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The Novel Open-Framework Vanadium Silicates K$_2$(VO)(Si$_4$O$_{10}$)·H$_2$O (VSH-1) and Cs$_2$(VO)(Si$_6$O$_{14}$)·3H$_2$O (VSH-2)**

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

Porous silicates that contain transition metals in octahedral or distorted octahedral framework sites have attracted interest in part stimulated by the catalytic properties of the Ti-doped microporous silicate TS-1 for epoxidation reactions.[1, 2] A prominent example of a mixed octahedral/tetrahedral compound is the titanium silicate ETS-10 that has a 12-ring channel system. The framework of ETS-10 contains single chains of corner-shared TiO$_6$ octahedra isolated from each other by silicate tetrahedra and as a consequence has unusual optical properties in addition to its absorption and catalytic properties.[3–8]

In contrast to octahedral/tetrahedral frameworks containing titanium and zirconium, analogous open-framework systems based on niobium and vanadium as the octahedral or distorted octahedral component are relatively rare. A vanadium silicate called AM-6 with the same structure as ETS-10 has been reported.[9] The only other known open-framework silicates containing vanadium are cavansite and

[*] Prof. A. J. Jacobson, Dr. X. Wang, L. Liu
Department of Chemistry
University of Houston
Houston, TX 77204-5641 (USA)
Fax: (+1)713-743-2787
E-mail: ajjacob@uh.edu

pentagonite, dimorphs of the mineral $Ca(VO)(Si_4O_{10}) \cdot 4H_2O$.[10,11] In both structures, silicate single layers are linked by $(H_2O)VO_5$ distorted octahedra into a three-dimensional framework that contains channels. Cavansite and pentagonite, to the best of our knowledge have not been synthesized in the laboratory. In ETS-10 and AM-6 the transition metal centers are not accessible from the channels, whereas in the cavansite and pentagonite frameworks, the vanadium cations are directly exposed to ions or molecules inside the channels.

We are currently investigating the synthesis of vanadium silicates. Microporous vanadium silicates are expected to be of catalytic interest because of the presence of a redox-active transition metal center. The valence-state of vanadium can easily be manipulated and consequently we also can anticipate novel magnetic and electric properties. Herein, we report the synthesis of two new open-framework vanadium silicates **1** and **2**, the structures of which are closely related to those of cavansite and pentagonite.

$K_2(VO)(Si_4O_{10}) \cdot H_2O$ **1**

$Cs_2(VO)(Si_6O_{14}) \cdot 3H_2O$ **2**
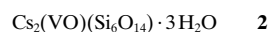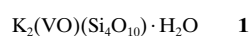
Crystals of **1** and **2** were prepared by hydrothermal reactions and were grown as pale blue polyhedra with a maximum dimension of about 0.2 mm. The structures of both compounds were determined by single-crystal X-ray diffraction,[12] and their compositions were measured by electron microprobe analysis.[13]

The orthorhombic structure of compound **1** has space group symmetry *Pbca*. Figure 1a shows the silicate single layer of **1** and Figure 1b shows a view of the structure along [110]. The silicate layer is composed of single chains of SiO_4 tetrahedra running along [100]. Neighboring chains are linked to form a layer that consists of only 6-rings. The SiO_4 tetrahedra in each single chain have an alternating *UUDD* orientation, where *U* refers to a terminal oxygen corner pointing up and *D* down, while in the 6-rings they have the rare *UUDDUD* orientation. The silicate layers are cross-linked into a three-dimensional framework by interlayer VO_5 tetragonal pyramids. Each pyramid shares its basal plane corners with two *UU* tetrahedra from one silicate layer and two *DD* tetrahedra from an adjacent layer. The pyramid is disordered over two orientations that have the same basal plane and opposite apex corners. The oxygen atoms of two disordered water molecules complete the vanadium coordination at V—O distances of 2.68 and 3.14 Å. The framework has two intersecting 8-ring channel systems running along [110] and [1̄10] that are related by a symmetry glide plane. The free aperture of the channels is about 2.6×4.0 Å. The K^+ ions and water molecules are located within the channels and both are disordered. Thermogravimetric analysis (TGA) data for **1** measured in air indicated that dehydration of the compound starts at about 200°C and is completed at about 460°C.

