

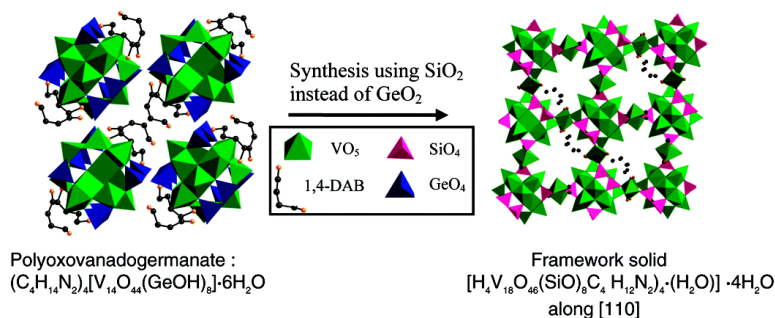
Communication

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The First Framework Solid Composed of Vanadosilicate Clusters

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Building oxide frameworks with increasing pore size and decreasing density is both demanding and rewarding.¹ These are promising materials in separation, catalysis, gas storage, and molecular recognition.^{1–4} A fruitful approach to such an endeavor is to use molecular building blocks with rigid molecular geometries.³ In one advance of this technique, Yaghi and co-workers have used metal carboxylate clusters for the design of metal–organic frameworks, in which chelating functional groups such as benzene dicarboxylates are used.⁴ Yet another advancement includes linking polyoxometalates via metal cations into three-dimensional (3D) structures.⁵ Incorporation of silicate and germanate into cluster anions can be a viable route to prepare 3D solids. However, so far only clusters and one-dimensional chain structures have been reported that incorporate Ge and/or Si in vanadium heteropolyanions.⁶ We recently presented the hydrothermal synthesis and structure of several novel polyoxovanadogermanates, with the cluster core as in $(\text{H}_2\text{DAB})_4[\text{V}_{14}\text{O}_{44}(\text{GeOH})_8]\cdot 6\text{H}_2\text{O}$ (DAB = 1,4-diaminobutane) (**1**)⁷ (Figure 1).

The substitution of GeO_2 by SiO_2 in the synthesis of **1** results in a novel framework solid, $[\text{H}_4\text{V}_{18}\text{O}_{46}(\text{SiO})_8(\text{DAB})_4\cdot(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$ (**2**), built from isotypic polyoxovanadosilicates (POVSSs). To our knowledge, **2** is the first realization of a 3D framework vanadosilicate composed of POVSSs (Figure 2). Interestingly and unlike **1**, the organic amine (DAB) does not act as a charge-compensating constituent in **2**; it is a bidentate ligand, covalently bonded to vanadium atoms, forming $(\text{VO})_2\text{N}_2$ pyramids that link the clusters into a 3D framework solid via nitrogen atoms.

In a typical synthesis of **1**, vanadium pentoxide (V_2O_5 , 0.7 g) and germanium oxide (GeO_2 , 0.4 g) were added to a mixture of DAB (9.12 mL) and water (2.0 mL). The final mixture, with mole ratio $\text{DAB}:\text{V}_2\text{O}_5:\text{GeO}_2:\text{H}_2\text{O} = 23.7:1:1:29$, was sealed in a Teflon-lined autoclave in air and heated at 170 °C for 5 days. After cooling to room temperature, the product was filtered and washed with deionized water. Dark green, virtually black cuboid crystals were recovered as a single phase in high yield (68.9% based on GeO_2). The synthesis of **2** is similar to that of **1**, wherein V_2O_5 (0.68 g) and fumed silica (SiO_2 , 0.224 g) were added to a mixture of DAB (9.12 mL) and water (2.06 mL). The final mixture, with mole ratio $\text{DAB}:\text{V}_2\text{O}_5:\text{SiO}_2:\text{H}_2\text{O} = 24:1:1:30$, was heated at 180 °C for 5 days. Dark green, virtually black octahedral crystals were obtained in 61% yield (based on SiO_2).

X-ray structural and chemical analysis of the compounds revealed the presence of the isostructural cluster anions $[\text{V}_{14}\text{O}_{44}(\text{GeOH})_8]^{8-}$ in **1** and $[\text{H}_4\text{V}_{14}\text{O}_{44}(\text{SiO})_8]^{12-}$ in **2**, with the latter being bridged by $(\text{VO})_2\text{N}_2$ pyramids in 3D.⁸ The cage has an idealized D_{2d} symmetry. Overall charge balance, bond valence calculations⁹ (BVC), IR, and average V–V distances were used to determine the oxidation state of the vanadium atoms.^{10,11} BVC give empirical oxidation states of 4.08, 4.18, 4.04, and 4.17 for V1, V2, V3, and V4, respectively, in **1**. In **2**, the corresponding values are 4.19, 4.01, 4.06, 4.17, and 4.11 for V1, V2, V3, V4, and V5, respectively. Similar BV values for V^{IV} have been reported by Müller et al.¹⁰

