

A three-dimensional neutral framework of a novel decavanadium cluster bridged by an AsO_4 tetrahedron: $[\text{AsV}^{\text{IV}}_8\text{V}^{\text{V}}_2\text{O}_{26}(\mu\text{-H}_2\text{O})]\cdot 8\text{H}_2\text{O}$

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A three-dimensional neutral framework of a novel decavanadate ion $[\text{V}^{\text{IV}}_8\text{V}^{\text{V}}_2\text{O}_{26}(\mu\text{-H}_2\text{O})]$ containing an AsO_4 tetrahedral bridge has been synthesized hydrothermally and structurally characterized by X-ray diffraction.

One of the great challenges of modern chemistry is to create multifunctional structures which have well defined cavities and surfaces with sites or areas of different reactivity by linking preorganised robust building blocks.¹ Given the significance of transition metal oxide surfaces² and proven roles of polyoxometalates and their derivatives in catalysis and materials science,³ it is conceivably valuable to attempt to design and prepare transition metal oxide based materials with desired and controllable properties by assembling metal oxide clusters which provide remarkably diverse and well defined building blocks.⁴ Although the mechanism by which the assembly is organised remains elusive, a popular strategy in the realisation of materials engineering involves combined applications of the hydrothermal synthesis method and structure-directing templates.⁵ On-going research has demonstrated that transition metal (*e.g.* Fe, Co, Ni, Cu, Zn and Mn) coordination complexes may serve as inorganic bridging ligands linking polyoxoanion clusters into one-, two- and three-dimensional networks.⁶

Owing to their exceptional ability to form mixed-valence compounds that exhibit rich electronic and magnetic properties, polyoxovanadates have been extensively studied with many structurally characterized examples now known.⁷ Recently, a decavanadium cluster with a $[\text{V}^{\text{V}}_{10}\text{O}_{22}]^{6-}$ core has been reported, and an X-ray structural analysis shows that it is a discrete ion with a chiral framework formed by nine square-pyramidal VO_5 polyhedra surrounding one VO_4 tetrahedron linked through the vertices.⁸ Although decavanadate ions as discrete entities are common, synthetically prepared examples of extended structures with decavanadate ions are relatively rare. According to our literature search, only one example, $[\text{Cu}(\text{en})_2]_2[\text{V}^{\text{IV}}_4\text{V}^{\text{V}}_6\text{O}_{25}]$, has been reported, which consists of $\text{Cu}(\text{en})_2^{2+}$ groups linked through layered vanadium oxides into a three-dimensional network.⁹ Khan *et al.* reported several three-dimensional frameworks which consist of spherical $[\text{V}_{18}\text{O}_{42}(\text{XO}_4)]$ clusters linked by bridging $[\text{M}(\text{H}_2\text{O})_4]$ groups ($\text{X}: \text{V}, \text{S}; \text{M}: \text{Fe}, \text{Co}, \text{Mn}, \text{Zn}$).¹⁰ Here, we report an entirely new type of mixed-valence decavanadate ion $[\text{V}^{\text{IV}}_8\text{V}^{\text{V}}_2\text{O}_{26}(\text{H}_2\text{O})]$ as a building block which is bridged by AsO_4 tetrahedra leading to a three-dimensional neutral network $[\text{AsV}^{\text{IV}}_8\text{V}^{\text{V}}_2\text{O}_{26}(\mu\text{-H}_2\text{O})]\cdot 8\text{H}_2\text{O}$ **1**. There are many structures reported in which AsO_4 tetrahedra are encapsulated in mixed-valence $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$ as well as V^{IV} polyoxoanions. To our knowledge, AsO_4 tetrahedra linking polyoxoanions in a bridging mode has not been described to date.

Compound **1** was prepared hydrothermally from a mixture of V_2O_5 , H_3AsO_4 , $\text{H}_2\text{C}_2\text{O}_4$, en and H_2O heated to 160 °C for three days.[†] The en is not incorporated into the structure of **1**, but is necessary to maintain the pH of the reaction. $\text{H}_2\text{C}_2\text{O}_4$ was employed as a reducing agent. The IR spectrum of the product exhibits characteristic bands at 972 and 958 cm^{-1} assigned to

$\nu(\text{V}=\text{O}_i)$ and a number of bands in the range 750–900 cm^{-1} associated with $\nu(\text{V}-\text{O}-\text{V})$ and $\nu(\text{V}-\text{O}-\text{As})$.