Compound **2** crystallizes in the orthorhombic space group *Cmca*. As shown in Figure 2a, the silicate single layer contains not only 6-rings similar to those of **1** but also 4-rings. The layer of **2** is composed of single tetrahedral chains running along [001] that are closely related to the [100] chains of **1**. In fact
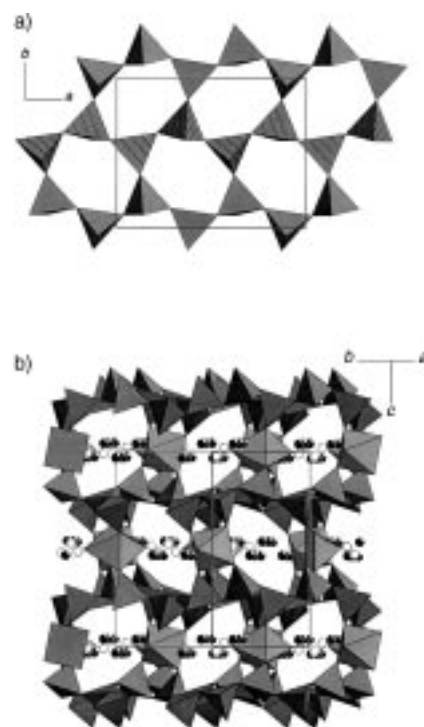

Figure 1. a) The silicate layer of **1**. A [100] chain is marked by hatching. b) A [110] view of the structure of **1**, showing the 8-ring channels. Open and solid circles represent water oxygen and potassium atoms, respectively.
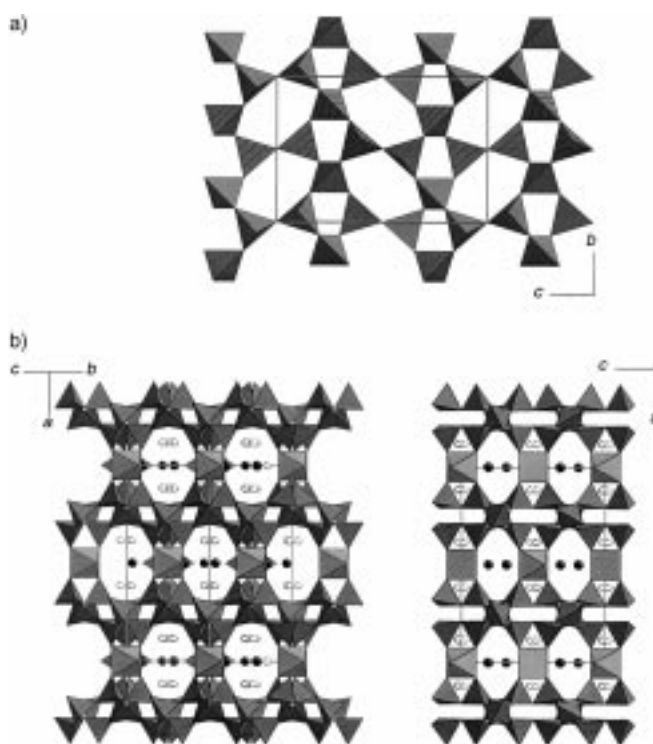

Figure 2. The silicate layer of **2**. A [001] chain is marked by hatching. b) Views of the structure of **2** along [011] (left) and [010] (right), showing the 8-ring channels. Open and solid circles represent water oxygen and cesium atoms, respectively.

the [001] chain of **2** can be derived by inserting an additional tetrahedron between the *UU* and *DD* pairs of the *UUDD* single chain of **1**. Therefore, the [001] chain in **2** has the

