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An extended chain structure formed by covalently linking polyoxovanadate cages with tetrahedral six rings

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The compound $Cs_{10.5}[(V_{16}O_{40})(Si_{4.5}V_{1.5}O_{10})]\cdot 3.5H_2O$ is the first example of an extended structure in which a polyoxometallate anion is linked by an extended tetrahedral unit.

A promising approach to the synthesis of new microporous compounds is to connect nanoscale 'cores' with extended linking groups *via* covalent bonds. Yaghi and coworkers have used this concept in the synthesis of a number of microporous phases in which metal–oxo cores have been connected with multifunctional organic linking groups. The compound (benzenedicaboxylate)$_3$Zn$_4$O is a recent example.[1] We have explored a similar approach using preformed vanadium borophosphate anions linked by metal cations into three-dimensional structures.[2] Others have synthesized compounds where polyoxovanadate ions are linked in a similar way.[3–5] A combination of both approaches in which polyoxoanion clusters are *covalently* linked to form stable microporous structures would be of special interest since polyoxovanadates are known to adopt a wide variety of structures with shapes ranging from cages to bowls, baskets, and belts.[6–8] A great diversity of framework topologies is therefore possible. Precedents for this strategy are found in the known compounds based on $Mo_4O_4^{4+}$ and $V_5O_9^{2+}$ 'cores' linked by single phosphate anions[9,10] and in the related structures of the minerals pharmacosiderite[11] and phosphovanadylite.[12] Here, we report the first example (to our knowledge) of an extended structure in which a polyoxovanadate ion is linked covalently by an extended tetrahedral linking unit. We note that chains of oxobridged cluster units have been previously reported.[13,14] The compound $Cs_{10.5}[(V_{16}O_{40})(Si_{4.5}V_{1.5}O_{10})]\cdot 3.5H_2O$ **1** contains a linear chain of $V_{16}O_{40}^{16-}$ anion shells linked by $(Si_{4.5}V_{1.5}O_{10})^{5.5+}$ six-rings and represents a first step towards the synthesis of three-dimensional expanded structures based on polyoxoanions.

In a typical synthesis of compound **1**, a mixture was prepared by mixing 0.14 g fumed silica, 0.26 g $VOSO_4\cdot 3H_2O$ and 1 ml H_2O. The mixture was then sealed together with 0.5 ml CsOH 50 wt% aqueous solution in a flexible Teflon bag in air. The bag was subsequently sealed in a steel reaction vessel filled with water to about 60% volume, and heated at 240 °C for 3 days. After cooling to room temperature over 3 h, the products were filtered off, washed with water, and dried in air. Dark-brown plate-like crystals of **1** were recovered as a minor phase together with blue crystals of $Cs_2(VSi_4O_{11})\cdot 3H_2O$ (VSH-2),[15] and were characterized with electron microprobe analysis, IR spectra† and single crystal X-ray diffraction.‡

In the crystal structure of **1**, two eight-membered rings of VO_5 tetragonal pyramids that share basal edges are fused together perpendicularly to form a cage. Two opposite windows of the cage are each capped by an additional VO_5 pyramid forming a spherical shell of composition $[V_{16}O_{40}]$ (Fig. 1).

The shell can be considered as a derivative of the α-Keggin cluster shell $[V_{12}O_{36}]$. The six square windows of the α-Keggin shell can be capped by V=O groups to form a $[V_{18}O_{42}]$ shell.[16] Substitution of two VO_5 pyramids of the $[V_{18}O_{42}]$ shell by Si_2O_7 dimers leads to the $[V_{16}Si_4O_{46}]$ unit of **1**. The spherical shell $[V_{16}Si_4O_{46}]$ in **1** has the symmetry 2/*m* and has a water molecule located at the shell center. The shortest distances from the water oxygen to the shell oxygen and vanadium atoms are 3.52 and 3.57 Å, respectively. Neighboring $[V_{16}Si_4O_{46}]$ shells are linked together by $(V_{1.5}Si_{0.5})O_4$ tetrahedra to form infinite chains running along [001]. The $(V_{1.5}Si_{0.5})O_4$ tetrahedra share corners with the SiO_4 tetrahedra of the shells to form a six-membered ring that has the symmetry 2/*m* (Fig. 2). Alternatively the chain may be described as made up of $[V_{16}O_{40}]$ cluster anions that are linked by single six-rings of composition $[Si_{4.5}V_{1.5}O_{10}]$. Efforts to solve the V,Si cation disorder in the $(V_{1.5}Si_{0.5})O_4$ tetrahedra by refinements in lower symmetry space groups were unsuccessful. Caesium cations and water molecules occupy the space between the chains.