The extended highly symmetrical structure of **1** (Fig. 1), consists of a three-dimensional neutral network of $[\text{V}^{\text{IV}}_8\text{V}^{\text{V}}_2\text{O}_{27}]$ cages with crystallographic T_d symmetry, with each cage connected to four other neighboring units *via* AsO_4 bridging groups. This generates a network of $[-\{\text{V}_{10}\text{O}_{27}\}-\text{AsO}_4-\{\text{V}_{10}\text{O}_{27}\}-]_{\infty}$ arrays running along two mutually perpendicular directions. The building block units in the structure of **1** may be viewed as a 'rugby ball'-like $[\text{V}^{\text{IV}}_8\text{V}^{\text{V}}_2\text{O}_{26}]$ shell encapsulating a central water molecule which is covalently bonded to two V(1) atoms in a μ -bridging mode with a V(1)–O(6) distance of 2.450 Å. The symmetry at O(6) is 222. Indeed, an unusual property of reduced polyvanadates is their tendency to form cages encapsulating a guest molecule.¹¹ Compound **1** represents a most unusual member of this class of clusters with the central bridging encapsulated water molecule.

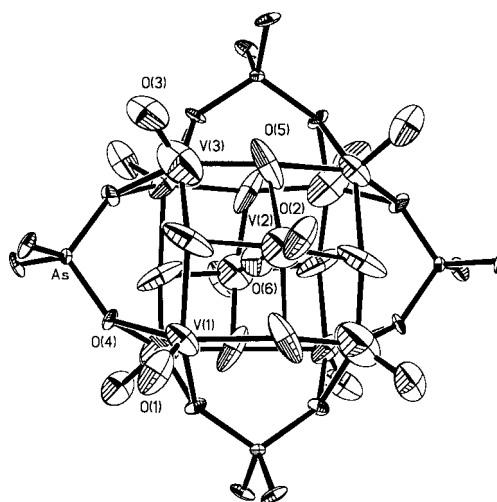


Fig. 1 Unit cell of structure **1** down the crystallographic *a* axis showing the rectangular channels parallel to this axis. Water molecules have been omitted for clarity.

The $[\text{V}^{\text{IV}}_8\text{V}^{\text{V}}_2\text{O}_{27}]$ unit is a new type of decavanadium ion. The vanadium exhibits two types of coordination: pyramidal [V(1) and V(3)] and octahedral [V(2)]. The octahedral geometry around vanadium V(2) is defined by a terminal oxo group [O(1)], four μ -oxygen atoms [O(5)] of the shell, and one μ -oxygen atom [O(6)]. The square-pyramidal geometry around V(1) and V(3) is formed by four basal μ_3 -oxo [O(4), O(5)] groups from the shell and an apical terminal oxo groups. Two V(1)O₅ and two V(3)O₅ pyramids are corner-shared by a μ_3 -O(5) atom to form a $[\text{V}_4\text{O}_{16}]$ ring. These vanadium atoms are all co-planar. Two such $[\text{V}_4\text{O}_{16}]$ rings are joined to each other by sharing edges in a parallel manner with two V(2)O₆ octahedra capping oppositely disposed faces of these two rings, respectively, forming a rugby ball-like structure. The surface of

the cluster exhibits four open windows. Curiously, the four AsO_4 tetrahedra cap on the windows by edge-sharing through a μ_3 -oxo group [O(4)] leading to a three-dimensional neutral network.

According to bond valence sum (BVS) calculations¹² and charge balance, compound **1** is formulated as $[\text{AsV}^{\text{IV}}_8\text{V}^{\text{V}}_2\text{O}_{26}(\text{H}_2\text{O})]\cdot 8\text{H}_2\text{O}$. The assignment of oxidation state for the vanadium and arsenic atoms are consistent with their coordination geometries and are confirmed by valence sum calculations which gives values for V1, V2, V3 and As of 4.06, 5.06, 4.15 and 5.10, respectively. The valence sum calculations associated with O(6) (BVS = 0.28) identify it as a water molecule, a feature consistent with the significant lengthened bond distance.

