Mixed-Valence Compounds

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$[Na_7U^{IV}O_2(U^{V}O)_2(U^{V/VI}O_2)_2Si_4O_{16}]$: A Mixed-Valence Uranium Silicate[**]

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Uranyl silicates are an important group of uranium(VI) minerals found in the altered zones of many uranium deposits.[1] Uranyl silicates have also attracted considerable interest because they are formed when spent nuclear fuel reacts with silicon-containing water under oxidizing conditions.[2] One naturally occurring uranium(IV) silicate also exists, namely coffinite ($USiO_4$).[3] In the last 10 years, a large number of uranyl silicates and germanates that contain alkali metals as counter cations have been synthesized,[4] and an organically templated uranyl silicate has also been reported.[5] The chemistry of compounds containing U^{5+} atoms is considerably less-developed compared to the extensive catalogue of U^{4+} and U^{6+} compounds. Apart from its fundamental structural interest, species containing U^{5+} atoms have environmental implications.[6] We previously reported the first uranium(V) silicates and germanates, $[K(UO)Si_2O_6]$ and $[A_3(U_3O_6)(X_2O_7)]$ (A = K, Rb; X = Si, Ge).[7] Mixed-valence uranium oxide materials are rare. On heating, the oxide UO_3 decomposes to the mixed oxidation state U_3O_8. X-ray absorption near-edge structure (XANES) analysis on uranates $[A_2U_4O_{12}]$ (A = K, Rb, or Tl) reveals that the uranium is present as U^{5+} and U^{6+} species.[8] The minerals ianthinite, $[U^{4+}{}_2(U^{6+}O_2)_4O_6(OH)_4(H_2O)_4]\cdot 5\,H_2O$,[9] and wyartite, $Ca[U^{5+}(U^{6+}O_2)_2(CO_3)O_4(OH)]\cdot 7\,H_2O$,[10] and the synthetic compounds $[U^{5+}(H_2O)_2(U^{6+}O_2)_2O_4(OH)]\cdot 4\,H_2O$ and $[U^{5+}(U^{4+}Y_5)O_{12}]$ were the other examples reported in the literature.[11,12] The dark coloration of $Cd_2(H_2O)_2[U(OH)(CH_3COO)(UO_2)_5(OH)_2O_8]\cdot 0.5\,H_2O$ and its magnetic susceptibility data indicate the presence of some U^{5+} sites in this uranyl acetate.[13] Recently, we reported mixed-valence uranium(V,VI) germanates, $[A_3(U_2O_4)(Ge_2O_7)]$ (A = Rb, Cs),[14] and uranium(IV,V) silicate, $[Cs_2K(UO)_2Si_4O_{12}]$.[15] Herein, we report the high-temperature, high-pressure hydrothermal synthesis of an extraordinary mixed-valence uranium silicate, $[Na_7UO_2(UO)_2(UO_2)_2Si_4O_{16}]$ (**1**), which contains three unique uranium sites for U^{4+}, U^{5+}, and U^{5+}/U^{6+} ions, respectively. The structure of **1** provides solid evidence of three different valence states for uranium in a single compound.

The valence state of uranium in **1** was studied by X-ray photoelectron spectroscopy (XPS). The U 4f XPS spectrum of **1** is shown in Figure 1. The binding energies (BEs) of all of the peaks were referenced to adventitious C 1s at 285.0 eV. A single, but variable full-width at half-maximum was used for all the peak components. The spectrum was fitted with three components and the satellites for U^{6+}, U^{5+}, and U^{4+}, where the BEs of U $4f_{7/2}$ peaks were at 382.0, 380.4, and 379.8 eV, respectively; these values can be compared with those in $[Cs_2U^{VI}{}_4O_{13}]$ (381.3), $[NaU^{V}O_3]$ (380.6), and $[U^{IV}O_2]$ (380.0 eV),[16] respectively. The separation between the satellite and primary peaks are also in agreement with the XPS analysis of values for the above compounds. The fitting parameters are given in Table S2 in the Supporting Information. The XPS spectrum of **1** indicates the presence of uranium sites with three different valence states. The $U^{IV}/U^{V}/U^{VI}$ $4f_{7/2}$ primary peak area ratio of 1:1.8:1.5 does not conform to that of 1:3:1 determined using the bond-valence method (see below). The reason for this mismatch may be the tendency of uranium for surface oxidation.

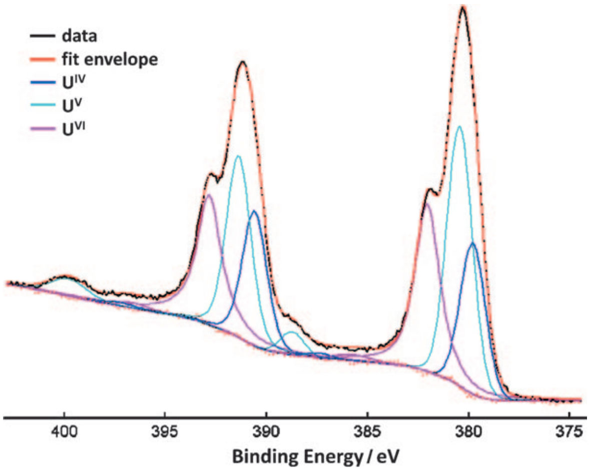

Figure 1. The U 4f XPS spectrum of **1**. The spectrum is modeled with three components.

