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COMMUNICATIONS

Published on Web 11/27/2002

$[(CH_3)_4N][(C_5H_5NH)_{0.8}((CH_3)_3NH)_{0.2}]U_2Si_9O_{23}F_4$ (USH-8): An Organically Templated Open-Framework Uranium Silicate

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Received October 5, 2002

Open-framework materials with ordered cavities of nanometer size are possible hosts for synthesis of nanocomposite materials in addition to their established importance in other areas such as ion exchange and catalysis.[1,2] The aluminosilicates (zeolites), the traditional examples of such materials, are particularly suitable because of their high thermal stability and good optical transparency.[3,4] Many attempts have been made to modify the physical and catalytic properties of zeolite frameworks by the incorporation of transition-metal ions.[5,6] These efforts have led to the discovery of a number of porous structures formed from both silicate tetrahedra and transition-metal-centered polyhedra.[7−15] Recently we reported a series of porous vanadosilicate compounds that are based on silicate sheets cross-linked by VO_5 square pyramids.[16,17] By substituting UO_6 tetragonal bipyramids for the VO_5 pyramids we obtained also a number of open-framework uranium silicates.[18,19] These new compounds were synthesized by using alkali metal cations as templating agents. We are investigating similar syntheses by using organic templates. In the development of zeolite synthesis, introduction of organic templates greatly increased the topology and composition spectrum of zeolite structures because of the huge variability of available template shapes and charge densities.[4] Here we report the first example of an open-framework uranium fluorosilicate $[(CH_3)_4N][(C_5H_5NH)_{0.8}((CH_3)_3NH)_{0.2}]U_2Si_9O_{23}F_4$ (*USH-8*) that has been synthesized by using organic templates.

In a typical synthesis, fumed silica was dissolved in a mixture of water, tetramethylammonium (TMA) hydroxide, HF, and pyridine. Uranium acetate was subsequently added. The final mixture with the molar ratios $TMAOH:SiO_2:UO_2(CH_3COO)_2:HF:pyridine:H_2O = 5:2:1:4:32:200$, was sealed in a Teflon-lined autoclave in air and heated at 180 °C for 10 days. After cooling to room temperature, the product was vacuum-filtered and washed with water. Yellow-brown needlelike crystals of *USH-8* were recovered as a single phase with high yield (65.9% based on U). Chemical analysis showed that the compound has a framework of composition $U_2Si_9O_{23}F_4$ consistent with the single-crystal X-ray diffraction data which indicates silicate double layers interlinked by chains of UO_3F_4 pentagonal bipyramids (Figure 1).[20]

The silicate double layer consists of two single layers that are related by a glide plane. The single layer can be described as formed from fundamental chains that run along [100] and are built by linking double five rings with single tetrahedra (Figure 2).[21] Interconnection of the chains results in large 10-ring voids in the single layer, but the voids are blocked by the other single layer because of the glide plane symmetry of the double layer. Two-ninths of the tetrahedra in the double layer are three-connected with their fourth terminal oxygen atom corners pointing to the outside of the double layer. These terminal oxygen atoms are further bonded to interlayer uranium atoms that have pentagonal bipyramidal coordination. The same silicate double layer is found in the structure of the zeolite ferrierite.[22] In ferrierite, the silicate oxygen atoms that form part of the UO_3F_4 pentagonal bipyramids in *USH-8* are shared to form 8-ring channels parallel to the layers. The UO_3F_4 pentagonal bipyramid has two apical uranyl oxygen atom corners and one equatorial oxygen atom corner that is shared with a silicate tetrahedron. Neighboring UO_3F_4 pentagonal bipyramids share an equatorial fluorine atom edge to form infinite chains along the [010] direction (Figure 2). The framework formed by connection of the uranate chains and the silicate double layers has 12-ring channels along [010] and 7-ring channels along [100]. The [010] 12-ring channels have a calabash-shaped cross-section with the middle part partially blocked by the uranyl oxygen atoms (Figure 1). The narrow side of the 12-ring channels is occupied by well-ordered TMA cations while the wide side is occupied by disordered pyridinium and trimethylammonium cations. The latter presumably were formed by decomposition of TMA during the synthesis reaction. Incorporation of the organic species was confirmed by infrared and ^{13}C NMR data and chemical analysis.[23]

