. EPR and magnetic data for complexes of this type, α-1,2-$[SiV_2W_{10}O_{40}]^{6-}$ and α-1,2,3-$[SiV_3W_9O_{40}H]^{6-}$, have been obtained and these show that the unpaired electrons of these anions are restricted to two or three oxygen-bridged vanadium atoms [151]. The preparation and some spectroscopic properties of several phosphorus-vanadium-molybdenum or tungsten heteropoly compounds have been published [152] and the compounds $Te_3Mo_2V_2O_{17}$ and $TeMoV_2O_{10}$ identified in the TeO_2-MoO_3-V_2O_5 system [153]. Hexagonal perovskites with cationic vacancies in the lattice, including $Ba_4Nb_2WO_{12}$ and $Ba_4M_6WO_{27}$ (M = Nb or Ta) have been characterised by X-ray crystallography [154] and the behaviour of $H_6[SiW_{10}Nb_2O_{40}]$ in aqueous solution has been studied [155]. Phase relationships in the Cr—W—O system and thermodynamic properties of $CrWO_4$ and Cr_2WO_6 have been reported [156]; $Rb_2CrO_4.MoO_3$ and $Rb_2CrO_4.Cr_2(MoO_4)_3$ have been characterised by their powder diffraction patterns [157]. A new $Cr^{III}As^VMo^{VI}$ heteropolyacid has been claimed with these elements present in the stoicheiometry 1:4:16 [158].

The importance of the surface bound species, formed in reactions between d^6 metal carbonyl complexes and metal oxide surfaces, has stimulated a study of metal carbonyl units bound to the oxide surfaces of polyoxoanion clusters. The first adducts of this type, $[(OC)_3M(Nb_2W_4O_{19})]^{3-}$ (M = Mn or Re), have been prepared by refluxing a solution of $[N(^nBu)_4]\ [Nb_2W_4O_{19}]$ and $[(OC)_3M(NCME)_3]$-$[PF_6]$ for 2 h in MeCN. ^{17}O NMR and IR spectroscopic studies indicate that these anions comprise $M(CO)_3$ moieties bonded to a triangle of oxygen atoms on the surface of the $[Nb_2W_4O_{19}]^{4-}$ anion [159].

The enthalpies of formation of $MnWO_4$ and $FeWO_4$ have been determined [160] and the crystal structure of $Fe_2(MoO_4)_3$ described [161,162]. Magnetic susceptibility measurements on this last compound indicate that it is an antiferromagnetic material with an ordering temperature below 80 K. The relationship between the structural order and the oxygen stoicheiometry of $Sr_3WFe_2O_9$ has been investigated [163], and hexamolybdate [164] and trihetero-polymolybdate [165] anions containing iron have been isolated. The progressive substitution of iron by cobalt in $Ba_3WFe_2O_9$ leads to substoicheiometric oxides and a structural evolution [166]. $M_6[Co_2Mo_{10}O_{34}(OH)_4].nH_2O$ (M = Na, Rb or Cs) have been obtained [167] and the crystal structure of $[NH_4]_{23}$-$[NH_4As_4W_{40}O_{140}Co_2(H_2O)_2].nH_2O$ (18 < n < 20) reported. The anion of the

latter compound consists of four AsW_9O_{33} subunits linked by four extra WO_6 octahedra, with the aggregate forming a cryptate (eight oxygen) site for the $[NH_4]^+$ ion; two Co^{2+} ions are also encapsulated, each of the latter being coordinated to four oxygens of the anion and a water molecule [168]. The crystal structure of $[Li(H_2O)_4]_2 H[Co_4I_3O_{24}H_{12}].3H_2O$ has been determined and the results used to propose characteristics atoms must have to become heteropolyanion addenda; these arguments were reinforced with reference to other available structural data, $e.g.$ $K_5[CoW_{12}O_{40}].20H_2O$ [169]. $K_{10}[NiW_{17}O_{55}F_4]-$ .33H_2O$ has been isolated [170] and phase relationships in the Cu_2O–CuO–MoO_3 system have been detailed [171]. The electron exchange at the tetrahedral copper centre in $[CuW_{12}O_{40}]^{7-/6-}$ has been shown to be slow, probably as a consequence of the different stereochemical requirements of copper(I) and copper(II) in this environment [172]. The formation and unit cell characteristics of $CdWO_4$ have been described [173].

The preparation and properties of a large number of molybdates and/or tungstates containing rare earth cations have been reported this year [174-181], including studies of the crystal structures of copper(I) rare earth tungstates [175], $LiY(MoO_4)_2$ [176], $Ba_2La_2ZnW_2O_{12}$ [177], $BaNd_2(MoO_4)_4$ [178], $Na_5Ln(MO_4)_4$ (M = Mo, Ln = Tb or Lu; M = W Ln = Lu) [179], polarized IR and Raman spectra of $KDy(MoO_4)_2$ single crystals, with a demonstration of the ^{92}Mo – ^{100}Mo isotope effects [180], and the crystal structure and magnetic properties of β-$Tb_2(MoO_4)_3$ [181]. The crystal structures of $CdTh(MoO_4)_3$ [182], UO_2MoO_4 [183] and α-$UO_2MoO_4.2H_2O$ [184] have been reported. $U_5W_{13}O_{50}$ [185], $M_{16}[U(As_2W_{17}O_{16})_2]$ (M = K, NH_4, Cs or Tl) [186], and $M'(UO_2)_3(MoO_4)_4.8H_2O$ [187] have been isolated and the complexes formed between neptunium, plutonium, or americium and molybdates [188] or phosphotungstates [189] have been investigated.

7.1.5   *Thiohalides*

The preparation and some properties of MoS_2Cl_2 have been reported [190]. $[AsPh_4][WSCl_5]$ has been prepared by the reaction of $WSCl_4$ with $[AsPH_4]Cl$ in CH_2Cl_2; the $[WSCl_5]^-$ anions have C_{4v} symmetry in this lattice and the structural *trans* effect of the sulphido group is found to be rather small [191].

7.1.6   *Sulphur chemistry*

$K_2[MoO_3S]$ has been prepared by reacting $Na_2[MoO_4].2H_2O$ with KOH in aqueous solution, followed by treatment with MeOH and a powerful stream of H_2S gas, and IR and Raman spectra and X-ray powder diffraction data have been obtained [192]. This synthesis is valuable because $[MoO_3S]^{2-}$ is the only ion

of the $[MoO_nS_{4-x}]^{2-}$ (x = 0-4) series which has been difficult to isolate in a crystalline solid. Kinetic studies have been reported for the formation and aquation of these anions; aquation becomes more difficult as x decreases and this has been attributed to the larger S^{2-} ions crowding the reaction site and making associative substitution more difficult [193]. SCF-Xα calculations have successfully accounted for the energy separations and relative cross section both below and above the molybdenum K-shell ionization threshold of $[MoS_4]^{2-}$ [96].

$[MS_4]^{2-}$ and, to a lesser extent, $[Mo_xS_{4-x}]^{2-}$ (M = Mo or W; x = 1 or 2) salts are widely used as starting materials in the syntheses of a number of interesting complexes with other metal(M') centres; the typical products either contain cores comprising $M'S_2MO_xS_{2-x}$ (x = 0, 1 or 2) groups or M'_3MS_4 (or related) cubane-like moieties. As last year [1], the principal developments have occurred for M' = Fe, stimulated by the search for a better understanding of the nature and properties of the Fe—Mo—S centre (the iron-molybdenum cofactor or FeMoco) of the nitrogenase enzymes. The developments in this area will be discussed in Section 7.12.3, alongside considerations of the nitrogenase enzymes, however, these may be summarised as follows. For tetrathiomolybate complexes, achievements include full descriptions of the preparations, structures, and properties of $[S_2MoS_2Fe(SR)_2]^{2-}$ (R = Ph or C_6H_4-4-Me) and $[S_2MoS_2FeCl_2]^{2-}$ complexes [194], the isolation and spectroscopic characterisation of $[(PhS)_2FeS_2FeS_2MoS_2]^{3-}$ [195], the preparation and structural characterisation of $[Fe(S_2MoS_2)_2]^{3-}$ [196,197], $[Cl_2FeS_2MoS_2FeCl_2]^{2-}$ [198] and $[S_5FeS_2MoS_2]^{2-}$ [199]. For Fe_3MS_4 (M = Mo or W) cubane-like clusters, full accounts of the synthesis, structure, spectroscopic and redox characteristics of $[Fe_6M_2S_8(SR)_9]^{3-}$ (R = Ph, C_6H_4-4-Cl, C_6H_4-4-Me, or Et), $[Fe_6M_2S_8(SPh)_6(OMe)_3]^{3-}$, $[Mo_2Fe_7S_8(SEt)_{12}]^{3-}$ and $[M_2Fe_7S_8(SCH_2Ph)_{12}]^{4-}$ complexes have been published [200-204]. The terminal, iron-bound thiolates of the complexes $[Fe_6Mo_2S_8(SR)_9]^{3-}$ (R = Et, CH_2CH_2OH, or CH_2Ph) can be exchanged for halide by reaction with PhCOX (X = Cl or Br) [205] and quantitative dihydrogen evolution occurs upon reacting $[Fe_6Mo_2S_8(SPh)_9]^{5-}$ with PhSH [206]. A polymer-bound Fe_6MoS_8 cluster has been claimed but not fully characterised [207].

The syntheses of $[Pd(MoS_4)_2]^{2-}$, $[Pd(WS_4)_2]^{2-}$, and $[Pt(MoS_4)_2]^{2-}$ have been achieved and improved methods for the preparation of the nickel analogues and $[Pt(WS_4)_2]^{2-}$ have been developed. These anions undergo electrochemical reductions; two well-separated one-electron reversible reductions are seen for the nickel complexes, these reductions are closer together in the palladium species and the second reduction becomes irreversible, and only one reduction wave is observed for the platinum complexes but appears to be an overlap of two different electrode processes [208]. The reaction of $[(Ph_3P)_2PtCl_2]$ with

Ph_3P and $[Ph_3PMe]$ $[WO_2S_2]$ has been shown to produce $[(Ph_3P)_2PtWS_4]$ and $[(Ph_3P)_3$-$PtWOS_3]$; $[(Et_3P)_2PtWS_4]$ was similarly prepared from $(Et_3P)_2PtCl_2$ and its structure confirmed as involving an approximately tetrahedral WS_4 unit bonded at one edge to $(Et_3P)_2Pt$ [209].

$[\{(Ph_3P)Cu\}_3 Mo(S)S_3Cl]$ (7) has been prepared by extracting an aqueous solution of $[NH_4]_2$ $[MoS_4]$ with a solution of $CuCl_2.2H_2O$ and PPh_3 in CH_2Cl_2 [210]. This complex has added interest because of Cu—Mo—S interactions which can have profound effects on the metabolism of many organisms, particularly ruminant animals. The related compound $[\{(Ph_3P)Cu\}_3Mo(O)S_3Cl]$, with a terminal oxo in place of the sulphido ligand in (7) has also been characterised [211]. $[(Ph_3P)_2AgS_2WS_2Ag(PPh_3)]$ has been prepared by reacting $Ag[NO_3]$, PPh_3, and $[NH_4]_2$ $[WS_4]$ in a $CH_2Cl_2 - H_2O$ system and the structure (8) of this compound determined [212]. A third structural type $[\{(Ph_3P)Cu\}_4\{W(O)\}_2$-$S_6]$ has been identified as a product of these facile reactions [213].

$[SW_4]^{2-}$ coordinated to tungsten(IV) has been identified in $[W_4S_{12}]^{2-}$, prepared by reacting $[PP_4]_2$ $[WS_4]$ with HOAc in CH_2Cl_2 for three days. This anion consists of two central edge-linked WS_5 square based pyramids, joined over a base edge, each also sharing a basal edge with a terminal WS_4 tetrahedron [214]. The structure and properties of amorphous MS_3 (M = Mo or W) have been investigated. WS_3 is considered to involve WS_6 clusters, as in crystalline WS_2 [215]. MoS_3 cathodes in lithium cells react with < 3.8 Li per MoS_3 under constant current conditions; this type of cell has a high theoretical energy density and good reversibility [216].

The complexes $[MoO(S_2CNR_2)_2]$ (R = Me, Et, or Pr) react with elemental sulphur smoothly in refluxing Me_2CO to give $[MoO(S_2CNR_2)_2(S_2)]$ [217]; an alternative procedure involves the reaction of $[Mo_2O_3(S_2CNR_2)_4]$ with Na_2S_4 in acetone. These complexes react with nucleophiles (e.g. $P(OEt)_3$, PPh_3, MeNC, CN^-, and $[SO_3]^{2-}$) and in each case the sulphur addended nucleophile and $[MoO(S_2CNR_2)_2]$ are produced. Reaction of $[MoO(S_2CNR_2)(S_2)]$ with $MeSO_3F$ has produced the new complex $[MoO(SSMe)(S_2CNR_2)_2]^+$, containing a persulphide ligand [218].

7.1.7   Nitride, nitrene and imide complexes

$[AsPh_4]$ $[MoNF_4]$ has been prepared by the reaction of $[AsPh_4]$ $[MoNCl_4]$ with AgF in MeCN and its crystal structure has been determined; Mo-N = 1.33 Å, N-Mo-F = 98.8 ° [219]. The reaction of $[MoCl_4(bipy)]$ with an excess of Me_3SiN_3 in $ClCH_2CH_2Cl$ results in the formation of a mixture of $[MoN(N_3)(bipy)]$ and $Mo(N_2)Cl_2(bipy)$. The structure of the former is composed of monomeric units with the molybdenum having a distorted octahedral coordination; the three
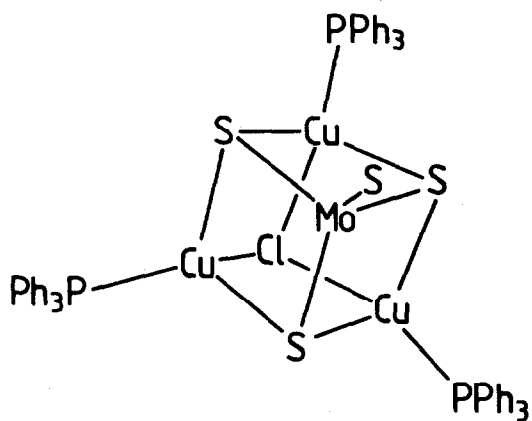
(7)
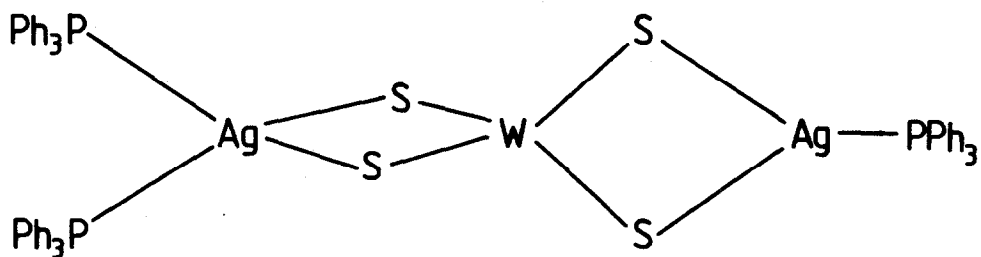
(8)
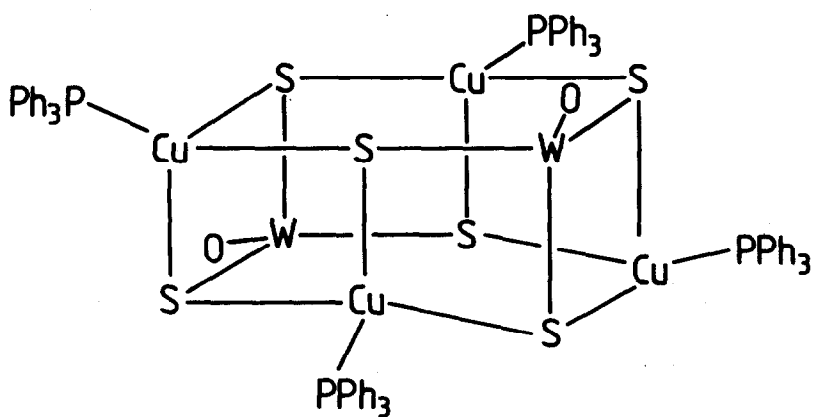
(9)

azide groups located *cis* to the nitride ligand [220]. The crystal structure of [AsPh$_4$]$_2$ [W$_2$NCl$_{10}$], a μ–nitride complex containing tungsten(VI) and (V) has been reported; the compound was obtained as a by-product of the preparation of [AsPh$_4$] ⌈WNCl$_4$] [221]. A new preparative route to WNCl$_3$ from WCl$_6$ and IN$_3$ has been described and [WNCl$_3$(POCl$_3$)]$_4$.2POCl$_3$ prepared by the reaction of WNCl$_3$ with an excess of POCl$_3$. The structure of the latter tungsten complex contains planar and almost square W$_4$N$_4$ eight-membered rings, with alternating W-N bond lengths; the distorted octahedral environment of each metal atom is completed by three terminal chloride ligands and the oxygen atom of a POCl$_3$ which is coordinated *trans* to the shorter W-N bond [222].

MoCl$_5$ in POCl$_3$ reacts with ClCN and CCl$_3$CN, in the presence of Cl$_2$ or NCl$_3$, to give [(Cl$_3$PO)Cl$_4$MoNCCl$_3$] and [(Cl$_3$PO)Cl$_4$MoNC$_2$Cl$_5$], respectively [223] and the [AsPh$_4$]$^+$ salts of the corresponding [Cl$_5$MoNR]$^-$ (R = CCl$_3$ or C$_2$Cl$_5$) ions have been reported [224]. Reaction of WCl$_6$ in POCl$_3$ with ClCN or Cl$_3$CN has been shown to lead to the formation of [(Cl$_3$PO)Cl$_4$WNR] (R = CCl$_3$ or C$_2$Cl$_5$, respectively); subsequent reaction with [AsPh$_4$]Cl produced the corresponding [AsPh$_4$] [Cl$_5$WNR] salt and the crystal structure for R = C$_2$Cl$_5$ has been determined (W-N = 1.68 Å) [225]. WCl$_6$ reacts with (CN)$_2$ diluted with N$_2$, and MoCl$_5$ reacts with (CN)$_2$ and Cl$_2$, in POCl$_3$ to yield the corresponding [(Cl$_3$PO)MCl$_4$(NCCl$_2$CCl$_2$N)MCl$_4$(OPCl$_3$)] complex [226].

Stable nitrene complexes of the type [Mo(NPh)X$_2$(S$_2$CNEt$_2$)$_2$] (X = Cl or Br) have been prepared by several different routes [227,228]. The structure of the chloride derivative has been determined at –150 °C and the short Mo—N distance of 1.734(4) Å suggests that this interaction should be described as a triple bond [228].

The reaction of MoO$_2$Cl$_2$ with *N*-(1-adamantyl)(trimethylsilyl)amine has been shown to form *trans*-[(AdNH)$_2$Mo(OSiMe$_3$)$_4$], the structure of which has been determined by X-ray crystallography (Mo-N = 2.057(3), Mo-O = 1.906(3) Å) [229].

Molybdenum and tungsten organo-dinitrogen ligand chemistry is considered in Section 7.13.

7.2 MOLYBDENUM(VI)/(V) AND TUNGSTEN(VI)/(V) OXIDES

The crystal structure of WO$_{~2.82}$ has been reported [230] and the properties of an intermediate blue oxide WO$_{2.8-2.9}$ investigated [231]. X-ray studies have shown that the blue material, isolated following the photo-reduction of [NH$_3$^{i}Pr]$_6$ [Mo$_7$O$_{24}$] in aqueous solution, contains [Mo$_{13}$O$_{40}$]$^{4-}$ (11Mo^{VI} + 2Mo^V) and [H$_4$Mo$_{12}$O$_{40}$]$^{4-}$ (Mo^{VI}) ions both having the Keggin structure, randomly distributed over the anion sites in 1:2 ratio [232].

^{1}H NMR relaxation times and spectra have been reported for the hydrogen molybdenum bronzes $H_{1.71}MoO_3$ and $H_{0.36}MoO_3$; both compounds are considered to contain proton pairs as coordinated H_2O groups in the former and pairs of HO groups in the latter [233]. The results of related studies have been described and discussed [234]. Lithium incorporation into molybdenum and tungsten oxides has been examined, with reference to the use of these materials as cathodes for lithium cells [235]. NMR studies of Na_xWO_3 ($x = 0.22 - 0.84$) [236] have been described.

The results of EPR studies of Mo^V centres in $CaMoO_4$ [237], $[NBu_4]_4-[PMo_{12}O_{40}]$ [238] and the products of the reduction of $H_3P_{12}O_{40}.xH_2O$ by ascorbic acid [239] have been reported. The reduction of the $[P_2Mo_{18}O_{62}]^{6-}$ anion by two electrons results in the mixed valence molybdenum form; use of ^{31}P and ^{17}O NMR high resolution spectroscopy has established that these electrons are trapped on two adjacent molybdenum atoms with a diamagnetic species being produced. For the one-electron reduced anion, $[P_2Mo_{18}O_{62}]^{7-}$, EPR spectra reveal the delocalization of an electron over an extensive part of the structure [240]. EPR studies have indicated localized electrons on molybdenum(V) in the reduced heteropolyanions $[AsMoW_{11}O_{40}]^{4-}$, $[AsMo_xW_{12-x}O_{40}]^{5-}$ ($x = 2$, 3, or 4) [241]. $Sb_2Mo_{10}O_{31}$ and Sb_4MoO_{31} have been prepared [242] and the crystal structure of the former determined and the Sb^{III} atom is shown to possess a stereochemically active lone pair [243]. The preparation and optical properties of a molybdotungstoselenite complex have been described [244].

The EPR spectrum of Mo^V in rutile has been obtained [245] and this spectroscopy used to establish that vanadium-molybdenum or -tungsten heteropoly blue anions involve reduced vanadium centres [148 - 151].

7.3 MOLYBDENUM(V) AND TUNGSTEN(V)

7.3.1 *Molybdenum pentafluoride and thiotrifluoride*

$[MoF_5]$ has been identified as the first product of UV photolysis of $[MoF_6]$ in an argon matrix; IR spectra were consistent with a C_{4v} structure for this molecule [24]. The thermodyamic stability of gaseous $[MoF_5]$ have been investigated and compared with those of $[MoF_6]$ [25].

A study of the species formed in the gas phase over $MoSF_3$ has shown that the predominant species are $(MoSF_3)_x$ ($x = 2$ or 3), with the monomer ($x = 1$) being only a minor constituent [246].

7.3.2   Monomeric complexes containing a terminal oxo group

SCF-Xα MO calculations have been carried out for $[MoOCl_4]^-$ and $[MoOBr_4]^-$ and the results used to interpret the chemical bonding and electronic spectra of these complexes [247]. The crystal structures of $[AsPh_4]_2[MoOCl_4]$-$[MoOCl_4(MeCN)]$ [224] and $[WOCl_3(Ph_3PO)_2]$ [248] have been determined. Single crystal EPR studies of this latter compound and $[AsPh_4][WOCl_4(H_2O)]$, diluted in the corresponding niobium analogue, have been accomplished and these data for $[WOCl_3(PPh_3O)_2]$, and previously recorded EPR data for $[MoOCl_3L_2]$ (L = Ph_3PO or hmpa), have been interpreted with the aid of an angular overlap model [248]. The preparations of $[MoOCl_3(NCPr)_2]$ [249], $[MoOCl_3(py)_2]$ [39] and $[WOCl_3(NCR)_2]$ (R = Me, Et, or Pr) [250] have been reported. This last material has been used in the synthesis of complexes such as $[WOClL]$ (H_2L = $2-C_6H_4N=CHC_6H_4-2-OH$) [250]. The preparation and crystal structure of $[MoOCl_3L']$ (L' = $2-HOC_6H_4CONHN=CHR$ where R = 2-pyridyl) have been reported; the complex has a distorted *mer*-octahedral geometry with L' being bidentate (*N,O*) [251].

The complexes (3), $[MoOL]^-$, have a very interesting redox behaviour; they undergo both one-electron oxidation and reduction, at a Pt electrode in dmf, and the corresponding oxidised products have been identified as $[MoO_2LH_2]$. The unusual stability of this monomeric molybdenum(V) centre is undoubtedly a consequence of the geometrical restraint of the ligand L [64]. Tripeptide (Gly-Gly-Met or Gly-Gly-His)-molybdenum(V) complexes have been characterised by EPR spectroscopy, following the reaction of $[NH_4]_2[MoOCl_5]$ with these tripeptides immobilized *via* the terminal glycine to a polystyrene matrix. These complexes are oxidised by $[NO_3]^-$ [69].

The UV-VIS spectra of several oxo(5,10,15,20-tetraphenylporphyrinato)-molybdenum(V) complexes $[MoO(TPP)X]$ (X = Cl, OMe, OEt, O^iPr, O^tBu) have been re-examined and the positions and intensities of the absorptions found to be extremely sensitive to the nature of the axial ligand X. The X = OH complex has been prepared by reaction of the X = Cl complex with aqueous NaOH and characterised by IR spectroscopy. The hydroxy complex reacts with CH_2N_2 to afford the X = OMe complex and concentration of CH_2Cl_2 solutions of the former in the presence of aromatic solvents preferentially yields $[\{MoO(TPP)\}_2O]$ [252]. $[MoO(TPP)X]$ (X^- = NCS^-, Br^- or O_2^-) have been reported [253] and EPR spectra for the complexes with X = Cl, OH, or OEt described and discussed [254]. Oxomolybdenum(V) complexes with corroles have been prepared and some of their spectroscopic properties measured [255].

A detailed, single crystal, EPR study of $[MoO(NCS)_5]^{2-}$, doped into different host materials, has been accomplished [256].

7.3.3   µ-Oxo and µ-sulphido complexes

A method has been described which allows precise isotropic analysis of the less labile oxygen atoms in the first coordination sphere of molybdenum(V) in aqueous media. Rapid conversion of Mo^V (*aq.*), as generated by Hg^0 reductions of Mo^{VI} in *ca.* 3M HCl solution, to $[Mo_2O_4(edta)]^{2-}$ in ^{18}O labelled H_2O, shows no appreciable transfer of solvent oxygens to the product ion. $Mo_2O_4^{2+}$ (*aq.*) contains 1.98 ± 0.03 slowly ($t_{\frac{1}{2}} \sim 100$ h at 40 °C) and 2.04 ± 0.6 rapidly ($t_{\frac{1}{2}} \sim 4$ min. at 0 °C) exchanging oxygens; IR and Raman studies have established that the former are the bridging and the latter are terminal oxo ligands of the cation. Solvent in the coordination sphere exchanges much more rapidly [257]. The ^{17}O NMR chemical shifts of the oxo ligands of molybdenum(V) and (IV) complexes are a useful means of comparing the relative Mo-O π-bond strengths, as previously established for molybdenum(VI) complexes. However, the effect of the lower oxidation states of molybdenum, upon the ^{17}O chemical shift, appears to be larger than the opposite to the effect due to increasing Mo-O bond multiplicity. For $[Mo_2O_3(Etcys)_4]$, the terminal and bridging ^{17}O resonances occur at 877 and 544 ppm (*vs.* H_2O), respectively, and for $[Mo_2O_4(Etcys)_2]$ the corresponding values are 850 and 530 ppm [258].

Interconversion of the mononuclear $[MoO(SR)_4]^-$ (R = aryl or alkyl) (10) and the binuclear $[Mo_2O_2(SR)_5Z]^-$ (Z = OMe, OEt, or SCH_2Ph) (11) anions has been shown to occur *via* redox process involving both the molybdenum and the ligand thiolate redox centres. The anions (10), R = alkyl, spontaneously convert into (11) at 25 °C [259]. Dimerization to the di-µ-oxo species

(10)   (11)
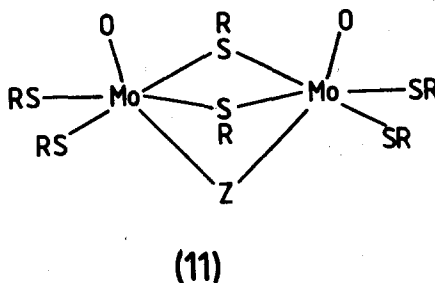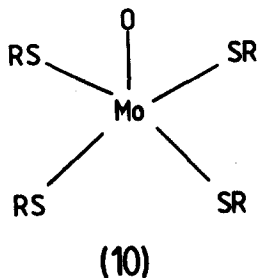
$[Mo_2O_4(cat)_2(H_2O)_2]^{2-}$ (H_2cat = catechol) occurs after $[MoO_2(cat)_2]^{2-}$ undergoes a one-electron/two proton reduction, according to the following stoicheiometry [63]; $2[MoO(H_2O)(cat)_2]^- \longrightarrow [Mo_2O_4(cat)_2(H_2O)_2]^{2-} + 2H_2cat$. Kinetic studies of the aquation of $[W_2O_4(edta)]^{2-}$ to $W_2O_4^{2+}$ (*aq.*) have been reported; the

process proceeds to completion in HCl $\geqslant 2$ mol l^{-1}. $[W_2O_4(edta)]^{2-}$ is a much stronger reducing agent than $[Mo_2O_4(edta)]^{2-}$ and oxidations of the former with $[IrCl_6]^{3-}$, $[Fe(phen)_3]^{3+}$, $[Fe(CN)_6]^{3-}$, and $[Co(bipy)_3]^{3+}$ have been investigated [260]. Electrochemical reductions of $[Mo_2O_4(edta)]^{2-}$ have been reported [71]. The crystal structure of $[pyH]_4[Mo_2O_4(NCS)_6]$ has been described and the anion involves a Mo—Mo separation of 2.582 Å [261]. The crystal structures of this compound and the $[pyH]^+$ salts of $[Mo_2O_3(NCS)_4-(C_2O_4)_2]^{4-}$, $[Mo_2O_3(NCS)_6(HCO_2)_2]^{4-}$, and $[Mo_2O_4(NH_2CH_2P(Me)O_2H)(NCS)_4]^{2-}$ have been determined in another study [262]. The magnetic susceptibilities of the complexes $Mo_2O_3L_4Cl_4$ (HL = $R_2C=NNHC=SNH_2$; $R_2 = Me_2$, Pr_2 or EtBu) have been measured [263]. A stable molybdenum(V) tripolyphosphate complex $[Mo_2O_4(P_3O_{10})_2H_n]^{n-8}$ has been identified in a ^{31}P NMR study [264] and ^1H NMR spectra reported for $[Mo_2O_4(cys)_2]^{2-}$ [265].

The tetranuclear complex $[Mo_4O_8(Me_2PO S)_4]$ has been prepared by reacting $MoCl_5$ with $Na(Me_2PO S)$ in $CHCl_3/CCl_4$. The complex consists of a highly distorted Mo_4O_4 cubane – like cluster, with each Mo atom having a terminal oxo group and the $Me_2PO S$ ligands are bidentate; the Mo atoms form two Mo_2 pairs through Mo—Mo bonding interactions. Partial substitution of the $Me_2PO S$ ligands by Me_2PO_2 has been achieved [266].

The CD spectra of fifteen μ-X-μ-Y – bis[oxo-molybdenum(V)](X = Y = O or S; X = O, Y = S) core complexes involving optically active ligands, such as (S)-cysteinate, its alkyl esters, (R)-penicillaminate, (S)-histidinate, and (R)-propylenediamine tetraacetate have been recorded. These spectra manifest two distinctive peaks with opposite signs at *ca.* 26,000 and 33,000 cm^{-1} and the sequence of the signs observed has been related to the nature of the asymmetric distortion around the Mo—Mo axis [267]. The crystal structure of μ-oxo-μ-sulphido-bis(1,2-dithiosquarate-S,S')oxomolybdate(V) has been determined with $[NBu_4]^+$ as the counterion; the anion adopts the *syn* configuration with a Mo—Mo separation of 2.700(1) Å.

