Control of Aggregation through Anion Encapsulation in Clusters of the V/O/RPO$_3$$^{2-}$ System: Synthesis and Crystal and Molecular Structures of the Tetranuclear Clusters [NBu$^n_4$][V$^V_4$O$_6$F(PhPO$_3$)$_4$] and [NBu$^n_4$]$_2$[V$^V_3$V^{VI}O$_6$F(PhPO$_3$)$_4$]

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The reaction of [(NBu$^n_4$)][V$_5$O$_7$(PhPO$_3$)$_5$(OMe)$_2$] with HBF$_4$·Et$_2$O in acetonitrile yields the tetranuclear vanadium(v) cluster [NBu$^n_4$][V$_4$O$_6$F(PhPO$_3$)$_4$] **1** which upon reduction with organohydrazine yields the mixed-valence cluster [NBu$^n_4$]$_2$[V$^V_3$V^{IV}O$_6$F (PhPO$_3$)$_4$] **2**.

The emergence of the oxovanadium organophosphonate system, V/O/RPO$_3$$^{2-}$, has revealed an unusually rich chemistry of both molecular clusters[1–7] and solid phases.[8–11] For either class of compounds, the influence of templating reagents in the organization of the oxovanadium organophosphonate framework has been noted.[6,12] In the case of the analogous vanadium oxide or 'naked' core clusters, an identical [V$_{15}$O$_{36}$]$^{5-}$ cage accommodates anions of significantly different ionic radii: Cl$^-$, Br$^-$ and CO$_3$$^{2-}$.[13] However, introduction of templates with different electronic or steric requirements will result in the organization of different cluster aggregates, providing cavities of appropriate dimensions, as noted, for example, in the case of [H$_2$V$_{22}$O$_{54}$(MeCO$_2$)].[7–14] While the clusters of the V/O/RPO$_3$$^{2-}$ system are largely limited to chloride encapsulating species, it was anticipated that the choice of alternative templates should result in the isolation of different cluster shells. This expectation has been realized in the preparation of the tetranuclear vanadium(v) cluster [NBu$^n_4$][V$_4$O$_6$F(PhPO$_3$)$_4$]·MeCN **1** and of the mixed-valence [NBu$^n_4$]$_2$[V$^V_3$V^{IV}O$_6$F(PhPO$_3$)$_4$]·1.4MeCN·1.3H$_2$O **2**.

The reaction of [NBu$^n_4$][V$_5$O$_7$(PhPO$_3$)$_5$](OMe)$_2$ with an excess of HBF4·Et$_2$O in acetonitrile at room temp. for 12 h yielded bright yellow crystals of **1** in 40% yield. The infrared spectrum of **1** exhibited a strong band at 968 cm^{-1} assigned to ν(V=O) and a group of three medium to strong bands in the range 997–1135 cm^{-1} associated with ν(P–O) of the organophosphonate group. The ^{51}V NMR spectrum in acetonitrile exhibits a single sharp resonance at δ −591 (VOCl$_3$ standard), while the ^{31}P NMR spectrum is characterized by a signal at δ 23.7 (H$_3$PO$_4$ reference). The cluster is electrochemically active, exhibiting successive reversible one-electron reductions at +0.06 and −0.56 V with respect to the ferrocene–ferrocenium couple. Controlled potential electrolysis at −0.05 V of an acetonitrile solution of **1** results in an emerald green solution of the one-electron reduced product [V$_4$O$_6$F(PhPO$_3$)$_4$]$^{2-}$ **2a**.

Chemical reduction with 1,2-diphenylhydrazine of a yellow solution of **1** in MeCN produces a dark green solution from which crystals of [NBu$^n_4$]$_2$[V$_4$O$_6$F(PhPO$_3$)$_4$]·1.4MeCN·1.3H$_2$O **2** are isolated in 45% yield. The infrared spectrum of **2** is very similar to that of **1** with ν(V=O) at 975 cm^{-1} and a group of three bands in the region 1000–1350 cm^{-1} attributed to ν(P–O). The room temp. magnetic susceptibility is consistent with the presence of a single unpaired electron.

The X-ray crystallographic study of [NBu$^n_4$][V$_4$O$_6$F(PhPO$_3$)$_4$]·MeCN **1**† reveals that the structure consists of isolated NBu$^n_4$ cations, MeCN molecules of crystallization and tetranuclear anionic clusters [V$_4$O$_6$F(PhPO$_3$)$_4$]$^-$, illustrated in Fig. 1. The structure exhibits of a spherical V/P/O shell of corner-sharing vanadium square pryramids and organophosphonate tetrahedra, encapsulating the fluoride anion which serves as a template for the cluster organization in the condensation process. Alternatively, the shell may be viewed as two binuclear {V$_2$O$_3$}$^{4+}$ units bridged by four organophosphonate groups, each contributing two oxygen donors to one binuclear site and one to the other. The vanadium square pyramids consist of the apical oxo-group with the basal plane defined by the bridging oxo-group and an oxygen donor from each of three organophosphonates. Two {(V$_2$O$_3$)(μ-O$_3$PPh)$_2$} structural motifs fuse through the third {P–O} moieties of each of the organophosphonate groups so as to dispose the {V–O–V} groups in a staggered orientation. The fluoride is not totally symmetrically disposed within the cavity, exhibiting three V–F distances averaging 2.418(6) Å and a fourth at the significantly longer distance of 2.477(4)Å. Valence sum calculations (15e) are consistent with the V^V formulation for all metal sites, providing an average valence of 4.99.

