PROGRESS IN INORGANIC CHEMISTRY

Edited by

KENNETH D. KARLIN

DEPARTMENT OF CHEMISTRY
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND

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Oxovanadium and Oxomolybdenum Clusters and Solids Incorporating Oxygen-Donor Ligands

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I. INTRODUCTION

A. General Considerations

All the elements of the periodic table except the lighter noble gases form oxides, and most elements form more than one binary compound with oxygen (1). The structural chemistry of oxides is extensive, encompassing simple molecular species, complex oligomeric clusters, and solid state phases exhibiting chain, layer, and three-dimensional (3D) network structures. Thus, the metal–oxo unit $\{M{=}O\}$ is a fundamental constituent both of soluble metal–oxo complexes of varying nuclearities and of complex metal oxide solids.

The metal oxide clusters known as the polyoxometalates or polyoxoanions constitute an important subclass of the metal oxide system. These clusters, which are characteristic of the early transition elements, exhibit an extensive chemistry including both isopolyanions $[M_xO_y]^{n-}$, which contain only a transition element together with oxygen and hydrogen, and the heteropolyanions $[X_aM_xO_y]^{n-}$, which contain one or more atoms of other elements in addition to M. While such "naked" core polyoxoanions, that is, metal oxide clusters that do not incorporate organic ligands, have provided the major focus in the development of the chemistry of metal oxide clusters, the past decade has witnessed the emergence of a considerable coordination chemistry of polyoxoanions, which is characterized by metal oxide cores incorporating a variety of organic ligands or fused to organometallic fragments.

B. Historical Perspective

While polyoxoanions have been known since the time of Berzelius (2), the first polyanions to contain covalently attached organic groups were not reported until the early twentieth century (3, 4) and their structures remained enigmatic until the mid-1970s (5, 6). The structural characterizations of $(NH_4)_6[(HCO)_2Mo_8O_{28}]\cdot 2H_2O$ (5), first described by Miolati (3) in 1908, and of $[(R_2AsO_2)Mo_4O_{13}H]^{2-}$ (6), prepared by Rosenheim and Belicki (4) in 1913 signaled the emergence of interest in the coordination chemistry of polyoxoanions. The dramatic developments in the area of polyoxoanion coordination chemistry received significant impetus from several seminal contributions:

1. The synthesis and characterization of a variety of metal–oxo–organophosphonato and metal–oxo–organoarsonato clusters by Pope and coworkers in the 1970s (7–9).
2. Systematic studies of polyoxoanions in inert, aprotic solvents by Day and Klemperer (10) in the early 1980s, which allowed the preparation of a number of novel covalent derivatives.

3. The introduction of templates to direct the self-assembly of complex metal oxide ligand shells and a new appreciation for the relationship of polyanion coordination chemistry to host–guest and host–hostage chemistry by Müller and co-workers (11–13) in the late 1980s.
4. The expansion of synthetic methodologies afforded by the exploitation of solvothermal methods introduced by Klemperer and co-workers (14) and Jacobson and co-workers (15, 16).

The dramatic expansion of the coordination chemistry of polyoxoanions in the past decade is also linked to a growing interest in these materials as models for surface bound intermediates in the selective catalytic oxidations and/or dehydrogenations of organic substrates by metal oxide solids, as versatile synthetic precursors for the preparation of complex solid state phases with designed properties, and as potential catalysts and sorbent materials. Furthermore, polyoxoanion coordination compounds are of intrinsic interest as a consequence of their diverse structures, complex magnetic properties, and rich electrochemistry.

C. Scope of This Chapter

In view of the extensive literature on polyoxoanions and the availability of a number of excellent reviews on the general subject, the scope of the discussion has been limited generally to oxovanadium and oxomolybdenum clusters incorporating simple organic ligands with oxygen-donor atoms. This choice is predicated on the dominant role of organic ligands with oxygen donors in the coordination chemistry of polyoxoanions and on the extensive chemistry of the oxovanadium and oxomolybdenum cores in comparison to other metal–oxo functionalities. To keep this chapter within manageable proportions, clusters derived from polyoxometalate cores by oxo-group substitution, such as nitrido (17), organoimido (18), nitrosyl (19), and hydrazido groups (20) have been excluded, as have the growing classes of polyoxometalates supporting organometallic subunits, whether of the transition metal or main group types (10, 21–25).

The general field of polyoxoanion chemistry is enormous, with over 1000 well-characterized complexes reported in the literature. An excellent overview of the area and a comprehensive literature review to 1983 is available in the monograph by Pope (26). The more recent literature has been discussed in updated reviews (27, 28), and the current status of the field is well represented in the book edited by Pope and Müller (29). More specialized reviews on the structural systematics of various classes of polyoxoanion clusters (30, 31) and on polyanion coordination chemistry (20, 32, 33) have also appeared in recent years.

In view of the rapid developments in the area of polyanion coordination chemistry and the absence of a comprehensive overview of the topic, this chapter is timely, exploring the literature up to the beginning of 1994. More specifically, the chapter discusses the ligand types and the rationales for their choice (see Section II), the synthetic methodologies adopted in the preparations of the clusters (see Section III), some general principles of the structural chemistry (see Section IV), and the detailed structural characteristics of the complexes (see Sections V–VII). This latter discussion is structured by ligand type, whether of the conventional organic classes (alkoxide, carboxylate, or carbon oxo anion) or of organophosphonate or organoarsonate types, and further subdivided according to cluster nuclearity (see Tables I–V). We have chosen not to discuss the enormous literature on complexes of nuclearity less than three, unless these are intimately related to the higher nuclearity species as synthetic precursors or structural prototypes. Triangular cores that possess reduced metal sites and fewer oxo groups than metal centers, such as the triangular Mo^{IV} and V^{III} carboxylate clusters, have also been excluded.

II. LIGAND TYPES

While an extensive coordination chemistry of polyoxoanions incorporating ligands with nitrogen, oxygen, and sulfur donors and supporting organometallic subunits has emerged in the past two decades, our discussion in this chapter will focus on two general classes of ligands with oxygen-donor groups: (a) the more or less conventional ''organic ligands, such as alkoxides, carboxylates, acetals, and carbon oxo anions; and (b) the organophosphonate, organoarsonate, and related ligand types.

Several general features of the coordination of these ligand types with polyoxoanions merit comment. The introduction of such ligand types vastly expands the coordination chemistry of polyoxoanions both by providing charge compensation by the substitution of peripheral O^{2-} oxo groups with mononegative ligands in ''classical'' compact polyanion structures (Section III) and by allowing structure expansion and/or modification through bridging interactions. While ''naked'' polyanion structures exhibit frameworks necessarily constructed exclusively from $\{MO_5\}$ square pyramids and/or $\{MO_6\}$ octahedra, the structural diversity of the coordination clusters reflects the introduction of ligand tetrahedra into the cluster framework. In addition to providing this diversity of structural types, metal oxide coordination clusters serve as models for the interactions of substrate molecules with metal oxides in heterogeneous catalysis, as potential precursors for the synthesis of new solid materials and supramolecular assemblies, and as materials with useful catalytic and sorptive properties of their own.

