The Missing Link in Low Nuclearity Pure Polyoxovanadate Clusters: Preliminary Synthesis and Structural Analysis of a New {V₁₆} Cluster and Related Products

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Two new metastable polyoxovanadate-based cluster compounds have been isolated and crystallographically characterized with nuclearities of {V₁₆} (**1**) and {V₁₈} (**2**). The {V₁₆} cluster represents a new framework type and incorporates two protons into the cluster framework whereas the {V₁₈} framework has been previously characterised, and the oxidation states of the {V₁₈} cluster can be assigned as $\{V_{15}^{IV}V_3^V\}$. Compound $K_{10}[H_2V_{16}O_{38}]\cdot 13H_2O$ (**1**) crystallizes in the monoclinic space group $P2_1/c$, $a = 12.12820(10)$, $b = 38.2302(3)$, $c = 12.35400(10)$ Å, $\beta = 115.0470(10)°$, $V = 5189.43(7)$ Å³, $D_c = 2.624$ g·cm⁻³. 10086 unique reflection and 702 refined parameters were used in structure refinement. $R1 = 0.039$, $R2 = 0.109$ (all data). From the same preparation the new compound $K_{11}[V_{18}O_{42}(SO_4)]\cdot 20H_2O$ (**2**) was also isolated and crystallographically characterized. Compound **2** crystallizes in the monoclinic space group $P2_1/n$, $a = 12.7854(3)$, $b = 20.2812(5)$, $c = 13.2386(4)$ Å, $\beta = 115.3400(10)°$, $V = 3102.53(14)$ Å³, $D_c = 2.650$ g·cm⁻³. 7115 unique reflections and 462 refined parameters were used in structure refinement. $R1 = 0.046$, $R2 = 0.121$ (all data).

KEY WORDS: Vanadium; vanadate; polyoxovanadate; polyoxometalate; x-ray crystal structure; mixed valence; cluster structure.

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INTRODUCTION

Polyoxovandates constitute an important subclass of metal-oxide based clusters that display a high propensity to form mixed valence species. Such cluster compounds have been found to contain vanadium ions in the V(IV) and V(V) oxidation states and their coordination geometries are often pyramidal, and comprise $\{O=VO_4\}$ units. Such building blocks have been seen to be extremely versatile in the formation of hollow cluster shells, with the incorporation of encapsulated anionic species of specified size, shape and charge [1]. In clusters that contain exclusively oxo-bridged vanadium centers, the $V\cdots V$ separations are normally larger than 3.5 Å. However there are some examples where there are some short V–V contacts at about 3.0 Å. These contacts fall in the range between single bonding and non-bonding separations and, with the aid of the bridging oxo ligands, form the pathway of strong intramolecular antiferromagnetic exchange interactions between vanadium atoms within the cluster shell. Therefore magnetic studies of these clusters are an interesting area of research [2–5]. To date many low nuclearity polyoxovanadate clusters that have been structurally characterized, including a range of clusters that have the metal atoms arranged in a closed cluster shell. Such clusters often incorporate anions or neutral guest molecules within the cluster. In the nuclearity range 14–18 several ''spherical'' clusters have been isolated including $\{V_{14}\}$, $\{V_{15}\}$, $\{V_{17}\}$, and $\{V_{18}\}$ clusters [6]. Herein, we report the synthesis and isolation of a hitherto unknown $\{V_{16}\}$ cluster compound, **1**, with the preliminary formula $K_{10}[H_2V_{16}O_{38}]\cdot 13H_2O$ that displays a spherical topology and interesting framework connectivity, along with a new $\{V_{18}\}$ cluster compound, **2**, with the preliminary formula $K_{11}[V_{18}O_{42}(SO_4)]\cdot 20H_2O$. Therefore the $\{V_{16}\}$ represents a fundamental new type of vanadate clusters in the nuclearity range of 10 to 34.