The structure of $[Mo_2O_2S_2(S_2)_2]^{2-}$ (12) has been determined for its $[NMe_4]^+$
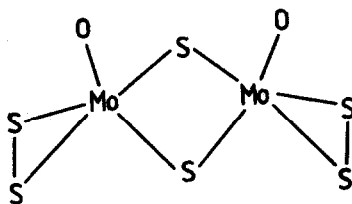
(12)

and $[NEt_4]^+$ [269] salts; the anion has essentially the same geometry in both
lattices, but in the former the $(S_2)^{2-}$ ligands are asymmetrically bonded
(Mo–S = 2.424(5), 2.432(5), 2.384(6), 2.390(5) Å) whereas in the latter the
asymmetry is slight (Mo–S = 2.409(1), 2.394(1), 2.390(1), 2.381(1) Å). The
Mo—Mo distances are 2.825(2) and 2.828(1) Å, respectively. Full details of
the crystal structure of $[NH_4]_2$ $[(S_2)_2Mo(S_2)_2Mo(S_2)_2]$.$2H_2O$ have been published;
Mo—Mo = 2.827(2) Å [270]. This compound has been shown to be a useful
synthetic intermediate for the preparation of complexes with the ${Mo_2S_4}^{2+}$
core [271]. When an aqueous solution containing $[WS_4]^{2-}$ is acidified, these
ions condense and reduction of the central atom(s) is observed. Thus,
$[S_2WS_2W(X)S_2WS_2]^{2-}$ (X = O or S) have been isolated and characterised [272].
Also, $[PPh_4]_2[WS_4]$ reacts with HOAc in CH_2Cl_2 over three days to give
$[PPh_4]_2$ $[S_2W^{VI}S_2W^V(S)S_2W^{VI}S_2]$, the anion may involve a W^V– W^V interaction
over the separation of 2.95 Å [214].

7.3.4 Complexes with metal–nitrogen multiple bonds

The crystal structure of $[AsPh_4]_2$ $[W_2NCl_{10}]$ a μ–nitrido complex containing
tungsten(VI) and (V) has been reported [221] and several complexes containing
W–N multiple bonds have been identified as products of the reaction between
$[WF_6]$ or $[WF_5(OR)]$ (R = Et or Ph) with $[Et_2NH_2]^+$ $[Et_3NH]^+$ [273].

The nature of the reaction between $[MoO(S_2P(OEt)_2)_2]$ and HN_3 has been
discussed. The decomposition of a purple intermediate, thought to be
$[Mo_2O_2(NH)(S_2P(OEt)_2)_4]$, results in the formation of $[Mo_2O_3(NH)(S_2P(OEt)_2)_2]$;
the latter involves bridging oxo and imido ligands. Reaction of this complex
with HX (X = Cl or $S_2P(OEt)_2$) produces the corresponding $[Mo_2O_2(NH_2)X$-
$(S_2P(OEt)_2)_2]$ derivative, by protonation of the imido ligands [274]. The
paramagnetic molybdenum(V) complexes $[Mo(NR)X(S_2P(OEt)_2)_2]$ (X = Cl or
$S_2P(OEt)_2$; R = Ph or tol) have been prepared from $[Mo(CO)_4Cl_2]$, $[NH_4]$-
$[S_2P(OEt)_2]$, and the corresponding aryl azide; *these* arylimido groups are stable
to protonation. The EPR spectra of these complexes are notable, since every
ligand donor atom (^{14}N, ^{31}P, and $^{35,37}Cl$) manifests a coupling to the $4d^1$
electron. $[Mo(Ntol)(S_2P(OEt)_2)_3]$ reacts with H_2S to produce the tetranuclear
complex $[Mo(Ntol)S(S_2P(OEt)_2)]_4$, which is believed to involve a Mo_4S_4 cubane –
like core, and dissociates to the dimeric complex [275].

7.3.5 Cyanide complexes

The crystal structure of $Cs_3[Mo(CN)_8]$.$2H_2O$ has been determined and a new
stereochemical configuration observed for this anion. The eight cyano groups

are arranged in a 4,4-dicapped trigonal prism about the molybdenum, with $\overline{Mo-C}$ = 2.17(2) Å [276]. The single crystal Q-band EPR spectrum of the D_{2d} anion of [NBu$_4$]$_3$[Mo(CN)$_8$] has been determined at room temperature. The sense of the anisotropy in g values ($g_{\parallel}$ > $g_{\perp}$) contradicts predictions based upon simple crystal field theory and possible reasons for this have been discussed [277]. EPR evidence has been presented for the formation of paramagnetic intermediates in the photolysis of [Mo(CN)$_8$]$^{3-}$ in MeOH solution [278] and the kinetics of reduction of this anion by [S$_2$O$_3$]$^{2-}$ have been investigated [279].

7.4 MOLYBDENUM(IV) AND TUNGSTEN(IV)

7.4.1   *Halide complexes*

The magnetic properties and nuclear γ-resonance of WF$_4$ have been obtained and the results discussed with reference to the polymeric, μ-F-bridged structure [280].[RR'PCl$_2$][WCl$_5$](R = Ph or Cl; R' = alkyl) have been prepared by the reaction of anhydrous tungsten chlorides with PhPCl$_2$ or PCl$_3$, in the presence of alkyl chlorides, and the magnetic and IR properties of the compounds have been obtained [281].

7.4.2   *Complexes with O-donor ligands*

Mo(OEt)$_4$ has been isolated as a product of the reaction between MoCl$_5$ and KOEt in EtOH. The presence of μ-OEt groups was proved by ^{1}H NMR spectroscopy and magnetic susceptibility and electronic spectral data have been interpreted in terms of octahedrally coordinated molybdenum(IV) [282]. [Mo(NMe$_2$)$_4$] reacts with 1-adamantanol (13) in Et$_2$O at room temperature to form, on standing,

(13)
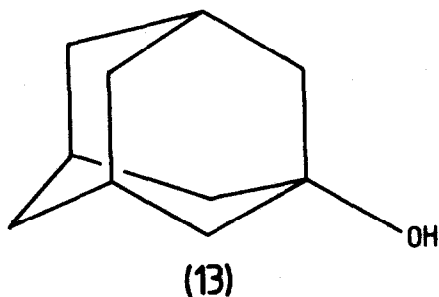
dark green crystals of [Mo(1-ado)(NHMe)$_2$]. The crystal structure of this complex involves molecules with a distorted trigonal bipyramidal environment

at the molybdenum, one alkoxo-group and the amine ligand occupying the axial sites. The difference (0.066 Å) between the Mo–O(axial) distance (1.963 Å) and the mean Mo–O(equatorial) distance (1.897 Å) is slightly less than that (0.1 Å) found between terminal axial and equatorial Mo–O distances in $[Mo_2(O^iPr)_8]$. The magnetic moment of $[Mo(1-ado)_4(NHMe_2)]$ in the solid state approximates to the spin-only value for a d^2 system [283].

New oxides containing molybdenum(IV) have been reported [284] and the structure of $Sn_{10}W_{16}O_{46}$ has been described and discussed [285].

7.4.3   Oxo and sulphido complexes

The ^{17}O NMR spectra of oxo-molybdenum complexes are useful in providing a measure of the Mo–O bond multiplicity and measurements have been extended to include molybdenum(IV); $[MoO(Et_2dtc)_2]$ and $[MoO(Et_2dtp)_2]$ (dtp = dithiophosphinate) exhibit resonances at 820 and 842 ppm (referenced to $H_2^{17}O$) [258].

Reaction of $[MoO(S_2CNR_2)_2]$ (R = Me or Et) with various acetylenes $C_2R'R''$ has been shown to produce the corresponding 1:1 complex $[MoO(S_2CNR_2)_2(C_2RR')]$. The reactions have equilibrium constants in the range ~20,000 M^{-1} (for R' = R'' = CO_2Me) to ~20 M^{-1} (for R' = R'' = H). On the basis of their IR spectra, the products are better described as complexes of molybdenum(VI), formed by oxidative addition of the acetylenic bond to molybdenum(IV). This conclusion is supported by the structure of $[MoO(S_2CNMe_2)_2(C_2(COC_6H_4-4-Me)_2)]$; the acetylenic C–C bond has a length of 1.267 Å and is perpendicular to the Mo–O bond (1.686 Å), and the Mo–C bonds are rather short (2.12 Å). Some reactions of these complexes have been described [286].

$[MoO(SCH_2CH_2PPh_2)_2]$ has been prepared by the reaction of $[MoO_2(acac)_2]$ with an excess of $Ph_2PCH_2CH_2SH$ in MeOH or toluene and the coordination geometry shown to be intermediate between triganol bipyramidal and square pyramidal. The oxo-group can be protonated with anhydrous $H[BF_4]$ in benzene to give $[Mo(OH)(SCH_2CH_2PPh_2)_2]$ but does not undergo condensation-type reactions with hydrazines even under forcing conditions [287].

The syntheses and electrochemical characteristics of some new molybdenum(IV) complexes, including $MoOCl_2L(MePPh_2)$ (L = bipy or phen) and $MoOL'(MePPh_2)$ (H_2L' = 8-hydroxy- or 8-mercaptoquinoline), have been described and all, except the last system, undergo essentially reversible one-electron oxidation [288].

$M'_3[MO(OH)(CN)_4].xH_2O$ (M' = Na or K; M = Mo or W) have been prepared by protonation of the corresponding $M'_4[MO_2(CN)_4]$ salt and the compounds characterised by vibrational and visible spectroscopy, DTA, and TGA.

Corresponding salts containing the $[M_2O_3(CN)_8]^{6-}$ anion have been isolated also [289]. Resonance Raman studies of $[W_2OBr_{10}]^{4-}$ have been reported and the $\pi \rightarrow \pi^*$ transition of the W-O-W system shown to be axially polarized; the high value of the W-O stretching force constant is indicative of multiple bond character [290].

$\{M_3XY_3\}^{n+}$ (M = Mo or W; X = a μ_3-atom $e.g.$ O, S, or F; Y = a μ_2-atom, $e.g.$ O or S, or group, $e.g.$ $MeCO_2$ or $S_2{}^{2-}$) moieties are now established as important structural elements, having a considerable integrity in molybdenum(IV) and tungsten(IV) chemistry. Further examples reported this year extend and enhance the occurrence of these centres. $Mo^{IV}(aq.)$ in 1-3M HCl or $MeSO_3H$ (obtained by reaction of $[MoO_4]^{2-}$ with $[MoCl_6]^{3-}$, followed by ion exchange separation) is suggested to contain the $[Mo_3O_4(H_2O)_9]^{4+}$ ion **(14)**, on the basis of results obtained from experiments using $H_2{}^{18}O$. The μ_2- and μ_3-oxo-groups are very slow to exchange and appear completely ($\pm$ 2%) in the $[Mo_3O_4(NCS)_9]^{5-}$ complex, precipitated by the addition of NaSCN and $[NMe_4]$ SCN to an aqueous solution containing Mo^{IV} $(aq.)$ at 0 °C [291]. A $W^{IV}{}_3O_{13}$ cluster has been suggested to occur in the six-electron-reduced form of metatungstate, $Rb_4H_8[H_2W_{12}O_{40}] . \sim 18H_2O$. This reduced anion exhibits the Keggin structure, but the tungsten atoms occupy two different positions in the WO_6 octahedra, with statistical disorder. Nine of the tungsten atoms occupy the usual position for a Keggin structure, while the three others are displaced by 0.48 Å in the direction of the centre of a W_3O_{13} group [292]. The crystal structure of $[W_3O(OAc)_6(H_2O)_3]$ $[CF_3SO_3]_4$ has been determined; the tungsten atoms form an equilateral triangle (W—W 2.747(1) Å), with two μ_2-acetato bridges per edge [293]. The first example of a μ_3-chloride atom occurring in this type of structure has been identified, in $[W_3O_3Cl_5(OAc)(P^nBu_3)_3]$ This complex, obtained upon treatment of $[W_2Cl_4(P^nBu_3)_4]$ with an excess of HOAc in a glyme-type solvent at 160 °C, involves a central $\{W_3ClO_3\}$ core ($\overline{W—W}$ = 2.609 Å) and the distorted octahedral coordination of these metal atoms is achieved by one μ_2-acetate, three phosphine and four chloride ligands [294]. The spectroscopic (XPS, UV/VIS., IR, and Raman) and cyclovoltammetric properties of $[Mo_3S(S_2)_6]^{2-}$ have been reported and interpreted in terms of a simple MO scheme involving a single Mo-Mo bond over each edge of the Mo_3 triangle [295]. This anion reacts with KCN through nucleophilic attack by CN^- on the three bridging $S_2{}^{2-}$ ligands, resulting in cleavage and S transfer; the final product of this attack, $K_5[Mo_3S(CN)_9]$ has been isolated and characterised [296].

[NEt$_4$]$_2$ [Mo(tdt)$_3$] (H$_2$tdt = 3,4-dimercaptotoluene) has been prepared by the addition of [MoOCl$_2$(MePPh$_2$)$_3$] in MeCN to H$_2$tdt in the presence of Et$_3$N, followed by precipitation with [NEt$_4$]Cl [288]. Reaction of MoCl$_5$ with (HSCH$_2$CH$_2$)$_2$S (mes) yields [Mo(mes)$_2$] (15), which possesses a trigonal prismatic geometry at the molybdenum(IV) with coordination of both mercapto and thioether

(14)   (15)
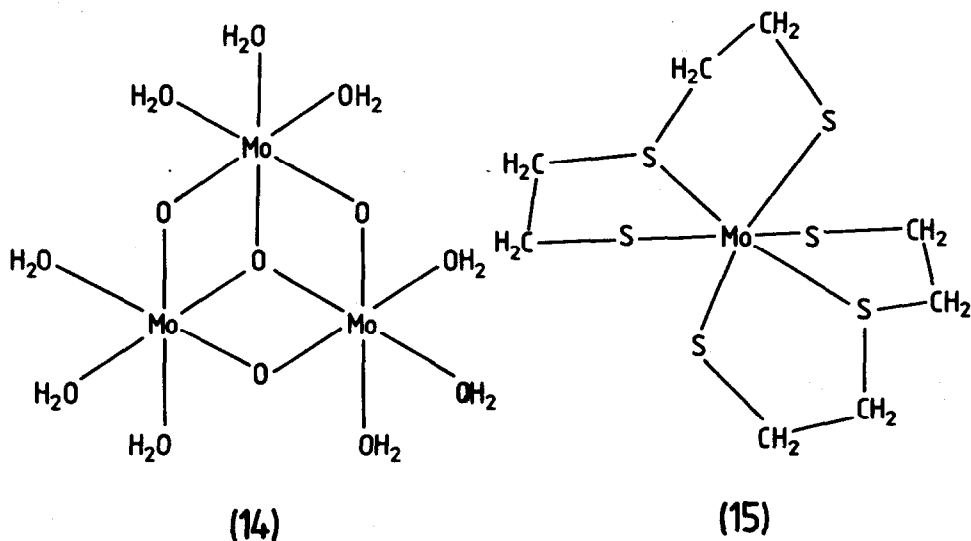
groups. This complex undergoes a reversible one-electron oxidation at + 0.53V and a reversible one-electron reduction at -1.07V [297].

WCl$_4$(SMe$_2$) reacts with Me$_3$SiSEt (1:2) in CH$_2$Cl$_2$ to form [(Me$_2$S)Cl$_2$W(SEt)$_3$-WCl$_2$(SMe$_2$)], a tungsten(III, IV) dimer, possessing a confacial bioctahedral molecular structure with three symmetrical μ$_2$-thiolate ligands. The W-W bond length is 2.505(1) Å and a short non-bonded contact (3.054(6) Å) between two of the μ$_2$-sulphur atoms occurs. The compound is EPR active (*g* = 2.00) [298].

[Mo(dtc)$_4$] has been prepared by refluxing [(η^6-C$_7$H$_8$)Mo(CO)$_3$] with (Et$_2$NCS$_2$)$_2$ in toluene under dinitrogen in the dark [299].

7.4.5   Chalcogenide phases

The dichalcogenides of molybdenum and tungsten are of special importance because of their existing and potential use as lubricants, catalyst precursors and supports (see Section 7.11), precursors of intercatalation superconductors,

and possible electrodes for photoelectrolysis. Therefore, the physical properties and the practical performance of these materials continue to attract much attention.

Electrochemical determinations of the free energy of formation of MoS_2 and WS_2 have been accomplished [300] and the magnetic properties of MoS_2 investigated [301]. X-ray emission spectra and valence-band PES of MoS_2 have been interpreted using a simple MO model based on the MoS_6 (D_{3h}) moiety 302 and the band structures of MoS_2 and α-$MoTe_2$ have been interpreted [303]. Crystal data for the full solid solution series $MoS_{2-x}Se_x$ ($0 < x < 2$) have been reported; a continuous series of solid solutions can be prepared, all having the same two-layer hexagonal structure [304].

n-Type MoS_2 and $MoSe_2$, have a direct band gap of 1.7 and 1.4 eV respectively, and each of these materials can be used as a stable photoanode for the oxidation of Cl^-, Br^-, or I^- MeCN solution. Further characteristics of these photooxidations have been reported recently [305,306]. The photochemical behaviour of n- and p-type WSe_2 single crystal electrodes in aqueous solutions containing a number of redox couples have been investigated [307] and other assessments of these materials as photoanodes have been completed [306,308].

7.4.6   *Complexes with N- and N,O-donor ligands*

The UVPES of [Mo(NR$_2$)$_4$] (R = Me or Et) contain a low energy ionization ($\sim$ 5.3 eV), which has been attributed to ionization from the essentially pure metal $4d_{x^2-y^2}$ orbital [309].

A polymer, bis(5,7-dichloro-8-quinolinolato)-5,8-quinoxalinediolato-tungsten(IV), of average molecular weight 40,000 – 50,000 Daltons has been prepared from the quinoxalinedione and a tungsten(II) intermediate. This and related systems, including molybdenum containing species, appear to have potential applications for energy-transfer [310].

7.4.7   *Octacyano complexes*

[Et$_3$NH]$_2$ [H$_3$O]$_2$ [Mo(CN)$_8$] contains anions with a coordination polyhedron which is about half-way a dodecahedron and a bicapped trigonal prism; the corresponding tungsten salt is isomorphous; the anions of [C$_6$H$_6$NO$_2$]$_4$ – [Mo(CN)$_8$], and the isomorphous tungsten derivative, have a dodecahedral structure [311].

A series of rare earth salts, Ln$_4$[Mo(CN)$_8$].nH$_2$O (Ln = rare earth), have been prepared by neutralisation of H$_4$[Mo(CN)$_8$] . 6 H$_2$O by the respective rare earth carbonate [312]. The pH dependent photolysis

of $[W(CN)_8]^{4-}$, leading to the formation of $[W(CN)_7(H_2O)]^{3-}$ and its protonated and deprotonated forms, has been investigated [313].

7.5 MOLYBDENUM(III) AND TUNGSTEN(III)

The material in this section will be organised according to the donor atom of the ligand considered to be of principal interest in the study, without subheadings and excluding complexes which involve a multiple (usually triple) bond between a pair of molybdenum(III) or tungsten(III) atoms. This latter material is included in Section 7.9.2.

Magnetic exchange within $[Mo_2Cl_9]^{3-}$ and the electronic spectra of $[M_2X_9]^{n-}$ (M = Mo or W; X = Cl or Br, n = 2, or 3) have been interpreted, [314]. A series of molybdenum(III) complexes has been examined by EPR spectroscopy and, at a temperature between 5 and 80 K, mononuclear six-coordinate systems with Cl, O, S, or N-donor ligands show broad axial or rhombic signals centred at g = 2 and 4. Substitution of ^{95}Mo results in a readily observable broadening of these signals and, for $[Mo(acac)_3]$, the estimated A values are 10 $\pm$ 1 (x,y) and 12.2 $\pm$ 0.5 (z) mK. Complexes with sulphur atoms which are part of an extended π-system (dtc, 2-aminothiophenolate, and 8-mercaptoquinolinate) have atypical EPR spectra, with all g values near 2 [315].

A gas chromatographic separation of the facial and meridional isomers of $tris$(1,1,1-trifluoro-2,4-pentanedionato)molybdenum(III) has been achieved, thus providing further evidence for the substitutional inertness of this metal centre [316]. $[Mo(H_2O)_2(cat)_2]^-$ has been obtained by electrochemical reduction of $[MoO_2(cat)_2]^{2-}$ in aqueous media pH 3.5-7; pyridine substitution at these aquo sites occurs and $[Mo(H_2O)(py)(cat)_2]^-$ and $[Mo(py)_2(cat)_2]^-$ have been identified [63]. The complex $[Mo_2(\mu-O)(\mu-C_2O_4)(alinate)_2(H_2O)_4].2H_2O$ has been prepared and characterised and isotopic exchange with $[^{14}C_2O_4]^{2-}$ investigated [317].

$[Mo(S_2CNEt_2)_3]$ has been prepared by refluxing $[(\eta^6-C_7H_8)Mo(CO)_3]$ with $(Et_2NCS_2)_2$ in toluene under dinitrogen in daylight [299]. The synthesis of $[Mo(S_2P(OEt)_2)_3]$ from $[Mo(CO)_4Cl_2]$, $HS_2P(OEt)_2$, and aryl azides has been described. This compound reacts with azobenzene in Et_2O containing HCl to form $[MoCl(S_2P(OEt)_2)_3]$ and benzidine rearrangement products, and with azobenzene in MeOH to produce $[Mo(OMe)_2(S_2P(OEt)_2]$ and hydrazobenzene [318].

A mixed oxidation state, dimeric tungsten(III,IV) compound, $[(Me_2S)Cl_2W(SEt)_3WCl_2(SMe_2)]$, has been prepared by the reaction of $WCl_4(Me_2S)_2$ and Me_3SiSEt (1:2) in CH_2Cl_2 solution (see Section 7.4.4) [298]. This compound forms part of an important study of the degredation of thiolate tungsten halide

complexes (see also [28] and Section 7.1.1), and a more extensive account of this type of reaction has been given. Thus, WCl_4L_2 (L = Me_2S or tetrahydrothiophene) reacts with Me_3SiSR (R = Me, Et, $PhCH_2$, ^iBu, or ^tBu) in CH_2Cl_2 to form $WCl_3(SR)L_2$; these complexes could not be isolated and, except for R = ^tBu, three products were obtained, one of which was $[WCl_2(\mu - SR)L]_2$ [319].

Details of the crystal structures of $[MoX_3(pic)_3]$ .0.5pic (X = Cl or Br; pic = 4-methylpyridine) [320] and $[pyH][WBr_4(py)_2]$ [321] have been reported. Molybdenum(III) forms the trischelated complexes $[Mo(LH)_3]X_3$ and the salts $[Mo(LH)_2X_2]^+$ $[Mo(LH)X_4]^-$ with 2-(2'-pyridyl)benzimidazole (LH) in the presence of anions (X = Cl, Br, or NCS) [322].

The crystal structure of $NaK_3[Mo(CN)_7].2H_2O$ involves the molybdenum(III) in a relatively undistorted pentagonal bipyramidal coordination geometry, with $\overline{Mo-C}$ = 2.160(3) $\overset{o}{A}$. Spectroscopic studies indicate that this geometry is maintained in aqueous solution, however, the symmetry of the anion may be lower in the lattice of $K_4[Mo(CN)_7].2H_2O$ [323]. Aerial oxidation of $K_6[Mo_2S_2(CN)_8].4H_2O$ in H_2O has been shown to lead to the formation of the diamagnetic, purple complex $[Mo(\mu_4 - S_2)(\mu_2 - SO_2)(CN)_8]^{4-}$ (16). In this complex, each molybdenum has a distorted pentagonal bipyramidal coordination

(16)
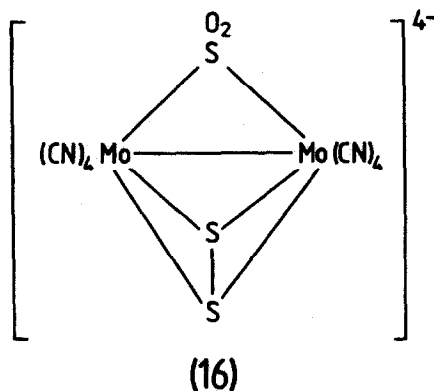
geometry, excluding any metal-metal bonded interaction over the Mo—Mo separation of 2.730(4) $\overset{o}{A}$ [324].

7.6 MOLYBDENUM(II) AND TUNGSTEN(II)

As with the previous section, this material will be presented without

subdivision and those studies advancing the knowledge of the chemistry of complexes containing a multiple (typically quadruple) bond between a pair of molybdenum(II) or tungsten(II) atoms, will be included in Section 7.9.3.

Carbonylation of [Mo₂(O^{t}Bu)₆] under mild conditions has been shown to lead to the formation of the green, air-sensitive compound [Mo(O^{t}Bu)₂(py)₂ - (CO)₂]. This complex involves mutually *trans* O^{t}Bu and mutually *cis* py and CO groups and is remarkable in that the ν(C–O) stretches appear at 1908 and 1768 cm^{-1}; the average ν(C–O) values (1838 cm^{-1}) is the lowest so far observed for a pair of *cis*-carbonyl groups coordinated to a molybdenum(II) centre [325]. The geometry of this complex has been included in an MO analysis, using extended Hückel calculations, of the electronic factors which influence the geometry of six-coordinate M(CO)₂L₄ and M(NO)₂L₄ complexes. These calculations have been stimulated by the novel observation that [Mo(CO)₂- (S₂CN^{i}Pr₂)₂] has a trigonal prismatic coordination geometry, previously unknown for metal carbonyl derivatives and with no obvious inter-ligand interactions favouring such a structure [326]. The crystal and molecular structure of [W(CO)₃(S₂CNMe₂)₂] has been determined; the tungsten has a seven-coordinate 4:3 "piano-stool" geometry with two carbonyl (*C*) and two dithiocarbonate (*S*) donor atoms in one plane and one carbonyl (*C*) and two dithiocarbamate (*S*) in the other. Dynamic ¹³C NMR studies of [W(CO)₃(S₂CNR₂)₂] (R = Me or Et) have revealed two distinct intramolecular rearrangement processes, the nature of which have been discussed with reference to the structure of [W(CO)₃(S₂CNMe₂)₂] in the solid state [327]. Tungsten alkyne complexes of the type [W(CO)(R'C≡CR'')- (S₂CNR₂)₂] (R = Me or Et) have been prepared for R' = R'' = H, Me, Et or Ph, and R' = H, R'' = Ph, by allowing the [W(CO)₃(S₂CNR₂)₂] complex to react with the appropriate alkyne in toluene at a ambient temperature. C₂H₄ does not react with [W(CO)₂(S₂CNR₂)₂] under these conditions and phosphine (PPh₃, PEt₃; P^{n}Bu₃, and P(OEt)₃) displace only one CO group, to form the corresponding [W(CO)₂L(S₂CNR₂)₂] product. With Ph₂PC≡CPPh₂, the reaction proceeds in two steps; the initial one involves phosphorus ligation with the displacement of one CO group and, subsequently, another CO group is lost and η²-alkyne coordination occurs. Detailed ¹H and ¹³C NMR studies have been accomplished for these complexes and the characteristics of alkyne rotation have been defined; also, a correlation of the ¹³C NMR chemical shift and the bonding of the alkyne ligand in these and related complexes has been noted [328].

[cpM(CO)₃Cl] and [M(CO)₃(PPh₃)₂Cl₂] (M = Mo or W) react with SPPh₂H to form [cpM(CO)₂(η²-SPPh₂)] and [M(CO)₂(PPh₃)(η²-SPPh₂)₂], respectively. An X-ray crystallographic study has revealed that [Mo(CO)₂(PPh₃)(SPPh₂)₂] has a seven-coordinate, pseudo-pentagonal bipyramidal geometry [329]. Nitrobenzene reacts with [Mo(CO)₂(S₂CNEt₂)₂] in CH₂Cl₂ to yield the previously reported

compound, [MoO(ONPh)(S$_2$CNEt$_2$)$_2$]. Reduction of this compound with PPh$_3$ yields [Mo(ONPh)(S$_2$CNEt$_2$)$_2$], which may also be prepared by reacting nitrosobenzene and [Mo(CO)$_2$(S$_2$CNEt$_2$)$_2$]. This new compound can be considered to be a valence isomer of the molybdenum(VI) complex [MoO(NPh)(S$_2$CNEt$_2$)$_2$] [330].

The structural complexities of seven-coordinate complexes involving both hard and soft donor ligands have been illustrated by the determination of the crystal structures of [W(CO)$_3$Cl(dcq)(PPh$_3$)] and [W(CO)$_2$(dcq)$_2$(PPh$_3$)] (dcq = 5,7-dichloro-8-quinolinate); in each case the coordination sphere about the metal does not approximate to any idealized geometry [331]. The crystal structures of [MI$_2$(CO)$_3${Ph$_2$P(CH$_2$)$_n$PPh$_2$}].xCH$_2$Cl$_2$ (M = Mo, n = 2, x = 1; M = Mo, n = 3, x = 0; M = W, n = 1, x = 0) have been determined. For the compounds with n = 2 or 3, the bidentate ligand has a large bite and the metal atom's stereochemistry is that usually found for complexes of this type, *i.e.* a capped trigonal prism with the bidentate ligand spanning one of the prism edges. For the compound with n = 1, the small ligand bite leads to a novel stereochemistry, a pentagonal bipyramid with the bidentate ligand spanning one of the pentagonal edges [332]. The molecular dynamics of [MoI(CO)$_2$(Me$_2$PC$_2$H$_4$PEt$_2$)$_2$]I have been investigated by ^{13}C and ^{31}P NMR spectroscopy and the results seen to be consistent with a non-dissociative, polytopal mechanism of interconversion between the two forms of the capped trigonal prismatic cation (17) [333].

(17)
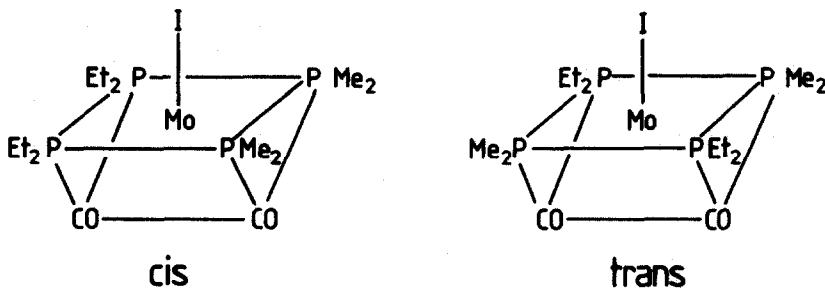
7.7   TUNGSTEN(0)

Carbonyl, dinitrogenyl and other formally molybdenum(0) and tungsten(0) complexes will be described in subsequent sections.

The new compound [W{P(OMe)$_3$}$_6$] has been prepared by agitating a mixture of WCl$_4$(py)$_2$.2py in C$_6$H$_6$ with K/KI at 80 °C for 2 h, removing the solvent *in vacuo* and adding an excess of P(OMe)$_3$. This material is analogous to the previously reported molybdenum compound but is much more susceptible to phosphite dissociation, and photolysis of hexane solutions in a dihydrogen atmosphere has yielded three new tungsten hydrides (see Section 7.8) [334].

7.8   HYDRIDE COMPLEXES

The products of hydrogenolysis of [WMe$_6$] in the presence of a tertiary phosphine are dependent upon the size of the ligand. Thus, while PPh^{i}Pr$_2$ an P^{i}Pr$_3$ yield the corresponding [WH$_6$(PR$_3$)$_3$] complex as the principal product, PMe$_2$Ph affords mainly [WH$_4$(PMe$_2$Ph)$_4$]. [WH$_6$(PPh^{i}Pr$_2$)$_3$] has been shown by ^{31}P NMR spectroscopy and X-ray diffraction to have approximate C_{2v} symmetry in the solid and in solution [335].