TABLE I
Oxovanadium Clusters with Alkoxide, Carboxylate, Carbon Oxo Anion and Related Ligand Types

Complex	Ligand Type[a]	References
a. Trinuclear Cores		
$[(VO)_3(thf)(PhCO_2)_6]$ **(1)**	C2	111
$[(VO)_3(sal)_3(MeOH)_3]$ **(2)**	A1, sal[b]	116
$[\{RC(CH_2O)_3V_3\}P_2W_{15}O_{59}]^{6-}$ **(3)**	TA3	120
b. Tetranuclear Cores		
$[V_4O_8(C_2O_4)_4(H_2O)_2]^{4-}$ **(4)**	Terminal bidentate	121
$[V_4O_8(NO_3)(\text{thiophene-2-carboxylate})_4]^{2-}$ **(5)**	C2	122
$[V_4O_7(OH)(O_2CR)_4K]^+$ **(6)**	C2	124
$[(VO)_4(H_2O)_2(SO_4)_2\{(OCH_2)_3CR\}_2]^{2-}$ **(7)**	TA5	127
$[V_4O_6Cl_2(OCH_2CR_2CH_2OH)_4]$ **(8)**	BA1	128
$[V_2Mo_2O_8(OMe)_2\{(OCH_2)_3CR\}_2]^{2-}$ **(9)**	A1, TA3	127
$[V_4O_2(acac)_4(OMe)_6]$ **(10)**	A2, Terminal bidentate acac	129
c. Pentanuclear Core		
$[V_5O_9Cl(\text{thiophene-2-carboxylate})_4]^{2-}$ **(11)**	C2	122
d. Hexanuclear Cores		
$[V_6O_{10}(PhCO_2)_9]$ **(22)**	C2	154
$[V_6O_{12}(OMe)_7]^{1-}$ **(12a)**	A2	141
$[V_6O_{13}(OMe)_3\{(OCH_2)_3CR\}]^{2-}$ **(12)**	A2, TA3	139
$[V_6O_{13}\{(OCH_2)_3CR\}_2]^{2-}$ **(13)**	TA3	142
$[V_6O_{11}(OH)_2\{(OCH_2)_3CR\}_2]$ **(14)**	TA3	146
$[V_6O_{10}(OH)_3\{(OCH_2)_3CR\}_2]^{2-}$ **(15)**	TA3	149
$[V_6O_9(OH)_4\{(OCH_2)_3CMe\}_2]^{2-}$ **(16)**	TA3	146
$[V_6O_7(OH)_6\{(OCH_2)_3CMe\}_2]^{2-}$ **(17)**	TA3	146
$[V_6O_8\{(OCH_2)_3CEt\}_2\{(OCH_2)_2CEt(CH_2OH)\}_4]^{2-}$ **(13a)**	BA2, TA5	139
$Ba[V_6O_7(OH)_3\{(OCH_2)_3CMe\}_3]$ **(18)**	TA3	152
$(Me_3NH)[V_6O_7(OH)_3\{(OCH_2)_3CMe\}_3]$ **(19)**	TA3	152, 153
$Na_2[V_6O_7\{(OCH_2)_3CEt\}_4]$ **(20)**	TA3	152, 153
$Na[(VO)_6F(OH)_3\{(OCH_2)_3CMe\}_3]$ **(21)**	TA3	152
$[V_6O_{10}(PhCO_2)_9]$ **(22)**	C2	154
$[(VO)_6(CO_3)_4(OH)_9]^{5-}$ **(23)**	CA1, CA2	155, 156
e. Octanuclear and Larger Nuclearity Cores		
$[(VO)_8(OMe)_{16}(C_2O_4)]^{2-}$ **(24)**	A2, O4	160
$[V_9O_{16}(bdta)_4]^{7-}$ **(28)**	bdta[c]	162
$[V^{IV}_{10}O_{13}\{(OCH_2)_3CMe\}_5]^{1-}$ **(32)**	TA3	163
$[V^{IV}_{10}O_{16}\{(OCH_2)_3CR\}_4]^{4-}$ **(29)**	TA3	163, 164
$[V^{IV}_8V^{V}_2O_{16}\{(OCH_2)_3CR\}_4]^{2-}$ **(30)**	TA3	165
$[V^{IV}_{10}O_{14}(OH)_2\{(OCH_2)_3CR\}_4]^{2-}$ **(31)**	TA3	165
$[V_{15}O_{36}(CO_3)]^{7-}$ **(25)**	CA2	161
$[H_6V_{10}O_{22}(RCO_2)_6]^{2-}$ **(26)**	C2	11
$[H_2V_{22}O_{54}(MeCO_2)]^{7-}$ **(27)**	Encapsulated RCO_2^-	11
$[V_{16}O_{20}\{(OCH_2)_3CR\}_8(H_2O)_4]$ **(33)**	TA3	166

TABLE I (*Continued*)

Complex	Ligand Type[a]	References
f. Polymeric Materials		
$(Ph_4P)[VOCl(C_2O_4)]$ **(36)**	O2	172
$K_2[VO(HCO_2)_4]$ **(35)**	C1 and anti-anti form of C2	171
$VO(OMe)_3$ **(34)**	A1, A2	167

[a] Ligand types refer to the common binding modes illustrated in Figs. 1, unless otherwise noted.
[b] Salicylhydroximate = sal, $-OC_6H_4C(O)NHO^-$.
[c] Butanediaminetetracetic acid = bdta, $\{(O_2CCH_2)_2N(CH_2)_4N(CH_2CO_2)_2\}^{4-}$.

TABLE II
Oxovanadium Organophosphonate, Organoarsonate, and Related Clusters

Complex	Ligand Type	References
a. Tetranuclear Cores		
$[V_4O_6(PhPO_3)_4F]^{1-/2-}$ **(39, 40)**	P4	178
$[(VO)_4\{PhP(O)_2OP(O)_2Ph\}_4Cl]$ **(41)**	See text	179
b. Pentanuclear Core		
$[V_5O_7(OMe)_2(PhPO_3)_5]^{1-}$ **(42)**	A1, P4	89
c. Hexanuclear Cores		
$[V_6O_{10}(PhAsO_3)_4(PhAsO_3H)_2]^{2-}$ **(45)**	P3, P4	180
$[V_6O_{10}(PhPO_3)_4(PhPO_3H)_2]^{2-}$ **(44)**	P3, P4	180
$[(VO)_6(t\text{-}BuPO_3)_8Cl]$ **(43)**	P4	179
d. Heptanuclear Core		
$[V_7O_{12}(PhPO_3)_6Cl]^{2-}$ **(46)**	P4	182
e. Decanuclear Core		
$[V_{10}O_{24}(H_2NC_6H_4AsO_3)_3]^{4-}$ **(47)**	P4	180
f. Dodecanuclear Cores		
$[H_{12}(VO_2)_{12}(PhPO_3)_8(H_2O)_4]^{4-}$ **(48)**	P4	15
$[2(MeOH)V_{12}O_{14}(OH)_4(PhAsO_3)_{10}]^{4-}$ **(51)**	P4	131
$[(VO)_{12}(OH)_2(PhAsO_3)_{10}(PhAsO_3H)_4]^{4-}$ **(50)**	P3, P4	131
$[(V_4O_8)_2\{(VO)_4(H_2O)_{12}\}(PhPO_3)_4Cl_2]^{2-}$ **(49)**	P4	184
g. Tetradecanuclear Cores		
$[2(NH_4Cl)V_{14}O_{22}(OH)_4(H_2O)_2(PhPO_3)_8]^{6-}$ **(52)**	P4	12
$[2(MeCN)_2V_{14}O_{22}(OH)_4(PhPO_3)_8]^{6-}$ **(53)**	P4	131
h. Hexadecanuclear Cores		
$[H_6(VO_2)_{16}(MePO_3)_8]^{8-}$ **(54)**	P4	15
$[H_8(VO_2)_{16}(PhAsO_3)_8]^{6-}$ **(55)**	P4	185
i. Octadecanuclear Core		
$[V_{18}O_{25}(H_2O)_2(PhPO_3)_{20}Cl_4]^{4-}$ **(56)**	P4	179