EXPERIMENTAL

Preparation of Compounds

All chemicals were of reagent grade and used as received from Aldrich and all reactions were carried out under a nitrogen atmosphere. $VOSO_4\cdot 5H_2O$ (1.00 g; 4.00 mmol) was dissolved in H_2O (60 ml) at room temperature in a large Erlenmeyer flask. KOH (95%) (1.38 g, 23.3 mmol) was then added in the clear solution which turned to dark red thereafter. This was followed by the addition of *N,N,N′,N′*-tetrakis(2-hydroxyethyl)ethylene-diamine (1.09 g; 4.62 mmol). The flask was sealed and left for several days to crystallize. Crystals of the **1** were isolated mechanically as bright red

plates, with a distinctive thicker inner region, and represent an estimated 2% of the precipitated material by weight. Crystals of **2** were isolated mechanically as red square plates and represent around 5% of the precipitated material by weight. The remaining crystalline precipitate was mainly found to be a previously reported $\{V_{18}\}$ cluster compound, **3** with the formula $K_{12}[V_{18}O_{42}(H_2O)] \cdot 16H_2O$ [5]. The identities of all three crystal types were confirmed by single crystal X-ray analysis. It was observed that when the solution containing the crystals of **1** and **2** was left to stand for more than two days after crystallization, both compounds **1** and **2** underwent dissolution and only compound **3** remained.

X-Ray Crystallography

Intensity data were measured at 150 K on a Bruker–Nonius Kappa-CCD diffractometer equipped with an area detector and using Mo-Kα monochromatized X-radiation ($\lambda = 0.71073$ Å). Data were corrected for absorption using the Gaussian quadrature method of Coppens *et al.* [7a]. The structures were solved by direct methods and refined by full matrix least-squares using the SHELX-97 package [7b]. Crystallographic data collection, intensity measurements and structure refinement parameters are given in Table I.

RESULTS AND DISCUSSION

Synthetic Strategy

The synthetic approach presented here incorporates *N,N,N′,N′*-tetrakis (2-hydroxy)ethylenediamine in the reaction system, and this appears to have interesting effects on the crystallization and isolation of several new cluster types. It is important to note that the incorporation of this ligand causes the isolation of many new crystalline compounds (at least five—as determined by initial unit cell measurements) of which only three could be fully crystallographically characterized. However, the majority of the crystalline material precipitated was found to be the previously characterized [5] $K_{12}[V_{18}O_{42}(H_2O)]$ (**3**) cluster whereas the two other identified components, compounds **1** and **2** contain the new the cluster types $\{V_{16}\}$ and $\{V_{18}\}$, respectively. Unfortunately both these clusters compounds are quite unstable and decompose in the mother liquor over a period of several days and within minutes when isolated.

Preliminary Formula Determinations

The determination of the formula of the compounds **1** and **2** was hindered by the fact that both the compounds are extremely unstable, decomposing in a matter of minutes after isolation from the mother liquor (attempts to investigate the clusters *via* redox titrations and elemental analysis was prevented due to the problems associated with cluster decomposition). Therefore the initial studies were limited to crystallographic analysis and assignment of the oxidation states of the vanadium ions by bond valence sums (BVS) analysis; fortunately the structures are of sufficiently high quality so that this analysis is meaningful. By considering the absolute numbers of cations present in the structures of compounds **1** and **2**, along with the number of the framework oxygen atoms (and the encapsulated sulphate anion in the case of **2**), it is possible to devise general formulas for **1** and **2**. From the structural analysis of **1** the original "crystallographic" formula can be given as $K_{10}[V_{16}O_{38}] \cdot 13H_2O$, which means fourteen vanadium ions in the V(IV) and two in the V(V) oxidation state.

Table I. Crystallographic Data Collection, Intensity Measurements, and Structure Refinement Parameters for **1** and **2**

Chemical formula	$K_{10}[H_2V_{16}O_{38}] \cdot 13H_2O$	$K_{11}[V_{18}O_{42}(SO_4)] \cdot 20H_2O$
M (g·mol^{-1})	2050.26	2475.40
Symmetry	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	12.12820(10)	12.7854(3)
b (Å)	38.2302(3)	20.2812(5)
c (Å)	12.35400(10)	13.2386(4)
β (°)	115.0470(10)	115.3400(10)
V (Å^3)	5189.43(7)	3102.53(14)
Z	4	2
D_c (g·cm^{-3})	2.624	2.650
μ (mm^{-1})	3.652	3.471
$F(000)$	3976	2414
Crystal size (mm)	$0.32 \times 0.30 \times 0.04$	$0.28 \times 0.14 \times 0.06$
Data collection ranges	$1.52 \leqslant \theta \leqslant 30.0$	$1.52 \leqslant \theta \leqslant 30.0$
No. data measured	58785	31167
No. unique data	10086	7115
No. observed data	9028	5064
No. variables	702	462
$R1$	0.039	0.046
$R2$ (all data)	0.109	0.121
Goodness of fit, S	1.029	1.030
Maximum shift/error	0.001	0.002