The crystal structures of [WH$_4$(PEtPh$_2$)$_4$] [336] and [WH$_4${P(O^{i}Pr)$_3$}$_4$] [337] have been determined and vibrational spectra reported for these and several related molybdenum and tungsten complexes [338]. The photolysis of [MoH$_4$(diphos)$_2$] and [MoH$_4$(PMe$_2$Ph)$_4$] under an N$_2$ atmosphere proceeds with the loss of 2H$_2$ to form *trans*-[Mo(N$_2$)$_2$(diphos)$_2$] and *trans*-[Mo(N$_2$)$_2$(PMe$_2$Ph)$_4$], respectively [339].

Photolysis of hexane solutions of [W{P(OMe)$_3$}$_6$] in an atmosphere of H$_2$, rapidly yields a mixture of three new higher coordinate tungsten hydrides, [WH$_2${P(OMe)$_3$}$_5$], and [WH$_4${P(OMe)$_3$}$_4$], and a very small amount of (probably) [WH$_2${P(OMe)$_3$}$_3${P(OMe)$_2$}$_2$] [334]. The crystal and molecular structure of [MoH{P(OMe)$_3$}$_4$(O$_2$CCF$_3$)] has been reported and the molybdenum atom found to have an approximate pentagonal bipyramidal coordination geometry, with the hydride ligand occupying an equatorial site. The molecule is stereochemically non-rigid and the dominant process appears to involve a non-pairwise exchange between inequivalent phosphorus sites [340].

[MoCl$_3$(thf)$_3$] reacts with PMe$_3$ in Et$_2$O or thf to form [MoCl$_3$(PMe$_3$)$_3$] which reacts with Na[BH$_4$] to yield [MoH(BH$_4$)(PMe$_3$)$_4$], whose structure has been determined by X-ray crystallography. The molecular unit involves a distorted octahedral environment at the molybdenum, with the bidentate [BH$_4$]$^-$ group considered to occupy one vertex, and Mo—H = 1.63 Å [341].

$[\mu-H\{Mo(CO)_4PMePh_2\}_2]^-$ has been obtained by reacting $[\mu-H\{Mo(CO)_5\}_2]^-$
with a ten-fold excess of $PMePh_2$ and its structure determined for the
$[NEt_4]^+$ salt; the Mo....Mo separation in the three-centre, two-electron
hydride bridge is 3.443(1) $\overset{o}{A}$, significantly shorter than that (3.7436(1) $\overset{o}{A}$)
in $[\mu-H(Mo_2(CO)_9PPh_3)]^-$ and only 0.02 $\overset{o}{A}$ longer than in $[\mu-H\{Mo(CO)_5\}_2]^-$
[342].   IR and Raman spectra of $[\mu-H\{M(CO_5)_2\}]^-$ and $[\mu-H\{M_2(CO)_9(NO)\}]$
(M = Mo or W) have been reported [343].   A combined structural and
spectroscopic study has been performed to examine the stereochemical
consequences resulting from the deprotonation of the bent Mo-H-Mo bond in
$[(\mu-H)(\mu-PMe_2)\{cp(Mo(CO)_2\}_2]$; the most significant structural change is
the reduction of the Mo—Mo separation from 3.262(2) $\overset{o}{A}$ in the hydride to
3.157(2) $\overset{o}{A}$ in $[(\mu-PMe_2)\{cpMo(CO)_2\}_2]^-$ [344].   The interaction of $[Mo_2(O_2CMe)_4]$
with Na/Hg in thf, in the presence of an excess of PMe_3 under H_2 (3 atm.),
yields $[(\mu-H)_2\{MoH(PMe_3)_3\}_2]$; the Mo-Mo separation at 2.194(3) $\overset{o}{A}$ is typical
of a quadruple bond. This compound reacts readily with alkyl halides, CO,
olefins, acetylenes, and H_2S [345].

$[(cp)_2MH_2]$ (M = Mo or W) reacts with $[RhH_2(PPh_3)_2(Me_2CO)_2]$ in Me_2CO or
CH_2Cl_2 at room temperature to yield the corresponding $[(cp)_2M(\mu-H)_2Rh(PPh_3)_2]$
complex. The crystal structure of the tungsten derivative has been determined
and the W—Rh distance shown to be 2.721(8) $\overset{o}{A}$; large metal-H coupling constants
to both metals are manifest in the ^1H NMR spectrum and confirm the structural
assignment of two bridging hydride ligands [346]. $[(cp)_2MoH_2]$ reacts with
MX_2 (M = Zn or Hg; X = Cl or I) to produce $(cp)_2MoH_2 \cdot MX_2 \cdot S$ (S = dmf or thf)
or the unsolvated polymer [347]. $[Mn_2(CO)_{10}]$ catalyzes the exchange between
D_2 and $[(cp)_2WH_2]$ [348] and UV photolysis of $[(cp)_2MH_2]$ (M = Mo or W) in an
argon matrix at 10 K leads to the loss of H_2 and the formation of $[(cp)_2M]$
[349].   Transient, paramagnetic radical cations have been detected as
products of the electrochemical oxidation of tungstanocene hydrides. The
anodic oxidation of $[\{(cp)_2WH_2]$ yields $[\{cp_2W\}_2H_3]^+$; a crystal structure
determination of its $[ClO_4]^-$ salt has revealed an unusually long W—W
distance of 3.628 $\overset{o}{A}$ and a symmetrical conformational distortion about each
cp-W-cp unit, which strongly suggest the presence of both bridging and terminal
hydrides in the structure cpW(H)-H-(H)Wcp [350]. Photoinduced insertion of
tungsten into aromatic and aliphatic C-H bonds has been developed using
$[(cp)_2WH_2]$ [351], $[(cp)_2WMe(H)]$ has been prepared and its reactions studied
[352], and the synthesis and reactions of $[\{(cp)_2MoHLi\}_4]$ have been reported
in full [353]. The crystal structure of $[(cp)_2Mo(H)CO][cpMo(CO)_3]$ has been
determined [354] and $[(cp)Mo(CO)_2H(L)]$ (L = $Ph(H)P(OCH_2CH_2)_2N$) has been
reported [355].

7.9 COMPLEXES CONTAINING ONE OR MORE METAL-METAL BONDS

7.9.1 *Higher oxidation state complexes*

Several of the molybdenum(V) dimeric complexes reported this year formally
involve a single Mo—Mo bond across a di-μ-oxo or -sulphido-bridge; these
include $[pyH]_4$ $[Mo_2O_4(NCS)_6]$ (Mo—Mo = 2.582 Å) [261] and the $[NMe_4]^+$ and
$[NEt_4]^+$ salts of $[Mo_2O_2S_2(S_2)_2]^{2-}$ ($\overline{Mo—Mo}$ = 2.828(2) Å) [269]. Similar
metal-metal bonding considerations would appear to apply in the anions of
$[NH_4]_2$ $[(S_2)_2Mo(S_2)_2Mo(S_2)]$.$2H_2O$ [270], $[PPh_4]_2$ $[S_2WS_2W(S)S_2W(S)S_2WS_2]$
[214], and $[PPh_4]_2$ $[S_2WS_2W(X)S_2WS_2]$ (X = O or S) [272], and across two of
the faces of the distorted cubane-like core of $[Mo_4O_8(Me_2POS)_4]$ [266].
The occurrence of direct metal-metal interactions in the complexes of $[MS_4]^{2-}$
and in $(\{M'_3MS_4\}$ (M = Mo or W; M' = Fe, Cu or Ag) [194-213] also seems likely.

The Mo—Mo separation of 2.730(4) Å in $[PPh_4]_4$ $[Mo_2(\mu_4-S_2)(\mu_2-SO_2)-$
$(CN)_8]$.$6H_2O$ implies the existence of a single metal-metal bond between these,
formally, molybdenum(III) atoms [324] and the possibility of a tungsten-
tungsten bond of fractional order (*e.g.* 2.5) in the tungsten(III,IV) compound
$[(Me_2S)Cl_2W(SEt)_3WCl_2(SMe_2)]$ [298] seems a realistic possibility.

The description [356] of the metal-metal bonding interactions in
$\{M^{IV}_3XY_3\}^{n+}$ (M = Mo or W, X = a μ_3-atom; Y = a μ_2-atom or group) has gained
general acceptance. Further examples of this class reported this year include,
$[W_3O(OAc)_6(H_2O)_3]$ $[CF_3SO_3]_4$ [293], $[W_3O_3Cl_5(OAc)(P^nBu_3)_3]$ [294],
$K_5[Mo_3S_4(CN)_9]$ [296], and the W_3O_{13} cluster identified in the six-electron-
reduced metatungstate $Rb_4H_4[H_2W_{12}O_{40}]$.~$18H_2O$ [292].

7.9.2 *Complexes with a metal-metal triple bond and their derivatives*

The generalized molecular orbital approach has been used to investigate
the bond energy and conformational preferences of Mo≡Mo bonds. The results
obtained lead to the conclusions that, in the hypothetical complex $[Mo_2H_6]$,
D(Mo≡Mo) = 526 ± 63 kJ mol^{-1}. Also, subsequent to predictions [357], based
on extended Hückel calculations, that Mo≡Mo and W≡W systems would prefer to be
eclipsed, it has been pointed out that this preference is slight (*ca.*
4.2 kJ mol^{-1}) and only obtains if correlation effects are neglected. When
correlation is included, this small preference vanishes and thus, the
conformation of M_2L_6 (M = Mo or W) complexes should be determined solely by the
ligands [358]. More details of the UVPES of $[Mo_2L_6]$ (L = OCH_2CMe_3, NMe_2, or
CH_2SiMe_3) have been given and the results interpreted with the aid of Xα-SCW

calculations. The results of these calculations have been used to further dispute the proposal [357] that the eclipsed rotational conformer should be preferred to the staggered conformer for small ligands [359]. The diamagnetic anisotropies of the metal-metal triple bonds in $[M_2(NMe_2)_6]$ (M = Mo or W) have been estimated as -142×10^{-36} and -156×10^{-36} m^3 (molecule)$^{-1}$, from ^{1}H NMR measurements [360].

A valuable experimental contribution to the continuing debate concerning the conformation of ligands in M_2L_6 dimers is the definition of an eclipsed geometry for $[Mo_2(MeNCH_2CH_2NMe)_3]$, over the Mo—Mo separation of 2.214(3) Å [361]. Also, the synthesis of 1,2-$[Mo_2X_2(CH_2SiMe_3)_4]$ (X = Me, O^iPr, or O^tBu), 1,1-$[Mo_2(NMe_2)_2(CH_2SiMe_3)_4]$, and 1,1-$[Mo_2(NMe_2)(O_2CNMe_2)(CH_2SiMe_3)_4]$, have led to the first direct observation of rotation about Mo≡Mo bonds *and* alkyl transfer between molybdenum atoms in these dimers [362]. The reaction of hexane solutions of 1,2-$[Mo_2Br_2(CH_2SiMe_3)_4]$ with $LiNMe_2$ or $HNMe_2$ gives 1,1- or 1,2-$[Mo_2(NMe_2)(CH_2SiMe_3)_4]$, respectively, which once formed do not isomerize readily [363].

$[Mo_2(O^tBu)_6]$ reacts with CO at room temperature and 1 atm. to form $[Mo(CO)_6]$ and $[Mo(O^tBu)_4]$; the reaction proceeds *via* the slow and reversible formation of $[Mo_2(O^tBu)_6(\mu-CO)]$ which involves a Mo=Mo bond of length 2.489(1) Å. This complex has been characterised by a series of spectroscopic measurements [364]. The analogous carbonylation of $[Mo_2(O^iPr)_6]$ also yields $[Mo(CO)_6]$ but proceeds to give the dinuclear molybdenum(IV) complex $[Mo_2(O^iPr)_8]$; this and related chemistry has been described and discussed [325]. A full account of the preparation and some reactions of $[CrMo(O^iPr)_6-(NO)_2]$ has been published [365], and the synthesis of $[Mo_2(O^iPr)_6(HNMe_2)_2(NO)_2]$, from $[Mo_2(O^iPr)_6(NO)_2]$ and $HNMe_2$ has been described [366].

$[M_2R_2(NMe_2)_4]$ (M = Mo or W; R = Me, Et, ^iPr, ^nBu, ^tBu, or CH_2CMe_3) have been prepared and their thermal stabilities and ^{1}H NMR spectra investigated; the complexes appear to be stable with respect to β-elimination. In hydrocarbon solutions, all of the compounds react with CO_2 to give selective insertion into the M-N bond; the molybdenum complexes afford the quadruply bonded dimers $[Mo_2(O_2CNMe_2)_4]$ but the corresponding reactions proceed differently for the tungsten systems to give, as yet, uncharacterised products [367].

$[Mo_2Cl_8]^{4-}$ reacts with $(F_2P)_2NMe_2$ to give $[Mo_2(F_2PN(Me)PF_2)_4Cl_2]$, which involves four μ_2-phosphine ligands and two axial chloride ligands bonded to an Mo_2 centre, with a metal-metal bond of length 2.470(1) Å. This molecule is of a new, and so far unique, type with a Mo-Mo triple bond arising from molybdenum(I) atoms, each forming a moderately strong axial bond to a chloride ligand [368].

7.9.3   Complexes with a metal-metal quadruple bond

The standard enthalpies of formation of [$Mo_2(OAc)_4$], [$CrMo(OAc)_4$], and [$Mo_2(OAc)_2(acac)_2$] have been determined by solution reaction calorimetry and the values used to obtain an estimate of D(Mo≡Mo) as 334 kJ mol^{-1} [369]. Calculations of the electronic structure and the Mo≡Mo bond energies in [Mo_2Cl_8]$^{4-}$ and [$Mo_2(O_2CH)_4$] have been published [370]. The assignment of the UVPES spectra of [$Mo_2(mhp)_4$] and [$Mo_2(mhp)_2(OAc)_2$] (Hmhp = 6-methyl-2-hydroxypyridine) have been aided by carrying out an *ab initio* MO calculation for the enol form of 2-hydroxypyridine. Clear evidence was obtained for the existence of a stronger Mo≡Mo bond in [$Mo_2(mhp)_4$], as compared to [$Mo_2(OAc)_4$] [371]. The crystal structure and polarized, low-temperature electronic absorption spectrum of [$Mo_2(L$-leucine$)_4$]$Cl_2(pts)_2$.$2H_2O$ (Hpts = 4-toluene-sulphonic acid) have been reported; the conclusion reached in this study is that the δ → δ* assignment of the lowest energy absorption of this and related complexes is consistent with all relevant experimental data [372].

A new, convenient, and efficient route to the formation of $Mo_2$$^{4+}$ complexes has been described, involving: (i) electrolytic reduction of molybdenum(VI) in HCl to form [$MoCl_6$]$^{3-}$, (ii) condensation of this anion to produce [Mo_2Cl_9]$^{3-}$, and (iii) quantitative reduction of the latter by a Jones reductor to produce the $Mo_2$$^{4+}$ species [373]. The synthesis and structural characterisation of complexes containing the $Mo_2$$^{4+}$ moiety continues unabated. This year, these characterisations include the relatively straightforward compounds, [pipH]$_2$[$Mo_2Br_6(H_2O)_2$] (Mo-Mo = 2.123(2) Å) [374], [$Mo_2(O_2CH)_4$].H_2O (Mo-Mo = 2.091(1) Å in the anhydrate and 2.100(1) Å in the dihydrate) [375], and [$Mo_2(OAc)_4$].NaOAc.HOAc (Mo-Mo = 2.093(1) Å) [376].

[$Mo_2(O_2CCF_3)_4$] catalyses the anti-Markovnikov addition of CF_3CO_2H to propylene in benzene at 50 °C, with a selectivity of >90% at optimum conditions [377]. The unique capacity of the $Mo_2$$^{4+}$ cation to form complexes with polypeptide ligands, in which only the carboxyl terminus is coordinated and the rest of the zwitterionic molecule is left conformationally free, has been described. This principal has been illustrated by the isolation and structural characterisation of [$Mo_2(glycylglycine)_4$]Cl_4.$6H_2O$ (Mo-Mo = 2.106(1) Å) [378].

The reactions of [$M_2(mhp)_4$] (M = Mo or W; H mhp = 6-methyl-2-hydroxy-pyridine) with gaseous HX (X = Cl or Br) have been investigated and the reaction products included [Mo_2X_8]$^{4-}$ and $W_2X_4(OMe)_2(MeOH)_4$ [379]; [Mo_2Cl_4(2,6-dimethylpyrazine$)_4$] has been prepared [380] and the crystal structure of [$Mo_2Cl_4(Et_2S)_4$] (Mo-Mo = 2.144(1) Å) has been reported [381].

The reaction of [Mo$_2$(OAc)$_4$] with the anion of N-(2-pyridyl)acetamide gives [Mo$_2${(C$_5$NH$_4$)NC(O)Me}$_4$]; this compound involves the ligands coordinated through two nitrogen atoms and possesses the shortest Mo≡Mo bond length, 2.037(3) Å, so far observed [382]. Other such dimers which have been structurally characterised by Cotton et al. include, [Mo$_2${PhNC(O)Me}$_4$] (Mo-Mo = 2.086(2) Å) [383], [Mo$_2${(2,6-xylyl)NC(O)Me}$_4$].2CH$_2$Cl$_2$ (Mo-Mo = 2.083(3) Å) in which the CH$_2$Cl$_2$ molecules occupy axial positions [384], [Mo$_2${2-xylylNC(O)-H}$_4$].2thf(Mo-Mo = 2.113(1) Å) with axial thf molecules, [Mo$_2${PhNC(O)CMe$_3$}$_4$] (Mo-Mo = 2.070(1) Å) [385], [Mo$_2$(OAc)$_2${PhNCMeCHC(O)Me}$_2$] (Mo-Mo = 2.131(1) Å) [386] and [Mo$_2${Me$_2$P(CH$_2$)$_2$}$_4$] (Mo-Mo = 2.082(2) Å) [387]. Cotton et al. have also reported the synthesis and structural characterisation of the homologous molybdenum and tungsten complexes [M$_2$(chp)$_4$] (H chp = 6-chloro-2-hydroxypyridine; Mo-Mo = 2.085(1) Å and W-W = 2.177(1) Å). These metal-metal bond lengths are significantly longer than in the corresponding mhp complexes, suggesting that inductive effects may play an important role in determining such M-M bond lengths [388]. [W$_2$(dmhp)$_4$] (H dmhp = 2,4-dimethyl-6-hydroxypyridine) reacts with Li[(PhN)$_2$N] to form [W$_2$(dmhp)$_2${(PhN)$_2$N}$_2$], which has been structurally characterised as its thf solvate (W-W = 2.169(1) Å) [389]. A breakthrough in the preparation of ditungsten(II) complexes has been achieved, by reacting WCl$_4$ suspended in thf at -20 °C in the presence of phosphines, to yield [W$_2$Cl$_4$(PR$_3$)$_4$] compounds. These materials are stable in air at room temperature [390] and the complexes for (PR$_3$)$_4$ = (PMe$_3$)$_4$, (dmpe)$_2$, or (dppe)$_2$ have been structurally characterised and the W-W distances range from 2.262 to 2.314 Å [294].

The complexes [Mo$_2$(O$_2$CCF$_3$)$_4$(L)$_2$] (where L = MePh$_2$P, Ph$_3$P, (cych)$_3$P, ^{t}Bu$_3$P, (Me$_3$Si)$_3$P, Me$_3$PO, quinuclidine; Me$_3$P, or Me$_2$PhP) have been prepared and classified according to whether the ligand L is axially (first group) or equatorially coordinated (second group), on the basis of ^{31}P{^{1}H} NMR spectroscopy [391]. Similar spectroscopic studies have led to the assignment of the stereochemistry of [Mo$_2$(OAc)$_2$(NR$_2$)(PR'$_3$)$_2$] (R$_2$ = (SiMe$_3$)$_2$, (SiMe$_2$H)$_2$, or (SiMe$_3$)(Me); R'$_3$ = Me$_3$, Me$_2$Ph, or Et$_3$) [392]. The crystal structure of [Mo$_2$(OAc)$_2$(SiMe$_3$)$_2$(PMe$_3$)$_2$] has been reported, the Mo-Mo separation found to be 2.0984(5) Å [393] and the stereochemistry seen to be in agreement with the ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR conclusions of Mainz and Anderson [392]. [(Me$_3$P)$_3$HMo(μ - H)$_2$MoH(PMe$_3$)$_3$] has been shown to have a Mo-Mo separation of 2.194(3) Å, suggesting the presence of a quadruple metal-metal bond, in addition to the dihydrido-bridge [345].

The nature of the green product, obtained from the reaction of [Mo$_2$(OAc)$_4$] with K$_2$[S$_2$COEt], has been reinvestigated and, according to ^{1}H NMR and conductometric studies, the complex should be formulated as a tetramer (A$^+$)$_2$-

$[Mo_4(S_2COEt)_{10}]$ $(A = [AsPh_4]^+$ $[PPh_3(PhCH_2)]^+)$; related complexes have been prepared [394].

7.9.4   Metal Clusters

Mo_6Cl_{12} and $Mo_6Br_{12}.2H_2O$ may be prepared conveniently by the high temperature conproportionation reactions of molybdenum metal with $MoCl_5$ and $MoBr_4$, respectively, in the presence of NaCl and NaBr, respectively [395]. SW-Xα calculations have been performed to interpret the XPES spectrum of $[Mo_6Cl_8]Cl_4$ [396]. Substitution by sulphide into $[Mo_6Cl_8]^{4-}$ has been achieved; compounds containing the $[Mo_6SCl_7]^{3+}$ and $[Mo_6S_6Cl_2]$ cores have been isolated and structurally characterised, e.g. $[pyH]_3[(Mo_6SCl_7)Cl_6].3pyHCl$, $[pyH]_3-$ $[(Mo_6SCl_7)Cl_6]$, and $[Mo_6S_6Cl_2(py)_6]$. This last compound is the first example of an Mo_6X_8 cluster which has < 24 electrons in its metal–metal bonding orbitals [397].

Chevrel phases, i.e. ternary molybdenum chalcogenides, $M_xMo_6X_8$ (typically M = Pb, Sn, or a rare earth element; X = S or Se) are of particular interest because of their physical properties – high superconducting critical temperatures, high critical fields, and coexistence of magnetic order and superconductivity [398]. Considerable flexibility in composition exists for, in addition to the variations indicated above, the ratio of Mo:X can be increased from the ideal 6:8 value. The relationships between the structure and physical properties of these phases have been reviewed [399] and ab initio calculations accomplished for MMo_6S_8 (M = Eu, Gd, or Sn) and $SnMo_6Se_8$ [400]. The effect of doping rare earth ions into $SnMo_6S_8$ on the superconducting properties of the material has been investigated [401] and the heat capacity of molybdenum chalcogenides with different Sn:Ga contents has been measured [402]. The effect of chalcogen non-stoicheiometry on superconductivity in the $SnMo_6S_8$ phase has been assessed [398] and the relationship between superconductivity, magnetic susceptibility and crystal structure in $PbMo(S_{1-x}Se_x)_8$ phases has been detailed [403].

$Mo_6S_6Br_2$ has been shown to be isostructural with Mo_6Se_8 [404]. The oxygen-containing Chevrel phases $M_xMo_6S_6O_2$ (M_x = Co_2, Ni_2, Cu_2, or Pb) and $Mo_6S_6O_2$ has been synthesised and their physical properties examined [405]. $M_xMo_4S_6$ (M = K, Rb, or Cs) and $M_2M_{15}S_{20}$ (M = K or Rb) have been prepared [406] and the crystal structure of $Tl_2Mo_6Se_6$ has been determined [407]. $InMo_6Se_8$ crystallises with the $PbMo_6S_8$ structure and $In_2Mo_{15}Se_{19}$ contains Mo_6Se_8 and Mo_9Se_{11} building blocks [408]; this latter type of structure is also found for $K_2Mo_{15}S_{19}$ and $M_2Mo_{15}Se_{19}$ (M = K, Ba, or Tl) [409]. MMo_3X_3 (M = In or Tl; X = Se or Te) have been synthesised and their crystal structure shown to

involve infinite chains of face-condensed Mo_6 clusters [410]. The structure of $M_2Mo_9S_{11}$ (M = K or Tl) is characterised by the presence of a completely new building block, $Mo_{12}S_{14}$, in addition to the Mo_6S_8 unit; $Mo_{12}S_{14}$ can be considered as a one-dimensional condensation of three Mo_6 octahedral clusters [411]. The crystal structure of $Fe_2Mo_6S_8$ has been described [412] and shown to be different from that of the low temperature modification of $Cu_{1.8}Mo_6S_8$ and the nature of the 270 K phase transformation of the latter has been described [413]. The homogeneity range of the Chevrel phase of the $Cu_xMo_6S_8$ system has been found to be $1.8 \leqslant x \leqslant 4$ at 850 °C [414], and solid solutions of $PBCu_xMo_6S_8$ ($x = 0-0.3$) and other Chevrel phases have been prepared and investigated [415].

7.9.5   Carbonyl and organometallic complexes

The $\nu(M-M)$ stretching frequencies of $[NEt_4]_2[M_2(CO)_{10}]$ (M = Mo or W) have been reported as 140 and 115 cm^{-1}, respectively [416]. The crystal structure of $[(cpMo)_2(\mu-\sigma,\eta^5-C_5H_4)_2]$ has been determined and the average Mo-Mo distance, in the two crystallographically independent molecules, is 2.885 $\overset{o}{A}$ [417]. μ-Alkylidene complexes of tungsten carbonyl dimers have been prepared and characterised; these include (18) which involves a W-W separation

$$Me_3P\ C\ Me_2$$

(18)
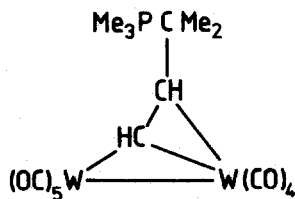
of 3.140(1) $\overset{o}{A}$ [418]. The dimetallocycle $[(cpW(CO)_2)_2\{\mu-\eta^2,\eta^2-C(O)C_2(CO_2Me)_2\}]$ involves a W-W bond of length 3.017(1) $\overset{o}{A}$ [419] and $[(cpMo(CO)_2)_2\{\mu-CH.CH.CMe_2\}]$ a Mo-Mo bond of length 3.106(1) $\overset{o}{A}$ [420].

$[\{cpMo(CO)_2)\}_2]$ (*i.e.* $[(cp)_2Mo_2(CO)_4]$) continues to attract much attention in view of its novel carbonyl bridged structure and its remarkable reactivity. The electronic structures of the $[cp_2M_2(CO)_4]$ complexes, with M = Cr, Mo or W, have been discussed by Hoffman *et al.* with the aid of extended Hückel MO calculations. They concluded that not much of a metal-metal triple bond exists in these molecules but two nice, low-lying acceptor orbitals exist and provide a seat of electrophilic activity [421]. Several of the following

studies exemplify this behaviour.

$[cp_2Mo_2(CO)_4]$ reacts with one equivalent of CN^- to give the $[cp_2Mo_2(CO)_4-(\mu - CN)]^-$ adduct; the cyanide ion bridges the Mo-Mo bond $(3.139(2) \text{ Å})$ in a σ,η^2-fashion, wherein two electrons are donated to one molybdenum from the carbon σ-orbital and two electrons are donated to the other molybdenum from the CN π-bond [422]. $[cp_2(Mo_2(CO)_4]$ reacts with either diphenyl- or bis(4-tolyl)diazomethane in CH_2Cl_2 at room temperature to form the corresponding green diazoalkane adduct $[cp_2Mo_2(CO)_4(N_2CR_2)]$. These complexes possess the structure (19) $(Mo-Mo = 2.987(4) \text{ Å})$, they are fluxional in solution, and can be thermally decomposed in benzene at 60 °C with loss of N_2 to afford the stable, red μ-diaryl-methylene complex, $[(cp)_2Mo(CO)_4(CR_2)]$ (20) $(Mo-Mo = 3.087(2) \text{ Å})$ [423].
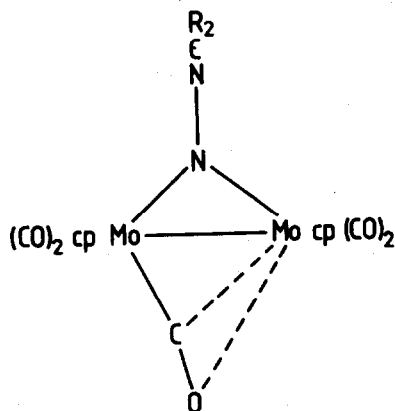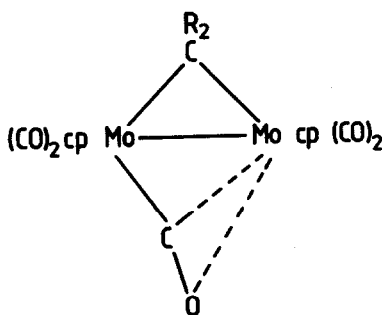
(19)   (20)

Ph_3PS reacts with $[cp_2M_2(CO)_4]$ (M = Mo or W) to produce $[cp_2M_2(CO)_4(Ph_3PS)_2]$, which can be considered to possess a metal-metal single bond [424]. Elemental sulphur reacts with $[cp_2Mo_2(CO)_4]$ to give $[cp_3Mo_3(CO)_6S]^+[cpMo(CO)_3]^-$, the cation possesses the structure (21), with $\overline{Mo-Mo} = 3.085(21) \text{ Å}$ [425].

Complexes of the formula $[(Me)_nC_5H_{5-n}Mo(S)SH]_2$ (where $n = 0, 1,$ or 5) have been prepared by the reaction of H_2 with several different cyclopentadienyl-molybdenum derivatives containing sulphido ligands. These complexes have interesting reactivities including the catalysis of HD exchange between H_2 and D_2, as well as betwee H_2 and D_2O, and the reduction of elemental sulphur to H_2S; C_2H_4 and C_2H_2 displace hydrogen from the SH ligands and form derivatives with bridging dithiolate ligands, and alkyl and aryl thiols

$(CO)_2$ cp Mo————Mo cp $(CO)_2$

Mo cp $(CO)_2$

(21)
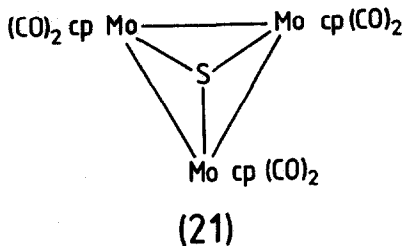
react to form H_2S and derivatives of the formula $[Me_nC_5H_{5-n}Mo(S)SR]$.
Spectroscopic information indicates that the latter have the same
structure as the SH complexes and the structure of the $n = 1$, R = Me derivative
has been determined (22); the molecule is centrosymmetric, with Mo–Mo =
2.582(1) Å, Mo–S = 2.352(2) and 2.479(2) Å, and the four sulphur atoms form
a plane perpendicular to the Mo–Mo vector, with S–S = 2.758(3) and 3.014(3) Å
[426]. The characteristics of the equilibria: $[MeC_5H_4MoSC_2H_4S]_2$ + nRNC ⇌
$[(MeC_5H_4Mo)_2(SC_2H_4S)_{2-n}(S_2CNR)_n]$ have been determined for $n = 1$ or 2 and

CH_3

S

S

Me C_5H_4Mo————Mo C_5H_4Me

S

S

CH_3

(22)
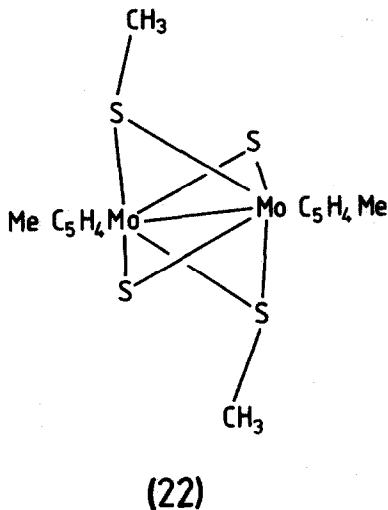
R = Bz. Other dimeric molybdenum complexes with bridging dithiocarbonimidate
ligands, $[cpMoS_2CNR]_2$ (where R = Me, Bz, ^{n}Bu or Hx) have been synthesized,
characterised, and their reactions with $MeOSO_2F$, $HOSO_2F$, CO, and reducing
agents described [427].