TABLE III

Oxovanadium Organophosphonate Solid State Phases

Complex	Ligand Type	References
a. One-Dimensional Phases		
$[H_2N(CH_2CH_2)_2NH_2][VO\{CH_2(PO_3)_2\}]$ (**57**)	P1	191
b. Two-Dimensional Phases		
$[VO(PhPO_3)(H_2O)]$ (**58**)	P4	186
$[Et_2NH_2][Me_2NH_2][(VO)_4(OH)_2(PhPO_3)_4]$ (**60**)	P4	188
$[Et_4N]_2[(VO)_6(OH)_2(H_2O)_2(EtPO_3)_6]$ (**61**)	P4	189
$[EtNH_3][(VO_3)(H_2O)(PhPO_3)_4]$ (**59**)	P4	187
$[(VO)_2\{CH_2(PO_3)_2\}(H_2O)_4]$ (**63**)	P4	190
$[H_3NCH_2CH_2NH_3][(VO)(O_3PCH_2CH_2PO_3)]$ (**64**)	P1	191
$[H_2N(CH_2CH_2)_2NH_2][(VO)_2(O_3PCH_2CH_2CH_2PO_3)_2]$ (**66**)	P4	*a*
$[V_2O_4(PhAsO_3H)(H_2O)]$ (**62**)	P3	181
c. Pillared Two-Dimensional Phases		
$(H_3NCH_2CH_2NH_3)[(VO)_4(OH)_2\{O_3PCH_2CH_2CH_2PO_3\}_2]$ (**65**)	P4	191

[a] V. Soghomonian, R.C. Haushalter, and J. Zubieta, unpublished results.

A. Alkoxides, Carboxylates, Carbon Oxo Anions, and Related Ligand Types

The major products of heterogeneous catalysis are formed by O_2 oxidations that employ transition metal oxides to effect dehydrogenation and/or oxygen atom transfer to the substrate (34). Given the versatility of metal oxides in catalyzing organic transformations, the chemical processes that occur on these surfaces are of considerable interest. Since oxide surfaces adopt complex structures that are difficult to characterize on a molecular level (35), particularly with respect to surface bound intermediates, the relatively simple soluble metal oxides have received increasing attention as models for the more complex systems. As Day and Klemperer (10) pointed out, the relationship between polyoxoanions and solid oxides extends beyond simple size considerations to fundamental aspects of structure and bonding, such that the chemical information elicited from the molecular systems is not only of intrinsic interest but may provide insights into the complex solid systems.

The recently described polyoxoalkoxymetalates $[M_aO_b(OR)_c]^{x-}$ represent a particularly prominent subclass of polyanion coordination compounds that are of considerable interest by virtue of their relationship to the oligomeric metal alkoxides, a major class of inorganic materials (36–41). Metal alkoxides display a range of reactivity patterns (42–48), including catalytic activity (48) and in their high oxidation states are versatile molecular precursors of oxides of high purity and a variety of "high tech" materials, including catalyst supports, biomaterials, and ceramics (49–58). The relationship of polyoxoalkoxymetalate to both the metal oxide and metal alkoxide systems identifies these clusters as

TABLE IV

Oxomolybdenum Clusters with Alkoxide, Carboxylate, Carbon Oxo Anion, and Related Ligand Types

Complex	Ligand Type	References
a. Trinuclear Cores		
$[Mo_3O_8(OMe)(C_4O_4)_2]^{3-}$ (**67**)	A3, SA1	192
$[Mo_3O_8(pinacolate)_2]^{2-}$ (**68**)	BA1	193
$[Mo_3O_7\{Me(OCH_2)_3CMe\}_2]^{2-}$ (**69**)	TA2, TA3	83
$[Mo_3O_6(OMe)\{(OCH_2)_3CMe\}_2]^{1-}$ (**70**)	A1	83
$[Mo_3O_9(dmso)_4]$ (**71**)	See text	196
b. Tetranuclear Cores		
$[Mo_4O_{10}(OMe)_6]^{2-}$ (**72**)	A1, A2, A3	84, 199
$[Mo_4O_{10}(OMe)_4Cl_2]^{2-}$ (**73**)	A2, A3	84, 199
$[Mo_4O_{10}(C_6H_2O_4)_2]^{2-}$ (**74**)	See text	217, 218
$[Mo_4O_8(OEt)_2\{(OCH_2)_3CR\}_2]$ (**75**)	A1, TA5	200
$[Mo_4O_{10}(OMe)_2(OC_6H_4O)_2]^{2-}$ (**76**)	A2, bidentate catecholate	199
$[Mo_4O_8(OMe)_2(HOMe)_2Cl_4]^{2-}$ (**77**)	A2	199
$[Mo_4O_8(OEt)_2(HOEt)_2Cl_4]^{2-}$ (**78**)	A2	200
$[Mo_4O_6(OPr)_4(HOPr)_2Cl_4]$ (**79**)	A1, A2	203
$[Mo_4O_8(OPr)_4(py)_4]$ (**80**)[a]	A2	204
$[Mo_4O_{11}(malate)_2]^{2-}$ (**81**)	C1, C3	210, 211
$[Mo_4O_{11}(citrate)_2\}^{4-}$ (**82**)	C1, C3	212, 213
$[Mo_4O_6Cl_2(O_2CR)_6][R = O_2CMe$ (**83a**) or $O_2C_6H_4Me$ (**83b**)	C3	214, 215
$[CH_2Mo_4O_{15}H]^{3-}$ (**84**)	CA3	207
$[(HCCH)Mo_4O_{15}X]^{3-}$ [X = F (**85a**) or HCO_2 (**85b**)]	CA4	208
$[(C_9H_4O)Mo_4O_{15}(OMe)]^{3-}$ (**86**)	A2, CA4	209
$[(C_{14}H_{10})Mo_4O_{15}(PRCO_2)]^{3-}$ (**87**)	C3, CA4	209
$[(C_{14}H_8)Mo_4O_{15}(OH)]^{3-}$ (**88**)	CA4	209
$[Mo_4O_8(OMe)_2(C_4O_4)_2(C_4O_4H)_2]^{4-}$ (**89**)	A2, SA1, and monodentate $HC_4O_4^-$	206
$[Mo_4O_6(OH)_4(CO_3)(CO)_2(PMe_3)_6]$ (**90**)	CA3	216
c. Pentanuclear Core		
$[Mo_5O_{16}(OMe)]^{3-}$ (**91**)	A2	192
d. Hexanuclear Core		
$[Mo_6O_{10}(OPr)_{12}]$ (**92**)	A1, A2	219
e. Octanuclear Cores		
$[Mo_8O_{26}(HCO)_2]^{6-}$ (**93**)	Monodentate	5
$[Mo_8O_{24}(OH)_4(sal)_2]^{2-}$ (**94**)	Monodentate through oxygen donor	220
$[Mo_8O_{24}(OH)_2(met)_2]^{4-}$ (**95**)	Monodentate through carboxylate oxygen	202
$[Mo_8O_{24}(OMe)_4]^{4-}$ (**96**)	A2	195
$[Mo_8O_{20}(OMe)_4\{(OCH_2)_3CR\}_2]^{2-}$ (**97**)	A1, A2, TA5	221
$[H_2Mo_8O_{24}(OMe)_2]^{4-}$ (**98**)	A2	205
$[Mg_2Mo_8O_{22}(OMe)_6(HOMe)_4]^{2-}$ (**99**)	A2	222
$[Mo_8O_{16}(OMe)_8(C_2O_4)]^{2-}$ (**100**)	A2, O4	223
$[Mo_8O_{16}(OMe)_8(PR_3)_4]$ (**101**)	A2	224
f. Dodecanuclear Cores		
$[Mo_{12}O_{36}(C_4O_4H)_4]^{4-}$ (**102**)	SA3	225
g. Superclusters		
$[Na(H_2O)_3H_{15}Mo_{42}O_{109}\{(OCH_2)_3CCH_2OH\}_7]^{7-}$ (**103**)	TA3	227a
$[Mo_{43}H_{13}O_{112}\{(OCH_2)_3CMe\}_7]^{10-}$ (**104**)	TA3	227b

