Coordination Chemistry of the Tetrametalate Core, $\{M_4O_{16}\}$: Syntheses from $[V_2O_2Cl_2\{(OCH_2)_2C(R)(CH_2OH)\}_2]$ and Structures of the Mixed-metal Cluster $[V_2Mo_2O_8(OMe)_2\{(OCH_2)_3CR\}_2]^{2-}$ and the Reduced Cluster $[V_4O_4(H_2O)_2(SO_4)_2\{(OCH_2)_3CR\}_2]^{2-}$

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The reactions of $[Ph_3PCH_2Ph][VO_2Cl_2]$ with $(HOCH_2)_3CR$ yield binuclear species of the type $[V_2O_2Cl_2\{(OCH_2)_2C(R)(CH_2OH)\}_2]$, which react in turn with $[Bu^n{}_4N]_2$ $[Mo_2O_7]$ to give the mixed-metal tetrametalates, $[V_2Mo_2O_8(OMe)_2\{(OCH_2)_3CR\}_2]^{2-}$ and with $[Bu^n{}_4N]HSO_4$ and $[Bu^n{}_4N]_3[H_3V_{10}O_{28}]$ to yield the reduced tetravanadium clusters $[V_4O_4(H_2O)_2(SO_4)_2\{(OCH_2)_3CR\}_2]^{2-}$.

The structures of many of the polyoxometalate clusters are basically constructed by the edge-sharing of $\{MO_6\}$ octahedra[1-3]. The fundamental structural motif is thus the pair of edge sharing octahedra, and the shapes of polyoxometalate anions can often be predicted by adding additional octahedra in an edge-sharing fashion to this core.[3] Compact structures of this type have also been described for polyoxometalate coordination complexes, $[M_xO_yL_z]^{n-}$, where L is an organic ligand, with cores ranging in size from three to forty-two metal octahedra.[3,4] The compact tetrametalate core $\{M_4O_{16}\}$ is represented in both the Mo/O/ligand and V/O/ligand systems by fully oxidized or d^0 clusters of which $[Mo_4O_{10}(OMe)_6]^{2-}$[5] and $[V_4O_4(OH)_2Cl_2\{OCH_2C(Me)_2CH_2O\}_4]$[6] are prototypical. In contrast, no mixed-metal or reduced clusters of this core have been described to date. In this work, we describe the preparations and structures of two new members of the tetrametalate class of clusters, $[Bu^n{}_4N]_2[V_2Mo_2O_8(OMe)_2\{(OCH_2)_3CCH_2OH\}_2]$ **2** and $[Bu^n{}_4N]_2[V_4O_4(H_2O)_2$-

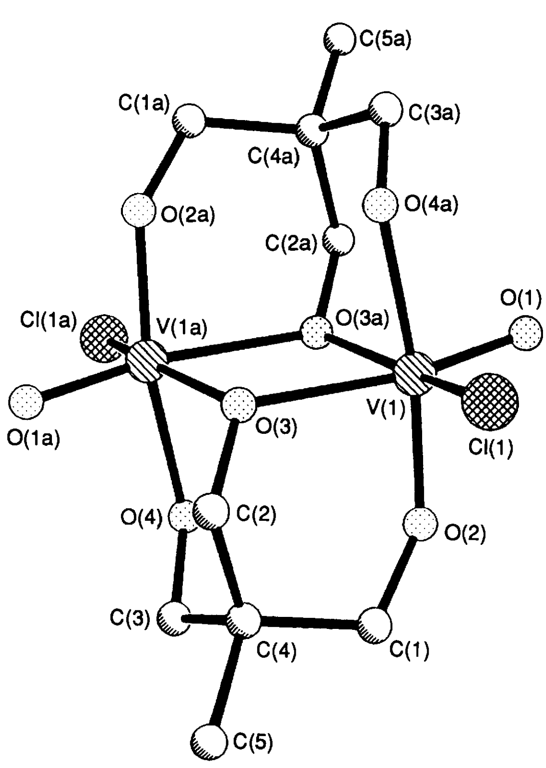

Fig. 1. View of the binuclear cluster $[V_2O_2Cl_2\{(OCH_2)_2CMe(CH_2OH)\}_2]$ **1a**, showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): V(1)–Cl(1) 2.326(1), V(1)–O(1) 1.592(4), V(1)–O(2) 1.781(3), V(1)–O(3) 2.184(3), V(1)–O(3a)1.906(3), V(1)–O(4a), 2.057(3), Cl(1)–V(1)–O(1) 100.8(1), V(1)–O(3)–V(1a) 105.4(1).

