Main-Group Element, Organic, and Organometallic Derivatives of Polyoxometalates

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I. Introduction

The early transition metals (V, Nb, Ta, Mo, W) in their highest oxidation states are able to form metal−oxygen cluster anions, commonly referred to as polyoxoanions[1] or polyoxometalates.[2] These species are remarkable for their molecular and electronic structural diversity and their significance in quite diverse disciplines, e.g., catalysis, medicine, and materials science.[3,4] Although the first polyoxometalates were reported over 150 years ago,[5] they continue to display novel structures, and unexpected reactivities and applications.[3,4] Increasing attention is currently devoted to supramolecular polyoxometalate chemistry, i.e., the self-assembly of large species from smaller fragments.[6−9]

The present review deals with derivatized polyoxometalates, especially those including organic and organometallic components. There are many reasons for the current interest in these derivatives. (i) Owing to the perceived structural analogies of polyoxometalates to metal oxide surfaces,[2,10,11] these species can be viewed as soluble metal oxide analogues and therefore are of special interest as models for the reactions and properties of oxides. Given the versatility of metal oxides in catalyzing organic transformations,[12] and the difficulty in determining the intimate mechanism of these reactions, the study of the stoichiometric reactivity of well-defined surface polyoxometalates might contribute toward an understanding of the elementary steps of heterogeneous reactions, particularly with respect to surface-bound intermediates. Therefore, the characterization of organic derivatives of polyoxoanions is relevant to the

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modeling of catalytic reactions taking place at metal oxide surfaces. Furthermore, polyoxoanion-supported transition-metal catalysts represent a new class of oxide-supported catalyst materials that can be fully investigated at the atomic level, both structurally and mechanistically.[13] (ii) Derivatization can result in the stabilization of otherwise unstable molecular architectures,[14] providing novel building blocks for the assembly of larger systems. (iii) The building of interconnected polyoxometalate networks could be achieved through the incorporation of ligands with a remote functionality,[15,16] and polysubstitution[17] could prove interesting in the context of the development of dendrimers. (iv) Functionalization may result in the activation of surface oxygen atoms.[18] (v) Derivatization might provide multifunctional oxidation catalysts that display selective recognition of substrates, thus higher selectivities, and might facilitate targeting of polyoxometalates in antiviral chemotherapy.[19]

II. Scope and Organization of the Review

In a restrictive sense, derivatized polyoxometalates might be defined as species where some oxo ligands have been replaced by other (inorganic or organic) ligands. However, this definition is worth extending so as to include derivatives where some $\{MO_x\}^{n+}$ units have been replaced by other groups. In view of the extensive literature on polyoxometalate chemistry and the quite rapid developments in the field of polyoxometalate coordination chemistry, the scope of the review has been restricted to a few areas. Our discussion will focus on polyoxometalates covalently attached with distinct subunits. Titanium-substituted polyoxometalates[20]—apart from cyclopentadienyl derivatives—and polyoxoalkoxotitanium complexes[21] have been excluded, as has the coordination chemistry of polyoxometalate-incorporated transition-metal complexes although the latter provide the basis of a variety of derivatives.[22] Derivatives involving noncovalent interactions such as host−guest systems, intermolecular complexes between polyoxometalates and organic substrates, and organic radical ion salts with polyoxometalates will be only briefly mentioned. The relationship of polyoxometalate coordination chemistry to host−guest and host−hostage chemistry has been discussed by Mitchell, Müller, Klemperer, and Pope.[23] The host−guest properties of polyoxometalates (largely polyoxovanadates) and the induced self-organization of large polyoxometalates have been recently reviewed by Müller,[9] and Zubieta has dealt with the control of oxide crystal growth by organic templates.[24b]

Early work on organic and organometallic derivatives of polyoxometalates has been reviewed by Pope,[2] and the coordination chemistry of soluble oxides of vanadium and molybdenum has been thoroughly reviewed by Zubieta in recent years.[24] Reference 4 includes several accounts on the coordination chemistry of polyoxoanions, e.g., polyoxoanion-supported organometallic complexes, polyoxometalate chemistry with main-group elements, polyoxomolybdates, and polyoxovanadates with organic ligands, and nitrosyl derivatives of polyoxomolybdates. Our purpose is to provide a systematic survey of derivatized polyoxometalates with special emphasis on derivatives with multiple bonded ligands. Mono-, di-, and trinuclear complexes will not be discussed, unless their structural and chemical features are related to those of higher nuclearity species or they might be indicative of directions for future research. The review focuses on structural relationships. The catalytic activity will not be reported unless it appears to be specific for a given derivative.

The review has been structured according to the classification of incorporated ligands as main-group element-centered ligands (Table 1). This classification, as any, is arbitrary in some respects, as the element under consideration may be not directly bound to a metal center, and as many derivatives

Table 1. Organization of the Review According to the Type of Incorporated Ligands

14	15	16	17
$C_nH_m^{z-}$	N^{3-}	E^{2-} (E = S, Se)	X^-
E^{2+} (E = Sn, Pb)	R_3N, RNH_2, RN^{2-}	RO^-	
	$RR'NN^{2-}$		
	NH_2OH, RR′CNOH, $RC(NH_2)NOH$		
	NO, RN_2^+		
$RCHO_2^{2-}$, $O_2RO_2^{4-}$	$RR'EO_2^-$ (E = As)	REO_2^- (E = S, Se)	
REO_3^{3-} (E = Si, Ge, Sn, Pb)	REO_3^{2-} (E = P, As)		
RCO_2^{2-}, $C_2O_4^{2-}$, $C_4O_4^{2-}$			
CO_3^{2-}, EO_4^{4-} (E = Si, Ge)	NO_3^-, XO_4^{3-} (X = P, As)	SO_4^{2-}	XO_4^-

include more than one kind of ligand. However, it offers the advantage of avoiding the debate on the definition of the ligands, e.g., are alkoxypolyoxometalates best described as O-alkylated polyoxometalates or as organic esters of polyoxometalates?

On the basis of their electronic structures, it should be possible to replace the oxo ligand by the isoelectronic ligands F^-, HO^-, HN^{2-}, N^{3-}, and HC^{3-}. Indeed these ligands are π-donor ligands that are effective in the stabilization of highest metal oxidation states. However, they differ in their propensity toward forming multiple bonds. Parallels in the chemistry of oxo, organoimido, and cyclopentadienyl complexes have been discussed with regard to the isolobal relationship.[25] Oxo, organoimido, and cyclopentadienyl ligands are σ,2π-bonding ligands, which form σ- and π-bonds with metal orbitals of the same symmetry, and it is the same for nitrido and carbyne ligands. The area of organoimido derivatives of polyoxometalates is steadily increasing (section V.B.2), but there are a very few examples of nitrido (V.B.1) and cyclopentadienyl (VII.A) polyoxometalates. To the best of our knowledge, polyoxoanions with HN^{2-} or HC^{3-} ligands are still unknown. However the chemistry of mononuclear oxo alkylidyne complexes of molybdenum and tungsten is currently an active area of research.[26] In contrast to imido and nitrido ligands, halide, hydroxo, and alkoxo ligands are reluctant to form multiple bonds with the same metal center, thus they cannot generally replace terminal multiply bonded oxo ligands.

III. Polyoxometalates Incorporating Halides

Polyoxometalates incorporating group 17 elements may be divided into two subclasses: (i) halide- and halogen oxoanion-encapsulating complexes (Table 2), and (ii) polyoxohalometalates.

Halide-encapsulating polyoxovanadates, e.g., $[V_{15}O_{36}X]^{6-}$ (X = Cl, Br), and $[H_xV_{18}O_{42}(X)]^{(13-x)-}$ (X = Cl, Br, and I) (Figure 1) have been prepared either by thermal reactions of KVO_3 or V_2O_5 with hydrazine in aqueous solutions,[27,28a] or by photolysis of aqueous solutions containing vanadates and alcohols.[29] The ClO_4^- ion provides a template for the self-induced organization of a larger cluster shell, e.g., $[HV_{22}O_{54}(ClO_4)]^{6-}$.[28b]

The conventional or solvothermal reactions of $[VO_2X_2]^-$ (X = F, Cl) with RPO_3H_2 in organic solvents yield a number of host–guest clusters, e.g., $[V_4O_6(PhPO_3)_4F]^-$,[30a] $[V_6O_6(t\text{-}BuPO_3)_8Cl]$,[30b] $[V_7O_{12}(PhPO_3)_6Cl]^{2-}$,[30c] $[V_{18}O_{25}(H_2O)_2(PhPO_3)_{20}Cl_4]^{4-}$,[30b] and $[V_{12}O_{20}(H_2O)_{12}(PhPO_3)_8Cl_2]^{2-}$ [30d] (section V.C.1). Halide-encapsulated clusters have also been obtained with carboxylate, e.g., $[V_5O_9(tca)_4Cl]^{2-}$ [31] (section VI.A.2) and trisalkoxide ligands, e.g., $[V^{IV}_6O_6F(OH)_3\{MeC(CH_2O)_3\}_3]^-$ [32] (section IV.B.2). The latter is to date the only example of a hexametalate core possessing a central anion other than oxide. However, its V_6O_{18} core may be defined as $[V_6(\mu_3\text{-}F)O_{18}]$ in contrast to the common $[M_6(\mu_6\text{-}O)O_{18}]$ core.

The reluctance of the fluoro ligand to expand its coordination number is also apparent in the structure of the $[(O_2CHCHO_2)Mo_4O_{11}F]^{3-}$ ion, [33a] where the

Table 2. Some Host–Guest Systems

system	ref(s)
$[V^{IV}_8V^V_7O_{36}(X)]^{6-}$ (X = Cl, Br)	27,28a
$[H_xV^{IV}_{18}O_{42}(X)]^{(13-x)-}$ (X = Cl, Br, I)	28a, 29b
$[V^{IV}_6O_6(OH)_3\{MeC(CH_2O)_3\}_3(F)]^-$	32
$[V^V_4O_6(PhPO_3)_4(F)]^{1-}$	30a
$[V^{IV}_5V^VO_6(t\text{-}BuPO_3)_8(Cl)]^{4-}$	30b
$[V^V_7O_{12}(PhPO_3)_6(Cl)]^{2-}$	30c
$[V^V_{18}O_{25}(H_2O)_2(PhPO_3)_{20}(Cl)_4]^{4-}$	30b
$[V^{IV}_{12}V^V_2O_{22}(OH)_4(H_2O)_2(PhPO_3)_8\{2M^+, 2Cl^-\}]^{6-}$ ($M^+ = NH_4^+$, Rb^+)	28c
$[(V^{IV}_4V^V_8O_{20}(H_2O)_{12}(PhPO_3)_8(Cl)_2]^{2-}$	30d
$[V^{IV}_4V^VO_9(tca)_4(X)]^{2-}$ (X = Cl, Br)	207
$[HV^{IV}_8V^V_{14}O_{54}(ClO_4)]^{6-}$	28b
$[V^{IV}_{14}As_8O_{42}(SO_3)]^{6-}$	3
$[V^{IV}_{12}V^V_6O_{42}(SO_4)]^{8-}$	28d
$[As^{III}_4Mo^{VI}_6V^{IV}_7O_{37}(SO_4)]^{4-}$	28e
$[V_4O_8(RCO_2)_4(NO_3)]^{z-}$	31, 207, 211
$[HV^{IV}_{12}V^V_6O_{44}(NO_3)]^{10-}$	23b, 213
$[H_2V^{IV}_8V^V_{10}O_{44}(N_3)]^{5-}$	28b
$[HV_{22}O_{54}(SCN)]^{6-}$	213
$[V^{IV}_8V^V_7O_{36}(CO_3)]^{7-}$	28a, 29a
$[V^{IV}_6O_6(OH)_9(CO_3)_4]^{5-}$	206
$[V_{12}As_8O_{40}(HCO_2)]^{5/3-}$	214
$[H_2V_{22}O_{54}(MeCO_2)]^{7-}$	213

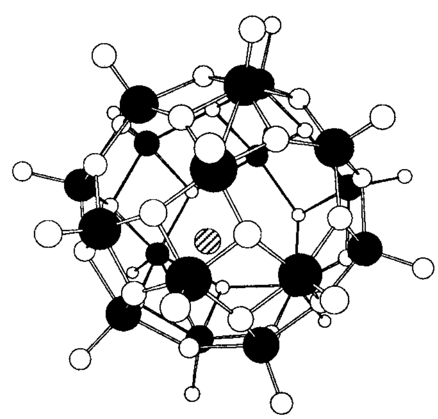


Figure 1. The structure of the $[V_{18}O_{42}(Cl)]^{13-}$ anion (ref 29b).

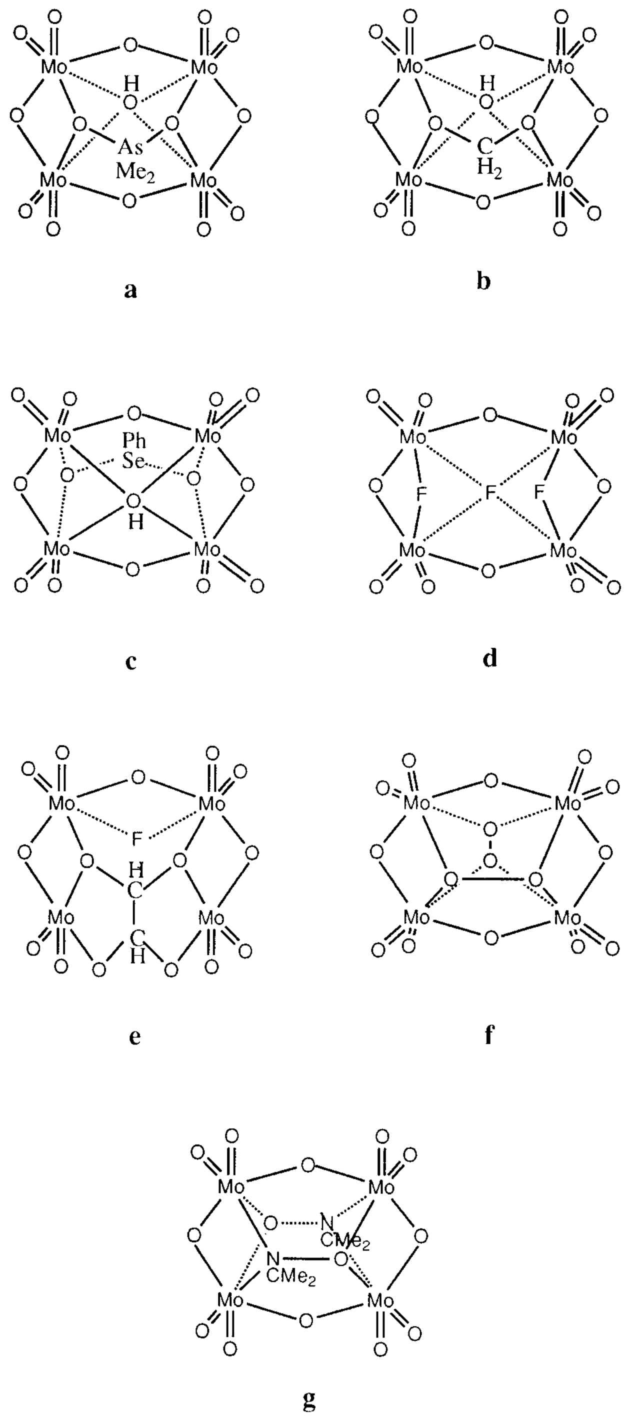


Figure 2. Schematic representations of some cyclic tetranuclear complexes: (a) $[(Me_2AsO_2)Mo_4O_{12}(OH)]^{2-}$ (ref 34), (b) $[(H_2CO_2)Mo_4O_{12}(OH)]^{3-}$ (ref 33b), (c) $[(PhSeO_2)Mo_4O_{12}(OH)]^{2-}$ (ref 88a), (d) $[Mo_4O_{12}F_3]^{3-}$ (ref 35a), (e) $[(O_2HCCHO_2)Mo_4O_{11}(F)]^{3-}$ (ref 33a), (f) $[Mo_4O_{12}(O_2)_2]^{4-}$ (ref 53), and (g) $[Mo_4O_{12}\{Me_2CNO\}_2]^{2-}$ (ref 113a).

capping F^- ligand is doubly bridging (Figure 2e) in contrast to the quadruply bridging OH^- group in the acetal derivative $[(H_2CO_2)Mo_4O_{12}(OH)]^{3-}$ (Figure 2b),[33b] and in the dimethylarsinate derivative $[(Me_2AsO_2)Mo_4O_{12}(OH)]^{2-}$ (Figure 2a).[34] However the cyclic tetramolybdate $[Mo_4O_{12}F_3]^{3-}$ contains a quadruply bridging capping fluoro ligand (Figure 2d).[35a] The structural relationship between the various cyclic tetramolybdates is analyzed in section V.A.2.

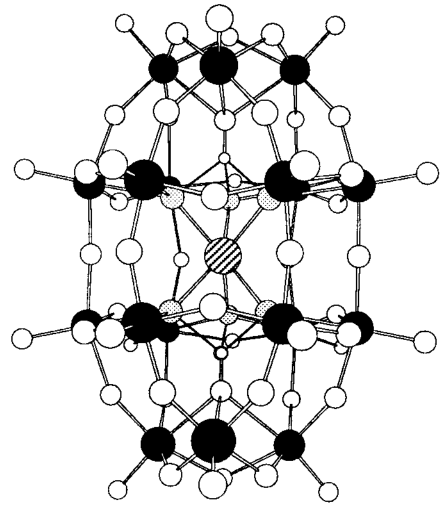


Figure 3. The structure of the $[H_2NaW_{18}O_{56}F_6]^{7-}$ anion (ref 37).

Several oligonuclear complexes formed in reactions of aqueous or methanolic solutions containing oxovanadium or oxomolybdenum species and fluoride or chloride ions, with squaric acid, have been recently reported. The structurally related complexes $[V_3O_4F_4(C_4O_4)_3]^{4-}$ and $[Mo_3O_8F(C_4O_4)_2]^{3-}$ display a $\{M_3(\mu_3\text{-}F)\}$ core.[35b]

Fluoropolyoxoanions have been characterized by Chauveau and co-workers,[36] Baker and co-workers,[37] and by Wasfi and co-workers.[38] Most of the compounds synthesized by Chauveau and Doppelt, e.g., $[H_2W_{12}O_{39}F]^{5-}$, $[H_2W_{12}O_{38}F_2]^{4-}$, $[HW_{12}O_{38}F_2]^{5-}$, and $[HW_{12}O_{37}F_3]^{4-}$, are derived from the metatungstate structure, while those obtained by Baker et al., *d,l*-α_1-$[(H_2O)M^{n+}O_5H_2F_6NaW_{17}O_{50}]^{(11-n)}$, wherein $M^{n+} =$ Co^{2+}, Co^{3+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, or Mn^{3+}, may be described as hypothetically derived from the Wells–Dawson α-$[P_2W_{18}O_{62}]^{6-}$.[37] The structure was elucidated by interdependent combination of structural X-ray crystallography, ^{183}W, ^{19}F, ^{1}H, and ^{23}Na NMR and optical spectroscopy, chemical analyses, isotopic exchanges, and electrochemistry.[37b] Six F atoms replace the six O atoms closest to the complex's center, yielding a trigonal prism of F atoms at the center of which is the Na atom. The two P atoms are replaced by two H atoms and one belt W atom is replaced by the M^{n+} heteroatom. Jorris et al. also showed that the species $[H_2F_6W_{18}O_{56}]^{8-}$ first reported by Chauveau et al.,[36c] is actually an isomorph the 17-tungsto heteropoly complexes, its true formula being $[H_2NaW_{18}O_{56}F_6]^{7-}$ (Figure 3).[37a] Five other members of this class of anions, $[Fe^{III}W_{17}O_{56}F_6NaH_4]^{8-}$,[38a] $[Cu^{II}W_{17}O_{57}F_5NaH_5]^{9-}$,[38b] $[Cu^{I}W_{17}O_{54}F_8NaH_4]^{8-}$,[38d] $[MgW_{17}O_{57}F_5NaH_6]^{8-}$,[38d] and $[Fe^{III}W^{V}W^{VI}_{16}O_{55}F_7NaH_4]^{8-}$,[38d] have been prepared and characterized by Wasfi et al. who have also reported several 1:1:11 and 1:11 heteropolyoxofluorotungstates as part of a program directed toward the preparation of potential antiviral agents. Evidence from analytical results, negative ion fast-atom bombardment mass spectra, visible and infrared spectroscopy, cyclic voltammetry, and X-ray diffraction patterns has shown that the complexes $[NiCoW_{11}O_{39}FH_2]^{7-}$,[38c] $[M^{II}NiW_{11}O_{38}F_2H_4]^{4-}$ (M^{II} = Cu, Mn),[38e] $[M^{II}W_{11}O_{38}F_2H_6]^{4-}$ (M^{II} = Cu, Mn),[38f] $[CoW_{11}O_{38}F_2H_4]^{6-}$,[38h]

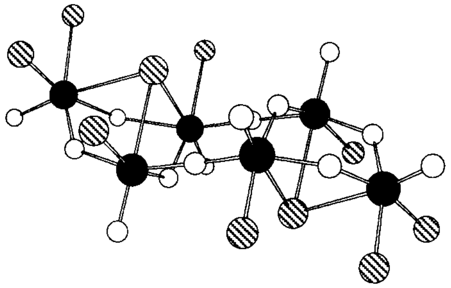


Figure 4. A view of the structure of the $[W_6O_{14}Cl_{10}]^{2-}$ ion (ref 40).

$[Mn^{III}W_{11}O_{37}F_3H]^{7-}$,[38g] and $[Fe^{III}ZnW^{V}W^{VI}_{10}O_{36}F_4]^{6-}$,[38i] have a Keggin structure. In the 1:11 complexes, the heteroatom is thought to replace one of the W atoms in the original Keggin structure. In all these fluoro derivatives, only those oxygens that form the central cavity of the Keggin and Dawson structures have been replaced by fluorine, i.e., the oxygens replaced are those not involved in π-bonding, which is in keeping with the known reluctance of fluorine to participate in multiple bonding.

Current studies in the system $V_2O_5-P_2O_5-HF-$organic base$-H_2O$ reflect the interest in oxyfluorinated microporous materials. $(H_3O)_2(NC_7H_{14})_6\{[V_4O_6F(HPO_4)(PO_4)_3]\}_2$ contains two kinds of clusters $[V_4O_6F(HPO_4)(PO_4)_3]^{4-}$ built up from the tetrahedral arrangement of VO_5F octahedra sharing edges and vertexes, capped by phosphorus tetrahedra.[39]

There is a single example of a fully oxidized polyoxochlorotungstate, $[W_6O_{14}Cl_{10}]^{2-}$, which was isolated from the reaction between $(n\text{-}Bu_4N)[W_2O_2Cl_7]$ and *p*-tolyl azide.[40] Its structure consists of two trinuclear $W_3O_3(\mu\text{-}O)_3Cl_4(\mu_3\text{-}Cl)$ fragments joined by two linear W$-$O$-$W linkages (Figure 4). Most other reported chloro derivatives are tetranuclear species that contain additional ligands. Whereas $[Mo_4O_{10}(OMe)_4Cl_2]^{2-}$,[41] $[Mo_4O_8(OR)_2(ROH)_2Cl_4]^{2-}$ (R = Me,[41] Et[42,43]), $[Mo_4O_6(OR)_4(ROH)_2Cl_4]$ (R = *n*-Pr,[43,44] and Et[45a]), $[Mo_4O_6(OEt)_4Cl_4(PMe_3)_2]$,[45b] and $[V_4O_6Cl_2\{Me_2C(CH_2O)_2\}_2\{Me_2C(CH_2O)CH_2OH\}_2]$,[46] all adopt a planar compact structure based on four edge-sharing octahedra (Figure 5a), carboxylate derivatives of the type $[Mo^{V}_4O_6Cl_2(O_2CR)_6]$ (R = Me[47a] or *p*-Tol[47b]) display different structures where there is one Mo$-$Mo bond.

IV. Polyoxometalates Incorporating Group 16 Element-Centered Ligands

A. Peroxopolyoxometalates

The $\eta^2\text{-}O_2^{2-}$ ligand is a π-donor like the oxo ligand and the $\{MO(O_2)\}$ and $\{MO(O_2)_2\}$ units are analogous to the *cis*-dioxo and *fac*-trioxo units, respectively. Peroxocomplexes of molybdenum,[48] tungsten,[48] and vanadium[49] have been recently reviewed, and Pope's review[48] includes a specific section on polyoxometalate derivatives. A comprehensive list of X-ray crystal structures for monuclear and polynuclear peroxo Mo(VI) and W(VI) complexes have also been published by Hill and co-workers.[50]

A systematic structural investigation of peroxo complexes of group 5 and group 6 elements has been carried out by Stomberg over more than 20 years.[51−53] Addition of H_2O_2 to aqueous solutions of polyoxomolybdates and -tungstates lead to the formation of polynuclear peroxo complexes if the concentration of H_2O_2 is kept low. Peroxide-rich structures are based on the $[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$ dinuclear species, whereas peroxide-poor species are related to known polyoxomolybdates. Thus $[Mo_7O_{22}(O_2)_2]^{6-}$ (Figure 6)[51,53] and $[Mo_8O_{24}(O_2)_2(H_2O)_2]^{4-}$ [52] are based on hepta- and octamolybdate frameworks, respectively, and $[Mo_4O_{12}(O_2)_2]^{4-}$ (Figure 2f)[53] displays the common cyclic $\{Mo_4O_{12}\}$ core.

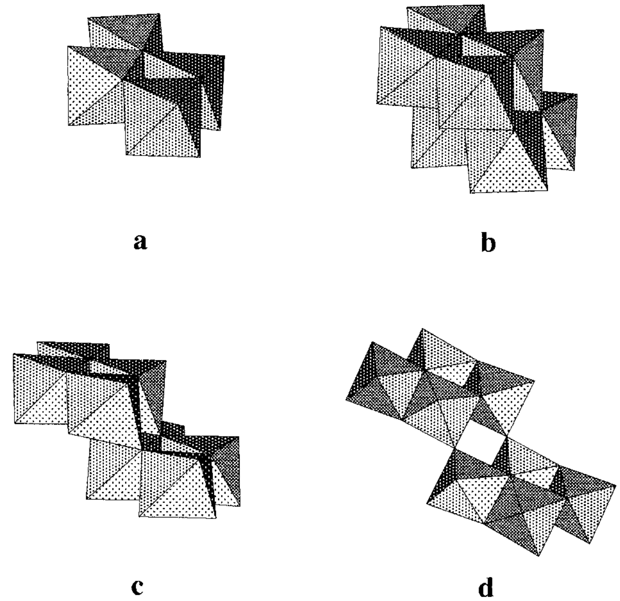


Figure 5. Polyhedral representations of the compact arrangement of four edge-sharing octahedra (a), the $\beta\text{-}[Mo_8O_{26}]^{4-}$ anion (b), and the hypothetical $[Mo_8O_{28}]^{8-}$ (c) and $[Mo_8O_{30}]^{12-}$ (d) anions

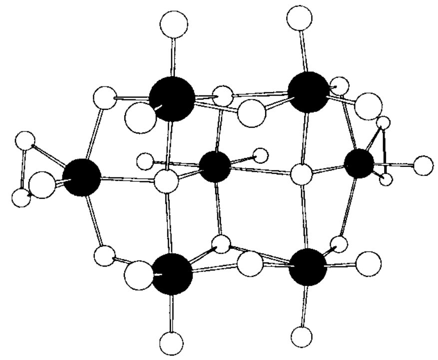


Figure 6. A view of the structure of the $[Mo_7O_{22}(O_2)_2]^{6-}$ anion (ref 51a)

The chemistry of iso- and heteropolyoxoperoxo complexes is of considerable current interest since some of these complexes catalyze the oxidations of a variety of organic substrates with H_2O_2 as cooxidant (Ishii$-$Venturello chemistry).[50,54−59] This involves the epoxidation of relatively electron poor terminal olefins by H_2O_2 and heteropolyacids, principally $H_3[PW_{12}O_{40}]$, using a phase-transfer catalyst. It is now clear that all Keggin-type precursors degrade in aqueous H_2O_2,[50,57a−c] but only $[PW_{12}O_{40}]^{3-}$ and $[PW_{11}O_{39}]^{7-}$ are effective epoxidation catalysts.[50] The speciation in the $H_3[PW_{12}O_{40}]/H_2O_2$ system has been evaluated UV$-$vis, NMR, and Raman spectroscopy.