The complexes $[cp_2Mo_2(CO)_4(\mu-SR)_2]$ (R = Me, ^{t}Bu, Ph, or 4-tolyl), which
do not contain a metal–metal bond, decarbonylate readily on heating to produce

[$cp_2Mo_2(CO)_2(\mu-SR)_2$] which contain a formal double metal–metal bond (Mo–Mo 2.616(2) Å for R = ^tBu) [428]. Studies on other complexes containing μ–thiolate ligands spanning a formal metal–metal bond reported this year include:
[$(\eta^7-C_7H_7)W(\mu-SR)_3(CO)_3$] and [$(\eta^7-C_7H_7W(\mu-SR)_3W(\mu-SR)_2W(CO)_3$] (R = Et, Bu, or Ph) [429] and [$(\eta^5-RC_6H_5CN)Mo(\mu-SMe)_4Mo(\eta^6-RC_6H_5)$]$^+$ (R = H or Me), the latter may be converted into the corresponding π–cyanoarene derivative by a two-electron oxidation-proton elimination process [430].

Complexes of the formula [$(\eta^5-C_5H_4R')_2M_2(CO)_4(R_2CS)$] (M = Mo or W; R' = H or Me; R = $4-X-C_6H_4$; X = OMe, Me, F, H, NMe_2) have been synthesised by a facile reaction of the thioketone with [$(\eta^5-C_5H_4R')_2M_2(CO)_4$]. The crystal structure of [$cp_2Mo_2(CO)_4\{4-Me-C_6H_5)_2CS\}$] has been determined and the molecule seen to involve one semi-bridging carbonyl ligand, and a Mo–Mo bond of length 3.145 Å which is involved in a metallathiocyclopropane moiety [431]. Reactions of these complexes with PR_3 and $P(OR)_3$ molecules have been described and discussed [432]. The hydrogenation of bridging alkyne ligands in [$cp_2Mo_2(CO)_4(RC_2R)$] and related complexes has been developed, in a study which included the preparation of [$cp_2Mo_2(CO)_2\{P(OMe_3)\}(RC_2R)$], a catalyst precursor for acetylene hydrogenation to *cis*-olefins [433].

The crystal structures of [$(\eta^7-C_7H_7)Mo(\mu-OMe)_3Mo(CO)_2(\eta^3-C_7H_7)$] and [$(\eta^3-C_7H_7)(CO)_2W(\mu-OMe)_3(CO)_2(\eta^4-C_7H_8)$] have been reported, and their Mo–Mo and W–W separations found to be in the range consistent with the presence of a single bond [434].

The presence of metal–metal bonding interactions in the crystallographically characterised μ–hydrido-complexes [$\mu-H(Mo_2(CO)_9PPh_3$]$^-$ [342], [$(\mu-H)(\mu-PMe_2)\{cpMo(CO)_2\}_2$] [344] and [$cp_2W(\mu-H)_2Rh(PPh_3)_2$] [346] has been commented upon in Section 7.8.

Hetero-nuclear metal–metal bonds, involving molybdenum or tungsten have been identified in a large number of complexes reported this year. These include:
[$M'(\mu-AsMe_2)Fe(CO)_3(\mu-AsMe)_2Mocp(CO)_3$] (M' = $cpFe(CO)_2$, $cpFe(CO)(PMe_3)$, or $cpM''(CO)_3$ = Cr, Mo or W) [435], [$Ru_3(CO)_{11}(\mu-AsMe_2)Mcp(CO)_3$] (M = Mo or W) and [$(OC)_4Ru(\mu-AsMe_2)Mocp(CO)_2$] [436], [$(OC)_5W\{\mu-C(OMe)Ph\}Pt(PMe_3)_2$] (W–Pt = 2.861(1) Å) [437], [$cp(CO)_2W\{\mu-CC_6H_4Me-4\}Pt(PMe_2Ph)_2$] (W–Pt = 2.751(1) Å) [438], [$Pt_2W\{\mu-C(OMe)Ph\}(CO)_6(P^tBu_2Me_2)_2$] **(23)** [439], [$(\eta^6-Me_6C_6)(OC)_2Cr(\mu-CC_6H_4Me-4)W(CO)_2cp$].$CH_2Cl_2$ (W–Cr = 2.941(1) Å)

Ph⟍ ⟍OMe
C
(Me Bu$_2$ P)(OC)Pt ———— Pt(CO) (P Bu$_2$ Me)
W
(CO)$_4$

(23)
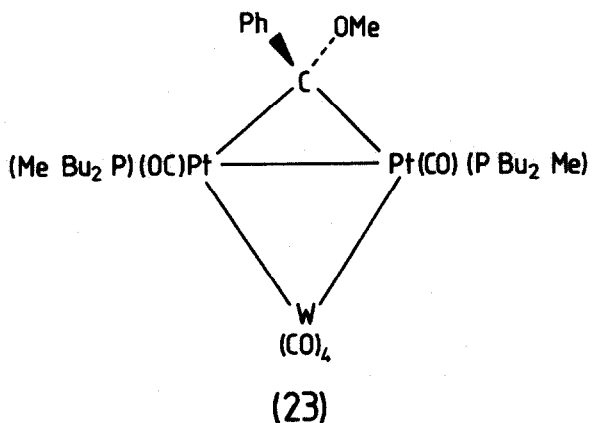
[440], [FePtW(μ_3 – CC$_6$H$_4$Me–4)(CO)$_6$(PEt$_3$)cp] (24) (W–Pt = 2.775(1) $\overset{o}{A}$,
W–Fe = 2.784(3) $\overset{o}{A}$) and [FeRhW(μ_3 – CC$_6$H$_4$Me–4)–(μ_2 – CO)(CO)$_5$cp(η^5–C$_9$H$_7$)]

C$_6$H$_4$ –4–Me
C
(Et$_3$ P)(OC)Pt
W cp(CO)$_2$
Fe
(CO)$_3$

(24)
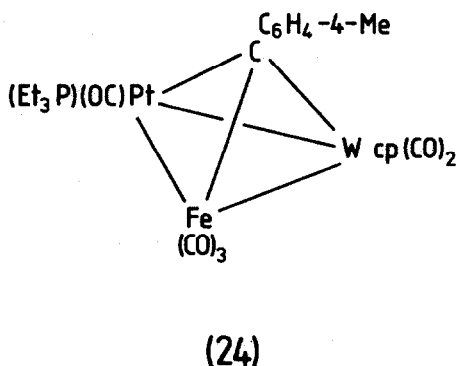
(W–Rh = 2.760(1) $\overset{o}{A}$, W–Fe = 2.772(1) $\overset{o}{A}$) [441], [{PdNMe$_2$CH$_2$C$_6$H$_4$}$_2\mu$–{Mocp(CO)$_3$}–
μ–Cl] (25) (Mo–Pd = 2.788(1) and 2.832(1) $\overset{o}{A}$) [442], and [Net$_4$]$_2$ [MoFe$_5$C(CO)$_{17}$]
(Mo–Fe = 2.915(2) $\overset{o}{A}$) [443]. Cathodic reduction of [PtL$_2${Mcp(CO)$_3$}$_2$] (L = ^{t}BuNC,
M = Mo or W) complexes leads to the paramagnetic platinum(I) complexes,
whereas the corresponding mercury(II) and gold(I) systems undergo metal–metal
bond cleavage [444].

cp
Mo

CO   CO

CO

Pd   Pd

Cl

N   N
Me₂   Me₂
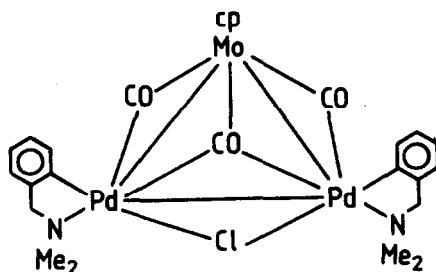
(25)

7.9.6   *Metallic moieties*

As indicated in the introduction to this review, new aggregates of
metal atoms containing molybdenum or tungsten, have been prepared and
spectroscopically characterised and further calculations of the electronic
structure of such species have been reported. These theoretical studies
include presentations of the potential energy curve for the $^1\Sigma_g^+$ ground state
and detailed descriptions of the nature of the sextuple bond in Mo_2 [12,13],
and an interpretation of the optical spectrum of the MoNb molecule [16].
The electronic spectrum of tungsten atoms isolted in an argon matrix has been
presented [17], and the bimetallic AgMo [18], Mo_2, and CrMo,and trimetallic
Mo_3, $CrMo_2$, and Cr_2Mo clusters [19] have been trapped in inert gas matrices
and characterised by optical spectroscopy. Unimetallic and bimetallic metal
clusters can be anchored efficiently to liquid poly(methylphenylsiloxanes);
manipulation of the experimental conditions can lead to the formation of other
species, including the bis(η^6-arene) metal complexes of molybdenum and
tungsten [14,15].

7.10   MISCELLANEOUS BINARY AND TERNARY PHASES

The standard heat of formation of W_2B_5 has been reported as 93 ± 9 kJ mol^{-1}
[445] and the new boride WB_{12} has been prepared [446]. The crystal structures
of the complex nitride $Mo(Ta,Mo)N_2$ [447] and the phosphide $Mo_2Ni_6P_3$ [448]
have been determined. The thermal decomposition of Mo_3Sb_7 [449], the
formation of $W_xNb_{1-x}Se_2$ [450], and the catalysis of CO hydrogenation over
Mo_2C [451], have been investigated.

7.11   HETEROGENEOUS CATALYST PRECURSORS

Molybdenum and, at the moment to a lesser extent, tungsten are used
widely in industrial catalysts. The majority of these materials are prepared
by the incoporation of a compound containing the metal onto or into an
oxide lattice, followed by suitable pre-treatment. The importance of these
materials has stimulated many chemical studies, aimed at duplicating the
properties of these heterogenous phases in homogeneous systems, and these
are described in other sections of the review. This section considers the
progress made in understanding the chemical nature of the molybdenum
(or tungsten) centres in these catalyst precursors.

Hydrodesulphurization is a catalytic process used industrially to remove
sulphur from petroleum feedstocks and coal. The commercial catalysts used
in this process are generally molybdenum supported on activated alumina,
with various promoters such as cobalt or nickel added to improve catalyst
performance. These oxides require sulphurization for dehydrosulphurization
activity. The physical studies of such systems accomplished this year are
extensive and only a selection will be presented here. One theme has been
to investigate how molybdenum interacts with the oxide support. ESCA,
XPS, Raman, and low-energy ion-scattering spectroscopy have been used to
characterise a series of $MoO_3/\gamma-Al_2O_3$ catalysts and three distinctly
different molybdenum species have been observed. At low concentrations, an
interaction species, possibly resulting from the reaction of molybic acid
with surface hydroxyl groups was found; this appears to involve both
octahedrally and tetrahedrally coordinated molybdenum atoms. After monolayer
coverage had been reached, $Al_2(MoO_4)_3$ was formed and, at higher concentrations,
the formation of bulk MoO_3 was observed [452]. The results of other
spectroscopic studies characterising $MoO_3/\gamma-Al_2O_3$ systems have been presented
[453] and a large number of similar studies have been accomplished for
$CoMo/\gamma-Al_2O_3$ materials, at various stages of preparation. These indicate
that the molybdenum oxide layer appears to be formed on top of the cobalt
oxide layer [454] and the corresponding sulphide systems appear to involve
MoS_2 and Co_9S_8 phases [455]. The vibrational spectra of hydrogen-sorbed
by MoS_2 and MoS_2/Al_2O_3 suggest that the hydrogen is bonded to $\geqslant$ one sulphur
atom [456] and the hydrodesulphurization activity of MoS_2 samples has been
correlated with their oxygen chemisorption capacity [457].

Catalysis of the hydrogenation of CO to alkanes by materials derived
from $[Mo(CO)_6]$ on Al_2O_3 has been discussed in terms of the $Mo(CO)_3-$
(dehydroxylated alumina) units forming molybdenum clusters, on heating to
500 °C in a He atmosphere [458]. Binuclear molybdenum centres with catalytic

activity are considered to be obtained when [{Mo(OEt)$_5$}$_2$] reacts with SiO$_2$ [459]. Well defined pairs of molybdenum centres are formed when [Mo$_2$(η^3-C$_3$H$_5$)$_4$] reacts with Al$_2$O$_3$ and SiO$_2$; these act as excellent catalysts for ethene hydrogenation at 200 - 293 K [460]. These materials also catalyse the partial oxidation of propene, by O$_2$ or N$_2$O and, in this case, the presence of coordinatively unsaturated *cis*-dioxomolybdenum(VI) centres are held to be crucial for activity [461]. Oxidation of propene on oriented and non-oriented catalysts shows a specificity for the reaction of the MoO$_3$ crystalline faces; catalytic sites for acrolein formation are located in the [020] direction [462]. Other studies of the oxidation of hydrocarbons over Mo–O catalysts have been described [463], with particular attention being devoted to Bi–Mo–O phases [464] which will also catalyse the oxidative ammonolysis of propylene [465]. The relationship between the oxygen exchange reactivity and catalytic oxidation ability of 3*d*-transition metal molybdates has been discussed [466].

Silica supported MoO$_3$ is photoreduced on irradiation at *ca.* 350 nm, provided that water vapour is present during the thermal treatment carried out at high temperature prior to irradiation; molybdenum(V) and, under certain conditions, molybdenum(IV) centres appear to be formed [467]. These oxidation states have also been identified by XPS for a series of MoO$_3$/SiO$_2$ catalysts, obtained by calcination of [Mo$_2$(O$_2$CR)$_4$]/SiO$_2$ (R = H, Me, CF$_3$ or Ph) mixtures, the measurements being undertaken before and after reaction with NO or CO [468].

The acidity of various MO$_3$/SiO$_2$ (M = Mo or W) systems has been measured by NH$_3$ adsorption [469] and gaseous hexamethyldisilazane has been shown to quantitatively and irreversibly poison the Brønsted acid sites on WO$_3$/SiO$_2$, without affecting the Lewis acid sites [470]. Reactions in which these Brønsted acid sites have been proposed as active centres include the metathesis of propene; stereoselectivity in the metathesis of but-2-ene has been observed on MoO$_x$/β-TiO$_2$ [471].

7.12   MOLYBDOENZYMES AND SOME RELATED CHEMICAL STUDIES

7.12.1   Oxo enzymes

The oxomolybdenum enzymes, principally xanthine oxidase and dehydrogenase, aldehyde and sulphite oxidase and nitrate reductase, constitute an important sub-group within the family of molybdoenzymes. These enzymes are linked by a common molybdenum-containing cofactor and exhibit very similar molybdenum(V) EPR signals. The title of this sub-group appears apt, since each enzyme is

involved in the net transfer of one oxygen atom between substrate and product, this behaviour clearly being related to the presence of one or more oxo-groups in the coordination sphere of the molybdenum(VI) centre (as detected by EXAFS studies) and the (probable) protonation of one oxo ligand upon reduction to molybdenum(V) or (IV). An additional molybdoenzyme has been identified in microbial sources, carbon monoxide oxidoreductase [472] and this reviewer has tentatively classified this as an oxo enzyme, pending further characterisation.

The detailed understanding of the catalysis which is accomplished at the molybdenum centres of these enzymes, and the development of authentic chemical analogues of these centres, are hampered by the lack of a definitive characterisation of the molybdenum cofactor (Moco). A major, and surprising, development in the characterisation of this entity is the identification of a reduced pterin as an integral component of the active cofactor [473]. Details for the isolation of Moco from the nitrate reductase of lupine bacteroids and milk xanthine oxidase have been described and a partial analysis of the amino acid content (aspartate:threonine:serine:glycine:alanine = 2:1:5:3:1) of Moco has been obtained [474]. Moco would appear to undergo some chemical modification from enzyme to enzyme, perhaps explaining the different redox potential of the molybdenum centres in the various enzymes. Such chemical modification is important for xanthine oxidase; thus, desulpho (and inactive) xanthine oxidase has a molybdenum(VI) centre, $MoO_2(SR)_x$ (x = 3-4), very similar to that in oxidised sulphite oxidase, whereas active xanthine oxidase possesses and $Mo^{VI}O(S)(SR)_x$ centre [65].

Active xanthine oxidase is converted into the desulpho form on treatment with CN^-, this involves the formation of CNS^- and the conversion of $MoO(S)^{2+}$ to MoO_2^{2+}; this behaviour is also encountered on cyanalysis of xanthine dehydrogenase and aldehyde oxidase. However, a different process occurs upon cyanolysis of sulphite oxidase and subsequent reactivation of this enzyme can be achieved by $[Fe(CN)_6]^{3-}$ oxidation [475].

The nature of the sites of interaction of oxidising substrates with xanthine oxidase and dehydrogenase and aldehyde oxidase have been reviewed [476]. The spectrum of the "rapid" Mo(V) EPR signal of xanthine oxidase, dissolved in ^{17}O-enriched H_2O, is indicative of strong hyperfine coupling of one oxygen atom to the molybdenum centre. A clear possibility exists that the oxygen is present in a Mo^V-OH group, the proton of which is also strongly coupled in this EPR signal [477]. Another type of "rapid" Mo(V) EPR signal has been observed for milk xanthine oxidase, which shows strong coupling to two protons; the signals were obtained either at pH 8.2 in the presence of borate or at pH 10.1 - 10.7 with or without this anion. The relationship between the two types of "rapid" EPR signals has been discussed;

they may represent coordination isomers; or the latter may arise from the presence of two hydroxide ions in the coordination sphere of the molybdenum(V) [478]. The oxidation/reduction potentials of the various prosthetic groups in native and desulpho chicken liver xanthine dehydrogenase have been determined by potentiometric titration, for samples dissolved in 0.05M K_3PO_4 buffer at pH 7.8; the values obtained were Mo(VI)/Mo(V) and Mo(V)/Mo(IV) native, -357 and -337 mV respectively, with corresponding values for the desulpho enzyme of -397 and -433 mV [479].

For chemical studies of possible relevance to the structure and function of these enzymes, the reader is referred to Sections 7.1.2 (especially references [64-71], 7.3.2, and 7.4.3.

7.12.2   Nitrogenases

Procedures for the isolation and characterisation of nitrogenases have been reviewed [480] and a large scale, rapid, high-yield purification for *Azotobacter vinelandii* nitrogenase proteins has been developed [481]. This latter study also included a description of the procedures for the isolation and concentration of the iron-molybdenum cofactor (FeMoco) of the molybdoferredoxin protein, and isolation procedures for this entity have been reviewed [482].

^{57}Fe Mössbauer and EPR studies of the molybdoferredoxin of *Clostridium pasteurianum* have been reported and, except for small differences in the hyperfine parameters, the results obtained were essentially the same as published previously for the *A. vinelandii* protein. Thus the thirty Fe atoms are partitioned into, two identical FeMoco centres (M, each probably containing one Mo and six Fe atoms), four P-clusters (each containing four Fe atoms) and one Fe atom (labelled S). The spectra were analyzed in terms of three oxidation states for FeMoco; M^{OX}, M^N (native, having the $S = {}^3/_2$ EPR signal) and M^{RED} [483]. The redox properties and some complexation reactions of FeMoco have been investigated. Addition of edta eliminates the $S = {}^3/_2$ EPR signal characteristic of dithionite reduced FeMoco to give a species which appears to be different from the EPR-silent substrate reducing (M^{RED}) dye-oxidised (M^{OX}) forms [484]. The molybdoferredoxin of *A. vinelandii* has been shown to undergo a six-electron oxidation by various dye oxidants, with full retention of initial activity. Subsequent reduction, by dithionite or controlled potential electrolysis, indicated the presence of two reduction regions, at -290 and -480 mV, each requiring three electrons for complete reaction. Selective reduction at -290 mV caused development of the $S = {}^3/_2$ EPR signal, whereas reduction at -480 mV produced a change in the visible

spectrum but no change in the EPR signal or its intensity [485].

FeMoco has been suggested to contain coenzyme A [486] and its location in the molybdoferredoxin has been studied using 2-phthalaldehyde [487]. Oxidative inactivation of the molybdoferredoxin of *C. pasteurianum* nitrogenase by $[Fe(CN)_6]^{3-}$ has been shown to release most of the metal and sulphur atoms from the protons; incubation with a mixture containing thiols, sulphide, $[MoO_4]^{2-}$, and Fe^{III} produced an EPR spectrum similar to that of the air-inactivated protein [488].

FeMoco has been shown to catalyse the electrochemical reduction of C_2H_2 to C_2H_4 [489].

7.12.3   Iron-molybdenum-sulphur clusters

The preparation and characterisation of complexes containing an Fe-Mo-S core has proceeded rapidly, following the isolation and molybdenum *K*-edge EXAFS investigation of FeMoco. As indicated in Section 7.1.6, these complexes are invariably prepared from $[MoS_4]^{2-}$, and an iron salt, and may be subdivided according to whether they contain (Type I) an $\{MoS_4\}$, tetrathiomolybdate, moiety coordinated as a bidentate ligand to one or two iron atoms, or (Type II) one or two Fe_3MoS_4 cubane – like clusters.

Several developments in the chemistry of Type I systems have been reported this year, including the comprehensive description of the syntheses, structures, and spectroscopic properties of the $[X_2FeS_2MoS_2]^{2-}$ (X = SPh or Cl) ions. The stability of these ions, the short Mo–Fe distance (2.756(1) and 2.716(1) Å, respectively), and the ^{57}Fe isomer shifts, all suggest that the bonding of $[MoS_2]^{2-}$ to iron(II) involves some net transfer of electron density to the former from the latter [194]. A conclusion which extends to other complexes of this type. $[NEt_4]_3[(PhS)_2FeS_2MoS_2]$ has been prepared by the reaction of $[NEt_4]_2[Fe_2S_2(SPh)_4]$ with $[NEt_4]_2[MoS_4]$, in MeCN at room temperature, and characterised by optical, ^1H NMR and Mössbauer spectroscopy, magnetic susceptibility and electrochemical oxidation and reduction. The results obtained were interpreted in terms of an Fe^{III} ($S = \frac{5}{2}$) centre, antiferromagnetically coupled to a formally $\{Fe^{II}S_2Mo^{VI}S_2\}$ ($S = 2$) unit, to give a net $S = \frac{1}{2}$ ground state [195].

An important basic unit in Fe-MoS$_4$ chemistry, $[Fe(MoS_4)_2]^{3-}$ has been isolated and characterised previous to this work, the simple complex formed between iron(II) and $[MoS_4]^{2-}$ was considered to be $[Fe(MoS_4)_2]^{2-}$ [490], however, this dianion still awaits conclusive identification. $[Fe(MoS_4)_2]^{3-}$ has been prepared by reacting $[NEt_4]_2[MoS_4]$ with FeL$_2$ (HL = 1-piperidine-carbodithioic acid) 2:1 [196], or $[Fe(S_2COEt)_3]^-$ [197], and the crystal structure of $[(Ph_3P)_2N]_2[NEt_4][Fe(MoS_4)_2]$ has been determined. The IR,

UV/VIS, and EPR spectra of this trianion have been recorded and the last is of special interest since the ground state has $S = \,^3/_2$ and g values of 4.6, 3.3 and 2.0. The electronic spectrum is identical to that previously reported for $[Fe_4Mo_4S_{20}]^{6-}$ [491], and thus negates the existence of this tetramer. The cyclic voltammogram of $[Fe(MoS_4)_2]^{3-}$ shows a quasi-reversible reduction at $ca.$ -1.8 V, and an oxidation at $ca.$ -0.10 V which is irreversible and thus further challenges the existence of $[Fe(S_2MoS_2)_2]^{2-}$.

The reaction of $[PPh_4]_2[(PhS)_2FeS_2MS_2]$ (M = Mo or W) complexes with $FeCl_3.6H_2O$ (1:2) in dmf, results in the oxidation of PhS^- to PhSSPh and the formation of iron(II); the compounds $[PPh_4]_2[Cl_2FeS_2MS_2FeCl_2]$ crystallise upon addition of Et_2O. A crystal structure determination for the molybdenum salt has indicated that the anions have a nearly linear Fe-Mo-Fe array $(\overline{Fe\!-\!Mo} = 2.775(6)\,\overset{\circ}{A})$, with distorted tetrahedral MoS_4 and Cl_2FeS_2 fragments. ^{57}Fe Mössbauer data suggest that the two iron atoms are in the +II formal oxidation state. This study also included a comprehensive documentation of the dimensions of Type I, Fe-Mo-S clusters [198]. $[PPh_4][(PhS)_2FeS_2MS_2]$ (M = Mo or W) react with $C_7H_7SSSC_7H_7$ in warm dmf to form $[PPh_4]_2[(S_5)FeS_2MS_2]$. These anions possess the structure (26); in which the two metal centres give
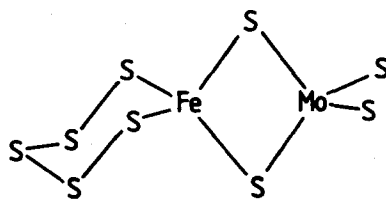
(26)

rise to a net $S = 2$ ground state, with the ^{57}Fe Mössbauer spectrum indicating that the iron atom is in an oxidation state intermediate between +II and +III [199].

A full account has been published describeing the synthesis of the Type II Fe-Mo-S clusters, $[Fe_6Mo_2S_8(SR)_9]^{3-}$ (R = Et, Ph, C_6H_4Cl-4, or C_6H_4Me-4), $[Fe_6Mo_2S_8(SPh)_6(OMe)_3]^{3-}$ and their tungsten counterparts, $[Fe_6W_2S_8(SEt)_9]^{3-}$ and $[Fe_6W_2S_8(SPh)_6(OMe)_3]^{3-}$. ^1H NMR spectra of these anions provide a clear distinction between bridging and terminal ligands and, within each set of bridging or terminal ligands, only one resonance is manifest for each chemically different proton; the bridging ligands exhibit much smaller isotropic shifts than for the corresponding ligands in terminal positions

[200,203]. [57]Fe Mössbauer parameters of the majority of the complexes have been obtained and are seen to be very similar to those obtained for $[Fe_4S_4(SR)_4]^{2-}$ complexes; thus each iron atom is considered to have a net oxidation state of *ca.* 2.5, implying that each molybdenum or tungsten atom has an oxidation state between +III and +IV. Electrochemical reductions of these trianions to the 4-,5-,6- and, in some instances 7- species have been observed and, rapid scan, staircase cyclic voltammetry showed that only the first two reductions of $[Fe_6M_2S_8(SEt)_9]^{3-}$ (M = Mo or W) in MeCN solution, approached good electrochemical reversibility [201,204]. The similarity in structure and electrochemical behaviour of these last two complexes has led to the reason for the inactivity of tungsten substituted (for molybdenum) nitrogenases [202]. The complexes $[Fe_6Mo_2S_8(SR)_9]^{3-}$ (R = Et, CH_2CH_2OH, or CH_2Ph) react with PhCOX (X = Cl or Br) to form the corresponding $[Fe_6Mo_2S_8(SR)_3X_6]^{3-}$ complex in good yield, with selective substitution of the thiolato groups attached to the iron atoms [205].

The full details concerning the structure of the iron-bridged "double-cubane" cluster complexes $[Fe_7Mo_2S_8(SEt)_{12}]^{3-}$ and $[Fe_7M_2S_8(SBz)_{12}]^{4-}$ (M = Mo or W) have been published [203]. $[Fe_7M_2S_8(SR)_{12}]^{3-}$ (M = Mo or W) clusters undergo their initial reduction at the central iron(III) atom, to generate the 4- anion with a central iron(II) atom [204]. An important development in the reaction chemistry of these clusters is the quantitative dihydrogen evolution which occurs when PhSH is added to $[Fe_6Mo_2S_8(SPh)_9]^{5-}$ [206].

A cluster, which is claimed to involve a Fe_6MoS_8 unit, has been obtained on a polystyrene support [207] and, if so, could be of a considerable interest.

7.12.4 *Dinitrogenyl chemistry*

The other important aspect of inorganic chemistry especially relevant to the function of the nitrogenases, involves the preparation, characterisation, and reactivity of dinitrogenyl complexes.

Ab initio MO calculations have been reported for $[Mo(N_2)_2(NH_3)_4]$, $[Mo(N_2)(NH_3)_5]$, and $[Mo(N_2)_2(PH_3)_4]$ and the results obtained indicate that the relative polarization of the bound dinitrogen molecule is in the sense $Mo\overset{\delta+}{-}N\overset{\delta-}{-}N$ [492]. A comparison of the bonding interactions for end-on and side-on coordinated dinitrogen has been made and the former preferred to the latter, principally because of the good σ-donating ability of the ligand [493]. The resonance Raman spectrum of $[\{Cl(PMe_2Ph)_4Re(N_2)\}_2MoCl_4]$ indicates that the intense absorption at 23,300 cm^{-1} should be assigned to an $e_g \longleftarrow e_u$, $^1A_{2u} \longleftarrow {}^1A_{1g}$, transition of the axial π-system of the linear chain; the

principal geometric changes within the complex on undergoing this transition, are a lengthening of the Re-N and a shortening of the N-N bonds [494].

[Mo(N₂)Cl₂(bipy)] has been obtained as one product of the reaction between [MoCl₄(bipy)] and an excess of Me₃SiN₃ in ClCH₂CH₂Cl₂, but its structure is unknown [220]. The crystal structure of [Mo(N₂)₂(Et₂PCH₂–CH₂PPh₂)₂] has been determined [495]. The effect of the wavelength of light upon the extent of N₂ exchange in [Mo(N₂)₂(dppe)₂] and [M(N₂)₂(depe)₂] (M = Mo or W) has been investigated [496] and the photoinduced elimination of H₂ from [MoH₄(PR₃)₄] (PR₃ = PEt₂Ph, PPh₂Me or 0.5 (dppe)) has been shown to produce the corresponding *trans*-[Mo(N₂)₂(PR₃)₄] complex [339,497]. New complexes, including *trans*-[M(CO)₃{P(cych)₃}₂(N₂)] (M = Mo or W), have been synthesized by the reaction of [Mo(CO)₃(cycloheptatriene)] with P(cych)₃ under dinitrogen; the binding is reversible and N₂ can be removed by flushing with argon at 40-60 °C, to form the apparently five-coordinate [M(CO)₃{P(cych)₃}₂] species [498]. The preparations of the complexes *trans*-[M(N₂)X(dppe)₂]⁻ (M = Mo or W; X = SCN, CN, or N₃) have been described. Relationships between $E_{\frac{1}{2}}^{ox}$ and ν(N-N) of these complexes and those of [M(N₂)(NCR)(dppe)₂] (with reference to the standard series [Cr(CO)₅(L or Y⁻)] [499]) have led to the identification of the labile ammine complex [Mo(N₂)(NH₃)(dppe)₂] in thf, *and* to the prediction of $E_{\frac{1}{2}}^{ox}$ and ν(N-N) for related but, as yet, unsynthesized complexes. Furthermore, in a most informative documentation, aspects of the reactivity of the coordinated dinitrogen ligand have been correlated with the "electron-richness" of the complex (as measured by $E_{\frac{1}{2}}^{ox}$), with particular reference to: (a) inner-sphere *versus* outer-sphere electron-transfer alkylation, and (b) protonation of the [M(N₂)(NCR)(dppe)₂] complexes to give the new hydrazido-salts, [M(N₂H₂)(NCR)(dppe)₂][HSO₄]₂, with retention of the *trans*-RCN ligand [500]. The oxidation of *trans*-[W(N₂)₂-(dppe)₂] with tcne or FeCl₃ has been achieved and *trans*-[W(N₂)₂(dppe)₂]⁺ salts isolated [501].

