

A Novel Hexavanadate Core: Synthesis and Structure of the Mixed Valence Cluster $[\text{V}_6\text{O}_8\{(\text{OCH}_2)_3\text{CEt}\}_2\{(\text{OCH}_2)_2\text{C}(\text{CH}_2\text{OH})(\text{Et})\}_4]^{2-}$ and a Comparison with the Hexametallate Core of $[\text{V}_6\text{O}_{13}(\text{OMe})_3\{(\text{OCH}_2)_3\text{CCH}_2\text{OH}\}]^{2-}$

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The reaction of $[\text{Bu}_4\text{N}]_3\text{V}_5\text{O}_{14}$ with $\text{RC}(\text{CH}_2\text{OH})_3$ in methanol yields red crystals of $[\text{Bu}_4\text{N}]_2[\text{V}_6\text{O}_{13}(\text{OMe})_3\{(\text{OCH}_2)_3\text{CR}\}]$ ($\text{R} = \text{Et}$, **1**; $\text{R} = -\text{CH}_2\text{OH}$, **1a**), a V^V cluster with the common hexametallate core $\{\text{V}_6\text{O}_{19}\}$, and a green filtrate from which were isolated light-green crystals of a mixed valence cluster $[\text{Bu}_4\text{N}]_2[\text{V}_6\text{O}_8\{(\text{OCH}_2)_3\text{CR}\}_2\{(\text{OCH}_2)_2\text{C}(\text{CH}_2\text{OH})\text{R}\}_4]$, **2**, consisting of a central $\{\text{V}_4\text{O}_{16}\}$ unit of edge-sharing octahedra linked to two peripheral vanadium square pyramids.

The structural chemistry of the polyoxometallate anion clusters^{1,2} has been dramatically expanded by the introduction of nitrogen- and oxygen-donor ligands in reactions carried out in aprotic, polar solvents.³ The use of multidentate alkoxy ligand types has proved most fruitful in the development of an extensive class of polyoxo alkoxide clusters,⁴⁻⁷ of which the hexavanadate species $[\text{V}_6\text{O}_{19-3n}\{(\text{OCH}_2)_3\text{CR}\}_n]^{x-}$ ($n = 2, 3,$ and 4) and the decavanadate compounds $[\text{V}_{10}\text{O}_{28-3n}\{(\text{OCH}_2)_3\text{CR}\}_n]^{x-}$ ($n = 4$ and 5) are representative. Although these latter clusters exhibit core structures derived from the classical hexametallate and decametallate structural types, $\{\text{M}_6\text{O}_{19}\}$ and $\{\text{M}_{10}\text{O}_{28}\}$, respectively, the isolation of other structural prototypes may be realized, as demonstrated by the recent characterization of the high nuclearity cluster $[\text{Na}(\text{H}_2\text{O})_3\text{H}_{15}\text{Mo}_{42}\text{O}_{109}\{(\text{OCH}_2)_3\text{CR}\}_7]^{7-}$.⁸ In this report, we describe the preparation and characterization of two hexavanadate clusters, $[\text{Bu}_4\text{N}]_2[\text{V}_6\text{O}_{13}(\text{OMe})_3\{(\text{OCH}_2)_3\text{CCH}_2\text{OH}\}]$, **1a** which exhibits the common $\{\text{M}_6\text{O}_{19}\}$ core geometry and $[\text{Bu}_4\text{N}]_2[\text{V}_6\text{O}_8\{(\text{OCH}_2)_3\text{C}$

$\text{Et}\}_2\{(\text{OCH}_2)_2\text{C}(\text{CH}_2\text{OH})\text{Et}\}_4]$, **2**, a novel mixed valence species with an unusual $\{\text{M}_6\text{O}_{22}\}$ framework.

The reaction of $[\text{Bu}_4\text{N}]_3\text{V}_5\text{O}_{14}$ ⁹ with $(\text{HOCH}_2)_3\text{CEt}$ (H_3trisEt) in methanol yields bright red crystals of $[\text{Bu}_4\text{N}]_2[\text{V}_6\text{O}_{13}(\text{OCH}_3)_3(\text{trisEt})]$ **1**⁺ in 50% yield and a green solution from which light green crystals of $[\text{Bu}_4\text{N}]_2[\text{V}_6\text{O}_8(\text{trisEt})_2(\text{HtrisEt})_4]$ **2**⁺ were recovered after 2 weeks. The IR spectrum of **1** exhibits a band at 944 cm^{-1} associated with $\nu(\text{V}=\text{O})$ and a feature at 1042 cm^{-1} consistent with the presence of the (trisEt) ligand. The observation of resonances at $\delta -483$ and -494 in the ⁵¹V NMR spectroscopy confirmed the presence of two distinct vanadium environments. The IR spectrum of **2** displays strong bands at 966 and 944 cm^{-1} attributed to ν_s and ν_{as} of the *cis* dioxo $[\text{VO}_2]^+$ groups and a feature at 985 cm^{-1} associated with the $\nu(\text{V}=\text{O})$ of the reduced centres.

