Inorganic Chemistry

Communication

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Mixed-Valence Uranium Germanate and Silicate: $Cs_x(U^{V}O)(U^{IV/V}O)_2(Ge_2O_7)_2$ ($x = 3.18$) and $Cs_4(U^{V}O)(U^{IV/V}O)_2(Si_2O_7)_2$

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Supporting Information

ABSTRACT: A new mixed-valence uranium germanate and the silicate analogue have been synthesized under hydrothermal conditions at 600 °C and 165 MPa. Their crystal structures contain infinite $-U^{V}-O-U^{IV/V}-O-U^{IV/V}-O-U^{V}-$ chains that are connected by Ge_2O_7 or Si_2O_7 groups to form a 3D framework with six-ring channels where the Cs^+ cations are located. Two of the Cs sites in the germanate are partially occupied. Bond-valence-sum calculation and an U 4f X-ray photoelectron spectroscopy study confirm the valence states of the uranium.

Uranyl silicates have attracted considerable interest because they are an important group of uranium(VI) minerals found in the altered zones of uranium deposits, they are formed when spent nuclear fuel reacts with silicon-containing water under oxidizing conditions, and they have shown a rich crystal chemistry.[1] A large number of uranyl silicates including an organically templated uranyl silicate have been synthesized.[2,3] Few uranium(IV) silicates and germanates were reported. The naturally occurring minerals coffinite, $USiO_4$,[4a,b] and arapovite, $U^{4+}(Ca,Na)_2(K_{1-x}\square_x)[Si_8O_{20}]$ ($\square$ denotes vacancy),[4c] a synthetic one, $Cs_2USi_6O_{15}$,[4d] and two synthetic germanates, $UGeO_4$ and $Cs_4UGe_8O_{20}$,[4e,f] are the only known uranium(IV) compounds. The synthesis of uranium(V) silicates and germanates is challenging because of the tendency of U^{5+} to either oxidize to U^{6+} or disproportionate to U^{4+} and U^{6+}. Recently, we synthesized two uranium(V) silicates, $K(UO)Si_2O_6$ and $K_3(U_3O_6)Si_2O_7$, and two germanates, $Rb_3(U_3O_6)Ge_2O_7$ and $Cs_3UGe_7O_{18}$, under high-temperature, high-pressure hydrothermal conditions.[5] In addition, several mixed-valence uranium silicates and germanates including uranium(IV,V), -(IV,VI), -(V,VI), and -(IV,V,VI) have been synthesized.[6] All mixed-valence uranium silicates and germanates with oxidation states of uranium from 4+ to 6+ have been observed. Among these compounds, two contain intermediate-valence uranium. The structure of $Cs_2K(UO)_2(Si_4O_{12})$ contains only one unique uranium in the oxidation state of 4.5+.[6b] $Na_7UO_2(UO)_2(UO_2)_2Si_4O_{16}$ is extraordinary in that three unique sites corresponding to uranium(IV), -(V), and -(V,VI) coexist.[6c] Herein, we report two new compounds in this system, $Cs_{3.18}(U^{V}O)(U^{IV/V}O)_2(Ge_2O_7)_2$ and $Cs_4(U^{V}O)(U^{IV/V}O)_2(Si_2O_7)_2$, which contain both mixed- and intermediate-valence uranium.

