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Hydrothermal Synthesis and Crystal and Molecular Structure of a Neutral Polyoxoalkoxyvanadium(IV) Cluster with a Hexadecametalate Core, $[V_{16}O_{20}\{(OCH_2)_3CCH_2OH\}_8(H_2O)_4]\cdot 3H_2O$

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Recent developments in the chemistry of polyoxovanadium clusters reflect their relevance to bioinorganic chemistry,[1-3] geochemistry,[4,5] sol–gel chemistry,[6,7] and catalysis and materials science.[8-10] While the "naked" isopolyanions $[V_xO_y]^{n-}$ have historically constituted the major focus of attention,[11,12] more recent investigations have revealed an extensive coordination chemistry, in which one or more cluster oxo groups have been replaced by organic ligands.[13] The polyoxoalkoxyvanadium clusters are represented by tetranuclear,[14,15] hexanuclear,[16-19] and decanuclear species,[20,21] constructed from edge-sharing of $\{VO_6\}$ or $\{VO_5L\}$ octahedra and containing fully oxidized V(V) cores, or fully reduced V(IV) cores, or mixed-valence V(V)/V(IV) sites, depending on the method of synthesis. While the "naked" polyoxovanadates are characterized not only by large mixed-valence aggregates constructed from edge-sharing of $\{VO_5\}$ square pyramids, such as $[V_{34}O_{82}]^{10-}$ [22] and $[V_{19}O_{41}(OH)_9]^{8-}$,[23] but also by fully oxidized compact clusters formed from edge-sharing of $\{VO_6\}$ octahedra and exhibiting a trend of increased nuclearity coupled to decreased cluster charge, as illustrated by the series $[M_6O_{19}]^{8-}$, $[M_{10}O_{28}]^{6-}$, and $[M_{13}O_{34}]^{3-}$,[24] aggregates of nuclearity greater than 10 have proved elusive for the $V/O/RO^-$ system. However, by exploiting the technique of hydrothermal synthesis, a unique neutral polyoxoalkoxyvanadium cluster with a hexadecametalate core, $[V_{16}O_{20}\{(OCH_2)_3CCH_2OH\}_8(H_2O)_4]\cdot 3H_2O$ (**1**·3H$_2$O), has been isolated. Curiously, the V_{16} core of **1**·3H$_2$O does not adopt the neutral $\{V_{16}O_{40}\}$ framework constructed by capping two faces of $[V_{10}A_{28}]^{6-}$ with $\{(\mu\text{-}O)V{=}O\}_3{}^{2+}$ units, as might be predicted by analogy to $[V_{13}O_{34}]^{3-}$ and the putative $[V_{16}O_{40}]^0$,[24] but rather a less compact neutral $\{V_{16}O_{48}\}$ core formed by the condensation through four corner-sharing interactions 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.

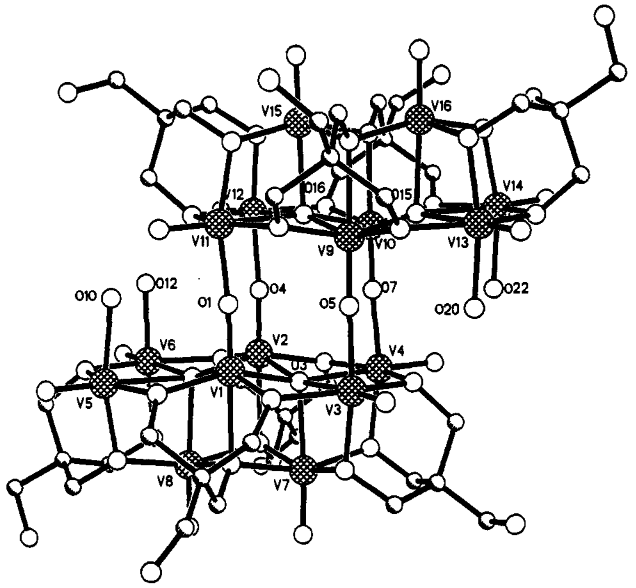

Figure 1. The structure of $[V_{16}O_{20}\{(OCH_2)_3CCH_2H\}_8(H_2O)_4]$ (**1**), showing the atom-labeling scheme.