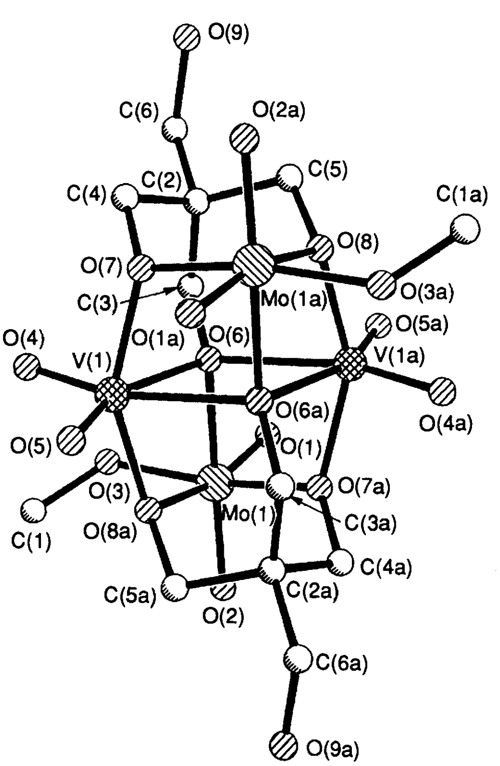

Fig. 2 ORTEP view of the molecular anion $[V_2Mo_2O_8(OMe)\{(OCH_2)_3CCH_2OH\}_2]^{2-}$. Selected bond lengths (Å) and angles (°): Mo(1)–O(1) 1.700(6), Mo(1)–O(2) 1.723(6), Mo(1)–O(3) 1.899(6), Mo(1)–O(6) 2.192(6), Mo(1)–O(7a) 2.074(5), Mo(1)–O(8a) 2.185(5), V(1)–O(4) 1.614(6), V(1)–O(5) 1.624(6), V(1)–O(6) 2.214(6), V(1)–O(7) 1.998(6), V(1)–O(6a) 2.303(6), V(1)–O(8a) 1.963(6), O(1)–Mo(1)–O(2) 106.5(3), O(4)–V(1)–O(5) 106.0(3), V(1)–O(6)–V(1a) 109.0(2), Mo(1)–O(6)–V(1) 101.1(2), Mo(1)–O(6)–V(1a) 96.0(2).

$(SO_4)_2\{(OCH_2)_3CEt\}_2]\cdot 2(HOCH_2)_3CEt$ **3**, and of the synthetic precursor $[V_2O_2Cl_2\{(OCH_2)_2CMe(CH_2OH)\}_2]\cdot 2Ph_3PCH_2PhCl\cdot 2MeOH$ **1a**.

The reactions of $[Ph_3PCH_2Ph][VO_2Cl_2]$ with the trishydroxymethylalkyl ligands $(HOCH_2)_3CR$ (R = Me, Et, OH) in methanol yield bright red diamagnetic crystals of binuclear V^V species of the type $[H_2V_2O_2Cl_2\{(OCH_2)_3CR\}_2]\cdot 2Ph_3PCH_2PhCl\cdot 2MeOH$ (**1a**, R = Me; **1b**, R = Et; **1c**, R = CH_2OH). The IR spectrum of **1a** exhibits bands at 1114 and 1054 cm^{-1} characteristic of ligand ν(C–O) and a strong absorption at 957 cm^{-1} assigned to ν(V=O) of the vanadate centres.