The one-electron reduced species **2** exhibits the same core structure as **1** with only minor differences in the metrical parameters. However, the consequences of reduction are most obviously manifested in V–F distances, three of which average 2.489(11) Å while the fourth is 2.406(9) Å, an observation consistent with an expansion of the cluster volume concomitant to introduction of an additional electron. Similar effects have been observed in the oxovanadium alkoxide class [V$_6$O$_{13}$\{OCH$_2$)$_3$CR\}$_2$]$^{n-}$ where cluster reduction is also reflected in expansion of cluster volume (16e). The metrical parameters associated with the vanadium sites confirm that the spin is not trapped at a single site but delocalized over the cluster metal centres. The average valence sum for the

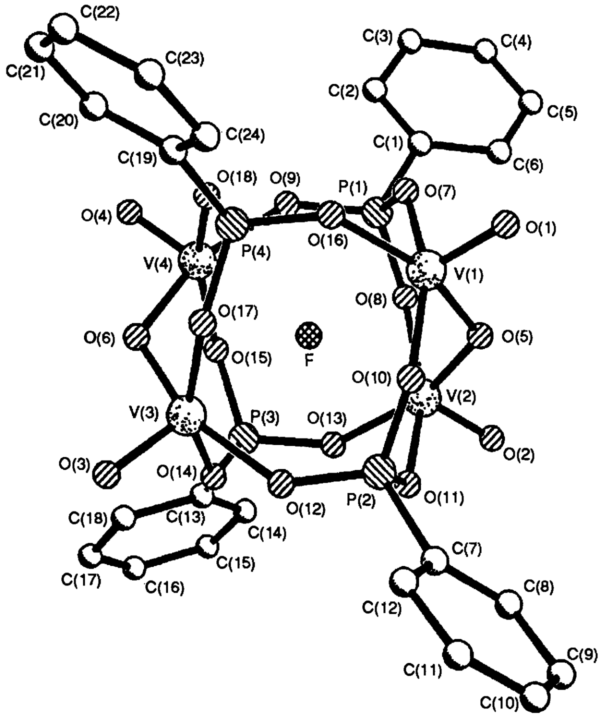

Fig. 1 A view of the structure of the molecular anion [V$_4$O$_6$F(PhPO$_3$)$_4$]$^{n-}$ of **1** and **2** (n = 1 and 2, respectively), showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): **1**, V–O$_t$ 1.581(8), V–O$_b$ 1.803(8), V–O(P) 1.929(7), V(1)–F 2.412(4), V(2)–F 2.427(3), V(3)–F 2.477(4), V(4)–F 2.414(4), V(1)–O(5)–V(2), 120.4(3), V(3)–O(6)–V(4) 120.1(2). **2**, V–O$_t$ 1.579(15), V–O$_b$ 1.824(13), 1.954(14), V(1)–F 2.493(9), V(2)–F 2.511(9), V(3)–F 2.463(9), V(4)–F, 2.406(9), V(1)–O(5)–V(2) 120.5(6), V(3)–O(6)–V(4) 118.0(6).

vanadium sites of **2** of 4.73 is consistent with this observation and with the introduction of a single electron.

The template influence in the organization of clusters of the $V/O/RPO_3^{2-}$ system is pronounced. While fluoride results in the isolation of tetranuclear cores **1a** and **2a**, the hexanuclear $[(VO)_6(RPO_3)_8Cl]$ **3** and heptanuclear $[V_7O_{12}(RPO_3)_6Cl]^-$ **4** are observed for chloride as template, reflecting the considerably larger ionic radius of Cl^- with respect to F^- (1.81 *vs.* 1.19 Å). It is noteworthy that while the tetranuclear core **1a** cannot accommodate Cl^-, the hexanuclear core $[(VO)_6(RPO_3)_8X]^-$ possesses dimensions adequate for the inclusion of Br^- or I^-. We are currently investigating the cluster chemistry of the $V/O/RPO_3^{2-}$ system with larger halides, pseudohalides such as N_{3-} and SCN^-, and carbon oxoanions.

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Footnotes

† *X-Ray data* for $[NBu^n_4][V_4O_6F(PhPO_3)_4]\cdot MeCN$ **1**: triclinic, space group $P\bar{1}$, a = 12.512(3), b = 12.637(3), c = 19.499(4) Å, α = 104.39(3), β = 92.20(3), γ = 113.43(3)°, V = 2707.3(14) Å^3, Z = 2, D_c = 1.505 g cm^{-3}, μ(Mo-Kα) = 8.60 cm^{-1}, structure solution and refinement based on 4944 reflections with $2\theta \leqslant 45°$ and $I_o \geqslant 3\sigma(I_o)$ converged at R = 0.0607. $[NBu^n_4]_2[V_4O_6F(PhPO_3)_4\cdot 1.4MeCN\cdot 1.3H_2O$ **2**: monoclinic, space group $P2_1/n$, a = 17.067(3), b = 21.833(4), c = 20.113(4) Å, β = 97.20(3)°, V = 7435(4) Å^3, Z = 4, D_c = 1.347 g cm^{-3}, μ(Mo-Kα) = 6.41 cm^{-1}, 2759 reflections, R = 0.0727. One of the acetonitrile molecules of crystallization in the structure of **2** is disordered and partially occupied.

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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