Spectral data give clear evidence for the formation of peroxophosphotungstates of composition $[PW_xO_y]^{z-}$ ($x = 1-4$).[57b] Complementary studies by Hill et al. have shown that similar species are generated directly from the epoxidation of alkene substrates in nonaqueous media and that $[PO_4\{WO(O_2)_2\}_4]^{3-}$ is the dominant species present under steady-state turnover conditions.[50] In addition to $[PO_4\{MO(O_2)_2\}]^{3-}$ (M = W,[55b] Mo,[57b]) and $[HPO_4\{WO(O_2)_2\}_2]^{2-}$,[57c] heteropolyoxoperoxometalates with organophosphonates,[56,58b,g] organophosphinates,[58e−g] arsenate,[57d,58a,g,59] organoarsonates,[57d] organoarsinates,[57d,58e,f] sulfate,[57e] and diphenylsilanediolate,[57g] assembling ligands have been structurally characterized. Many of these complexes have one or two neutral $\{M_2O_2(\mu\text{-}O_2)_2(O_2)_2\}$ (M = W or Mo) moieties with one bridging and one nonbridging peroxo groups on each W or Mo center, and a number are active oxidation catalysts with H_2O_2. Extended Hückel molecular orbital calculations support an outer-shere mechanism for active oxygen-to-olefin transfer as the best mechanistic model.[57f]

Reduction of the lacunary anion α-$[Co^{III}W_{11}O_{39}]^{9-}$ with H_2O_2 leads to β_3-$[Co^{II}W_{11}O_{35}(O_2)_4]^{10-}$ where four *cis*-$\{WO(\eta^2\text{-}O_2)\}$ units surround the vacancy created by the loss of WO^{4+} from β-$[Co^{II}W_{12}O_{40}]^{6-}$.[60] Other examples of peroxopolyoxoanions include $[(H_2)W_{12}O_{39}(O_2)]^{6-}$, for which IR and ^1H NMR data are consistent with the metatungstate structure,[61] the substituted peroxoniobium and peroxotantalum Keggin polyoxotungstates, $[SiNb(O_2)W_{11}O_{39}]^{5-}$, $[Si\{Nb(O_2)\}_3W_9O_{37}]^{7-}$, and $[SiTa(O_2)W_{11}O_{39}]^{5-}$, and the hexasubstituted peroxoniobium Wells−Dawson polyoxotungstate, $[P_2\{Nb(O_2)\}_6W_{12}O_{56}]^{12-}$.[62,63] The anti-HIV-1 activity and toxicity of the peroxoniobium-substituted heteropolytungstates has been evaluated.[63]

B. Polyoxoalkoxometalates

Polyoxoalkoxometalates, since the pioneering work at du Pont in the early 1980s,[64,65] have attracted continuous attention and now form the largest subclass of polyoxometalate derivatives.[24a,c,d] They can be obtained in a variety of ways e.g. (i) O-alkylation of polyoxometalates with trialkyloxonium salts,[64a,68a] dialkyl sulfates,[18,67,68a] or alkyl halides;[68b] (ii) thermolysis of trialkyloxonium salts,[64b] and aryldiazonium salts;[66] (iii) esterification of polyoxometalates with alcohols;[19,67] (iv) controlled hydrolysis of metal alkoxides;[69] (v) reaction of oxides with alcohols;[65] and (vi) self-assembly from polyoxometalates and alcohols. Reaction of polyoxometalates with organic ligands in methanol often results in the formation of methoxo derivatives which are reported under the relevant heading.

1. Polyoxoalkoxometalates Involving Unidentate Alcohols

Reaction of $MoO_3{\cdot}2H_2O$ with methanol yields isopoly-oxo-methoxomolybdates, $Mo_2O_5(OMe)_2$, $Mo_2O_5{\cdot}2MeOH$, and $Na_4[Mo_8O_{24}(OMe)_4]{\cdot}8MeOH$, which proved to be adequate models for the selective oxidation of methanol to formaldehyde over molybdate catalysts.[65] The compound $(Ph_3MeP)_2[Mo_4O_{10}(OMe)_6]$ has been isolated from the reaction of $(Ph_3MeP)_4[Mo_8O_{26}]$ with methanol in the presence of an organic base.[41b] The anion $[Mo_4O_{10}(OMe)_6]^{2-}$ (Figure 7) displays the compact structure (Figure 5a) common to many tetramolybdates (Table 3). It is noteworthy that the thermal decomposition of $Na_4[Mo_8O_{24}(OMe)_4]{\cdot}8CH_3OH$,[65b,c] and of $(Ph_3MeP)_2[Mo_4O_{10}(OMe)_6]$,[41b] yields formaldehyde in addition to water, and dimethyl ether, methanol, and water, respectively, which is consistent with the presence of significant C−H···O contacts, indicating possible paths for proton transfer. It has been similarly proposed that bridging methoxy groups are the key species in the formation of formaldehyde, dimethyl ether, and methyl formate, upon the thermal decomposition of $[(Cp^*Rh)_2Mo_3O_9(OMe)_4]$ (section VII.C.3).[70]

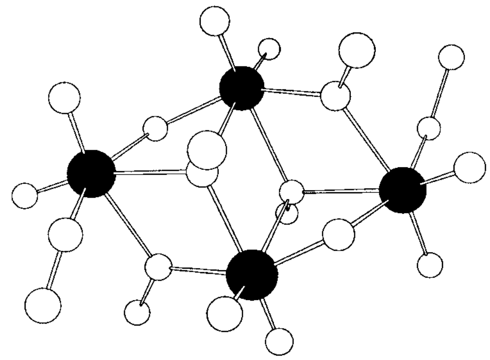


Figure 7. A view of the structure of the $[Mo_4O_{10}(OMe)_6]^{2-}$ anion (ref 41b).

Table 3. Tetranuclear Complexes with the Compact Planar Arrangement Based on Four Edge-sharing Octahedra

complex	ref(s)
$[Mo_4O_{10}(OMe)_6]^{2-}$	41
$[Mo_4O_{10}(OMe)_4Cl_2]^{2-}$	41
$[Mo_4O_8(OMe)_2(MeOH)_2Cl_4]^{2-}$	41
$[Mo_4O_8(OEt)_2(EtOH)_2Cl_4]^{2-}$	42, 43
$[Mo_4O_6(OEt)_4(EtOH)_2Cl_4]$	45a
$[Mo_4O_6(OPr\text{-}n)_4(n\text{-}PrOH)_2Cl_4]$	43,44
$[Mo_4O_{10}(OMe)_2(OC_6H_4O)_2]^{2-}$	41
$[Mo_4O_{10}(OMe)_2(PhCONO)_2]^{2-}$	112a
$[Mo_4O_{10}(OMe)_2\{RC(NH)NO\}_2]^{2-}$ (R = 2-thienyl)	107
$[Mo_4O_{10}(OMe)_4(Me_2CNO)_2]$	113a
$[Mo_4O_6(OEt)_4Cl_4(PMe_3)_2]$	45b
$[Mo_4O_8(OEt)_2\{MeC(CH_2O)_3\}_2]$	72
$[Mo_4O_{10}\{MeC(CH_2O)_3\}_2]^{2-}$ (M = Mo, W)	73
$[V_2Mo_2O_8(OMe)_2\{C(CH_2OH)(CH_2O)_3\}_2]^{2-}$	74a
$[V_4O_6Cl_2\{Me_2C(CH_2O)_2\}_2\{Me_2C(CH_2OH)CH_2O\}_2]$	46, 24d
$[V_4O_4(OMe)_6\{MeC(CH_2O)_3\}_2]$	75
$[V_4O_4(OEt)_3\{MeC(CH_2O)_3\}_3]$	75
$[V_4O_4(H_2O)_2(SO_4)_2\{EtC(CH_2O)_3\}_2]^{2-}$	74a

A few other (polyalkoxy)polyoxometalates with unidentate alcohols have been characterized. The compound $[Mg(MeOH)_6][Mg_2Mo_8O_{22}(MeO)_6(MeOH)_4]{\cdot}6MeOH$ has been isolated from a methanolic solution containing $MoCl_5$ and $MgCl_2$.[71b] When reduced electrochemically to Mo(III), the complex forms an active catalyst for N_2 reduction by sodium amalgam at room temperature and atmospheric pressure. In the mixed-valence cluster $[Mg_2Mo_8O_{22}(MeO)_6(MeOH)_4]^{2-}$, the $\{MgO_6\}$ octahedra occupy the cavities formed by the arrangement of $\{MoO_6\}$ octahedra, completing the $\{M_{10}O_{28}\}$ core.[71b] The formation of $[V_6O_{12}(OMe)_7]^-$ from $(n\text{-}Bu_4N)_3[H_3V_{10}O_{28}]$ in refluxing methanol, reflects the stabilization of the hexavanadate core provided by the charge reduction that follows the incorporation of alkoxo ligands.[71a]

The reactivity of polyoxometalates toward alkylating agents reflects the relative labilities of different types of metal–oxygen bonds, the steric environments of different surface oxo ligands, and the surface charge distribution in the metal–oxygen framework. Alkylation of $(n\text{-}Bu_4N)_3[PM_{12}O_{40}]$ (M = Mo, W) with trimethyloxonium tetrafluoborate in 1,2-dichloroethane yields $(n\text{-}Bu_4N)_2[PM_{12}O_{39}(OMe)]$. A crystal-structure determination of the molybdenum complex has shown that the methyl group is bonded to an oxygen which bridges two edge-sharing molybdenum octahedra.[64a] Alkylation of $[Nb_2W_4O_{19}]^{4-}$ with dialkyl sulfate yields a mixture of five distinct diastereomeric $[Nb_2W_4O_{18}(OR)]^{3-}$ (R = Me, Et) anions containing alkoxy groups in the five possible doubly bridging sites in $[Nb_2W_4O_{19}]^{4-}$. This contrasts with the acid esterification of $[Nb_2W_4O_{19}]^{4-}$, which yields a single isomer where the alkoxy group, depending on its bulk, either occupies the bridging position between the two niobium atoms or is terminally bound to a single niobium center.[67] It is noteworthy that the methoxy group is terminally bound to the niobium center in the $[(MeO)NbW_5O_{18}]^{2-}$ anion formed in the controlled hydrolysis of a mixture of $[WO_4]^{2-}$, $[WO(OMe)_4]$, and $[Nb(OMe)_5]$.[69]

Methylation of $[Mo_6O_{18}(NO)]^{3-}$ [18a] and $[W_5O_{18}\{Mo(NO)\}]^{3-}$,[18b] with dimethyl sulfate is stereoselective, contrary to that of other hexametalates, e.g., $[Nb_2W_4O_{19}]^{4-}$.[67] Only one isomer of $[M_5O_{17}(OMe)\{Mo(NO)\}]^{2-}$ (M = Mo, W) is formed. With regard to the methylation site, three isomers are possible depending on whether the bridging methoxo ligand is adjacent or opposite to the nitrosyl, or lies in the equatorial plane. X-ray diffraction structure determinations ruled out the third possibility but could not distinguish the adjacent from the remote site because the anions are located at inversion centers. NMR studies[18b] have provided definite evidence for the location of the methoxo group in adjacent site to the nitrosyl unit in $[W_5O_{17}(OMe)\{Mo(NO)\}]^{2-}$. These results are consistent with the ab initio determined distribution of the electrostatic potential for $[M_6O_{18}(NO)]^{3-}$ which shows that the most basic oxygen atoms are those adjacent to the M(NO) unit.[18c]

2. Polyoxoalkoxometalates Involving Chelating Triols

A number of polymetalate derivatives incorporating trisalkoxo ligands of the type $\{RC(CH_2O)_3\}^{3-}$ (tris; R = Me, NO_2, NH_2, CH_2OH, $CHNC(O)CH{=}CH_2$) have been prepared either by conventional or hydrothermal syntheses, and structurally characterized.[24d] Their structures reflect the steric requirements of the trialkoxy groups which preferentially bridge three metals in a triangular arrangement, or cap the triangular faces of the tetrahedral cavities of the polyoxometalate frameworks.

Conventional synthetic methods involve hydrolysis and fragment condensation of aggregates from simpler molecular precursors in solution. Trisalkoxide ligands are effective in stabilizing dinuclear complexes $[Mo_2O_4(tris)_2]^{2-}$ (Figure 8a), which may in turn

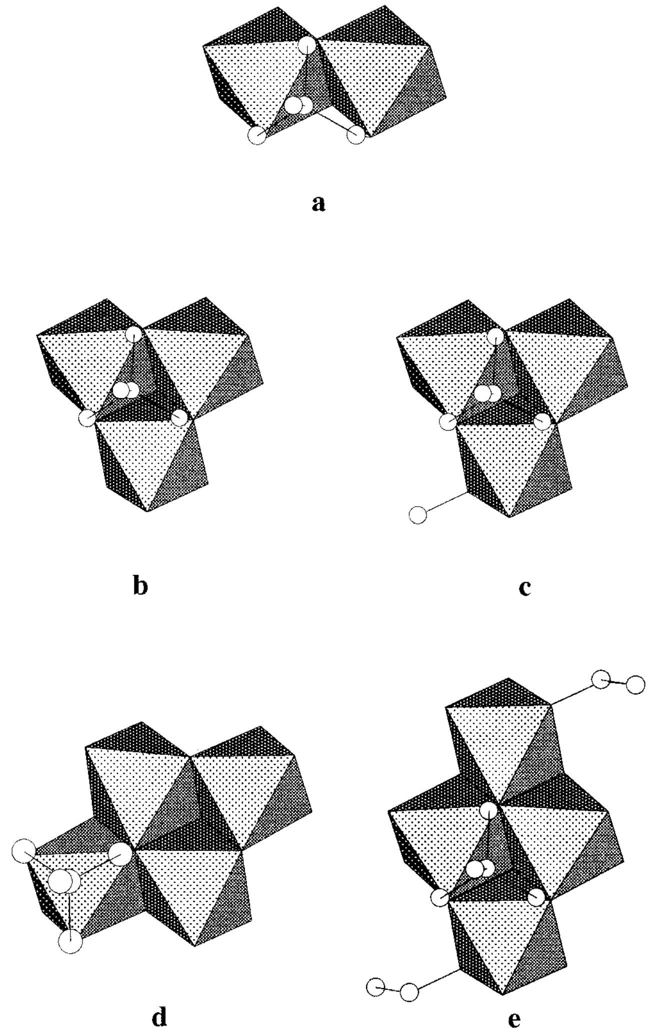


Figure 8. Illustration of the structural relationship among the complexes $[Mo_2O_4\{MeC(CH_2O)_3\}_2]^{2-}$ (a), $[Mo_3O_7\{MeC(CH_2O)_3\}_2]^{2-}$ (b), $[Mo_3O_6(OMe)\{MeC(CH_2O)_3\}_2]^{-}$ (c), $[Mo_4O_{10}\{MeC(CH_2O)_3\}_2]^{2-}$ (d), and $[Mo_4O_8(OEt)_2\{MeC(CH_2O)_3\}_2]$ (e) (from refs 68c and 73).

aggregate to form higher nuclearity clusters, e.g., $[Mo_3O_7(tris)_2]^{2-}$ (Figure 8b),[68] $[Mo_3O_6(OR)(tris)_2]^{-}$ (Figure 8c),[68] $[Mo_4O_8(OR)_2(tris)_2]$ (Figure 8e),[68c,72] and $[Mo_8O_{20}(OMe)_4(tris)_2]^{2-}$.[68d] The sequential synthesis of the di-, tri-, and tetranuclear complexes when R = NO_2,[68c] nicely reflects the structural relationship between these complexes. This series of complexes has been extended by our group to include $[M_4O_{10}(tris)_2]^{2-}$ (Figure 8d), $[Mo_6O_{10}(NO)_2(tris)_4]^{2-}$,[177] $[H_xM'Mo_6O_{18}\{RC(CH_2O)_3\}_2]^{(6-m-x)-}$ ($M'^{m+} = Fe^{3+}, Mn^{3+}, Ni^{2+}, Zn^{2+}$; R = Me, NO_2, NH_2, CH_2OH; x = 0, 2), $[Mo_8O_{18}Cl_4(tris)_2]^{2-}$, $[H_2Mo_8O_{24}(tris)_2]^{4-}$, and $[Mo_{14}O_{36}(tris)_6]^{6-}$.[73a]

The compound $(n\text{-}Bu_4N)_2[Mo_2O_4\{O_2NC(CH_2O)_3\}_2]\cdot 2O_2NC(CH_2OH)_3$ has been prepared by reaction of $(n\text{-}Bu_4N)_2[Mo_2O_7]$ with $O_2NC(CH_2OH)_3$ in methanol,[68c] and the related tungsten compound $(n\text{-}Bu_4N)_2[W_2O_4\{MeC(CH_2O)_3\}_2]$ has been obtained by reaction of $WO_3\cdot H_2O$ with $MeC(CH_2OH)_3$ in the presence of triethylamine and $(n\text{-}Bu_4N)OH$ in refluxing methanol.[73a] An unusual feature of the structure of the

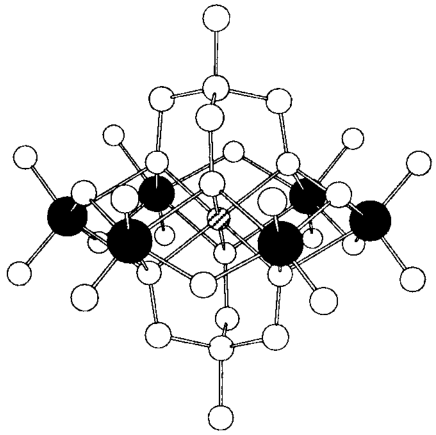


Figure 9. Structure of $[MnMo_6O_{18}\{MeC(CH_2O)_3\}_2]^{3-}$ (ref 73a).

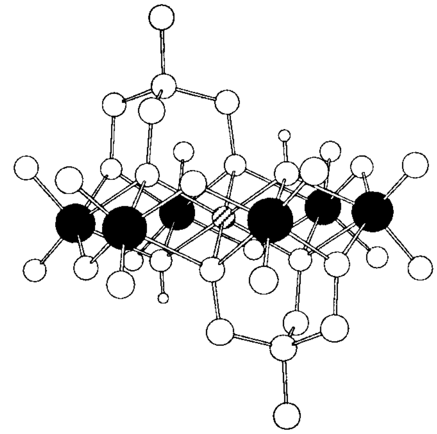


Figure 10. Structure of $[H_2ZnMo_6O_{18}\{MeC(CH_2O)_3\}_2]^{2-}$ (ref 73a).

$[M_2O_4(tris)_2]^{2-}$ anions is the absence of bridging oxo groups (Figure 8a).

The structure of the trinuclear anion $[Mo_3O_7\{MeC(CH_2O)_3\}_2]^{2-}$ displays the central triangular $\{Mo_3(\mu_3\text{-}O)\}$ core (Figure 8b).[68] The unique anti-Lipscomb MoO_3 unit is sufficiently nucleophilic to provide a site for further condensation reactions, which is examplified in the synthesis of $[Mo_3O_6(OMe)\{MeC(CH_2O)_3\}_2]^-$ (Figure 8c) from reaction of $[Mo_3O_7H\{MeC(CH_2O)_3\}_2]^-$ with methanol,[68a] and in the formation of the tetradecanuclear species $[Mo_{14}O_{36}\{MeC(CH_2O)_3\}_6]^{6-}$.[73a]

All the tetranuclear oxotrisalkoxo complexes characterized to date display a compact $\{M_4O_{16}\}$ core with the four M atoms in a single plane. However, they may differ in the coordination mode of the trisalkoxo ligands. While both ligands display the $\mu_4\text{-}\kappa{:}^2\kappa{:}^2\kappa^3$ mode in $[Mo_4O_8(OEt)_2\{MeC(CH_2O)_3\}_2]$ (Figure 8e),[72] $[V_4O_4(H_2O)_2(SO_4)_2\{EtC(CH_2O)_3\}_2]^{2-}$,[74a] $[V_2Mo_2O_8(OMe)_2\{HOCH_2C(CH_2O)_3\}_2]^{2-}$,[74a] and $[V_4O_4(OMe)_6(MeC(CH_2O)_2]$,[75] they display the $\mu_3\text{-}\kappa{:}^1\kappa{:}^1\kappa^3$ coordination mode in the $[M_4O_{10}\{MeC(CH_2O)_3\}_2]^{2-}$ (M = Mo, W) anions (Figure 8d).[73a] A salient feature in the structure of $[V_4O_4(MeC(CH_2O)_3\}_3(OEt)_3]$ is the diversity in the coordination modes of the three alkoxo ligands: $\mu_2\text{-}\kappa{:}^1\kappa{:}^1\kappa^2$, $\mu_4\text{-}\kappa{:}^1\kappa{:}^2\kappa^3$, and $\mu_4\text{-}\kappa{:}^2\kappa{:}^2\kappa^3$.[75] The structure of the mixed-valence cluster $[V_6O_8\{(OCH_2)_3CEt\}_2\{(OCH_2)_2C(CH_2OH)Et\}^{2-}$ is based on a tetranuclear core of edge-sharing octahedra linked via edge sharing to two peripheral vanadium square pyramids.[79d]

Complexes of formula $[H_xM'Mo_6O_{18}\{RC(CH_2O)_3\}_2]^{(6-m-x)-}$ ($M'^{m+} = Fe^{3+}$, Mn^{3+}, Ni^{2+}, Zn^{2+}; R = Me, NO_2, NH_2, CH_2OH; x = 0, 2) have been characterized. All these complexes possess the Anderson structure.[76] The trisalkoxo ligands may either symmetrically cap the central octahedron (Figure 9), or cap two opposite tetrahedral cavities of the oxometalate framework (Figure 10).[73a,b]

The structure of the mixed-valence species $[Mo_8O_{18}Cl_4\{MeC(CH_2O)_3\}_2]^{2-}$,[73a] and that of the fully oxidized complex $[Mo_8O_{20}(OMe)_4\{MeC(CH_2O)_3\}_2]^{2-}$,[68d] can be related to that of the β-$[Mo_8O_{26}]^{4-}$ anion (Figure 5b). The geometry of $[Mo_8O_{18}Cl_4\{MeC(CH_2O)_3\}_2]^{2-}$ is related to that of the hitherto unknown $[Mo_8O_{28}]^{8-}$, which can be derived from β-$[Mo_8O_{26}]^{4-}$ by shearing of the Mo_4 subunits of the latter parallel to one another (Figure 5c).[77] Further shearing would produce the hypothetical $[Mo_8O_{30}]^{12-}$ anion with two corner-linked subunits (Figure 5d), which is the actual geometry of $[Mo_8O_{20}(OMe)_4\{MeC(CH_2O)_3\}_2]^{2-}$.[68d] In contrast, the anion $[H_2Mo_8O_{24}\{MeC(CH_2O)_3\}_2]^{4-}$ may be viewed as composed of two $[Mo_3O_{10}\{MeC(CH_2O)_3\}]^{5-}$ units formally related to $[Mo_3O_7\{MeC(CH_2O)_3\}_2]^{2-}$, linked by two MoO_2^{2+} units.[73a] On the other hand, the anion $[Mo_{14}O_{36}\{MeC(CH_2O)_3\}_6]^{6-}$ may be viewed as the product of the condensation of one $[Mo_8O_{24}\{MeC(CH_2O)_3\}_2]^{6-}$ unit with two $[Mo_3O_7\{MeC(CH_2O)_3\}_2]^{2-}$ units by sharing corners.[73a]

The variety of clusters can be extended by the use of hydrothermal methods. Hydrothermal reactions of $Na_2MoO_4{\cdot}2H_2O$, MoO_3, and Mo with polyalcohols in the presence of Me_3NHCl and Me_4NCl yield two series of mixed-valence clusters, the hexadecanuclear species $[XH_{12}(Mo^{VI}O_3)_4Mo^{V}{}_{12}O_{40}]^{m-}$ ($X = Na^+$, $m = 7$; $X = 2H^+$, $m = 6$), and the superclusters $[XH_nMo^{VI}{}_6Mo^{V}{}_{36}O_{109}\{RC(CH_2O)\}_7]^{m-}$ ($X = Na(H_2O)_3{}^+$, $m = 9$, $n = 13$; $X = Na(H_2O)_3{}^+$, $m = 7$, $n = 15$ (see Figure 69 of Kahn and Zubieta's work, ref 24d); $X = MoO_3$, $m = 9$, $n = 14$; $X = MoO_3$, $m = 10$, $n = 13$). It is noteworthy that the $\{Mo_{16}O_{52}\}$ unit of the hexadecanuclear clusters provides the structural core for the construction of the supercluster frameworks.[78]

Reaction of $(n\text{-}Bu_4N)_3[H_3V_{10}O_{28}]$ with trisalkoxo ligands in acetonitrile yields the hexavanadate clusters $[V_6O_{13}(tris)_2]^{2-}$, which can be next (i) protonated or silylated to give the derivatives $[V_6O_{11}(OR')_2(tris)_2]$, (ii) electrochemically reduced to yield the one-electron reduced products $[V^{IV}V^{V}{}_5O_{13}(tris)_2]^{3-}$, and (iii) chemically reduced with organohydrazines to give the reduced protonated derivatives $[V^{IV}{}_3V^{V}{}_3O_{10}(OH)_3(tris)_2]^{2-}$, $[V^{IV}{}_4V^{V}{}_2O_9(OH)_4(tris)_2]^{2-}$, and $[V^{IV}{}_6O_7(OH)_6(tris)_2]^{2-}$.[79]

The hexametalates of the type $[V^{IV}{}_nV^{V}{}_{6-n}(OH)_nO_{13-n}(tris)_2]^{2-}$ can exist in isomeric cis and trans forms referring to the arrangement of the trisalkoxo groups. While all the species obtained in nonaqueous solvents are trans forms (Figure 11), reduced cis forms, $[V^{IV}{}_6O_7(OH)_6(tris)_2]^{2-}$ and $[V^{IV}V^{V}{}_5O_{13}(tris)_2]^{3-}$

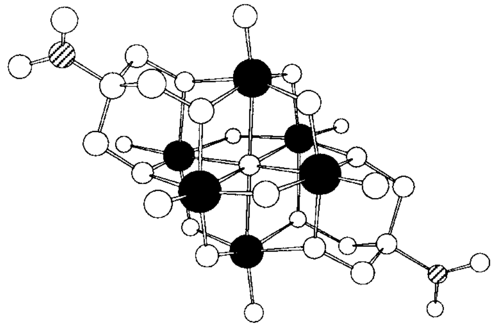


Figure 11. Structure of *trans*-$[V_6O_{13}\{O_2NC(CH_2O)_3\}_2]^{2-}$ (ref 79a).