An important clarification of the protonolysis of [M(N₂)₂(PR₃)₄] (M = Mo or W) has been accomplished, in that, for the first time, the fate of the metal has been determined. [Mo(N₂){PhP(CH₂CH₂PPh₂)₂}(PPh₃)] reacts with HBr (2:8) to produce 2[NH₄]Br, 3N₂, 2PPh₃ and 2[MoBr₃{PhP(CH₂CH₂PPh₂)₂}]. Thus the six electrons required for the reduction of N₂ to 2NH₃ are supplied from the 2Mo⁰ to 2Mo^III conversion [502]. Treatment of *cis*-[W(N₂)₂(PMe₂-Ph)₄] with 2-propanol/KOH yields N₂H₄, whereas use of normal alcohols instead of 2-propanol gives NH₃ [503], and the formation of NH₃ and N₂H₄ has been detected subsequent to the reaction of this complex with acidic hydridometal carbonyls, H₂Fe(CO)₄ or HFeCo₃(CO)₁₂, and treatment with aqueous KOH [504]. The reduction of N₂ to N₂H₄ by Na/Hg in MeOH, as catalyzed by a molybdenum(V)

complex, has been investigated [505]. A reaction mechanism has been presented for the reduction of N_2 to N_2H_4 and NH_3 by a $Ti(OH_3)/Mo(OH)_3$ system [506] and the electrolytic reduction of N_2 in a $Ti^{III}/Mo^{III}/$guanidine system has been described [507].

7.13 COMPLEXES OF ORGANODINITROGEN AND RELATED LIGANDS

Reactions of the coordinated dinitrogen, of molybdenum or tungsten phosphine complexes, to form carbon-nitrogen bonds are well known, with the formation of diazenido (-N=N-R) and hydrazido(2-) complexes being obtained as in the following sequence:

$$[M(N_2)_2(dppe)_2] \quad \xrightleftharpoons{k_1} \quad [M(N_2)(dppe)_2] \quad + \quad N_2$$

$$[M(N_2)X(dppe)_2] \quad + \quad R\cdot \quad \longrightarrow \quad [M(N_2)(XR)(dppe)_2]$$

$$[M(N_2R)X(dppe)_2] \quad + \quad RX \quad \xrightarrow{k_2} \quad [M(N_2R_2)X(dppe)_2]X$$
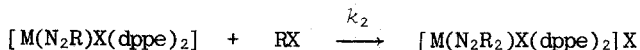
Dinitrogen loss is the rate-determining step (k_1) in the primary alkylation forming the diazenido complex, whereas the secondary alkylation (k_2) to form the hydrazido(2-) complex has been shown to be a typical S_N2 reaction [508].

Diazenide derivatives seem likely to be the stable analogues of the first intermediate, -N=N-H, in the reduction of dinitrogen to ammonia; also, these ligands are formally isoelectronic with the nitrosyl group and manifest interesting variations in their modes of bonding, [$Mo(N_2Ph)_2(TPP)$] involves N_2Ph groups that are "half doubly bent", with $Mo-N-N = 149.1(9)$ ° and $N-N-C = 128.6(9)$ ° [509]. A further report of the crystal structure of [$Mo(N_2Ph)(S_2CNMe_2)_3$], accompanied by that for [$Mo(N_2C_6H_4NO_2-4)(S_2CNMe_2)_3$] [510], agrees with the singly bent (linear $Mo-N-N$) arrangement obtained earlier for this compound. The same geometry, $Mo-N-N = 177(1)$ and $N-N-C = 132(1)$ °, has been confirmed for [$MoI(N_2cych)(dppe)_2$], in a reinvestigation of the crystal of the benzene solvate [511]. The materials formulated as [$Mo_2(N_2Ph)(S_2CNR_2)_4$] [512] have been shown, by ^1H NMR and cyclic voltammetric studies to be a mixture of the compounds [$Mo(N_2Ph)(S_2CNR_2)_3$] and [$Mo(N_2Ph)_2(S_2CNR_2)_2$] [513]. The complexes [$cpM(CO)_2(N_2Me)$] (M = Mo or W) react with [$Cr(CO_5(thf)$] and [$cpMn(CO)_2(thf)$], via coordination of the basic nitrogen function, to yield, respectively, the trinuclear [$cpM(CO)_2\{N_2MeCr(CO)_5\}$] and [$cpM(CO)_2\{N MeMncp(CO)_5\}$] complexes [514]. The potentially

chelating bis(aryldiazenate) ligands (2) (R = H or ^{t}Bu) = L have been
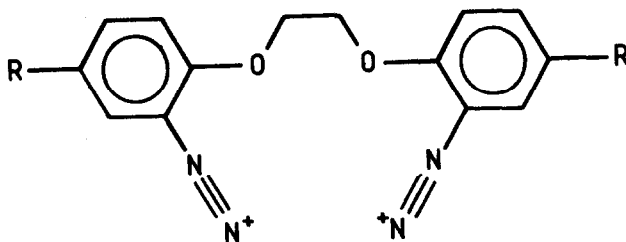
(27)

prepared and their reactions, leading to the formation of the binuclear complexes [L{cpM(CO)$_2$}$_3$] (M = Mo or W) and [L{cpMo(CO)(PPh$_3$)}$_2$], have been investigated [515].

[Mo(N$_2$)$_2$(dppe)$_2$] reacts with MeBr, ^{n}BuBr, and Me$_3$CCH$_2$CH$_2$Br, to form the corresponding 2-alkyldiazenido-N derivative [MoBr(N$_2$R)(dppe)$_2$]; whereas, the analogous reaction with 6-bromo-1-hexene yields the cyclopentylmethyldiazenido complex, thus providing additional support for the formation of the diazenido complexes via an alkyl radical pathway. Protonation of these alkyldiazenido complexes by H[BF$_4$], in which the proton is attached to the carbon-bound nitrogen atom. [MoBr(N$_2$^{n}Bu)(dppe)$_2$] reacts with Na[BH$_4$] or NaOMe, in C$_6$H$_6$-MeOH solution at an elevated temperature, to produce almost equal quantities of ^{n}BuNH$_2$ and NH$_3$ [516]. The reactions of $trans$-[M(N$_2$)$_2$(dppe)$_2$] (M = Mo or W) with Br(CH$_2$)$_n$Br, under irradiation in C$_6$H$_6$, yield products, the nature of which is a function of n. For n = 3, [MBr{N$_2$(CH$_2$)$_3$Br}(dppe)$_2$] is obtained and for n = 4 or 5, [MBr{NN(CH$_2$)$_{n-1}$CH$_2$}(dppe)$_2$]Br is formed; for n = 6-12 two series of complexes, [MBr{N$_2$(CH$_2$)$_n$Br}(dppe)$_2$] and [{μ - N$_2$(CH$_2$)$_n$N$_2$}{MBr(dppe)$_2$}$_2$] are produced and both of these can be protonated reversibly to hydrazido(2-) forms [517].

The hydrazido(2-) complex [WBr$_2$(NNH$_2$)(PMe$_2$Ph)$_3$] reacts with HCl (1:1) to form the hydrido hydrazido(2-) complex [WHClBr(NNH$_2$)(PMe$_2$Ph)$_3$]Br, as confirmed by IR and NMR spectra and X-ray crystallography. Anion exchange with Na[BPh$_4$] gives the novel diazenido complex [WHClBr(=N=N(→BPh$_3$)H)(PMe$_2$Ph)$_3$].−CH$_2$Cl$_2$ in low yield, in addition to [WHClBr(NNH$_2$)(PMe$_2$Ph)$_3$][BPh$_4$] the crystal structure of which has been determined by X-ray analysis [518]. [MoO$_2$L$_2$] (L = S$_2$CNR$_2$; R = Me, Et, or Ph, or R$_2$ = (CH$_2$)$_5$; or L = 8-O-quin) react with hydrazines (R'$_2$NH$_2$; R'$_2$ = Me$_2$, (CH$_2$)$_5$, or Ph$_2$) to form the corresponding hydrazido(27) complex, [Mo(NNR'$_2$)OL$_2$]. A crystal structure determination for

[Mo(NNMe$_2$)O(S$_2$CNMe$_2$)] has shown the molybdenum to have a distorted octahedral coordination geometry, with the hydrazido ligand bonded linearly in a position *cis* to the oxo-group [519]. [MCl$_4$(PR$_3$)$_2$] (M = Mo or W; PR$_3$ = PPh$_3$ or PMePh$_2$) react with an excess of Me$_3$SiNHNMe$_2$, in MeCN at room temperature to form [MCl(NNMe$_2$)$_2$(PR$_3$)$_2$] [BPh$_4$]; use of one equivalent of Me$_3$SiNHNMe$_2$ gives [MCl$_3$(NNMe$_2$)(PR$_3$)$_2$]. The analogous reactions of [MCl$_4$(PR$_3$)$_2$] with Me$_3$SiN$_2$Ph (1:2) produces the corresponding [MCl$_2$(N$_2$Ph)(Pr$_3$)$_2$] complex [520]. [W(NNH$_2$)(dppe)$_2$X]Y (X = F, Br, or CF$_3$CO$_2$, respectively, for Y = BF$_4$, Br or H(O$_2$(CF$_3$)$_2$) react with 2,4-dinitrobenzene to yield the 2,4-dinitrophenyl-diazenido (=L) complexes, [WL(dppe)$_2$X]. Spectroscopic properties of these complexes have been obtained [521] and a general consideration of the ^{15}N NMR spectra hydrazido(2-) complexes of molybdenum and tungsten have been published [522]. The preparation and some reactions of hydrazine ([cpMo(NR$_2$NR$_2$)-(NO)X$_2$]), hydrazido(1-) ([cpMo(NRNR$_2$)(NO)X]), and hydrazido(2-) ([μ-NNR$_2${cpMo(NO)X}$_2$]) complexes have been described [523], and the crystal structure of [μ-NNMe$_2${cpMo(NO)I}$_2$] has been shown to comprise molecules with an unsymmetrically bridging dimethylhydrazido group (Mo-N = 1.907(5) and 2.070(6) Å) [524].

[Mo(NNMePh)$_2$(S$_2$CNMe$_2$)$_2$] reacts with HCl (1:1) to form [Mo(NNMePh)-(NHNMePh)(S$_2$CMe$_2$)$_2$]$^+$; an X-ray crystal structure determination of the [BPh$_4$]$^-$ salt has shown that the complex is seven-coordinate, with the coordination of both end-on hydrazido(2-) and unsymmetrically (Mo-N = 2.069(8) and 2.175(9) Å) side-on hydrazido(1-) groups [525]. The complex [(cp)$_2$WH-(NN(H)C$_6$H$_4$F-4)]$^+$, prepared by the insertion of [4-FC$_6$H$_4$N$_2$]$^+$ into one W-H bond of [(cp)$_2$WH$_2$] below -20 °C, has been shown, by an X-ray crystallographic study of its [PF$_6$]$^-$ salt at -100 °C, to contain (formally) a 4-fluorophenyl-hydrazido(2-) ligand with a distinctly bent (W-N-N = 146.3(6)°) skeleton [526]. Repetition of this synthesis at *ca.* 0 °C, or stirring solutions of [(cp)$_2$WH(NNHAr)]$^+$ (Ar = Ph or X-XC$_6$H$_5$, X = F, Me or MeO) near this temperature, produces an isomeric product, [(cp)$_2$W(H$_2$NNAr)]$^+$, which contains an arylhydrazido(1-) ligand bound to the tungsten through both nitrogen atoms [527]. In the case of [(cp)$_2$W(H$_2$NNPh)]$^+$ an X-ray crystallographic study of its [BF$_4$]$^-$ salt has shown that the two W-N bonds are inequivalent (W-N = 2.156(9) and 2.034(9) Å), with the shorter distance corresponding to the phenyl-bonded nitrogen atom [528].

A relatively recent development, in the reactions of coordinated dinitrogen leading to the formation of nitrogen-carbon bonds, has been the synthesis of complexes containing the diazoalkane (=N-N=CR'R) grouping. Thus, treatment of [M(N$_2$)$_2$(dppe)$_2$] (M = Mo or W) with MeBr in thf affords, after protonation of the product, [MBr{=N-N=CH(CH$_2$)$_3$OH}(dppe)$_2$]Br. These materials were

originally considered to contain the tetrahydropyridazido-ligand
($-\overline{N-N}$=CH-CH$_2$-CH$_2$) [529], however, further investigations, including
determinations of the crystal structures of [WBr(N-N=CHCH$_2$CH$_2$CH$_2$OH)(dppe)$_2$]$^-$
[PF$_6$].0.5CH$_2$Cl$_2$ and [WBr(N-N=CMe$_2$)(dppe)$_2$]Br.0.5MeOH [530] have clarified
this situation. This study also explained the unusual ^{1}H and ^{13}C NMR
parameters of these complexes and difficulties encountered in the preparation
of diazoalkane complexes, where R and R' groups are larger than methyl.
The reactions of *trans*-[W(N$_2$)$_2$(dppe)$_2$] with *gem*-dibromides, Br$_2$CRR', to yield
the *trans*-[WBr(N$_2$CRR')(dppe)$_2$]Br diazoalkane complex, have been described.
These complexes do not react with protonic acids, but the unique diazoalkane
carbon atoms are attacked by nucleophiles, such as LiMe, to yield diazenido-
complexes, some of which cannot be obtained by conventional means. The
reactions of *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] with *gem*-dibromides are more complex,
and diazioalkane complexes are, at best, minor products [531]. [WBr(N$_2$H$_2$)-
(dppe)$_2$]Br reacts with CXCl$_3$ (X = Br or H) in the presence of a [Ph$_2$I]$^+$ salt
and an aqueous base, to form the dichlorodiazomethane complex [WBr(N$_2$CCl$_2$)-
(dppe)$_2$]$^+$. This cation has been characterised by X-ray crystallography as
its [PF$_6$]$^-$ salt (W-N = 1.75(2) Å, N-N = 1.35(3) Å, N-C = 1.28(3) Å, W-N-N =
1.69(2) °, N-N-C = 122(2)°) ; the cation has been shown to undergo rapid
reaction with nucleophiles to give a range of interesting organodinitrogen
complexes. These included the vinyl diazenido complex [WBr{N$_2$C(Cl)C(CN)$_2$}-
(dppe)$_2$], by reaction with [CH(CN)$_2$]$^-$, and the structure of this complex has
been determined [532]. *Trans*-[W(N$_2$)$_2$(dppe)$_2$] reacts with MeBr in thf and
related solvents, to produce diazenido-complexes which undergo reversible ring
opening with protic acids to yield substituted-diazoalkane complexes.
Similarly, *N*-methylpyrrolidine and tetrahydrothiophen form diazenido-
derivatives, which react with acids to form hydrazido(2-) complexes and do not
undergo ring opening [533]. The complexes [MoX$_2$(NNH$_2$)(PMe$_2$Ph)$_3$] (X = Cl or
Br) react with aldehydes or ketones to form diazoalkane complexes, [MoX$_2$-
(NN:CRR')(PMe$_2$Ph)$_3$] [534].

The preparations of [W(CO)$_5$L] (L = MeNHNHMe; *cis*- or *trans*- MeN:NMe)
and [*trans*- MeN:NMe{W(CO)$_5$}$_2$] have been described and preferential oxidation
of the coordinated hydrazine to the *cis*-diazene has been observed [535].
Monomeric and dimeric complexes, involving M(CO)$_5$ and M(CO)$_4$ (M = Mo or W)
moieties with diazirines have been synthsised [536]. The complexes
[MoOCl(P-P)]$^+$[MoOCl$_3$(RCON$_2$Ph)]$^-$ (P-P = dppe or dppre; R = Me, Ph, 4-ClC$_6$H$_4$ or
4-MeCC$_6$H$_4$) have been obtained by reacting the hydrazines RCONHNHPh with
[{MoOCl$_2$(P-P)}$_2$], or [MoOCl$_3$(P-P)], in refluxing MeOH. A crystal structure
determination, for P-P = dppe and R = 4-ClC$_6$H$_4$, has shown the anion to have a
distorted octahedral geometry, with an *N,O* bond diazene ligand [537].

Treatment of $[Mo(XC_6H_4CSN_2H)_3]$ (X = H, 4-Me, 4-OMe, or 4-Cl) with acetone, in the presence of dilute acid, yields the complexes $[Mo(4-XC_6H_4CSN)-(4-XC_6H_4SN_2H)(4-XC_6H_4CSNNMe_2)]$ possessing a condensed hydrazonide ligand. The crystal structures have been determined for X = 4-Me or 4-Cl; these molecules involve a coordination polyhdron intermediate between trigonal prismatic and octahedral and (for X = 4-Me) the chelate rings involve Mo-N dimensions of 1.786(5) Å and 142.8(3)° for the diazenido(1-) ligand, 1.967(5) Å and 131.6(4)° for the diazene group, and 2.216(5) Å and 116.9(4) ° for the hydrazonide ligand [538].

7.14 NITROSYL COMPLEXES

The interaction of NO with molybdenum(IV) centres on SiO_2 [539] and Al_2O_3 [540] have been investigated, and the latter considered to involve a dinitrosyl complex. A mechanism, whereby molybdenum-nitrosyl complexes could catalyse the formation of HCN, from NH_2OH and HCHO has been described; this mechanism is considered to involve the initial coordination of NH_2OH [541]. The structure of (hydroxylamido-O,N)nitrosyl complex $[Mo(phen)_2-(NO)(ONH_2)]I_2.H_2O$ has been determined and several new, related complexes have been synthesised [542]. Reduction by Zn/Hg of $[Mo(ttp)Cl_2]$ in C_6H_6 (H_2ttp = meso-tetra-4-tolylporphyrin) under NO leads to the formation of two complexes $[Mo(ttp)(NO)_2].C_6H_6$; the structures of both of these compounds have been determined. The former involves a cis-arrangement of the nitrosyl ligands, with the Mo-N-O groups significantly bent (average bond angle 158.0(8)°) $towards$ each other; the latter possesses a $trans$ arrangement of the MeOH and an essentially linear Mo-N-O (bond angle = 179.8(4)°) group [543]. An excess of $[NO]Y$ (Y = BF_4 or PF_6) reacts with $[Mo(CO)_6]$ in MeCN to form the paramagnetic salt $[Mo(NO)(NCMe)_5]Y_2$ which reacts with NO gas to produce the diamagnetic cis-$[Mo(NO)_2(NCMe)_4]Y_2$ compound. The reactivity of these compounds has been explored and several new nitrosyl complexes isolated, these include: $[Mo(NO)(NCMe)(dppe)_2]Y_m$ (m = 1 or 2) and $[MoCl(NO)(dppe)_2]Y_n$ (n = 0 or 1) [544]. $[MoH_4(dppe)_2]$ reacts with $[NO][PF_6]$ in C_6H_6/MeOH solution to form the protonated nitrosyl complex $[MoF(HNO)(dppe)_2]-[PF_6]$, and the normal nitrosyl complex $trans$-$[MoF(NO)(dppe)_2].0.5C_6H_6$; the reactivity of these complexes has been investigated and other nitrosyl derivatives prepared [545].

A full account of the preparation and reactivity of $[CrMo(O^iPr)_6(NO)_2]$ has been published [365] and the synthesis of $[Mo_2(O^iPr)_6(HNMe_2)_2(NO)_2]$, from $[Mo_2(O^iPr)_6(NO)_2]$ and $HNMe_2$, has been described. This new molecule is centrosymmetric and the lcoal geometry about each molybdenum is that of a

distorted octahedron; comprised of two $\mu_2 - O^i Pr$, one terminal $O^i Pr$ and
$HNMe_2$ group, and one linearly (Mo-N-O = 179.4(5) °) bound nitrosyl ligand
[366]. The compounds $[(Ph_3P)_2N]_3[Na\{Mo_3(CO)_6(NO)_3(\mu_2 - OMe)_3(\mu_3 - O)\}_2]$
and $[NMe_4][Mo_3(CO)_6(NO)_3(\mu_2 - OMe)_3(\mu_3 - OMe)]$ have been synthesised by
refluxing $[Mo(CO)_6]$, $NaNO_2$, $NaOH$ in MeOH and adding the appropriate cation.
The crystal structure of each of these novel materials has been determined.
The anions of both consist of equilateral triangles of molybdenum atoms,
with two carbonyl and one nitrosyl ligand terminally bound to each molybdenum;
the non-bonding Mo-Mo distances (3.297(2) and 3.428(1) Å, respectively) are
bridged by $\mu_2 - OMe$ ligands and a $\mu_3 - O$ atom or a $\mu_3 - OMe$ group, respectively,
caps the triangle; the anion of the former compound contains two such units
linked by a Na^+ ion octahedrally coordinated by the six oxygen atoms of the
$\mu_2 - OMe$ ligands [546].

Comments concerning the hydrazido-complex, $[\mu - NNMe_2\{cpMo(NO)X\}_2]$,
and related monomeric cyclopentadienyl-nitrosyl complexes of molybdenum
[523,524] have made earlier (Section 7.13). The crystal structure of the
"piano-stool" molecule $[cpW(NO)_2Cl]$ has been detailed [547]. $[cpW(NO)I_2]_2$
has been prepared and shown to react with various Lewis bases (L = PPh_3,
$P(OPh)_3$, $SbPh_3$, or CO) to produce the monomeric $[cpW(NO)I_2L]$ complex, but
the carbonyl complex slowly reverts to the original reactants. $[cpW(NO)I_2]_2$
reacts with $Tl^+ cp^-$ or $Na^+ cp^-$ to form the novel, stereochemically non-rigid,
complexes $[(cp)_2W(NO)I]$ and $[(cp)_3W(NO)]$ [548]. $[cpW(NO)I_2\{P(OPh)_3\}]$ and
$[cpW(NO)I_2]_2$ react with $Na[AlH_2(OCH_2CH_2OMe)_2]$ to form the hydrido-nitrosyl
complexes, $[cpW(NO)(H)I\{P(OPh)_3\}]$ and $[cpW(NO)(H)I]_2$, respectively [549].
The complexes $[(\eta^5 - C_5Me_5)M(CO)_2(NO)]$ (M = Mo or W) have been synthesised,
and spectroscopically and structurally characterised; the crystals involve
disordered $M(CO)_2(NO)$ moieties, in which the ligands are *C*- or *N*- bonded to
the metal in a linear fashion [550]. The reactions of $[cpM(NO)(CO)PPh_3]$
with $HgCl_2$ and $SnCl_4$ proceed *via* electrophilic attack at the metal centre
with retention of configuration [551]. The displacement of carbonyl ligands
from $[cpMo(\eta^3 - C_3H_5)(CO)NO]^+$ and other allyl-containing complexes has been
discussed [552], and the attack of nucleophiles on this type of complex has
been the subject of an extensive investigation [553].

7.15 CARBONYL AND THIOCARBONYL COMPLEXES

The polar tensors, effective charges and vibrational intensities of
$[M(CO)_6]$ (M = Mo or W) molecules have been considered [554] and comparative
mass spectrometry has been detailed for these compounds and their
monothiocarbonyl counterparts [555]. ^{95}Mo NMR spectra of molybdenum carbonyl

complexes have been detailed, in an elegant and important study which has clearly demonstrated the ability to observe [95]Mo-X (for X = [31]P) coupling constants in such spectra [6]. ^{17}O NMR spectra of enriched metal carbonyl complexes, such as cis-[Mo(CO)$_4$L$_2$] (L = PPh$_3$, AsPh$_3$, SbPh$_3$ or PPhMe$_2$) have been obtained [556] and the synthesis of molybdenum and tungsten carbonyl complexes enriched in ^{13}C has been developed using the CO-labilizing ability of (^{n}Bu)$_3$PO [557].

The preparation, spectroscopic properties and resonance Raman profiles of [μ-pyrazine{W(CO)$_5$}$_2$], the preresonance Raman spectrum of [W(CO)$_5$-(pyridazine)] [558], the resonance Raman, electronic, photochemical reactivity and MCD spectra of [M(CO)$_{4-x}$L{P(OMe)$_3$}$_x$] (M = Mo or W; x = 0 or 1; L = 1,4-diazabutadiene, pyridine-2-carbaldehyde imine, bipy, or phen) have been described and discussed [559], and the MCD spectra alkylaminopentacarbonyl complexes of molybdenum and tungsten have been presented and interpreted [560]. The quenching of emission and photochemistry of [W(CO)$_5$(4-cyanopyridine)] by anthracene has been described, this relationship implying that the emitting state of this molecule is implicated in its photochemistry [561]. Further studies of the photolysis of molecular molybdenum and tungsten carbonyl complexes, isolated in an inert gas matrix at low temperature, have been accomplished [562-564]; in 2-methyltetrahydrofuran (mthf) at 77 K, evidence has been obtained for the photoconversion of Mo(CO)$_5$ into [Mo(CO)(mthf)] [565].

The Mo $3d_{5/2}$, C $1s$, and O $1s$ binding energies of [LMo(CO)$_5$] (L = PX$_3$ or CO) compounds have been measured and found to be linearly related to each other and to the phosphorus lone-pair IP of the free PX$_3$ molecule [566]. The UVPES and ^{13}C NMR spectra of [W(CO)$_5$(PR$_3$)] (R = C$_6$H$_{11}$, Ph, or OPh) have been presented and assigned by comparison with the spectra of free PR$_3$ and [W(CO)$_6$] [567]. The heats of formation of a number of [M(CO)$_{6-x}$L$_x$] (M = Mo or W; L = piperidine, py, pyrazine, pyrazole, or thiazole; x = 1, 2 or 3) compounds have been reported [568].

[M(CO)$_6$] (M = Mo or W) have been found to be active homogeneous catalyst for the water gas shift reaction, CO(g) + H$_2$O(l) $\rightleftharpoons$ H$_2$(g) + CO$_2$(g), in the presence of a large excess of sulphides generated by Na$_2$S dissolved in aqueous methanol [569]. Phase-transfer catalysed nucleophilic reactions of hydroxide ions at metal-bound carbonyl centres, [M(CO)$_{6-x}$L$_x$] (M = Mo or W) have been discussed [570], as have the requirements for multinuclear centres to catalyze the hydrogenation of CO [571]. M$_2$[W(CO)$_5$] (M = Li or Na) salts in thf have been shown to reduce CO$_2$ to CO [572]. Lewis acid promoted CO insertion into a metal-aryl bond has been observed with [PhW(CO)$_5$]$^-$ [573], and the nature of the catalytically active species, for homogeneous

acetylene metathesis, in the [Mo(CO)₂]/PhOH system has been discussed [574].
Thiols can be desulphurized in good yield by treatment with [Mo(CO)₆]
either in HOAc or when pre-adsorbed on SiO₂ [575].

The half-wave oxidation and reduction potentials have been determined
for [M(CO)₆] (M = Mo or W) and for [W(CO)₆₋ₓ(MeCN)ₓ] (x = 1-3) in various
aprotic solvents [576], and the electrochemical synthesis of [M(CO)₆]
(M = Mo or W) and their phosphine derivatives, from suitable metal complexes
in the +III oxidation state, has been developed [577].

The crystal structure of [Mo(CO)₃(phen)(η²-SO₂)] and [Mo(CO)₂(bipy)-
(η²-SO₂)₂] have been determined and the η²-SO₂ bonding has been considered
in relationship to the dimensions observed [578]. [NEt₄] [(μ-C₆Cl₅S){W(CO)₅}₂]
involves a bent W-S-W (132.1(1)°) bridge and the ν(C-O) stretching frequencies
observed in the IR are consistent with this structure [579]. [W(CO)₄(S,S-
dimethylsulphonium 2-picolinyl(methylide)] has been shown by X-ray
crystallography to involve the ylide coordinated through the pyridine N and
carbonyl O atoms [580]. The syntheses and the structures of [(Ph₃P)₂N] -
[Na{Mo₃(CO)₆(NO)₃(μ₂-OMe)(μ₃-O)}₂] and [NMe₄] [Mo₃(CO)₆(NO)₃(μ₂-OMe)₃-
(μ₃-OMe)] [546] have been presented earlier (Section 7.14). Histidinato-
carbonyl complexes of molybdenum and tungsten have been prepared [581] and the
activation volume for the reaction of [Mo(bipy)(CO)₄] with CN⁻ has been
measured [582]. Tetracarbonylbis(P,P-diphenyl-N-methylphosphino-
thioformamido)bis(μ-P,P-diphenyl-N-methylphosphinathio formamido)dimolybdenum.
4CH₂Cl₂ has been characterised by X-ray crystallography, and one ligand found
to be tridentate with the S and N atoms coordinated to one molybdenum and the
P bonded to the other molybdenum of the dimeric molecule [583],

The relative stabilities of the geometric isomers of [Mo(CO)₂(PPh₃)₄]
have been assessed in terms of electronic factors [42]. The new five-
coordinated complexes [M(CO)₃(P(cych)₃)₂] (M = Mo or W) have been prepared and
shown to reversibly add dinitrogen, dihydrogen, and other small molecules
[498]. The crystal structure of [Mo{Ph₂P(CH₂)₂PPh(CH₂)₂PPh₂}(CO)₃] has been
determined [584] and ³¹P NMR data have been used to assign the structure of
the complexes formed between {(diphenylphosphino)methyl}-ethylenediamine and
molybdenum and tungsten carbonyls [585]. The complete series of fifteen
compounds of the type Ph₂P(X)CH₂P(Y)Ph₂ (L) (X = Y and X ≠ Y for O, S, Se, or
Me⁺) have been synthesised and their [M(CO)₄L] (M = Mo or W) derivatives
have been prepared [586]. The unsymmetrical bis(tertiary phosphine) ligand,
Ph₂PCH₂PᵗBu₂ and its mono- and disulphides have been prepared and used as
ligands (L) in [M(CO)₄L] (M = Mo or W) complexes [587]. Other complexes,
involving molybdenum or tungsten carbonyl moieties coordinated by P-donor
ligands reported this year, have included: [M(CO)₅(PX₃)] (M = Mo or W;

X = Cl or Br) [588], [(OC)$_4$Mo{PhPH(CH$_2$)$_3$PPhH}] and its oligomers [589], *cis*-[{R$_2$PCH$_2$PR$_2$}M(CO)$_4$] (M = Mo or W; R = Me$_2$CHO or Me$_2$N) and [{R$_2$P(S)-CH$_2$PR$_2$}$_2$Mo(CO)$_4$] [590], [M(CO)$_3$L] (where M = Mo or W; L = 2-Ph$_2$PC$_6$H$_4$CH:CRC$_6$H$_4$-PPh$_2$, R = H or Me) [591], [(OC)$_m$Mo(PhP(H)PR$_2$)$_n$] (*m* = 4 or 5; *n* = 2 or 1, respectively; R = Ph or ^{t}Bu) and [(OC)$_5$MPPhHPPhPPhHMo(CO)$_5$] [592]. The crystal structure of [Mo(CO)$_2$(dppe)$_2$F] [PF$_6$] has established a seven-coordinate geometry for the cation [593]. Reactions of the ligands of *cis*-[Mo(CO)$_4$(Me$_2$PLi)$_2$] [594], [(OC)$_5$MoPPh$_2$Cl] and *cis*-[(OC)$_4$Mo(PPh$_2$Cl)$_2$] [595] have been explored and the photochemical ligand substitutions of *trans*-[W(CO)$_4$LL'] (L ≠ L' = ^{i}Pr$_3$P, Ph$_3$P, (Me$_2$N)$_3$P, (^{i}PrO)$_3$P) have been categorised [596]. The reaction of [(OC)$_5$WPPhCl$_2$] with Hacac results in substitution of the Cl by the oxygen atom of the enolized dione [597]; the modes of coordination of (PXNR)$_2$ (X = F or Cl) to metal centres, including M(CO)$_5$, (M = Mo or W) [598] have been investigated and 3,5-dimethylpyrazolyl-phosphine has been shown to coordinate as a mono- bi-, or tridentate ligand in molybdenum and tungsten carbonyl complexes [599]. Phosphole [2+2] and [4+2] dimerisations have been observed around molybdenum and tungsten carbonyl moieties [600], and the coordination of P$_4$(SiMe$_2$)$_3$ [601] and di- and triaza-σ^2-phosphole [602] to these and other metal centres have been investigated.