It is noteworthy that the structure of **1** possesses large rectangular and hexagonal channels, which are filled with water molecules of crystallization (eight water molecules per unit cell) (Fig. 1 and 2). The rectangular channels run along all three crystallographic axes with mean diameters of 10.508 Å while hexagonal channels extend along the diagonal direction of the unit cell with a mean diameter of 11.986 Å. The arsenic atoms reside on a 4 axis. In addition, two perpendicular 4 axes pass through the center of the $[\text{V}_{10}\text{O}_{27}]$ unit. Owing to the crystallographically imposed 4 symmetry, these channels may be viewed as a cylinder, not observed previously in other metal oxide cluster frameworks. Whereas transition metal coordination complexes acting as bridges are well established, it is seen here that AsO_4 tetrahedra may play an important role in the assembly of a specific structural motif.

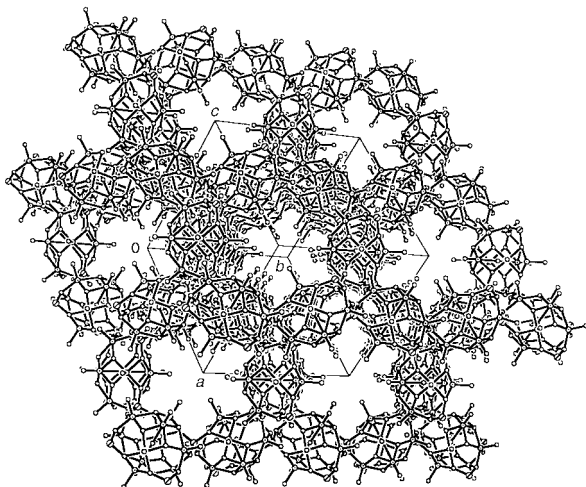


Fig. 2 The hexagonal channels viewed along the diagonal direction of the unit cell.

The room-temperature EPR spectrum of a crystalline sample of **1** consists of one signal (g 2.034), indicating the presence of V^{IV} centers. Although no hyperfine structure was observed, the linewidth was extremely narrow, which suggests significant exchange coupling.

The magnetic susceptibility χ_m of **1** was measured between 2 and 300 K. The value of $\chi_m T$ shows a gradual decrease as the temperature is decreased, indicative of weak antiferromagnetic exchange coupling. Because no suitable theoretical model is available in the literature¹³ for such a complex system, detailed magnetic analyses were not performed for the present compound.

This work has important implications for the conversion of discrete cluster anions into three-dimensional networks¹⁴ and demonstrates that the use of hydrothermal techniques is a vital tool for the realisation of materials design. This novel structure

and building principle may provide further insight into designing new porous materials as well as other supramolecular architectures.

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Notes and references

† A mixture of V_2O_5 (5.5 g), H_3AsO_4 (1.5 g), $\text{H}_2\text{C}_2\text{O}_4$ (1 g) and H_2O (20 ml) was neutralized to pH = 8 with en (2 ml). The sample was then sealed in a Teflon-lined reactor which was heated to 160 °C for three days. After cooling to room temperature, black prism-shaped crystals were isolated in ca. 40% yield (based on vanadium). Anal. Calc. for $\text{H}_{18}\text{As}_2\text{V}_{10}\text{O}_{35}$: As, 12.11; V, 41.17; H, 1.47. Found: As, 11.92; V, 41.10; H, 1.52%.

‡ Crystal data for **1**: $[\text{AsV}^{\text{IV}}_8\text{V}^{\text{V}}_2\text{O}_{26}(\text{H}_2\text{O})]\cdot 8\text{H}_2\text{O}$: cubic, space group: $I\bar{4}3m$ (no. 217), $a = 16.7083$ Å, $V = 4360.6$ Å³, $Z = 4$. A black crystal of dimensions $0.23 \times 0.21 \times 0.11$ mm was mounted on a glass fiber. Data were collected on Siemens P4 four circle diffractometer at room temperature in the range $2 < 2\theta < 50^\circ$ using the ω scan technique. A total of 4600 reflections was collected of which 978 with $I > 2\sigma(I_o)$ were used. No attempt was made to locate the water hydrogen atoms. The structure was solved by direct methods and refined using SHELXTL (Version 5.01). Attempts to resolve the structure in the centric space group $Im\bar{3}m$ proved unsatisfactory. Structure solution and refinement based on 587 reflections and 31 parameters gave $R(R_w) = 0.0567$ (0.1098).

CCDC 182/1671. See <http://www.rsc.org/suppdata/cc/b0/b003359f/> for crystallographic files in .cif format.

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