The structure of the binuclear unit $[H_2V_2O_2Cl_2\{(OCH_2)_3CMe\}_2]$ of **1a**,† Fig. 1, is seen to consist of two edge-sharing $\{VO_5Cl\}$ octahedra.[6] Each V^V centre is coordinated to a terminal oxo-group, a terminal chloride, two bridging alkoxy oxygens from each of the two trisalkoxy ligands, and two terminally coordinated oxygen donors provided by the trisalkoxy groups. The significant differences in the V(1)–O(2) and V(1)–O(4) distances of 1.781(3) Å and 2.057(3) Å, respectively, clearly identify O(4) as the site of protonation. The structure of **1a** is reminiscent of that of the binuclear Mo^{VI}-trisalkoxide complex $[Mo_2O_4\{(OCH_2)_3CMe\}_2]^{2-}$ [7] 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 shiny yellow diamagnetic crystals of **2** from the reaction of **1c** with $[Bu^n{}_4N]_2Mo_2O_7$ in refluxing wet methanol. The IR spectrum of **2** exhibited bands at 1056 cm^{-1} and 1009 cm^{-1} associated with ν(C–O) of the ligand and a complex pattern of bands between 790 and 968 cm^{-1} characteristic of ν(Mo=O) and ν(V=O). The ^{51}V NMR spectrum exhibited a single line at δ −502 with respect to $VOCl_3$.

As shown in Fig. 2, the structure of the anion of **2**† consists of a tetranuclear core constructued by condensing two $[MoO_2(OMe)]^+$ units onto the two triangular alkoxide oxygen faces of the $[V_2O_4\{(OCH_2)_3CCH_2OH\}_2]^{4-}$ core provided by hydrolysis of **1c**. The structure of the anion of **2** is isotypic with that of $[Mo_4O_8(OR)_2\{(OCH_2)_3CR\}_2]^8$ with the two central Mo^{VI} centres replaced by V^V.

Under conditions of solvothermal synthesis,[9] **1b** reacts with $[Bu^n{}_4N]_3\,[H_3V_{10}O_{28}]$ and $[Bu^n{}_4N]HSO_4$ in methanol at 120 °C and autogenous pressure to give blue paramagentic crystals of the V^{IV} cluster **3**. The presence of formaldehyde in the reaction mixture confirms the role of methanol as the reducing agent.[10] The IR spectrum of **3** exhibits strong intensity bands at 1116, 1103, 1053 and 1019 cm^{-1} associated with ν(S–O) and

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† *Crystal data* for $[V_2O_2Cl_2\{(OCH_2)_2CMe(CH_2OH)\}_2]\cdot 2Ph_3PCH_2PhCl\cdot 2MeOH$ **1a**: triclinic space group $P\bar{1}$ with a = 10.316(2), b = 15.762(3), c = 10.125(2) Å, α = 105.72(3), β = 90.02(3), γ = 79.86(3)°, V = 1558.1(8) $Å^3$, Z = 1, D_c = 1.368 g cm^{-1}; structure solution and refinement based on 3550 reflections with $F_0 \geqslant 6\sigma(F_0)$(Mo–Kα, λ = 0.71073 Å) converged at R = 0.0510.

For $[Bu^n{}_4N]_2[V_2Mo_2O_8(OMe)_2\{(OCH_2)_3CCH_2OH\}_2]$ **2**: monoclinic space group $P2_1/c$ with a = 10.069(2), b = 20.268(4), c = 14.227(3) Å, β = 101.96(3)°, V = 2840(1) $Å^3$, Z = 2, D_c = 1.444 g cm^{-3}; 2363 reflections, R = 0.0537.

For $[Bu^n{}_4N]_2[V_4O_4(H_2O)_2(SO_4)_2\{(OCH_2)_3CEt\}_2]\cdot 2(HOCH_2)_3CEt$ **3**: triclinic space group $P\bar{1}$ with a = 12.564(3), b = 12.845(3), c = 12.012(3) Å, α = 67.14(3), β = 70.17(3), γ = 73.31(3)°, V = 1928(1) $Å^3$, Z = 1, D_c = 1.299 g cm^{-3}; 3468 reflections, R = 0.0788.

