# Synthesis and molecular structure of a new arsenic rich polyoxovanadium anion, $[As^{III}{}_8V^{IV}{}_6O_{26}]^{4-}$

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**Reaction of arsenic(III) oxide with vanadate in aqueous solution under reducing conditions leads to the formation of the molecular anion $[As^{III}{}_8V^{IV}{}_6O_{26}]^4$, built up from two semicircular fragments which fit into each other to form a cage structure.**

Since Müller *et al.* showed in 1987 that polyoxovanadates, which contain square $V^{IV}O_5$ pyramids, possess an unusual structural chemistry leading to the formation of spherical cages, attention has been focused on the chemistry of reduced iso- and hetero-polyoxovanadates.[1] To date, the literature contains numerous examples of cage-like molecular anions which often act as cryptates encapsulating neutral molecules or anions.[2–7] Here, we report the synthesis, molecular structure and magnetic properties of $[As^{III}{}_8V^{IV}{}_6O_{26}]^{4-}$, which contains only six vanadium atoms and is therefore one of the smallest cage anions of the rich polyoxovanadate family.[8] The stability of the molecular structure, with a poor metallic skeleton, is ensured by the presence of four handle-like $As_2O_5$ moieties. This anion is the first molecular arsenovanadate which contain more arsenic than vanadium atoms (As/V = 4/3).[9]

$[As_8V_6O_{26}]^{4-}$ has been isolated as a tetrabutylammonium salt and was synthesized at room temperature by reduction of an equimolar aqueous solution of $NaVO_3$ and $NaAsO_2$ (0.5 mol $dm^{-3}$) with an excess of hydrazine. Addition of tetrabutylammonium bromide to the solution leads to precipitation of a green powder corresponding to the desired compound (50% yield based on As).† Recrystallization of the green powder from DMF–acetonitrile (1 : 1) gave large bright green crystals of $[NBu^n_4]_4[As_8V_6O_{26}]$. The structure of the compound was determined by X-ray diffraction of a single crystal.‡ The solid, which crystallizes in the tetragonal space group $P\bar{4}n2$, contains $[As_8V_6O_{26}]^{4-}$ anions and $NBu^{n+}_4$ cations. The anion is located on the $\bar{4}$-axis while the organic molecule is on a general position, leading to an $(anions)^{4-}$–$NBu^{n+}_4$ ratio of 1:4 in the unit cell. The oxidation states of the vanadium atoms, which are expected to be four for charge compensation, were confirmed by redox titration. Thermogravimetric analysis was consistent with the presence of four $NBu^{n+}_4$ cations and the absence of water molecules in the compound.

The molecular anion, $[As_8V_6O_{26}]^{4-}$, is built up from six distorted $VO_5$ square pyramids and eight $AsO_3$ trigonal pyramids (Fig. 1). The six vanadium pyramids are divided into two trimeric units made from three edge-sharing pyramids, $\{V_3O_{11}\}$. All the arsenite pyramids are linked in pairs, through a vertice, forming handle-like $\{As_2O_5\}$ moieties. The $\{V_3O_{11}\}$ building block, sandwiched by two $\{As_2O_5\}$ units, forms a semicircular fragment. Therefore, this anion can be described as two semicircular halves, related by a $\bar{4}$-axis, fitting into each other. Condensation of the two half-rings forms a cavity at the centre of the anion (Fig. 2). The structure of $[As_8V_6O_{26}]^{4-}$ is closely related to the spherical anion $[As_8V_{14}O_{42}{\cdot}0.5H_2O]^{4-}$ previously described by Huan *et al.*[10] In this anion a central ring made up eight edge-sharing $VO_5$ pyramids is connected by two units made of $\{V_3O_{11}\}$ trimers. The structure of $[As_8V_6O_{26}]^{4-}$ can be easily derived from $[As_8V_{14}O_{42}{\cdot}0.5H_2O]^{4-}$ by removal of the central ring.[11]

In the molecular anion, the distances between vanadium(IV) atoms suggested the existence of a magnetic coupling within the $d^1$ centres of the trimers ($d_{V-V}$ = 3.09 Å).[12,13] The temperature dependences of $\chi$ and $\chi^{-1}$, measured with a SQUID susceptometer, are shown in Fig. 3. At room temperature, as expected from the bright green colour of the compound, the $\mu_{eff}$ value of 3.95 $\mu_B$ (1.61 per $V^{IV}$ atom) is in agreement with the existence of six localized electrons. The compound is paramagnetic down to 25 K and above 50 K the data fit a Curie–Weiss law (C = 2.3

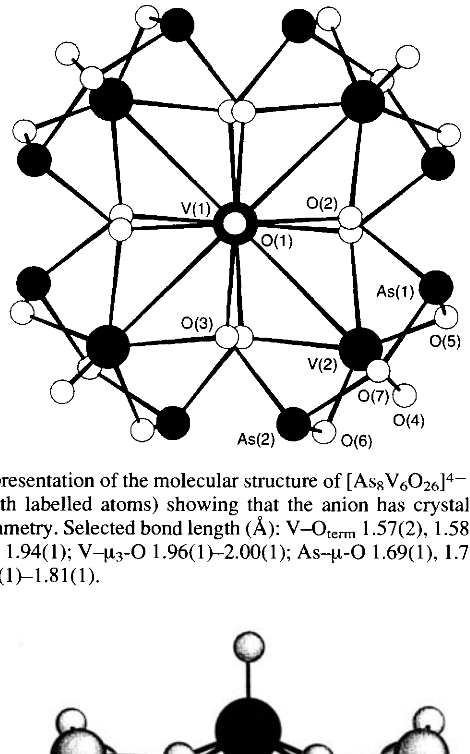

**Fig. 1** Representation of the molecular structure of $[As_8V_6O_{26}]^{4-}$ along the $\bar{4}$-axis (with labelled atoms) showing that the anion has crystallographic $\bar{4}$-axis symmetry. Selected bond length (Å): V–$O_{term}$ 1.57(2), 1.58(1); V–μ-O 1.92(1), 1.94(1); V–$\mu_3$-O 1.96(1)–2.00(1); As–μ-O 1.69(1), 1.71(1); As–$\mu_3$-O 1.79(1)–1.81(1).