While the hydrothermal reaction of a mixture of vanadium(III) oxide, vanadium(V) oxide, pentaerythritol, and $(CH_3)_3NHCl$ in H_2O at 150 °C produces the decavanadium cluster $(Me_3NH)_2[V_{10}O_{14}(OH)_2\{(OCH_2)_3CCH_2OH\}_4]\cdot 2H_2O$,[21] the reaction of V_2O_5, V_2O_3, $C(CH_2OH)_4$, Me_2NH_2Cl, $EtNH_3Cl$, and H_2O at 170 °C for 48 h yields light green crystals of $[V_{16}O_{20}\{(OCH_2)_3CH_2OH\}_8(H_2O)_4]\cdot 3H_2O$ (**1**·3H$_2$O) in 20% yield.[25] The infrared spectrum of **1**·3H$_2$O exhibits bands in the 1000–1200-cm^{-1} region characteristic of the tris(alkoxide) ligand and strong absorbances at 966 and 913 cm^{-1} associated with $\nu(V{=}O)$ and $\nu(V{=}O\cdots V)$, respectively.

As shown in Figure 1, the structure of **1**[26] consists of two $[V_8O_8\{(OCH_2)_3CCH_2OH\}_4(H_2O)_2]^{4+}$ (**1a**) units connected through four μ^2-oxo groups. The topology of each $[V_8O_8\{(OCH_2)_3CCH_2OH\}_4(H_2O)_2]^{4+}$ motif is clearly related to the decametalate core $\{V_{10}O_{28}\}$ by removal of two of the polar capping $\{(\mu\text{-}O)V{=}O\}$ groups. Face to face condensation of two of the $[V_8O_8\{(OCH_2)_3CCH_2OH\}_4(H_2O)_2]^{4+}$ units through four μ^2-oxo groups produces the neutral core of **1**. Twenty doubly-bridging and four triply-bridging oxo groups of the hypothetical $\{V_{16}O_{48}\}$ core have been

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(26) Crystal data for $[V_{16}O_{20}\{(OCH_2)_3CCH_2OH\}_8(H_2O)_4]\cdot 3H_2O$ (**1**·3H$_2$O): monoclinic space group $P2_1/n$ with $a = 13.995(2)$ Å, $b = 23.378(4)$ Å, $c = 23.197(4)$ Å, $\beta = 105.36(2)°$, $V = 7318.4(14)$ Å^3, $Z = 4$, $D_{calc} = 2.111$ g cm^{-3}; structure solution and refinement based on 3477 reflections with $I_o \geq 3\sigma(I_o)$ (Mo Kα radiation, $\lambda = 0.710\,73$ Å) converged at $R = 0.0601$.

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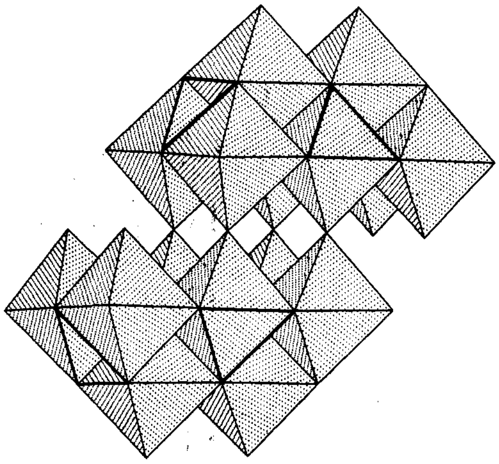

Figure 2. Polyhedral representation of the $\{V_{16}O_{48}\}$ core of **1**, highlighting the two types of triangular faces of the framework occupied by the oxygen donors of the tris(alkoxy)ligands.

replaced by alkoxy donors from the eight tris(alkoxy) ligands. In addition, there are four aquo ligands sited on the two exterior vanadium centers of the central hexavanadium ring of each $[V_8O_8\{(OCH_2)_3CCH_2OH\}_4(H_2O)_2]^{4+}$ layer and directed toward the interlayer region. On consequence of the aquo coordination is that the two $[V_8O_8\{(OCH_2)_3CCH_2OH\}_4 (H_2O)_2]^{4+}$ layers do not align with the hexavanadium ring of one unit directly above the hexavanadium face of the second but with the layers sheared via a parallel displacement to produce four {V—O═V} interactions with long–short V–O distances.

Within each $[V_8O_8\{(OCH_2)_3CCH_2OH\}_4 (H_2O)_2]^{4+}$ subunit, the $\{VO_6\}$ octahedra aggregate by edge-sharing into a compact arrangement, while the two octavanadium units are interconnected by corner-sharing of four pairs of vanadium octahedra. This arrangement produces an unusual central $\{V_4O_6\}$ parallelepiped with two pairs of short V–V distances (2.671(5) and 2.684(5) Å compared to a range of 3.03–3,30 Å for the distance between other V–V pairs). The vanadium centers involved in these short interactions are also displaced from the planes through the hexavanadium rings into the region between two **1a** structural units, so as to produce short V–O distances to the four oxo groups bridging these units.