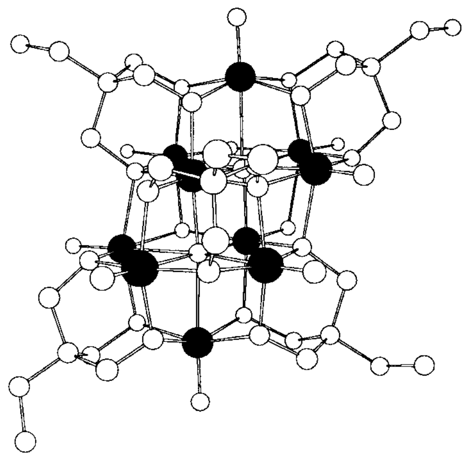


Figure 12. The structure of the $[V_{10}O_{13}\{EtC(CH_2O)_3\}_5]^{-}$ anion (ref 82).

(tris^{3-} = $\{HOCH_2C(CH_2O)_3\}^{3-}$) have been obtained in aqueous medium.[80] Hydrothermal synthesis has been exploited in the preparation of hexavanadium clusters with three and four trisalkoxo groups, e.g., $[V^{IV}_5VO_7(OH)_3(tris)_3]^{-}$, $[V^{IV}_6O_7(OH)_3(tris)_3]^{2-}$, $[V^{IV}_6O_6F(OH)_3(tris)_3]^{-}$, and $[V^{IV}_6O_7(tris)_4]^{2-}$.[32,81] All these clusters retain the $\{V_6O_{19}\}$ structural core. The structural effects of reduction and/or protonation are most apparent in the overall expansion of the cluster. The relative positions of the trisalkoxo ligands, the substituent R of these ligands and the protonation of doubly bridging oxo ligands produce significant effects on the redox properties of the compounds.[79−81]

Fully reduced clusters of general composition $[V_{10}O_{28-3n}(tris)_n]^{x-}$ ($n = 4$, $x = 4$; $n = 5$, $x = 1$, Figure 12), and mixed-valence clusters $[V^{IV}_8V^{V}_2O_{16}(tris)_4]^{2-}$, all based on the decavanadate core $\{V_{10}O_{28}\}$, have been obtained by hydrothermal synthesis.[82] Although six of the 12 tetrahedral cavities associated with the $\{V_{10}O_{28}\}$ core could be conceivably capped with trisalkoxo groups, occupation of the sixth site has not been achieved. A unique neutral polyoxoalkoxovanadium cluster, $[V_{16}O_{20}(tris)_8(H_2O)_4]\cdot 3H_2O$ has also been obtained by hydrothermal synthesis. The $\{V_{16}O_{48}\}$ core is formed by the condensation through four μ_2-oxo groups of two $\{V_8O_{24}\}$ cores, formally generated by the removal of two adjacent $\{VO_2\}$ polar caps from each of two $\{V_{10}O_{28}\}$ clusters (Figure 13).[74b]

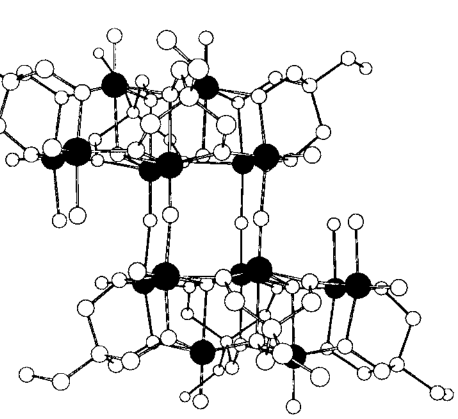


Figure 13. Structure of $[V_{16}O_{20}\{RC(CH_2O)_3\}_8(H_2O)_4]$ (ref 74b).

C. Heavier Group 16 Element-Centered Ligands

1 Thiopolyoxometalates

The differences in the chemistry between oxo- and thiometalates can be largely attributed to facile intramolecular redox processes in thiometalates.[3] Consequently, attempts to isolate polyoxothiometalates from polyoxometalates by oxygen−sulfur exchange have been frequently frustrated by metal center reduction and/or metal−oxygen framework degradation. Replacement of oxygen by sulfur has proved possible only in polyoxometalates that contain labile metal−oxygen subunits, such as $\{MO\}^{3+}$ (M = Nb, Ta), incorporated in substitution-inert polyoxotungstates. Thus, $[W_5M'SO_{18}]^{3-}$ and $[PW_{11}MSO_{39}]^{4-}$ (M′ = Nb, Ta) have been obtained by reacting $[W_5M'O_{19}]^{3-}$ and $[PW_{11}NbO_{40}]^{4-}$ with hexamethyldisilathiane,[83,84] or, with regard to the Keggin derivative, with 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide.[85] The seleno derivatives $[W_5NbSeO_{19}]^{3-}$ and $[PW_{11}M'SeO_{39}]^{4-}$ (M′ = Nb, Ta) have been similarly obtained by reacting the parent oxo compounds with $\{(n\text{-octyl})Me_2\}_2Se$.[84] The increased hydrolytic stability of $[PW_{11}O_{39}ME]^{4-}$ compared to $[W_5O_{18}M'E]^{3-}$ (M′ = Nb, Ta; E = S, Se) has been rationalized by the lower surface charge density of the former.[84]

Another route to polyoxothiometalates has been used by Sécheresse and co-workers[86] who obtained γ-$[XW_{10}M_2S_2O_{38}]^{n-}$ (M = Mo^{V}, W^{V}; X = Si,[86a] $n = 6$; X = P,[86b] $n = 5$) through stereospecific addition of the dication $\{M_2S_2O_2\}^{2+}$ to the corresponding divacant γ-$[XW_{10}O_{36}]^{(n+2)-}$ anion,[87] in DMF. These anions are formed by a γ-XW_{10} unit acting as a tetradentate ligand toward a $\{OM(\mu\text{-}S)_2)MO\}^{2+}$ fragment which has retained the parent structure (Figure 14). The anions $[P_2M_6W_{18}S_6O_{74}(H_2O)_6]^{12-}$ (M = Mo^{V}, W^{V}) have been similarly obtained by reaction of $\{M_2S_2O_2\}^{2+}$ with α-*A*-$[PW_9O_{34}]$.[9−] They consist of two α-$[PW_9O_{34}]^{9-}$ units linked by three $\{M_2O_2S_2(H_2O)_2\}^{2+}$ units.[86c]

2. Organosulfur and Organoselenium Ligands

Phenylsulfinic acid reacts with $(n\text{-}Bu_4N)_2[Mo_2O_7]$ in acetonitrile to yield a mixture of $(n\text{-}Bu_4N)_2[Mo_6O_{19}]$

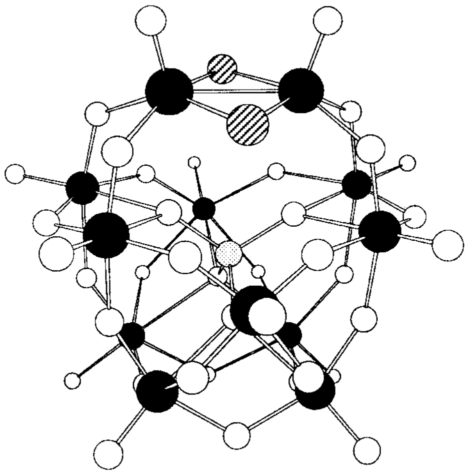


Figure 14. The structure of the γ-$[SiW_{10}Mo_2S_2O_{38}]^{6-}$ anion (ref 86a).

and $(n\text{-}Bu_4N)_2[(PhSO_2)_2Mo_5O_{15}]$.[88] The structure of the anion $[(PhS)_2Mo_5O_{19}]^{2-}$ resembles that of the anions $[S_2Mo_5O_{21}]^{4-}$,[89a] $[P_2Mo_5O_{23}]^{6-}$,[89b] and $[(RP)_2Mo_5O_{21}]^{4-}$.[90] However, it consists of a cyclic arrangement of three $\{MoO_6\}$ octahedra and two $\{MoO_5\}$ polyhedra, whereas the latter anions are formed only of $\{MoO_6\}$ octahedra. The reaction of $PhSeO_2H$ with sodium molybdate in hot water, followed by addition of $(n\text{-}Bu_4N)Cl$ yields $(n\text{-}Bu_4N)_2[(PhSeO_2)Mo_4O_{12}(OH)]$.[88] The structure of the anion $[(PhSeO_2)Mo_4O_{12}(OH)]^{2-}$ (Figure 2c) is similar to that of the anions $[(H_2CO_2)Mo_4O_{12}(OH)]^{3-}$(Figure 2b),[33b] and $[(Me_2AsO_2)Mo_4O_{12}(OH)]^{2-}$ (Figure 2a).[34]

V. Polyoxometalates Incorporating Group 15 Element-Centered Ligands

A. Singly Bonded Nitrogen-Donating Ligands

1. Amine and Related Ligands

A few octamolybdates incorporating singly bonded nitrogen-donating ligands, e.g., pyridine,[77] imidazole,[92] pyrazole,[91] and thiocyanate,[93] have been structurally characterized, and polyoxomolybdate salts $(R_3NH)_4[Mo_8O_{26}(R_3N)_2]$, where R_3N = (+)-cinchonine, (+)-hydroquinidine, or (−)-quinine,[94] are thought to be isostructural with the pyridine derivative. They are representative of a class of derivatized octamolybdates with the $[Mo_8O_{26}X_2]^{(2n+4)-}$ generic formula, where n is the charge of X (Table 4). Their structure may be compared to those of the parent octamolybdates. While the α-$[Mo_8O_{26}]^{4-}$ anion is made up of a six edge-sharing $\{MoO_6\}$ octahedra ring capped above and below by a $\{MoO_4\}$ tetrahedron,[95,96,153] the β-$[Mo_8O_{26}]^{4-}$ anion is built up from eight edge-sharing $\{MoO_6\}$ octahedra (Figure 5b).[96] Recently, the γ-$[Mo_8O_{26}]^{4-}$anion, which was postulated to be an intermediate in the α−β interconversion,[95c] has been characterized in $[Me_3N(CH_2)_6NMe_3]_2[Mo_8O_{26}]\cdot 2H_2O$ and found to consist of six $\{MoO_6\}$ octahedra interlinked along edges and two $\{MoO_5\}$ trigonal bipyramids, each sharing two edges with the octahedra.[97] Since then, the δ-isomer which has an approximate α−γ or β−γ intermediate structure has been reported,[98] and the ϵ-isomer, which consists of six $\{MoO_5\}$ square pyramids and two $\{MoO_6\}$ octahedra,[99] have been reported. The $[Mo_8O_{26}X_2]^{(2n+4)-}$ anions display structures which are reminiscent of the γ-type but with two additional terminal positions. Two linkage isomers have been observed (Figure 15). The stereochemical positions of the groups X are the same in $[Mo_8O_{26}X_2]^{4-}$ (X = pyridine [77] imidazole,[92] pyrazole [92]), $[Mo_8O_{26}X_2]^{6-}$ (X = NCS,[93] HCO_2,[100]),

Table 4. Octanuclear Complexes Deriving from the Assembly of Two Compact Tetranuclear Subunits

parent structure	derivative	ref
β-$[Mo_8O_{26}]^{4-}$		96
$[Mo_8O_{28}]^{8-\ a}$	$[Mo_8O_{26}(py)_2]^{4-}$	77
	$[Mo_8O_{26}(R_3N)_2]^{4-}$ (R_3N = (+)-cinchonine, (+)-hydroquinidine, (−)-quinine)	94
	$[Mo_8O_{26}(imH)_2]^{4-}$	92
	$[Mo_8O_{26}(pzH)_2]^{4-}$	91
	$[Mo_8O_{26}(NCS)_2]^{6-}$	93
	$[Mo_8O_{26}(lysH_2)_2]^{2-}$	101b
	$[Mo_8O_{26}(HCO_2)_2]^{6-}$	100
	$[Mo_8O_{24}(OH)_2(metO)_2]^{4-}$	102
	$[Mo_8O_{22}(OH)_4\{OC_6H_4CH{=}NPr\text{-}n)\}_2]^{2-}$	102
	$[Mo_8O_{24}(OMe)_4]^{4-}$	65a
	$[Mo_8O_{18}Cl_4\{MeC(CH_2O)_3\}_2]^{2-}$	73
	$[Mo_8O_{22}(NO)_2(acac)_2]^{4-}$	177
	$[Mo_8O_{16}(OMe)_6(NNMePh)_6]^{2-}$	148
$[Mo_8O_{30}]^{12-\ a}$	$[Mo_8O_{20}(OMe)_4\{MeC(CH_2O)_3\}_2]^{2-}$	68d

[a] Unknown in that form.

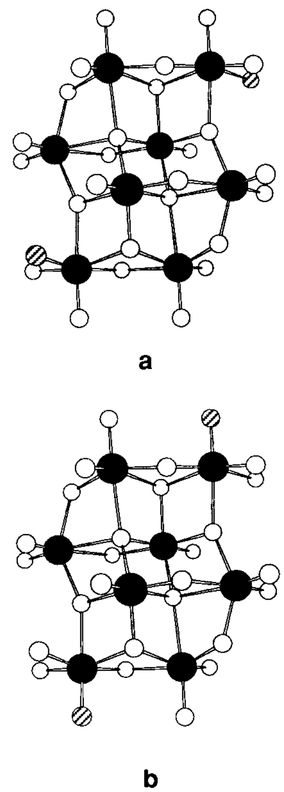


Figure 15. The different stereochemical positions of the ligands X in $[Mo_8O_{26}X_2]^{(2n+4)-}$ (ref 77).

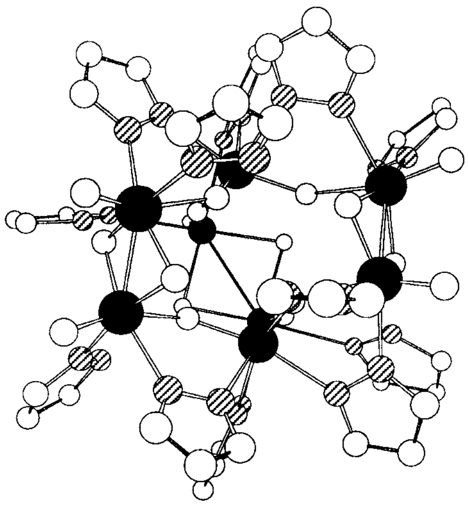


Figure 16. Structure of $[Mo_8(pz)_6O_{18}(pzH)_6]$ (ref 104).

$[Mo_8O_{26}(OH)_2]^{6-}$,[101a] $[Mo_8O_{26}X_2]^{2-}$ (X = D- or L-lysH_2),[101b] $[Mo_8O_{24}(OH)_2(metO)_2]^{4-}$, and $[Mo_8O_{22}(OH)_4X_2]^{2-}$ (X = *N*-propylsalicylideneiminate)[102] but are different from those found in $[Mo_8O_{24}(OMe)_4]^{4-}$ [65a] and $[Mo_8O_{26}(MoO_4)_2]^{8-}$.[103]

Two octamolybdenum clusters, $[Mo_8(pz)_6O_{21}(pzH)_6]$ and $[Mo_8(pz)_6O_{18}(pzH)_6]$, containing both bridging pyrazolate and terminal pyrazole ligands, have been prepared by the reaction of molten pyrazole with molybdenum oxides.[104] The first one possesses a skeleton of corner-linked MoX_6 octahedra (where X = O or N), which results in a rather open structure. The second one contains two Mo(VI) centers and three dimeric Mo(V) units (Figure 16). From an empirical bond length−bond strength correlation based on the valence-bond formalism, it is apparent that the Mo−N bonds are generally weak, with bond orders less than 0.5.[104]

The tetranuclear compound, $[Mo_4O_{12}(C_{12}H_{30}N_4S_2)_2]\cdot$DMF, has been obtained upon recrystallization of $[Mo_2O_5(Me_2NCH_2CH_2NHCH_2CH_2S)_2]$ in DMF. Its structure consists of a cyclic Mo_4O_{12} core with the two pairs of diagonal molybdenum atoms linked by NNNN donors.[105]

2. Amide Oximes

Although a very few complexes of amide oximes had been reported in the early literature,[106] these ligands now appear to have unique complexing properties. They can ligate either as neutral RC(NH$_2$)NOH, zwitterionic RC(NH$_2$)NHO, RC(NH$_2$)NO$^-$, RC(NH)NHO$^-$, or RC(NH)NO^{2-} species. They display a range of coordination modes (Table 5).[107] They present unusual acid−base features such as the presence of both the neutral zwitterionic and anionic forms of the ligand in the same species.[107,108] In addition, they can act as nitrosylating reagents,[110] and they can transform into amides or amidines, which further increases the diversity of products. The coordination chemistry of amide oximes with oxomolybdenum compounds offers a unique illustration of the versatile behavior of these ligands. They stabilize various oxomolybdenum cores, such as the compact $\{Mo_4O_{10}(OMe)_2\}^{2+}$ core, the cyclic $\{Mo_4O_{12}\}$ core, and the open $\{Mo_nO_{3n-1}\}^{2+}$ (n = 2 and 4) and $\{Mo_5O_{12}(NO)_2\}^{2+}$ cores.

Acetamide oxime reacts with $(n\text{-}Bu_4N)_4[\alpha\text{-}Mo_8O_{26}]$ in methanol to yield the tetranuclear species $(n\text{-}Bu_4N)_2[Mo_4O_{12}\{MeC(NH_2)NO\}_2]\cdot 2MeOH$.[111a] The tungsten analogue is similarly obtained from $(n\text{-}Bu_4N)_2[W_6O_{19}]$.[111a] Most of the amide oximes react in the same way and a number of compounds of the type $(NBu_4)_2[Mo_4O_{12}\{RC(NH_2)NO\}_2]$ have been obtained.[14,107,112] However, the tungsten series is still restricted to the above example. In several cases, the molybdenum complexes have been obtained by reaction of $[MoO_2(acac)_2]$ with the appropriate amide oxime in methanol or acetonitrile and isolated as amide oximium or amidinium salts.[107,110] $[MeC(NH_2)_2]_2[Mo_4O_{12}\{MeC(NH_2)NO\}_2]$ has also been obtained through the deoxygenation of acetamide oxime by $[Mo_2(MeCO_2)_4]$.[111b] Reaction of acetone oxime with $(n\text{-}Bu_4N)_4[\alpha\text{-}Mo_8O_{26}]$ in refluxing methanol yields $(n\text{-}Bu_4N)_2[Mo_4O_{12}(Me_2CNO)_2]$ while that with $[MoO_2(acac)_2]$ at room temperature results in the formation of $[Mo_4O_{10}(OMe)_4(Me_2CNO)_2]$.[113a] The reaction of acetone oxime with various oxomolybdenum complexes in alcohols, under reflux, leads to the formation of nitrosyl complexes.[113b]

The anions $[M_4O_{12}\{RC(Z)NO\}_2]^{2-}$ (Z = NH$_2$, Me) display a cyclic $[(MO_2)_4(\mu\text{-}O)_4]$ core capped by either two amide oximate or oximate (Figure 2g) ligands.[111,113a] In all cases, the coordination of the capping ligands involve both the nitrogen and oxygen atoms of the oximate group, but the metal−nitrogen interaction displays some flexibility. Indeed, while the acetone oximate ligand is linked in a μ_4-$\kappa^2 N$:$\kappa^2 O$ mode,[113a] the coordination mode of the acetamide oximate ligand is halfway between the μ_4-$\kappa^2 N$:$\kappa^2 O$ and the μ_3-κN:$\kappa^2 O$ modes.[111] Significant variations in the location of the capping ligand relative to the cyclic $[(MO_2)_4(\mu\text{-}O)_4]$ core have been observed for the $[Mo_4O_{12}\{MeC(NH_2)NO\}_2]^{2-}$ in different compounds and can be ascribed to packing effects.[111b] The specific coordination mode also depends on the substituent R. While $[MeC(NH_2)NHOH]_2[Mo_4O_{12}\{MeC(NH_2)NO\}_2]$ displays nearly symmetrical two-electron-three-center Mo−N−Mo bonds,[111a] the Mo−N interaction is best described as a 2e−2c Mo−N bond in $(n\text{-}Bu_4N)_2[Mo_4O_{12}\{N{\equiv}C{-}CH{=}CH{-}C(NH_2)NO\}_2]$.[112c]

The cyclic $[(MO_2)_4(\mu\text{-}O)_4]$ core is rather common in molybdenum chemistry (Figure 2, Table 6). However, the type of junction of the coordination polyhedra depends on the bridging capacity of the capping ligands. A cyclic assembly of alternately face- and corner-sharing octahedra is displayed by the anions $[M_4O_{12}\{RC(Z)NO\}_2]^{2-}$ (Z = NH$_2$, Me) when the capping ligands are linked in the μ_4-$\kappa^2 N$:$\kappa^2 O$ mode, while that of four edge-sharing octahedra is displayed by the peroxo species $[Mo_4O_{12}(O_2)_2]^{4-}$.[53] On the other hand, the structures of $[(H_2CO_2)Mo_4O_{12}(OH)]^{3-}$,[33b] and $[(R_2AsO_2)Mo_4O_{12}(OH)]^{2-}$,[34] can be described as two pairs of face-sharing octahedra, fused by corner-sharing, while in $[Mo_4O_{12}(C_{12}H_{30}N_4S_2)_2]$,[105] the four octahedra are connected only by corners. The cyclic M_4O_{12} ring also occurs in polyoxovanadate chemistry, e.g., in metavanadate and metavanadate-supported organometallic complexes (section VII.C.2.d).

Table 5. Coordination Modes of Amidoximes and Oximes in Polyoxometalate Complexes

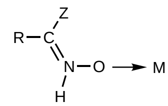
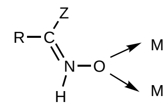
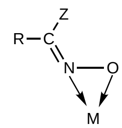
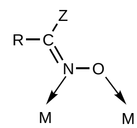
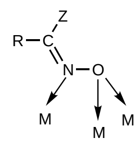
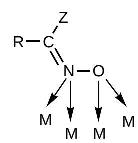
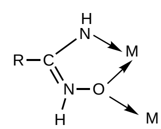
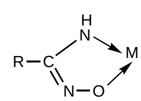
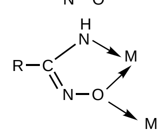
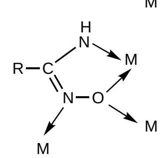
protonation state	coordination mode		ref
zwitterionic form, RC(Z)NHO, Z = NH_2 or Me		*κO*	113a
		*μ-κ²O*	107,108
singly deprotonated form, $RC(Z)NO^-$, Z = NH_2 or Me		*κ²N,O*	113b
		*μ-κN:κO*	113b
		*μ₃-κN:κ²O*	113b
		*μ₄-κ²N:κ²O*	111,113a
singly deprotonated form, $RC(NH)NHO^-$, Z = NH_2 or Me		*μ-κN′:κ²O*	107, 108
doubly deprotonated form, $RC(NH)NO^{2-}$, Z = NH_2 or Me		*κ²N′,O*	107
		*μ-κN′:κ²O*	107,108
		*μ₃-κN:κN′:κ²O*	109

Table 6. Tetranuclear Complexes Containing the Cyclic [{MoO_2)(*μ*-O)}$_4$] Core

complex	structure	ref
$[Mo_4O_{12}(C_{12}H_{30}N_4S_2)_2]$	*a*	105
$[Mo_4O_{12}(O_2)_2]^{4-}$	*b*	53
$[Mo_4O_{12}\{RC(NH_2)NO\}_2]^{2-}$	*c*	111
$[Mo_4O_{12}(Me_2CNO)_2]_2]^{2-}$	*c*	113a
$[Mo_4O_{12}(H_2CO_2)(OH)]^{3-}$	*d*	33b
$[Mo_4O_{12}(Me_2AsO_2)(OH)]^{2-}$	*d*	34
$[Mo_4O_{12}F_3]^{3-}$	*d*	35a

[a] Corner-sharing octahedra. [b] Edge-sharing octahedra. [c] Alternately face- and corner-sharing octahedra. [d] Two pairs of face-sharing octahedra fused by corner sharing.

Oximes and amide oximes also form compact tetranuclear complexes, as shown by $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$[113a] and $[Mo_4O_{10}(OMe)_2\{RC(NH)NO\}_2]^{2-}$,[107] where R = 2-thienyl. The former derives formally from $[Mo_4O_{10}(OMe)_6]^{2-}$ by replacement of the two terminal methoxo groups by zwitterionic acetone oxime ligands. The structure of the latter is closely related to those of the catecholate and benzohydroximate derivatives, $[Mo_4O_{10}(OMe)_2(OC_6H_4O)_2]^{2-}$ [41b] and $[Mo_4O_{10}(OMe)_2(C_6H_5CONO)_2]^{2-}$.[112a]

In addition, amide oximes are effective in stabilizing $\{Mo_nO_{3n-1}\}^{2+}$ cores. Three complexes containing the $\{Mo_2O_5\}^{2+}$ core, $[Mo_2O_5\{PhC(NH)NHO\}_2]$,[108] $[Mo_2O_5\{RC(NH)NHO\}\{RC(NH)NO\}]^-$, and $[Mo_2O_5\{RC(NH)NO\}_2]^{2-}$ (R = 2-thienyl),[107,112b] have been characterized by X-ray crystallography. The flexibility of the dinuclear core is reflected in the fact that the two ligands display different coordination modes, i.e., *κ²-N′,O* and *μ-κN′:κ²O* in $[Mo_2O_5\{PhC(NH)NHO\}_2]$, while both ligands display the *μ-κN′:κ²O* coordination mode in $[Mo_2O_5\{RC(NH)NHO\}$-

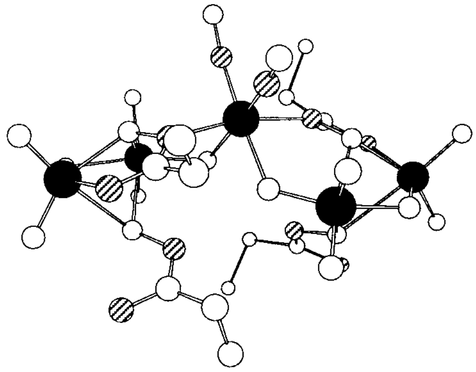


Figure 17. Structure of $[Mo_5O_{12}(NO)_2\{EtC(NH)NO\}_2\{EtC(NH_2NO\}_2]^{2-}$ (ref 109).

