

# Synthesis and Crystal and Molecular Structure of $(\text{NH}_4)_4[\text{V}_{10}\text{O}_{16}\{\text{EtC}(\text{CH}_2\text{O})_3\}_4]\cdot 4\text{H}_2\text{O}$ , a Decavanadyl Cluster

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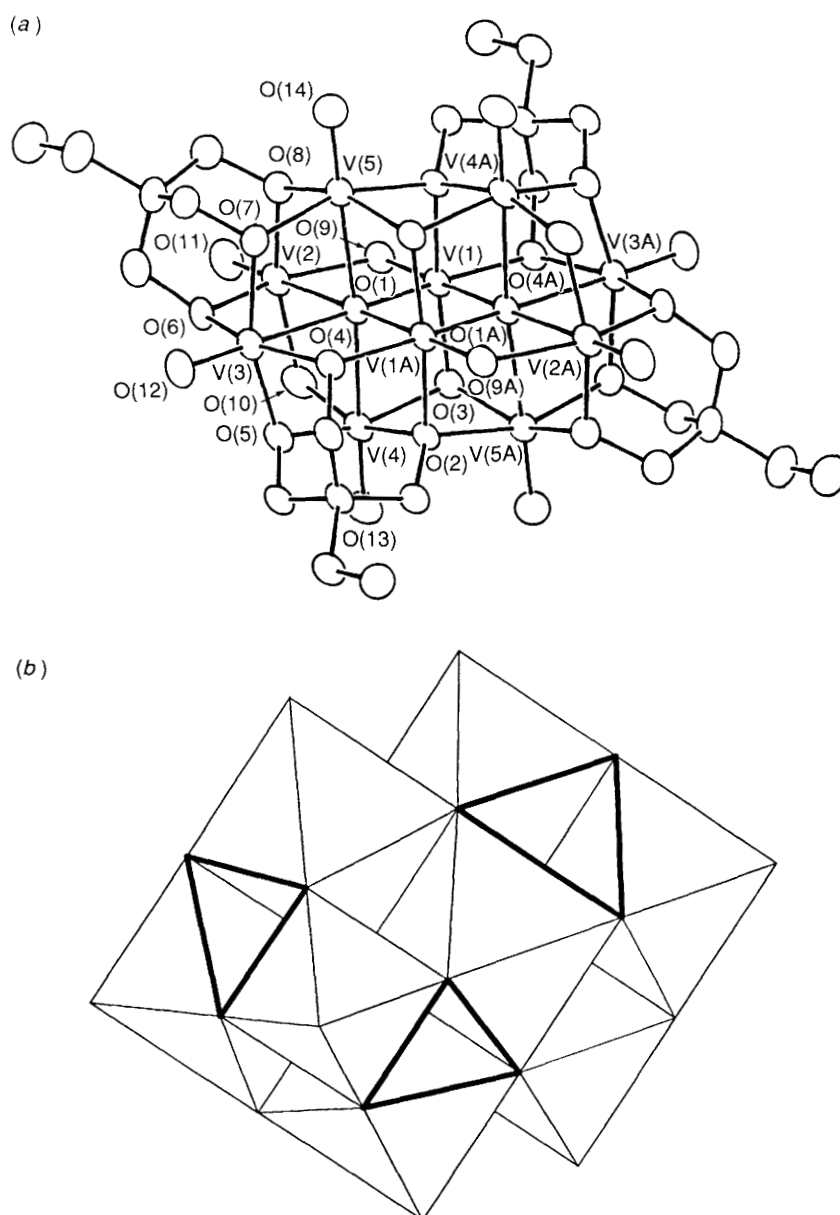
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The hydrothermal reaction of  $(\text{NH}_4)\text{VO}_3$  with  $\text{EtC}(\text{CH}_2\text{OH})_3$  yields the oxoalkoxovanadium(IV) cluster,  $(\text{NH}_4)_4[\text{V}_{10}\text{O}_{16}\{\text{EtC}(\text{CH}_2\text{O})_3\}_4]\cdot 4\text{H}_2\text{O}$ , an unusual polyoxoanion coordination complex with a reduced  $\{\text{V}_{10}\text{O}_{28}\}$  core.

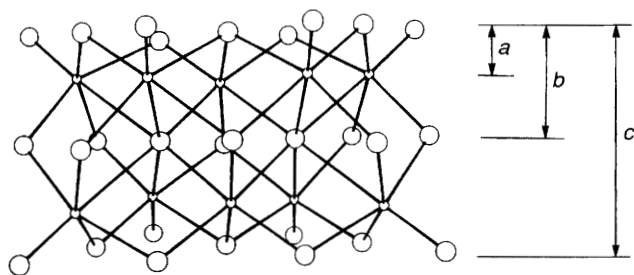
The reduced polyoxovanadates represent a new class of metal–oxygen cluster<sup>1</sup> which exhibit nearly all ratios of  $\text{V}^{\text{IV}}$  to  $\text{V}^{\text{V}}$ , from as few as two weakly coupled  $\text{V}^{\text{IV}}$  sites in  $\text{V}_{10}\text{O}_{26}^{4-2}$  to as many as eighteen  $\text{V}^{\text{IV}}$  sites in  $\text{V}_{18}\text{O}_{42}^{12-3}$ . We have recently described an emerging structural class of oxoalkoxovanadium oligomers<sup>4</sup> and have sought to extend their chemistry by employing the techniques of hydrothermal chemistry which have been demonstrated to produce numerous unusual

polyoxomolybdates and polyoxovanadates of phosphorus which incorporate reduced metal sites.<sup>5,6</sup> In this paper we describe the synthesis and structure of the new oxoalkoxovanadyl cluster  $(\text{NH}_4)_4[\text{V}_{10}\text{O}_{16}\{\text{EtC}(\text{CH}_2\text{O})_3\}_4]\cdot 4\text{H}_2\text{O}$  **1** prepared by the hydrothermal method.

