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

Xiqu Wang, Lumei Liu, Ge Zhang and Allan J. Jacobson*

Department of Chemistry and Materials Research Science and Engineering Center, University of Houston, Houston, TX 77204-5641, USA. E-mail: ajjacob@uh.edu

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The compound Cs$_{10.5}$[(V$_{16}$O$_{40}$)(Si$_{4.5}$V$_{1.5}$O$_{10}$)]·3.5H$_2$O 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 process 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$_4$O$_{12}^{4+}$ and V$_5$O$_{9}^{2+}$ ‘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$_{10}$)]·3.5H$_2$O I contains a linear chain of V$_{16}$O$_{40}^{2-}$ 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 I, a mixture was prepared by mixing 0.14 g fumed silica, 0.26 g VOSO$_4$·3H$_2$O and 1 ml H$_2$O. 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 I were recovered as a minor phase together with blue crystals of Cs$_8$V$_{15}$O$_{45}$H$_2$O.\(^15\) and single crystal X-ray diffraction.\(^‡\) The compound (benzenedicaboxylate)$_3$Zn$_4$O is a recent example.\(^1\) We have explored a similar process 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.

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from the X-ray data. The VO₅ 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 V⁴⁺ characters.

The [V₁₆Si₄O₆₄⁻] unit of I 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 [As₃O₇]₄⁻, n = 3, 4 where n VO₅ pyramids of a [V₁₈O₄₃⁻] shell are replaced by As₂O₅/VO₅ pyramids of a [V₁₈O₄₂⁻] shell, the clusters cannot link because of the presence of the electron lone pairs on As(III). The tetrahedral configuration of the four As₂O₅ groups in [As₃O₇]₄⁻, however, points to possibilities for similar substitution by Si₂O₇ groups to form, for example, clusters of [Si₆V₁₄O₃₅⁻]. 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 polyanvadate 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 microprobe analysis was carried out with a JEOL 6800 electron microprobe operating at 15 kV with a 10 µm beam diameter and a beam current of 30 nA. Observed atomic ratios (based on V = 17.5): Cs : Si : V = 19.351(2), 12.803(1), 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, 2θ max = 57°, R(F) = 0.055/0.143 for 1911/3964 observed (I > 2σ(I)) all unique reflections and 269 variables. Intensities were measured on a SMART program 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. CCDC reference number 171147. See http://www.ccdc.cam.ac.uk/chemistry/suppdata/cc/hb108303a/ for crystallographic data in CIF or other electronic format.

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