[a] Pyridine = py.

TABLE V

Oxomolybdenum Clusters with Organophosphonate, Organoarsonate, and Related Ligand Types

Complex	Ligand Type	References
a. Trinuclear Core		
$[Mo_3O_9(O_3PCMe(O)PO_3)]^{5-}$ **(105)**	XXIV	228
b. Tetranuclear Cores		
$[Mo_4O_8\{MeC_6H_4AsO_2(Cl)\}_4Cl]$ **(106)**	See text (P1)	230
$[Mo_4O_8\{PhAsO_2(Cl)\}_4Cl][MoOCl_4]$ **(106a)**		230
$[Mo_4O_{13}H(Me_2AsO_2)]^{2-}$ **(107)**	P3	6
$[Mo_4O_{10}(PhPO_3)_4]^{4-}$ **(108)**	P2	230
$\alpha - [Mo_4O_{10}(PhAsO_3)_4]^{4-}$ **(109)**	P1, P5	230
$\beta - [Mo_4O_{10}(C_7H_7AsO_3)_4]^{4-}$ **(110)**	P1, P5	230
b. Pentanuclear Cores		
$[Mo_5O_{15}(RPO_3)_2]^{n-}$ **(111)**	P7	7,231
$R = -Me, -Ph; n = 4$		
$R = -CH_2N(CH_2)_4O; n = 2$		232
$[Mo_5O_{15}(C_3H_7AsO_3)_2]^{4-}$ **(111a)**	P7	100
c. Hexanuclear Cores		
$[Mo_6O_{18}(RAsO_3)_2]^{4-}$ **(112)**	P6	9
$[Mo_6O_{18}(RPO_3)_2]^{4-}$ **(118)**	P7	
$[Mo_6O_{18}(H_2O)(PRAsO_3)_2]^{4-}$ **(113)**	P5, P6	8
$[Mo_6O_{18}(H_2O)_6(MeAsO_3)]^{2-}$ **(114)**	P6	238
$[Mo_6O_{17}\{HOCH(PO_3)_2\}_2]^{6-}$ **(115)**	P2	234
$[Mo_6O_{17}\{OCH(PO_3)_2\}_2]^{8-}$ **(116)**	P2	228
$\{M[Mo_6O_{15}(PhPO_3H)_3(PhPO_3)]_2\}^{9-}$ **(117)** $M = Na^+$ or K^+	P1, P6	236-237
d. Dodecanuclear Core		
$[Mo_{12}O_{34}(H_3NC_6H_4AsO_3)_4]$ **(119)**	P6	6(d)

models for the initial stages in the sol–gel process (59). As such, the development of the chemistry of the polyoxoalkoxymetalates may provide insights into controlling the aggregation process and providing useful synthetic precursors amenable to some degree of molecular engineering.

B. Organophosphonates, Organoarsonates, and Related Ligand Types

The organophosphonates and organoarsonates provide effective bridging groups linking metal–oxo fragments $\{MO\}_n$ in unusual oligomeric species and even solid phases of various dimensionalities. Indeed, the metal–organophosphonate system specifically spans a rich variety of coordination chemistry including mononuclear coordination compounds (60, 61), linear one-dimensional (ID) complexes (62), and layered solid compounds (63–65). The layered metal organophosphonates exhibit unusual sorptive and catalytic properties and serve as catalyst supports and ion exchangers (66–70). Most specifically, the oxovanadium organophosphonate solids, exemplified by $[VO(PhPO_3)] \cdot H_2O$, possess structurally well-defined internal void spaces and coordination sites that intercalate alcohols by coordination of the substrate molecule to the vanadium centers of the inorganic V/P/O layer. The shape selectivity of these phases in absorbing alcohols is related to the steric constraints imposed by the organic residues of the phosphonates surrounding the metal sites and to the interplay of hydrophobic and hydrophilic domains in the structure (71). Since the functional groups of these solids may be introduced through the organic moiety of the

