Investigations of the Vanadium–oxo–organophosphonato System: Preparation and Structural Characterization of a Mixed-valence V^V–V^{IV} Cluster encapsulating Chloride Anions, $(Bu_4N)_2[(V_8O_{16})\{V_4O_4(H_2O)_{12}\}(PhPO_3)_8Cl_2]\cdot 2Et_2O\cdot 2MeOH\cdot 4H_2O$

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The reaction of $(Bu_4N)[V_5O_7(OMe)_2(PhPO_3)_5]$ with aqueous HCl in methanol followed by treatment with diethyl ether yields dark brown crystals of $(Bu_4N)_2[(V_8O_{16})\{V_4O_4(H_2O)_{12}\}(PhPO_3)_8Cl_2]\cdot 2Et_2O\cdot 2MeOH\cdot 4H_2O$ **1**, a mixed-valence V^V–V^{IV} cluster consisting of two $(V_4O_8)^{4+}$ caps each bridged through four $PhPO_3^{2-}$ groups to a central girdle of four $[VO(H_2O)_3]^{2+}$ units, and encapsulating two chloride anions in the molecular cavity.

The diverse chemistry of the vanadium–oxo–organophosphonate system ($V–O–RPO_3^{2-}$) is represented by both solid materials with practical applications as sorbents[1–3] and a complex polyanion chemistry manifested in a variety of cluster shells constructed from the edge- and corner-sharing of vanadium square pyramids and/or octahedra and phosphorus tetrahedra.[4] We have recently demonstrated that, by exploiting hydrolysis–condensation reactions, relatively simple molecular precursors may be used in the preparation of complex clusters, as exemplified by the preparations of $[V_5O_7(OMe)_2(PhPO_3)_5]^-$ from $[(VO_2)_2(PhPO_3)_2]^{2-}$ and of the super cluster $[V_{18}O_{25}(H_2O)_2(PhPO_3)_{20}Cl_4]^{4-}$ from $[V_5O_7(OMe)_2(PhPO_3)_5]^-$.[4,5] The pentanuclear species $(R_4N)[V_5O_7(OMe)_2(PhPO_3)_5]$ represents a readily prepared and easily handled synthetic precursor for the investigation of the $V–O–RPO_3^{2-}$ system, and our continuing studies have revealed an extensive chemistry with a variety of anionic templates which serve to direct the aggregation processes. We report here the synthesis and structure of one member of this class of host-guest complexes of the $V–O–RPO_3^{2-}–X$ system (X = halide or pseudohalide), $(Bu_4N)_2[(V_8O_{16})\{V_4O_4(H_2O)_{12}\}(PhPO_3)_8Cl_2]\cdot 2Et_2O\cdot 2MeOH\cdot 4H_2O$ **1**.

The reaction of $(Bu_4N)[V_5O_7(OMe)_2(PhPO_3)_5]$ with 4 equiv. of aqueous HCl in methanol yields a dark brown solution from which crystals of **1** are isolated in 20–30% yield after treatment with diethyl ether.† The infrared spectrum of **1** exhibits two strong bands in the 900–970 cm^{-1} range associated with ν(V=O) and four strong bands in the 1000–1200 cm^{-1} range assigned to the PO_3 goup.

The X-ray crystallographic study of **1** reveals a structure consisting of discrete $(Bu_4N)^+$ cations, $[(V_8O_{16})\{V_4O_4(H_2O)_{12}\}(PhPO_3)_8Cl_2]^{2-}$ **1a** molecular anions, and Et_2O, H_2O and MeOH molecules of crystallization.‡ The structure of the anion **1a** shown in Fig. 1, consists of two $(V_4O_8)^{4+}$ caps, each bridged through four $(PhPO_3)^{2-}$ tetrahedra to a central girdle of four $[VO(H_2O)_3]^{2+}$ groups. Each tetranuclear cap exhibits a ring of V^V square pyramids, corner-sharing through bridging oxo-groups and linked in a pairwise fashion by corner-sharing to $(RPO_3)^{2-}$ tetrahedra adopting the symmetrically bridging bidentate mode (Fig. 2). The remaining oxygen donors of the eight organophosphonate groups serve to bridge the (V_4O_8) caps to the four central V^{IV} octahedra. These sites are most unusual in that the coordination about each of the V^{IV} centres consists of a terminal oxo-group, two organophosphonate oxygens and three aquo ligands, one of which projects into the interior of the molecular cavity so as to partition the interior volume into two compartments, each of which is occupied by a chloride anion. Charge requirements suggest that **1a** is a mixed valence species $V_8{}^VV_4{}^{IV}$ and valence sum calculations[6] clearly identify the capping vanadium centres as V^V, while the four vanadium atoms of the central girdle are in the +4 oxidation state. The room-temperature magnetic moment of 2.60 μ_B is close to the spin-only value for four isolated V^{IV} sites. It is also noteworthy that the $(V_4O_8)^{4+}$ units of **1** are topologically related to the $(V_5O_9)^{3+}$ groups observed in $[V_{14}O_{22}(OH)_4(H_2O)_2(PhPO_3)_8]^{6-}$ [7] and $[H_4V_{18}O_{42}X]^{9-}$ [8] by removal of the central $(VO)^{3+}$ and