orientation of tetrahedra *UUQDD* where Q is a four-connected tetrahedron that has no terminal corner. The connection of adjacent silicate layers by VO_5 pyramids in **2** is very similar to that in **1**, that is, each pyramid shares its basal plane corners with two *UU* tetrahedra from one silicate layer and two *DD* tetrahedra from an adjacent layer. The orientational disorder of the VO_5 pyramids of **1** is also found in **2**. In **2**, the oxygen atom of the nearest water molecule is at 3.50 Å from the vanadium atom. The framework of **2** contains two intersecting channel systems running along [011] and [0Ī1] that are symmetry equivalent. These channels have a width defined by 8-rings and a free aperture of 3.0×3.6 Å. A third system of channels runs along [010] that also has a free width of 3.0×3.6 Å (Figure 2b). The Cs^+ ions and the water molecules occupy the space within the channels. TGA of **2** at a heating rate of $5\,K\,min^{-1}$ shows loss of water molecules from the framework begins immediately on heating. By 350°C all of the water is removed. An X-ray powder pattern of the TGA sample after heating to a final temperature of 523°C was similar to that of the starting material. After dehydration at 500°C, the sample reabsorbs water on cooling in the presence of water vapor. The dehydration–rehydration behavior is reversible.

Bond valence sums[14] calculated for the vanadium atoms are 4.1 and 3.8 v.u. for **1** and **2**, respectively, indicating their V^{4+} character similar to the vanadium atoms in cavansite and pentagonite. The silicate layers of both cavansite and pentagonite consist of alternating *UUDD* tetrahedral single chains similar to those of **1** (Figure 3). Different ways of linking such
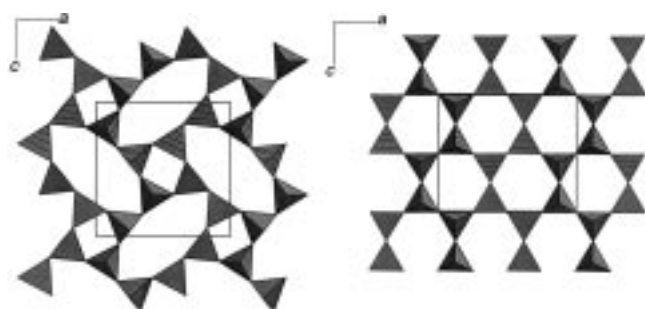

Figure 3. The silicate layers in cavansite (left) and pentagonite (right). The *UUDD* chains similar to that of **1** are marked by hatching.

chains lead to the different geometrical features of the layers in these compounds. The silicate layer of pentagonite comprises only 6-rings similar to that of **1**. However, the 6-rings in pentagonite have an *UUUUDD* orientation of tetrahedra. The silicate layers of cavansite consist of both 4-rings and 8-rings. The ways of connecting adjacent silicate layers by the VO_5 pyramids in cavansite and pentagonite are the same to those in **1** and **2**. The *UU* and *DD* tetrahedra pairs apparently fit well to the pyramids and favor the formation of such structures. There are many hypothetical tetrahedral layers that can be built by interconnecting the single chains of **1** or its derivatives. Therefore, a series of open-framework structures similar to **1** and **2** are anticipated.

In conclusion, compounds **1** and **2** have small pore frameworks that can be considered as based on the same building principles as the mineral cavansite and pentagonite. The fact that pentagonite has wider channels defined by 10-rings points to the possibility of synthesizing similar compounds with middle- and large-pore frameworks.[15] Employing organic templates should be helpful in synthesizing such highly porous materials.

Experimental Section

1: A 0.5 M aqueous solution of $VOSO_4 \cdot 3H_2O$ (0.5 mL), 45% KOH (0.5 mL), H_2O (0.5 mL), and ethylene glycol (1 mL) was mixed together. The solution was sealed together with 0.64 g fumed silica and heated at 240°C for 3 days in a 23 mL Teflon-lined autoclave. Pale blue crystals of **1** were recovered by vacuum-filtering together with impurities of green powder.

2: A 0.5 M aqueous solution of $VOSO_4 \cdot 3H_2O$ (0.5 mL), 50% CsOH (0.5 mL), H_2O (0.5 mL), and ethylene glycol (1 mL) was mixed together. The solution was sealed together with 0.62 g fumed silica and heated at 240°C for 3 days in a 23 mL Teflon-lined autoclave. Pale blue crystals of **2** were recovered by vacuum-filtering together with impurities of brown powder.

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[13] Electron microprobe analysis: JEOL JXA-8600 instrument operating at 15 KeV with a 10 μm beam diameter and a beam current of 30 nA. The measured atomic ratios are K:V:Si = 1.9:1.0:4.2 for **1** and Cs:V:Si = 1.9:1:6.5 for **2**.

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