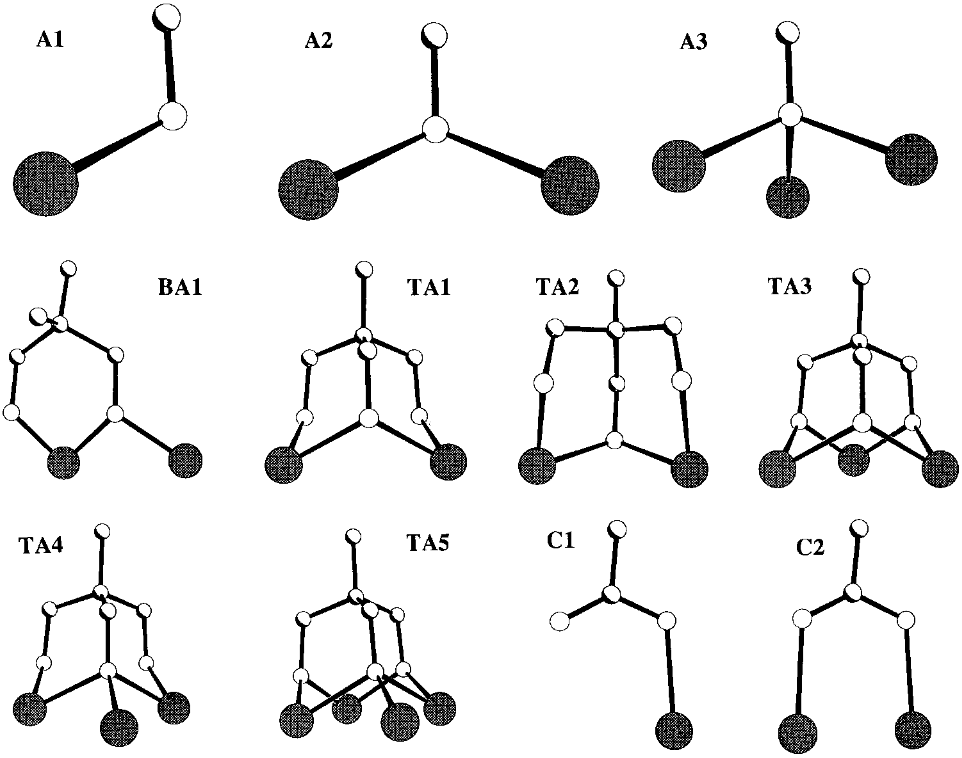


Figure 1. Schematic views of representative coordination modes adopted by the oxygen-donor ligands discussed in this chapter. The atom-labeling scheme, which is consistently maintained throughout this chapter, depicts vanadium or molybdenum atoms as cross-hatched circles, phosphorus or arsenic as circles lined from bottom left to top right, oxygen atoms as open circles, and carbon atoms as highly highlighted circles. A1: terminal alkoxide; A2: μ^2-bridging alkoxide; A3, μ^3-bridging alkoxide; BA1, mixed bridging and terminal mode adopted by bisalkoxides; TA1–TA5, coordination modes adopted by trisalkoxide ligand types; C1–C3, coordination modes adopted by carboxylate ligands; SA1–SA3, common coordination modes for squaric acid and hydrogen squarate; O1–O4, oxalate coordination modes; CA1 and CA2, common coordination modes for carbonate; CA3 and CA4, acetal or ketal coordination types; P1–P7, organoarsonate and organophosphonate coordination modes.

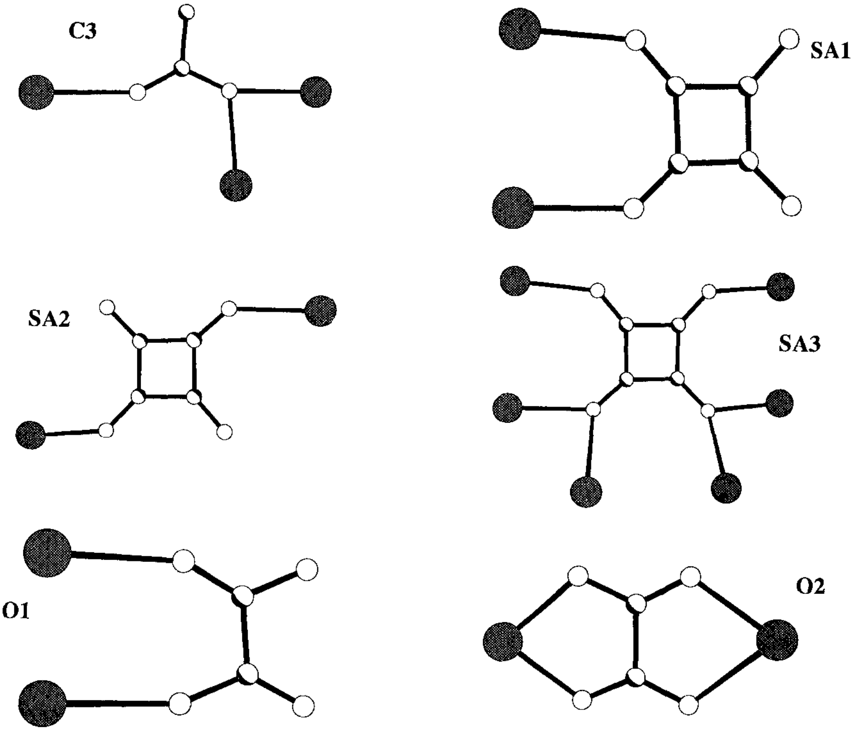


Figure 1. (*Continued*)

phosphonate or incorporated by postsynthesis reactions, a wealth of chemistry may be exploited in the preparation of new materials. Furthermore, since layered phosphonates undergo both Brønsted and Lewis intercalative chemistry (72), the optical and electronic properties of the host may be modified. While the chemistry of the molecular systems of the M/O/REO$_3^{2-}$ system (E = P or As) remains relatively undeveloped, it is tempting to speculate on the potential role of such molecular species in the design of solid phases with tailored properties (73, 74) for applications as catalyst supports, sorbent materials, and electronic or optical devices.

C. Classification of Ligand Types and Coordination Modes

The representative members of the two general classes of ligands discussed in this chapter and the major coordination types adopted are summarized in Fig. 1. Although other coordination modes are possible, the polyanion coordination compounds are generally limited to those of the figure. Several unique cases are discussed in subsequent sections. Although examples of ligands with mixed-

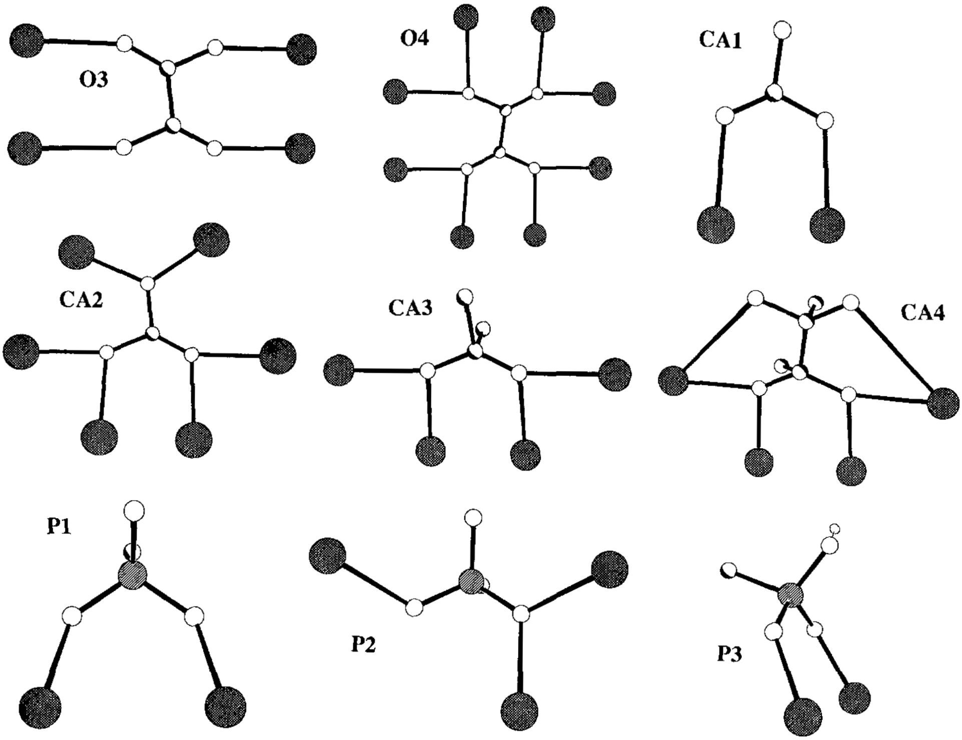


Figure 1. (*Continued*)

donor groups (O and N, and O and S) are known (75, 76): these groups have been excluded from this discussion.