High-temperature, high-pressure hydrothermal synthesis was performed in gold ampules contained in a Tem-Pres autoclave where the pressure was provided by water. The degree of filling of the autoclave by water at room temperature was 55%. A reaction mixture of 0.253 mL of CsOH(aq) (50 wt %), 41.1 mg of UO_3, 120.0 mg of GeO_2, and 1.9 mg of Al (molar ratio Cs:U:Ge:Al = 10:1:8:0.5) in a 4.5-cm-long gold ampule (inside diameter = 0.48 cm) was heated at 600 °C for 2 days. Aluminum metal was included in the reaction mixture as a reducing agent. The pressure was estimated to be 165 MPa at the reaction temperature according to the $P-T$ diagram of pure water. The autoclave was then cooled to 350 °C at 5 °C/h and quenched at room temperature by removal of the autoclave from the furnace. The product was filtered, washed with water, rinsed with ethanol, and dried under ambient conditions. The reaction produced brown plate crystals of $Cs_{3.18}(U_3O_3)(Ge_2O_7)_2$ (denoted as **1**) as a major product along with some colorless GeO_2 crystals. A qualitative energy-dispersive X-ray analysis of several brown crystals did not show any aluminum and confirmed the presence of cesium, uranium, and germanium. A suitable crystal was selected for single-crystal X-ray diffraction, from which the chemical formula was determined.[7] The brown crystals were manually separated from the others, giving a pure sample, as indicated by powder X-ray diffraction (PXRD; Figure S1 in the Supporting Information). The yield of **1** was 62% based on UO_3. Total-reflection X-ray fluorescence (TXRF) spectroscopy was applied to determine the relative element content. A powder sample of **1** was transferred into a liquid form by dissolving it in 50% HF(aq). For a single measurement, 5 μL of the solution was transferred to a sample carrier made of acrylic glass and dried by heating with a hot plate. TXRF analysis of seven samples showed the compound to contain cesium, uranium, and germanium in the molar ratio $(3.24 \pm 0.14):3:(4.14 \pm 0.13)$, which is in agreement with that determined from X-ray diffraction. The corresponding silicate $Cs_4(U_3O_3)(Si_2O_7)_2$ (**2**) could also be synthesized but in a very low yield. An optimum reaction condition has not been found. A suitable crystal was selected for structural analysis.[7] However, we were unable to collect enough sample for spectroscopy studies.

The valence states of uranium in **1** were analyzed by X-ray photoelectron spectroscopy (XPS). A large crystal was selected and etched using a 1 kV Ar^+ ion beam for 5 s before measurement. The U 4f XPS spectrum is shown in Figure 1,

Received: May 24, 2012
Published: July 5, 2012

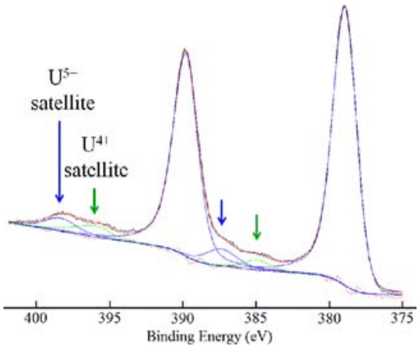

Figure 1. U 4f XPS spectrum of **1**. The spectrum is modeled with one component. (black line, observed data; red line, fit envelope; blue line, UV; green line, satellites for U^{IV}; red dotted line, deviation).

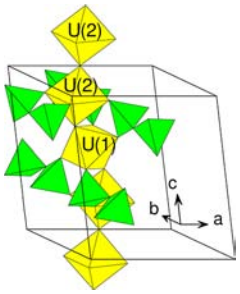

Figure 2. Section of an infinite chain in **1**. The yellow and green polyhedra are UO_6 octahedra and GeO_4 tetrahedra, respectively.

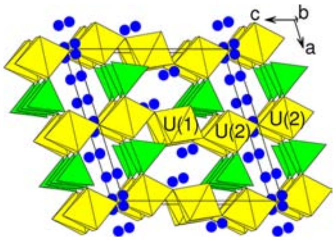

Figure 3. Structure of **1** viewed along the *b* axis. The blue circles are Cs atoms.