Molybdenum carbonyl complexes with three new tertiary-arsine-containing macrocycles have been prepared and characterised [603] and extensive studies of the productions of the reactions of phosphine, arsine, and stibine donor ligands with molybdenum and tungsten carbonyl complexes have been accomplished [604]. New germylene [605] and stannylene [606] complexes have been described and novel gallium-containing ligands have been prepared and reacted with organo-molybdenum carbonyl complexes [607].

Other carbonyl complexes of these metals have been described in earlier sections, including those dealing with : molybdenum(II) and tungsten(II) (7.6 [326-329, 332, 333]), hydride complexes (7.8 [342-345, 355]), metal-metal bonds (7.9.5 [416, 418-425, 428-444]), organodinitrogen ligands (7.13 [513-515]) and nitrosyl complexes (7.14 [546, 550-553]).

REFERENCES

1   C. D. Garner, *Coord. Chem. Rev.*, 37 (1981) 117.
2   F. E. Mabbs, *Coord. Chem. Rev.*, 37 (1981) 157.
3   M. P. Coughlan (Ed.), "Molybdenum and Molybdenum Containing Enzymes",
    Pergamon, Oxford, 1980.
4   W. E. Newton and S. Otsuka (Eds.), "Molybdenum Chemistry of Biological
    Significance", Plenum, New York (1980).
5   H. F. Barry and P. C. H. Mitchell (Eds.), "Chemistry and Uses of
    Molybdenum", *Proc. Climax Third Int. Conf.*, Climax Molybdenum Company,
    Ann Arbor, Michigan (1979).
6   A. F. Masters, R. T. C. Brownless, J. D. Cotton, M. J. O'Connor and
    A. G. Wedd, *J. Organometal. Chem.*, 195 (1980) C17, and references
    therein.
7   J. Kronenbitter, INIS Atomindex, 11 (1980) Abstr. No. 515208,
    Chem. Abstr. 93 (1980) 84501.
8   J. C. J. Bart and V. Ragaini, *Acta Crystallogr., Sect. B*, 36 (1980)
    1351.
9   J. C. J. Bart and V. Ragaini, Phosphorus Sulfur, 8 (1980) 161.
10 A. M. Emel'yanov, A. V. Gusarov, and L. N. Gorokhov, *Vses. Konf.
    Kalorim., 7th*, 2 (1977) 325, *Chem. Abstr.*, 92 (1980) 11943.
11 J. K. Bates and D. M. Gruen, *J. Mol. Spectrosc.*, 78 (1979) 284.
12 P. M. Atha, I. H. Hillier, and M. F. Guest, *Chem. Phys. Lett.*, 75
    (1980) 84.
13 B. E. Bursten, F. A. Cotton, and M. B. Hall, *J. Am. Chem. Soc.*,
    102 (1980) 6349.
14 C. G. Francis and P. L. Timms, *J. Chem. Soc., Dalton Trans.*, (1980)
    1401.
15 C. G. Francis, H. Huber, and G. A. Ozin, *Inorg. Chem.*, 19 (1980) 219.
16 W. E. Klotzbücher and G. A. Ozin, *Inorg. Chem.*, 19 (1980) 2848.
17 W. E. Klotzbücher and G. A. Ozin, *Inorg. Chem.*, 19 (1980) 3767.
18 W. E. Klotzbücher and G. A. Ozin, *Inorg. Chem.*, 19 (1980) 3776.
19 W. E. Klotzbücher and G. A. Ozin, NBS Spec. Publ. (U.S.) 561 (1979) 567.
    Chem. Abstr. 92 (1980) 87295.
20 A. J. Woytek, *Kirk-Othmer Encycl. Chem. Technol.*, 3rd Ed., M. Grayson,
    and D. Eckroth (Eds.), Wiley, New York, 10 (1980) 823 and 764.
21 J. C. Cumming, *J. Mol. Spectrosc.*, 83 (1980) 417.
22 G. L. Gutsev and A. A. Levin, *Chem. Phys.*, 51 (1980) 459.
23 V. H. Shui, P. I. Singh, B. Kivel, and E. R. Bressel, AIAAJ, 17
    (1979) 1178, *Chem. Abstr.*, 92 (1980) 47356.
24 O. V. Blinova and Yu. B. Predtechenskii, *Opt. Spektrosk.*, 47 (1979) 1120.
25 P. D. Kleinschmidt, K. H. Lau, and D. L. Hildenbrand, *J. Chem. Thermodyn.*,
    11 (1979) 765.
26 C. J. Barbour, J. H. Cameron, and J. H. Winfield, *J. Chem. Soc.,
    Dalton Trans.*, (1980) 2001.
27 J. Fawcett, R. D. Peacock, and D. R. Russell, *J. Chem. Soc., Dalton
    Trans.*, (1980) 2294.
28 P. M. Boorman and B. D. O'Dell, *J. Chem. Soc., Dalton Trans.*, (1980)
    257.
29 J. C. Taylor and A. B. Waugh, *J. Chem. Soc., Dalton Trans.*, (1980)
    2006.
30 K. Iijima and S. Shibata, *Bull. Chem. Soc. Jpn.*, 48 (1975) 666.
31 I. A. Topol, N. F. Stepanov, and V. M. Kovba, *Theor. Chim. Acta.*,
    56 (1980) 297.
32 S. S. Eliseev and L. E. Malysheva, *Izv. Akad. Nauk Tadzh. SSR.,
    Otd. Fiz.-Mat. Geol.-Khim. Nauk*, 1 (1980) 28, *Chem. Abstr.*, 93 (1980)
    55049.
33 J. H. Holloway and G. J. Schrobilgen, *Inorg. Chem.*, 19 (1980) 2632.

34   A. K. Sengupta and S. K. Nath, *Indian J. Chem.*, Sect. A, 19 (1980) 166.
35   Yu. V. Kokunov, V. A. Bochkareva, Yu. D. Chubar and Yu. A. Buslaev, *Koord. Khim.*, 6 (1980) 1205.
36   A. A. Konovalova, S. V. Bainova and Yu. A. Buslaev, *Koord. Khim.*, 6 (1980) 1423.
37   N. D. Ivanova and K. B. Kladnitskaya, *Ukr. Khim. Zh. (Russ. Ed.)* 45 (1979) 1061.
38   A. J. Edwards, D. R. Slim, J. E. Guerchais, and R. Kergoat, *J. Chem. Soc., Dalton Trans.*, (1980) 289.
39   M. M. Azizov, A. Kushakbaev, and N. A. Parpiev, *Dokl. Akad. Nauk. Uzb. SSR.*, (1978) 43, *Chem. Abstr.*, 93 (1980) 87577.
40   B. Viossat and N. Rodier, *Acta Crystallogr., Sect. B*, 35 (1979) 2715.
41   K. Tatsumi and R. Hoffmann, *Inorg. Chem.*, 19 (1980) 2656.
42   D. M. P. Mingos, *J. Organomet. Chem.*, 179 (1979) C29.
43   K. Tani, M. Hanafusa, and S. Otsuka, *Tetrahedron Lett.*, (1979) 3017.
44   T. Mashiko, S. Terashima, and S. Yamada, Yakugaku Zasshi, 100 (1980) 319 and 328, *Chem. Abstr.*, 93 (1980) 192718 and 131963.
45   F. Di Furio, G. Modena, R. Curci, and J. O. Edwards, *J. Chem. Soc., Perkin Trans. 2*, (1980) 457.
46   W. Winter, C. Mark, and V. Shurig, *Inorg. Chem.*, 19 (1980) 2045.
47   A. D. Westland, F. Hague, and J.-M. Bouchard, *Inorg. Chem.*, 19 (1980) 2255.
48   S. U. Kreingold and A. N. Vasnev, *Zh. Neorg. Khim.*, 25 (1980) 2451.
49   S. B. Etcheverry and E. J. Baran, *Z. Anorg. Allg. Chem.*, 465 (1980) 153.
50   H. Ledon, M. Bonnet, and J.-Y. Lallemand, *J. Chem. Soc., Chem. Commun.*, (1979) 702.
51   B. F. Mentzen, M. C. Bonnet, and H. J. Ledon, *Inorg. Chem.*, 19 (1980) 2061.
52   H. Arzoumanian, R. Lai, R. L. Alvarez, J.-F. Petrigani, J. Metzger, and J. Fuhrop, *J. Am. Chem. Soc.*, 102 (1980) 845.
53   A. P. Filippov and O. A. Polishchuk, *Zh. Neorg. Khim.*, 25 (1980) 2711.
54   A. S. Reddy and B. R. Reddy, *Indian J. Chem., Sect. A*, 19 (1980) 200.
55   J. Anwar, M. Umar, M. Younas, and M. K. Mukhtar, *Arabian J. Sci, Eng.*, 5 (1980) 97.
56   Yu. K. Tselinskii, B. V. Pestryakov and T. M. Pekhtereva, *Zh. Obshch. Khim.*, 50 (1980) 347.
57   V. M. S. Gil, M. E. T. L. Saraiva, M. M. Caldiera, and A. M. D. Pereira, *J. Inorg. Nucl. Chem.*, 42 (1980) 389.
58   V. M. S. Gil, M. M. Caldeira and M. E. T. L. Saraiva, *Inorg. Nucl. Chem. Lett.*, 16 (1980) 65.
59   Y. Abe, T. Takizawa, and T. Kunieda, *Chem. Pharm. Bull.*, 28 (1980) 1324.
60   K. I. Suleimanova, N. P. Ismailov, and Kh. R. Rustamov, *Uzb. Khim. Zh.*, 6 (1979) 72.
61   S. Natansohn, J. I. Krugler, J. E. Lester, M. S. Chagnon, and R. S. Finocchario, *J. Phys. Chem.*, 84 (1980) 2972.
62   J. M. Poirier and J. F. Verchere, *J. Chem. Res. Synop.*, 3 (1980) 80.
63   L. M. Charney and F. A. Schultz, *Inorg. Chem.*, 19 (1980) 1527.
64   J. T. Spence, M. Minelli, and P. Kroneck, *J. Am. Chem. Soc.*, 102 (1980) 4538.
65   J. Bordas, R. C. Bray, C. D. Garner, S. Gutteridge, and S. S. Hasnain, *Biochem. J.*, 191 (1980) 499.
66   C. A. Cliff, G. D. Fallon, B. M. Gatehouse, K. S. Murray, and P. J. Newman, *Inorg. Chem.*, 19 (1980) 773.
67   E. I. Stiefel, K. F. Miller, A. E. Bruce, J. L. Corbin, J. M. Berg, and K. O. Hodgson, *J. Am. Chem. Soc.*, 102 (1980) 3624.
68   J. M. Berg and K. O. Hodgson, *Inorg. Chem.*, 19 (1980) 2180.
69   J. Topich, *Inorg. Chim. Acta.*, 46 (1980) L97.
70   I. Pawlowska and W. Wojciechowski, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.*, 27 (1979) 203.

71   M. Chaudhury, P. Banerjee, R. De, and K. Nag, *Transition Met. Chem.*
      (Weinheim. Ger.), 5 (1980) 117.
72   C. Knobler, B. R. Penfold, W. T. Robinson, C. J. Wilkins, and S. H. Young,
      J. Chem. Soc., Dalton Trans., (1980) 248; A. J. Matheson and
      B. R. Penfold, *Acta Crystallogr., Sect. B*, 35 (1979) 2707.
73   J. P. N. Srivastava and M. N. Srivastava, *Talanta*, 27 (1980) 763.
74   P. S. Zacharias and C. Subramani, *Indian J. Chem., Sect. A*, 19 (1980)
      71.
75   H. Singh, U. K. Rathi, and N. Singh, *J. Indian Chem. Soc.*, 57 (1980)
      475.
76   J. K. Howie, P. Bosserman, and D. T. Sawyer, *Inorg. Chem.*, 19 (1980)
      2293.
77   S. N. Poddar, S. Ghosh, and G. C. Samanta, *J. Indian Chem. Soc.*, 57
      (1980) 92.
78   L. Saussine, H. Mimoun, A. Mitschler, and J. Fisher, *Nouv. J. Chim.*,
      4 (1980) 235.
79   K. Weighardt, E. Hofer, W. Holzbach, B. Nuber, and J. Weiss, *Inorg.*
      Chem., 19 (1980) 2927.
80   J. Topich, *Inorg. Chim. Acta.*, 46 (1980) L37.
81   W. E. Hill, N. Atabay, C. A. McAuliffe, F. P. McCullough and
      S. M. Razzoki, *Inorg. Chim. Acta*, 35 (1979) 35.
82   M. M. Azizov, A. Kushakbaev, and N. A. Parpiev, *Koord. Khim.*, 6 (1980)
      1417.
83   M. M. Azizov, A. Kushakbaev, and N. A. Parpiev, *Dokl. Akad. Nauk Uzb.*
      SSR, (1979) 19.
84   B. Viossat, N. Rodier, and P. Khodadad, *Acta Crystallogr., Sect. B*,
      35 (1979) 2712.
85   P. Mouron, *Rev. Chim. Miner.*, 16 (1979) 449.
86   E. L. Muetterties and E. Band, *J. Am. Chem. Soc.*, 102 (1980) 6572.
87   J. R. M. Kress, M. J. M. Russell, M. G. Wesolek, and J. A. Osborn,
      J. Chem. Soc., Chem. Commun., (1980) 431.
88   J. H. Wengrovius, R. R. Schrock, M. R. Churchill, J. R. Missert, and
      W. J. Youngs, *J. Am. Chem. Soc.*, 102 (1980) 4515.
89   A. K. Rappé and W. A. Goddard III, *J. Am. Chem. Soc.*, 102 (1980) 5115.
90   S. Mohan, *Ind. J. Pure Appl. Phys.*, 17 (1979) 774.
91   L. A. Alesho-Ozhevskaya, M. K. Il'in, A. V. Makarov, and O. T. Nikitin,
      Vestn. Mosk. Univ. Ser. 2, Khim., 21 (1980) 248, *Chem. Abstr.*, 93
      (1980) 249162.
92   A. A. Ivanov, A. V. Demidov, N. I. Popenko, E. Z. Zasorin,
      V. P. Spiridonov, and I. Hargittai, *J. Mol. Struct.*, 63 (1980) 121.
93   C. D. Jaeger, F.-R. F. Fan, and A. J. Bard, *J. Am. Chem. Soc.*, 102
      (1980) 2592; A. Giraudeau, F.-R. F. Fan, and A. J. Bard, *ibid.*,
      102 (1980) 5137.
94   V. G. Pitsyuga, L. A. Pozharskaya, M. V. Mokhosoev, and E. D.
      Serdyukova, *Zh. Neorg. Khim.*, 25 (1980) 891.
95   S. Son, N. Kinomura, F. Kanamura, and M. Koizumi, *J. Chem. Soc.*,
      Dalton Trans., (1980) 1029.
96   F. W. Kutzler, C. R. Natoli, D. K. Misemer, S. Doniach, and
      K. O. Hodgson, *J. Chem. Phys.*, 73 (1980) 3274.
97   H. Gamsjäger, G. A. K. Thompson, W. Sagmüller, and A. G. Sykes,
      Inorg. Chem., 19 (1980) 997.
98   K. H. Tytko, G. Petridis, and B. Schönfield, *Z. Naturforsch.*,
      B: Anorg. Chem., Org. Chem., 35b (1980) 45.
99   J. J. Cruywagen, *Inorg. Chem.*, 19 (1980) 552.
100   A. F. Masters, S. F. Gheller, R. T. C. Brownlee, M. J. O'Connor, and
      A. G. Wedd, *Inorg. Chem.*, 19 (1980) 3866.
101   W. A. LaRue, A. T. Liu, and J. San Filippo, Jr., *Inorg. Chem.*, 19
      (1980) 315.
102   V. W. Day, M. R. Thompson, C. S. Day, W. G. Klemperer, and R.-S. Liu,
      J. Am. Chem. Soc., 102 (1980) 5971.

103   H. Horiuchi, N. Morimoto, and S. Shinobu, *J. Solid State Chem.*, 33
       (1980) 115.
104   K. Okada and J. Ossaka, *Acta Crystallogr.*, *Sect. B*, 36 (1980) 657.
105   F. Knee and R. A. Condrate, *J. Phys. Chem. Solids.*, 40 (1979) 1145.
106   H. Hasegawa and M. Imaoka, see *Chem. Abstr.*, 93 (1980) 30675.
107   M. Spoliti, V. Piacente, L. Bencivenni, D. Ferro, and S. N. Cesaro,
       High Temp. Sci., 12 (1980) 215.
108   H. J. Becher, *J. Chem. Res. Synop.*, 3 (1980) 92; H. J. Becher,
       C. Brendel, and W. Scheuermann, *ibid.*, 3 (1980) 93.
109   V. Massarotti, G. Flor, A. Marini, and R. Riccardi, *Z. Naturforsch. A*,
       35 (1980) 500.
110   L. I. Zakharkina, N. A. Korotchenko, V. F. Chuvaev, and G. A. Bogdanov,
       Zh. Fiz. Khim., 53 (1979) 2964.
111   K. R. Poeppelmeier, A. J. Jacobson, and J. M. Longo, *Mater. Res. Bull.*,
       15 (1980) 339.
112   V. A. Levitskii, Yu. Hekimov, and Ya. I. Gerasimov, *J. Chem.
       Thermodyn.*, 11 (1979) 1075.
113   D. K. Breitinger, L. Emmert, and W. Kress, *J. Mol. Struct.*, 61
       (1980) 195.
114   W. Depmeier, *J. Appl. Crystallogr.*, 12 (1979) 623.
115   L. G. Maksimova, L. V. Tumurova, and M. V. Mokhosoev, *Zh. Neorg. Khim.*,
       25 (1980) 2416.
116   O. W. Rollins and B. J. Haynes, *J. Inorg. Nucl. Chem.*, 41 (1979) 1797.
117   M. Goreaud, P. Labbe, J. C. Monier, and B. Raveau, *J. Solid State Chem.*,
       30 (1979) 311.
118   A. P. Perepelitsa and M. V. Mokhosoev, *Zh. Neorg. Khim.*, 25 (1980)
       2848.
119   H. Ichida, A. Kobayashi, and Y. Sasaki, *Acta Crystallogr.*, *Sect. B*,
       36 (1980) 1382.
120   M. Feist, V. N. Molchanov, L. P. Kazanskii, E. A. Torchenkova, and
       V. I. Spitsyn, *Zh. Neorg. Khim.*, 25 (1980) 733.
121   F. Robert, A. Tézé, G. Herve, and Y. Jeannin, *Acta Crystallogr.*, *Sect. B*,
       36 (1980) 11.
122   V. W. Truesdale, P. J. Smith, and C. J. Smith, *Analyst (London)*
       104 (1979) 897.
123   Zh. G. Bazarova, M. V. Mokhosoev, and E. A. Kirillov, *Izv. Akad. Nauk*,
       SSSR. Neorg. Mater., 16 (1980) 717; E. V. Tkachenko, L. M. Fedorova,
       V. T. Gabrielyan, N. S. Nikogosyan, and L. Bazhenova, *Zh. Neorg. Khim.*,
       25 (1980) 1443.
124   L. G. Sevast'yanova, K. P. Burdina, E. V. Zubova, and Yu. N. Venevtsev,
       Izv. Akad. Nauk SSSR, Neorg. Mater., 15 (1979) 2022.
125   O. Gansow, R. K. C. Ho, and W. G. Klemperer, *J. Organomet. Chem.*, 187
       (1980) C27.
126   Gh. Marcu, A. Botar, and M. Rusu, *Rev. Roum. Chim.*, 24 (1979) 1465;
       Gh. Marcu and I. Ciogolas, *ibid.*, 24 (1979) 1049.
127   D. E. Katsoulis, A. N. Lambrianidou, and M. T. Pope, *Inorg. Chim. Acta.*,
       46 (1980) L55.
128   L. A. Fernando, M. L. Miles, and L. H. Bowen, *Anal. Chem.*, 52 (1980)
       1115.
129   K. Sakata, M. Misono, and Y. Yoneda, *Chem. Lett.*, (1980) 151.
130   K. M. Barkigia, L. M. Rajković-Blazer, M. T. Pope, E. Prince, and
       C. O. Quicksall, *Inorg. Chem.*, 19 (1980) 2531.
131   K. Y. Matsumoto, *Bull. Chem. Soc. Jpn.*, 52 (1979) 3284.
132   B. Hedman, *Acta Crystallogr.*, *Sect. B*, 36 (1980) 2241.
133   W. G. Klemperer and R.-S. Liu, *Inorg. Chem.*, 19 (1980) 3863.
134   E. T. Shuvaeva and E. T. Fesenko, *Kristallografiya*, 25 (1980) 408.
135   A. Watanabe and H. Kodema, *Koen Yoshishu–Jinko Kobutsu Toronkai, 24th*,
       (1979) 57; *Chem. Abstr.*, 92 (1980) 172668; H. Kodema and I. Fujo, *ibid.*,
       (1979) 59; *Chem. Abstr.*, 92 (1980) 172514.
136   J. Fuchs, H. U. Krüsler, and A. Förster, *Z. Naturforsch., B: Anorg. Chem.*,

Org. Chem., 34 (1979) 1683.

137 P. Forzatti and P. Tittarelli, *J. Solid State Chem.*, 33 (1980) 421.

138 F. Chauveau, P. Doppelt, and J. Lefebvre, *Inorg. Chem.*, 19 (1980) 2803.

139 H. Kondo, A. Kobayashi, and Y. Sasaki, *Acta Crystallogr.*, Sect. B, 36 (1980) 661.

140 R. C. Fay, *Coord. Chem. Rev.*, 37 (1981) p. 20-21.

141 R. K. Srivastava, B. Pal, B. B. Raizada, and K. B. Pandeya, *J. Indian Chem. Soc.*, 57 (1980) 391.

142 P. V. Klevtsov, E. S. Zolotova, L. A. Glinskaya, and R. F. Klevtsova, *Zh. Neorg. Khim.*, 25 (1980) 1844.

143 R. F. Klevtsova, A. A. Antonava, and L. A. Glinskaya, *Kristallografiya*, 25 (1980) 161.

144 S. K. Roy and P. P. Jha, *J. Indian Chem. Soc.*, 57 (1980) 927.

145 D. Labonnette, *J. Chem. Res. Synop.*, 8 (1979) 252.

146 A. Björnberg, *Acta Crystallogr.*, Sect. B, 35 (1979) 1989.

147 A. Björnberg, *Acta Crystallogr.*, Sect. B, 36 (1980) 1530.

148 A. Björnberg and B. Hedman, *Acta Crystallogr.*, Sect. B, 36 (1980) 1018.

149 G. Hervé, A. Tézé, and M. Leyrie, *J. Coord. Chem.*, 9 (1979) 245.

150 F. Y. Robb, W. S. Glausinger, and P. Courtine, *J. Solid State Chem.*, 30 (1979) 171.

151 M. M. Mossoba, C. J. O'Connor, M. T. Pope, E. Sinn, G. Hervé, and A. Tézé, *J. Am. Chem. Soc.*, 102 (1980) 6866.

152 E. N. Yur'chenko, *J. Mol. Struct.*, 60 (1980) 325; A. K. Il'yasova, D. U. Bagalieva, and S. E. Bekmakhanov, *Zh. Neorg. Khim.*, 24 (1979) 3274, A. K. Il'yasova, O. A. Molchanova, I. N. Nurlybaev, and M. N. Kentaeva, *ibid.*, 24 (1979) 3269; V. S. Sergienko, M. A. Porai-Koshits, and E. N. Yurchenko, *Zh. Strukt. Khim.*, 21 (1980) 111.

153 M. Marinov, V. Kozhukharov, G. Bliznakov, D. Klisurski, and I. Pavlova, *Z. Anorg. Allg. Chem.*, 463 (1980) 213.

154 S. Kemmler-Sack, *Z. Anorg. Allg. Chem.*, 461 (1980) 146; S. Kemmler-Sack and U. Treiber, *ibid.*, 462 (1980) 166; H. J. Rother, S. Kemmler-Sack, U. Treiber, and W. R. Cyris, *ibid.*, 466 (1980) 131.

155 L. Ghizdava and G. Marcu, *Rev. Roum. Chim.*, 24 (1979) 569.

156 K. T. Jacob, *J. Mater. Sci.*, 15 (1980) 2167.

157 V. L. Butukhanov, M. V. Mokhosoev, and S. R. Sambueva, *Zh. Neorg. Khim.*, 25 (1980) 2455.

158 C. Cuong and B. N. Thuyea, *Tap Chi Hoa Hoc.*, 14 (1976) 17; *Chem. Abstr.*, 92 (1980) 51114.

159 C. J. Besecker and W. G. Klemperer, *J. Am. Chem. Soc.*, 102 (1980) 7600.

160 J. Amosse and J. C. Mathieu, *J. Chem. Themodyn.*, 12 (1980) 683.

161 H. Chen, *Mater. Res. Bull.*, 14 (1979) 14.

162 M. H. Rapposch, J. B. Anderson, and E. Kostiner, *Inorg. Chem.*, 19 (1980) 3531.

163 G. Matzen, F. Seveque, and P. Poix, *Z. Anorg. Allg. Chem.*, 457 (1979) 5.

164 V. P. Sagalovich, T. N. Tikhonova, N. B. Kupletskaya, and L. A. Kazitsyna, *Zh. Obshch. Khim.*, 50 (1980) 1424.

165 K. Nomiya, M. Sugaya, and M. Miwa, *Bull. Chem. Soc.*, Jpn., 52 (1979) 3107.

166 G. Matzen and P. Poix, *C. R. Hebd. Seances Acad. Sci.*, Ser. C, 290 (1980) 219.

167 Q. S. Olgiun, B. N. Ivanov-Emin, and G. Z. Kaziev, *Zh. Neorg. Khim.*, 24 (1979) 3279.

168 F. Robert, M. Leyrie, G. Hervé, A. Tézé, and Y. Jeanin, *Inorg. Chem.*, 19 (1980) 1746.

169 L. C. W. Baker, L. Lebioda, J. Grochowski, and H. G. Mukherjee, *J. Am. Chem. Soc.*, 102 (1980) 3274.

170 G. Marcu, I. Ciogolas, I. Todorut, *Rev. Roum. Chim.*, 24 (1979) 715.

171 T. Machej and J. Ziolkowski, *J. Solid State Chem.*, 31 (1980) 135; *idem.*, *ibid.*, 31 (1980) 145.

172 G. A. Lappin and R. D. Peacock, *Inorg. Chim. Acta.*, 46 (1980) L71.

222

173   D. J. Morell, J. S. Cantrell, and L. L. Y. Chang, *J. Am. Ceram. Soc.*,
      63 (1980) 2967; D. S. Robertson, I. M. Young, and J. R. Tefler,
      J. Mater. Sci., 14 (1979) 2967.
174   M. V. Mokhosoev, A. D. Gorbalyuk, A. P. Perepelitsa, and F. P. Alekseev,
      Zh. Neorg. Khim., 25 (1980) 2407. E. S. Razgon, I. V. Shakno,
      T. I. Bel'skaya, E. M. Avzhieva, and L. R. Portugal'skaya, *ibid.*,
      25 (1980) 1479; T. A. Tunik, L. A. Bezukladnikova, E. G. Grigor'ev,
      Yu. P. Udalov, and N. F. Fedorov, *ibid.*, 24 (1979) 3091; N. F. Fedorov,
      V. V. Ipatov, and O. V. Kvyatovskii, *ibid.*, 25 (1980) 1630; V. L.
      Butukhanov, M. V. Mokhosoev, S. R. Sambueva, *ibid.*, 24 (1979) 2978;
      L. Yu. Kharchenko and V. I. Protasova, *ibid.*, 25 (1980) 851; A. A.
      Evdokimov, V. K. Trunov, and B. M. Sokolovskii, *ibid.*, 25 (1980) 710;
      A. Watanabe, Z. Inoue, and T. Ohsaka, *Mater. Res. Bull.*, 15 (1980) 397;
      Yu. L. Suponitskii. V. M. Lazarev, and M. Kh. Karapet'yants,
      Zh. Fiz. Khim., 53 (1979) 3055; K. Blacklock, H. W. White, and E. Guerman,
      J. Chem. Phys., 73 (1980) 1966; A. Watanabe, Z. Inoue, and T. Ohsaka,
      Koen. Yoshishu-Jinko Kobutsu Toronkai, 24th (1979) 15, *Chem. Abstr.*,
      92 (1980) 189285.
175   P. V. Klevtsov, A. P. Perepelitsa, and A. V. Sinkevich, *Kristallografiya*,
      25 (1980) 624.
176   Y. Le Page and P. Strobel, *Acta Crystallogr., Sect. B*, 36 (1980) 1919.
177   H. J. Rother, A. Fadini, and S. Kemmler-Sack, *Z. Anorg. Allg. Chem.*,
      463 (1980) 137.
178   I. I. Kiseleva, M. I. Sirota, R. P. Ozerov, T. P. Balakireva, and
      A. A. Maier, *Kristallografiya*, 24 (1979) 1277.
179   V. A. Efremov, T. A. Berezina, I. M. Averina, and V. K. Trunov,
      Kristallografiya, 25 (1980) 254.
180   J. Hanuza and V. V. Fornitsev, *J. Mol. Struct.*, 66 (1980) 1.
181   C. Svensson, S. C. Abrahams, and J. L. Bernstein, *J. Chem. Phys.*,
      71 (1979) 5191.
182   S. Launay and A. Rimsky, *Acta Crystallogr., Sect. B*, 36 (1980) 910.
183   V. N. Serezkhin, V. K. Trunov, and L. G. Makarevich, *Kristallografiya*,
      25 (1980) 858.
184   V. N. Serezkhin, V. A. Efremov, and V. K. Trunov, *Kristallografiya*, 25
      (1980) 861.
185   M. V. Angelyuk, L. M. Kovba, and O. N. Rozanova, *Radiokhimiya*, 22
      (1980) 595.
186   G. Marcu, M. Rusu, and M. Oneaga, *Stud. Univ. Babes-Bolyai [Ser.] Chem.*,
      24 (1979) 51, *Chem. Abstr.*, 93 (1980) 60057.
187   V. N. Serezkhin and N. A. Rasshchepkina, *Radiokhimiya*, 21 (1979) 824.
188   A. Tabuteau and M. Pages, *J. Inorg. Nucl. Chem.*, 42 (1980) 401.
189   V. P. Shilov, T. N. Bukhtiyarova, O. P. Zhuravleva, and N. N. Krot,
      Radiokhimiya, 21 (1979) 714.
190   J. Rinjsdorp, G. J. De Lange, and G. A. Wiegers, *J. Solid State Chem.*,
      30 (1979) 365.
191   F. Weller, P. Rushke, and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 467
      (1980) 89.
192   A. Müller, H. Dornfeld, H. Schulze, and R. C. Sharma, *Z. Anorg. Allg.
      Chem.*, 468 (1980) 193.
193   M. A. Harmer and A. G. Sykes, *Inorg. Chem.*, 19 (1980) 2881.
194   R. H. Tieckelmann, H. C. Silvis, T. A. Kent, B. H. Huynh, J. V. Waszczak,
      B.-K. Teo, and B. A. Averill, *J. Am. Chem. Soc.*, 102 (1980) 5550.
195   R. H. Tieckelmann and B. A. Averill, *Inorg. Chim. Acta.*, 46 (1980) L35.
196   J. W. McDonald, G. D. Friesen, and W. E. Newton, *Inorg. Chim. Acta.*,
      46 (1980) L79.
197   D. Coucouvanis, E. D. Simhon, and N. C. Baenziger, *J. Am. Chem. Soc.*,
      102 (1980) 6646.
198   D. Coucouvanis, N. C. Baenziger, E. D. Simhon, P. Stremple, D. Swenson,
      A. Sinopoulos, A. Kostikas, V. Petrouleas, and V. Papaefthymiou,
      J. Am. Chem. Soc., 102 (1980) 1732.