We have noted previously in the structures of the $[V_6O_{19-3n}\{(OCH_2)_3CR\}_n]^{x-}$ and $[V_{10}O_{28-3n}\{(OCH_2)_3CR\}_n]^{x-}$ classes of polyoxoalkoxyvanadium clusters[16–21] that the preferred substitution pattern of the tris(alkoxide) ligands adopts a bridging mode between three metals in a triangulo arrangement, so as to cap the triangular faces of the tetrahedral cavities of the metal–oxide framework (Figure 2). Such an arrangement in the case of **1** would limit tris(alkoxide) occupancy to six sites. However, by adopting a ligation mode of alternating occupancy of triangular cavities, which bridge three V sites, and of triangular faces of the central vanadium sites of each hexavanadium ring, thus bridging such vanadium sites to four adjacent vanadium centers, eight alkoxide ligands are accommodated about the framework.

Calculated valence sums[27] for the sites of **1** confirm that all are V(IV) centers. While the two short V–V distances associated with the central sites are relatively uncommon for V(IV) sites, which unlike Mo(V) species rarely exhibit pronounced metal–metal interactions,[11] similar pairing has been observed for $[V_{34}O_{82}]^{10-}$ [22] and monoclinic VO_2, where distances of 2.62 Å have been reported.[28]

Variable temperature solid-state magnetic susceptibility studies were performed on powdered samples of $\mathbf{1}\cdot 3H_2O$ in the range

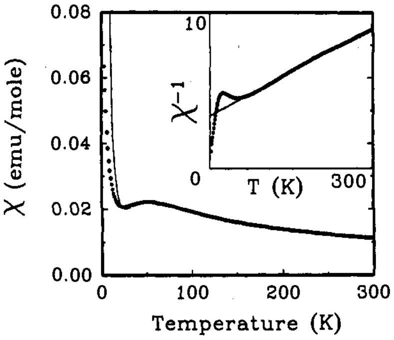

Figure 3. The magnetic susceptibility of $\mathbf{1}\cdot 3H_2O$ plotted as a function of temperature over the 2–300 K temperature range. The curve drawn through the data is the fit to the theoretical model as described in the text. The inset illustrates the inverse magnetic susceptibility plotted as a function of temperature, and the line through the data in the inset is the result of the Curie-Weiss fit as described in the text.

2–300 K (see Figure 3). The high-temperature magnetic susceptibility data ($T > 200$ K) exhibits Curie–Weiss paramagnetism.[29] While the effective magnetic moment of the cluster is *ca.* 6 μ_B at room temperature, extrapolation of the data reveals that a higher moment would be realized at higher temperature.

The broad maximum at lower temperatures is expected for short-range antiferromagnetic interactions and is consistent with magnetic exchange within the short-contact V(IV) binuclear units while the remaining V(IV) centers would be expected to show more of a paramagnetic behavior that results from significantly less magnetic exchange. The behavior of the two pairs of V(IV) ions and the 12 paramagnetic V(IV) sites, corrected for a molecular exchange field, is illustrated in Figure 3 as a smooth curve.

A noteworthy characteristic of $\mathbf{1}\cdot 3H_2O$ is the loss of both lattice and coordinated water at the relatively low temperature of 230 °C, without significant decomposition as monitored by infrared spectroscopy and X-ray powder diffraction. To determine if it were possible for small molecules to access the internal void volume of samples thus treated, water absorption isotherms were measured on material degassed at 200 °C under vacuum. The type 1 absorption isotherm,[30] a characteristic common to many polyoxoanions,[31] showed absorption of 5–6% water, indicating that water can readily penetrate the internal volume of crystals of this material, that the dehydrations are reversible, and that coordinatively unsaturated V(IV) sites of the cluster are accessible to substrate molecules. Further investigations of the substrate absorption and reactivity properties are in progress.

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Supplementary Material Available: Tables of atomic positional parameters and isotropic thermal parameters, anisotropic thermal parameters, bond lengths, bond angles, and calculated hydrogen atom positions for $\mathbf{1}\cdot 3H_2O$ and details of the magnetic susceptibility measurements and analysis (18 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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