which is best fitted with one component of U^{5+}. The fitting parameters are given in Table S1 in the Supporting Information. The binding energies (BEs) of all peaks were referenced to the adventitious C 1s at 285.0 eV. The BEs of U^{5+} were at 379.8 eV (U $4f_{7/2}$), with the shakeup satellite peak at 388.3 eV, and 390.7 eV (U $4f_{5/2}$), with the satellite peak at 399.3 eV. These values are comparable with those of U^{5+} in $Cs_3UGe_7O_{18}$.[5c] For uranium, both of the U 4f core-level peaks show shakeup satellites at higher BEs, with the values of the separations depending on the oxidation states of uranium. Typically, the separations are in the range of 6−7 eV for U^{4+}, 7.8−8.5 eV for U^{5+}, and 4 and 10 eV for U^{6+}.[8] The separations between the satellite and primary peaks in **1** are comparable with the values for U^{5+}. The XPS spectrum also shows the satellites for U^{4+}, which is evidence for a small amount of U^{4+} in **1**. A UV−vis−near-IR (NIR) absorption spectrum was measured on a plate crystal using a microspectrophotometer, but the f−f transitions for U^{IV} were not clearly observed. This is because the measurement was on a small crystal and only a small amount of U^{IV} is present.

The structure of **1** is constructed from the following distinct structural elements: two UO_6 octahedra, one GeO_4 tetrahedron, and three Cs^+ ions. U(1) is at inversion centers, U(2) and all Cs^+ ions lie in mirror planes, and Ge(1) is in general positions. Each GeO_4 shares a corner with another GeO_4 to form a Ge_2O_7 dimer, with the bond angle at the bridging oxygen atom being 136.4(7)°. Both UO_6 octahedra are only slightly distorted, with U−O distances between 2.063 and 2.173 Å for $U(1)O_6$ and between 2.099 and 2.209 Å for $U(2)O_6$. Bond-valence sums at U(1) and U(2) sites, calculated by using the bond-valence parameters R_{ij} = 2.051 Å and b = 0.519 Å of Burns et al.,[9] are 5.10 and 4.87 vu (vu = valence unit), respectively, in accordance with the occurrence of U^{5+} and $U^{4+/5+}$ ions in these sites.

As shown in Figure 2, every UO_6 has four equatorial silicate O atoms and two axial O atoms that act as common vertices to neighboring octahedra to form infinite $-U^{V}-O-U^{IV/V}-O-U^{IV/V}-O-U^{V}-$ chains along the *c* axis. The U(1)−O(5)−U(2) and U(2)−O(6)−U(2) bond angles are 140.3(5)° and 180°, respectively. Adjacent U−O chains are linked together through corner-sharing by Ge_2O_7 groups to form a 3D framework that delimits two types of six-ring channels along the *b* axis, where the Cs^+ cations are located (Figure 3). Each Ge_2O_7 acts as a bidentate ligand to one U(2) atom within a chain and as a bridging ligand to two pairs of U(1) and U(2) atoms in two neighboring chains. The distance between adjacent Cs(1) and Cs(2) sites is too short to allow simultaneous occupancy and, therefore, they are partially occupied, whereas the Cs(3) site is fully occupied. There are 3.18 Cs atoms per formula unit, and the average oxidation state of U is 4.94+. This is consistent with the bond-valence-sum calculation results that U(1) is pentavalent and 10% of U^{5+} at the U(2) site is reduced to U^{4+}. The structure of compound **2** is essentially the same as that of **1** except that there are only two unique Cs sites in the structural channels of **2** and both sites are ordered and fully occupied. In this structure, half of U^{5+} at the U(2) site is reduced to U^{4+}. Presumably, the void volume of the silicate is smaller such that the Cs−O interaction is stronger and, therefore, the Cs sites are fully occupied.

Previously, we reported a mixed-valence uranium(IV,V) silicate, $Cs_2K(UO)_2(Si_4O_{12})$,[6b] whose structure contains straight chains of UO_6 octahedra sharing opposite corners. Crystal structure analysis results do not reveal the presence of two distinct coordination environments, and there is only one unique uranium in the oxidation state of 4.5+. One explanation for the locations of U^{IV} and U^{V} is that they are disordered within the chain. This is possible because the coordination geometries for the two cations are similar. In the structure of **1**, dimers of corner-sharing $U(2)^{IV,V}O_6$ octahedra are connected by a $U(1)^{V}O_6$ octahedron. The common vertex within the octahedral dimer is at an inversion such that the two U atoms are symmetry-equivalent. The average oxidation state of U(2) is 4.9+. Presumably, 90% of U(2) is U^{5+} and the remaining 10% is U^{4+}, and they are disordered at the U(2) site.