199 *Idem., ibid.,* 102 (1980) 1730.

200 G. Christou and C. D. Garner, *J. Chem. Soc., Dalton Trans.,* (1980) 2354.

201 G. Christou, C. D. Garner, R. M. Miller, C. E. Johnson, and J. D. Rush, *J. Chem. Soc., Dalton Trans.,* (1980) 2363.

202 G. Christou, C. D. Garner, R. M. Miller, and T. J. King, *J. Inorg. Biochem.,* 11 (1979) 349.

203 T. E. Wolff, J. M. Berg, P. P. Power, K. O. Hodgson, and R. H. Holm, *Inorg. Chem.,* 19 (1980) 430.

204 T. E. Wolff, P. P. Power, R. B. Frankel, and R. H. Holm, *J. Am. Chem. Soc.,* 102 (1980) 4694.

205 G. Christou and C. D. Garner, *J. Chem. Soc., Chem. Commun.,* (1980) 613.

206 G. Christou, R. V. Hageman, and R. H. Holm, *J. Am. Chem. Soc.,* 102 (1980) 7601.

207 C. Ungurenasu, C. Cotzur, and V. Harabagiu, *Polym. Bull. (Berlin)* 2 (1980) 521; *Chem. Abstr.,* 93 (1980) 186970.

208 K. P. Callahan and P. A. Piliero, *Inorg. Chem.,* 19 (1980) 2619.

209 A. R. Siedle, C. R. Hubbard, A. D. Mighell, R. M. Doherty, and J. M. Stewart, *Inorg. Chim. Acta.,* 38 (1980) 197.

210 A. Müller, H. Bögge, and U. Schimanski, *J. Chem. Soc., Chem. Commun.,* (1980) 91.

211 A. Müller, H. Bögge, H. G. Tölle, R. Jostes, U. Schimanski, and M. Dartman, *Angew. Chem.,* 92 (1980) 665.

212 A. Müller, H. Bögge, and E. König-Ahlborn, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.,* 34B (1979) 1698.

213 A. Müller, H. Bögge, and T. K. Hwang, *Inorg. Chim. Acta.,* 39 (1980) 71.

214 F. Secheresse, J. Lefebvre, J. C. Daran, and Y. Jeannin, *Inorg. Chim. Acta.,* 45 (1980) L45.

215 K. S. Liang, J. P. De Neufville, A. J. Jacobson, R. R. Chianelli, and F. Betts, *J. Non-Cryst. Solids,* 35-36 (1980) 1249.

216 A. J. Jacobson, R. R. Chianelli, S. M. Rich, and M. S. Whittingham, *Mater. Res. Bull.,* 14 (1979) 1437.

217 J. W. McDonald and W. E. Newton, *Inorg. Chim. Acta.,* 44 (1980) L81.

218 K. Leonard, K. Plute, R. C. Haltiwanger, and M. R. DuBois, *Inorg. Chem.,* 18 (1979) 3246.

219 D. Fenske, W. Liebelt, and K. Dehnicke, *Z. Anorg. Allg. Chem.,* 469 (1980) 83.

220 E. Schweda and J. Strähle, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.,* 35 (1980) 1146.

221 F. Weller, W. Liebelt, and K. Dehnicke, *Angew. Chem.,* 92 (1980) 211.

222 W. Musterle, J. Strähle, W. Liebelt, and K. Dehnicke, *Z. Naturforsch, B: Anorg. Chem., Org. Chem.,* 34 (1979) 942.

223 K. Dehnicke, U. Weiher, and D. Fenske, *Z. Anorg. Allg. Chem.,* 456 (1979) 71.

224 F. Weller, U. Müller, U. Weiher, and K. Dehnicke, *Z. Anorg. Allg. Chem.,* 460 (1980) 191.

225 U. Weiher, K. Dehnicke, and D. Fenske, *Z. Anorg. Allg. Chem.,* 457 (1979) 105.

226 P. Rushke and K. Dehnicke, *Z. Anorg. Allg. Chem.,* 466 (1980) 157.

227 G. J. J. Chen, J. W. McDonald, and W. E. Newton, *Inorg. Chim. Acta.,* 41 (1980) 49.

228 E. A. Maatta, B. L. Haymore, and R. A. D. Wentworth, *Inorg. Chem.,* 19 (1980) 1055.

229 W. A. Nugent and R. L. Harlow, *Inorg. Chem.,* 19 (1980) 777.

230 M. Sundberg, *Chem. Scr.,* 14 (1979) 161.

231 L. Bartha, G. Gyarmati, A. B. Kiss, T. Nemeth, A. Salamon, and T. Szalay, *Acta Chim. Acad. Sci. Hung.,* 101 (1979) 127.

232 T. Yamase, T. Ikawa, Y. Ohashi, and Y. Sasada, *J. Chem. Soc., Chem. Commun.,* (1979) 697.

233 R. C. T. Slade, T. K. Halstead, and P. G. Dickens, *J. Solid State Chem.,*

34 (1980) 183.

234 A. C. Cirillo, Jr., L. Ryan, B. C. Gerstein, and J. J. Fripiat, *J. Chem. Phys.*, 73 (1980) 3060; A. J. Nicol, D. Tinet, and J. J. Fripiat, *J. Phys. (Orsay, Fr)*, 41 (1980) 423; R. E. Taylor, M. M. S. Crawford, and B. C. Gerstein, *J. Catal.*, 62 (1980) 401.

235 P. A. Christian, J. N. Carides, F. J. DiSalvo, and J. V. Waszczak, *J. Electrochem. Soc.*, 127 (1980) 2315; K. H. Cheng and M. S. Whittingham, *Solid State Ionics*, 1 (1980) 151; G. Pistoia, C. Temperoni, P. Cignini, M. Icovi, and S. Panero, *J. Electroanal. Chem.*, 108 (1980) 169; P. Fiordiponti, G. Pistoia, C. Temperoni, M. Icovi, and S. Panero, *J. Electroanal. Chem. Interfacial Electrochem.*, 108 (1980) 181.

236 D. P. Tunstall and W. Ramage, *J. Phys. C.*, 13 (1980) 725.

237 M. Friedrich and W. Karthe, *Phys. Status Solidi, B*, 97 (1980) 113.

238 J. P. Launay, M. Fournier, C. Sanchez, J. Livage, and M. T. Pope, *Inorg. Nucl. Chem. Lett.*, 16 (1980) 257.

239 V. I. Spitsyn, K. I. Popov, V. F. Chuvaev, T. A. Karpukhina, G. K. Mailieva, and V. L. Zefirova, *Zh. Neorg. Khim.*, 25 (1980) 163.

240 L. P. Kazansky and M. A. Fedotov, *J. Chem. Soc., Chem. Commun.*, (1980) 644.

241 L. P. Tsyganok, I. N. Marov, and L. V. Sorokina, *Zh. Neorg. Khim.*, 25 (1980) 1840.

242 M. Parmentier, C. Gleitzer, and R. J. D. Tilley, *J. Solid State Chem.*, 31 (1980) 305.

243 M. Parmentier, C. Gleitzer, A. Courtois, and J. Protas, *Acta Crystallogr., Sect. B*, 35 (1979) 1963.

244 L. V. Derkach, I. K. Latichevskii, F. P. Ivoglo, and T. D. Gutsul, *Zh. Neorg. Chem.*, 25 (1980) 476.

245 P. Meriaudeau, *Chem. Phys. Lett.*, 72 (1980) 551.

246 I. P. Malkerova, A. S. Alikhanyan, V. S. Perov, V. D. Butskii, and V. I. Gorgoraki, *Zh. Neorg. Khim.*, 25 (1980) 2067.

247 J. Weber and C. D. Garner, *Inorg. Chem.*, 19 (1980) 2206.

248 L. H. Hill, N. C. Howlader, F. E. Mabbs, M. B. Hursthouse, and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, (1980) 1475.

249 C. A. McAuliffe and A. Werfalli, *Inorg. Chim. Acta.*, 44 (1980) L36.

250 C. A. McAuliffe, A. C. Rice, and W. E. Hill, *Inorg. Chim. Acta*, 45 (1980) L133.

251 P. Domiano, A. Musatti, M. Nardelli, C. Pelizzi, and G. Predieri, *Transition Met. Chem. (Weinheim Ger.)* 5 (1980) 172.

252 H. J. Ledon, M. C. Bonnet, Y. Brigandat, and F. Varescon, *Inorg. Chem.*, 19 (1980) 3488.

253 T. Imanura, T. Terui, Y. Takahashi, T. Numatatsu, and M. Fujimoto, *Chem. Lett.*, (1980) 89.

254 M. S. Bains and D. G. Davis, *Inorg. Chim. Acta*, 37 (1979) 53.

255 Y. Murakami, Y. Matsuda, S. Yamada, T. Goto, and M. Kuramoto, *Kenkyu. Hokoku-Asahi Garasu Kogyo Gijutsu Shoreikai*, 34 (1979) 295; *Chem. Abstr.*, 93 (1980) 160405.

256 M. J. Nilges and R. L. Belford, *J. Mag. Reson.*, 35 (1979) 259.

257 R. K. Murmann, *Inorg. Chem.*, 19 (1980) 1765.

258 K. F. Miller and R. A. D. Wentworth, *Inorg. Chem.*, 19 (1980) 1818.

259 J. R. Bradbury, A. G. Wedd, and A. M. Bond, *J. Chem. Soc., Chem. Commun.*, (1979) 1022.

260 A. B. Soares, R. C. Taylor, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, (1980) 1101.

261 B. Kamenar and M. Penavic, *Z. Kristallogr.*, 150 (1979) 327.

262 T. Glowiak, *Int. Semin. Cryst. Chem. Coord. Organomet. Compd., [Proc.], 3rd*, (1977) 244; *Chem. Abstr.*, 92 (1980) 224658.

263 V. V. Zelentsov and N. A. Subbotina, *Tr. Buryat. Inst. Estestv. Nauk Buryat. Fil., Sib. Otd. Akad. Nauk SSSR*, 24 (1978) 32; *Chem. Abstr.*, 93 (1980) 160208.

264 H. So, *Taeham Hwahakhoe Chi.*, 24 (1980) 86; *Chem. Abstr.*, 93 (1980) 174670.

265   V. M. S. Gil, M. M. M. Caldiera, M. E. L. Saraiva, and A. M. V. S.
       Cavaleiro, *Cienc. Biol., (coimbra)* 5 (1980) 181; *Chem. Abstr.,* 93
       (1980) 199650.
266   R. Mattes and K. Mühlsiepen, *Z. Naturforsch. B: Anorg. Chem. Org. Chem.,*
       35 (1980) 265.
267   K. Suzuki, Y. Sasaki, S. Ooi, and K. Saito, *Bull. Chem. Soc. Jpn.,* 53
       (1980) 1288.
268   D. Altmeppen and R. Mattes, *Acta Crystallogr., Sect. B,* 36 (1980) 1942.
269   W. Clegg, N. Mohan, A. Müller, A. Neumann, W. Rittner, and G. M.
       Sheldrick, *Inorg. Chem.,* 19 (1980) 2066; W. Clegg, G. M. Sheldrick,
       C. D. Garner, and G. Christou, *Acta Crystallogr., Sect. B,* 36 (1980)
       2784.
270   A. Müller, W. O. Nolte, and B. Krebs, *Inorg. Chem.,* 19 (1980) 2835.
271   K. F. Miller, A. E. Bruce, J. L. Corbin, S. Wherland, and E. I. Stiefel,
       J. Am. Chem. Soc., 102 (1980) 5104.
272   A. Müller, R. G. Bhattacharyya, E. König-Ahlborn, R. C. Sharma, W. Rittner,
       A. Neuman, G. Henkel, and B. Krebs, 37 (1979) L493; A. Müller,
       W. Rittner, A. Neumann, E. König-Ahlborn, and R. G. Bhattacharyya,
       Z. Anorg. Allg. Chem., 461 (1980) 91.
273   Yu. V. Kokunov, V. A. Bochkareva, Yu. D. Chubar, and Yu. A. Buslaev,
       Koord. Khim., 6 (1980) 1213.
274   A. W. Edelblut and R. A. D. Wentworth, *Inorg. Chem.,* 19 (1980) 2006.
275   A. W. Edelblut and R. A. D. Wentworth, *Inorg. Chem.,* 19 (1980) 1110.
276   S. S. Basson, J. G. Leipoldt, L. D. C. Bok, J. S. Van Vollenhoven,
       and P. J. Cilliers, *Acta Crystallogr., Sect. B,* 36 (1980) 1765.
277   C. D. Garner and F. E. Mabbs, *J. Inorg. Nucl. Chem.,* 41 (1979) 1125.
278   D. Rehorek, J. Salvetter, A. Hantschmann, H. Hennig, Z. Stasicka, and
       A. Chodkowska, *Inorg. Chim. Acta.,* 37 (1979) L471.
279   G. J. Lamprecht, J. G. Leipoldt, C. R. Dennis, and S. S. Basson,
       React. Kinet. Catal. Lett., 13 (1980) 269.
280   V. S. Perov, Yu. V. Rakitin and V. M. Novotorsev, *Zh. Neorg. Khim.,*
       25 (1980) 2327.
281   M. S. Saini and D. M. Puri, *Indian J. Chem., Sect. A,* 18 (1979) 439.
282   U. Hillebrand and E. Stumpp, *Z. Naturforsch., B: Anorg. Chem., Org.*
       Chem., 35 (1980) 245.
283   M. Bochmann, G. Wilkinson, G. B. Young, M. B. Hursthouse, and K. M. A.
       Malik, *J. Chem. Soc., Dalton Trans.,* (1980) 901.
284   A. Manthiram and J. Gopalkrishnan, *Mater. Res. Bull.,* 15 (1980) 207;
       idem., J. Less-Common Met., 68 (1979) 167.
285   M. Goreaud, P. Labbe, and B. Raveau, *Acta Crystallogr., Sect. B,* 36
       (1980) 15; 19.
286   W. E. Newton, J. W. McDonald, J. L. Corbin, L. Ricard and R. Weiss,
       Inorg. Chem., 19 (1980) 1997.
287   J. Chatt, J. R. Dilworth, J. A. Schmutz, and J. A. Zubieta, *J. Chem. Soc.,*
       Dalton Trans., (1979) 1595.
288   C. A. Rice and J. T. Spence, *Inorg. Chem.,* 19 (1980) 2845.
289   A. Samotus, A. Kanas, and A. Samotus, *J. Inorg. Nucl. Chem.,* 41 (1979)
       1135; A. Samotus, A. Kanas, and M. Dudek, *ibid.,* 41 (1979) 1129.
290   J. R. Campbell and R. J. H. Clark, *J. Chem. Soc., Faraday Trans. 2,*
       76 (1980) 1103.
291   R. K. Murmann and M. E. Shelton, *J. Am. Chem. Soc.,* 102 (1980) 3984.
292   Y. Jeannin, J. P. Launay, and M. A. Seid Sedjadi, *Inorg. Chem.,* 19
       (1980) 2933.
293   A. Bino, K. F. Hesse, and H. Kueppers, *Acta Crystallogr., Sect. B,* 36
       (1980) 723.
294   F. A. Cotton, T. R. Felthouse, and D. G. Lay, *J. Am. Chem. Soc.,* 102
       (1980) 1431.
295   A. Müller, R. Jostes, W. Jägermann and R. G. Bhattacharyya, *Inorg. Chim.*
       Acta., 41 (1980) 259.
296   A. Müller and U. Reinsch, *Angew. Chem.,* 92 (1980) 69.

297   J. Hyde, L. Magin, and J. Zubieta, *J. Chem. Soc., Chem. Commun.,* (1980)
       204.
298   P. M. Boorman, V. D. Patel, K. A. Kerr, P. W. Codding, and P. Van Roey,
       Inorg. Chem., 19 (1980) 3508.
299   D. A. Brown, W. K. Glass, and K. S. Jasim, *Inorg. Chim. Acta.,* 45
       (1980) 97.
300   S. C. Shaefer, *Rep. Invest. - U.S. Bur. Mines,* 1980, RI 8405; *Chem. Abstr.,*
       92 (1980) 204412.
301   P. Belougne and J. V. Zanchetta, *Rev. Chim. Miner.,* 16 (1979) 565.
302   D. E. Haycock, D. S. Urch, and G. Wiech, *J. Chem. Soc., Faraday, Trans.,*
       2, 75 (1979) 1692.
303   S. P. Hind and P. M. Lee, *J. Phys. C,* 13 (1980) 349; I. T. McGovern,
       R. H. Williams and A. W. Parke, *ibid.,* 12 (1979) 2689.
304   L. F. Schneemeyer and M. J. Sienko, *Inorg. Chem.,* 19 (1980) 789.
305   L. F. Schneemeyer and M. S. Wrighton, *J. Am. Chem. Soc.,* 101 (1979)
       6496; *idem., ibid.,* 102 (1980) 6964; L. F. Schneemeyer, M. S. Wrighton,
       A. Stacy, and M. J. Sienko, *Appl. Phys. Lett.,* 36 (1980) 701; *idem.,*
       Govt. Rep. Announce Index (U.S.) 80 (1980) 1674; C. P. Kubiak,
       L. F. Schneemeyer and M. S. Wrighton, *J. Am. Chem. Soc.,* 102 (1980)
       6898.
306   W. Kautek and H. Gerischer, *Ber. Bunsenges. Phys. Chem.,* 84 (1980) 645.
307   F.-R. F. Fan, H. S. White, B. L. Wheeler, and A. J. Bard, *J. Am. Chem.*
       Soc., 102 (1980) 5142.
308   H. J. Lewerenz, A. Heller and F. J. DiSalvo, *J. Am. Chem. Soc.,* 102
       (1980) 1877.
309   M. H. Chisholm, A. H. Cowley, and M. Lattman, *Gov. Rep. Announce Index*
       (U.S.), 79 (1979) 66.
310   R. D. Archer, *Gov. Rep. Announce Index (U.S.),* 79 (1979) 71.
311   T. G. Leipoldt, S. S. Basson, L. D. C. Bok, *Inorg. Chim. Acta.,* 44 (1980)
       L99; S. S. Basson, J. G. Leipoldt, and A. J. Van Wyk, *Acta Crystallogr.,*
       Sect. B, 36 (1980) 2025.
312   D. I. Zubritskaya, A. N. Sergeeva, and Yu. V. Pisak, *Koord. Khim.,* 6
       (1980) 405.
313   B. Sieklucka and A. Samotus, *J. Inorg. Nucl. Chem.,* 42 (1980) 1003.
314   A. P. Ginsberg, *J. Am. Chem. Soc.,* 102 (1980) 111; W. C. Trogler,
       Inorg. Chem., 19 (1980) 697.
315   B. A. Averill and W. H. Orme-Johnson, *Inorg. Chem.,* 19 (1980) 1702.
316   G. R. Brubacker and J. A. Romberger, *Inorg. Chem.,* 19 (1980) 1087.
317   S. Wajda and B. Kurzak, *Pol. J. Chem.,* 54 (1980) 179.
318   A. W. Edelblut and R. A. D. Wentworth, *Inorg. Chem.,* 19 (1980) 1117.
319   P. M. Boorman and V. D. Patel, *Inorg. Chim. Acta.,* 44 (1980) L85.
320   J. V. Brencic and I. Leban, *Acta Crystallogr. Sect. B,* 36 (1980) 698;
       idem., Z. Anorg. Allg. Chem., 465 (1980) 173.
321   J. V. Brencic, B. Ceh, and I. Leban, *Acta Crystallogr., Sect. B,* 35
       (1979) 3028.
322   S. P. Gosh and K. M. Prasad, *J. Indian Chem. Soc.,* 56 (1979) 660.
323   M. B. Hursthouse, K. M. A. Malik, A. M. Soares, J. F. Gibson, and
       W. P. Griffiths, *Inorg. Chim. Acta.,* 45 (1980) 81.
324   C. Potvin, J.-M. Brégeault, and J.-M. Manoli, *J. Chem. Soc., Chem. Commun.,*
       (1980) 664.
325   M. H. Chisholm, J. C. Huffman, and R. L. Kelly, *J. Am. Chem. Soc.,*
       101 (1979) 7615.
326   J. L. Templeton and B. C. Ward, *J. Am. Chem. Soc.,* 102 (1980) 6568.
327   J. L. Templeton and B. C. Ward, *Inorg. Chem.,* 19 (1980) 1753.
328   B. C. Ward and J. L. Templeton, *J. Am. Chem. Soc.,* 102 (1980) 1532;
       3288.
329   H. P. M. M. Ambrosius, J. H. Noordik, and G. J. A. Ariaans, *J. Chem.*
       Soc., Chem. Commun., (1980) 832.
330   E. A. Maatta and R. A. D. Wentworth, *Inorg. Chem.,* 19 (1980) 2597.

331 R. O. Day, W. H. Batschelet, and R. D. Archer, *Inorg. Chem.*, 19 (1980) 2113.

332 R. M. Foy, D. L. Kepert, C. L. Raston, and A. H. White, *J. Chem. Soc., Dalton Trans.*, (1980) 440.

333 P. J. Domaille and S. S. Wreford, *Inorg. Chem.*, 19 (1980) 2188.

334 H. W. Choi, R. M. Gavin, and E. L. Muetterties, *J. Chem. Soc., Chem. Commun.*, (1979) 1085.

335 D. Gregson, J. A. K. Howard, J. N. Nicholls, J. L. Spencer, and D. G. Turner, *J. Chem. Soc., Chem. Commun.*, (1980) 572.

336 E. B. Lobovskii, V. D. Makhaev, A. P. Borisov, and K. N. Semenenko, *Zh. Strukt. Khim.*, 20 (1079) 944.

337 E. B. Lokovskii, A. P. Borisov, V. D. Makhaev, and K. N. Semenenko, *Zh. Strukt. Khim.*, 21 (1980) 126.

338 V. B. Polyakova, A. P. Borisov, V. D. Makhaev, and K. N. Semenenko, *Koord. Khim.*, 6 (1980) 743.

339 R. Pierantozzi and G. L. Geoffroy, *Inorg. Chem.*, 19 (1980) 1821.

340 S. S. Wreford, J. K. Kouba, J. F. Kirner, E. L. Muetterties, I. Tavanaiepour, and V. W. Day, *J. Am. Chem. Soc.*, 102 (1980) 1558.

341 J. L. Atwood, W. E. Hunter, E. Carmona-Guzman, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, (1980) 467.

342 M. Y. Darensbourg, J. L. Atwood, W. E. Hunter, and R. R. Burch, Jr., *J. Am. Chem. Soc.*, 102 (1980) 3290.

343 J. Sheikholeslami, P. Teulon, and J. Roziere, *Proc. Int. Conf. Raman Spectrosc. 6th*, (1978) 68; *Chem. Abstr.*, 92 (1980) 206451.

344 J. L. Petersen and R. P. Stewart, Jr., *Inorg. Chem.*, 19 (1980) 186.

345 R. A. Jones, K. W. Chiu, G. Wilkinson, A. M. R. Galas, and M. B. Hursthouse, *J. Chem. Soc., Chem. Commun.*, (1980) 408.

346 N. W. Alcock, O. W. Howarth, P. Moore, and G. E. Morris, *J. Chem. Soc., Chem. Commun.*, (1979) 1160.

347 A. V. Aripovskii and B. M. Bulychev, *Zh. Neorg. Khim.*, 25 (1980) 1687.

348 J. R. Blickensderfer, R. J. Hoxmeier, and H. D. Kaesz, *Inorg. Chem.*, 18 (1979) 3606.

349 P. Grebenik, A. J. Downs, M. L. H. Green, and R. N. Perutz, *J. Chem. Soc., Chem. Commun.*, (1979) 742.

350 R. J. Klingler, J. C. Huffman, and J. K. Kochi, *J. Am. Chem. Soc.*, 102 (1980) 208.

351 M. Berry, K. Elmitt, and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, (1980) 1950.

352 N. J. Cooper, M. L. H. Green, and R. Mahtab, *J. Chem. Soc., Dalton Trans.*, (1980) 1557.

353 M. Berry, N. J. Croper, M. L. H. Green, and S. J. Simpson, *J. Chem. Soc., Dalton Trans.*, (1980) 29.

354 M. A. Adams, K. Folting, J. C. Huffman, and K. G. Caulton, *Inorg. Chem.*, 18 (1979) 3020.

355 J. Wachter, F. Jeanneaux, and J. G. Riess, *Inorg. Chem.*, 19 (1980) 2169.

356 A. Bino, F. A. Cotton, and Z. Dori, *J. Am. Chem. Soc.*, 100 (1978) 5252.

357 T. A. Albright and R. Hoffmann, *J. Am. Chem. Soc.*, 100 (1978) 7736.

358 M. B. Hall, *J. Am. Chem. Soc.*, 102 (1980) 2104.

359 B. E. Bursten, F. A. Cotton, J. C. Green, E. A. Seddon, and G. G. Stanley, *J. Am. Chem. Soc.*, 102 (1980) 4579.

360 M. J. McGlinchey, *Inorg. Chem.*, 19 (1980) 1392.

361 T. P. Blatchford, M. H. Chisholm, K. Folting, and J. C. Huffman, *Inorg. Chem.*, 19 (1980) 3175.

362 M. H. Chisholm and I. P. Rothwell, *J. Am. Chem. Soc.*, 102 (1980) 5950.

363 M. H. Chisholm and I. P. Rothwell, *J. Chem. Soc., Chem. Commun.*, (1980) 985.

364 M. H. Chisholm, F. A. Cotton, M. W. Extine, and R. L. Kelly, *J. Am. Chem. Soc.*, 101 (1979) 7645.

365 D. C. Bradley, C. W. Newing, M. H. Chisholm, R. L. Kelly, D. A. Haitko, D. Little, F. A. Cotton, and P. E. Fanwick, *Inorg. Chem.*, 19 (1980) 3010.

366 M. H. Chisholm, J. C. Huffman, and R. L. Kelly, *Inorg. Chem.*, 19
     (1980) 2762.
367 M. H. Chisholm and D. A. Haitko, *J. Am. Chem. Soc.*, 101 (1979) 6784.
368 F. A. Cotton, W. H. Ilsley, and W. Kaim, *J. Amer. Chem. Soc.*, 102
     (1980) 1918.
369 K. J. Cavell, C. D. Garner, G. Pilcher, and S. Parkes, *J. Chem. Soc.*,
     Dalton Trans., (1980) 1714.
370 J. G. Norman, Jr., and R. B. Ryan, *J. Comput. Chem.*, 1 (1980) 59;
     K. Yamaguchi, *Chem. Phys. Lett.*, 68 (1979) 477.
371 C. D. Garner, I. H. Hillier, M. J. Knight, A. A. MacDowell, and
     I. B. Walton, *J. Chem. Soc.*, *Faraday Trans.*, 2, 76 (1980) 885.
372 A. Bino, F. A. Cotton, and P. E. Fanwick, *Inorg. Chem.*, 19 (1980) 1215.
373 A. Bino and D. Gibson, *J. Am. Chem. Soc.*, 102 (1980) 4277.
374 J. V. Brencic and P. Segedin, *Vestn. Slov. Kem. Drus.*, 26 (1979) 367;
     Chem. Abstr., 92 (1980) 224642.
375 P. A. Koz'min, M. D. Surazhskaya, T. B. Larina, A. S. Kotel'nikova, and
     E. L. Akhmedov, *Zh. Neorg. Khim.*, 24 (1979) 3383; 25 (1980) 1261.
376 D. L. Kepert, B. W. Skelton, and A. H. White, *Aust. J. Chem.*,
     33 (1980) 1847.
377 I. I. Moiseev, A. E. Gekhman, and I. V. Kalechits, *Kinet. Katal.*, 21
     (1980) 284.
378 A. Bino and F. A. Cotton, *J. Am. Chem. Soc.*, 102 (1980) 3014.
379 D. DeMarco, T. Nimry, and R. A. Walton, *Inorg. Chem.*, 19 (1980) 575.
380 D. A. Edwards, G. Uden, W. S. Mialki, and R. A. Walton, *Inorg. Chim.*
     Acta., 40 (1980) 25.
381 F. A. Cotton and P. E. Fanwick, *Acta Crystallogr.*, *Sect. B*, 36 (1980) 457.
382 F. A. Cotton, W. H. Ilsley, and W. Kaim, *Inorg. Chem.*, 18 (1979) 2717.
383 A. Bino, F. A. Cotton, and W. Kaim, *Inorg. Chem.*, 18 (1979) 3030.
384 F. A. Cotton, W. H. Ilsley, and W. Kaim, *J. Am. Chem. Soc.*, 102 (1980)
     3475.
385 F. A. Cotton, W. H. Ilsley, and W. Kaim, *Inorg. Chem.*, 19 (1980) 3586.
386 F. A. Cotton, W. H. Ilsley, and W. Kaim, *Inorg. Chim. Acta.*, 37
     (1979) 267.
387 F. A. Cotton, B. E. Hanson, W. H. Ilsley, and G. W. Rice, *Inorg. Chem.*,
     18 (1979) 2713.
388 F. A. Cotton, W. H. Ilsley, and W. Kaim, *Inorg. Chem.*, 19 (1980) 1453.
389 F. A. Cotton, W. H. Ilsley, and W. Kaim, *Inorg. Chem.*, 19 (1980) 1450.
390 P. R. Sharp and R. R. Schrock, *J. Amer. Chem. Soc.*, 102 (1980) 1430.
391 G. S. Girolami, V. V. Mainz, and R. A. Anderson, *Inorg. Chem.*, 19
     (1980) 805.
392 V. V. Mainz and R. A. Anderson, *Inorg. Chem.*, 19 (1980) 2165.
393 M. B. Hursthouse and K. M. A. Malik, *Acta Crystallogr.*, *Sect. B*, 35
     (1979) 2709.
394 J. A. Goodfellow and T. A. Stephenson, *Inorg. Chim. Acta.*, 44
     (1980) L45.
395 F. W. Koknat, T. J. Adaway, S. I Erzerum and S. Syed, *Inorg. Nucl. Chem.*
     Lett., 16 (1980) 307.
396 G. Seifert, J. Finster, and H. Mueller, *Chem. Phys. Lett.*, 75 (1980)
     373.
397 J. B. Michel, *Energy Res. Abstr.*, 5 (1980) Abstr. 16250; *Chem. Abstr.*,
     93 (1980) 196803.
398 F. S. Delk, II, and M. J. Sienko, *Inorg. Chem.*, 19 (1980) 788 and
     references therein.
399 K. Yvon, *Curr. Top. Mater. Sci.*, 3 (1979) 53.
400 T. Jarlborg and A. J. Freeman, *Phys. Rev. Lett.*, 44 (1980) 178.
401 R. Chevrel, C. Rossel, and M. Sergent, *J. Less-Common Met.*, 72 (1980) 31.
402 N. E. Alekseevskii, G. Wolf, V. I. Tsebro, N. M. Drobrovolskii,
     K. Bohmhammel, and S. Krautz, *J. Low Temp. Phys.*, 38 (1980) 243.
403 F. S. Delk, II, and M. J. Sienko, *Inorg. Chem.*, 19 (1980) 1352.
404 C. Perrin, R. Chevrel, M. Sergent, and O. Fischer, *Mater. Res. Bull.*,
     14 (1979) 1505.

