The Synthesis and Crystal Structure of a New Polyoxovandium Cluster Anion: $[As^{III}{}_8V^{IV}{}_{14}O_{42}(0.5H_2O)]^{4-}$

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The dark-brown compound $[N(Me)_4]_4[As^{III}{}_8V^{IV}{}_{14}O_{42}(0.5H_2O)]$, containing a spherical anion $[As^{III}{}_8V^{IV}{}_{14}O_{42}(0.5H_2O)]^{4-}$ containing condensed VO_5 square pyramids and As_2O_5 units, is synthesized hydrothermally from As_2O_3, V_2O_5 and $(Me)_4NOH$ and structurally characterized by X-ray diffraction.

Iso- and hetero-polyvanadates that contain square pyramidally coordinated vanadium atoms often contain molecular anions with interesting cage structures. In several instances, these polyvanadate cage anions form inclusion compounds with neutral molecules (*e.g.* $[V_{12}O_{36}(MeCN)]^{4-}$[1] and $[V_{18}O_{42}(H_2O)]^{12-}$[2]). Other examples are known in which anions are included in polyvanadate structures (*e.g.* $[H_9V_{18}O_{42}(VO_4)]^{6-}$, $[V_{18}O_{42}(SO_4)]^{8-}$, $[H_4V_{18}O_{42}(X)]^{9-}$; X = Cl, Br, I, and $[V_{15}O_{36}(Y)]^{6-}$; Y = Cl, Br[3-5]). Similar complex anions are also formed by heteropolyvanadates in which the square pyramidally coordinated vanadium atoms are connected by other structural units. The anions $[H_{12}(VO_2)_{12}(C_6H_5PO_3)_8]^{4-}$,[6] $[H_6(VO_2)_{16}(MePO_3)_8]^{8-}$[7] and $[As_6V_{15}O_{42}(H_2O)]^{6-}$[8] are recent examples in which the connections are organophosphonate (RPO_3) and As_2O_5 units, respectively. In this communication, we describe the synthesis and structure of a new compound, $[N(Me)_4]_4[As^{III}{}_8V^{IV}{}_{14}O_{42}(0.5H_2O)]$ **1** which contains an anion closely related to $[V_{18}O_{42}(H_2O)]^{12-}$.

Compound **1** was synthesized by the reaction of 0.791 g As_2O_3, 0.910 g V_2O_5 and 2.0 g $(Me)_4NOH$ (25% in H_2O) in a 23 ml Teflon lined autoclave. The autoclave was filled to 60% by addition of distilled water and the reactants were heated at 200 °C for 48 h. The reaction product in the form of dark-brown prismatic crystals (1.46 g, *ca.* 89% yield based on vanadium)† was filtered, washed several times with distilled water and air-dried.

X-Ray structural analysis‡ of **1** revealed the presence of discrete tetramethylammonium cations, and anions $[As^{III}{}_8V^{IV}{}_{14}O_{42}(0.5H_2O)]^{4-}$, **2** (Fig. 1) with a disordered water molecule at the centre of the anion cage. The 'ball-like' structure of **2** consists of condensed vanadium oxygen square pyramids, (VO_5), connected by As_2O_5 units through sharing oxygen atoms. Eight vanadium [four V(4), two V(1) and two V(2)] oxygen square pyramids share their opposite edges to form a ring. These vanadium atoms are all co-planar in the plane of the ring within ± 0.06 Å. In addition, three vanadium [two V(5) and one V(2)] oxygen square pyramids share their opposite edges to form a trimer. One trimer is connected across the ring by sharing edges to two V(4) containing square pyramids. The other trimer is similarly connected on the opposite side of the ring to the other two V(4) atoms. The overall composition of this unit is $[(VO)_{14}O_{24}]$. The twenty-four oxygen atoms occupy the vertices of a rhombicuboctahedron, which has a total of eighteen square faces. Fourteen of these are formed by the bases of VO_5 square pyramids arranged as described above. The remaining four square faces are formed by the bases of the As_2O_5 units to give a total anion composition of $[As_8V_{14}O_{42}]^{4-}$.