III. SYNTHETIC METHODOLOGIES

A. General Features

There are no general synthetic routes for preparing cluster compounds and solid materials of predictable features. Rational synthetic methods available for molecular and soluble complexes are more developed compared to somewhat primitive approaches that have thus far been adopted for preparing solids. Since organic ligands do not survive under the typical solid state reaction conditions, which often involve highly refractory amorphous materials that diffuse together very slowly, even at high temperatures, the scope of these methods is generally

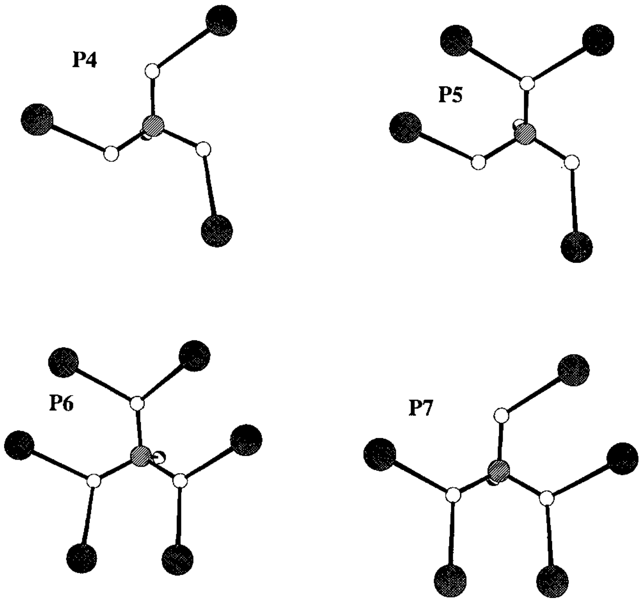


Figure 1. *(Continued)*

limited to the preparation of metal oxides and refractory materials. Furthermore, under solid state reaction conditions, only the most stable reaction product(s) are isolated, and, therefore the possibility of achieving analogous syntheses from simple molecular precursors of materials with desired features appears impractical. In other terms, the solid state analogue of organic functional group chemistry is still in an embryonic state.

Reaction fluxes or molten salts, which behave as high-temperature solvents to provide reaction media at elevated temperatures, promote the reactions of starting materials and crystallization of final product by enhancing diffusion rates and particle mobility of the reactants. Such conditions have been widely employed for preparing metal oxides and metal–chalcogenide based solid materials (77). However, this technique poses serious problems for the preparation of molecular species containing conventional organic ligands and even for solid phase materials incorporating organic substituents. Not only are most organic precursors decomposed at the high temperatures required, but the activation energy for diffusion is a substantial fraction of the individual bond strengths in the products and exceeds the activation energy for the conversion of metastable products into the thermodynamically favored product. Thus, there is no access to the kinetic products that are stable at lower temperatures.

Another common preparative method, the sol–gel technique, consists of making a homogenous solution of precursors in a suitable solvent, followed by controlled hydrolysis to form a gel. The technique has found wide applications in the preparation of oxide glasses and ceramics by the controlled hydrolyses of solvents (usually alcohols), to produce the gel, which after drying and pyrolysis produces the final products as glassy solids or ceramics (40). However, the products of sol–gel synthesis are characteristically amorphous polymeric materials, a distinct disadvantage in the design of complex molecular clusters and related solid phases with ordered arrays.

Conventional synthetic methods, on the other hand, involve hydrolysis and fragment condensation reactions or ''self-assembly'' of complex products from simpler molecular precursors in solution. Under these conditions molecular species present at the initial stages of hydrolysis–condensation processes may be isolated, and the structures and properties of these species may be related to those of solid materials formed under more forcing conditions. Furthermore, these simpler molecular products may in turn serve as the precursors for some of the low-temperature, nonconventional reactions, to be discussed in the following sections. Also, by bringing together these soluble building blocks, supramolecular materials and designer solids can be synthesized (13). The molecular building block approach is quite attractive since it provides not only a conceptional framework for the design of topologically controlled materials but also several synthetic advantages:

1. There is an extensive chemistry of coordination complexes and clusters that provide precursors for the synthesis of more complex assemblies.
2. Functional group chemistry and molecular symmetry of the precursors may be exploited in the synthesis of the product cluster.
3. The use of such soluble starting materials allows low-reaction temperatures, favoring the kinetic trapping of interesting metastable structures.
4. Reactions proceed by transformation of some of the functional groups of the organic and inorganic starting materials while retaining the covalent bonding relationships between most of the atoms, a feature that tends to direct the assembly of the more complex frameworks.

Furthermore, the structure-directing character of ionic bonds, through which these individual units may also be linked, provides an alternative approach to conventional solution synthesis of supramolecular materials, as evidenced by the success of ''Lego chemistry'' (73). However, the high degree of success that conventional synthetic methods enjoy in preparing simple molecular species is not uniformly paralleled in the preparation of supramolecular materials and solid phases. The current interest in giant clusters, and supramolecular, lamellar, and zeolitic materials has resulted in significant activity directed towards development of more effective synthetic procedures. Consequently, relatively low-temperature (100–400°C) nonconventional synthetic techniques suitable for a variety of both molecular and nonmolecular materials have evolved over the past decade.

Nonconventional hydrothermal syntheses are conveniently employed for molecular complexes of varying degrees of complexity, 1D and lamellar solids, as well as 3D open-framework solid materials. Hydrothermal reactions, typically carried out at a temperature range 140–260°C under autogenous pressure, exploit the self-assembly of the product from soluble precursors (78). The reduced viscosity of the solvent under these conditions results in enhanced rates of solvent extraction of solids and crystal growth from solution. Since differential solubility problems are minimized, a variety of simple precursors may be introduced, as well as a number of organic and/or inorganic structure-directing (templating) agents from which those of appropriate shape(s) and size(s) may be selected for efficient crystal packing during the crystallization process. Use of nonaqueous solvents such as alcohols, acetonitrile, acids, and mixtures of organic solvents in solvothermal synthesis (79), has received considerable attention in applications requiring the exclusion of water to prevent hydrolysis of desired products or for which effective solubility of reactants in nonaqueous solvents is practical or in which the solvent is itself a reactant (78). Solvothermal reactions are typically carried out at lower temperature (100–160°C) than hydrothermal counterparts in sealed, thick-walled quartz or glass tubes. The technique is particularly suitable for air and moisture sensitive reactions.