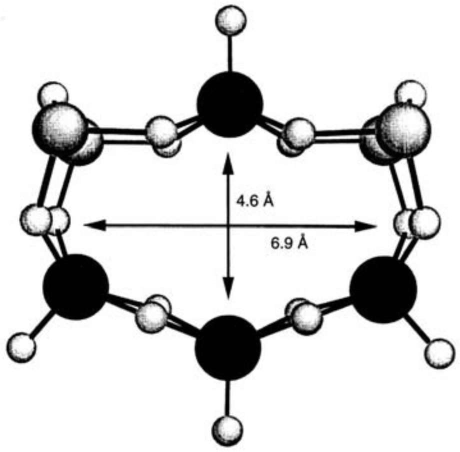

**Fig. 2** Representation of a fragment of the anion illustrating the molecular cavity (two $VO_5$ and four $AsO_3$ groups have been removed for clarity)[16]

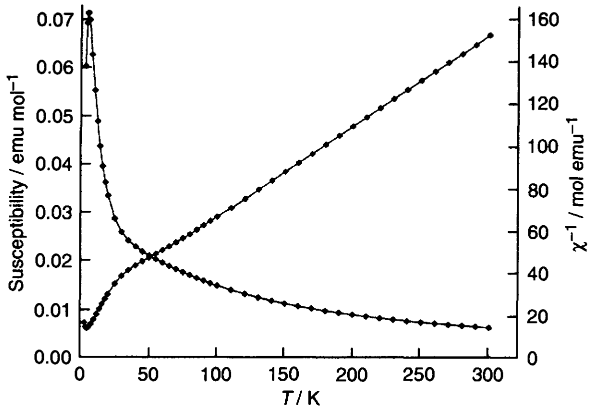

**Fig. 3** Temperature dependence of $\chi$ and $\chi^{-1}$ for $[NBu^n_4]_4[As_8V_6O_{26}]$. The sample was made up only of single crystals. The experimental data were corrected for diamagnetism.

emu mol$^{-1}$, $\theta_p = 53$ K) with a Curie constant in excellent agreement with six spins per molecular anion. At 25 K a marked change in the curve, characterized by an important increase of the susceptibility, indicates the existence of a magnetic coupling. The curve exhibits a second significant change around 5 K, with an abrupt decrease of susceptibility, characteristic of an antiferromagnetic coupling. Structural analysis is in agreement with the existence of two types of interactions in the molecular anion: a relatively strong one within the spins of the vanadium trimers and a weaker interaction between trimers (shortest distance $V^{IV}$–$V^{IV}$ 4.5 Å). Accordingly, the increase of susceptibility, observed at 25 K, could be compatible with a non-compensated antiferromagnetic coupling between the three vanadium atoms of the trimer and the second antiferromagnetic coupling, observed at 5 K, with an antiferromagnetic coupling between trimers.

The molecular structure of $[As_8V_6O_{26}]^{4-}$ is another example of the tendency of $V^{IV}O_5$ pyramids to form curved fragments, even without the templating effect of a molecule at the centre of the cavity.

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## Footnotes

† *Characterising data* for $[NBu^n_4]_4[As_8V_6O_{26}]$: IR (solid/KBr pellet, $\nu$/cm$^{-1}$): 1485vs, 1460s, 1383s, 1153m, 1110w, 1058w, 1032w, 981vs, 971vs, 880s, 847vs, 809vs, 764m, 738w, 676vs, 633s, 565m, 495vs, 401m, 360s. Satisfactory elemental analysis was obtained.

‡ *Crystal data* for $C_{64}H_{144}As_8N_4O_{26}V_6$: tetragonal, space group $P\bar{4}n2$ (no. 118), $a = 16.653(4)$, $c = 17.275$ Å, $U = 4789(2)$ Å$^3$, $Z = 2$, $D_c = 1.55$ g cm$^{-3}$; $\mu = 33.4$ cm$^{-1}$. Intensity data were collected at room temperature with an $\omega$–$2\theta$ scan technique on an Enraf-Nonius CAD4 diffractometer (Mo-K$\alpha$ radiation, graphite monochromator). A total of 2302 independent reflections were measured in the range $2 < 2\theta < 50°$ from which 1400 reflections with $I > 3\sigma(F_o)^2$ were considered observed. An empirical absorption correction was applied by DIFABS.[14] The structure was solved by direct methods using the SHELX-86 program and successive difference Fourier maps with anisotropic thermal parameters for all the atoms of the anion (As, V, O).[15] Owing to the considerable motion of the $NBu^{n+}_4$ cations, nitrogen and carbon atoms were refined with isotropic thermal parameters. The reliability factors converge to $R = 0.050$ and $R_w = 0.058$. In the final density map the deepest hole was $-0.46$ e Å$^{-3}$ and the highest peak 0.58 e Å$^{-3}$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/244.

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