$\{RC(NH)NO\}]^-$ and the κ^2-*N′*,*O* coordination mode in $[Mo_2O_5\{RC(NH)NO\}_2]^{2-}$ (R = 2-thienyl).[107]

Dinuclear units appear as transferable building blocks in compounds with extended open cores. Indeed, the structure of $[Mo_4O_{11}\{RC(NH_2)NHO\}_2\{RC(NH)NHO)\{RC(NH)NO\}]^-$ is composed of two closely related dinuclear units, $Mo_2O_5\{RC(NH_2)NHO\}\{RC(NH)NO\}$ and $Mo_2O_5\{RC(NH_2)NHO\}\{RC(NH)NO\}^+$, linked by one bridging oxo ligand. Both zwitterionic ligands display the μ-κ^2O coordination mode while both (1−) and (2−) ligands exhibit the μ-$\kappa N'$:κ^2O coordination mode.[108] The structure of the complexes $[M_5O_{12}(NO)_2\{RC(NH)NO\}_2\{RC(NH_2)NHO\}_2]^{2-}$ (M = Mo, W) may be viewed in terms of an open $\{M_5O_{12}(NO)_2\}^{2+}$ core which derives from the parent $\{M_5O_{14}\}^{2+}$ core by replacing the terminal oxo groups of the central atom by nitrosyl ligands. Each of the two $[M_2O_5\{RC(NH)NO\}\{RC(NH_2)NHO\}]$ units is linked to the $\{Mo^0(NO)_2\}^{2+}$ unit by its hydroxylamino nitrogen atom and by an additional bridging oxo ligand (Figure 17).

B. Multiply Bonded Nitrogen Ligands

1. Nitrido Derivatives

Nitrido complexes of transition metals have been reviewed by Dehnicke and Strähle[114] and by Nugent and Mayer.[115] Despite the isolobal analogy between the oxo and nitrido ligands, there is a single report of a nitridopolyoxometalate, viz., $[Mo_6O_{18}N]^{3-}$.[116] However, a nitrido−technetium-substituted phosphotungstate has been reported.[117] Although obviously not being a polyoxometalate, the poly(amido imido) nitride $[Zr_5N(NH)_4(NH_2)_4(OR)_5]$,[118] is noteworthy in that its framework is the same as that of defect Lindqvist-type complexes, e.g., $[W_5O_{18}]^{6-}$ [119] and $[Mo_5O_{13}(OR)_4(NO)]^{3-}$.[14] Also the cubane nitride cluster $[\{Cp^*V(\mu_3\text{-}N)\}_4]$ deserves to be mentioned since it displays a structure which is common for organometallic oxides.[120] The current status of this field of nitridopolyoxometalates probably reflects the lack of convenient synthetic methods rather than some intrinsic hindrance to its development. It is expected that the interest in catalytic activity of nitrido complexes and the search for preceramic materials will provide impetus to the chemistry of nitrido derivatives of polyoxometalates.

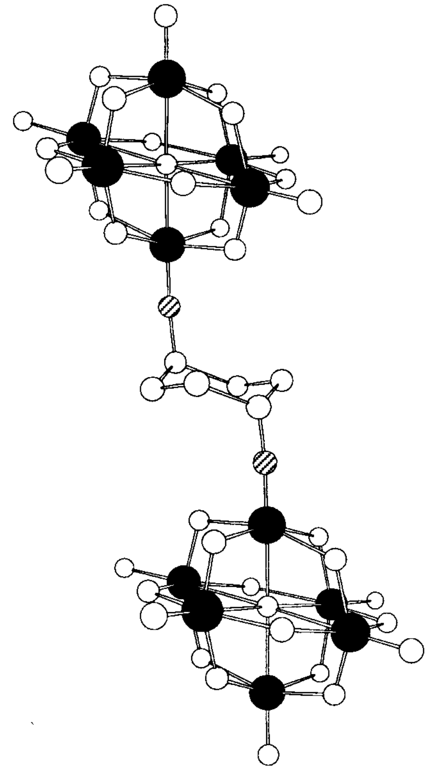


Figure 18. The structure of the $[(Mo_5O_{18})MoN(1,4\text{-}c\text{-}C_6H_{10})NMo(Mo_5O_{18})]^{4-}$ anion (ref 15).

2. Organoimido Derivatives

Transition metal imido chemistry has experienced a remarkable growth in recent years.[121] Although oxo−imido complexes of early transition metals have been known for some time, imido derivatives of polyoxometalates have only been characterized very recently. A fairly large number of imido derivatives of $[Mo_6O_{19}]^{2-}$ have now been synthesized.[15−17,116,122−126] Imido derivatives of polyoxomolybdates can be obtained in several ways: (i) imido metathesis via Wittig-like (net) [2 + 2] exchange reactions of Mo═O bonds with isocyanates,[15,17,123,124] phosphinimines,[122,125a] or sufinylamines;[125b] (ii) α-hydrogen transfer reactions with amines;[126] and (iii) the displacement of labile ligands from a imido-containing precursor by oxometalates, followed by aggregation.[116] The most significant achievement is the bridging of two hexametalate cages by a diimido ligand (Figure 18).[15] A unique example of organoimido hexatungstate has been reported.[127]

The X-ray crystal structures of several compounds of the type $(n\text{-}Bu_4N)_2[Mo_6O_{18}(NR)]$ have been determined (R = *p*-Tol;[122] R = *t*-Bu;[124,126a] R = *o*-Tol, (*i*-Pr)$_2$-2,6-C_6H_3, and Cy;[124] R = Fc;[123] R = Ph;[125a] R = (O_2N)-*p*-C_6H_4[125b]). The structure of the anions $[Mo_6O_{18}(NR)]^{2-}$ resembles that of their $[Mo_6O_{19}]^{2-}$ parent, but the internal Mo−O bond trans to the imido ligand is substantially shorter than those trans to a terminal oxo ligand. The Mo−N bond lengths are consistent with linear linkages although the Mo−N−C angles depart from linearity more than expected.

Electrochemical data and ^{95}Mo, ^{17}O, and ^{14}N NMR data have been recorded for a range of $[Mo_6O_{18}(NR)]^{2-}$ complexes.[124,125] The following trends have been

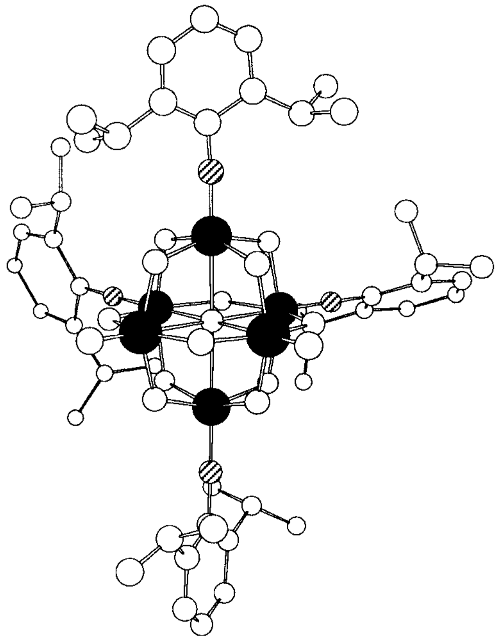


Figure 19. The structure of the $[Mo_6O_{15}(NAr)_4]^{2-}$ anion (Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$) (ref 17).

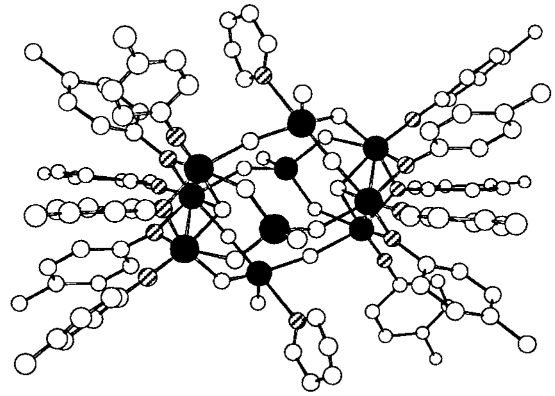


Figure 20. Structure of $[Mo_{10}(N\text{-}p\text{-}Tol)_{12}(py)_2O_{18}]$ (ref 130).

observed: (i) All species display a one-electron reduction process, the potential of which undergoes a cathodic shift in the order O < NAr < NR and, for arylimido complexes of the type $[Mo_6O_{18}(NC_6H_4\text{-}p\text{-}Z)]^{2-}$, in the order of increasing electron-donating properties of the substituent Z. (ii) The *Mo*=N resonance is shifted upfield in the order O < NAr < NR, and in the series of arylimido complexes, in the order of increasing electron-attracting properties of the substituent. (iii) The ^{17}O NMR spectrum of any imido complex is globally shielded with respect to that of $[Mo_6O_{19}]^{2-}$. These data are consistent with the trend in π-donor ability of the ligands, O < NAr < NR. For arylimido derivatives, molybdenum and nitrogen shieldings increase with increase in the ($\sigma + \pi$) acceptor ability of the substituent, which is in agreement with the trends observed in the series of mononuclear complexes $[WCl_4(NC_6H_4\text{-}p\text{-}Z)]$,[128] and $[VCl_3(NC_6H_4\text{-}p\text{-}Z)]$.[129]

A characteristic feature of the derivatization of polyoxomolybdates with organoimido ligands is the capacity for polyfunctionalization.[17,124,125a] Derivatives of the type $[Mo_6O_{19-x}(NAr)_x]$,$^{2-}$ with $x \leq 6$, have been characterized ($x = 4$, Figure 19).[17,124a] The substitution pattern (*cis*-bis, *fac*-tris, *cis*-tetrakis) is counter to steric expectations. The formation of the bis-imido derivative even when only one equivalent of Ph$_3$P=NPh is used means either that $[Mo_6O_{18}(NPh)]^{2-}$ is less stable than $[Mo_6O_{17}(NPh)_2]^{2-}$, which seems rather unlikely, or that the former is more reactive than $[Mo_6O_{19}]^{2-}$ and reacts competitively with it. The separation of the successive derivatives may be difficult, which is best illustrated by the cocrystallization of $(n\text{-}Bu_4N)_2[Mo_6O_{19}]$, $(n\text{-}Bu_4N)_2[Mo_6O_{18}(NPh)]$, and $(n\text{-}Bu_4N)_2[Mo_6O_{17}(NPh)_2]$.[125a]

The reaction of *p*-tolyl isocyanate with $(n\text{-}Bu_4N)_3[\alpha\text{-}PMo_{12}O_{40}]$ in pyridine yields a mixture of products, among which are the highly functionalized neutral species $[Mo_{10}(Ntol)_{12}(py)_2O_{18}]$ (Figure 20), *p*-Tol-N=NTol-*p*, and reduced derivatives of $\alpha\text{-}[PMo_{12}O_{40}]^{3-}$.[130] The decamolybdenum complex can be viewed as composed of two $\{Mo_3O_7(Ntol)_6\}$ groups similar to the structurally characterized discrete tritungstate $[W_3(N\text{-}t\text{-}Bu)_3(NPh)_3Cl_7]^-$,[131] linked by four extra molybdenum units. These groups are made of three edge-sharing distorted octahedra and are reminiscent of the $\{Mo_3O_{13}\}$ building blocks of the $\alpha\text{-}[PMo_{12}O_{40}]^{3-}$ Keggin anion.

The reaction of $(n\text{-}Bu_4N)_4[H_3PW_{11}O_{39}]$ with $[W(N\text{-}Tol\text{-}p)Cl_4]_2$ in 1,2-dichloroethane yields a mixture of $(n\text{-}Bu_4N)[W(NTol\text{-}p)Cl_5]$ and $(n\text{-}Bu_4N)((p\text{-}TolNH_3)[W_2OCl_8(NTol\text{-}p)]$ which both react with H$_2$O to give $(n\text{-}Bu_4N)_2[W_4O_4(NTol\text{-}p)_4Cl_{10}]$.[132] A related compound, $(Ph_3BzP)_2[W_4O_4(N\text{-}t\text{-}Bu)_4Cl_{10}]$, has been obtained by reacting $[WOCl_4]$ with *t*-BuNH$_2$ in the presence of (Ph$_3$BzP)Cl.[40] The distorted tetrahedron of four tungsten atoms is bridged across two opposite edges by chlorine atoms and across the remaining edges by oxygen atoms.[40]

3. Hydrazido and Diazenido Derivatives of Polyoxometalates

a. General Considerations. Organodiazenido and organohydrazido transition metal complexes have been extensively studied largely because the NNR and NNRR′ ligands are of interest as potential models of NNH and NNH$_2$ respectively, which are intermediates in the chemical and enzymatic conversion of coordinated dinitrogen into ammonia.[133−135] They have been synthesized through a variety of processes, including alkylation of dinitrogen and organodiazenido complexes, reactions of diazonium salts with metal carbonyls, reactions of substituted hydrazines or their trimethylsilyl derivatives with metal halides, and condensation-type reactions of organohydrazines with oxometal complexes, notably oxomolybdenum complexes and polyoxomolybdates.[133−138]

Reactions of organohydrazines with oxomolybdenum complexes of the type $[MoO_2L_2]$ have been found to depend upon (i) the basicity of the hydrazine which may be used as RR′NNH$_3$X, as RR′NNH$_2$ with or without an additional base, e.g., NEt$_3$, (ii) the ancillary ligand L, thus the redox characteristics of the complex, and (iii) the electronic count of the metal center. The versatility of this synthetic route is best illustrated by the reactions of organohydrazines with $[MoO_2(acac)_2]$. With disubstituted hydrazines, RR′N-NH$_2$, mononuclear bis(hydrazido) complexes,[139a] mononuclear and dinuclear oxo(hydrazido) complexes,[139b,c] and mononuclear complexes containing both hydrazido(1−) and hydrazido(2−) ligands[139d] have been obtained depending on the solvent, the temperature and the hydrazine. With monosubstituted hydrazines, $ArNHNH_2$, mononuclear bis(diazenido) complexes,[140a] dinuclear complexes,[140b,c,d] and tetranuclear complexes[140c] have been obtained depending on Ar, the solvent, and the excess of hydrazine.

The reactions of substituted hydrazines with oxomolybdenum complexes presumably involve initial coordination of the hydrazine followed by proton transfer to the oxo group.[141] In this way, the reactions of $[MoO_2L_2]$ with $RR'NNH_2$ can yield either $[MoO(NNRR')L_2]$ or $[M(NNRR')_2L_2]$. The terminal hydrazido ligand is formally isoelectronic with the terminal imido ligand and with the terminal oxo ligand, and there are many examples of essentially isostructural metal−oxo and metal−hydrazido complexes. In the $\{MoO(NNRR')\}^{2+}$ and $\{Mo(NNRR')_2\}^{2+}$ units, as well as in the $\{MoO_2\}^{2+}$ unit, the cis arrangement is invariably observed as it allows to maximize π-bonding interactions between the Mo center and the strongly π-donating oxo and hydrazido ligands. ^{95}Mo NMR data on hydrazido complexes of polyoxomolybdates are fully consistent with Mo(VI) centers.[142] However, the internal geometry of the RR′NN units in most hydrazido(2−) complexes supports the current view that these ligands are described more accurately as neutral isodiazene than as hydrazido(2−).[143,144] The bis(hydrazido) complexes $[Mo(NNHAr)_2L_2]$ that would be expected from the reaction of $[Mo^{VI}O_2L_2]$, with monosubstituted hydrazines $ArNHNH_2$ have not been isolated. Instead complexes $[Mo(NHNHAr)(NNAr)L_2]$ which undergo aerobic oxidation to $[Mo(NNAr)_2)L_2]$ have been characterized.[145] The *cis*-$\{Mo(NNAr)_2\}^{2+}$ exhibits structural characteristic similar to those of the *cis*-$\{MoO_2\}^{2+}$ and *cis*-$\{Mo(NNRR')_2\}^{2+}$ units. In some cases complexes containing a $\{Mo(NNAr)\}^{3+}$ unit, e.g., $[Mo(NNAr)(dtc)_3]$[146] or $[Mo_6O_{18}(NNAr)]^{3-}$,[142,147] have been isolated. In both $\{Mo(NNAr)\}^{3+}$ and $\{Mo(NNAr)_2\}^{2+}$ units, the short Mo−N and N−N distances, and the linearity of the Mo−N−N linkages, suggest extensive delocalization and significant multiple bond character thoughout the MoNNAr units. In this coordination mode, diazenido ligands are commonly considered as RNN^+ species.[136] According to this formalism, $\{Mo(NNAr)\}^{3+}$ and $\{Mo(NNAr)_2\}^{2+}$ units would contain Mo(II) and Mo(0) centers, respectively.

b. Organohydrazido Derivatives. Only a few organohydrazido complexes of polyoxomolybdates have been characterized.[148−150] Reaction of $(n\text{-}Bu_4N)_2[Mo_2O_7]$ or $(n\text{-}Bu_4N)_4[Mo_8O_{26}]$ with $RR'NNH_2$ in dry methanol/CH_2Cl_2 solution yields $(n\text{-}Bu_4N)_2[Mo_4O_{10}(OMe)_2(NNRR')_2]$.[148,149] The structure of the tetranuclear species $[Mo_4O_{10}(OMe)_2(NNRR')_2]^{2-}$ (R = R′ = Ph;[148] R = Ph, R′ = Me[149]) consists of a dinuclear unit of edge-sharing octahedra bridged by two MoO_4^{2-} tetrahedra (Figure 21a). The reaction of $(n\text{-}Bu_4N)_2[Mo_2O_7]$ with 1-hydrazinophthalazine yields the analogous tetranuclear species $(n\text{-}Bu_4N)_2[Mo_4O_{12}(C_8H_6N_4)]$.[149] The structure of $[Mo_4O_{12}(C_8H_6N_4]^{2-}$

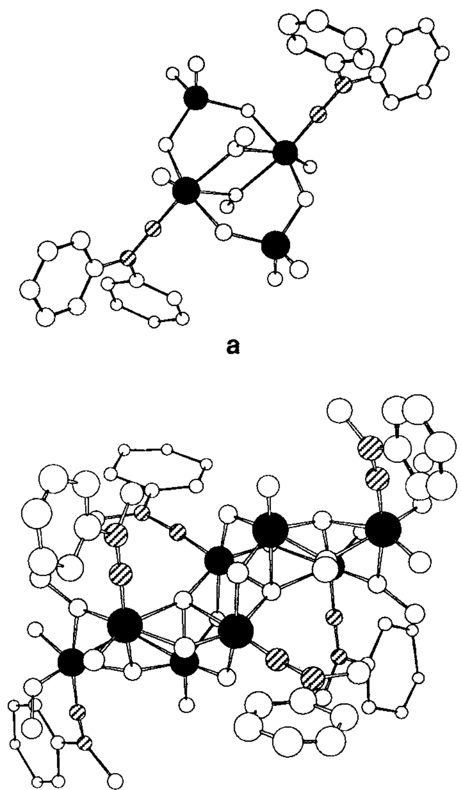
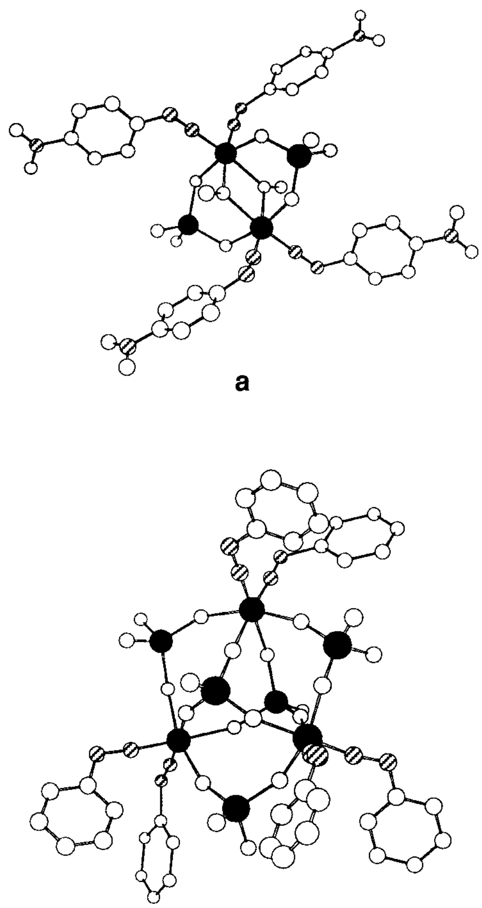


Figure 21. Structures of two hydrazido derivatives: (a) $[Mo_4O_{10}(OMe)_2(NNPh_2)_2]^{2-}$, and (b) $[Mo_8O_{16}(OMe)_6(NNMePh)_6]^{2-}$ (ref 148).

consists of a planar $\{Mo_2O_4(C_8H_6N_4)\}^{2+}$ core bridged by two MoO_4^{2-} units. Although the nitrogen-bound hydrogen could not be located, the bidentate bridging phthalazine moiety is best described as a doubly deprotonated hydrazido ligand, $(C_8H_5)NHN(2-)$. A related tetramolybdate $[Mo_4O_{11}(C_8H_6N_6)]^{2-}$, containing the quadruply deprotonated form of 1,4-dihydrazinophthalazine, has been reported.[150] The structure of the octanuclear species, $[Mo_8O_{16}(OMe)_6(NNMePh)_6]^{2-}$ (Figure 21b), formed by hydrolysis of $[Mo_4O_{10}(OMe)_2(NNMePh)_2]^{2-}$, is related to that of derivatives of the type $[Mo_8O_{26}X_2]^{(2n+4)-}$.[148] The structure of the hexamolybdate $[Mo_6O_{18}(NNMePh)]^{2-}$ resembles that of $[Mo_6O_{19}]^{2-}$ with one terminal oxo ligand replaced by the hydrazido(2−) ligand.[116]

c. Organodiazenido Derivatives. Dinuclear, tetranuclear, and octanuclear species containg *cis*-$[Mo(NNAr)_2]^{2+}$ units have been reported. The dinuclear[140b−d] and tetranuclear[140c,151−153] complexes contain the $[\{Mo(N_2Ar)_2(\mu\text{-}OR)\}_2]^{2+}$ core, in which the molybdenum atom is ligated to two bridging alkoxo and two terminal aryldiazenido ligands. It achieves six coordination either with a bidentate ligand as in $[\{Mo(N_2Ph)_2(acac)(\mu\text{-}OR)\}_2]$,[140b,c] or with two unidentate ligands as in $[\{Mo(N_2Ph)_2(NH_2NHPh)(OR)(\mu\text{-}OR)\}_2]$.[140d] In the first case, the geometry around the molybdenum center is imposed by the chelate ring. In the second case, two different geometries are conceivable according to whether the unidentate ligands are cis or trans. However, only the latter has ever been found. Another kind of isomerism arises from the orientation of the diazenido ligands. Two diastereoisomers of $[\{Mo(N_2Ph)_2(acac)(\mu\text{-}OR)\}_2]$ have


a

b

Figure 22. Structures of two diazenido derivatives (a) $[Mo_4O_8(OMe)_2(NNC_6H_4\text{-}p\text{-}NO_2)_4]^{2-}$ and (b) $[Mo_8O_{20}(NNC_6H_5)_6]^{4-}$ (ref 153).

been characterized by X-ray crystallography; they interconvert by syn−anti isomerization at the outer nitrogen atom of one of the two phenyldiazenido ligands.[140b]

Although the tetranuclear species $[Mo_4O_8(OR)_2(NNAr)_4]^{2-}$ have been occasionally obtained from mononuclear dioxomolybdenum complexes,[140c,151] they are more conveniently prepared by reaction of $(n\text{-}Bu_4N)_4[\alpha\text{-}Mo_8O_{26}]$ with arylhydrazines in alcohols.[152,153] A related tetranuclear species containing a single *cis*-$Mo(NNAr)_2{}^{2+}$ unit has been obtained by reaction of $[Mo_4O_{10}(OMe)_2(NNPh_2)_2]^{2-}$ with excess phenylhydrazine in methanol,[153,154] and tetranuclear complexes $[Mo_4O_6(OMe)_2(XC_6H_4Y)_2(NNAr)_4]^{2-}$ (X = Y = O; X = O, Y = NH) have been obtained by reaction of the parent oxo compounds $[Mo_4O_{10}(OMe)_2(XC_6H_4Y)_2]^{2-}$ with $PhNHNH_2$.[41b] A comparison of the structural features of $[\{Mo(NNAr)_2(\mu\text{-}OR)(\mu\text{-}MoO_4)\}_2]^{2-}$ (R = Me, Ar = $O_2N\text{-}p\text{-}C_6H_4$, Figure 22a) and $[Mo_4O_6(OMe)_2(XC_6H_4Y)_2(NNAr)_4]^{2-}$ reveals that the $\{Mo_4O_4\}$ ring common to these structures adopts a chair configuration wth some degree of flexibility.[41b]

The structure of $[Mo_8O_{20}(NNPh)_6]^{4-}$ (Figure 22b) may be derived from that of the parent ion $\alpha\text{-}[Mo_8O_{26}]^{4-}$ by replacement of two terminal oxo groups on each of three alternate molybdenum atoms in the $\{Mo_6O_6\}$ crown by two phenyldiazenido groups and rotation of the capping $\{MoO_4\}$ units.[153,155]

Although polyoxomolybdate derivatives containing the $\{Mo^{II}(NNAr)\}^{3+}$ unit are less easily formed that those containing the *cis*-$\{Mo^0(NNAr)_2\}^{2+}$ unit, a number of hexamolybdates $[Mo_6O_{18}(NNAr)]^{3-}$ have been reported.[142,147,156] It appears that they are most easily obtained from arylhydrazines bearing electron-attracting substituents.[157] Several of these complexes have been structurally characterized. Although the structures of $[Mo_6O_{18}(NNAr)]^{3-}$ (Ar = Ph,[147] C_6F_5,[142] $C_6H_4\text{-}p\text{-}NO_2$,[156,157] $C_6H_4\text{-}o\text{-}NO_2$,[157]) may be derived from that of the parent ion $[Mo_6O_{19}]^{2-}$ by replacement of a single terminal oxo group by an aryldiazenido ligand, there are significant differences in the electronic spectra, redox electrochemistry, and structural parameters. Thus, in contrast to the electrochemical behavior of $[Mo_6O_{19}]^{2-}$, which displays two successive one-electron reduction processes, the cyclic voltammograms of the diazenido derivatives are characterized by two successive one-electron oxidation processes. The Mo(NNAr) resonance, lying at about 800 ppm, is highly deshielded with respect to those of the Mo(VI) centers at about 180 ppm, which has been ascribed to an enhanced contribution of the paramagnetic term in shielding.[157]

The controlled reaction of $[Mo_6O_{18}(NNAr)]^{3-}$ with sodium hydroxide in methanol yields the lacunary pentamolybdate species $[Mo_5O_{13}(OMe)_4(NNAr)]^{3-}$ which has been isolated as $(n\text{-}Bu_4N)_2[Mo_5O_{13}(OMe)_4(NNAr)\{Na(MeOH)\}]\cdot x MeOH$ where Ar = C_6F_5 and $O_2N\text{-}p\text{-}C_6H_4$. Although the sodium complex has not been structurally characterized, in contrast to the nitrosyl analogue, the identity of the pentamolybdate species has been definitively established by the X-ray crystal structure analysis of $(n\text{-}Bu_4N)_3[Bi\{Mo_5O_{13}(OMe)_4(NNC_6H_4\text{-}p\text{-}NO_2)\}_2]$.[157]

4. Nitrosyl Derivatives

Early work on oxo nitrosyl complexes has been reviewed.[158,159] The reactions of hydroxylamine with oxo complexes of transition metals were first studied by Hofmann at the turn of the century.[160] It was thought at this time that the behavior of hydroxylamine was similar to that of water; the reported formulas of complexes, e.g., $MoO_2\cdot 4KCN\cdot NH_2OH\cdot H_2O$,[160a] $MoO_3(NH_3O)_2(NH_3)$,[160b] and $MoO_4H_2(NH_3O)_3(NH_2OK)$,[160b] clearly need to be reconsidered and some of them have been already.[161] Then these systems were studied from time to time, but it was not until the mid-1900s that the nitrosylating action of hydroxylamine was firmly established.[161] Since then, a lot of results were gathered by the groups of K. Wieghardt,[162] A. Müller,[163] and R. Bhattacharyya,[164] and hydroxylamine is now known as one of the most convenient sources for nitrosyl complexes.[165]

The reductive nitrosylation of oxomolybdenum species, including polyoxomolybdates, with hydroxylamine can be performed in nonaqueous as well as in aqueous solutions. Amide oximes[110] and ketone oximes[113b] can be used as substitutes for hydroxylamine. Although the actual pathway of the reductive nitrosylation with amide oximes and oximes has not been unambiguously established, it probably involves the initial formation of hydroxylamine.