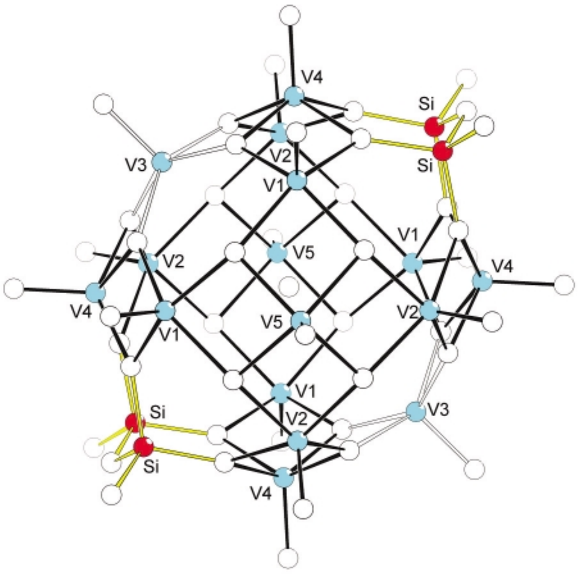

Fig. 1 The spherical shell $[V_{16}Si_4O_{46}]$ in **1**. Empty circles are oxygen atoms. The two eight-rings of square pyramids (vertical and horizontal) are plotted with black solid bonds.

The SiO_4 tetrahedron in **1** has regular Si–O bond lengths 1.604–1.630 Å and O–Si–O angles 105.8–112.3°. The $(V_{1.5}Si_{0.5})O_4$ tetrahedron has an average V–O bond length of 1.69 Å and a bond valence sum (bvs) of 5.45 v.u. calculated using bond valence parameters for V^{5+}–O bonds.[17] The high bvs value is a result of the partial substitution of Si^{4+} for V^{5+}. The chemical composition was confirmed by electron microprobe analysis and is consistent with the occupancies refined

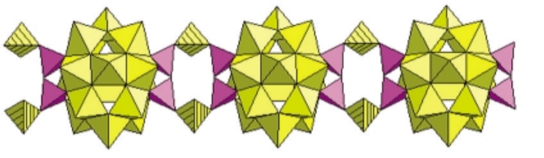

Fig. 2 The one-dimensional chain in **1**; $(V_{1.5}Si_{0.5})O_4$ tetrahedra are hatched.

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from the X-ray data. The VO_5 pyramids have apical V=O bond lengths 1.602–1.633 Å and basal V–O bond lengths 1.908–2.017 Å. Bond valence sums calculated for the V atoms of the pyramids are in the range 4.03–4.20 v.u., in agreement with their V^{4+} characters.

The $[V_{16}Si_4O_{46}]$ unit of **1** has four silicate tetrahedral corners available for further covalent bonding, and therefore, can readily be linked into a chain. In contrast, in the related Keggin cluster derivatives $[As^{III}_{2n}V^{IV}_{18-n}O_{42}]^{4-}$, n = 3, 4 where n VO_5 pyramids of a $[V_{18}O_{42}]$ shell are replaced by As_2O_5 trigonal pyramid dimers, the clusters cannot link because of the presence of the electron lone pairs on As(III).[18,19] The tetrahedral configuration of the four As_2O_5 groups in $[As^{III}_8V^{IV}_{18}O_{42}]^{4-}$, however, points to possibilities for similar substitution by Si_2O_7 groups to form, for example, clusters of composition $[Si_8V_{14}O_{50}]$. Such clusters could favor formation of three-dimensional framework structures in which each cluster functions as a super-tetrahedron.

In summary, we have synthesized hydrothermally a novel one-dimensional silicovanadate that demonstrates the possibility of decorating cage-like polyvanadate clusters with silicate tetrahedra and linking them covalently into extended structures. This example suggests a synthetic route to novel microporous materials by using polymetalate nanoclusters as building units.

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Notes and references

† Electron mocroprobe analysis was carried out with a JEOL 8600 electron microprobe operating at 15 keV with a 10 μm beam diameter and a beam current of 30 nA. Observed atomic ratios (based on V = 17.5): Cs : Si : V = 10.20 : 4.52 : 17.5. Infrared data (cm^{-1}): 629(w), 702(s), 945(s), 980(vs), 1020(s), 1633(m), 3462(m).

‡ *Crystal data* for **1**: M = 3276.4, orthorhomic, space group *Pnnm*, a = 19.351(2), b = 12.803(1), c = 13.189(1) Å. Dark-brown plate, crystal size 0.11 × 0.07 × 0.02 mm. Mo-Kα radiation (λ = 0.71073 Å), μ = 8.32 mm^{-1}, $2\theta_{max}$ = 57°, $R(F)$ = 0.055/0.143 for 1911/3964 observed ($I > 2\sigma(I)$)/all unique reflections and 269 variables.

Intensities were measured on a SMART platform diffractometer equipped with a 1K CCD area detector using graphite-monochromatized Mo-Kα radiation at 20 °C. Absorption correction was made using the program SADABS. The structure was solved with direct methods and refined using SHELXTL.[20–22]

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See http://www.rsc.org/suppdata/cc/b1/b108303a/ for crystallographic data in CIF or other electronic format.

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