405   A. M. Umarji, G. V. S. Rao, V. Sankaranarayanan, G. Rangarajan, and
     R. Srinivasan, *Mater. Res. Bull.*, 15 (1980) 1025.

406   M. Kümpers and R. Schöllhorn, *Z. Naturforsch. B, Anorg. Chem.,*
     Org. Chem., 35 (1980) 929.

407   M. Potel, R. Chevrel, and M. Sergent, *Acta Crystallogr., Sect. B,*
     36 (1980) 1545.

408   A. Lipka and K. Yvon, *Acta Crystallogr., Sect. B,* 36 (1980) 2123.

409   R. Chevrel, M. Potel, M. Sergent, M. Decroux, and O. Fischer,
     Mater. Res. Bull., 15 (1980) 867.

410   W. Hönle, H. G. Von Schnering, A. Lipka, and K. Yvon, *J. Less-Common. Met.,*
     71 (1980) 135.

411   R. Chevrel, M. Potel, M. Sergent, M. Decroux, and O. Fischer, *J. Solid*
     State Chem., 34 (1980) 247; M. Potel, R. Chevrel, and M. Sergent,
     Acta Crystallogr., Sect. B, 36 (1980) 1319.

412   K. Yvon, R. Chevrel, and M. Sergent, *Acta Crystallogr., Sect. B,* 36
     (1980) 685.

413   K. Yvon, R. Baillif, and R. Flükiger, *Acta Crystallogr., Sect. B,* 35
     (1979) 2859.

414   R. Flükiger, R. Baillif, J. Müller and K. Yvon, *J. Less-Common. Met.,*
     72 (1980) 193.

415   F. J. Culetto, *Speculations Sci. Technol.*, 3 (1980) 275; *Chem. Abstr.,*
     93 (1980) 195862.

416   S. Onaka, C. B. Cooper, III, and D. F. Shriver, *Inorg. Chim. Acta.,*
     37 (1979) L467.

417   B. Meunier and C. K. Prout, *Acta Crystallogr., Sect. B,* 35 (1979) 2558.

418   J. Levisalles, F. Rose-Munch, H. Rudler, J.-C. Daran, Y. Dromzee, and
     Y. Jeannin, *J. Chem. Soc., Chem. Commun.*, (1980) 685; J. Levisalles,
     H. Rudler, Y. Jeannin, and F. Dahan, *J. Organomet. Chem.*, 178 (1979)
     C8; *idem., ibid.*, 187 (1980) 233.

419   S. R. Finnimore, S. A. R. Knox, and G. E. Taylor, *J. Chem. Soc.,*
     Chem. Commun., (1980) 411.

420   G. K. Barker, W. E. Carroll, M. Green, and A. J. Welch, *J. Chem. Soc.,*
     Chem. Commun., (1980) 1071.

421   E. D. Jemmis, A. R. Pinhas, and R. Hoffmann, *J. Am. Chem. Soc.,*
     102 (1980) 2576.

422   M. D. Curtis, K. R. Han, and W. M. Butler, *Inorg. Chem.*, 19 (1980) 2096.

423   L. Messerle and M. D. Curtis, *J. Am. Chem. Soc.*, 102 (1980) 7789.

424   H. Alper and J. Hartgerink, *J. Organomet. Chem.*, 190 (1980) C25.

425   M. D. Curtis and W. M. Butler, *J. Chem. Soc., Chem. Commun.*, (1980) 998.

426   M. Rakowski Dubois, M. C. Van Derveer, D. L. Dubois, R. C. Haltiwanger,
     and W. K. Miller, *J. Am. Chem. Soc.*, 102 (1980) 7456.

427   D. J. Miller and M. Rakowski Dubois, *J. Am. Chem. Soc.*, 102 (1980) 4925.

428   I. B. Benson, S. D. Killops, S. A. R. Knox, and A. J. Welch,
     J. Chem. Soc., Chem. Commun., (1980) 1137.

429   L. R. Krauth-Siegel, W. Schulze, and M. L. Ziegler, *Angew. Chem.*, 92
     (1980) 403.

430   W. E. Silverthorn, *J. Am. Chem. Soc.*, 102 (1980) 842.

431   H. Alper, N. D. Silavwe, G. I. Birnbaum, and F. R. Ahmed, *J. Am. Chem.*
     Soc., 101 (1979) 6582.

432   J. Hartgerink, N. D. Silavwe, and H. Alper, *Inorg. Chem.*, 19 (1980) 2593.

433   S. Slater and E. L. Muetterties, *Inorg. Chem.*, 19 (1980) 3337.

434   K. Weidenhammer and M. L. Ziegler, *Z. Anorg. Allg. Chem.*, 455 (1979) 43.

435   H. J. Langenbach and H. Vahrenkamp, *Chem. Ber.*, 113 (1980) 2200.

436   E. Roland and H. Vahrenkamp, *Chem. Ber.*, 113, (1980) 1799.

437   T. V. Ashworth, J. A. K. Howard, M. Laguna, and F. G. A. Stone,
     J. Chem. Soc., Dalton Trans., (1980) 1593.

438   T. V. Ashworth, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc.,*
     Dalton Trans., (1980) 1609.

439   T. V. Ashworth, M. Berry, J. A. K. Howard, M. Laguna, and F. G. A. Stone,
     J. Chem. Soc., Dalton Trans., (1980) 1615.

440 M. J. Chetcuti, M. Green, J. C. Jeffery, F. G. A. Stone, and A. A. Wilson, *J. Chem. Soc., Chem. Commun.,* (1980) 948.

441 M. J. Chetcuti, M. Green, J. A. K. Howard, J. C. Jeffery, R. M. Mills, G. N. Pain, S. J. Porter, F. G. A. Stone, A. A. Wilson, and P. Woodward, *J. Chem. Soc., Chem. Commun.,* (1980) 1057.

442 M. Pfeffer, J. Fischer, A. Mitschler, and L. Ricard, *J. Am. Chem. Soc.,* 102 (1980) 6338.

443 M. Tachikawa, A. C. Sievert, and E. L. Muetterties, *J. Am. Chem. Soc.,* 102 (1980) 1725.

444 P. Lemoine, A. Giraudeau, M. Gross, and P. Braunstein, *J. Chem. Soc., Chem. Commun.,* (1980) 77.

445 V. Ya. Leonidov, O. M. Gaisinskaya, and V. S. Pervov, *Vses. Konf. Kalorim.* [*Rasshir. Tezisy, Dokl*] , *7th* 1 (1977) 21, *Chem. Abstr.,* 92 (1980) 11948.

446 J. A. Avlokhashvili, F. N. Tavadze, G. F. Tavadze, D. N. Tsikaridze, D. L. Gabunia, and K. P. Tsomaya, *J. Less-Common. Met.,* 67 (1979) 367.

447 P. Ettmayer and A. Vendl, *Monatsch. Chem.,* 111 (1980) 547.

448 S. V. Orishchin and Yu. B. Kuz'ma, *Kristallografiya,* 25 (1980) 1066.

449 P. L. Mart, J. J. Murray, and J. B. Taylor, *J. Less-Common. Met.,* 65 (1979) 71.

450 V. L. Kalikhman, *Izv. Akad. Nauk. SSSR Neorg. Mater.,* 16 (1980) 437.

451 I. Kojima, E. Miyazaki, and I. Yasumori, *J. Chem. Soc., Chem. Commun.,* (1980) 573.

452 P. Gajardo, P. Grange, and B. Delmon, *J. Catal.,* 63 (1980) 201; D. S. Zingg, L. E. Makovsky, R. E. Tischer, F. R. Brown, and D. M. Hercules, *J. Phys. Chem.,* 84 (1980) 2898.

453 T. Edmonds and P. C. H. Mitchell, *J. Catal.,* 64 (1980) 491; Y. Okamoto, H. Tomioka, Y. Katoh, T. Imanaka, and S. Teranishi, *J. Phys. Chem.,* 84 (1980) 1833.

454 F. Delannay, E. N. Haeuessler, and B. Delmon, *Bull. Soc. Chim. Belg.,* 89 (1980) 255.

455 F. Delannay, P. Gajardo, P. Grange, and B. Delmon, *J. Chem. Soc., Faraday Trans.,* 1, 76 (1980) 988; G. Delvaux, A. Leonard, M. Genet, P. Grange, and B. Delmon, *Rev. Port. Quim.,* 19 (1977) 199; S. S. Pollack, L. E. Makovsky, and F. R. Brown, *Prepr. Can. Symp. Catal.,* 6 (1979) 213; S. S. Pollack, L. E. Makovsky, and F. R. Brown, *J. Catal.,* 59 (1979) 452.

456 C. J. Wright, C. Sampson, D. Fraser, R. B. Moyes, P. B. Wells, and C. Riekel, *J. Chem. Soc., Faraday Trans.,* 1, 76 (1980) 1585.

457 S. J. Tauster, T. A. Pecoraro, and R. R. Chianelli, *J. Catal.,* 63 (1980) 515.

458 R. G. Bowman and R. L. Burwell, Jr., *J. Catal.,* 63 (1980) 463.

459 D. Gutschick, O. N. Kimkhai, B. N. Kuznetsov, A. N. Startsev, V. G. Shinkarenko, and G. K. Boreskov, *Kinet. Katal.,* 21 (1980) 436.

460 Y. Iwasawa, M. Yamagishi, and S. Ogasawara, *J. Chem. Soc., Chem. Commun.,* (1980) 871.

461 Y. Iwasawa, T. Nakamura, K. Takamatsu, and S. Ogasawara, *J. Chem. Soc., Faraday Trans.,* 1, 76 (1980) 939.

462 J.-C. Volta and B. Moraweck, *J. Chem. Soc., Chem. Commun.,* (1980) 338.

463 J. Guidot, Y. Arnaud, and J. E. Germain, *Bull. Soc. Chim. Fr.,* (1980) 209; K. M. Abd. El-Salaam and E. A. Hassan, *Surf. Technol.,* 9 (1979) 195; O. V. Isaev and K. N. Spiridonov, *Khim. Kinet. Katal.,* (1979) 153; K. Yu. Adzhamov, F. M. Poladov, and T. G. Alkhazov, *Kinet Katal.,* 20 (1979) 1350.

464 I. Matsuura, R. Schut, and K. Hirakawa, *J. Catal.,* 63 (1980) 152; P. K. Sinhamahapatra, and S. K. Bhattacharyya, *Kinet. Katal.,* 20 (1979) 1261; A. M. Chaze, and P. Courtine, *J. Chem. Res. Synop.,* (1980) 96; J. Kumar and E. Ruckenstein, *J. Solid State Chem.,* 31 (1980) 41.

465 K. H. Schnabel and A. A. Kadushin, *Kinet. Katal.,* 20 (1979) 1597.

466   D. G. Klissurski, R. A. Ross, and T. J. Griffith, *Rev. Port. Quim.*, 19 (1977) 7; D. G. Klissurski, R. A. Ross and T. J. Griffith, *Prepr. Can. Symp. Catal.*, 6 (1979) 247.

467   A. N. Pershin, B. N. Shelimov, and V. B. Kazanskii, *Kinet. Katal.*, 21 (1980) 494; P. Forzatti, C. Aktardo, and F. Trifiro, *J. Chem. Soc., Chem. Commun.*, (1979) 747.

468   S. A. Best, R. G. Squires, and R. A. Walton, *J. Catal.*, 60 (1979) 171.

469   F. Janowski, A. Sofianos, and F. Wolf, *React. Kinet. Catal. Lett.*, 12 (1979) 157.

470   A. J. Van Roosmalen and J. C. Mol, *J. Chem. Soc., Chem. Commun.*, (1980) 704.

471   K. Tanaka, K.-I. Tanaka, and K. Miyahara, *J. Chem. Soc., Chem. Commun.*, (1980) 666.

472   O. Meyer and H. G. Schlegel, *J. Bacteriol.*, 141 (1980) 74.

473   J. L. Johnson, B. E. Hainline, and K. V. Rajagopalan, *J. Biol. Chem.*, 255 (1980) 1783.

474   Z. A. Alikulov, N. P. L'vov, Sh. S. Bun'khanov, and V. L. Kretovich, *Izv. Akad. Nauk. SSSR. Ser. Biol.*, (1980) 712.

475   M. P. Coughlan, J. L. Johnson, and K. V. Rajagopalan, *J. Biol. Chem.*, 255 (1980) 2694.

476   M. P. Coughlan, and I. N. Fhaolain, *Proc. R. Ir. Acad., Sect. B*, 79B (1979) 169.

477   S. Gutteridge, J. P. G. Malthouse, and R. C. Bray, *J. Inorg. Biochem.*, 11 (1979) 355.

478   J. P. G. Malthouse, S. Gutteridge, and R. C. Bray, *Biochem. J.*, 185 (1980) 767.

479   M. J. Barber, M. P. Coughlan, M. Kanda, and K. V. Rajagopalan, *Arch. Biochem. Biophys.*, 201 (1980) 468.

480   R. R. Eady, *Methods Enzymol.*, 69 (1980) 753.

481   B. D. Burgess, K. B. Jacobs, and E. I. Stiefel, *Biochem. Biophys. Acta.*, 614 (1980) 196.

482   V. K. Shah, *Methods Enzymol.*, 69 (1980) 792.

483   B. Huynh, M. T. Henzl, J. A. Christner, R. Zimmerman, W. H. Orme-Johnson, and E. Münck, *Biochem. Biophys. Acta.*, 623 (1980) 124.

484   B. K. Burgess, E. I. Stiefel, and W. E. Newton, *J. Biol. Chem.*, 255 (1980) 353.

485   G. D. Watt, A. Burns, S. Lough, and D. L. Tennent, *Biochemistry*, 19 (1980) 4926.

486   L. A. Levchenko, O. S. Roschupkina, A. P. Sadkov, S. A. Marakushev, G. M. Mikhailov, and Yu. G. Borod'ko, *Biochem. Biophys. Res. Commun.*, 96 (1980) 1384.

487   I. Z. Mitsova, T. A. Kondrat'eva, and R. I. Gvozdev, *Dokl. Akad. Nauk SSSR.*, 251 (1980) 494.

488   C. Gomez-Moreno, and B. Ke, *Mol. Cell. Biochem.*, 26 (1979) 111.

489   G. N. Petrova, L. M. Uzenskaya, L. A. Syrtsova, and O. N. Efimov, *Elektrokhimiya*, 16 (1980) 1079.

490   A. Müller and S. Sarkar, *Angew. Chem. Int. Ed. Engl.*, 16 (1977) 705.

491   H. C. Silvis, R. H. Tieckelmann, and B. A. Averill, *Inorg. Chim. Acta.*, 36 (1979) L423.

492   J. N. Murrell, A. Al-Derzi, G. J. Leigh, and M. F. Guest, *J. Chem. Soc., Dalton Trans.*, (1980) 1425.

493   T. Yamabe, K. Hori, T. Minato, and K. Fukui, *Inorg. Chem.*, 19 (1980) 2154.

494   J. R. Campbell and R. J. H. Clark, *J. Chem. Soc., Chem. Commun.*, (1980) 772.

495   C.-H. Hsai, C.-C. Ni. Y. L. Ma, and T. M. Chang, *K'O Hsueh T'ung Pao*, 25 (1980) 23; *Chem. Abstr.*, 92 (1980) 189508.

496   L. J. Archer and T. A. George, *Inorg. Chim. Acta.*, 44 (1980) L129.

497   A. P. Pivovarov, Yu. V. Gak, Yu. M. Shul'ga, V. D. Makhaev, A. P. Borisov, and Yu. G. Borod'ko, *Izv. Akad. Nauk. SSSR., Ser. Khim.*,

(1979) 2590.

498 G. J. Kubas, *J. Chem. Soc., Chem. Commun.*, (1980) 61.

499 J. Chatt, C. T. Kan, G. J. Leigh, C. J. Pickett, and D. R. Stanley,
J. Chem. Soc., Dalton Trans., (1980) 2032.

500 J. Chatt, G. J. Leigh, H. Neukomm, C. J. Pickett, and D. R. Stanley,
J. Chem. Soc., Dalton Trans., (1980) 121.

501 H. M. Colquhoun and R. A. Head, *Inorg. Chim. Acta.*, 45 (1980) L123.

502 J. A. Baumann and T. A. George, *J. Am. Chem. Soc.*, 102 (1980) 6153.

503 M. Hidai, J. Takahashi, I. Yokotake, and Y. Uchida, *Chem. Lett.*, 6
(1980) 645.

504 H. Nishihara, T. Mori, T. Saito, and Y. Sasaki, *Chem. Lett.*, 6 (1980) 667.

505 L. P. Didenko, A. E. Shilov, and A. K. Shilova, *Kinet. Katal.*, 20
(1979) 1488.

506 N. T. Denisov, S. I. Kobelev, and N. I. Shuvalova, *Kinet Katal.*, 21
(1980) 1251.

507 S. I. Kulakovskaya, L. P. Vasil'eva, and O. N. Efimova, *React. Kinet.
Catal. Lett.*, 14 (1980) 181.

508 J. Chatt, W. Hussain, G. J. Leigh, H. Neukomm, C. J. Pickett, and
D. A. Rankin, *J. Chem. Soc., Chem. Commun.*, (1980) 1024.

509 J. Colin, G. Butler, and R. Weiss, *Inorg. Chem.*, 19 (1980) 3828.

510 G. A. Williams and A. R. P. Smith, *Aust. J. Chem.*, 33 (1980) 717.

511 C. S. Day, V. W. Day, T. A. George, and I. Tavanaiepour, *Inorg. Chem.
Acta.*, 45 (1980) L54.

512 A. Nakamura, M. Nakoyama, K. Sugihashi, and S. Otsuka, *Inorg. Chem.*,
18 (1979) 394.

513 J. R. Dilworth, B. D. Neaves, and C. J. Pickett, *Inorg. Chem.*, 19
(1980) 2859.

514 W. A. Herrman and S. A. Bistram, *Chem. Ber.*, 113 (1980) 2648.

515 R. A. Michelin and R. J. Angelici, *Inorg. Chem.*, 19 (1980) 3850.

516 G. E. Bossard, D. C. Busby, M. Chang, T. A. George, and
S. D. A. Iske, Jr., *J. Chem. Am. Soc.*, 102 (1980) 1001.

517 J. Chatt, W. Hussain, G. J. Leigh, and F. P. Terreros, *J. Chem. Soc.,
Dalton Trans.*, (1980) 1408.

518 T. Takahashi, Y. Mizobe, M. Sato, Y. Uchida, and M. Hidai, *J. Am. Chem.
Soc.*, 102 (1980) 7461.

519 M. W. Bishop, J. Chatt, J. R. Dilworth, M. B. Hursthouse, and M. Motevalli,
J. Chem. Soc., Dalton Trans., (1979) 1600.

520 B. A. L. Crichton, J. R. Dilworth, P. Dahlstrom, and J. Zubieta,
Transition Met. Chem., *(Weinheim, Ger.)* 5 (1980) 316.

521 H. M. Colquhoun, *J. Chem. Res., Synop.*, (1979) 325.

522 J. Chatt, M. E. Fakley, R. L. Richards, J. Mason, and I. A. Stenhouse,
J. Chem. Res., Synop., (1979) 322.

523 P. D. Frisch, M. M. Hunt, W. G. Kita, J. A. McCleverty, A. E. Rae,
D. Seddon, D. Swann, and J. Williams, *J. Chem. Soc., Dalton Trans.*,
(1979) 1819.

524 P. R. Mallinson, G. A. Sim, and D. I. Woodhouse, *Acta Crystallogr.*,
Sect. B, 36 (1980) 450.

625 J. Chatt, J. R. Dilworth, P. L. Dahlstrom, and J. Zubieta, *J. Chem. Soc.,
Chem. Commun.*, (1980) 786.

526 T. Jones, A. J. L. Hanlan, F. W. B. Einstein, and D. Sutton, *J. Chem.
Soc., Chem. Commun.*, (1980) 1078.

527 J. A. Carroll and D. Sutton, *Inorg. Chem.*, 19 (1980) 3137.

528 J. A. Carroll. D. Sutton, M. Cowie, and M. D. Gauthier, *J. Chem. Soc.,
Chem. Commun.*, (1979) 1058; M. Cowie and M. D. Gauthier, *Inorg. Chem.*,
19 (1980) 3142.

529 A. A. Diamantis, J. Chatt, G. A. Heath, and G. I. Leigh, *J. Chem. Soc.,
Chem. Commun.*, (1975) 27.

530 R. A. Head and P. B. Hitchcock, *J. Chem. Soc., Dalton Trans.*, (1980)
1150.

531 R. Ben-Shoshan, J. Chatt, G. J. Leigh, and W. Hussain, *J. Chem. Soc.*,

Dalton Trans., (1980) 771.

532   H. M. Colquhoun, *J. Chem. Soc., Chem. Commun.*, (1980) 879.

533   J. Chatt, R. A. Head, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, (1980) 1129.

534   Y. Mizobe, Y. Uchida, and M. Hidai, *Bull. Chem. Soc. Jpn.*, 53 (1980) 1781.

535   M. N. Ackermann, D. J. Dobmeyer, and L. C. Hardy, *J. Organomet. Chem.*, 182 (1979) 182.

536   R. Battaglia, H. Matthaeus, and H. Kisch, *J. Organomet. Chem.*, 193 (1980) 57.

537   M. W. Bishop, J. Chatt, J. R. Dilworth, M. B. Hursthouse, and M. Motevalli, *J. Chem. Soc., Dalton Trans.*, (1979) 1603.

538   P. Dahlstrom, M. Kustyn, J. Zubieta, and J. R. Dilworth, *Transition Met. Chem. (Weinheim Ger.)*, 4 (1979) 396; J. R. Dilworth, P. Dahlstrom, J. R. Hyde, M. Kustyn, P. A. Vella, and J. Zubieta, *Inorg. Chem.*, 19 (1980) 3562.

539   A. N. Pershin, B. N. Shelimov, and V. B. Kazanski, *Kinet. Katal.*, 21 (1980) 753.

540   A. Kazusaka and R. F. Howe, *J. Catal.*, 63 (1980) 447.

541   P. Subramanian, *Inorg. Chim. Acta.*, 46 (1980) L69.

542   K. Wieghardt, W. Hotzbach, B. Nuber, and J. Weiss, *Chem. Ber.*, 113 (1980) 629.

543   T. Diebold, M. Schappacher, B. Chevrier, and B. Weiss, *J. Chem. Soc., Chem. Commun.*, (1979) 693.

544   S. Clamp, N. G. Connelly, G. E. Taylor, and T. S. Louttit, *J. Chem. Soc., Dalton Trans.*, (1980) 2162.

545   T. Tatsumi, K. Sekizawa, and H. Tominaga, *Bull. Chem. Soc. Jpn.*, 53 (1980) 2297.

546   S. W. Kirtley, J. P. Chanton, R. A. Love, D. L. Tipton, T. N. Sorrell, and R. Bau, *J. Am. Chem. Soc.*, 102 (1980) 3451.

547   T. J. Greenhough, B. W. S. Kolthammer, P. Legzdins, and J. Trotter, *Acta. Crystallogr., Sect. B*, 36 (1980) 795.

548   P. Legzdins, D. T. Martin, and C. R. Nurse, *Inorg. Chem.*, 19 (1980) 1560.

549   B. W. Hames, P. Legzdins, and J. C. Oxley, *Inorg. Chem.*, 19 (1980) 1565.

550   J. T. Malito, R. Shakir, and J. L. Atwood, *J. Chem. Soc., Dalton Trans.*, (1980) 1253.

551   A. G. Ginzburg, V. N. Setkina, and D. N. Kursanov, *J. Organomet. Chem.*, 182 (1979) C1.

552   J. W. Faller and Y. Shvo, *J. Chem. Soc.*, 102 (1980) 5396.

553   J. A. McCleverty and A. J. Murray, *Transition Met. Chem.*, (Weinheim, Ger.), 4 (1979) 273.

554   R. E. Bruns, Y. Hase, and I. M. Brinn, *J. Phys. Chem.*, 84 (1980) 3593.

555   G. D. Michels, G. D. Flesch, and H. J. Svec, *Inorg. Chem.*, 19 (1980) 479.

556   R. L. Kump and L. J. Todd, *J. Chem. Soc., Chem. Commun.*, (1980) 292.

557   D. J. Darensbourg, N. Walker, and M. Y. Darensbourg, *J. Am. Chem. Soc.*, 102 (1980) 1213.

558   H. Daamen, D. J. Stufkens, and A. Oskam, *Inorg. Chim. Acta.*, 39 (1980) 75.

559   R. W. Balk, D. J. Stufkens, and A. Oskam, *J. Chem. Soc., Chem. Commun.*, (1979) 604; R. W. Balk, D. J. Stufkens, and A. Oskam, *J. Mol. Struct.*, 60 (1980) 387; R. W. Balk, T. Snoeck, D. J. Stufkens, and A. Oskam, *Inorg. Chem.*, 19 (1980) 3015.

560   A. F. Schreiner, S. Amer. W. M. Duncan, G. Ober, R. M. Dahlgren, and J. Zink, *J. Am. Chem. Soc.*, 102 (1980) 6871.

561   A. J. Lees and A. W. Adamson, *J. Am. Chem. Soc.*, 102 (1980) 6874.

562   J. D. Black and P. S. Braterman, *Inorg. Chim. Acta.*, 44 (1980) L181.

563   G. Boxhoorn, A. Oskam, T. M. McHugh, and A. J. Rest, *Inorg. Chim. Acta.*, 44 (1980) L1.

564   G. Boxhoorn, G. C. Schoemaker, D. J. Stufkens, A. Oskam, A. J. Rest, and D. J. Darensbourg, *Inorg. Chem.*, 19 (1980) 3455.

565   J. D. Black, M. J. Boylan, P. S. Braterman, and A. Fullarton, *J. Chem. Soc.*,

Dalton Trans., (1980) 1651.

566   S. C. Avanzino, H.-W. Chen, C. J. Donahue, and W. L. Jolly, *Inorg. Chem.*, 19 (1980) 2201.

567   H. Daamen, A. Oskam, and D. J. Stufkens, *Inorg. Chim. Acta.*, 38 (1980) 71.

568   H. Daamen, H. Van der Poel, D. J. Stufkens, and A. Oskam, *Thermochim. Acta.*, 34 (1979) 69.

569   A. D. King, R. B. King, and D. B. Yang, *J. Chem. Soc., Chem. Commun.*, (1980) 529.

570   D. J. Darensbourg, B. J. Baldwin, and J. A. Froelich, *J. Am. Chem. Soc.*, 102 (1980) 4688.

571   A. Brenner and D. A. Hucul, *J. Am. Chem. Soc.*, 102 (1980) 2484.

572   J. M. Maher and N. J. Cooper, *J. Am. Chem. Soc.*, 102 (1980) 7604.

573   S. B. Butts, S. H. Strauss, E. M. Holt, R. E. Stimson, N. W. Alcock, and D. F. Shriver, *J. Am. Chem. Soc.*, 102 (1980) 5093.

574   S. Devarajan, D. R. M. Walton, and G. J. Leigh, *J. Organomet. Chem.*, 181 (1979) 99.

575   H. Alper and C. Blais, *J. Chem. Soc., Chem. Commun.*, (1980) 169.

576   A. Seurat, P. Lemoine, and M. Gross, *Electrochim. Acta.*, 25 (1980) 675.

577   J. Grobe and H. Zimmerman, *Z. Naturforsch. B: Anorg. Chem., Org. Chem.*, 35 (1980) 533.

578   G. J. Kubas, R. R. Ryan, and V. McCarty, *Inorg. Chem.*, 19 (1980) 3003.

579   M. K. Cooper, P. A. Duckworth, M. Saporta, and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, (1980) 570.

580   G. Matsubayashi, I. Kawafune, T. Tanaka, S. Nishigaki, and K. Nakatsu, *J. Organomet. Chem.*, 187 (1980) 113.

581   W. Beck, W. Petri, andJ. Meder, *J. Organomet. Chem.*, 191 (1980) 73.

582   J. Burgess, A. J. Duffield, and R. Sherry, *J. Chem. Soc., Chem. Commun.*, (1980) 350.

583   W. P. Bosman, J. H. Noordik, H. P. M. M. Ambrosius, and J. A. Cras, *Cryst. Struct. Commun.*, 9 (1980) 7.

584   M. C. Favas, D. L. Kepert, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, (1980) 447.

585   S. O. Grim, D. P. Shah, and L. J. Matienzo, *Inorg. Chem.*, 19 (1980) 2475.

586   S. O. Grim and E. D. Walton, *Inorg. Chem.*, 19 (1980) 1982.

587   S. O. Grim, P. H. Smith, I. J. Colquhoun, and W. McFarlane, *Inorg. Chem.*, 19 (1980) 3195.

588   H. Meinert, H. Vogt, B. Pahnke, and G. Schulenburg, *Z. Chem.*, 20 (1980) 110.

589   M. Baacke, S. Morton, O. Stelzer, and W. S. Sheldrick, *Chem. Ber.*, 113 (1980) 1343.

590   M. Fild, W. Handke, and W. S. Sheldrick, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 35B (1980) 838.

591   M. A. Bennett, S. Corlett, G. B. Robertson, and W. L. Steffen, *Aust. J. Chem.*, 33 (1980) 1261.

592   M. Baacke, S. Morton, G. Johannsen, M. Weferling, and O. Stelzer, *Chem. Ber.*, 113 (1980) 1328.

593   T. Chandler, G. R. Kriek, A. M. Greenaway, and J. H. Enemark, *Cryst. Struct. Commun.*, 9 (1980) 557.

594   O. Stelzer and N. Weferling, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 35 (1980) 74.

595   G. M. Gray and C. S. Kraihanzel, *J. Organomet. Chem.*, 187 (1980) 51.

596   W. A. Schenk, *J. Organomet. Chem.*, 184 (1980) 205.

597   J. Von Seyerl, D. Neugebauer, G. Huttner, G. Krueger, and Y.-H. Tsay, *Chem. Ber.*, 112 (1979) 3637.

598   J. C. T. R. Burckett St. Laurent, H. E. Hosseini, J. Sinclair, and J. F. Nixon, *Inorg. Chim. Acta.*, 44 (1980) L17.

599   H. B. Davis, J. K. Hoyano, P. Y. Leung, L. K. Peterson, and B. Wolstenholme, *Can. J. Chem.*, 58 (1980) 151.

600   C. C. Santini, J. Fischer, F. Mathey, and A. Mitschler, *J. Am. Chem. Soc.*,

102 (1980) 5809.

601   G. Fritz and R. Uhlman, *Z. Anorg. Allg. Chem.*, 465 (1980) 59.

602   J. H. Weinmaier, H. Tautz, A. Schmidpeter, and S. Pohl, *J. Organomet. Chem.*, 185 (1980) 53.

603   E. P. Kyba and S. S. P. Chou, *J. Chem. Soc., Chem. Commun.*, (1980) 449.

604   W. A. Schenk, *J. Organomet. Chem.*, 184 (1980) 195; J. Grobe and L. Van Duc, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 35 (1980) 694; D. Fenske, H. Teichert, H. Prokscha, W. Renz, and H. J. Becher, *Monatsh. Chem.*, 111 (1980) 177; H. J. Breunig and W. Fichtner, *Z. Anorg. Allg. Chem.*, 454 (1979) 167.

605   P. Jutzi, W. Steiner, and K. Stroppel, *Chem. Ber.*, 113 (1980) 3357.

606   W. W. DuMont and B. Neudert, *Angew. Chem.*, 92 (1980) 561.

607   K. S. Chong, S. J. Rettig, A. Storr, and J. Trotter, *Can. J. Chem.*, 58 (1980) 1080; K. S. Chong and A. Storr, *Can. J. Chem.*, 58 (1980) 2278.