XANES spectra were recorded on a Wiggler 01C1 beamline at the National Synchrotron Radiation Research Center (NSRRC), Taiwan, in transmission mode at 293 K. The U L_3-edge XANES spectra of **1** and four reference materials: $U^{VI}O_3$, $[K_3(U^{V}{}_3O_6)(Si_2O_7)]$, mixed-valence

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uranium(IV,V) silicate [$Cs_2K(UO)_2Si_4O_{12}$], and $U^{IV}O_2$ are shown in Figure S2 in the Supporting Information. The edge of **1**, measured at the position of the half-edge step, is at 17167.7 eV, a value which is between those for [$K_3(U^{V}{}_3O_6)(Si_2O_7)$] and [$Cs_2K(U^{IV,V}O)_2Si_4O_{12}$] (see Table S1 in the Supporting Information).

The overall structure of **1** is layered with slabs of uranium silicate, separated by Na^+ cations. The structure is formed from the following structural elements: four sodium sites, one UO_6 octahedron, two UO_7 pentagonal bipyramids, and two SiO_4 tetrahedra. Na(1) and U(1) atoms are at inversion centers and all other atoms are in general positions. In contrast to uranium(VI) compounds, which contain two strongly bonded uranyl oxygen atoms with U−O bond lengths of approximately 1.8 Å, the U(1)O_6 octahedron in **1** is considerably more regular with d(U(1)−O) = 2.228–2.282 Å, close to the predicted U^{4+}−O bond lengths of 2.25 Å according to the effective ionic radius for a six-coordinate U^{4+} ion.[17] The mean U(1)−O bond length of 2.256 Å is comparable to those of 2.197 and 2.29 Å for the U^{4+}−O octahedra in [$Cs_2K(UO)_2Si_4O_{12}$] and the mineral ianthinite,[9] respectively. U(2) is seven-coordinate in a pentagonal bipyramid geometry with two axial U−O distances of 1.897 and 2.010 Å, and five equatorial U−O distances in the range 2.294–2.499 Å. The axial U(2)−O bond lengths are considerably longer than the average U−O bond length of 1.793 Å in the uranyl ion for a pentagonal bipyramid. U(3) is also in a seven-coordinate pentagonal bipyramidal geometry. However, the axial U−O distances of 1.868 and 1.869 Å in U(3)O_7 are significantly shorter than those in U(2)O_7, thus indicating that U(3) is in a higher oxidation state than U(2). The bond-valence approach is a powerful tool for the interpretation of bond lengths in the solid state. The bond-valence sums at the U(1), U(2), and U(3) sites, calculated using the bond-valence parameters $R_{ij} = 2.051$ Å and $b = 0.519$ Å reported by Burns et al.,[18] were 4.05, 5.14, and 5.58 valence units, respectively, thus indicating the presence of U^{4+}, U^{5+}, and U^{5+}/U^{6+} ions at these sites. To balance the charge, the average oxidation state of U(3) must be +5.5. The oxidation states of +5 and +6 are disordered throughout the U(3) sites in the lattice. Compound **1** is highly unusual in that it contains three different valence states of an element within a compound. Bond-valence analysis on ianthinite shows that a U^{4+} site probably contains U^{5+} and, therefore, all three oxidation states of U may in fact be present.[9b] Finnie et al. provided XPS evidence for U(IV,V,VI) in a uranium-doped thorium analogue of brannerite, [$U_xTh_{1-x}Ti_2O_6$].[19] Very recently, Albrecht-Schmitt and co-workers reported two very interesting neptunium borates.[20] An evaluation of both the neptunyl Np=O bond length and bond-valence sums suggests that the NpO_6, NpO_7, and NpO_8 units in their structures are primarily +4, +5, and +6, respectively. Additionally, compound **1** is the first example of an inorganic compound that contains U^V atoms in a uranyl structure. All the other pentavalent-uranium silicates and germanates have U^V atoms in a uranate coordination scheme.

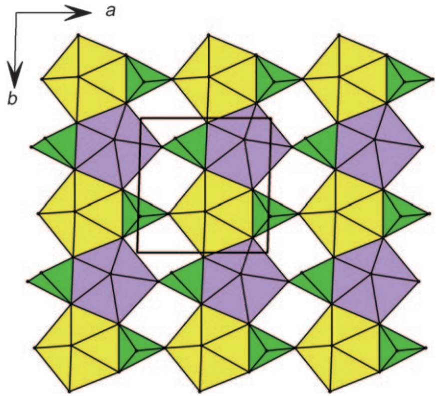

Figure 2. Section of a uranium silicate sheet in **1**. The purple and yellow polyhedra represent $U(2)^{V}O_7$ and $U(3)^{V/VI}O_7$ pentagonal bipyramids, respectively. Silicate tetrahedra are in green.