While there are examples of the synthesis of large molecular clusters by stepwise fragment condensation processes, generally through hydrolysis–condensation reactions of simple precursors, the most common synthetic routes rely upon "self-assembly," the spontaneous formation of higher ordered structures (80). Self-assembly may involve simply the spontaneous formation of product upon combining the component parts under the proper conditions or may be regulated in a variety of ways such as precursor modification, postsynthesis modification of functional groups introduced into the product, direct self-assembly involving a buttressing agent, which itself does not appear in the final product, the introduction of structure directing templates, which often appear as guests in host–guest assemblies of molecular clusters or as charge compensating and space-filling entities in solid phase materials.

B. Representative Examples of Syntheses of Clusters and Solid Phase Materials

These general synthetic principles may be illustrated by several selected examples of the preparations of clusters and solid-phase materials of the general classes discussed in this chapter. Although the principles underlying polyanion accretion are not understood in detail, fragment condensation processes have been invoked (81, 82). The aggregation process is demonstrated most convincingly in the synthesis of higher oligomers from $[Mo_2O_4\{(OCH_2)_3CR\}_2]^{2-}$ (83–88). The structural interrelationships of the bi-, tri-, and tetranuclear species are shown in Fig. 2, which illustrates schematically the course of the aggregation process viewed as successive condensations of $[MoO_2(OR)]^+$ units.

$$[Mo_2O_7]^{2-} + 2H_3L \longrightarrow [Mo_2O_4L_2]^{2-} + 3H_2O$$

$$2[Mo_2O_4L_2]^{2-} + [Mo_2O_7]^{2-} + H_3L + MeOH \rightarrow [Mo_3O_6(OMe)L_2]^{-}$$
$$+ [Mo_3O_7L_2]^{2-} + 2H_2O + L^{3-}$$

$$2[Mo_3O_6(OMe)L_2]^{-} + [Mo_2O_7]^{2-} + 6MeOH \longrightarrow [Mo_4O_8(OMe)_2L_2]$$
$$+ [Mo_4O_{10}(OMe)_6]^{2-} + H_2O + 2H_2L^{-}$$

$$2[Mo_4O_8(OMe)_2L_2] + 4H_2O \longrightarrow [H_2Mo_8O_{20}(OMe)_4L_2] + 2H_3L$$

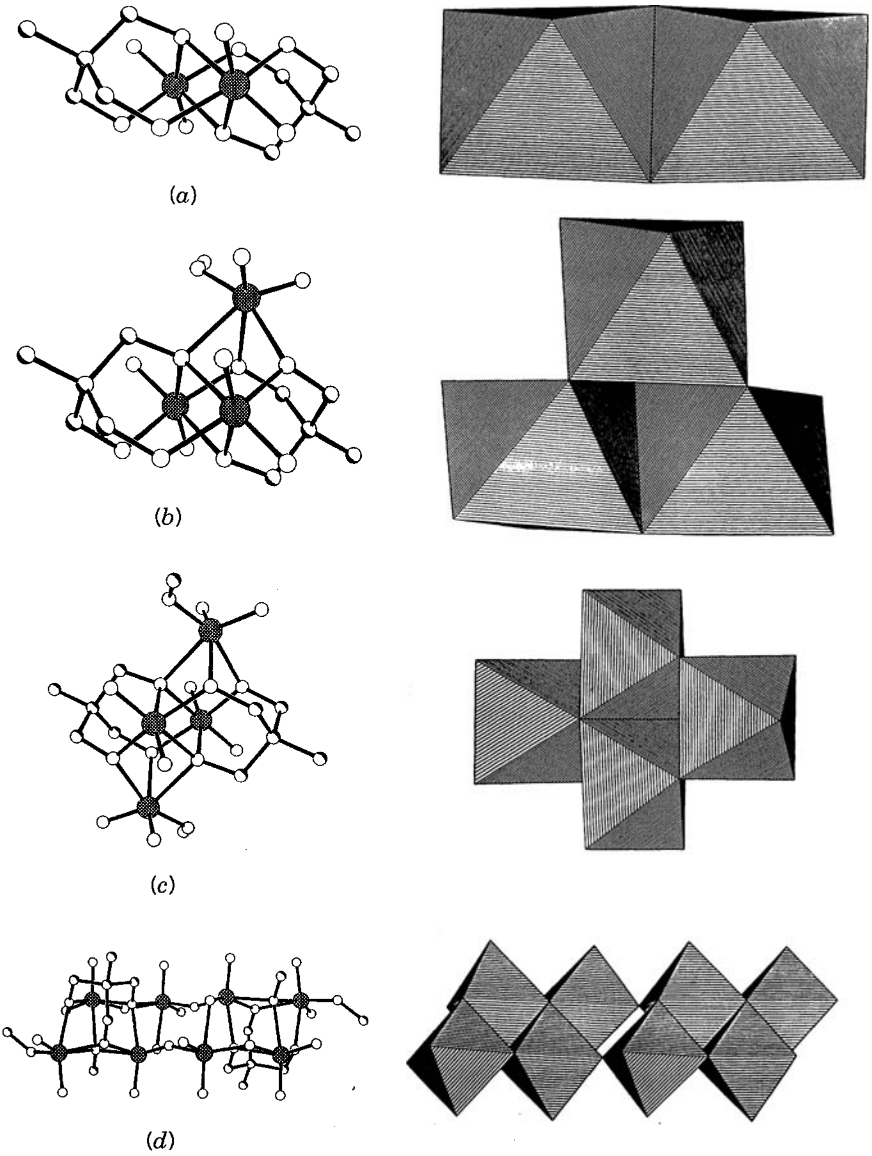
Similar fragment condensation processes are apparent in the vanadium chemistry. The reaction of tris(hydroxymethyl)alkane ligands with $[VO_2Cl_2]^{2-}$ under oxidizing conditions yields the binuclear $[(VO)_2Cl_2\{(OCH_2)_2CR(CH_2OH)\}_2]$, as shown in Fig. 3. The structure is reminiscent of that of $[Mo_2O_4\{(OCH_2)_3CR\}_2]^{2-}$ discussed above in exhibiting two sets of three alkoxy oxygen donors, each so disposed as to provide facial tridentate coordination. Further aggregation to produce higher oligomers should then be possible by condensation of appropriate units onto these faces. This expectation was realized in the preparation of a variety of tetranuclear species.

$$[(VO_2)Cl_2\{(OCH_2)_2CR(CH_2OH)\}_2] + Mo_2O_7^{2-} + 2MeOH \longrightarrow$$
$$[V_2Mo_2O_8(OMe)_2\{(OCH_2)_3CR\}_2]^{2-} + 2HCl + H_2O$$

$$2[(VO)_2Cl_2\{(OCH_2)_2CR(CH_2OH)\}_2] + 2HSO_4^{-} + 2H_2O + 2MeOH \longrightarrow$$
$$[(VO)_4(H_2O)_2(SO_4)_2\{(OCH_2)_3CR\}_2]^{2-} + 4HCl + 2H_2CO$$
$$+ 2\{(HOCH_2)_3CR\}$$

$$2[(VO)_2Cl_2\{(OCH_2)_2CR(CH_2OH)\}_2] + 3HOR \longrightarrow$$
$$[(VO)_4(OR)_3\{(OCH_2)_3CR\}_3] + 4HCl + (HOCH_2)_3CR$$

The tetranuclear species in turn undergo hydrolysis–condensation reactions to form higher oligomers.