However, this assumes that all the framework oxygen atoms are not protonated. If the possibility of protonation is taken into account then a general formula can be given as $K_{10}[H_{2-x}V^{IV}_{16-x}V^{V}_{x}O_{38}] \cdot 13H_2O$. This analysis implies that there are three possible formulations for the $\{V_{16}\}$ where $x = 2, 1$, or 0 and this changes the number of V(IV) and V(V) states respectively. Analysis of the bond valence sums gives an average BVS value of 4.063 per vanadium centre in the cluster which means that the cluster is almost totally reduced with $\{V^{IV}_{16}V^{V}_{0}\}$ ($x = 0$) or possibly comprises $\{V^{IV}_{15}V^{V}_{1}\}$ and $x = 1$. However, we have managed to locate two proton positions per cluster cage, see the structural analysis section, which means that the formula for the cluster framework can be considered to be $[H_2V^{IV}_{16}O_{38}]^{10-}$. Applying the same logic to **2,** where the "crystallographic" formula is $K_{11}[V_{18}O_{42}(SO_4)] \cdot 20H_2O$, yields the general formula $K_{11}[V^{IV}_{18-x}V^{V}_{x}H_{3-x}O_{42}(SO_4)] \cdot 20H_2O$. This implies four possible formulations for the $\{V_{18}\}$ cluster, corresponding to $x = 3, 2, 1$ and 0, respectively. Examination of the bond valence sums gives an average BVS value of 4.166 per vanadium centre which corresponds to the formula $\{V^{IV}_{15}V^{V}_{3}\}$ so that $x = 3$ and there are no protons incorporated into the shell.

Structural Analysis

The structure of the $\{V_{16}\}$ cluster present in compound **1** is shown in Fig. 1 as a $[V_{16}O_{38}]$ shell made of sixteen square-pyramidal VO_5 units. Of
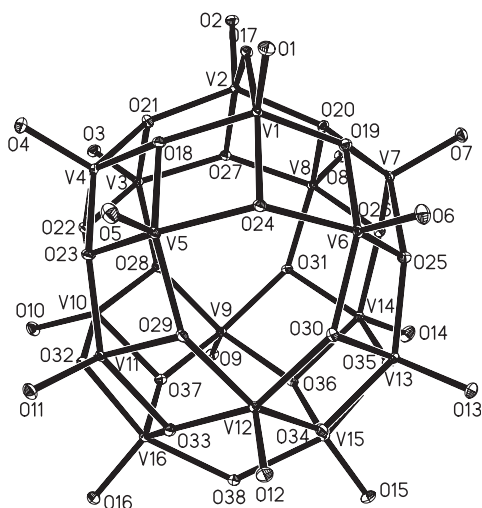

Fig. 1. ORTEP view of the $\{V_{16}\}$ cluster anion found in compound **1**.

the five oxo ligands, four are bridging ligands between vanadium atoms with the remaining oxo ligand in a terminal coordination mode. Most of the twenty-two bridging oxygen atoms adopt a μ_3 coordination and only two (O17 and O38) adopt a μ_2 bridging mode. The bond lengths of the terminal V=O bonds fall in the range from 1.621(3) to 1.649(3) Å. Those μ_3 bridging oxo ligands have V–O distances that range from 1.910(3) to 1.984(3) Å while those for μ_2 bridging oxo ligands range 2.012(3) to 2.020(3) Å.

The shortest V–V contact within the cluster is 2.7827(11) Å observed between V5 and V11; most other close V–V contacts are in the range 2.8729(11) to 3.0386(11) Å, which are intermediate values compared to those expected for a V–V single bond (ca. 2.5 Å), and non-bonded interactions (ca. 3.5 Å). Fig. 2 shows the structure of the skeleton of the vanadium cluster built up *via* these short V–V contacts. This framework of roughly D_{2d} symmetry has an unprecedented topology and it differs from all other known polyoxovanadate structures.