* Satisfactory elemental analyses were obtained.

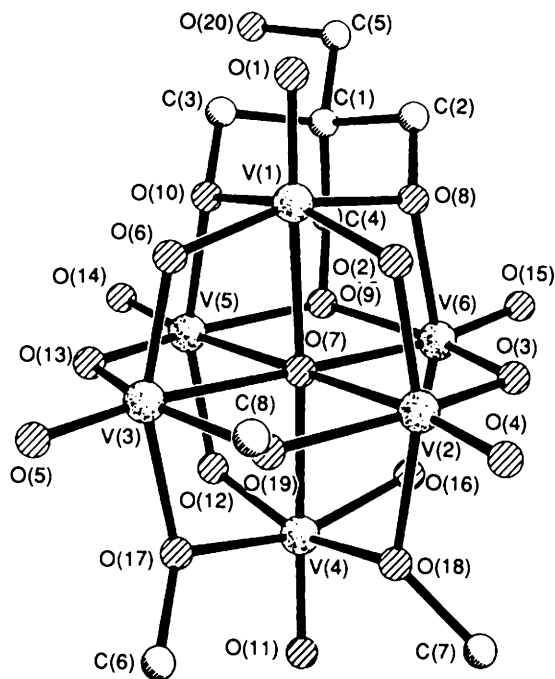


Fig. 1 A view of the anion cluster $[V_6O_{13}(OMe)_3\{(OCH_2)_3CCH_2OH\}]^{2-}$ of **1a**. Average bond lengths (Å): V–O, 1.59(1); V–O (doubly bridging), 1.83(1); V–O(7): 2.24(1); V–O (alkoxy), 2.01(1).

Since crystals of **1** were not of high quality, the structure of the isomorphous derivative $[Bu_4N]_2[V_6O_{13}(OMe)_3\{(OCH_2)_3CCH_2OH\}]^{2-}$ **1a** was undertaken.† As shown in Fig. 1, the structure of the anion of **1a** consists of the hexavanadate core $\{V_6O_{19}\}$ with six doubly bridging oxo group replaced by the bridging alkoxy donors of the (trisCH₂OH) ligand and by three methoxy ligands. The clusters of type **1** complete the series of polyanion types based on the $\{V_6O_{19}\}$ core, for which cores with one, two, three and four trisalkoxy ligands have now been reported.

As shown in Fig. 2, the structure of the anion of **2** presents a novel hexavanadium framework based on a tetranuclear $\{V_4O_{16}\}$ core of edge-sharing octahedra linked *via* edge-sharing to two peripheral vanadium square pyramids.§ The geometry of the tetranuclear framework of **2** is reminiscent of that observed for $[Mo_4O_{10}(OCH_3)_6]^{2-}$,¹⁰ which also displays a compact arrangement of four edge-sharing octahedra. The structure of the anion cluster of **2** is realized by fusing two $\{VO_5\}$ square pyramids to the two exterior octahedra for the central core. The resultant hexavanadium cluster exhibits three distinct vanadium geometries: the V(1) site which is distinguished by the *cis* dioxo $[VO_2]^+$ unit, an unusual instance of this structural motif in polyvanadate clusters; the octahedral V(2) centre which participates in bonding to four polyalkoxide ligands, two which bridge sites within the