(a)

(b)

(c)

(d)

Figure 2. Ball-and-stick and polyhedral representations of the structures of (a) $[Mo_2O_4\{RC(CH_2O)_3\}_2]^{2-}$, (b) $[Mo_3O_7\{RC(CH_2O)_3\}_2]^{2-}$, (c) $[Mo_4O_8(OR)_2\{RC(CH_2O)_3\}_2]$, and (d) $[H_2Mo_8O_{20}(OR)_4\{RC(CH_2O)_3]_2$.

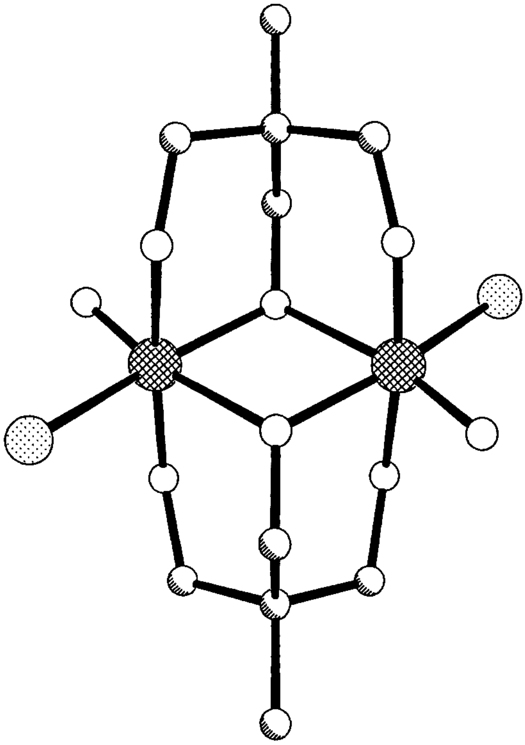


Figure 3. A view of the structure of $[V_2O_2Cl_2\{(OCH_2)_2CR(CH_2OH)\}_2]$. The chloride donors are represented as stippled spheres.

$$2[(VO)_4(OR)_3\{(OCH_2)_3CR\}_2] + 2[V_5O_{14}]^{3-} + 3H_2O \longrightarrow$$

$$3[V_2O_{13}\{(OCH_2)_3CR\}_2]^{2-} + 6HOR$$

$$3[(VO)_4(OR)_3\{(OCH_2)_3CR\}_2] + 4H_2O + 4MeOH + 4R_3N \longrightarrow$$

$$2[V_6O_8\{(OCH_2)_3CR\}_2\{(OCH_2)_2CR(CH_2OH)\}_4]^{2-} + 9MeOH$$

$$+ 4H_2CO + (HOCH_2)_3CR + 4R_3NH^+$$

The isolation of reduced and mixed-valence species, $[(VO)_4(H_2O)_2(SO_4)_2\text{-}\{(OCH_2)_3CR\}_2]^{2-}$ and $[V_6O_8\{(OCH_2)_3CR\}_2\{(OCH_2)_2CR(CH_2OH)\}_4]^{2-}$, respectively, reflects the facile reduction of V^V species in alcoholic solutions and demonstrates the additional structural complexity, which is introduced by the rich redox chemistry of the metal oxides.

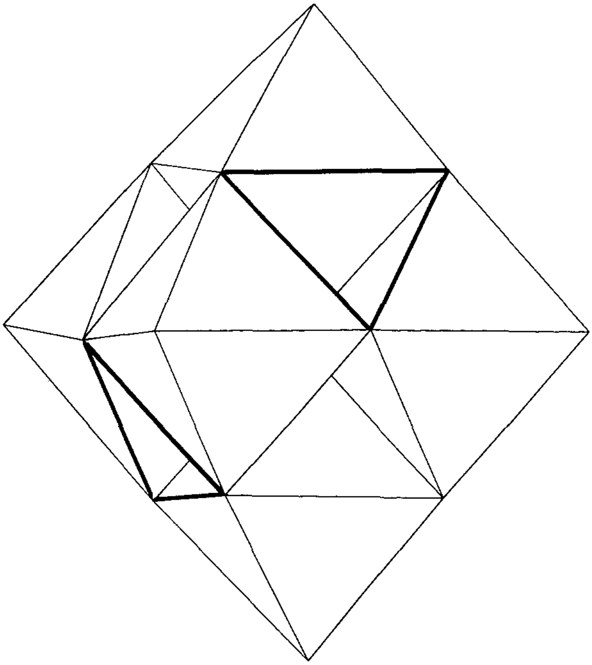


Figure 4. A polyhedral representation of the hexanuclear core, $\{M_6O_{19}\}$, highlighting the triangular faces commonly occupied by the oxygen donors of trisalkoxide ligand types.

Two features of the hexametalate core are noteworthy. As shown in Fig. 4, the tris(hydroxymethyl)alkane ligands occupy the triangular faces of the tetrahedral cavities of the hexametalate framework. Although there are eight triangular faces of this type associated with the $\{V_6O_{19}\}$ core, only four may be occupied at any one time by the trisalkoxy ligands. Under the conditions of conventional synthesis, the only derivatives isolated were those of the classes with one or two trisalkoxy ligands, $[V_6O_{13}(MeO)_3\{(OCH_2)_3CR\}]^{2-}$ and $[V_6O_{13}\{(OCH_2)_3CR\}_2]^{2-}$ respectively. Similarly, the $\{V_6O_{19}\}$ core should serve as a framework for further condensation to yield higher oligomers. Again, under the conditions of conventional synthesis, no clusters of higher nuclearity could be isolated. However, by adopting the conditions of hydrothermal synthesis both the progressively substituted hexametalate cores and higher oligomers were readily isolated. Thus, in the presence of Ba^{2+} cations, vanadate, and $(HOCH_2)_3CMe$ react at 150°C in H_2O to give $Ba[V_6O_7(OH)_3\{(OCH_2)_3CMe\}_3]$, while the reaction under similar conditions with Na^+ yields the tetra-substituted product $Na_2[V_6O_7\{(OCH_2)_3CMe\}_4]$. By raising the temperature and increasing reactions times, decanuclear cores of the classes $[V_{10}O_{16}\{(OCH_2)_3CR\}_4]^{n-}$ and $[V_{10}O_{13}\{(OCH_2)_3CR\}_5]^{1-}$ are isolated.