The $\{Mo(NO)\}^{3+}$ unit and the $\{Mo(NNH)\}^{3+}$ units are isoelectronic,[136] and so are the $\{Mo(NO)_2\}^{2+}$ and

$\{Mo(NNH)_2\}^{2+}$ units. The reductive nitrosylation of polyoxomolybdates by hydroxylamine provides a convenient way to polynuclear nitrosyl oxomolybdates, just as the reaction of monosubstituted hydrazines yield polynuclear diazenido oxomolybdates. However, whereas the reduction by arylhydrazines gives chiefly diazenido derivatives containing $\{Mo(NNAr)_2\}^{2+}$ units, the reductive nitrosylation gives mainly nitrosyl derivatives containing $\{Mo(NO)\}^{3+}$ units. There are now several pairs of structurally related clusters where $\{MoO\}^{4+}$ units are replaced by $\{Mo(NO)\}^{3+}$ units, e.g. $[Mo_6O_{19}]^{2-}$ and $[Mo_6O_{18}(NO)]^{3-}$,[14a,18a] $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$,[166] and $[Mo_{36}O_{108}(NO)_4(H_2O)_{16}]^{12-}$,[167] $[Mo_{154}O_{462}(H_2O)_{70}H_x]^{y-}$,[168] and $[Mo_{154}O_{420}(NO)_{14}(OH)_{28}(H_2O)_{70}]^{(25\pm5)-}$.[169]

The reduction of acidified molybdate aqueous solutions with hydroxylamine provides an impressive illustration of the molecular building block approach to giant clusters. The $\{Mo_{17}O_{58}(NO)_2(H_2O)_2\}^{20-}$ units formed upon reductive nitrosylation of acidified molybdate are linked to various cationic species such as $\{MoO_2\}^{2+}$, $\{VO(H_2O)\}^{2+}$, $\{Fe(H_2O)_2\}^{3+}$, and $\{Mo(\mu\text{-}H_2O)_2(\mu\text{-}OH)Mo\}^{9+}$. These aggregation processes lead to the formation of very large clusters, e.g., $[\{MoO_2\}_2\{H_{12}Mo_{17}O_{58}(NO)_2(H_2O)_2\}_2]^{12-}$, i.e., $[Mo_{36}O_{108}(NO)_4(H_2O)_{16}]^{12-}$, $[\{VO(H_2O)\}_6\{Mo(\mu\text{-}H_2O)_2(\mu\text{-}OH)Mo\}_3\{Mo_{17}O_{58}(NO)_2(H_2O)_2\}_3]^{21-}$, and $[\{Fe(H_2O)_2\}_6\{Mo(\mu\text{-}H_2O)_2(\mu\text{-}OH)Mo\}_3\{Mo_{17}O_{58}(NO)_2(H_2O)_2\}_3]^{15-}$.[170] Incorrect formulas had been previously assigned to theses species.[171a,b] A novel one-dimensional polymer $\{(H_3O^+)_{12}\{(H_2O)MoO_{2.5}[Mo_{36}O_{108}(NO)_4(H_2O)_{16}]O_{2.5}Mo(H_2O)\}^{12-}\}_n$ has been obtained by the reaction of the discrete nanospecies $(H_3O^+)_{12}[Mo_{36}O_{108}(NO)_4(H_2O)_{16}]^{12-}$ with hydroxylamine chlorhydrate in water.[171d] The cluster $[\{VO(H_2O)\}_6\{Mo(\mu\text{-}H_2O)_2(\mu\text{-}OH)Mo\}_3\{Mo_{17}O_{58}(NO)_2(H_2O)_2\}_3]^{21-}$ itself might act as a template for the formation of the giant cluster $[Mo_{154}O_{420}(NO)_{14}(OH)_{28}(H_2O)_{70}]^{(25\pm5)-}$, the so-called "big wheel".[169] The related cluster $[Mo_{154}O_{462}(H_2O)_{70}H_x]^{y-}$ appears to represent the major structural motif in molybdenum blue species.[168]

Reactions of hydroxylamine with isopolyoxomolybdates in methanol or ethanol yield nitrosyl polyoxomolybdates of the type $[Mo_5O_{13}(OR)_4(NO)]^{3-}$ (R = Me, Et). The structures of $(n\text{-}Bu_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]\cdot3MeOH$, $K_2[Mo_5O_{13}(OMe)_4(NO)\{Na(H_2O)(MeOH)\}]$, $(Me_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(H_2O)\}]$, and $(n\text{-}Bu_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(DMF)\}]$ have been determined by X-ray crystallography (Figure 23).[14] The $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ anion has an approximate C_{4v} symmetry. It contains a linear $\{Mo^{II}(NO)\}^{3+}$ unit and may be viewed as deriving from the hitherto unknown lacunar $[Mo_5O_{18}]^{6-}$ Lindqvist anion. The sixth position is occupied by a sodium cation. Recrystallization of $(n\text{-}Bu_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]\cdot3MeOH$ in acetonitrile or dichloromethane affords $(n\text{-}Bu_4N)_3[Mo_6O_{18}(NO)]$.[14a] Reductive nitrosylation of $(n\text{-}Bu_4N)_2[Mo_2O_7]$ with hydroxylamine chlorhydrate in acetonitrile provides a more straightforward synthesis of the latter.[18a] Other members of the Lindqvist-type nitrosyl series $(n\text{-}Bu_4N)_3[M_5O_{18}\{M'(NO)\}]$ (M, M′ = Mo, W) have been synthesized through the reaction of $[Mo(NO)\{MeC(NH_2)NO\}(acac)_2]$,[110] or $[W(NO)Cl_3(MeCN)_2]$,[172] with $(n\text{-}Bu_4N)_2[Mo_2O_7]$ or $(n\text{-}Bu_4N)_2[WO_4]$ in MeCN.[173] The electronic features of the $[M_5O_{18}\{M'(NO)\}]^{3-}$ anions have been investigated by vibrational, electronic, and multinuclear (^{14}N, ^{17}O, ^{95}Mo, and ^{183}W) magnetic resonance spectroscopy, and by electrochemistry.[18a,173] A full assignment of the NMR spectra has been achieved. Chemical shifts are dominated by the paramagnetic term of the shielding. ^{17}O NMR data and electrochemical reduction data show that the expected effect of the whole charge increase with respect to the parent oxoanions $[M_6O_{19}]^{2-}$ is partly offset by the electron-withdrawing effect of the nitrosyl ligand. All four species are essentially localized mixed-valence complexes, with five d^0-M(VI) centers and one d^4-M′(II) center; however, some electronic delocalization is supported by ^{95}Mo and ^{183}W NMR data and by electrochemical data.[173] As already discussed (section IV.B.1), activation of the hexametalates $[M_6O_{19}]^{2-}$ upon nitrosylation is supported by the observation that $[Mo_6O_{18}(NO)]^{3-}$ [18a] and $[W_5O_{18}\{Mo(NO)\}]^{3-}$ [18b] can be methylated by dimethyl sulfate in acetonitrile, while $[Mo_6O_{19}]^{2-}$ is unreactive.

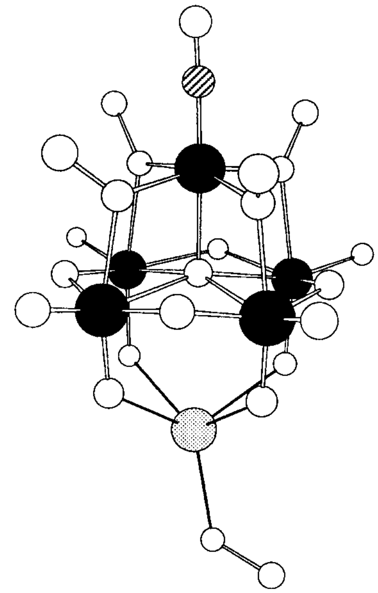


Figure 23. Structure of $[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]^{2-}$ (ref 14).

Reduction of $(n\text{-}Bu_4N)_3[Mo_6O_{18}(NO)]$ with various reducing agents, including hydrazine dichlorohydrate, in methanol or in a mixture of methanol and acetonitrile, yields decamolybdates, among which the two-electron reduced $(n\text{-}Bu_4N)[Mo_{10}O_{25}(OMe)_6(NO)]$ and two diasteroisomers of the four-electron reduced $(n\text{-}Bu_4N)_2[Mo_{10}O_{24}(OMe)_7(NO)]$ have been crystallographically characterized. The molecular structures of $[Mo_{10}O_{25}(OMe)_6(NO)]^-$ and $[Mo_{10}O_{24}(OMe)_7(NO)]^{2-}$ are closely related to that of $[W_{10}O_{32}]^{4-}$ and consist of two halves of five edge-sharing octahedra connected through four quasi-linear Mo−O−Mo bridges (Figure 24). Besides the four electrons essentially residing at the Mo(II) center bearing the nitrosyl ligand, they further accommodate two and four delocalized "blue" electrons, respectively. On the basis of their optical spectra, they are best described as class II mixed-valence complexes according to the classification of Robin and Day.[174]

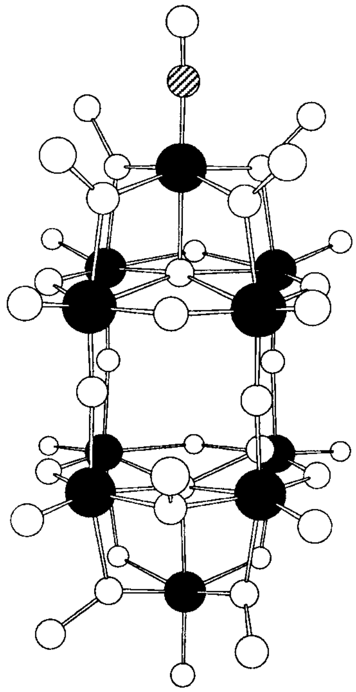


Figure 24. Structure of one diastereomer of $[Mo_{10}O_{24}(OMe)_7(NO)]^{2-}$ (ref 174).

The lacunary nitrosyl derivatives exhibit a rich coordination chemistry.[175a,b] They coordinate to a variety of cationic species, including organic cations, e.g. $ArNH_3^+$ [175a] and $RC(NH_2)_2^+$;[107] main-group cations, e.g. Na^+,[14] Ba^{2+}, Bi^{3+};[175b] f-block cations, e.g., Eu^{3+}, Ce^{4+};[159] d-block cations, e.g., Mn^{2+}, Ag^+;[175b] and unsaturated organometallic fragments (section VII.C.2.b) displaying various coordination modes.

In addition, the defect $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ species is a potential source of the $\{Mo(NO)\}^{3+}$ group, thus a convenient starting material for the synthesis of a number of other oxo-nitrosyl polyoxometalates. This is demonstrated by its spontaneous conversion into $[Mo_6O_{18}(NO)]^{3-}$ in MeCN or dichloromethane[14a,18a] and by the synthesis of $(n\text{-}Bu_4N)_4[PM_{11}\{Mo(NO)\}]$ (M = Mo, W) through its reaction with $(n\text{-}Bu_4N)_4[PM_{12}O_{40}]$ in MeCN in the presence of $n\text{-}Bu_4NOH$.[176] The ability of $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ to act as a source of the $\{Mo(NO)\}^{3+}$ unit is further illustrated by its reactions with other potential ligands.[177] Thus its reacts with $[MoO_2(acac)_2]$ in MeCN to yield $(n\text{-}Bu_4N)_2Na_2[Mo_8O_{22}(NO)_2(acac)_2]\cdot 2H_2O$ and with $MeC(CH_2OH)_3$ in MeCN to yield $(n\text{-}Bu_4N)_2[Mo_6O_{10}(NO)_2\{MeC(CH_2O)_3\}_4]$. The framework of the $[Mo_8O_{22}(NO)_2(acac)_2]^{4-}$ anion is related to those of other derivatized-octamolybdates of the type $[Mo_8O_{26}X_2]^{(2n+4)-}$, while the $[Mo_6O_{10}(NO)_2\{MeC(CH_2O)_3\}_4]^{2-}$ anion is made of two $Mo_3O_5(NO)\{MeC(CH_2O)_3\}^-$ units connected by two nearly linear Mo−O−Mo bridges. Provided prior formal substitution of NO^+ for a terminal oxo ligand at the MoO_3 moiety, the anion may be viewed as the product of a condensation of two $[Mo_3O_7\{MeC(CH_2O)_3\}_2]^{2-}$ anions by sharing of two corners. Both $[Mo_8O_{22}(NO)_2(acac)_2]^{4-}$ and $[Mo_6O_{10}(NO)_2\{MeC(CH_2O)_3\}_4]^{2-}$ anions can be viewed as localized Mo^{II}/Mo^{VI} species.[177]

Such condensation reactions between nitrosyl complexes and oxometalates appear to be an attractive and promising alternative route to novel oxo-nitrosyl complexes. As a further example, $[\{Mo(NO)(Me_2CNO)_2(OMe)\}_2]$, obtained by reductive nitrosylation of $(n\text{-}Bu_4N)_2[Mo_6O_{19}]$ with acetone oxime in ethanol, reacts with $(n\text{-}Bu_4N)_2[Mo_2O_7]$ to yield $(n\text{-}Bu_4N)_2[Mo_4O_{10}(NO)(OMe)(Me_2CNO)_2]$. In the latter, the acetone oximato ligand exhibits a hitherto unprecedented $\mu_3\text{-}\kappa N{:}\kappa^2 O$ coordination mode.[113b]

While the diazenido clusters $[Mo_4O_8(OR)_2(NNAr)_4]^{2-}$ are well established, the analogous nitrosyl species $[Mo_4O_8(OR)_2(NO)_4]^{2-}$ have yet to be isolated. The formation of oxo-nitrosyl polymetalates containing *cis*-$\{M^0(NO)_2\}^{2+}$ units apparently requires additional ligands, such as amide oxime ligands (section V.A.2).[107,109]

C. Organophosphorus, Organoarsenic, and Organoantimony Ligands

The current interest in the $M/O/RPO_3^{2-}$ systems reflects the significance of both the cluster and solid-state chemistry of these materials.[24b,d,178,179] The exploitation of solvothermal techniques and the introduction of various templates into the Mo/$ORPO_3^{2-}$ and $Mo/O/RAsO_3^{2-}$ systems systems have allowed an impressive expansion of structural types, notably within oxovanadium clusters which exhibit a remarkable versatility in providing electronically normal, inverse, bifunctional, or neutral hosts capable of accommodating cations, anions, or neutral molecules.[24b,d,9] The topological relationships of these clusters to solid phases[24b,d] and the self-organization of host−guest systems[9] have been discussed. The structural diversity of polyoxovanadates[180a] is further enhanced by the introduction of organophosphonate and organoarsonate ligands. Dinuclear complexes of the class $[(VO)_2Cl_2(H_2O)_2(RPO_3H)_2]$[181a] serve as precursors for condensation into larger oligomers.[24d] The spherical, cyclic, bowlike or barrel-shaped structures adopted by the clusters can be described in terms of vanadium-centered square pyramids and, more rarely, ocatahedra, phosphonate tetrahedra, and arsonate tetrahedra or square pyramids. These structures reflect the reaction conditions, the influence of the template, and the substitution of As for P: in contrast to the shorter $\{RP\}^{4+}$ unit, the $\{RAs\}^{4+}$ unit is topologically identical with the $\{VO\}^{3+}$ unit and may replace the latter in structural motifs.[181b]

1. Organophosphonate and Organoarsonate Ligands

The following discussion will be restricted to oxomolybdenum and oxotungsten complexes.

The tetranuclear complex $[Mo_4O_{10}(PhPO_3)_4]^{4-}$ has been prepared by reaction of $[MoO_2(acac)_2]$ with $PhPO_3H_2$ in refluxing acetonitrile in the presence of excess triethylamine. Its structure is based on two pairs of face-sharing octahedra symmetrically bridged by two phosphonate ligands. The resultant ring is capped above and below by the two remaining phosphonate ligands. The phenyl arsonate analogue, $[Mo_4O_{10}(PhAsO_3)_4]^{4-}$, has an identical structure, while the *p*-tolylarsonate derivative, $[Mo_4O_{10}(p\text{-}MeC_6H_4AsO_3)_4]^{4-}$, displays a different structure based on two $\{Mo_2O_3\}$ and $\{Mo_2O_5\}$ units bridged by the arsonate groups.[181c]

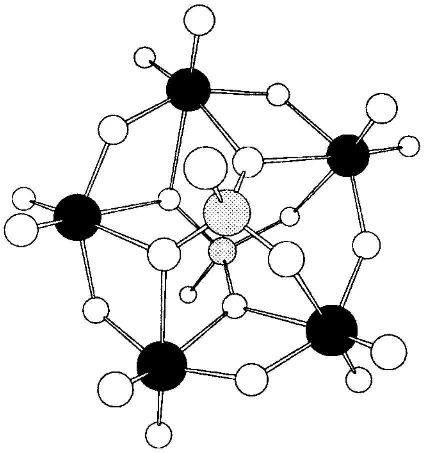


Figure 25. Structure of $[(MeP)_2Mo_5O_{21}]^{4-}$ (ref 90).

The speciation of the $H^+/MoO_4^{2-}/REO_3^{2-}$ systems (E = P, R = Ph;[182a] R = As, R = Me and Ph[182b]) has been investigated by combined emf-NMR techniques. The following tentative formulas of the species found in solution have been given: $[(RP)_2Mo_5O_{21}]^{4-}$, $[(RP)_2Mo_5O_{20}(OH)]^{3-}$, $[(RP)Mo_6O_{21}(H_2O)_6]^{2-}$, and $[(RP)Mo_7O_{25}(OH_x)]^{(6-x)-}$ ($x = 1$ and 2) in the aqueous molybdophenylphosphonate system,[182a] $[(RAs)_2Mo_6O_{24}(OH_x)]^{(6-x)-}$ ($x = 1$ and 2) and $[(RAs)_2Mo_5O_{21}]^{4-}$ in the molybdomethylarsonate system.[182b]

The pentamolybdobisphosphonates, $[(RP)_2Mo_5O_{21}]^{4-}$, are readily formed in aqueous solutions at pH 2–6, but the isolation of pure salts requires recrystallization from nonaqueous solvents or the appropriate choice of the counterion.[183] Since the X-ray crystal structure determinations of the methyl- and the ethylammonium phosphonate complexes, which were the first examples of organic derivatives of polyoxometalates to be structurally characterized[90] (R = Me, Figure 25), the crystal structures of four other conjugates, R = Ph,[184] *n*-amyl,[185a] and c-$\{X(CH_2CH_2)_2NHCH_2\}^+$ (X = O, S, and CH_2)[186] have been reported. Although there is very little deviation in the basic structure of the $[(RP)_2Mo_5O_{21}]^{4-}$ ions, which is very similar to that reported for the $[P_2Mo_5O_{23}]^{6-}$ anion,[89b] the various organic moieties occupy different positions for preferred steric and electrostatic reasons.[186b] A noteworthy feature of the crystal structure of the (aminomethyl)phosphonate conjugates is the formation of an intramolecular hydrogen bond from the protonated nitrogen to one terminal oxygen. This has the effect of bending over the appending ligand toward the metal–oxygen surface. Since analogous phosphonomolybdates with macrocycles have been synthesized,[186a] this might offer the possibility of bringing a second metal atom in close contact to the metal–oxygen surface. The tungstate analogues, $[(RP)_2W_5O_{21}]^{4-}$, have been reported and shown to exhibit intramolecular exchange behavior.[187]

The H^+/MoO_4^{2-}/(1-hydroxyethylidene)diphosphonic acid system has been investigated by Russian workers.[188a] A wide diversity of compounds have been isolated from aqueous solutions and characterized by X-ray diffraction. The hexanuclear species $[Mo_6O_{17}\{HOCH(PO_3)_2\}_2]^{6-}$ [188b] and $[Mo_6O_{17}\{MeC(O)(PO_3)_2\}_2]^{8-}$ [188c] consist of two $[Mo_3O_9\{XCH(PO_3)_2\}]$ fragments, similar to that present in the $[Mo_3O_9\{MeC(O)(PO_3)_2\}]^{5-}$ anion,[188c] linked by one bridging oxo ligand. The open structure of these hexamolybdodiphosphonates contrasts with the cyclic structure of the methylenediphosphonate complex, $[(O_3PCH_2PO_3)Mo_6O_{18}(H_2O)_4]^{4-}$ (Figure 26), recently reported by Kortz and Pope.[189a] The latter consists of a six-membered ring of $\{MoO_6\}$ octahedra which alternate in sharing edges and corners. The diphosphonate ligand is bound with one group in the center of the ring and the second off-center and bound above the ring to two adjacent molybdenum atoms. Each of the four molybdenum atoms has a terminal water ligand on the same side as the off-center phosphonate group.[189a] The macrocyclic dodecatungstate, $[(O_3PCH_2PO_3)_4W_{12}O_{36}]^{16-}$ displays an open cyclic structure based upon a folded dodecatungstate ring. This structure has two saddle-shaped cavities, which incorporate cations (Figure 27).[189b]

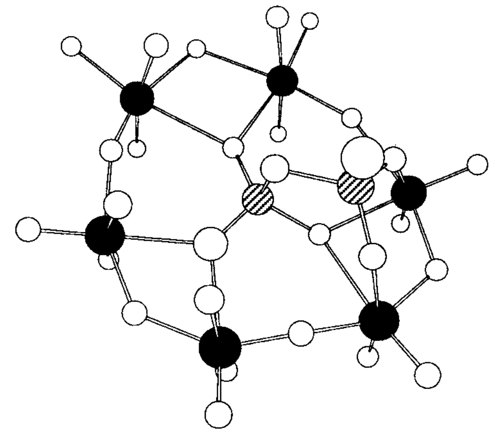


Figure 26. Structure of $[(O_3PCH_2PO_3)Mo_6O_{18}(H_2O)_4]^{4-}$ (ref 189a).

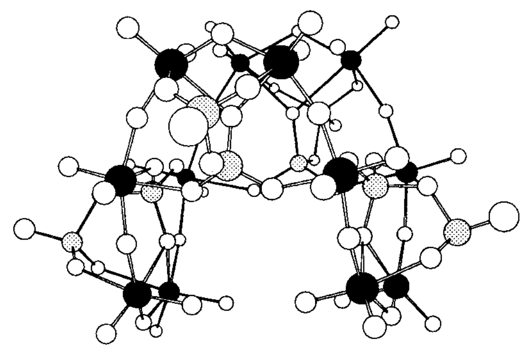
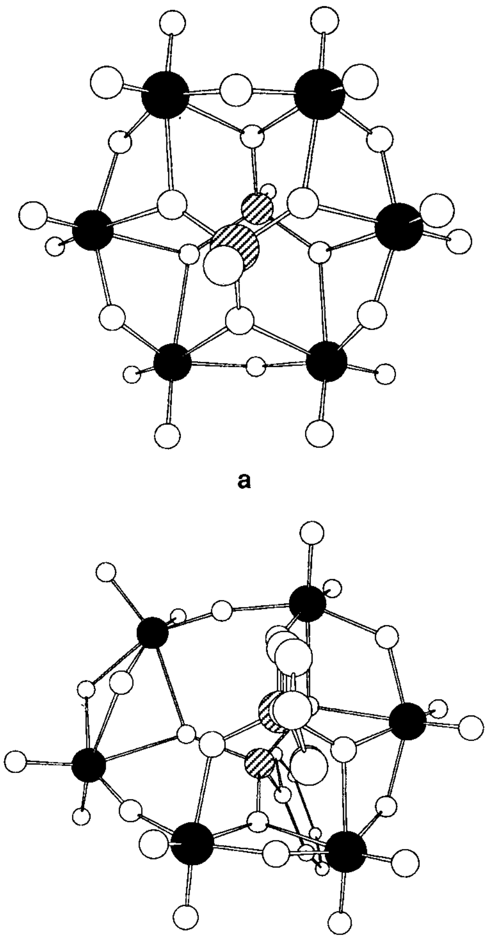


Figure 27. A view of the anion $[(O_3POPO_3)_4W_{12}O_{46}]^{12-}$ in $Cs_{13}Na_3[(O_3POPO_3)_4W_{12}O_{36}]\cdot24H_2O$ (ref 189b).

The hexamolybdobis(organoarsonates) are the predominant species in aqueous solutions at pH ~4. Although the first structurally characterized member of this series of complexes, $[(MeAs)_2Mo_6O_{24}]^{4-}$, consists of a ring of six edge-sharing Mo_6 octahedra capped above and below by the arsonate groups (Figure 28a),[190a] it has been subsequently found that the $[(RAs)_2Mo_6O_{24}]^{4-}$ complexes take up a water molecule in aqueous solution.[190b] On the basis of the X-ray crystal structure of $(CN_3H_6)_4[(PhAs)_2Mo_6O_{24}(H_2O)]\cdot4H_2O$,[190c] the "hydrated" structure $[(RAs)_2Mo_6O_{24}(H_2O)]^{4-}$ derives from that of $[(RAs)_2Mo_6O_{24}]^{4-}$ by incorporation of a bridging water ligand adjacent to two of the oxygen atoms of an arsonate group (Figure 28b). Although the hydrated form is pre-



a

b

Figure 28. Structures of $[(MeAs)_2Mo_6O_{24}]^{4-}$ (a, ref 190a) and $[(PhAs)_2Mo_6O_{24}(H_2O)]^{4-}$ (b, ref 190c).

dominant in aqueous solution, dehydration may be achieved by heating in acetonitrile.[190b] The related deprotonated complexes $[(RAs)_2Mo_6O_{24}(OH)]^{5-}$, wherein R = Ph, *o*-, *m*-, *p*-$(O_2N)C_6H_4$, have been characterized. The phenylarsonate complex, $[(PhAs)_2Mo_6O_{25}H]^{5-}$,[185a] is isostructural with its tungsten analogue,[191] while the *o*-nitrophenylarsonate derivative displays a variant of this structure.[185d] The fluxional behavior of the $[(RAs)_2W_6O_{25}H]^{5-}$ complexes involves protonation of the bridging hydroxy oxygen and subsequent exchange of water as for the molybdate analogues.[191] The solution structure of $[(PhAs)_2Mo_6O_{24}]^{4-}$ derived from ^{17}O NMR spectroscopy in acetonitrile is consistent with a D_{3d} symmetry.[192]

Although it was first thought that the arsenic analogues of the pentamolybdobis(organophosphonates) did not exist due to the larger size of As vis-à-vis P,[190a] two complexes of the class $[(RAs)_2Mo_5O_{21}]^{4-}$ (R = *n*-Pr,[185b] $CH_2{=}CHCH_2$[185c]) have been characterized since. While the 2:6 complexes are the predominant species in weakly acid solution, the complexes $[(RAs)_4Mo_{12}O_{46}]^{4-}$ are formed at pH < 1.[193] The dodecamolybdate cluster in the structurally characterized compound $[(H_3N\text{-}p\text{-}C_6H_4As)_4Mo_{12}O_{46}]\cdot 10CH_3CN\cdot 6H_2O$ is composed of four groups of three edge-sharing MoO_6 octahedra that are bridged by four $\{H_3N\text{-}p\text{-}C_6H_4AsO_3\}$ unit. The structure of the metal oxide core may be viewed as an inverted Keggin structure.[193]

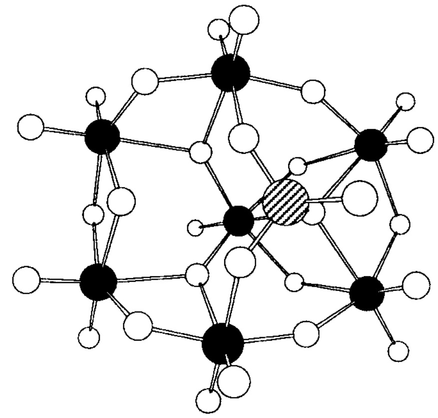


Figure 29. Structure of $[(MeAs)W_7O_{27}H]^{7-}$ (ref 194).