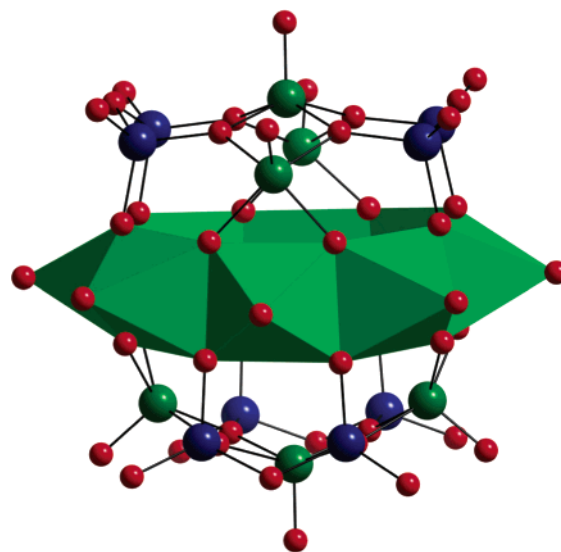


Figure 1. Ball-and-stick representation of the cluster in **1**, highlighting the midsection in polyhedral view. The clusters are surrounded by H_2DAB cations and water molecules. The encapsulated water molecules are omitted for clarity; V, green; Ge, blue; O, red.

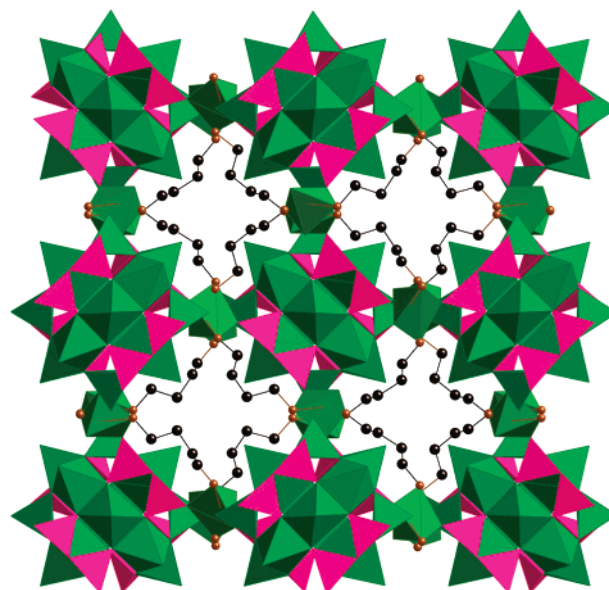


Figure 2. Polyhedral representation of the network formed by $[\text{H}_4\text{V}_{14}\text{O}_{44}(\text{SiO})_8]^{12-}$ clusters viewed along $[001]$. Each cluster is linked to eight others through $(\text{VO})_2\text{N}_2$ units. Water molecules in the channels and inside the clusters are omitted for clarity; VO_5 pyramids, green; SiO_4 tetrahedra, pink; N, brown; C, black.

The close V–V contacts (detailed below) imply the possibility of intramolecular antiferromagnetic spin coupling. The results of magnetic measurements will be published elsewhere.

The structure of the nearly spherical cage includes 14 tetravalent VO₅ square pyramids sharing edges via basal oxygen atoms with their short, axial V–O bonds, characteristics of a vanadyl group, directed outward (Figure 1). In **1**, the V–O bond distances of these terminal oxygen atoms range from 1.58 to 1.61 Å, while those for the basal, shared oxygens range from 1.91 to 2.00 Å. The Ge–O bond distances are in the range of 1.68–1.76 Å. Each V atom has at least one neighboring V atom within 3.09 Å in **1** and **2**. The V–V contacts range from 2.85 to 3.09 Å in **1** and from 2.83 to 3.09 Å in **2**. Whitfield et al. recently reported a vanadogermanate cluster anion similar to **1** that is surrounded by piperazinium cations.¹²

The cage structure of these anions closely resembles that of the [V₁₈O₄₂]¹²⁻ anion.¹³ The two cages are built up of a common midsection of a central octagonal ring, approximately 7 Å in diameter, consisting of eight VO₅ pyramids linked by basal edges (Figure 1). It is fused to three VO₅ pyramid fragments above and below in two different fashions. In [V₁₈O₄₂]¹²⁻, the midsection is fused to a three-VO₅ pyramid chain on top and a like chain on bottom, oriented ca. 45° to the first one. In the clusters of **1** and **2**, the three-pyramid chains on top and bottom are rotated by 90° with respect to each other and are flanked by two corner-connected A₂O₇ (A = Ge(**1**), Si(**2**)) dimers, thus generating a cluster of D_{2d} symmetry. Each dimer shares two corners with the VO₅ pyramid on the central ring and two corners with the perpendicular chain. In [V₁₈O₄₂]¹²⁻, each chain is flanked by a single VO₅ pyramid that shares one basal edge with the midsection and one with the top pyramid of the chain to generate a cluster of D_{4d} symmetry.

