

# The first polyoxoalkoxovanadium germanate anion with a novel cage-like structure: solvothermal synthesis and characterization

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The first example of polyoxoalkoxovanadium germanate,  $(\text{NH}_4)_2[\text{H}_2\text{V}_9\text{Ge}_6\text{O}_{26}(\text{L})_6] \cdot 0.65\text{H}_2\text{O}$  ( $\text{H}_2\text{L} = \text{HOCH}_2\text{CH}_2\text{OH}$ ), was solvothermally synthesized, and its polyanion is made up of six  $\text{VO}_6$  octahedra, three  $\text{VO}_5$  square pyramids and six  $\text{GeO}_4$  tetrahedra with six bridging ethylene glycol ligands projecting outwards from the central core.

## Introduction

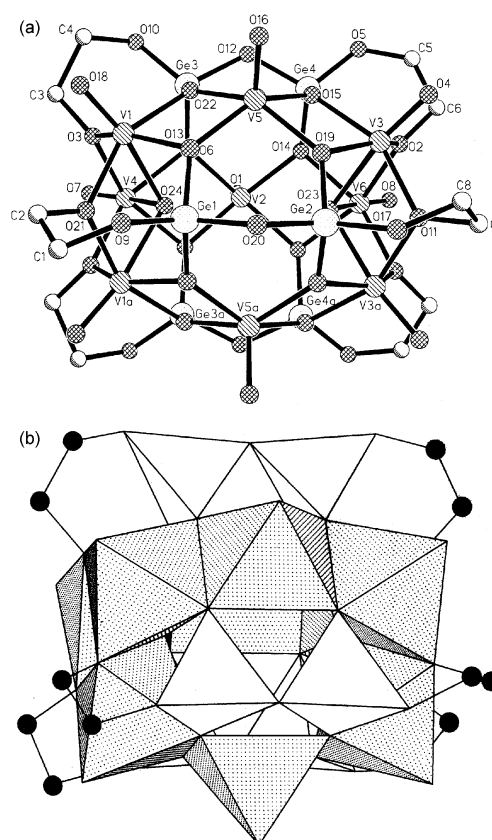
Because of the rich variety of their components, structures, and properties, significant attention continues to be focused on polyoxometallic anions in many research fields.<sup>1–3</sup> Polyoxometalates with organic oxygen-donor groups show an impressive structural and electronic diversity, and extensive synthetic research has been carried out in this field over the past few years. The incorporated ligands include alkoxides, acetals, organophosphonates, organoarsonates, etc.<sup>4–16</sup> Substituting mono-negative ligands for the peripheral  $\text{O}^{2-}$  groups in classical compact or cage-like cluster structures would vastly expand the coordination chemistry of polyoxoanions with interesting magnetic or catalytic properties.<sup>15</sup> Typical examples are the polyoxoalkoxometalates with chelating trisalkoxy ligands,  $[\text{V}_{16}\text{O}_{20}\{(\text{OCH}_2)_3\text{C}(\text{CH}_2\text{OH})\}_8(\text{H}_2\text{O})_4]$ ,<sup>8</sup>  $[\text{XH}_m\text{Mo}_{42}\text{O}_{109}\{(\text{OCH}_2)_3\text{CR}\}_7]^{m-}$ ,<sup>9</sup>  $[\text{V}_{10}\text{O}_{16}\{(\text{CH}_2)_3\text{C}(\text{CH}_2\text{O})_3\}_4]$ ,<sup>4–10</sup>  $[\text{V}_4\text{O}_4\{(\text{OCH}_2)_3\text{CCH}_3\}_3(\text{OC}_2\text{H}_5)_3]$ ,  $[\text{V}_4\text{O}_4\{(\text{OCH}_2)_3\text{CCH}_3\}_3(\text{OCH}_3)_6]$ ,<sup>11</sup>  $[(\text{H}_4\text{V}_6\text{P}_4\text{O}_{30})\{(\text{CH}_2)_3\text{CCH}_2\text{OH}\}_2]^{6-}$  and  $[(\text{H}_7\text{V}_{12}\text{V}_7\text{O}_{50})(\text{CH}_2)_3\text{CCH}_2\text{OH}]$ .<sup>7–12</sup> However, polyoxoalkoxometalate cluster chemistry remains relatively undeveloped and polyoxoalkoxometalates with a cage-like structure are very few, and a polyoxoalkoxovanadate with ethylene glycol as the organic oxygen-donor group has not been reported to date. On the other hand, it has been demonstrated that the application of solvo- and hydro-thermal synthesis techniques can lead to such new materials.<sup>13,16–20</sup> Herein we report the solvothermal synthesis and structural characterization of the first polyoxoalkoxovanadium germanate,  $(\text{NH}_4)_2[\text{H}_2\text{V}_9\text{Ge}_6\text{O}_{26}(\text{L})_6] \cdot 0.65\text{H}_2\text{O}$  ( $\text{H}_2\text{L} = \text{HOCH}_2\text{CH}_2\text{OH}$ ), **1**, where the polyanion clusters possess a novel cage structure and all the V atoms are in reduced states.