This framework can be described as two octagonal rings (one from V1 to V8 and the other from V9 to V16) linked together *via* four other close contacts, namely V3–V10, V5–V11, V6–V13, and V8–V14. The shape of the
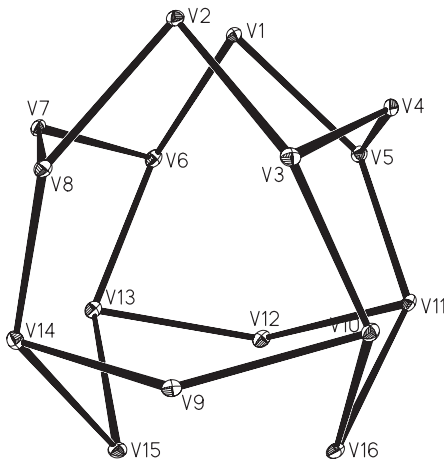

Fig. 2. The metal framework built up *via* V–V close contacts of ca 3.0 Å in $[V_{16}O_{38}]$ of **1**. Short contacts between vanadium atoms: V1–V5 2.9885(11), V1–V6 2.8729(11), V2–V3 2.9659(11), V2–V8 2.9664(10), V3–V10 2.9065(11), V3–V4 2.9907(10), V4–V5 2.9991(11), V5–V11 2.7827(11), V6–V13 2.9042(11), V6–V7 3.0242(11), V7–V8 3.0054(11), V8–V14 2.9481(11), V9–V10 2.9929(11), V9–V14 3.0127(11), V10–V16 2.9439(11), V11–V12 3.0386(11), V11–V16 2.9934(11), V12–V13 3.0287(11), V13–V15 2.9727(11), V14–V15 2.9189(11) Å.
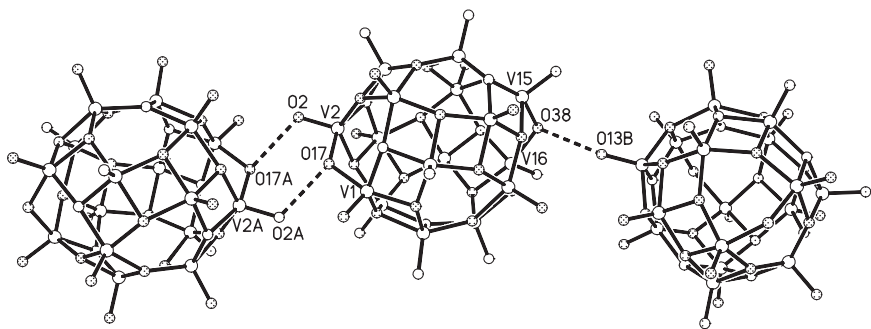
Fig. 3. A ball and stick diagram showing the hydrogen bonding interactions between $\{V_{16}\}$ clusters that allows confirmation of protonation at the two μ_2 bridging oxygen atoms O17 and O38. Symmetry codes: A $= 1 - x$, $1 - y$, $1 - z$; B $= x$, $0.5 - y$, $0.5 + z$.

metal framework consists of 2 kinds of vanadium atom nodes: 3-connected and 2-connected. The separations of V1–V2 and V15–V16 are 3.577(2) and 3.618(2) Å, respectively and two μ_2 oxygen atoms O17 and O38 bridge these vanadium ions respectively, as shown in Fig. 1. Examination of the intermolecular contacts between the clusters reveals that two protons can be located on the μ_2 bridging oxygen atoms, O17 and O38. This is because both these oxygen atoms are involved in hydrogen-bonded interactions with terminal oxo-ligands of adjacent clusters [O17$\cdots$O2A $= 2.807(3)$ Å, symmetry operation A: $1-x$, $1-y$, $1-z$ and O38$\cdots$O13B $= 2.758(3)$, symmetry operation B: x, $0.5-y$, $0.5+z$]. Because of this arrangement it is possible to assign protonation states to both O17 and O38 in an unambiguous manner, see Fig. 3.

Most previously reported vanadium clusters with similar nuclearities encapsulate some kind of anion or molecule such as H_2O [5], but the cage in the present $\{V_{16}\}$ cluster is empty (although a small peak could be identified in the Fourier difference map that equals to ca. 0.2 oxygen atom's occupancy in structure refinement). In light of the analysis of the cluster structure it is clear that the polyoxovanadate is coordinated to ten potassium cations which coincidently co-ordinate to other clusters within the crystal structure to form a three-dimensional network structure. Water molecules are either coordinated to potassium atoms or solvated in the crystal lattice.