The anions $[(RAs)W_7O_{27}H]^{7-}$, which are formed in solutions of WO_4^{2-} and $RAsO_3^{2-}$ at pH 7–8.5, have an unusual stoichiometry.[194] An X-ray crystal structure analysis of $(CN_3H_6)_7[(MeAs)W_7O_{27}H]\cdot 3H_2O$ has been performed. The anion is composed of a $\{W_7O_{24}\}$ group topologically related to the paratungstate-A structure, and a $MeAsO_3$ moiety which sits above one or the other of two chemically distinct triangles of edge-sharing octahedra (Figure 29). The relationships among the species $[W_7O_{24}]^{6-}$, $[(RAs)W_7O_{27}H]^{7-}$, and $[(RAs)_2W_6O_{25}H]^{5-}$ have been discussed.[194] An $AsMo_7$ species with a different overall stoichiometry, $[(PhAs)Mo_7O_{25}]^{4-}$, has been obtained from the reaction of $(n\text{-}Bu_4N)_4[\alpha\text{-}Mo_8O_{26}]$ with $(n\text{-}Bu_4N)_4[(PhAs)_2Mo_6O_{24}]$ in acetonitrile.[195] The structurally related anions $\alpha\text{-}[Mo_8O_{26}]^{4-}$, $[(PhAs)Mo_7O_{25}]^{4-}$, and $[(PhAs)_2Mo_6O_{24}]^{4-}$ contain tridentate oxoanions MoO_4^{2-} or $PhAsO_3^{2-}$, bonded on opposite sides of a puckered Mo_6O_{18} ring. A dynamic ^{17}O NMR study has provided evidence for rapid intramolecular Mo_6O_{18} ring inversion in $[(PhAs)Mo_7O_{25}]^{4-}$.[195] The crystal and molecular structure of an $AsMo_6$ complex have also been reported.[196]

The compounds $(Et_4N)_2Na_3(H_3O)_4[Na\{Mo_6O_{15}(PhPO_3)(PhPO_3H)_3\}_2]\cdot{\sim}14H_2O$,[197] $(NH_4)_5Na_4[Na\{Mo_6O_{12}(OH)_3(PhPO_3)_4\}_2]\cdot 6H_2O$,[198a,b] $Na_7(N_2H_4)_2[Na\{Mo_6O_{12}(OH)_3(PhPO_3)_3(PhPO_3H)\}_2]\cdot 26H_2O$,[198c] and $(BzMe_3N)_4K_4[K_2\{Mo_6O_{12}(OH)_3(PhPO_3)_4\}_2]\cdot 10H_2O$,[198a,b] contain hexanuclear Mo(V) species whose cyclic core is reminiscent of the Anderson structure. In the sodium compounds, one Na^+ cation is sandwiched between a pair of hexanuclear units,[197,198] while in the potassium compound, one of the hexanuclear units is shifted slightly to accommodate the larger K^+ cation.[198b]

Organophosphonyl and organoarsonyl derivatives have also been obtained from lacunary heteropolyoxometalates. Hill et al. have reported the synthesis of the complexes $[\{PhP(O)\}_2XW_{11}O_{39}]^{(8-n)-}$ ($X^{n+} = P^{5+}$, Si^{4+}) by reaction of the monovacant complex anions $\alpha\text{-}[XW_{11}O_{39}]^{(12-n)-}$ with $PhPOCl_2$ in acetonitrile solution. The X-ray structure of $(n\text{-}Bu_4N)_2H[\{PhP(O)\}_2PW_{11}O_{39}]$ has been reported.[199] The two equivalent PhP(O) groups each bridge two terminal oxygen atoms of the four that define the hole in the XW_{11} lacunary structure (Figure 30). The collective ^1H, ^{31}P, and ^{183}W NMR data provide evidence establishing that the $[\{PhP(O)\}_2XW_{11}O_{39}]^{(8-n)-}$ complexes retain

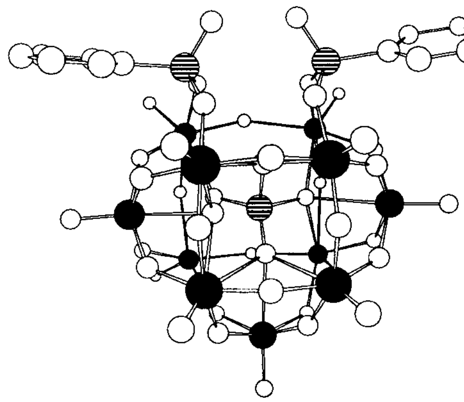


Figure 30. Structure of $[\{PhP(O)\}_2PW_{11}O_{39}]^{3-}$ (ref 199).

the C_s symmetry in solution. The $(n\text{-}Bu_4N)_2H[\{PhP(O)\}_2PW_{11}O_{39}]$ compound converts to $(n\text{-}Bu_4N)_2H_2[\{PhP(O)\}\{PhP(O)(OH)\}PW_{11}O_{39}]$ when dissolved in wet dimethyl sulfoxide. This partially hydrolyzed compound slowly reverts to the original compound in acetonitrile.[199] In the presence of $(n\text{-}Bu_4N)Br$ acting as phase-transfer reagent, organophosphonic acids react in acetonitrile with the trivacant compound β-*A*-$Na_8[HPW_9O_{34}]\cdot 24H_2O$ to give α-*A*-$(n\text{-}Bu_4N)_3Na_2[\{RP(O)\}_2PW_9O_{34}]$ (R = Et, *n*-Bu, *t*-Bu, Ph). The solution structure of the anions has been inferred from multinuclear (^{31}P, ^{183}W) NMR studies. Each RP(O) group is connected to two terminal oxygen atoms belonging to a same diad.[200]

2. Organophosphinate and Organoarsinate Ligands

The tetramolybdoarsisinate complexes $[R_2AsMo_4O_{14}(OH)]^{2-}$ are formed in aqueous solution at pH 4−5 from stoichiometric mixtures of the arsinic acid and sodium molybdate.[34] Salts of anions with this stoichiometry were first prepared by Rosenheim and Bilecki.[201] The $H^+/MoO_4^{2-}/Me_2AsO_2^-$ system has been recently reinvestigated by the combined emf−NMR thechnique. Data confirmed the existence of $[Me_2AsMo_4O_{14}(OH)]^{2-}$ in solution. The structure of $(CN_3H_6)_2[Me_2AsMo_4O_{14}(OH)]\cdot H_2O$ has been determined by single-crystal X-ray diffraction[34,196] and neutron diffraction.[202] The anion may be viewed as a ring of face- and edge-sharing $\{MoO_6\}$ octahedra capped by the tetrahedral $Me_2ASO_2^-$ group (Figure 2a). The ^{17}O NMR spectra of the dimethyl and diphenyl derivatives have been reported by Klemperer et al.[203] Polyperoxometalates with phosphinate and arsinate assembling ligands have been reported (section IV.A).

A few organoantimony and organobismuth derivatives have been reported.[204,205]

VI. Polyoxometalates Incorporating Group 14 Element-Centered Ligands

A. Oxocarbon Ligands

1. Carbonate

The carbonate group acts as a template in the self-assembly of the V^{IV} species $[V_6O_6(OH)_9(CO_3)_4]^{5-}$,[206] and of the mixed-valence cluster $[V^{IV}_8V^V_7O_{36}(CO_3)]^{7-}$.[28a] The former displays a crown-shaped framework with one μ_6- and three μ_2-bridging carbonato ligands while the structure of the latter consists of a spherical shell of corner-sharing $\{VO_5\}$ square pyramids encapsulating the CO_3^{2-} anion.

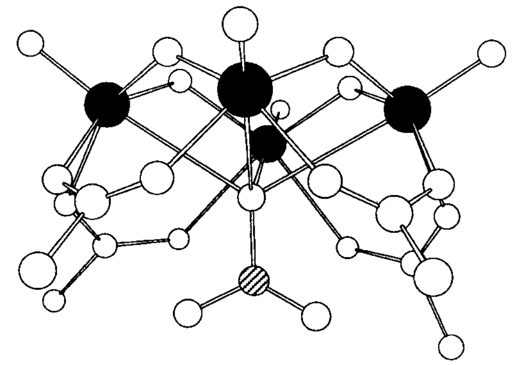


Figure 31. Structure of $[V_4O_8(tca)_4(NO_3)]^{2-}$ (thiophene groups omitted, ref 207).

2. Carboxylates

A rich class of vanadium clusters with carboxylate ligands has emerged in recent years.[207] These species are of interest owing to their structures and magnetic properties[207] and to the biological relevance of vanadium.[208] In addition to oxo-centered trinuclear complexes,[207] these include $[V_4O_2(EtCO_2)_7(bpy)_2]^+$,[209] $[KV_4O_8\{t\text{-}BuCH_2CO_2)_4]^+$,[210a] $[V_4O_8(RCO_2)_4(NO_3)]^{z-}$ (*z* = 1[211] or 2[31]), $[V_5O_9(RCO_2)_4(X)]^{2-}$ (X = Cl, Br),[207] $[V_6O_{10}(PhCO_2)_9]$,[210b] $[V_4Zn_4O_4(PhCO_2)_{12}(THF)_4]$,[212] and $[H_6V_{10}O_{22}(MeCO_2)_6]^{2-}$.[213]

The structures of $[KV_4O_8(RCO_2)_4]^+$ and $[V_4O_8(RCO_2)_4(NO_3)]^{2-}$ (Figure 31) may be viewed as a ring of corner-sharing square pyramids, and the $\{V_5O_9\}$ core in $[V_5O_9(RCO_2)_4(X)]^{2-}$ may be derived by capping the cyclic $\{V_4O_8\}$ unit of the former with a {VO} unit. It is noteworthy that the cavity provided by the carboxylate groups on the square face of the tetravanadate species or the basal face of the pentavanadate species can accommodate either cationic (X = K^+) or anionic (X = Cl^-, Br^-, NO_3^-) guests. In the mixed-valence cluster $[H_6V^{IV}_8V^V_2O_{22}(MeCO_2)_6]^{2-}$, the carboxylato ligands occupy the exterior of the cluster so as to link $\{VO_6\}$ octahedra.[213] Encapsulation of a carboxylate template requires larger shells, e.g., $[As_8V_{12}O_{40}(HCO_2)]^{z-}$ (*z* = 3 and 5)[214] and $[H_2V_{22}O_{54}(MeCO_2)]^{7-}$.[213]

A few molybdenum carboxylate complexes with metal nuclearities >3 have been reported. These include the tetranuclear species $[(HCCH)Mo_4O_{15}(HCO_2)]^{3-}$ and $[(C_{14}H_{10})Mo_4O_{15}(PhCO_2)]^{3-}$ [215] and the octanuclear complexes $[Mo_8O_{26}(HCO_2)_2]^{6-}$,[100] $[Mo_8O_{26}(lysH_2)_2]^{2-}$,[101b] and $[Mo_8O_{24}(OH)_2(metO)_2]^{4-}$.[102] Malate and citrate ligands are effective in stabilizing the $\{Mo_4O_{11}\}^{2+}$ core.[216−219]

3. Oxalate and Squarate

Vanadium and molybdenum oxalate complexes have been obtained either from oxalic or from rhodizonic acid. The bridging abilities of the oxalate and squarate ligands often lead to the generation of cyclic structures rather than the compact structures generally favored in polyoxometalates. The oxalato ligands may adopt the chelating mode, as in $[V_4O_8(H_2O)_2(C_2O_4)_4]^{4-}$,[220] or the μ_8-bridging mode, as in $[(VO)_8(OMe)_{16}(C_2O_4)]^{2-}$ [221a] and $[(Mo_8O_{16}(OMe)_8$-

$(C_2O_4)]^{2-}$.[221b] The squarate moiety is found as μ_2-bridging $C_4O_4^{2-}$ ligands in $[Mo_3O_8(OMe)(C_4O_4)_2]^{3-}$,[221c] $[V_3O_4F_4(C_4O_4)_3]^{4-}$, and $[Mo_3O_8F(C_4O_4)_2]^{3-}$,[35b] as singly bonded $C_4O_4H^-$ and μ_2-$C_4O_4^{2-}$ ligands $[Mo_4O_8(OMe)_2(C_4O_4)_2(C_4O_4H)_2]^{4-}$,[221d] as μ_4-bridging $C_4O_4^{2-}$ ligand in $[Mo_4O_{10}F_4(C_4O_4)]^{4-}$,[35b] and as μ_6-bridging $C_4O_4H^-$ ligands in the cluster $[Mo_{12}O_{36}(C_4O_4H)_4]^{4-}$.[221e]

4. Carbonyl Derivatives

The reactions of aldehydes with $(n\text{-}Bu_4N)_2[Mo_2O_7]$ yield $(n\text{-}Bu_4N)_3[RCHMo_4O_{15}H]$ (R = H, CH_3, CF_3, Ph, CHO, CH_3CO)[33] which are assumed to contain isostructural anions best formulated as acetal derivatives $[(RCHCO_2)Mo_4O_{12}(OH)]^{3-}$ according to the X-ray diffraction study of $(n\text{-}Bu_4N)_3[CH_2Mo_4O_{15}H)]$ (Figure 2b).[33b] Indeed, the $H_2CO_2^{2-}$ and OH^- groups are connected by weak Mo−O bonds to opposite sides of an Mo_4O_{12} ring. Attempts to synthesize ketal derivatives $[R_2CMo_4O_{15}H]^{3-}$ were unsuccessful.[33b] The tungsten analogue $[CH_2W_4O_{15}H]^{3-}$ has been prepared from $(n\text{-}Bu_4N)_2[WO_4]$ by recrystallization from dichloromethane,[222] or by reaction of $(n\text{-}Bu_4N)_2[WO_4]$, SeO_2 and a small excess of formaldehyde in acetonitrile,[88a] and found to be isostructural with $[CH_2Mo_4O_{15}H]^{3-}$.

The subsequent reaction of $[(OHCCHO_2)Mo_4O_{12}(OH)]^{3-}$ with HX (HX = HF or HCO_2H) results in the displacement of OH^- by X^- and insertion of the pendent carbonyl group into a Mo−O bond. The flexible $\{RCCHMo_4O_{15}\}^{2-}$ unit is able to accommodate either the F^- anion or the larger HCO_2^- anion.[33a] In contrast to glyoxal and methylglyoxal, the reactions of organic substrates containing the α-diketones, e.g., ninhydrin, benzyl, and phenanthraquinone, with $(n\text{-}Bu_4N)_2[Mo_2O_7]$ proceed directly to the diketal products of the type $[RMo_4O_{15}X]^{3-}$ (R = C_9H_4O, X = OMe; R = $C_{14}H_{10}$, X = $PhCO_2$; R = $C_{14}H_8$, X = OH). In all cases, the α-diketone subunit of the organic ligand is incorporated into the $[RMo_4O_{15}X]^{3-}$ structure by insertion into the Mo−O bonds of adjacent metal centers, to give species which may be alternatively formulated as diketals $[(O_2RO_2)(Mo_4O_{11})X]^{3-}$. The tetranuclear core associated with these complexes possesses sufficient conformational flexibility to accommodate a variety of anions.[215]

B. Silicon Derivatives

Organosilyl derivatives of polyoxometalates were first reported by Knoth who obtained anions of the composition $[SiW_{11}O_{39}\{O(SiR)_2\}]^{4-}$ by reacting $RSiCl_3$ (R = Et, Ph, C_3H_5) with $[SiW_{11}O_{39}]^{8-}$ in unbuffered aqueous solution.[223] These reactions have been reproduced and extended by Nadjo[224] and Hill.[225a] Although no X-ray crystal structures are available on any of these complexes, spectroscopic data provide structural evidence: (i) IR data indicate the presence of a μ-oxo disilyl linking unit;[223,225a] (ii) ^{183}W NMR data establish that all the complexes retain the lacunary unit α-$\{SiW_{11}O_{39}\}^{8-}$;[225a] (iii) ^{29}Si NMR data indicate that the most probable structure has equivalent SiR groups bound perpendicular to the mirror plane bisecting the α-$\{SiW_{11}O_{39}\}^{8-}$ subunit,[225a] as originally proposed by Knoth.[223] Similar compounds have been obtained from α-$[PW_{11}O_{39}]^{7-}$ [225b,c] and α-$[SiW_9Mo_2O_{39}]^{8-}$.[226] These derivatives exhibit substantial hydrolytic stability,[223−225] and high therapeutic indices in cell culture against HIV-1.[225b,c]

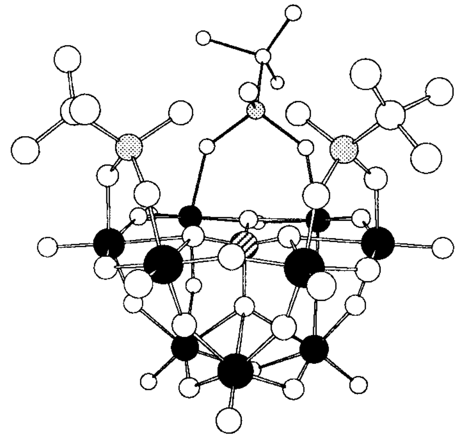


Figure 32. Structure of α-*A*-$[PW_{11}O_{34}(t\text{-}BuSiOH)_3]^{3-}$ (ref 228).

The reactions of chlorosilanes with trivacant polyoxotungstates are currently investigated by Thouvenot and co-workers.[227−229] Under phase-transfer conditions, dichlorosilanes, R_2SiCl_2 (R = Me or Ph), react with α-*A*-$[XW_9O_{34}]^{n-}$ trivacant Keggin species (X = Si, n = 10; X = P or As, n = 9) to give the silyl derivatives $[(\alpha\text{-}A\text{-}XW_9O_{34})(SiR_2)_3]^{(n-6)-}$, which have been characterized by multinuclear NMR spectroscopy.[227,229a] The proposed structure with C_{3v} symmetry has been confirmed by the X-ray diffraction structure determination of $(n\text{-}Bu_4N)_4[SiW_9O_{34}(SiMe_2)_3]$.[229a] Under similar conditions, trichlorosilanes, $RSiCl_3$ yield the anions $[(\alpha\text{-}A\text{-}XW_9O_{34})(SiR)_3(O_3SiR)]^{(n-6)-}$ which are assumed to be isostructual. The C_{3v} structure proposed on the basis of a thorough multinuclear NMR study of $[(\alpha\text{-}A\text{-}SiW_9O_{34})(SiH)_3(O_3SiH)]^{4-}$,[227] has been confirmed by the X-ray diffraction structure determination of α-*A*-$(n\text{-}Bu_4N)_3(Me_2NH_2)[SiW_9O_{34}(SiEt)_3(O_3SiEt)]$.[229a] Whereas n-$BuSiCl_3$ reacts with α-*A*-$[PW_9O_{34}]^{9-}$ to give $[(\alpha\text{-}A\text{-}PW_9O_{34})(SiBu\text{-}n)_3(O_3SiBu\text{-}n)]^{3-}$, the corresponding reaction with t-$BuSiCl_3$ yields only $[(\alpha\text{-}A\text{-}PW_9O_{34})(t\text{-}BuSiOH)_3]^{3-}$ presumably because of steric crowding (Figure 32).[228] The complex $[(\alpha\text{-}B\text{-}AsW_9O_{33})(t\text{-}BuSiOH)_3]^{3-}$ has been similarly obtained by reacting t-$BuSiCl_3$ reacts with α-*B*-$[HAsW_9O_{33}]^{8-}$. These two derivatives have been crystallographically characterized as tetrabutylammonium salts. Both anions display an approximate C_{3v} symmetry and the structure of the parent trivacant polyoxotungstate is retained. Each of the three chemically equivalent t-BuSiOH units is attached to the polyoxotungstate backbone through two W−O−Si bridges. These "open-structure" anions react cleanly with $RSiCl_3$ in DMF to yield $[(\alpha\text{-}A\text{-}PW_9O_{34})(t\text{-}BuSi)_3(RSiO_3)]^{3-}$ and $[(\alpha\text{-}B\text{-}AsW_9O_{33})(t\text{-}BuSi)_3(RSiO_3)]^{3-}$, respectively.[228] Of special interest in the context of the development of novel organic−inorganic hybrids is the reaction of $[(\alpha\text{-}A\text{-}PW_9O_{34})(t\text{-}BuSiOH)_3]^{3-}$ with bis(trichlorosilanes) $Cl_3SiRSiCl_3$, which gives species containing two organically bridged polyoxotungstate subunits.[229b]

Organosilicate-metalate complexes are of interest in modeling oxide surface hydroxyl groups. The simplest conceivable complexes of this type, $R_3SiOMoO_3^-$ (R = Ph, t-Bu) have been reported.[230]

C. Germanium Derivatives

Oganogermyl derivatives of polyoxotungstates were independently reported by Knoth[223,231] and Pope[232] in 1979. Some trichlorogermanes $RGeCl_3$ (R = CpFe-$(CO)_2$ or $Co(CO)_4$) react with lacunary $[XM_{11}O_{39}]^{n-}$ polyanions (X = Si, M = Mo or W, n = 8; X = P, M = W, n = 7) to yield $[XM_{11}O_{39}\{O(GeR)_2\}]^{(n-3)-}$ analogous to the reaction products of $RSiCl_3$.[231] The anion $SiW_{11}O_{39}[O\{GeCo(CO)_4\}_2]^{4-}$ undergoes rapid disproportionation, which gives rise to an inorganic polymer $[\{SiW_{11}O_{40}Ge_2Co(CO)_3\}^{5-}]_n$.[231] In contrast to this behavior, alkyl- and aryltrichlorogermanes react with lacunary $[XW_{11}O_{39}]^{n-}$ polyanions (X = P, Si, Ge, or B) to give $[XM_{11}O_{39}\{O(GeR)_2\}]^{(n-3)-}$ in which a $\{WO\}^{4+}$ unit is replaced by an GeR group (R = Et,[223] Ph[232]). Similar reactions occur with lacunary $[X_2W_{17}O_{61}]^{10-}$ polyanions.[232] The Lindqvist-type derivative $[W_5O_{18}(GePh)]^{3-}$ has been obtained by reacting (n-$Bu_4N)_2[WO_4]$, $PhGeCl_3$, and stoichiometric amounts of HCl in acetonitrile.[88a]

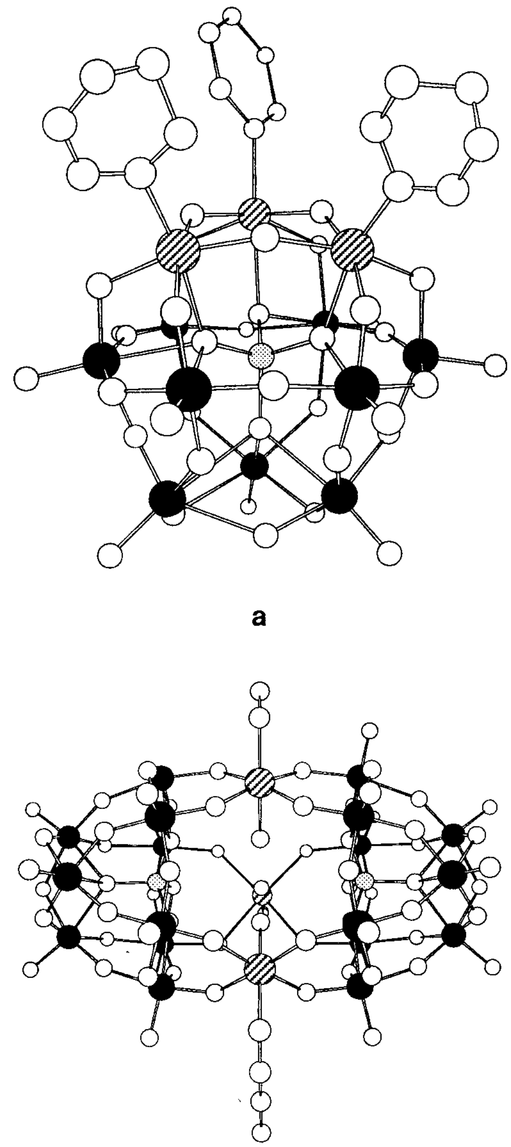
D. Tin and Lead Derivatives

The reports by Knoth[223] and Pope[232] also dealt with the reactions of trichorostannanes $RSnCl_3$ with monovacant Keggin-type[223,232] and Dawson-type[232] lacunary polyanions. These reactions give either mono-(organotin) derivatives $[XM_{11}O_{39}(SnR)]^{(n-3)-}$ (X = Si, n = 8: M = W, R = Me,[223,232] Et, Ph, C_3H_5, $HOCOCH_2$-CH_2CH_2,[223] n-Bu;[232] M = Mo, R = Et[223]) or bis-(organotin) derivatives $[PW_{10}O_{38}(SnR)_2]^{5-}$ (R = Me, Ph),[223] depending on the pH. A number of metal–tin-bonded derivatives $[XW_{11}O_{39}(SnR)]^{(n-3)-}$ (R = Cp-$Fe(CO)_2$, $CpW(CO)_3$, $IrH_2(CO)(PPh_3)_2$, $Rh(C_7H_8)_2$, $Pt(C_6H_4F$-$p)(PEt_3)_2$) have also been reported.[231] Spontaneous disproportionation reaction is observed for R = $Co(CO)_4$, $Fe(NO)(CO)_3$, and $Pd(PPh_3)(\eta^3$-$C_3H_5)$.[231] The 1,5 and 1,4 isomers of $[PW_{10}O_{38}\{SnFeCp(CO)_2\}_2]^{5-}$ have been characterized.[234,235] The chlorotin derivative $[PW_{11}O_{39}(SnCl)]^{3-}$ has also been obtained.[233] These complexes have been isolated as potassium, cesium, trimethylammonium, tetramethylammonium, tetrabutylammonium, trimethylsulfonium, or guanidinium salts and characterized by chemical analysis, vibrational, electronic, ^1H NMR,[223,231,232] and ^{183}W NMR[233–235] spectroscopy, polarography, and X-ray diffraction.[232]

The anion $[P_2W_{17}O_{61}]^{10-}$ reacts with $RSnCl_3$ to give $[P_2W_{17}O_{61}(SnR)]^{7-}$ (R = Ph;[223] R = n-Bu[232]). A single-crystal X-ray diffraction structure determination of the potassium salt of $[P_2W_{17}O_{61}(SnBu$-$n)]^{7-}$ prepared from the α_2-isomer,[236] has shown that the tin occupies a "polar" position in the $P_2W_{12}O_{62}{}^{10-}$ framework.[232] The reaction of $PhSnCl_3$ with $[P_2W_{16}O_{59}]^{12-}$ similarly yields $[P_2W_{16}O_{60}(SnPh)_2]^{8-}$.[223]

Although it was anticipated that γ-$[SiW_{10}O_{36}]^{8-}$ would react with $RSnCl_3$ to give γ-$[SiW_{10}O_{38}(SnR)_2]^{6-}$, only $[\{\gamma$-$SiW_{10}O_{36}\}_2\{PhSn(OH_2)\}_2]^{10-}$ has been obtained by reaction of $PhSnCl_3$ with $K_8[\gamma$-$SiW_{10}O_{36}]\cdot xH_2O$. Its structure of virtual C_{2h} symmetry with two phenyltin groups sandwiched between two γ-SiW_{10} units, is different from all other reported polytungstates derived from $[\gamma$-$SiW_{10}O_{36}]^{8-}$.[237]

The reactions of organotin trichloride with α- or β-$[SiW_9O_{34}]^{10-}$ and with α-$[PW_9O_{34}]^{9-}$ have also been investigated. Two kinds of products, $[SiW_9O_{37}$-$(SnR)_3]^{7-}$ and $[\{SiW_9O_{34}\}_2(RSnOH)_3]^{14-}$, are formed from α- or β-$[SiW_9O_{34}]^{8-}$, depending upon the ratio of $RSnCl_3$ and SiW_9 used. It has been shown that $[SiW_9O_{37}(SnR)_3]^{7-}$ is kinetically stable, but $[\{SiW_9$-$O_{34}\}_2(RSnOH)_3]^{14-}$ is the thermodynamically stable product. The compounds retain the same α- or β-structures as the starting trivacant species. The anion $[\beta$-$SiW_9O_{37}(SnPh)_3]^{7-}$ has a structure with three corner-shared WO_6 octahedra of the β-Keggin anion replaced by three $PhSnO_5$ groups (Figure 33a), and the $[(\alpha$-$SiW_9O_{34})_2(BuSnOH)_3]^{14-}$ has the anticipated symmetry with three BuSnOH groups sandwiched between α-A-$SiW_9O_{34}{}^{10-}$ anions (Figure 33b).[238] The reaction of the metastable A-$[PW_9O_{34}]^{9-}$ anion with n-$BuSnCl_3$ yields $[\{PW_9O_{34}\}_2(n$-$BuSnOH)_3]^{12-}$ which contains three n-BuSnOH groups sandwiched between β-A-$PW_9O_{34}{}^{9-}$ anions.[239] In contrast, the complexes $[\{PW_{11}O_{34}\}_2\{RSn(OH_2)\}_3]^{9-}$ (R = Ph or $CpFe(CO)_2$) are presumed to contain α-A-$PW_{11}O_{34}{}^{9-}$ anions.[235]



a

Figure 33. Structures of $[\beta$-$SiW_9O_{37}(SnPh)_3]^{7-}$ (a) and $[(\alpha$-$SiW_9O_{34})_2(n$-$BuSOH)_3]^{14-}$ (b) (ref 238).