The general description (above) for polyvanadate structures in terms of regular convex polyhedra with oxygen atoms occupying their vertices was first discussed by Day *et al.*[1] All of the anions $[As^{III}{}_6V^{IV}{}_{15}O_{42}(H_2O)]^{6-}$[8], $[PV_{14}O_{42}]^{9-}$,[9] $[V_{18}O_{42}H_9(VO_4)]^{6-}$ and $[V_{18}O_{42}H_9(SO_4)]^{8-}$[3] are related to the rhombicuboctahedron whereas the $[V_{18}O_{42}(H_2O)]^{12-}$[2] anion is derived from the elongated square gyrobicupola as

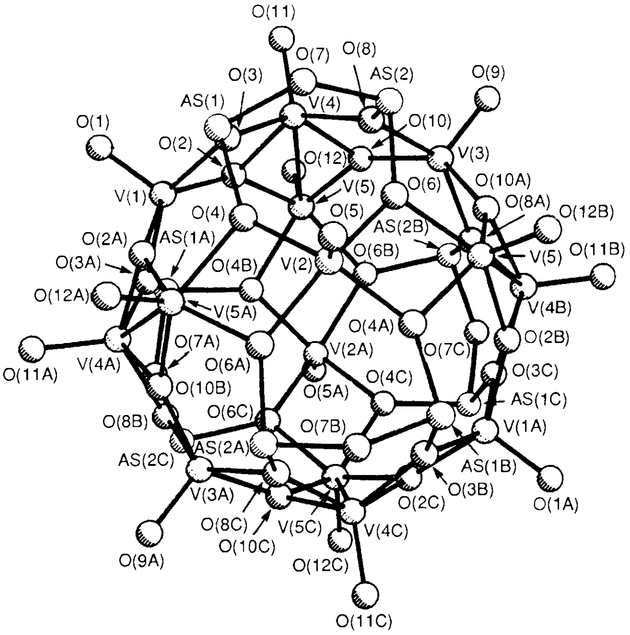

Fig. 1 A view of the $[As^{III}{}_8V^{IV}{}_{14}O_{42}(0.5H_2O)]^{4-}$ anion in **1**. Selected bond distances (Å) and angles (°) of interest: $V–O_{term}$ 1.56(1)–1.62(1), V-(μ_3-O) 1.89(1)–2.02(1), As-(μ_3-O) 1.76(1)–1.82(1), As-(μ_2-O) 1.74(1)-1.78(1), V(4)–V(5) 2.840(4), V(1)–V(4) 3.020(4), V(3)–V(4) 3.059(4), V(2)–V(5) 3.138(4); O_{term}–V-(μ_3-O) 107.8 (2)–112.6(2), O_{term}–V-(μ_3-O) 105.9(2)–108.0(2), (μ_3-O)–V-(μ_3-O) 74.6(5)–91.2(5), (μ_3-O)–As-(μ_3-O) 98.1(5)–98.7(5), (μ_3-O)–As-(μ_2-O) 98.2(5)–100.3(5), As-(μ_2-O)–As 132.2(7).

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† *Selected analytical data* for **1**: Chemical analysis (Galbraith Laboratories, Inc.) gave: Found: C 8.56, H 2.06, N 2.39, V 30.56, As 26.21% and Calc. for $C_{16}H_{49}N_4V_{14}As_8O_{42.5}$, C 8.39, H 2.16, N 2.45, V 31.14 and As 26.17%. IR (solid/KBr pellet): ν/cm^{-1} = 1490 (vs), 1110 (vs), 995 (vs), 970 (s), 965 (s), 950 (m), 830 (s), 765 (vs), 715 (vs), 670 (s), 632 (s), 560 (s), 465 (s). Redox titration result gave a vanadium valence of 4.00 ± 0.02.

‡ *Crystal data* (solved at Molecular Structure Corporation, The Woodlands, Texas 77381, USA) for **1**: $C_{16}H_{49}N_4V_{14}As_8O_{42.5}$, M = 2290.12, orthorhombic, space group *Fddd*; a = 20.482(5), b = 41.54(1), c = 14.156(6) Å, V = 12037(6) Å^3, and Z = 8; D_c = 2.526 g cm^{-3}; μ = 64.54 mm^{-1} for Mo-Kα radiation (λ = 0.71069 Å). A total of 2902 reflections having $2\theta < 50.0°$ were collected at −80 ± 1 °C on a Rigaku AFC6R diffractometer with graphite monochromated Mo-Kα radiation and a 12-kW rotating anode generator. The structure was solved by direct methods utilizing the SHELX software package. The resulting structural parameters have been refined to R = 0.069 for 1618 unique absorption-corrected reflections having $I > 3\sigma(I)$ using full-matrix least-squares techniques and a structural model that incorporated anisotropic thermal parameters for all non-hydrogen atoms. Methyl hydrogen atoms were calculated assuming ideal positions. Since the oxygen atom of the water molecule is at a position with 222 site symmetry, the hydrogen atoms of the water molecule must be disordered. These hydrogen atoms could not be located. The water molecules are half-occupied at the centres of the cages. 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.