## Results and discussion

Blue block-shaped crystals of **1** were prepared in ca. 58% yield based on Ge from the solvothermal reaction of a mixture of  $\text{NH}_4\text{VO}_3$ ,  $\text{GeO}_2$ ,  $\text{H}_2\text{O}$ , 45% HF and ethylene glycol at 170 °C for 3 d. Although  $\text{F}^-$  is not incorporated in the final structure, this species appears to be needed in the synthesis. Without HF, attempts to synthesize **1** proved fruitless. Because no additional reducing agent was provided, ethylene glycol employed in the solvothermal synthesis of **1** not only acts as the reaction medium and the organic oxygen-donor ligands, but also functions as the reducing agent to reduce  $\text{V}^{\text{V}}$  to  $\text{V}^{\text{IV}}$ . Compound **1** was characterized by elemental analyses and IR spectroscopy (see Experimental section).

X-Ray crystallography revealed that the structure of **1** is built

up of ammonium cations, polyoxoalkoxovanadium germanate  $[\text{H}_2\text{V}_9\text{Ge}_6\text{O}_{26}(\text{L})_6]^{2-}$  anions and lattice water molecules. As shown in Fig. 1, the vanadogermanate anion consists of a cage-like cluster fused by six edge- and corner-sharing  $\text{VO}_6$  octahedra, three edge-sharing  $\text{VO}_5$  square pyramids and six corner-sharing  $\text{GeO}_4$  tetrahedra, with six bridging ethylene glycol ligands projecting outward from the central core. Six  $\text{VO}_6$  octahedra can be grouped into two trimers. Each  $\text{VO}_6$



**Fig. 1** The structure of the  $[\text{H}_2\text{V}_9\text{Ge}_6\text{O}_{26}(\text{L})_6]^{2-}$  polyanion in **1**. (a) A ball and stick representation with the atom labeling scheme; (b) A polyhedral representation where the dotted and blank polyhedra are for units around V and Ge, respectively. Selected bond lengths (Å): Ge(1)–O(9) 1.677(7), Ge(1)–O(20) 1.742(6), Ge(1)–O(13) 1.753(3), Ge(1)–O(13a) 1.753(3), V(1)–O(18) 1.585(4), V(1)–O(22) 1.981(3), V(1)–O(13) 1.988(4), V(1)–O(3) 2.011(4), V(1)–O(21) 2.013(3), V(1)–O(24) 2.167(2), V(2)–O(1) 1.597(6), V(2)–O(6) 1.978(4), V(2)–O(6a) 1.978(4), V(2)–O(14a) 1.991(4), V(2)–O(14) 1.991(4). Symmetry code: a  $x, y, -z$ .

octahedron within a trimer shares its two edges with the other two units producing a common corner, O(23) or O(24). The two trimers are held together to form a cage through three VO<sub>5</sub> square pyramids, where each VO<sub>5</sub> pyramid shares its two opposite basal edges with a VO<sub>6</sub> octahedron of the two opposite trimers. Three six-membered ring windows of the cage are each capped by an additional corner-sharing Ge<sub>2</sub>O<sub>7</sub> tetrahedral dimer (Fig. 1b), forming a spherical shell of composition [V<sub>9</sub>Ge<sub>6</sub>O<sub>38</sub>] with approximate D<sub>3h</sub> symmetry. While one O atom of each alkoxide ligand coordinates to one germanium ion, the other is shared by two octahedral vanadium sites of a trimer. The chelating fashion of the alkoxide in the structure of **1** is significantly different from that of the polyoxoalkoxometalates with trisalkoxy ligands, where three alkoxide O atoms are shared by three metal atoms<sup>8–12</sup> and also from that of the benzoate cluster [V<sub>6</sub>O<sub>10</sub>(PhCO<sub>2</sub>)], where the ligand PhCO<sub>2</sub> coordinates to two vanadium ions.<sup>21</sup>