Trisorganotin-substituted Dawson tungstophosphates $[P_2W_{15}O_{59}(SnR)_3]^{9-}$, where R = Ph or n-Bu, have been prepared by reaction of $RSnCl_3$ with Na_{12}-[α-$P_2W_{15}O_{56}$]·24H_2O,[239] and the Lindqvist-type derivative, $[W_5O_{18}(SnPh)]^{3-}$ has been obtained by reaction of $(n\text{-}Bu_4N)_2[WO_4]$ with $PhSnCl_3$ and HCl in acetonitrile.[88a]

Keggin- $[[XW_{11}O_{39}Sn]^{n-}$ (X = P, Si, Ge, B, Ga)] and Dawson-type α_2-$[P_2W_{17}O_{61}Sn]^{8-}$ tungstostannates(II) have been prepared by reaction of $SnSO_4$ with the parent lacunary polyanion at pH ~4. IR spectra, cyclic voltammograms, and ^{31}P NMR spectra indicate that the Sn(II) is too large to fit into the octahedral vacancy but is attached to the exterior of the vacancy as seen in the structure of the Pb(II) derivative, $[GaW_{11}O_{39}Pb]^{7-}$. Oxidation of the preformed tungstostannates(II), e.g. by aqueous Br_2, yields the corresponding tin(IV) derivatives $[XW_{11}O_{39}(SnOH)]^{(n-1)-}$. The tungstostannates(II) react as nucleophiles toward both organic and organometallic compounds.[240] The compound $K_{11}[HSn^{II}_3(PW_9O_{34})_2]\cdot 27H_2O$ has been synthesized in a "one-pot reaction" from $SnCl_2$, $NaH_2PO_4\cdot 7H_2O$, and $Na_2WO_4\cdot 2H_2O$. The anions contains three Sn(II) sandwiched between **A**-$PW_9O_{34}{}^{9-}$ anions.[241]

Organolead-substituted tungstates, e.g., $[BW_{11}O_{39}(PbPh)]^{6-}$, have been reported by Pope,[232] and a Pb(II) derivative, $[GaW_{11}O_{39}Pb]^{7-}$, has been reported by Tourné et al.[242]

VII. Organometallic Derivatives of Polyoxometalates

The chemistry of organometallic oxides is an area of growing interest.[115,243−245] There are two major interests in this field: (i) they may provide models for solid oxide supported organometallic compounds; (ii) the combination of the hard oxo ligand with soft ligands may result in novel properties. Organometallic oxo clusters may be obtained in a variety of ways including (i) oxidative aggregation of low-valent complexes, (ii) reductive aggregation of high-valent organometallic oxo complexes, (iii) reaction of organometallic moieties with preformed complete or defect polyoxometalates, and (iv) self-assembly via acid−base condensation processes involving both hard and soft metal centers.

A. Cyclopentadienyl Derivatives of Polyoxometalates

Oxo and cyclopentadienyl ligands are $\sigma,2\pi$-bonding ligands, which form σ- and π-bonds with metal orbitals of the same symmetry. Despite this analogy, there are only a few authentic cyclopentadienyl polyoxometalates, i.e., species that can be formally derived from polyoxometalates by replacement of oxo ligands by cyclopentadienyl ligands. On the other hand, a significant number of organometallic oxide clusters of groups 5 and 6, and a lot of organometallic polyoxometalates containing M′Cp units where M′ ≠ V, Mo, or W, have been reported. It is also worth noting the recent use of the dicarbollide anion [*nido*-7,8-$C_2B_9H_{11}$]$^{2-}$, which is isolobal with the η^5-C_5R_5 ligands, as an ancillary ligand in the synthesis of metal oxo complexes. The complexes $[(\eta^1\text{-}C_2B_9H_{11})MoO_3]^{2-}$ and $[\{(\eta^5\text{-}C_2B_9H_{11})MoO_2\}_2(\mu\text{-}O)]^{2-}$ have been

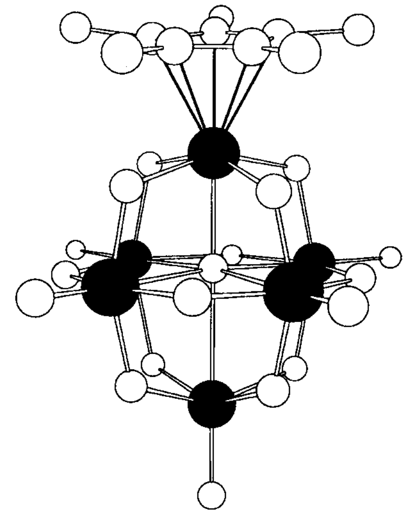


Figure 34. Structure of $[Cp^*Mo_6O_{18}]^-$ (ref 247).

obtained by oxidation of $[[(\eta^5\text{-}C_2B_9H_{11})Mo(CO)_2(SPh)_2]^{2-}$ with PhIO, and structurally characterized.[246] The geometry of the $Mo_2O_5{}^{2+}$ core in $[\{(\eta^5\text{-}C_2B_9H_{11})MoO_2\}(\mu\text{-}O)]^{2-}$ is comparable with that in the analogous complex $[(Cp^*MoO_2)_2(\mu\text{-}O)]$.

Oxidation of $[\{Cp^*Mo(CO)_2\}_2]$ by O_2 in $CHCl_3$ solution yields $[Cp^*Mo_6O_{18}]^-$, as well as $[Cp^*MoOCl_2]$ and $[(Cp^*MoO_2)_2(\mu\text{-}O)]$,[247] while oxidation with $[MeAsO]_4$ yields $[Cp^*{}_6Mo_8O_{16}]$.[248] The oxidation of the tungsten analogue with $[MeAsO]_4$ forms $[Cp^*{}_2W_6O_{17}]$.[248] The anion $[Cp^*Mo_6O_{18}]^-$ (Figure 34) and the neutral cluster $[Cp^*{}_2W_6O_{17}]$ are cyclopentadienyl derivatives of the hexametalates $[M_6O_{19}]^{2-}$ (M = Mo, W) in which one or two O^{2-} have been formally replaced by $(\eta^5\text{-}C_5Me_5)^-$. In both cases, the central oxo ligand is displaced significantly toward the $(\eta^5\text{-}C_5Me_5)$-coordinated metal center(s).[247,248]

B. Cyclopentadienyl Oxide Clusters of Groups 5 and 6

A number $[\{(\eta^5\text{-}C_5R_5)M\}_mO_n]$ clusters, notably of groups 5 and 6 have been synthesized by Bottomley and co-workers, either by oxidative aggregation of low-valent cyclopentadienyl derivatives, e.g., $[M(\eta^5\text{-}C_5R_5)_2]$ (M = V or Cr) and $[\{(\eta^5\text{-}C_5R_5)Mo(CO)_2\}_2]$, with N_2O or O_2, or by reductive aggregation of cyclopentadienyl oxo complexes, e.g., $[(\eta^5\text{-}C_5R_5)MOCl_2]$ (M = V or Mo) with zinc or phosphines.[243,244] The most common structural types are the cubane-type $\{M_4(\mu_3\text{-}O)_4\}$ core, e.g., $[\{CpCr(\mu_3\text{-}O)\}_4]$,[249] the adamantane-type $\{M_4(\mu_2\text{-}O)_6\}$ core, e.g., $[(Cp^*V)_4(\mu_2\text{-}O)_6]$,[250,251] and the alternative $\{M_4(\mu_3\text{-}O)_3(\mu_2\text{-}O)_3\}$ core, which occurs in the clusters $[Cp^*{}_4Mo_5O_{11}]$[251,252] and $[Cp^*{}_6Mo_8O_{16}]$.[248] It is noteworthy that the cluster $[\{CpMo(\mu_3\text{-}O)\}_4]$ has presented a considerable synthetic challenge. Reduction of $[CpMoOCl_2]$ has now given $[(CpMoO)_4]$, but this is not a cubane.[120]

C. Organometallic Polyoxometalates

Complexation of organometallic cations by polyoxometalates has been developed mainly by Knoth,[223] Day and Klemperer,[11,253] Finke,[254] and Isobe.[70] Polyoxometalates provide models for metal oxide surfaces. Given the difficulties in determining the structures

Table 7. Polyoxometalate-Incorporated Organometallic Complexes

complex	ref
$[(CpTi)Mo_5O_{18}]^{3-}$	257−259
$[(Cp^*Ti)Mo_5O_{18}]^{3-}$	260
$[(CpTi)W_5O_{18}]^{3-}$	259
$[(Cp^*Ti)W_5O_{18}]^{3-}$	261
$[PW_{11}O_{39}(TiCp)]^{4-}$	223,256
$[PW_{11}O_{39}(M'Cp^*)]^{4-}$ (M′ = Ti, Zr, Hf)	253
$[SiM_{11}O_{39}(TiCp)]^{5-}$	223
$[\{Mn(CO)_3\}Mo_2O_4\{MeC(CH_2O)_3\}_2]^-$	73a,175b
$[\{Mn(CO)_3\}_2Mo_2O_4\{MeC(CH_2O)_3\}_2]$	
$[\{Mn(CO)_3\}_2Mo_6O_{16}(OMe)_2\{MeC(CH_2O)_3\}_2]^{2-}$	

and therefore the mechanisms of oxide-supported catalysts, polyoxoanion-supported transition metal complexes might provide a correlation between atomic-level structure and function for catalysis by solid oxide-supported analogues. Perhaps more importantly, they also provide new types of catalyst systems where rational catalyst design and molecular fine-tuning is possible, and have their own potentially unique reactivity and chemistry.[254]

The difference between organometallics supported on, and incorporated into, a polyoxometalate, has been emphasized by Finke.[255] Polyoxoanion-supported organometallics mean species that are firmly attached to a κ^3-O site of surface oxygens of the support, while in polyoxometalate-incorporated organometallics, the organometallic moiety is incorporated into a vacancy in the polyoxometalate framework by four, approximately square-planar, oxo ligands. However, there are a few cases where the organometallic moiety is attached to the polyoxometalate framework by either one or two oxo ligands.

1. Polyoxometalate-incorporated Organometalic Complexes (Table 7)

The first reported organometallic polyoxometalate, $[PW_{11}O_{39}(TiCp)]^{4-}$, was obtained by reaction of $(n\text{-}Bu_4N)_4[H_3PW_{11}O_{39}]$ with $[CpTiCl_3]$ in 1,2-$C_2H_4Cl_2$.[256] This derivative, as well the silicate analogues, $[SiM_{11}O_{39}(TiCp)]^{5-}$ (M = W or Mo), have also been prepared by an aqueous route.[223] Reaction of $(n\text{-}Bu_4N)_4[H_3PW_{11}O_{39}]$ with $[Cp^*MCl_3]$ proceeds similarly to give the $[PW_{11}O_{39}(MCp^*)]^{4-}$ anions (M = Ti, Zr, and Hf).[253] The solid-state structure of $(n\text{-}Bu_4N)_4[PW_{11}O_{39}(TiCp^*)]$ has been determined.[253] The Lindqvist-type derivatives $[\{(\eta^5\text{-}C_5R_5)Ti\}M_5O_{19}]^{3-}$ (M = Mo, R = H,[257−259] and Me;[260] M = W, R = H,[259] and Me[261]) have been obtained by mixing stoichiometric quantities of $(n\text{-}Bu_4N)_2[WO_4]$ or $(n\text{-}Bu_4N)_2[Mo_2O_7]$, $[Cp_2TiCl_2]$ or $[Cp^*TiCl_3]$, and H_2O, HCl or $(n\text{-}Bu_4N)OH$ in CH_2Cl_2 or CH_3CN. The species $[(CpTi)Mo_5O_{19}]^{3-}$ [258,259] and $[H(Cp^*Ti)Mo_5O_{19}]^{2-}$ [260] have been structurally characterized. The trans bond length alternation pattern that results from the metal center substitution, provides a mechanism for surface charge delocalization.[259] In contrast to the $[PW_{11}O_{39}(TiCp)]^{4-}$ anion,[256] the $[(CpTi)Mo_5O_{18}]^{3-}$ is decomposed by atmospheric moisture.[257] This instability may arise in part from relatively high negative charge density on the surface of the $Mo_5O_{18}^{6-}$ unit.[258] The Cp* derivatives[260,261] are significantly more stable, which has been ascribed to the bulk of the Cp* ligand.[260] The complexes $[\{(\eta^5\text{-}C_5R_5)Ti\}Mo_5O_{19}]^{3-}$ (R = H, Me) have higher basicity than the tungsten analogues.

Cyclopentadienyltitanium Keggin- and Dawson-type phosphotungstates bearing reactive organic groups on the Cp ring suitable for selective attachment to macromolecular sites have been prepared by Keana and co-workers by reacting $[(\eta^5\text{-}C_5H_4R)Ti(NMe_2)_3]$ derivatives with preformed defect polyoxoanions $[PW_{11}O_{39}]^{7-}$ and α_2-$[P_2W_{17}O_{61}]^{10-}$.[262] These proved to be stable under a variety of conditions that lead to modification of the organic appendage, and visible individually by using conventional transmission electron microscopy.[262c] Moreover, the nonspecific electrostatic precipitation of these anionic species with cationic biomolecules could be prevented by specially designed alkylammonium ligands.[262d]

Quite recently, we have obtained a novel series of polyoxometalate-incorporated organometallic complexes from mixtures of $(n\text{-}Bu_4N)_2[Mo_2O_7]$, $[MnBr(CO)_5]$, and $MeC(CH_2OH)_3$ in methanol. The species $[\{Mn(CO)_3\}Mo_2O_4(tris)_2]^-$, $[\{Mn(CO)_3\}_2Mo_2O_4(tris)_2]$, and $[\{Mn(CO)_3\}_2Mo_6O_{16}(OMe)_2(tris)_2]^{2-}$ can be derived formally from $[Mo_3O_7(OR)(tris)_2]^-$, $[Mo_4O_8(OR)_2(tris)_2]$, and $[Mo_8O_{20}(OMe)_4(tris)_2]^{2-}$, respectively, by replacing one or two *fac*-$\{MoO_2(OR)\}^+$ units by *fac*-$\{Mn(CO)_3\}^+$ units.[73a,175b,c]

2. Polyoxometalate-Supported Organometallic Complexes (Table 8)

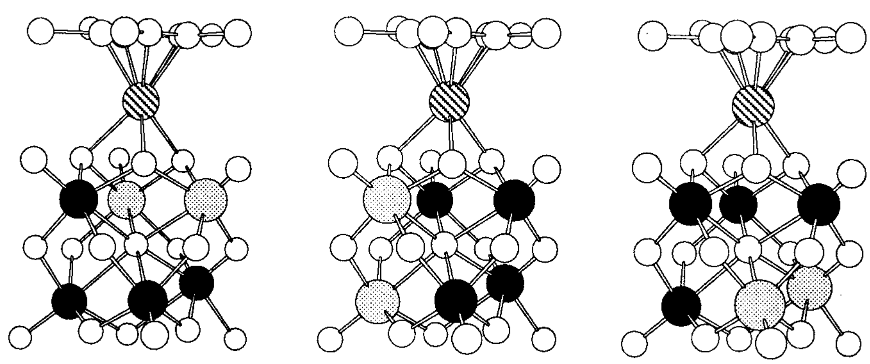
There are a limited number of polyoxometalates containing sufficient charge density at their surface oxygens to covalently bind metals or organometallics. However, surface activation may be achieved by replacing Mo(VI) or W(VI) centers by one or more lower valent metals. For example, whereas the hexametalates $[M_6O_{19}]^{2-}$ are unreactive, the $[\{(\eta^5\text{-}C_5R_5)Ti\}M_5O_{19}]^{3-}$, $[NbW_5O_{19}]^{3-}$, and *cis*-$[Nb_2W_4O_{19}]^{4-}$ ions form stable adducts with a variety of cations.

Since the report of the first metal carbonyl adducts, $[(OC)_3M\cdot Nb_2W_4O_{19}]^{3-}$ (M = Mn and Re) in 1980,[263a] the synthesis and characterization of polyoxometalate-supported organometallic derivatives has received much attention. In most cases, the synthetic strategy has been to react organic-soluble forms of the polyoxometalates, generally via tetrabutylammonium counterions, with organometallic reagents in organic solvents such as CH_3CN or CH_2Cl_2. However, the aqueous route has also been exploited.

a. Complete Lindqvist-Type Polyoxometalate-Supported Complexes. Studies by Klemperer and Day's group have been mainly concerned with Lindqvist-type species such as the *cis*-$[Nb_2W_4O_{19}]^{4-}$, $[\{(\eta^5\text{-}C_5R_5)Ti\}M_5O_{18}]^{3-}$ (M = Mo, W), and $[M'W_5O_{19}]^{3-}$ (M′ = Nb, Ta) ions. Reaction of these hexametalates, as tetrabutylammonium salts, with a number of organometallic complexes in nonaqueous solvents yield adducts which have been isolated as tetrabutylammonium salts and characterized using single-crystal X-ray diffraction, and IR and ^{17}O NMR spectroscopy. The *cis*-$[Nb_2W_4O_{19}]^{4-}$ forms 1:1 adducts with d^6 metal centers such as $M(CO)_3^+$ (M = Mn and Re),[263] $Ru(Arene)^{2+}$ (Arene = C_6H_6 and *p*-cymene),[264] and Cp^*Rh^{2+}.[265] As anticipated based on previous work

Table 8. Polyoxoanion-Supported Organometallic Complexes

support	organometallic moiety	stoichiometry	ref
cis-$[Nb_2W_4O_{19}]^{4-}$	$(OC)_3M^+$ (M = Mn, Re)	1:1	263
	Cp^*Rh^{2+}	1:1	265
	$(\eta^6\text{-Arene})Ru^{2+}$	1:1	264
	$(NBD)Rh^+$	2:5	267
	$(1,5\text{-COD})Ir^+$	1:1	268
	$(1,5\text{-COD})Ir^+$	2:2	268
	$(OC)_2Rh^+$	2:5, 2:3	269
	$(OC)_2Ir^+$	2:2	269
	$(1,5\text{-COD})(MeCN)ClRu^+$	2:5	270
$[Mo_5O_{18}(TiCp)]^{3-}$	$(OC)_3Mn^+$	1:1	258
	Cp^*Rh^{2+}	1:1	253
$[Mo_5O_{18}(TiCp^*)]^{3-}$	$(1,5\text{-COD})Ir^+$	1:1	260
$[W_5O_{18}(TiCp^*)]^{3-}$	$(C_6H_6)Ru^{2+}$	1:1	264
	$Ru_2(CO)_4{}^{2+}$	2:1	271
$[M'W_5O_{19}]^{3-}$ (M′ = Nb, Ta)	Cp_3Ac^+ (Ac = U, Th)	2:1	272
$[TiW_5O_{19}]^{4-}$	Cp_2U^{2+}	2:2	273
$[V_6O_{19}]^{8-}$	Cp^*Rh^{2+}, Cp^*Ir^{2+}	1:4	274,275
$[Mo_5O_{13}(OMe)_4(NO)]^{3-}$	$Cp^*Rh(H_2O)^{2+}$, $(Cp^*Rh)_2(\mu\text{-X})^{3+}$	1:1	277
	$(OC)_3Mn^+$	1:1	175b
β-$[SiW_9V_3O_{40}]^{7-}$	$CpTi^{3+}$	1:1	255,281
β-$[SiW_9Nb_3O_{40}]^{7-}$	Cp^*Rh^{2+}		282
	$(1,5\text{-COD})Ir^+$	1:1	286
$[P_2W_{15}V_3O_{62}]^{9-}$	$CpTi^{3+}$	1:1	281
$[P_2W_{15}Nb_3O_{62}]^{9-}$	$CpTi^{3+}$	1:1	281
	Cp^*Rh^{2+}	1:1	283,285
	$(\eta^6\text{-}C_6H_6)Ru^{2+}$	1:1	283,285
	$(OC)_3Re^+$	1:1	288
	$(OC)_2Ir^+$	1:1	288
	$(1,5\text{-COD})Ir^+$	1:1	13,254,280,287
$[P_4W_{30}Nb_6O_{123}]^{16-}$	$Ir_{\sim 300}$ cluster		280
$[V_4O_{12}]^{4-}$	$(1,5\text{-COD})Ir^+$	1:1, 1:2	293
	$(1,5\text{-COD})Rh^+$	1:1, 1:2	295
	$(\eta^4\text{-}C_4H_7)_2Rh^+$	1:2	294a
	$(\eta^4\text{-}C_8H_{14})Rh^+$	1:2	294a
	$(\eta^4\text{-}C_6H_{10})Rh^+$	1:2	296
	$(1,5\text{-COD})(MeCN)_2Ru^{2+}$	1:1	270



a b c

Figure 35. The three diastereomers of $[(OC)_3Mn{\cdot}Nb_2W_4O_{19}]^{3-}$ (from ref 263).

by Stucky, using $[Nb_6O_{19}]^{8-}$,[266] the $[Nb_2W_4O_{19}]^{4-}$ ligand is coordinated to the metal center by a triangle of three adjacent bridging OM_2 oxygens. ^{17}O NMR spectroscopy provides conclusive evidence for the three possible diastereomers of $[(OC)_3M{\cdot}Nb_2W_4O_{19}]^{3-}$ (Figure 35),[263] while either two- or three-diastereomer mixtures were obtained in other cases. A disordered arrangement is observed in the solid state for all X-ray structurally characterized compounds.

In contrast, d^8 metal centers such as $Rh(NBD)^+$,[267] $Ir(1,5\text{-COD})^+$,[268] and $M(CO)_2{}^+$ (M = Rh, Ir)[269] form 5:2 adducts in which two $[Nb_2W_4O_{19}]^{4-}$ ions are linked together in a face-to-face fashion by five organometallic centers (Figure 36). The 3:2 adduct $[\{(OC)_2Rh\}_3(Nb_2W_4O_{19})_2]^{5-}$ [269] and the 2:2 adducts $[\{(1,5\text{-COD})Ir\}_2H(Nb_2W_4O_{19})_2]^{5-}$ [268] and $[\{(OC)_2Ir\}_2H(Nb_2W_4O_{19})_2]^{5-}$ [269] have also been characterized. The latter contains two $[Nb_2W_4O_{19}]^{4-}$ ions linked together in an edge-to-edge fashion by two organometallic units and one proton.[269] The compound $(n\text{-}Bu_4N)_3[\{RuCl(1,5\text{-COD})(MeCN)\}_5\{(Nb_2W_4O_{19})_2]{\cdot}3H_2O$, obtained by reaction of $(n\text{-}Bu_4N)_4[Nb_2W_4O_{19}]{\cdot}1.5H_2O$ with $[RuCl(COD)(MeCN)_3]BF_4$ in CH_2Cl_2, was similarly supposed to contain two $[Nb_2W_4O_{19}]^{4-}$ anions linked, face-to-face by five organometallic centers.[270]

The $[(CpTi)Mo_5O_{18}]^{3-}$ ions form 1:1 adducts with metal units such as $Mn(CO)_3{}^+$,[258] Cp^*Rh^{2+},[253] and MoO_2Cl^+,[258] which are all bonded to a triangle of three doubly bridging OMo_2 oxygens. The similar 1:1 adducts, $[(1,5\text{-COD})Ir{\cdot}Mo_5O_{18}(TiCp)]^-$ and $[(\eta^6\text{-}C_6H_6)$-

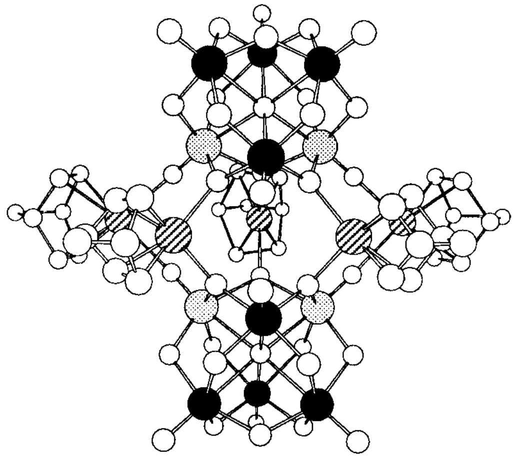


Figure 36. Drawing of the C_{2v} structure proposed for an isolated nondisordered $[\{(NBD)Rh\}_5(Nb_2W_4O_{19})_2]^{3-}$ anion (ref 267).