The reaction of two equivalents of  $(\text{NH}_4)\text{VO}_3$  with one equivalent of  $\text{EtC}(\text{CH}_2\text{OH})_3$  in water at 200 °C for four days gave shiny black crystals of  $(\text{NH}_4)_4[\text{V}_{10}\text{O}_{16}\{\text{EtC}-$



**Fig. 1** (a) ORTEP view of the structure of  $[\text{V}_{10}\text{O}_{16}\{\text{EtC}(\text{CH}_2\text{O})_3\}_4]^{4-}$ . This particular anion lies on a crystallographic inversion centre. Bond length ranges (Å): V–O(1), 2.014(3)–2.447(3); V–O (terminal), 1.599(3)–1.656(3); V–O (alkoxy), 1.935(3)–2.135(3); V–O (bridging oxo), 1.656(3)–2.017(3). (b) Schematic representation of the  $\{\text{V}_{10}\text{O}_{28}\}$  core, highlighting the triangular cavities available for occupancy by the oxygen donors of the tris-alkoxy ligand types.



**Fig. 2** Schematic representation of the  $\{V_{10}O_{28}\}$  core viewed as planar layers of negatively charged close-packed oxygen atoms separated by layers of vanadium cations. For  $[V_{10}O_{28}]^{6-}$ :  $a = 0.89$ ,  $b = 2.18$ ,  $c = 4.36$  Å; for  $[V_{10}O_{16}\{EtC(CH_2O)_3\}_4]^{4-}$ :  $a = 0.87$ ,  $b = 2.24$ ,  $c = 4.48$  Å.

$(CH_2O)_3\}_4\cdot 4H_2O$  **I**.<sup>†</sup> The IR spectrum of **I** exhibits a strong band at  $1042\text{ cm}^{-1}$ , characteristic of  $\nu(C-O)$  of the ligand, and features at  $968$  and  $777\text{ cm}^{-1}$  associated with  $\nu(V-O_t)$  and  $\nu(V-O-V)$ , respectively.

The structure of the molecular anion of **I**,<sup>‡</sup> shown in Fig. 1, consists of the decavanadate core  $\{V_{10}O_{28}\}$  in which ten doubly bridging oxo groups and two triply bridging oxo groups have been replaced by twelve alkoxy donors from the four ligands. The substitution pattern exhibited by the trisalkoxy donors of the ligands conforms to the ligand steric requirements which dictate adoption of a bridging mode between three metal sites in a triangular arrangement when possible. Three donors will cap the triangular faces of the tetrahedral cavities of the decametallate framework, as shown schematically in Fig. 1(b). Of the twelve potential ligand sites, six may be occupied by bridging tridentate ligands and, of these, four sites are occupied symmetrically about the core. Of the stoichiometries possible for the reduced decavanadium core substituted by trisalkoxy ligand types,  $[V_{10}O_{28-3n}\{RC(CH_2O)_3\}_n]^{-16+(3n)}$ , two have now been observed,  $n = 4$  and  $n = 5$ .<sup>7</sup> Other stoichiometries are possible, and the existence of at least three substitution types in the hexavanadate series,  $[V_6O_{19-3n}\{RC(CH_2O)_3\}_n]^{x-}$ ,  $n = 2, 3$  and  $4$ ,<sup>4,8</sup> suggests that

<sup>†</sup> Satisfactory elementary analyses.

<sup>‡</sup> Crystal data for  $C_{24}H_{68}N_4O_{32}V_{10}$ : monoclinic,  $C2/c$ ,  $a = 17.320(2)$ ,  $b = 24.904(4)$ ,  $c = 12.430(2)$  Å,  $\beta = 106.32(1)^\circ$ ,  $V = 5145.6(12)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.85\text{ g cm}^{-3}$ . Structure solution and refinement based on 4054 reflections with  $I \geq 3\sigma(I_o)$  converged at a residual of 0.042. 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.

these may also be isolable. A cation dependence is apparent since in the presence of alkylammonium salts only the  $[V_{10}O_{13}\{RC(CH_2O)_3\}_5]^{1-}$  cluster types are formed, while with  $NH_4^+$  the  $[V_{10}O_{16}\{RC(CH_2O)_3\}_4]^{4-}$  species are readily isolated.

It is noteworthy that the complex anion contains exclusively  $V^{IV}$  d<sup>1</sup> sites. The consequences of reduction of the metal sites and ligand substitution on the  $\{V_{10}O_{28}\}$  central core are illustrated in Fig. 2, which compares the interplanar spacings between layers of negatively charged, closed-packed oxygen atoms separated by layers of cationic vanadium centres for  $[V_{10}O_{28}]^{6-9}$  and  $[V_{10}O_{16}\{EtC(CH_2O)_3\}_4]^{4-}$ . The overall expansion of the cluster core of  $[V_{10}O_{16}\{EtC(CH_2O)_3\}_4]^{4-}$  relative to that of  $[V_{10}O_{28}]^{6-}$  is most clearly reflected both in the distances between outermost planes of oxygen atoms, 4.48 and 4.36 Å, respectively, and in the interplanar separation between planes of vanadium centres, 2.74 and 2.58 Å, respectively.

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