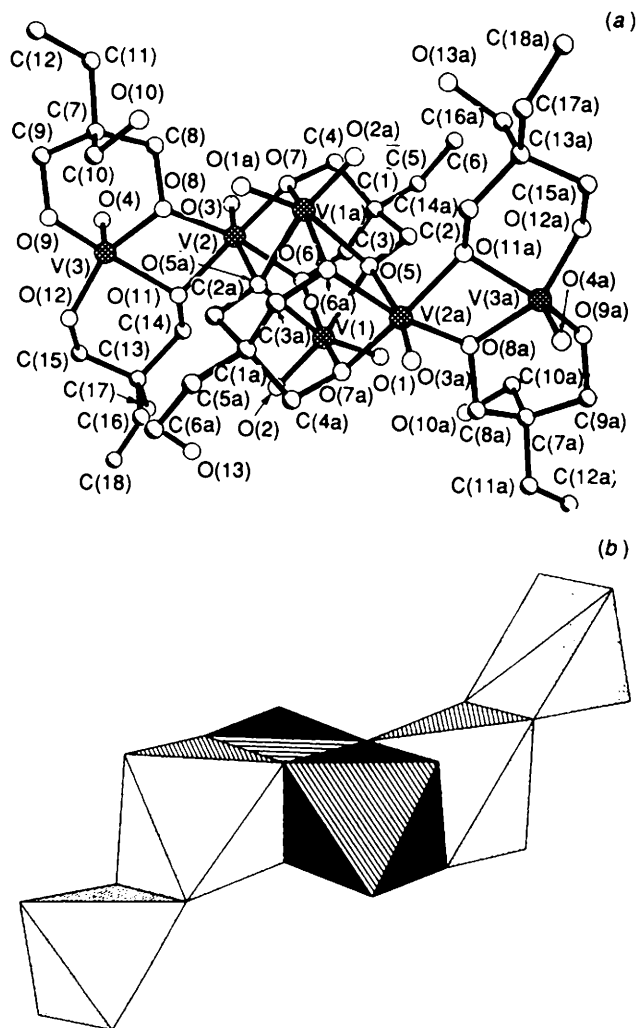


Fig. 2 (a) A view of the structure of the anion cluster $[V_6O_8\{(OCH_2)_3CET\}_2\{(OCH_2)_2C(CH_2OH)(Et)\}]^{2-}$ of **2**. Selected bond lengths (Å): V(1)–O(1), 1.615(8); V(1)–O(2), 1.619(8); V(1)–O(5), 2.183(8); V(1)–O(6), 1.969(8); V(1)–O(5a), 2.206(8); V(1)–O(7), 1.977(8); V(2)–O(3), 1.592(8); V(2)–O(6), 2.008(8); V(2)–O(7), 2.003(8); V(2)–O(8), 1.983(8); V(2)–O(11), 1.98(8); V(2)–O(5a), 2.229(8); V(3)–O(4), 1.62(1); V(3)–O(8), 1.996(8); V(3)–O(9), 1.80(1); V(3)–O(11), 2.009(8); V(3)–O(12), 1.804(9). (b) A polyhedral representation of the structure; the V(1) octahedra are represented with parallel lines while the V(2) octahedra and the V(3) square pyramids are shown as polyhedra with dots.

tetranuclear core and two which bridge V(2) and the exterior V(3) centre; and the square-pyramidal V(3) site, which bonds to two bidentate (HtrisEt) ligands. Valence sum calculations¹¹ confirm that the V(1) site is in the +5 oxidation state while V(2) and V(3) exhibit an intermediate oxidation state +4.5, suggesting that the electrons associated with the reduced metal sites are delocalized.

The (trisEt) moiety adopts the geometry commonly associated with this ligand type in polyoxometallate structures, wherein a triangular arrangement of three metal centres is linked by doubly bridging oxygen donors. One alkoxide oxygen, O(5), bridges to the fourth vanadium centre of the $\{V_4O_{16}\}$ unit to complete the geometric requirements of the central core. The (HtrisEt) ligands assume a bridging bidentate mode with one oxygen donor bridging V(2) and V(3) while another provides terminal ligation to V(3). The pendant oxygens of these ligands are protonated.

While other members of the hexavanadate family of clusters $[V_6O_{19-3n}(tris)_n]^{2-}$ ($n = 2, 3$ and 4) are characterized by reversible redox processes and coupled electron/proton

† Crystal data for $[Bu_4N]_2[V_6O_{13}(OMe)_3\{(OCH_2)_3CCH_2OH\}]^{2-}$ **1a**: monoclinic space group $P2_1/c$, $a = 16.854(2)$, $b = 17.730(3)$, $c = 19.366(4)$ Å, $\beta = 101.89(2)^\circ$, $V = 5663(3)$ Å³, $Z = 4$, $D_c = 1.439$ g cm⁻³; structure solution and refinement based on 2908 reflections [$I_0 \geq 3\sigma(I_0)$]; Mo–K α , $\lambda = 0.71073$ Å] converged at $R = 0.0662$.

§ Crystal data for $[Bu_4N]_2[V_6O_8\{(OCH_2)_3CET\}_2\{(OCH_2)_2C(CH_2OH)(Et)\}]^{2-}$ **2**: orthorhombic space group $Pbca$, $a = 19.622(4)$, $b = 20.524(4)$, $c = 20.800(4)$ Å, $V = 8377(2)$ Å³, $Z = 4$, $D_c = 1.35$ g cm⁻³; structure solution and refinement based on 2441 reflections [$I_0 \geq 3\sigma(I_0)$]; Mo–K α , $\lambda = 0.71073$ Å] converged at $R = 0.0666$.

Atomic coordinates, bond lengths and angles, and thermal parameters for both compounds have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

transfer, clusters **1** and **1a** are electrochemically inactive. On the other hand, **1** reacts with lacunary polymetallates to supply a capping {V₃O₃(tris)} unit, providing substituted polyoxometallates of the type [V₃O₃(tris)PW₉O₃₄]³⁻ 3⁺ and related Dawson types. Cluster **2** is highly reactive and hydrolyses to form higher oligomers the structures and magnetic properties of which are currently under investigation.

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