The structure of **1** contains distinct alternating U(2)O_7 and U(3)O_7 pentagonal bipyramids that share edges to form infinite chains along the b axis (Figure 2). Silicate tetrahedra share edges with the pentagonal bipyramids of a given chain and vertices with an adjacent chain to form sheets in the ab plane. This uranium silicate sheet has a uranophane anion topology, which is a common topology for many sheets in addition to uranyl silicates. Three different types of sheets that contain the uranophane anion topology that differ in the orientation of the silicate tetrahedra have been reported, namely α uranophane, oursinite, and β uranophane.[21] The sheets that are formed in **1** are different from the above three structures because all of the silicate tetrahedra within a sheet point in the same direction. U(1)O_6 octahedra are located between two sheets and share two vertices with silicate tetrahedra from each adjacent sheets, and two vertices with the U(2)O_7 pentagonal bipyramids to form thick layers in the ab plane (Figure 3). The intralayer region contains $Na(1)^+$ and $Na(2)^+$ ions. Adjacent layers are linked through bonds from the interlayer $Na(3)^+$ and $Na(4)^+$ ions to the oxygen atoms of the uranium silicate sheets. The interlayer region does not contain any water molecules. The high-temperature synthesis may preclude the incorporation of water, which has also been observed in other cases.[4d]

In summary, we have synthesized a novel mixed-valence uranium silicate under high-temperature, high-pressure hydrothermal conditions. The structure and uranium oxidation states of **1** were confirmed by single-crystal X-ray

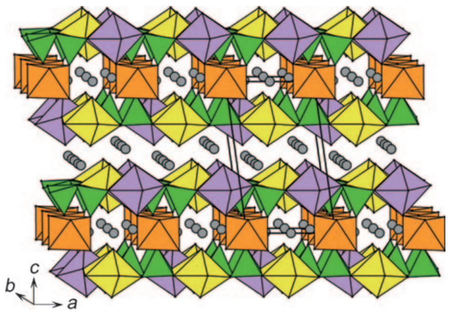

Figure 3. Structure of **1** viewed along the b-axis. The orange, purple, yellow, and green polyhedra represent $U(1)^{IV}O_6$ octahedra, $U(2)^{V}O_7$ and $U(3)^{V/VI}O_7$ pentagonal bipyramids, and SiO_4 tetrahedra, respectively. Gray circles, Na^+ ions.

diffraction, XPS, and XANES. Compound **1** is extraordinary in that three unique uranium sites corresponding to three different oxidation states coexist. In the course of researching the synthesis of pentavalent-uranium silicates and germanates, we observed other new phases whose dark color is indicative of mixed-valence compounds. We anticipate that more compounds in this very interesting and complex system will be synthesized.

Experimental Section

A reaction mixture of 10 M NaOH(aq) (210 μL), 5 M CsF(aq) (210 μL), UO_3 (30 mg), and SiO_2 (76 mg) in the molar ratio Na/Cs/U/Si = 10:5:0.5:6 was sealed in a 5.7 cm long gold ampule (i.d. = 4.85 mm) inside an autoclave and counter-pressured with water at a fill level of 55 %. The autoclave was heated at 600 °C for 2 days, cooled to 350 °C at $5\,°C\,h^{-1}$, and then rapidly cooled to RT by turning off the power to the tube furnace. The pressure was estimated to be 170 MPa according to the pressure-temperature diagram for pure water. The reaction yielded black lamellar crystals of **1** along with some dark-red crystals of $[Cs_2Na(UO)_2Si_4O_{12}]$, which is isostructural with the mixed-valence uranium(IV,V) silicate $[Cs_2K(UO)_2Si_4O_{12}]$[15] and some unidentified colorless solid. The black crystals of **1** could be manually separated from the side products, giving a pure sample as indicated by powder X-ray diffraction (see the Supporting Information, Figure S1). Energy dispersive X-ray analysis of several black crystals showed only the presence of sodium, uranium, and silicon. The yield was 23 % based on uranium. A suitable black crystal was selected for single-crystal X-ray diffraction analysis, from which the chemical formula was determined.[22]

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[22] Crystal data for **1**: triclinic, space group $P\bar{1}$ (No. 2), $M_r = 1847.44$, $a = 6.7931(1)$, $b = 6.9685(1)$, $c = 11.9157(2)$ Å, $\alpha = 95.471(1)$, $\beta = 98.371(1)$, $\gamma = 90.688(1)°$, $V = 555.32(2)$ Å^3, $Z = 1$, $\rho_{calcd} = 5.524\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 367.95\ cm^{-1}$, 8979 reflections measured on a CCD diffractometer at 293 K, 2655 independent reflections with $R_{int} = 0.0454$, $R1 = 0.0203$, and $wR2 = 0.0556$ for 2612 reflections with $I > 2\sigma(I)$ and 185 parameters. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-421530.