The structure of the cluster in compound **2** is shown in Fig. 4, which consists of $[V_{18}O_{42}(SO_4)]$ cages linked by solvated K^+ ions. Each cage hosts a twofold disordered tetrahedral SO_4 group, which is located on a crystallographic special position at the center of the cluster.
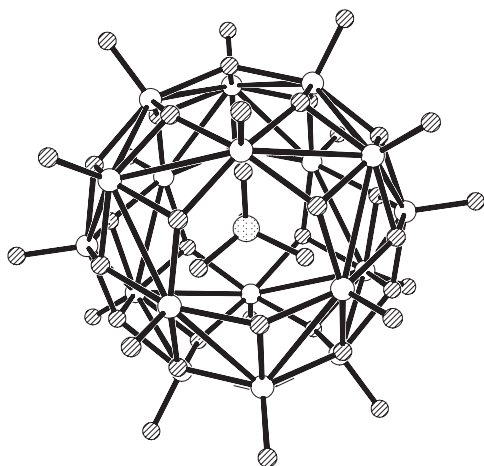
Fig. 4. A ball and stick representation of the $\{V_{18}\}$ cluster in compound **2**.

The S–O bond lengths are in the range 1.440(6) to 1.519(7) Å, which are intermediate between the values for double-bonded and single-bonded interactions. The host shell has a composition of $V_{18}O_{42}$, constructed from eighteen $\{O=VO_4\}$ square pyramids sharing edges through twenty-four μ_3-oxygen atoms. The bond lengths of the eighteen terminal V=O bonds fall in the range from 1.610(3) to 1.664(3) Å. The bridging μ_3-oxo ligands have V–O distances that range from 1.911(3) to 1.983(3) Å. The close V–V contacts within the cluster fall in the range of 2.8436(12) to 2.9907(11) Å and Fig. 5 shows the framework structure of the vanadium cluster built up *via* these short V–V contacts. This framework displays approximately O_h symmetry with a topology of six vanadium 4-connected and twelve 2-connected nodes. Such $[(VO)_{18}O_{24}]$-type shells have been previously observed in the fully reduced molecular species $Cs_{12}[V_{18}O_{42}(H_2O)]\cdot 9H_2O$ and related compounds [5]. Interestingly there is another configuration for the $[(VO)_{18}O_{42}]$ cluster shell, which has D_{4d} symmetry and is illustrated in Fig. 6(e), $(NEt_4)_5[V_{18}O_{42}(I)]$ [5] being one example of such structures. These two configurations can be exchanged by a rotation of 45° of one of the shell halves around one of the four-fold axes.

The $[(VO)_{18}O_{42}]$ cluster shell encapsulates anions or neutral molecules, examples include H_2O [5], X^- ($X = Cl$, Br, I and SH^-) [5], NO_2^- [5], N_3^- [8, 9], NO_3^- [10], PO_4^{3-} [10], SO_4^{2-} and VO_4^{3-} [11, 12]. Such an encapsulation has been suggested by Müller *et al.* to be a form of self-organisation resulting from unusual weak repulsive interactions [1]. In compound **2**, a $[SO_4]^{2-}$ group has been found to be encapsulated, whereby the
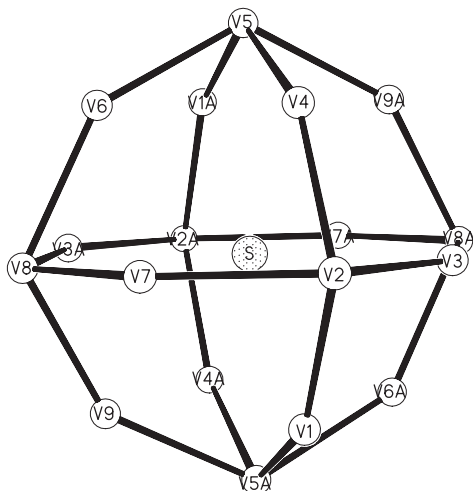
Fig. 5. The metal framework built up *via* V–V close contacts of ca 3.0 Å in $[V_{18}O_{42}(SO_4)]$ of **2**. Oxygen atoms omitted for clarity. Short contacts between vanadium atoms: V1–V2 2.9777(11), V1–V5A 2.8458(11), V2–V3 2.9272(11), V2–V4 2.8954(11), V2–V7 2.9692(11), V3–V8A 2.9408(11), V4–V5 2.9907(11), V5–V6 2.8931(11), V5–V9A 2.9175(11), V6–V8 2.9428(11), V7–V8 2.8436(12), V8–V9 2.8527(12) Å. Symmetry operation A: $-x, 2-y, 2-z$.

average $O \cdots O$ separation between the $[(VO)_{18}O_{42}]$ cluster shell and SO_4 group is ca. 2.481(7) Å. At the same time the average value for the $SO \cdots V$ contacts is ca. 2.590 (7) Å, which is slightly larger than that of $O \cdots O$ separation, verifying the existence of weak repulsive interactions between host anion and guest anion.