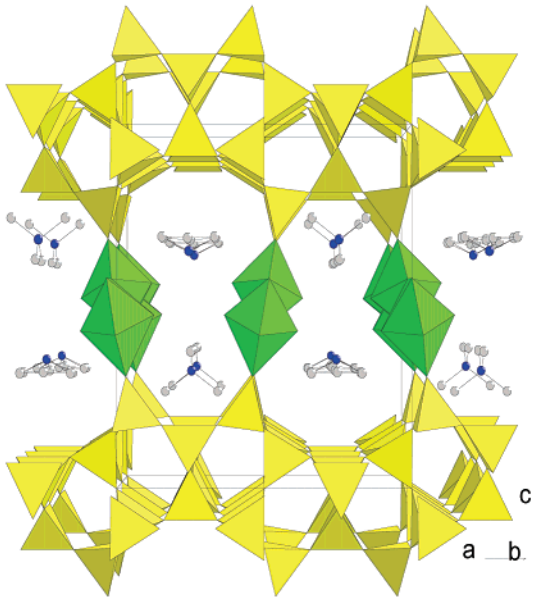

Figure 1. View of the structure of *USH-8*. Silicate tetrahedra are yellow and uranate pentagonal bipyramids green. Blue and gray circles represent nitrogen and carbon atoms, respectively.

The observed Si−O bond lengths (1.542−1.617 Å, average 1.594 Å) are somewhat shorter than typical values but are still within the normal range.[21] We noted that the thermal parameters of the framework atoms are larger than expected under the low-temperature (−50 °C) conditions used for the X-ray measurement (for oxygen atoms, U_{iso}:0.020(4)−0.045(4), average 0.033 Å^2). These thermal parameters suggest some local static disorder at the

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10.1021/ja0288284 CCC: $22.00 **© 2002 American Chemical Society**

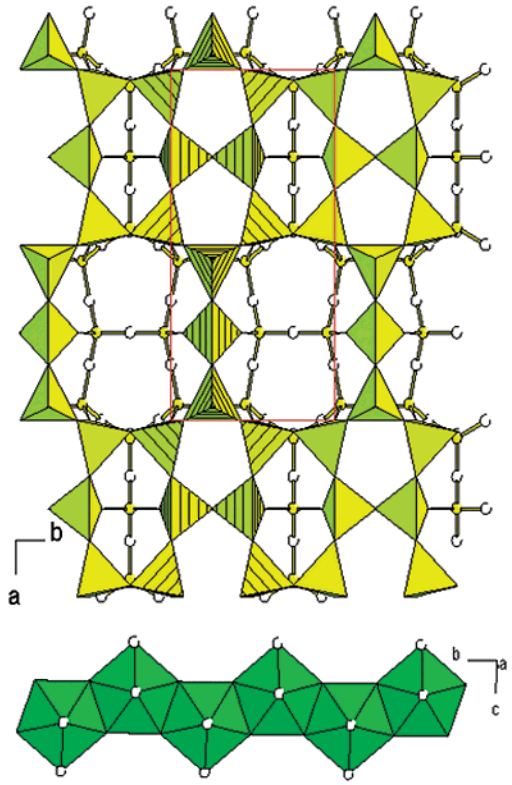

Figure 2. Silicate double layer (top) and the uranate chain (bottom) of *USH-8*. The two single layers of the double layer are shown as ball-and-stick and polyhedral presentations, respectively. A fundamental chain is marked by hatching. Open circles represent oxygen atoms.

framework atom sites, which may cause the observed atom distances to appear shorter than their real values.[21] The terminal Si−O bonds have the shortest bond length. The observed O−Si−O bond angles of 106.7−111.9° are well within the expected range. The two apical uranyl U═O bonds have bond lengths 1.744−1.760 Å and an O−U−O angle 178.8°. The equatorial U−O and U−F bond lengths are 2.23 and 2.354−2.363 Å, respectively.