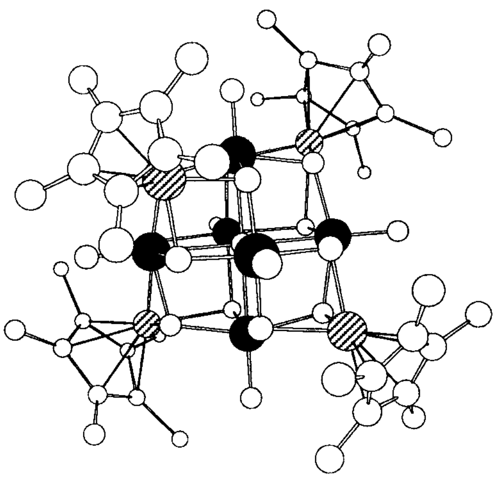


Figure 37. Structure of $[(Cp^*Rh)_4V_6O_{19}]$ (ref 274).

$Ru{\cdot}W_5O_{18}(TiCp^*)]^-$,[264] and the $Ru^I{-}Ru^I$ tetracarbonyl complex $[(Cp^*Ti)W_5O_{18}\}_2\{Ru_2(CO)_4\}]^{4-}$ [271] have also been characterized and are assumed to contain κ^3-O-$[(Cp'Ti)M_5O_{18}]^{3-}$ (Cp′ = Cp, Cp*; M = Mo, W) ligands.

The $[M'W_5O_{19}]^{3-}$ ions (M′ = Nb, Ta) react with Cp_3-AcCl (Ac = Th^{IV} and U^{IV}) to form an isostructural series of $[Cp_3Ac(MW_5O_{19})_2]^{5-}$ anions where the actinide center is σ-bonded to the terminal ONb oxygens of two $MW_5O_{19}{}^{3-}$ ions.[272] In contrast, the reaction of $[ClTiW_5O_{19}]^{3-}$ with Cp_3UCl gives the dimeric $[(Cp_2U)_2(\mu$-κ^2-O-$TiW_5O_{19})_2]^{4-}$ anion.[273]

Neutral organometallic oxide clusters $[(Cp^*Rh)_4$-$V_6O_{19}]$ (M = Rh,[274,275] Ir[275]) have been obtained by aqueous routes. They can be viewed as one hexavanadate $\{V_6O_{19}\}^{8-}$ unit capped by four Cp^*M^{2+} groups, or alternatively as amphiphilic quadruple-cubane-type clusters (Figure 37). Together with trisalkoxo derivatives they represent the only examples of the $\{V_6O_{19}\}$ core. Mixed clusters $[(Cp^*Rh)_{4-n}(Cp^*Ir)_nV_6O_{19}]$ ($0 \leq n \leq 4$) have been obtained by dissociation and substitution of RhCp* in $[(Cp^*Rh)_4V_6O_{19}]$.[275b] $[(Cp^*Rh)_4V_6O_{19}]$ catalyzes the oxidation of cyclohexene with *tert*-butyl hydroperoxide to give mainly allylic oxidation products.[276]

b. Lacunary Lindqvist-Type Polyoxometalate-Supported Complexes. The lacunary Lindqvist-type derivative $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$,[14] is sufficiently basic to react with organometallic cations. Two complexes, $[Mo_5O_{13}(OMe)_4(NO)\{RhCp^*(H_2O)\}]^-$ (Figure 38) and $[Mo_5O_{13}(OMe)_4(NO)\{(RhCp^*)_2(\mu$-$Br)\}]$, have been structurally characterized. They represent unique polyoxoanion-supported organometallic complexes where the organometallic moiety is bound to the terminal oxygen atoms of the open face of a lacunary polyoxoanion.[277] Different coordination modes are observed in $(n$-$Bu_4N)_3[Na\{Mo_5O_{13}(OMe)_4(NO)\{Mn$-$(CO)_3\}_2]$ which has been obtained by reaction of $(n$-$Bu_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]{\cdot}x$MeOH with $[MnBr(CO)_5]$ in methanol. The $Mn(CO)_3{}^+$ moiety is bound to two methoxo ligands and to one bridging oxo ligand, while the sodium cation achieves eight coordination by interaction with the terminal oxygen atoms of two $[Mo_5O_{13}(OMe)_4(NO)\{Mn(CO)_3\}]^{2-}$ units.[175b]

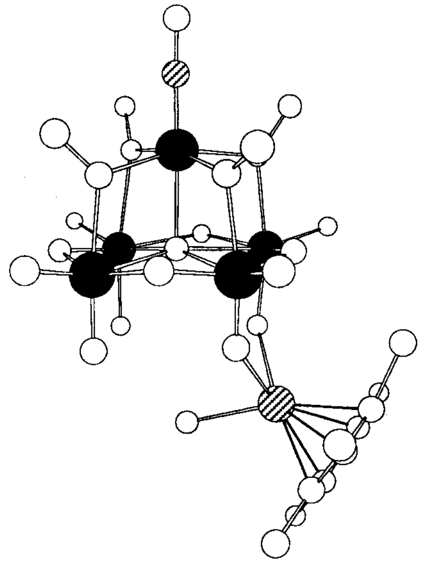


Figure 38. A view of the structure of the anion $[Mo_5O_{13}$-$(OMe)_4(NO)\{RhCp^*(H_2O)\}]^-$ (ref 277).

c. Keggin- and Dawson-Type Polyoxometalate-Supported Complexes. Finke and co-workers have extensively developed the chemistry of custom-designed trisubstituted heteropolyoxotungstates, β-$[SiW_9M_3O_{40}]^{7-}$ and $[P_2W_{15}M_3O_{62}]^{9-}$ (M = V and Nb), as soluble metal analogues.[278,279] Their efforts have been directed toward the synthesis and characterization of these polyoxoanions and their supported organometallics, and catalytic studies of these precatalysts. This work has led to the first polyoxoanion-supported catalyst precursor, $[(1,5\text{-COD})Ir{\cdot}P_2W_{15}$-$Nb_3O_{62}]^{8-}$.[254,280]

$CpTi^{3+}$,[255,281] Cp^*Rh^{2+},[282−285] $(C_6H_6)Ru^{2+}$,[283,285] (1,5-COD)Ir^+,[13,254,280,286,287] (1,5-COD)Rh^+,[13] $Re(CO)_3{}^+$, and $Ir(CO)_2{}^+$,[288] complexes have been isolated as their all-$(n$-$Bu_4N)^+$, all-Na^+, or mixed $(n$-$Bu_4N)^+/Na^+$ salts. These complexes have been characterized by complete elemental analyses, FAB-MS, IR, and multinuclear NMR spectroscopy. Solution structures have been derived from spectroscopic data. In addition, the X-ray crystallographic analysis of $(n$-$Bu_4N)_6Na$-$[Cp^*Rh{\cdot}P_2W_{15}Nb_3O_{62}]{\cdot}10MeCN{\cdot}10Me_2CO$ has provided the only solid-state structure of a Dawson-type polyoxometalate-supported organometallic complex

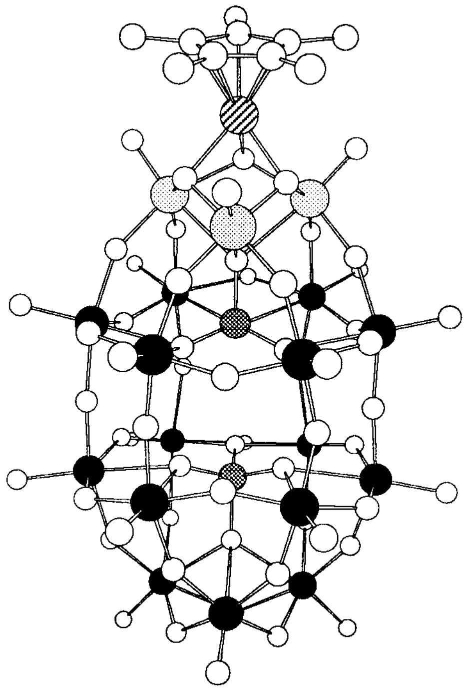


Figure 39. Structure of $[Cp^*Rh\cdot P_2W_{15}Nb_3O_{62}]^{7-}$ (ref 285).

(Figure 39).[285] All three $[Cp^*Rh\cdot SiW_9Nb_3O_{40}]^{5-}$,[282] $[CpTi\cdot SiW_9V_3O_{40}]^{4-}$,[255] and $[CpTi\cdot P_2W_{15}V_3O_{62}]^{6-}$ [281] ions have overall C_s symmetry. The structure derived from spectroscopic data for $[Cp^*Rh\cdot SiW_9Nb_3O_{40}]^{5-}$ is the one where the Cp^*Rh^{2+} group is attached to three Nb—O—W bridging oxygens of a B-type triad of NbW_2 edge-sharing octahedra; the most probable structure for $[CpTi\cdot SiW_9V_3O_{40}]^{4-}$ is the one where the $CpTi^{3+}$ group is attached to two V—O—W bridging oxygens plus one V═O terminal oxygen of a B-type triad array of VW_2 octahedra,[255,281] while that for $[CpTi\cdot P_2W_{15}V_3O_{62}]^{6-}$ is the one where the $CpTi^{3+}$ group is attached to two V—O—V bridging oxygens plus one V═O terminal oxygen.[281] The C_s symmetry of $[CpTi\cdot P_2W_{15}V_3O_{62}]^{6-}$ contrasts the C_{3v} or pseudo-C_{3v} symmetry of the related triniobium complexes $[Cp^*Rh\cdot P_2W_{15}Nb_3O_{62}]^{6-}$, $[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}]^{7-}$,[283,285] and $[(1,5\text{-COD})Ir\cdot P_2W_9Nb_3O_{62}]^{8-}$.[287] It has been suggested that the C_s site is the sterically least congested site of kinetic attack, while the C_{3v} product might be the more stable, thermodynamic product. The $[(1,5\text{-COD})M\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ complex is fluxional in a process that makes the three Ir—O bonds all equivalent on the ^{17}O NMR time scale.

The Dawson-type polyoxoanion-supported $Re(CO)_3^+$ and $Ir(CO)_2^+$ complexes, $[(OC)_3Re\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ and $[(OC)_2Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ have been synthesized and characterized in two different countercation compositions.[288] While both all-$(n\text{-}Bu_4N)^+$ compounds exist as a single C_{3v} isomer in solution, added Na^+ can induce the formation of non C_{3v} symmetry isomers. When Na^+ is removed from these systems, the non C_{3v} isomers convert back to the single, C_{3v} isomer with heating, thereby providing a model system for the mobility of $M(CO)_n^+$ cations on an oxide surface.[288]

The air sensitivity of the $[(1,5\text{-COD})Ir\cdot P_2W_9Nb_3O_{62}]^{8-}$ complex has been exploited in developing its

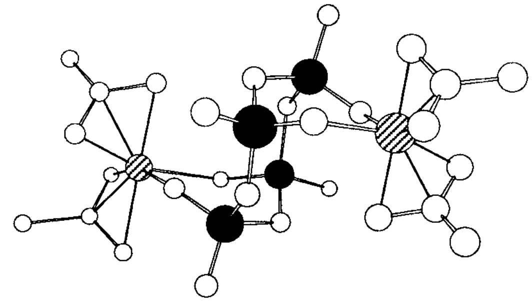


Figure 40. Structure of $[\{\eta^3\text{-}C_4H_7)_2Rh\}_2(V_4O_{12})]^{2-}$ (ref 294a).

catalytic oxidation chemistry with O_2.[255,289] This complex is as efficacious a precatalyst for O_2/isobutyraldehyde/cyclohexene coepoxidation as any reported.[289] Mechanistic studies confirm that the actual catalyst is indeed polyoxoanion supported. In contrast, the true catalysts in the active hydrogenation system, which evolves from cyclohexene, hydrogen, and $(n\text{-}Bu_4N)_5Na_3[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]$, are polyoxoanion/$n\text{-}Bu_4N^+$ stabilized $Ir_{\sim 300}$ nanoclusters.[280] Spectroscopic evidence indicates that the $[P_2W_{15}Nb_3O_{62}]^{9-}$ has been converted to its well-known Nb—O—Nb-bridged aggregate form, $[P_4W_{30}Nb_6O_{123}]^{16-}$. These $Ir_{\sim 300}\cdot$polyoxoanion nanoclusters are unique in terms of their combination of isolability, well-defined composition, and yet high catalytic activity and relatively long catalytic lifetimes in solution.[290] A novel polyoxoanion-stabilized $Rh^0{}_n$ 1 to 4 nm nanocluster is formed upon photolysis of the unstable rhodium complex $(n\text{-}Bu_4N)_8[Rh(CO)_2\cdot P_2W_{15}Nb_3O_{62}]$.-$(n\text{-}Bu_4N)BF_4$ under H_2 in anhydrous EtOH in the presence of cyclohexene.[288] These results bear a strong analogy to Yate's work studying atomically dispersed $Rh(CO)_2^+$ on solid alumina, which establishes one of the best connections between the reaction chemistry of a polyoxoanion-supported and a solid oxide-supported organometallic.[291]

The so-called ϵ-Keggin structure is observed in the complex $[(Cp^*Rh^{III})_8(Mo_{13}O_{40})]^{2+}$ which has been prepared hydrothermally as a chloride salt from $[(Cp^*Rh)_2(\mu\text{-}OH)_3]Cl$ and $MoO_3\cdot 2H_2O$. This complex can be viewed as a hexamer of $Mo^V{}_2O_{10}$ units encapsulating a tetrahedral $Mo^{VI}O_4^{2-}$ anion. The eight Rh(III) centers cap the eight faces of the $Mo^V{}_{12}$ truncated tetrahedron and form two interpenetrating $Rh^{III}{}_4$ tetrahedra.[292]

d. Metavanadate-Supported Complexes. A number of $[M_n(V_4O_{12})]^{(4-n)-}$ complexes (M = (1,5-COD)Ir, n = 1, 2;[293] M = $(\eta^3\text{-}C_4H_7)_2Rh$ (Figure 40), $(\eta^4\text{-}C_8H_{14})Rh$, n = 2;[294a] M = (1,5-COD)Rh, n = 1, 2;[295] M = $(\eta^4\text{-}C_6H_{10})Rh$, n = 2[296]) have been reported. They have related structures consisting of a $\{V_4O_{12}\}^{4-}$ ring with one or two M^+ moieties bonded to two terminal oxygen atoms of two adjacent vanadium centers. Dynamic NMR suggests an intramolecular mechanism such as pivoting is responsible for the fluxionality of these complexes in solution.[296] Fluxional behavior has also been observed for $[Ru(1,5\text{-COD})(MeCN)_2(V_4O_{12})]^{2-}$ and $[Ru(1,5\text{-COD})(MeCN)_2(HV_4O_{12})]^-$.[270]

In the presence of $P(OEt)_3$, the complex $[\{(\eta^3\text{-}C_4H_7)_2Rh\}_2(V_4O_{12})]^{2-}$ undergoes C—C coupling to give

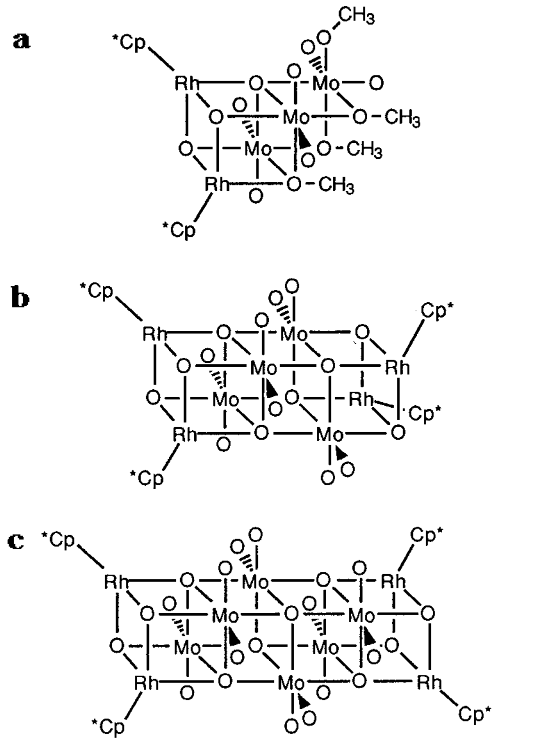


Figure 41. Schematic representations of $[(Cp^*Rh)_2Mo_3O_9(OMe)_4]$ (a), $[(Cp^*Rh)_4Mo_4O_{16}]$ (b), and $[(Cp^*Rh)_4Mo_6O_{22}]$ (c) (ref 298).

$[\{(\eta^4\text{-}C_8H_{14})Rh\}_2(V_4O_{12})]^{2-}$. This compares to the release of 1,5-hexadiene from oxide-supported bis(allyl)rhodium complexes by the action of a nucleophile, but contrasts the reaction of $[(\eta^3\text{-}C_4H_7)_2Rh(acac)]$ with $P(OEt)_3$ which produces a mixture of organic compounds. These results show that the vanadate support has a significant influence on the reactivity of organometallic complexes.[294b] SiO_2-grafted $(n\text{-}Bu_4N)_2[\{(\eta^3\text{-}C_4H_7)_2Rh\}_2(V_4O_{12})]$ and $[(Cp^*Rh)_4V_6O_{19}]$, as molecular models of supported Rh catalysts characterized by EXAFS and FTIR studies, exhibit high selectivities for the selective oxidation of propene to acetone.[276b]

3. Integrated Cubane-Type Clusters

Isobe and co-workers have developed the synthesis of integrated cubane-type clusters as potential models for inorganic solid surfaces.[70] They have demonstrated the possibility of triggering the condensation of monomeric oxometalates by Lewis acidic coordination compounds which have vacant coordination sites. This results in the building of an oxide framework on the Lewis acidic center. In this fashion, the reaction of $[\{Cp^*IrCl(\mu\text{-}Cl)\}_2]$ with Na_2MoO_4 in water gives $[(Cp^*M)_4Mo_4O_{16}]\cdot nH_2O$ (M = Rh, $n = 2$; M = Ir, $n = 0$) (Figure 41b). These clusters consist of a triple cubane framework with a central Mo_4O_4 core and two external $M_2Mo_2O_4$ cores. The M atoms have a distorted octahedral geometry and achieve 18-electron configuration by binding three adjacent bridging O atoms and a Cp* ring. This triple cubane-type structure can be viewed as a representation of the infinite layer structure of MoO_3.[297]

Methanol in the presence of *p*-hydroquinone partly breaks the triple fused cubic framework of $[(Cp^*Rh)_4Mo_4O_{16}]$ to give an incomplete double cubane-type cluster $[(Cp^*Rh)_2Mo_3O_9(OMe)_4]$ (Figure 41a). There are several short interactions between doubly bridged methoxy carbons and terminal Mo=O oxygens in the structure of $[(Cp^*Rh)_2Mo_3O_9(OMe)_4]$, indicating the existence of short C–H···O intramolecular contacts.[298] The proton transfer between these methoxy groups and oxygen atoms would lead to the formation of HCHO molecules, which is observed on dissolving the cluster in CH_2Cl_2 and results in the formation of the linear quadruple cubane-type cluster $[(Cp^*Rh)_4Mo_6O_{22}]$ (Figure 41c). Short contacts are also observed between the oxygen atom of a bridging methoxy group and the carbon atom of another. Methyl transfer between these methoxy groups would yield Me_2O and other organic molecules, e.g., HCOOMe, observed on heating the compound.[298] On the other hand, methanethiol induces a reconstruction of the triple cubane-type framework of $[(Cp^*Rh)_4Mo_4O_{16}]$, separating the organometallic and oxide parts with formation of the new octamolybdate salt $[(Cp^*Rh)_2(\mu_2\text{-}SMe)_3]_4[Mo_8O_{26}]$.[98] A novel organometallic oxide cluster $(n\text{-}Bu_4N)_2[(Cp^*Rh)_2Mo_6O_{20}(OMe)_2]$ with multivalley sites has been recently reported.[299] Its framework is in some respect similar to that of the $\gamma\text{-}[Mo_8O_{26}]^{4-}$ isomer.[98] It reacts with $[\{Cp^*RhCl)(\mu\text{-}Cl)\}_2]$ and with $(n\text{-}Bu_4N)_2[Mo_2O_7]$ in methanol to produce $[(Cp^*Rh)_2Mo_3O_9(OMe)_4]$ and $[(Cp^*Rh)_4Mo_4O_{16}]$, respectively. The cluster $[\{(p\text{-}Pr^iC_6H_4Me)Ru\}_4Mo_4O_{16}]$ which is isoelectronic to $[(Cp^*Rh)_4Mo_4O_{16}]$, has a different structure: the $Ru_4Mo_4O_{12}$ framework can be described as a central cube with 4-folded ORuO flaps resembling the sails of a windmill.[300]

4. Organometallic Cation Salts of Keggin-Type Anions

Siedle and co-workers have developed the solid-state chemistry of materials derived from Keggin-type anions. $[L_nM(PG)]_x[XM_{12}O_{40}]$ (X = P, $x = 3$; X = Si, $x = 4$) where $L_nM(PG)^+$ represents a metal center, M, bonded to an accompanying array of ligands L, and a protective group PG chosen that it can be easily removed, have been prepared by metathetic reaction of $[L_nM(PG)]^+$ salts with hydrated $(H_3O)_x[XM_{12}O_{40}]$ in organic solvents.[301] The compound $[(Ph_3P)_3Ir(1,5\text{-}COD)]_3[PW_{12}O_{40}]$ represents a prototypical catalytic system. The cyclooctadiene protective group can be removed by heterogeneous hydrogenolysis, forming $[(Ph_3P)_2IrH_2]_3[PW_{12}O_{40}]$.[302a] The analogous reaction with D_2 produces cyclooctane containing up to 16 deuterium atoms. This has been interpreted in terms of C–H activation involving Ir–*D*–C–*H* exchange in an intermediate species containing coordinated cyclooctene.[303] Orthometalation and hydrogen transport in $[(Ph_3P)_2IrH_2]_3[PW_{12}O_{40}]$ have been probed by ^{31}P long-range deuterium isotope effects.[302b]

Iridium and rhodium EXAFS data on $[(Ph_3P)_2IrH_2]_3[PMo_{12}O_{40}]$[301] and $[(Ph_3P)_2Rh(CO)]_4[SiW_{12}O_{40}]$[304] have been interpreted to mean that the Ir···Mo and Rh···W separations are ≥4 Å, and that, in turn, there is no significant Ir–O–Mo or Rh–O–W bonding. Thus, it is believed that these compounds contain interstitial 14-electron $(Ph_3P)_2IrH_2^+$ and $(Ph_3P)_2Rh$-

(CO)$^+$ ions, respectively.[304] The heterogeneous reactions of $[(Ph_3P)_2IrH_2]_3[PW_{12}O_{40}]$ with small organic molecules have been reported and described in terms of either addition of iridium to a C—H bond or addition of Ir—H to a C═C bond. It has been proposed that the reactants gain access to the iridium sites by dissolving in the hydrophobic regions of the lattice. Solid state ^{2}H NMR show that, even at low temperature, small organic molecules have substantial motional freedom.[305] It has been shown that $[(Ph_3P)_2Rh(CO)]_x[XW_{12}O_{40}]$ are bifunctional catalysts for hydroformylation of olefins and subsequent oxidation of aldehydes to carboxylic acids.[304]

The compound $[(Cp^*Rh)_2(\mu\text{-}Cl)_3](PPN)_2[PMo_{12}O_{40}]\cdot$4DMF which has been obtained by reaction of $[\{Cp^*RhCl_2\}_2]$ with $(PPN)_3[PMo_{12}O_{40}]\cdot Me_2CO$ in DMF, represents the only X-ray structurally characterized example of an organometallic salt of a Keggin polyoxoanion.[306]

VIII. Concluding Remarks

Functionalization of polyoxometalates is quite attractive for its relevance to quite diverse disciplines. Although the first organic derivatives of polyoxometalates were obtained at the turn of the century, this field really began to develop in the late 1970s. A quite large number of organic and organometallic derivatives have now been synthesized and characterized in solution and in the solid state. In addition to further expanding the structural diversity of polyoxometalates, derivatization provides complex species with novel and multifunctional properties. One of the most challenging objectives is that of obtaining derivatives with predetermined structures and properties. Although systematic studies in nonaqueous solutions have allowed the synthesis of a number of covalent derivatives, hydrolytically stable derivatives are clearly needed in order to enhance the potential utility of polyoxometalates in catalysis, chemotherapy, and material science.

Quite promising results have been already obtained in the context of catalytic applications.[307] Organometallic derivatives of polyoxometalates represent a growing class of oxide-supported catalysts or precatalyts that can be fully investigated at the atomic level, both structurally and mechanistically, and close connections between the chemistry of polyoxoanion-supported organometallics and that of solid oxide-supported organometallics have been established.

Increasing attention is currently being paid to intermolecular complexes between polyoxometalates and organic substrates. These include model compounds for polyoxometalate-protein interactions,[308] photensensitive complexes between polyoxometalates and electron-rich organic substrates, and compounds with a nonlinear optical response.[309] Worthy noncatalytic applications of polyoxometalates include their use as electronic materials.[310,311] Indeed, polyoxometalates have attractive features for the synthesis of molecular materials with unusual associations of properties, e.g., electrical and magnetic properties. With respect to the field of molecular materials, derivatization of polyoxometalates might provide efficient pathways to favor electronic coupling within charge-transfer materials based on organic donors and might allow the incorporation of polyoxometalates in conducting polymers.

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X. Abbreviations

X	halide
Z	variable group
R	alkyl
Me	methyl
Et	ethyl
Pr	propyl
Bu	butyl
Ar	aryl
Ph	phenyl
Bz	benzyl
Tol	tolyl
Cp	$(\eta^5\text{-}C_5H_5)$
Cp*	$(\eta^5\text{-}C_5Me_5)$
1,5-COD	$(\eta^4\text{-}C_8H_{12})$
NBD	norbornadiene
DMF	dimethylformamide
THF	tetrahydrofuran
acac	acetylacetonate
tca	thiophene-2-carboxylate
metO	methioninate
py	pyridine
bpy	2,2′-bipyridine
pzH	pyrazole
imH	imidazole
PPN	bis(triphenylphosphine)nitrogen(1+) cation

Note Added in Proof

A number of polyoxovanadates with structurally equivalent $[V_{18}O_{42}]$ shells but different electron populations and with unusual host−guest chemistry, including a cluster compound with an encapsulated SH^- ion, have been recently reported (Müller et al. *Inorg. Chem.* **1997**, *36*, 5239). A new type of hybrid inorganic−organometallic host, composed of a cubane-type $[W_4O_{16}]^{8-}$ unit capped by size $[Zr(1,5\text{-}COD)]^+$ groups, has been recently reported (Finke et al. *J. Am. Chem. Soc.* **1997**, *119*, 11401).

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