For all three clusters atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

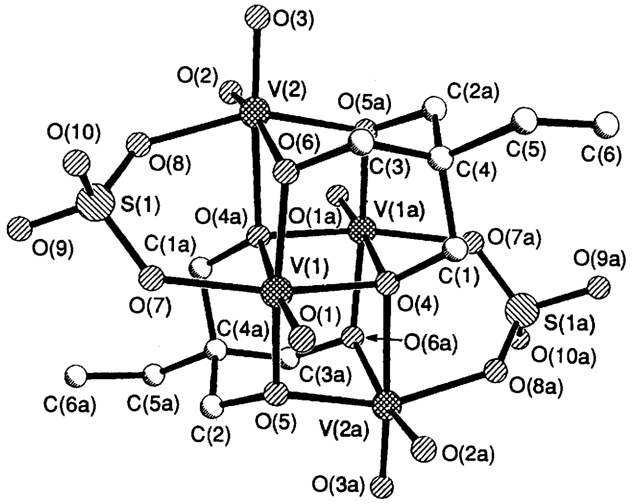

Fig. 3 Structure of the molecular anion cluster of **3**, $[V_4O_4(H_2O)_2(SO_4)_2 = \{(OCH_2)_3CEt\}_2]^{2-}$. Selected bond lengths (Å) and angles (°); V(1)–O(1) 1.609(6), V1–O(4) 2.304(5), V(1)–O(4a) 1.994(6), V(1)–O(5) 2.013(7), V(1)–O(6) 1.973(8), V(1)–O(7a) 1.995(6), V(2)–O(2) 2.105(5), V(2)–O(3) 1.592(9), V(2)–O(4) 2.259(7), V(2)–O(5a) 1.996(6), V(2)–O(6a) 1.982(5), V(2)–O(8) 2.001(7), O(1)–V(1)–O(7) 104.0(3), O(2)–V(2)–O(3) 98.0(3), V(1)–O(4)–V(1a) 105.4(2), V(2)–O(4)–V(1) 90.1(2), V(2)–O(4)–V(1a) 97.3(3).

ν(C–O) of the ligands and features characteristic of ν(V=O) at 966 and 945 cm^{-1}.

While the structure of the anion of **3**,† illustrated in Fig. 3, shares with **2** the compact arrangement of edge-sharing $\{MO_6\}$ octahedra characteristic of the tetrametalate core, a number of unusual and unique features emerge. The cluster represents the first example of a fully-reduced tetravanadium species of this class. The $[V_2O_2\{(OCH_2)_3CEt\}_2]^{2-}$ binuclear core provides two faces, each defined by a triangular arrangement of three alkoxy oxygen donors, which fuse with the two $[VO(H_2O)(SO_4)]$ moieties which complete the aggregate. The result is an unusual reduced cluster incorporating both organic and inorganic ligand sets.

The trisalkoxy ligands assume the common coordination-mode previously observed for this core: two alkoxy oxygen donors of each ligand exhibit the μ^2 bridging mode, while the third adopts the μ^3-type. A noteworthy feature of the structure in the presence of the $(SO_4)^{2-}$ ligands which assume a bidentate bridging geometry, linking a V^{IV} site of the binuclear core motif to one of the $[VO(H_2O)]$ fragments condensed to the faces of this core. The V(2)–O(2) bond distance of 2.105(5) Å identifies O(2) as an aquo ligand, an assignment with the charge requirements of the cluster.

The syntheses of tetranuclear clusters **2** and **3** from binuclear precursors of type **1** demonstrate that, while the principles underlying polyanion accretion are not understood in detail, a degree of rational design may be introduced by exploiting the properties of coordinated ligands and simple fragment addition processes. The isolation of cluster **3** also provides an unusual example of a polyoxometalate structure incorporating both organic and inorganic ligand types, suggesting that cluster chemistry of the $M/O/alkoxide/H_xEO_4$ systems (M = V, Mo, W; E = P, As, S) can be developed and that analogous extensions to the solid phases may be possible.

This work was supported by a grant from the National Science Foundation (CHE 9119910).

Received, 10th August 1993; Com. 3/04827F

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