Chem. Mater. **2007,** *19,* 132−134

Cs^+-Selective Ion Exchange and Magnetic Ordering in a Three-Dimensional Framework Uranyl Vanadium(IV) Phosphate

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Received October 18, 2006
Revised Manuscript Received December 11, 2006

Uranium-based open-framework materials continue to captivate material chemists because of their remarkably diverse architectures. The challenge in obtaining three-dimensional framework structures is that most U(VI) compounds are found to be layered because of the terminal nature of the uranyl, UO_2^{2+}, oxo atoms that are seldom involved in bridging to additional metal centers, effectively terminating one direction of structure propagation.[1] Several strategies have been adopted for overcoming this hurdle. The first of these is to use organic structure-directing agents, especially organoammonium cations, to influence the formation of uranyl-containing frameworks. In particular, some of these agents cause perpendicular alignment of uranyl polyhedra to create framework structures, which is aptly illustrated by the oxyfluorides $[N(CH_3)_4][(UO_2)_2F_5]$[2] and $[C_4H_{12}N_2][U_2O_4F_6]$,[3] as well as by the phosphate and fluorophosphate, $[Et_2NH_2]_2[(UO_2)_5(PO_4)_4]$[4] and $[C_6H_{14}N_2]_2[(UO_2)_6(H_2O)_2F_2(PO_4)_2(HPO_4)_4]\cdot 4H_2O$.[5] There is also a family of uranyl silicates[6] with alkali metal cations, such as $RbNa(UO_2)(Si_2O_6)\cdot H_2O$[7] and $Rb_4(UO_2)_2(Si_8O_{20})$,[8] that are known to adopt open-framework structures.

The addition of main group and transition metal building units into both purely inorganic and organic−inorganic hybrid materials has been shown to lead to the formation of three-dimensional framework compounds with vastly different topologies. In uranyl phosphates alone, the metal centers range from tetrahedral Ga^{3+} in $Cs[UO_2Ga(PO_4)_2]$,[9] to square planar Cu^{2+} in $Cs_{3+x}[(UO_2)_3CuH_{4-x}(PO_4)_5]\cdot H_2O$,[10] to square pyramidal V^{5+} in $Cs_2[(UO_2(VO_2)_2(PO_4)_2]\cdot 0.59H_2O$,[11] to octahedral Ga^{3+} and Co^{2+} in $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$[9] and $Cs_2\{(UO_2)_4[Co(H_2O)_2]_2(HPO_4)(PO_4)_4\}$.[10] The recently reported uranyl niobates $AUNbO_6$ (A = Na, K, Cs) also fit well within this group of compounds.[12] Although these materials have answered the synthetic and structural challenges of preparing three-dimensional framework uranyl compounds, it is of equal importance to demonstrate that these structures lend themselves to important physicochemical properties. Indeed, these compounds have risen to this test as well, and a variety of structure−property relationships have been established, including ionic conductivity in $A(UO_2)_4(VO_4)_3$ (A = Li, Na),[13] selective ion exchange in $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$,[9] NLO optics in $K_2[(UO_2)_2(VO)_2(IO_6)_2O]\cdot H_2O$[14] and $Cs_2[UO_2(VO_2)_2(PO_4)_2]\cdot 0.59H_2O$,[11] and chirality in $[(C_2H_5)_2NH_2]_2[(UO_2)_4(MoO_4)_5(H_2O)](H_2O)$.[15] The magnetic properties of mixed-metal uranyl phosphates have yet to be reported. In this communication, the synthesis,[16] structure, magnetic properties, and Cs^+-selective ion exchange of the three-dimensional framework uranyl vanadyl phosphate, $A_{3.48}[(UO_2)(VO)_4H_{1.52}(PO_4)_5]$ (A = K, Rb), are reported.