The four independent vanadium centers in trioctahedra of the cluster anion in **1** have distorted octahedral environments, defined by one terminal oxo-group with short V–O distances ranging from 1.570(6) to 1.585(4) Å and five triply bridging O atoms with V–O distances between 1.977(4) and 2.167(4) Å. In the VO<sub>5</sub> square pyramid, the basal plane is formed by four triply bridging O atoms each shared by two vanadium atoms and one germanium atom with V–O bond lengths of 1.977(3)–1.991(4) Å, and the apical position is located by a terminal O with short V–O distances of 1.597(6) and 1.589(3) Å. Valence sum calculations<sup>22</sup> resulted in an oxidation state in the range 3.96–4.28 (4.12 in average) for the vanadium centers, suggesting that all vanadium sites in compound **1** have been reduced to V(IV). This observation is in accord with the formula given by the single crystal X-ray structure determination. It should be noted that the V–V distances between the octahedral and pyramidal V atoms in **1** range from 3.0697(12) to 3.070(2) Å. In general, such short distances mean that the unpaired electrons in the shell are delocalized, as often-observed in most polyoxometalate clusters.<sup>2,23</sup> It is surprising, however, that a signal at  $g = 1.9688$  was observed in the ESR spectrum of **1** measured at room temperature. It at least indicates that not all of the nine unpaired d<sup>1</sup> electrons of the polyanion unit in **1** are delocalized. Studies on the temperature dependence of the magnetic behavior are in progress.

## Conclusions

This paper reports the first polyoxoalkoxovanadium germanate incorporating ethylene glycol as organic oxygen-donor groups. The coordination mode of the alkoxide ligands in the structure of **1** is significantly different from that of the observed polyoxoalkoxometalates. To our knowledge, no previous examples of the polyoxoalkoxometalates with chelating ethylene glycol ligands have been reported. It indicates that ethylene glycol can be participate in the syntheses of polyoxoalkoxometalates, and then develop the polyoxometalate chemistry.

## Experimental

### Synthesis of **1**

Blue block-shaped crystals of **1** were prepared in ca. 58% yield based on Ge from the solvothermal reaction of a mixture of NH<sub>4</sub>VO<sub>3</sub> (0.23 g, 2 mmol), GeO<sub>2</sub> (0.104 g, 1 mmol), H<sub>2</sub>O (0.5 ml), 45% HF (0.2 ml) and ethylene glycol (5 ml) at 170 °C for 3 d. Anal. calc. for C<sub>12</sub>H<sub>35.3</sub>Ge<sub>6</sub>N<sub>2</sub>O<sub>38.65</sub>V<sub>9</sub> **1**: H, 2.06; C, 8.38; N, 1.63; V, 26.65. Found: H, 2.10; C, 8.35; N, 1.62; V, 26.56%. IR (KBr, cm<sup>-1</sup>) for **1**: 3435s, 2932w, 2877w, 1642w, 1485w, 1255vw, 1083s, 1043m, 1004s, 888m, 835s, 784vs, 605s, 512m, 442w. Thermogravimetric analysis showed a weight loss of ca. 2.23% for **1** on heating from room temperature to ~210 °C attributed to the loss of the ammonium cations and water, with

a further weight loss of ca. 10.35% for the C and H atoms of the organic ligands in the range 300–540 °C.

## X-Ray crystallography

Diffraction data for **1** were collected on a Rigaku R-Axis RAPID IP diffractometer (Mo-K $\alpha$ ,  $\lambda = 0.71069$  Å) with  $\omega$ -scan mode in the range of  $2 < \theta < 28^\circ$  at 293(2) K. Crystal habit = orthorhombic, space group = *Pnmm*,  $M_r = 1720.12$ ,  $a = 18.5773(6)$ ,  $b = 22.7989(9)$ ,  $c = 14.5097(4)$  Å,  $V = 6145.5(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.859$  g cm<sup>-3</sup>,  $\mu = 4.266$  mm<sup>-1</sup>. Of 12985 data collected, 7151 were unique ( $R_{int} = 0.0340$ ) and 5285 reflections were observed [ $I > 2\theta(I)$ ]. An empirical absorption correction from  $\phi$ -scans was applied. All non-hydrogen atoms, except N of the ammonium cations, O of the lattice water molecule, and two C atoms [C(7) and C(8)], were refined anisotropically. The occupancy parameter for the lattice water molecule was refined to 0.65. While the hydrogen atoms riding on C atoms were located in calculated positions, those on O and N atoms were located from the Fourier map. At convergence,  $R_1 = 0.0556$ ,  $wR_2 = 0.1632$  and GOF = 1.111 for the observed reflections and 328 parameters. It should be noted that two C atoms [C(1) and C(8)] in two chelating ethylene glycol ligands showed disorder in space group *Pnmm*, but efforts to solve the disorder by refinement in a lower symmetry space group were unsuccessful.

CCDC reference number 186635.

See <http://www.rsc.org/suppdata/dt/b2/b208489a/> for crystallographic data in CIF or other electronic format.

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