In **1**, the A₂O₇ dimer has two unshared oxygen atoms that terminate with a hydroxyl group. In **2**, they contribute to VO₃N₂ pyramids that are bonded to another such cluster by like oxo groups, to yield the cross-linked 3D structure (Figures 1 and 2). This arrangement in **2** results in 14 VO₅ pyramids, sharing edges through eight μ₃-oxygen atoms, and eight SiO₄ tetrahedra, sharing corners through 16 μ₃-oxygen atoms, that are edge-shared by VO₅ pyramids. The cluster-linking (VO)₂N₂ pyramid is bonded to two N atoms of DAB on each side besides being bonded to the Si atom of the nearby clusters via a μ₂-oxygen. The fifth bond is the short V–O bond (V–O, 1.64(1); V–O, 1.81(1), 1.86(1); V–N, 2.15(2), 2.22(2) Å). The bridging DABs are bidentate and are covalently bonded to the linking vanadium polyhedra through V–NH₂–(CH₂)₄–NH₂–V connections. Thus, the overall 3D network structure of **2** consists of [H₄V₁₄O₄₄(SiO)₈]¹²⁻ clusters that are linked by eight (VO)₂[NH₂(CH₂)₄NH₂]₂ units (Figures 1 and 2). The clusters in **2** are formed by four triply and 10 doubly fused VO₅ pyramids, each having an oxo group (V–O, 1.58–1.64 Å) pointing outward and four equatorial V–O bonds (V–O, 1.89–2.03 Å). They are capped by eight corner-sharing Si tetrahedra (Si–O, 1.56–1.67 Å). Incorporation of organic amines was confirmed by infrared data.¹¹

The cluster of **2** encapsulates tumbling water molecules. The average position of these disordered water molecules was located at the center of the cluster. Disordered water molecules were also located in the channels along [001] and [110]. TGA for **1** exhibits a total mass loss of 20.9% between 25 and 593 °C due to the loss of water molecules (including hydroxyls) and DAB (calculated 20%) with no clear distinction. The powder diffraction data, obtained after heating a sample of **1** to 200 °C, indicate a partial loss of crystallinity. In **2**, the weight loss starts from 25 °C and continues steadily up to 433 °C. It is difficult to ascertain the identity of the species that is fragmented after the loss of water in **2**. It appears that the water in the channels and encapsulated in the cluster is lost in two steps between 30–97 and 97–245 °C.

We have synthesized a polyoxovanadogermanate and extended this work to the preparation of the first network structure consisting

of isotopic vanadosilicate clusters connected by means of vanadium polyhedra along the three axes. This opens up possibilities for the syntheses of other templated vanadogermanate and vanadosilicate network solids as well as their heteropolyanions. The magnetochemistry and ion-exchange studies of **1** and **2** will be detailed in a forthcoming paper.

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Supporting Information Available: Crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) (a) Elemental analysis, calcd/found for (H₂DAB)₄[V₁₄O₄₄(GeOH)₈]·6H₂O (**1**): C, 7.38/7.47; H, 2.92/3.15; N, 4.30/4.52; Ge, 22.32/20.46; V, 27.40/28.64. For [H₄V₁₈O₄₆(SiO)₈(DAB)₄·(H₂O)]·4H₂O (**2**): C, 7.83/7.96; H, 2.53/2.74; N, 4.56/4.62; Si, 29.33/28.15; V, 37.40/39.36 (b) Crystallographic data for **1** and **2**: Bruker XPS diffractometer (CCD area detector, Mo Kα radiation, T = 110(2) K, graphite monochromator), empirical absorption correction using symmetry-equivalent reflections (SADABS), direct methods, difference Fourier syntheses. The initial structures were refined against F² (Bruker-SHELXTL, version 5.1, 1998). Single crystals of **1** were cuboidal, while those of **2** were octahedral in shape. **1**: tetragonal, space group P4₂/n (No. 86), a = 15.588(2) Å, c = 16.268(3) Å, V = 3953.1(11) Å³, Z = 8, ρ_{calcd} = 2.136 g cm⁻³, μ(Mo Kα) = 46.60 cm⁻¹, R₁ = 0.041 and wR₂ = 0.122, GOF = 1.063, F(000) = 2428. Of the 25 450 reflections collected, 4805 were unique (R_{int} = 0.0577), 272 parameters were refined, max/min residual electron density 1.719/–1.272 e Å⁻³. **2**: tetragonal, space group P4₂/c (No. 114), a = 16.169(2) Å, c = 18.199(4) Å, V = 4758.0(13) Å³, Z = 4, ρ_{calcd} = 1.695 g cm⁻³, μ(Mo Kα) = 18.63 cm⁻¹, R₁ = 0.065 and wR₂ = 0.145, GOF = 1.106, F(000) = 2754. Of the 16 354 reflections collected, 2486 were unique (R_{int} = 0.0667), 260 parameters were refined, max/min residual electron density 1.520/–1.352 e Å⁻³. Hydrogen atoms were geometrically placed for all the amines. In both structures, the water molecules are disordered.
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