The synthesis of $K_{3.48}[(UO_2)(VO)_4H_{1.52}(PO_4)_5]$ (**K−UVP−2**) was achieved by reacting $UO_2(NO_3)_2\cdot 6H_2O$ with V metal, phosphoric acid, and KCl under mild hydrothermal conditions.[16] This reaction results in the formation of large clusters of blue prisms of **K−UVP−2**. The synthesis of **UVP−2** is very similar to that of $Cs_2[(UO_2(VO_2)_2(PO_4)_2]\cdot 0.59H_2O$ (**UVP−1**), with the exception of replacing CsCl with KCl.[11] The alkali metal cations not only have a structure-directing effect, but also control the ultimate oxidation state of the vanadium in these compounds (vide infra). The Rb analog of **UVP−2** can also be prepared.

The structure[17] of $K_{3.48}[(UO_2)(VO)_4H_{1.52}(PO_4)_5]$ consists of two-dimensional vanadyl phosphate layers in the [*ab*]

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(1) (a) Burns, P. C.; Miller, M. L.; Ewing, R. C. *Can. Mineral.* **1996**, *34*, 845. (b) Burns, P. C. In *Uranium: Mineralogy, Geochemistry and the Environment;* Burns, P. C., Finch, R., Eds.; Mineralogical Society of America: Washington, D.C., 1999; Chapter 1. (c) Burns, P. C. *Mater. Res. Soc. Symp. Proc.* **2004**, *802*, 89. (d) Burns, P. C. *Can. Mineral.* **2005**, *43*, 1839.

(2) Ok, K. M.; Doran, M. B.; O'Hare, D. *J. Mater. Chem.* **2006**, *16*, 3366.

(3) Walker, S. M.; Halasyamani, P. S.; Allen, S.; O'Hare, D. *J. Am. Chem. Soc.* **1999**, *121*, 10513.

(4) Danis, J. A.; Runde, W. H.; Scott, B.; Fettinger, J.; Eichhorn, B. *Chem. Commun.* **2001**, *22*, 2378.

(5) Doran, M. B.; Stuart, C. L.; Norquist, A. J.; O'Hare, D. *Chem. Mater.* **2004**, *16*, 565.

(6) Li, Y.; Burns, P. C. *J. Nucl. Mater.* **2001**, *299*, 219.

(7) Wang, X.; Huang, J.; Liu, L.; Jacobson, A. J. *J. Mater. Chem.* **2002**, *12*, 406.

(8) Huang, J.; Wang, X.; Jacobson, A. J. *J. Mater. Chem.* **2003**, *13*, 191.

(9) Shvareva, T. Y.; Sullens, T. A.; Shehee, T. C.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2005**, *44*, 300.

(10) Shvareva, T. Y.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2006**, *45*, 1900.

(11) Shvareva, T. Y.; Beitz, J. V.; Duin, E. C.; Albrecht-Schmitt, T. E. *Chem. Mater.* **2005**, *17*, 6219.

(12) Surblé, S.; Obbade, S.; Saad, S.; Yagoubi, S.; Dion, C.; Abraham, F. *J. Solid State Chem.* **2006**, *179*, 3238.

(13) Obbade, S.; Dion, C.; Rivenet, M.; Saadi, M.; Abraham, F. *J. Solid State Chem.* **2004**, *177*, 2058.

(14) Sykora, R. E.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2003**, *42*, 2179.

(15) Krivovichev, S. V.; Cahill, C. L.; Nazarchuk, E. V.; Burns, P. C.; Armbruster, Th.; Depmeier, W. *Microporous Mesoporous Mater.* **2005**, *78*, 209.