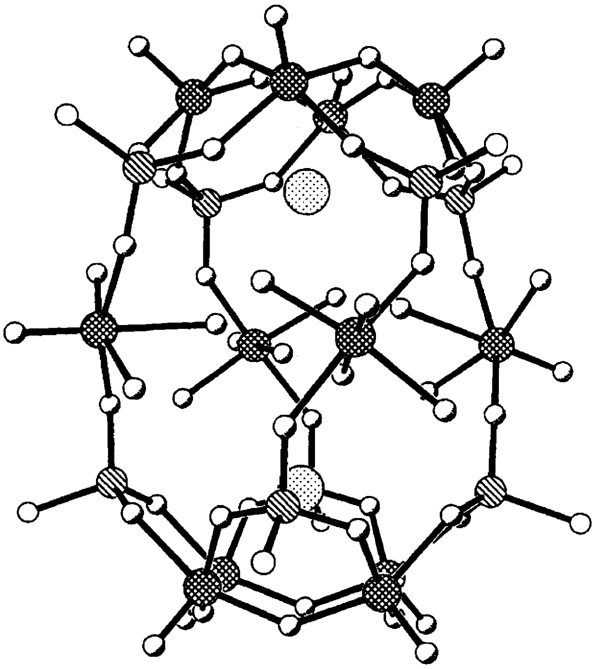

Fig. 1 A view of the structure of the molecular anion of **1** (phenyl groups removed for clarity). Selected bond distance ranges (Å): V^V sites of the two $(V_4O_8)^{4+}$ caps: $V–O_t$ 1.54–1.57(2), V–(μ-O) 1.77–1.85(2), V–O(phosphonate) 1.94–2.01(2); V^{IV} sites of the four central $[VO(H_2O)_3]$ units: $V–O_t$ 1.59–1.65(2), V–O(phosphonate) 1.97–2.06(2), V–O(aquo) 2.02–2.32(2).

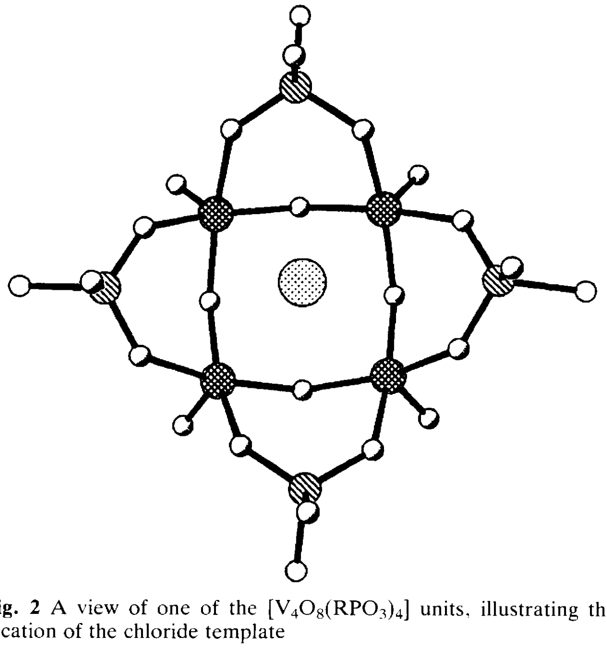

Fig. 2 A view of one of the $[V_4O_8(RPO_3)_4]$ units, illustrating the location of the chloride template

flattening of the (V_4O_4) ring, an observation which reveals the structural relationship of **1** with $[V_{14}O_{22}(OH)_4(H_2O)_2(PhPO_3)_8]^{6-}$. the latter is formally constructed from **1a** by reduction of the V^V centres, capping of each (V_4O_8) unit by a $(VO)^{3+}$ group, and pairwise condensation of the four $[VO(H_2O)_3]^{2+}$ units to give two bridging $[V_2O_2(OH)_2(H_2O)]^{2+}$ groups. We are investigating the synthesis of the tetradecanuclear species from **1a** or directly from $[V_5O_7(OMe)_2(PhPO_3)_5]^-$.

While the preparation of **1** from $(Bu_4N)[V_5O_7(OMe)_2(PhPO_3)_5]$ provides an additional example of organization of vanadium polyhedra and $(RPO_3)^{2-}$ tetrahedra about a template, the role of different anions as templates remains undeveloped. Since the topological flexibility of the V–O–RPO_3^{2-} system may exceed that of the 'naked' V–O clusters,[9] the encapsulation of a variety of anionic, neutral and even cationic templates is being realized in the isolation of molecular and supramolecular species of remarkably diverse structures.

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Footnotes

† Satisfactory elementary analyses were obtained. Thermal gravimetric analysis exhibited mass losses at temperatures below 150 °C, consistent with the loss of the molecules of crystallization.

‡ *Crystal data* for $C_{90}H_{152}Cl_2N_2O_{64}P_8V_{12}$: monoclinic, space group $P2/n$, $a = 22.132(4)$, $b = 13.584(3)$, $c = 22.685(5)$ Å, $\beta = 103.58(2)°$, $V = 6629(11)$ Å^3, $Z = 2$, $D = 1.604$ g cm^{-3}; structure solution and refinement based on 2393 reflections $[I_o \geq 3\theta(I_o)]$ converged at $R = 0.0782$. Data were collected at 213 K on a Rigaku AFC5S diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å). Data were corrected for absorption effects using ψ scans on five reflections with χ angles near 90 or 270°. Structure solution and refinement was performed using the PC version of SHELXTL PLUS. The Bu_4N^+ cation and the molecular anion **1a** exhibit no signs of disorder. The final difference Fourier maps revealed the presence of Et_2O, MeOH and H_2O molecules of crystallization. The large temperature factors associated with these sites suggest some disorder. However, placing the atoms at the sites of maximum peak heights in the electron density map and allowing the temperature factors to vary undamped resulted in a featureless difference Fourier map, suggesting that no further modelling was required. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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