Thermogravimetric analysis combined with X-ray powder diffraction indicates that the structure collapses after loss of the organic species between 300 and 600 °C in air. The openings in the channel systems of the framework are apparently too narrow for free removal of the bulky organic cations by oxidative decomposition.

In contrast to the *VSH-n* and some of other *USH-n* phases which are based on silicate single layers containing 4- and 6-ring channels, *USH-8* is based on silicate double layers containing 5-ring channels.[17,18] The structural difference is related to the different synthesis conditions. The *VSH-n* phases are synthesized with high concentrations of alkali metal cations that were replaced by organic cations in the synthesis of *USH-8*. A similar correlation between structure and synthesis conditions has also been observed in zeolite synthesis.[4] The uranate chains of *USH-8* are commonly found in uranium-rich minerals such as uranophane $Ca(UO_2)(SiO_3OH)(H_2O)_5$[24] but are rare in compounds with high Si/U ratios that usually contain isolated uranium centered polyhedra.[25] The condensation of the uranate bipyramids, which is facilitated by F^- ions in *USH-8*, favors the high proportion of 4-connected silicate tetrahedra and, therefore, lowers the framework charge density to accommodate the organic templates.

In summary, we have synthesized a new open-framework uranosilicate *USH-8*. The framework is characterized by silicate double layers with high density of 5-ring channels and single chains of fluorouranate pentagonal bipyramids. The successful use of organic templates suggests further opportunities for synthesizing microporous uranium silicates in a systematic way.

Acknowledgment. We thank the National Science Foundation (DMR-0120463) and the R.A. Welch Foundation for financial support. This work made use of MRSEC Shared Experimental Facilities supported by the National Science Foundation under Award Number DMR-9632667.

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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(20) (a) Analysis. Calcd/Found for $[(CH_3)_4N][(C_5H_5NH)_{0.8}((CH_3)_3NH)_{0.2}]U_2Si_9O_{23}F_4$: C 7.80/7.93; H 1.42/1.79; N 2.12/2.30; F 5.75/5.73; Si 19.10/17.92; U 36.07/37.13. (b) Crystallographic data. Orthorhombic, space group P*mmn*, $a = 14.063(3)$ Å, $b = 7.409(2)$ Å, $c = 15.285(3)$ Å, $V = 1592.6(6)$ Å^3, $Z = 2$, $d_{cal} = 2.759$ g cm^{-3}, μ (Mo Kα) $= 10.61$ mm^{-1}. A total of 5333 reflections were measured on a Siemens SMART/CCD single-crystal diffractometer at 223 K, which gave 2006 independent reflections with $R_{int} = 0.137$. The high R_{int} value may be due to the small size of the needlelike crystal (0.13 mm × 0.03 mm × 0.02 mm). An absorption correction was made by using the SADABS program. The structure was solved and refined with the SHELXTL software package. Final refinements converged at $R = 0.0558$ for 992 reflections with $I > 2\zeta(I)$ and 89 parameters.
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(23) Infrared bands observed: 434(s), 461(s), 546(w), 598(m), 677(w), 731-(m), 812(w), 837(w), 891(m), 910(s), 930(s), 951(m), 1084(s), 1190(m), 1255(s), 1381(w), 1421(w), 1485(s), 1639(m), 3074(w), 3164(w), 3458-(m) cm^{-1}. The bands above 1255 cm^{-1} are indicative of the organic cations. ^{13}C NMR spectrum: three peaks at 7.41, 6.97, and 6.89 ppm for pyridinium and two stronger ones at 0.38 and 0.37 ppm for TMA and trimethylammonium were observed.
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JA0288284