(16) $\mathbf{K_{3.48}[(UO_2)(VO)_4H_{1.52}(PO_4)_5]}$**.** $UO_2(NO_3)_2\cdot 6H_2O$ (0.395 g, 0.787 mmol), V (0.080 g, 1.60 mmol), H_3PO_4 (0.231 g, 2.36 mmol), KCl (0.293 g, 3.94 mmol), and 1 mL of Millipore-filtered water were loaded into the 23 mL autoclave. The reaction was run at 190 °C in a box furnace for 5 days and then cooled at a rate of 9 °C/h to room temperature. Clusters of bright blue prismatic crystals of $K_{3.48}[(UO_2)(VO)_4H_{1.52}(PO_4)_5]$ were isolated, washed with methanol, and allowed to dry. Yield: 340 mg (40.5% yield based on U). EDX analysis provided a K:U:V:P ratio of 4:1:4:5. The Rb analog of this compound can also be prepared by replacing KCl with RbCl. Elemental analysis results for the Rb-analog showed (calcd/found): P 11.86/11.66, V 15.61/15.53. Rb content from refinement of occupancy is 3.40.

10.1021/cm062490l CCC: \$37.00

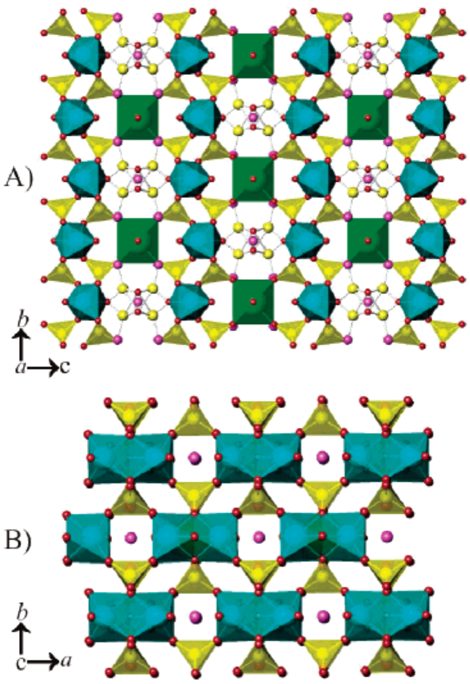

Figure 1. (a) View down the *a*-axis of two-dimensional vanadyl phosphate layers that extend in the [*ab*] plane in the structure of $K_{3.48}[(UO_2)(VO)_4H_{1.52}(PO_4)_5]$. These layers are joined by UO_6 tetragonal bipyramids in the *c* direction into a three-dimensional framework structure. (b) Depiction of the small channels that extend along the *c*-axis (2.8 × 4.4 Å^2). VO_6 units are shown in blue, UO_6 in green, and PO_4 in yellow. Oxygen atoms are depicted in red, and K^+ cations in magenta.

plane, depicted in Figure 1, that are joined by UO_6 tetragonal bipyramids in the *c* direction into a three-dimensional framework structure (Figure 1A). The structure has small channels extending down the *c*-axis that are filled by K^+ cations (Figure 1B). The individual layers are complex and consist of distorted octahedral VO_6 units that share faces to form dimers, which are in turn bridged by phosphate anions into a 2D network. The complexity and nonstoichiometry of $K_{3.48}[(UO_2)(VO)_4H_{1.52}(PO_4)_5]$ is the result of two important features. The first of these is that one of the phosphate anions is disordered with four different orientations. These layers and their inherent problems with disorder are similar to those found in $[NH_4][Zn(H_2O)(VO)_2(PO_4)_2(H_2PO_4)]$[18] and $MZn(H_2O)(VO)_2(PO_4)_2(H_2PO_4)$ (M = K, Rb, Cs).[19] The second feature leading to a nonideal stoichiometry is that there are two crystallographically distinct K^+ sites. Those in the channels appear to be fully occupied, whereas the second K^+ cation coincides with the disorder phosphate anion and has an occupancy of 0.624(7). The remaining positive charge needed to counterbalance the anionic framework is accomplished by protonating the terminal oxo atoms on the disordered phosphate anion in a method similar to that of $Cs_{3+x}[(UO_2)_3CuH_{4-x}(PO_4)_5]\cdot H_2O$.[10]