In summary, we have successfully synthesized a new uranium germanate and the silicate analogue, $Cs_{3.18}(U^{V}O)(U^{IV/V}O)_2(Ge_2O_7)_2$ and $Cs_4(U^{V}O)(U^{IV/V}O)_2(Si_2O_7)_2$, which contain pentavalent and intermediate-valence states of uranium. The structure of previously reported uranium(IV,V) silicate, $Cs_2K(UO)_2Si_4O_{12}$,[6b] contains corner-sharing infinite chains of intermediate valence uranium ($-U^{IV/V}-O-U^{IV/V}-O$) and that of the mixed-valence uranium(V,VI) germanates, $A_3(U_2O_4)Ge_2O_7$ (A = Rb, Cs),[6a] contains corner-sharing infinite chains of alternatively pentavalent and hexavalent uranium ($-U^{V}-O-U^{VI}-O$). In contrast, compounds **1** and **2** contain infinite chains of alternatively pentavalent and intermediate-valence uranium (−U^{V}−O−$\text{U}^{\text{IV/V}}$−O−$\text{U}^{\text{IV/V}}$−O−U^{V}−). They are the first examples in the literature. The high-temperature, high-pressure hydrothermal method has been successfully used in the synthesis of uranium silicates and germanates with unusual oxidation states of uranium and interesting crystal structures. Further research on this interesting class of compounds is in progress.

■ ASSOCIATED CONTENT

Supporting Information

X-ray data in CIF format, PXRD pattern, and XPS fitting parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Science Council of Taiwan for financial support, Prof. Walter Vogel at National Central University for PXRD measurements, S.-L. Cheah at National Tsing Hua University for XPS measurements, and J. N. Cross and Prof. T. E. Albrecht-Schmitt at University of Notre Dame for UV−vis−NIR spectral measurements.

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(7) Crystal data of **1**: A total of 9746 reflections of a brown plate crystal with dimensions of 0.10 × 0.06 × 0.06 mm^3, monoclinic, $C2/m$ (No. 12), a = 11.7377(4) Å, b = 7.7257(3) Å, c = 11.9543(4) Å, β = 107.671(2)°, V = 1032.89(6) Å^3, Z = 2, d_{calc} = 5.463 g·cm^{-3}, μ(Mo Kα) = 34.76 mm^{-1}, were measured on a Kappa APEXII diffractometer at 296 K, which gave 1359 independent reflections with R(int) = 0.0566. An empirical absorption correction based on the symmetry equivalent was applied with $T_{\text{min}}/T_{\text{max}}$ = 0.424/0.746. The final cycles of refinement converged at R1 = 0.0237 and wR2 = 0.0545 for 1329 reflections with $I > 2\sigma(I)$. GOF = 1.166, and ρ_{max} and ρ_{min} = 2.51 and −1.76 e·Å^{-3}, respectively. Crystal data of **2**: 7452 reflections, brown plate crystal, 0.16 × 0.06 × 0.04 mm^3, monoclinic, $C2/m$, a = 11.594(2) Å, b = 7.544(2) Å, c = 11.894(2) Å, β = 107.43(3)°, V = 992.5(3) Å^3, Z = 2, d_{calc} = 5.455 g·cm^{-3}, μ(Mo Kα) = 31.96 mm^{-1}, 1315 independent reflections, R(int) = 0.0369, $T_{\text{min}}/T_{\text{max}}$ = 0.345/0.985, R1 = 0.0247, wR2 = 0.0661 for 1284 reflections with $I > 2\sigma(I)$, GOF = 1.133, and ρ_{max} and ρ_{min} = 1.53 and −3.23 e·Å^{-3}. The values of U_{11} and U_{33} of the bridging O atom in the Ge_2O_7 group in **1** are considerably larger than that of U_{22}, which is because the bridging atom prefers to vibrate in directions at right angles to the Si···Si vector. For the Si_2O_7 group in **2**, the differences between the values of U_{11} and U_{33} of the bridging O atom and that of U_{22} are smaller.

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