For the $[V_{18}O_{42}(SO_4)]$ cluster, there is a much more stable compound $(NH_4)_8[V_{18}O_{42}(SO_4)] \cdot 25H_2O$ previously reported by Müller *et al.* [12]. Direct comparison of the cluster shells in **2** and that in $(NH_4)_8[V_{18}O_{42}(SO_4)] \cdot 25H_2O$ reveals that the structure frameworks are identical, however the compound previously reported is an ammonium salt whereas **2** is a potassium salt. Furthermore, the new $\{V_{18}\}$ cluster in **2** has a different reduction state with $\{V_{15}^{IV}V_3^{V}\}$, (average BVS value per vanadium centre = 4.16), whereas the compound $(NH_4)_8[V_{18}O_{42}(SO_4)] \cdot 25H_2O$ appears to have the following assignment of oxidation states of $\{V_{12}^{IV}V_6^{V}\}$, corresponding to the observed BVS value of 4.37 per vanadium centre.

Comparison of Structural Types

As the $\{V_{16}\}$ cluster reported here has a new spherical framework structure it seems appropriate to make comparisons with previously

reported polyoxovanadates of similar nuclearities. Therefore a group of polyoxovanadates with nuclearities from $\{V_{14}\}$ to $\{V_{18}\}$ were selected and their vanadium "skeleton" frameworks have been drawn by using the V–V close contacts of ca. 3.0 Å; a comparison with the $\{V_{16}\}$ structure is shown in Fig. 6. The framework structures of $\{V_{14}\}$, $\{V_{15}\}$, $\{V_{17}\}$, and $\{V_{18}\}$ cluster shells found in $(CH_6N_3)_7(CH_7N_3)[PV_{14}O_{42}] \cdot 7H_2O$ [13], $K_5[H_2V_{15}O_{36}(CO_3)] \cdot 14.5H_2O$ [14], $(Bu_4N)_4[V_{17}O_{42}]$ [15] and $(Et_4N)_5$ $[V_{18}O_{42}(I)]$ [5], in which the short V–V contacts of ca. 3.0 Å are shown as solid line in Fig. 6. Basically these clusters all have spherical shells but the geometrical features of the frameworks are quite different. A few examples of $\{V_{14}\}$ clusters have been reported in literature [13, 16–18]; in all examples anions encapsulated in the cluster cages. The framework shown in Fig. 6(a) is a typical $\{V_{14}\}$ shell which forms two main parts each
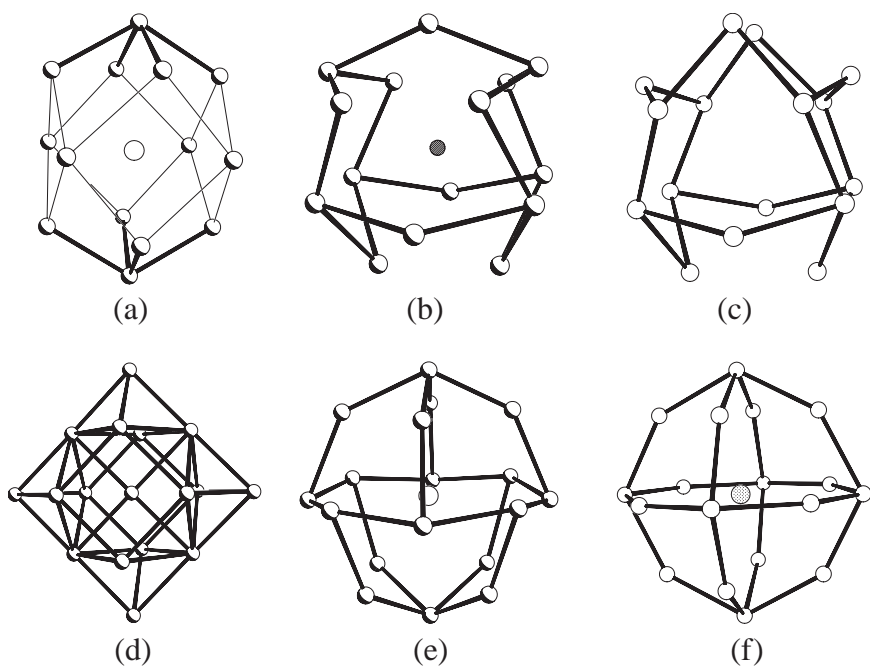