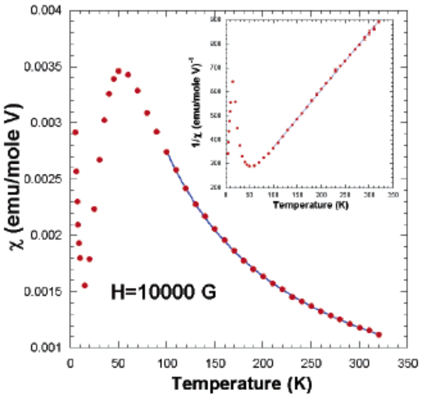

Figure 2. Magnetic susceptibility of **Rb−UVP−2** as a function of temperature. Line is the fit to Curie−Weiss behavior. Inset shows the temperature dependence of the inverse magnetic susceptibility. The line is also the fit to Curie−Weiss behavior.

The V−O bond distances in the distorted VO_6 octahedra are classical for a VO_{5+1} polyhedron where there is one long bond trans to a vanadyl V═O group. In this case, the short V═O bond distance is 1.590(4) Å, whereas the *trans*-V−O bond distance is 2.297(5) Å. The remaining four V−O distances are 1.958(3) (×2) and 2.061(3) (×2) Å. These bond distances were used to arrive at a bond-valence sum of 4.13, which is consistent with V(IV).[20,21]

As a result of the face-sharing between two VO_6 octahedra, the V centers are pushed away from the center of the octahedra toward opposite edges of the dimer. Nevertheless, there is a short V···V distance of 3.0352(18) Å. The UO_6 tetragonal bipyramids shows normal U−O bond distances with two terminal U═O distances of 1.786(6) Å, and four longer distances of 2.260(4) Å in the equatorial plane. The uranyl oxo atoms are terminal. Using the bond-valence parameters of Burns et al., we found a BVS of 6.22 for U(1) that is typical for a U(VI) compound.[22]

Further confirmation of the +4 oxidation state for vanadium is provided by magnetic susceptibility measurements on **Rb−UVP−2**. Magnetization measurements, obtained at 5 K, increase linearly with magnetic field up to the highest measured field, 10 000 G. About 75% of the magnetic signal arises from the background at high temperatures, necessitating susceptibility data acquisition in a 10 000 G field. The temperature dependence of the magnetic susceptibility, together with its inverse, is depicted in Figure 2. The data show complex behavior with temperature. Susceptibility data obtained at lower fields, 500 and 2000 G, show a similar temperature dependence. The data indicate a long-range ordering of the moments at 52(2) K. Above that temperature, the sample appears paramagnetic. The data between 100 and 320 K are fit to the modified Curie law; the effective

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(17) (a) X-ray structural analyses: $K_{3.48}[(UO_2)(VO)_4H_{1.52}(PO_4)_5]$: blue prism (fragment), crystal dimensions 0.055 × 0.029 × 0.014 mm^3, orthorhombic, *Immm*, $Z = 2$, $a = 7.3803(7)$ Å, $b = 9.1577(8)$ Å, $c = 17.0898(16)$ Å, $V = 1155.04(18)$ Å^3 ($T = 193$ K), $\mu = 96.41$ cm^{-1}, $R_1 = 0.0258$, $wR_2 = 0.0622$. Bruker APEX CCD diffractometer: $\theta_{max} = 56.58°$, MoKα, $\lambda = 0.71073$ Å, 0.3° ω scans, 5940 reflections measured, 843 independent reflections, all of which were included in the refinement. The data were corrected for Lorentz polarization effects and for absorption, solutions were solved by direct methods, anisotropic refinement of F^2 was completed by full-matrix least-squares, 105 parameters. (b) Sheldrick, G. M. *SHELXTL PC, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*, version 6.12; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 2001.

(18) Le Fur, E.; Peña, O.; Pivan, J. Y. *J. Mater. Chem.* **2002**, *12*, 132.