first noted by Day *et al.* The anions $[H_4V_{18}O_{42}(X)]^{9-}$; X = Cl, Br, I were also observed to be based on this polyhedron.[5]

The structures of both $[As^{III}_8V^{IV}_{14}O_{42}(0.5H_2O)]^{4-}$ and $[As^{III}_6V^{IV}_{15}O_{42}(H_2O)]^{6-}$, can be derived from the rhombicuboctahedron in $[V_{18}O_{42}H_9(VO_4)]^{6-}$ structure by replacing $[OVO_4]^{6-}$ with $[OAs_2O_4]^{4-}$ units and omitting the central tetrahedron. The oxygen–oxygen atom distances in the base of the $[OVO_4]$ square pyramid (*ca.* 2.5–2.8Å) are similar to those in the $[OAs_2O_4]$ group (*ca.* 2.7–2.8Å) and consequently the two units behave in a close structurally analogous fashion. Formal replacement of V=O groups by As–O–As units was noted by Müller *et al.*[5] In the As_8 compound, all four As_2O_5 units occupy positions above and below the ring of eight VO_5 square pyramids (see Fig. 2). In contrast, in the previously reported As_6 anion,[8] one As_2O_5 group replaces a VO_5 pyramid in the eight ring; the other two As_2O_5 units are located one on either side. Anions with compositions corresponding to $[(VO)_{18-n}(As_2O)_nO_{24}]^{(12-2n)-}$ with n = 0, 3 and 4 are now known and attempts to synthesize other members of the series are currently in progress.

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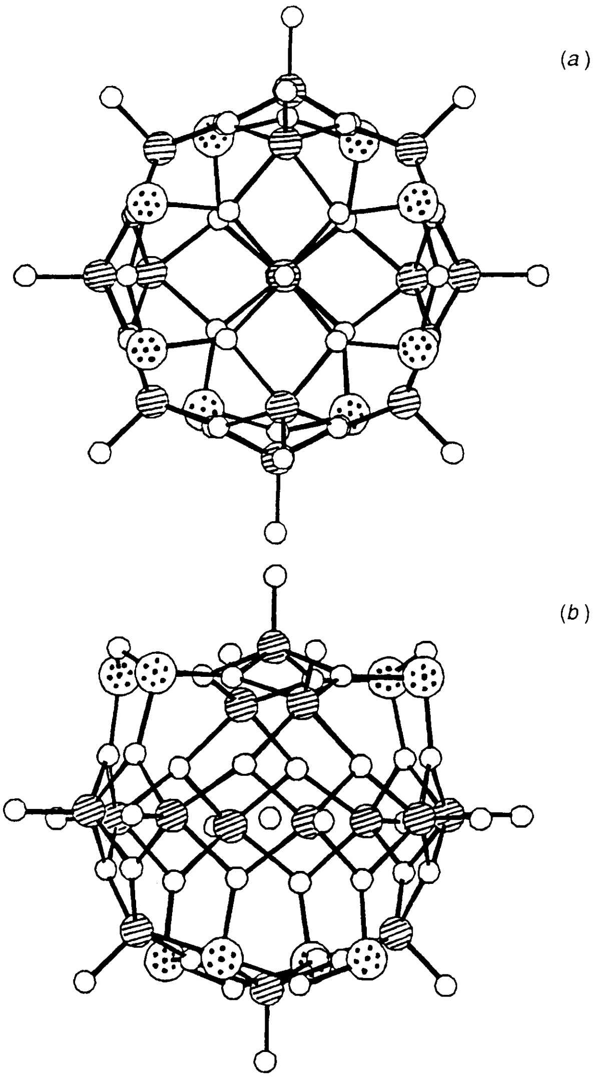

Fig. 2 Two perpendicular views of the structure of the anion **2** with As, V and O atoms represented by dotted, shaded and open circles, respectively. The eight membered ring of VO_5 square pyramids can be seen in 2(*a*); the arrangement of As_2O_5 units above and below the 8-membered ring is shown in 2(*b*).

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