Fig. 6. Comparison of vanadium position arrangements in clusters. Solid lines show the short V⋯V contacts of ca. 3.0 Å within the clusters; thin lines in (a) show the V⋯V contacts between 3.2 and 3.6 Å. (a) $\{V_{14}\}$ in $(CH_6N_3)_8[PV_{14}O_{42}] \cdot 7H_2O$ [13]; (b) $\{V_{15}\}$ in $K_5[H_2V_{15}O_{36}(CO_3)] \cdot 14.5H_2O$ [14]; (c) $\{V_{16}\}$ in $K_{10}[H_2V_{16}O_{38}] \cdot 13H_2O$ (**1**) reported here; (d) $\{V_{17}\}$ in $(Bu_4N)_4[V_{17}O_{42}]$ [15]; (e) $\{V_{18}\}$ in $(Et_4N)_5[V_{18}O_{42}(I)]$ [6]; (f) $\{V_{18}\}$ $K_{11}[V_{18}O_{42}(SO_4)] \cdot 20H_2O$ (**2**) reported here. The central atoms in (a), (b), (e), and (f) are P, C, I, and S respectively.

having five vanadium atoms. Between these two parts, there are four other vanadium atoms equally located forming a square of side length ca. 4.5 Å and having two main interactions between 3.2 and 3.6 Å [13]. Fig. 6(d) shows the framework of $\{V_{17}\}$ in $(Bu_4N)_4[V_{17}O_{42}]$ [15], which could be described as two-fold tetra-capped body-centred cubic type framework. The isomers of the $\{V_{18}\}$ shown in Fig. 6 (e) and (f) have been described in structure analysis section. It is interesting to compare the new $\{V_{16}\}$ (Fig. 6(b)) with the known $\{V_{15}\}$ clusters (Fig 6(c)) as they have very similar frameworks. However there is a key difference between these two frameworks which can be seen by careful examination of Fig. 6(e) and (f), where there is only one vanadium bridge at the top of the framework in the $\{V_{15}\}$, while in $\{V_{16}\}$ there are two. Therefore, in the $\{V_{15}\}$ framework there are three octagons, plus two hexagons, whilst in the $\{V_{16}\}$ there are two octagons plus four hexagons.

CONCLUDING REMARKS

We have been able to isolate two new vanadate compounds, one of which has a $\{V_{16}\}$ spherical structure not previously seen and another with a well-known $\{V_{18}\}$ type framework. Although both structures are extremely unstable, and this has limited the amount of analytical data that can be collected, the high quality of the crystal structures determinations has allowed a preliminary analysis. In this way we were able to examine these metastable cluster-compounds and compare their frameworks with more stable analogues. In particular, the identification of protons in $\{V_{16}\}$ cluster framework represents a dilemma as the cluster synthesis was done under very basic conditions (pH $\approx$ 12–14). Therefore presenting a formula in which protonation is a possibility appears to be against chemical intuition, but the bond-valence-sums and the arrangement of the hydrogen-bonded network between the clusters has clearly shown that the $\{V_{16}\}$ cluster framework supports at least two protons. The reasons for the metastable nature of these clusters is not understood and it could be suggested that these could be reaction intermediates towards the cluster found in **3**, as this appears to be the main stable product from this reaction system.

In future work we will aim to further characterize these clusters so that full formula determination and magnetic investigations can yield information about the precise nature of their electronic structures. However it would appear that the use of multidenate nitrogen donor ligands has allowed the isolation of these metastable clusters–in this respect further work will continue to exploit this strategy in the discovery of other types of cluster-compound.

SUPPLEMENTARY MATERIALS AVAILABLE

Crystallographic data for the structural analysis of compounds **1** and **2** has been deposited with the Inorganic Crystallographic Database at FIZ Karlsruhe, CSD nos. 413145 (compound **1**) and 413146 (compound **2**).

ACKNOWLEDGMENTS

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