(19) Messaoudi, S.; Furet, E.; Gautier, R.; Le Fur, E.; Peña, O.; Pivan, J. Y. *Chem. Mater.* **2004**, *16*, 435.

(20) Brese, N. E.; O'Keefe, M. *Acta Crystallogr., Sect. B* **1991**, *47*, 192.

(21) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *41*, 244.

(22) Burns, P. C.; Ewing, R. C.; Hawthorne, F. C. *Can. Mineral.* **1997**, *35*, 1551.

magnetic moment is determined to be 1.73(10) μ_B, which is consistent with this compound containing V(IV). χ_{TIP} and θ are also determined from the modified Curie law fit as −0.00008(4) emu/mol and −41(8) K, respectively. The large negative Weiss constant is consistent with an antiferromagnetic component to the ordering, as is the shape of the χ vs T plot. There is an additional feature in the data that occurs at about 15(1) K that could be a reordering of the moments as the temperature is lowered through the ordered state from 52 K, or it could be a paramagnetic impurity phase. The effective moment at 5 K, determined from the M vs H curve, is 0.34 μ_B.

The presence of K^+ cations in the channels of the framework in $K_{3.48}[(UO_2)(VO)_4H_{1.52}(PO_4)_5]$ lends this compound well to ion-exchange studies. These measurements were conducted using a combination of ion-selective electrodes and atomic absorption (AA). There is no uptake of Ca^{2+} or Sr^{2+} from 1×10^{-2} M and 1×10^{-3} M solutions of $CaCl_2$ and $SrCl_2$. A small exchange with Na^+ cations with an uptake value of 0.25(6) meq/g was observed in a 1×10^{-2} M NaCl solution. In mixed 1:1 molar ratio solution pairs of NaCl:$CaCl_2$ and NaCl:$SrCl_2$, slightly smaller Na^+-exchange capacities of 0.18(5) and 0.17(5) meq/g, respectively, were detected. Ca^{2+} and Sr^{2+} uptake were not found in the mixed solutions either. Ion-exchange experiments with Cs^+ from a 1×10^{-2} M CsCl solution reveals a notable uptake value of 0.87(10) meq/g. We suggest that the small size of the channels that extend along the *c*-axis (2.8 × 4.4 Å^2) precludes their involvement in exchange unless the framework is highly flexible. However, channels are also present as the result of the orientational disorder of the phosphate anions within the layers. The selectivity can be explained in terms of radii and hydration energy for competing cations. In the hydrated state, the radii of K^+ and Cs^+ are the same and correspond to 3.3 Å. Because of its lower dehydration energy, Cs^+ is able to lose its hydration sphere and enter the channels more easily than K^+.[23] PXRD data taken before and after ion exchange do not suggest significant structural changes. Taken together, these data suggest that $K_{3.48}[(UO_2)(VO)_4H_{1.52}(PO_4)_5]$ is a Cs^+-selective ion-exchange material that might play a key role in ^{137}Cs sequestration.

In conclusion, we have shown that $K_{3.48}[(UO_2)(VO)_4H_{1.52}(PO_4)_5]$, a compound readily available from common starting reagents, is a multifunctional material undergoing both magnetic ordering and Cs^+-selective ion exchange. This work also provides further expansion of the structural building units that can be used to construct three-dimensional uranyl-containing frameworks. Future work on this compound will investigate whether or not the luminescence from the uranyl units can be used as a straightforward probe of ion exchange.

Acknowledgment. This work was supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, Heavy Elements Program, U.S. Department of Energy, under Grant DE-FG02-01ER15187 at Auburn University and under Contract W-31-109-ENG-38 at Argonne National Laboratory. We thank Prof. A. Y. Shvarev for assistance with preparing ion-selective electrodes.

Supporting Information Available: X-ray crystallographic file for $K_{3.48}[(UO_2)(VO)_4H_{1.52}(PO_4)_5]$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[23] Nightingale, E. R. *J. Phys. Chem.* **1959**, *63*, 1381.