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$Cs_8U^{IV}(U^{VI}O_2)_3(Ge_3O_9)_3\cdot 3H_2O$: A Mixed-Valence Uranium Germanate with 9-Ring Channels

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S Supporting Information

ABSTRACT: A mixed-valence uranium(IV,VI) germanate has been synthesized under high-temperature, high-pressure hydrothermal conditions. The structure contains discrete $U^{IV}O_6$ octahedra and $U^{VI}O_6$ tetragonal bipyramids, which are connected by three-membered single-ring $Ge_3O_9{}^{6-}$ anions to form a three-dimensional framework with 9-ring channels. The U 4f X-ray photoelectron spectroscopy spectrum was measured to identify the valence states of the uranium.

The structural chemistry of uranium compounds is very diverse because of the possibility of different oxidation states and the richness of uranium coordination geometries.[1] Among these compounds, many uranium silicate phases have been found as minerals and certain synthetic examples of uranyl silicates and germanates have been reported,[2,3] together with an organically templated uranyl silicate.[4] Recently, two uranium(V) silicates, $K(UO)Si_2O_6$ and $K_3(U_3O_6)Si_2O_7$,[5] and a germanate analogue, $K_3(U_3O_6)Ge_2O_7$,[5b] have been synthesized in which the oxidation state of uranium was considered as metastable pentavalent uranium in an aqueous solution and existed as $UO_2{}^+$ in a narrow stability field. Naturally occurring uranium(IV) silicate exists, namely, coffinite ($USiO_4$),[6] which is the most important ore mineral of uranium after uraninite (UO_{2+x}), whereas a uranium(IV) germanate, $UGeO_4$, has been synthesized by solid-state reaction.[7] In addition, a number of interesting mixed-valence uranium silicates and germanates have been reported, for example, a mixed-valence uranium(IV,V) silicate, $Cs_2K(UO)_2Si_4O_{12}$,[8] uranium(V,VI) germanates, $A_3(U_2O_4)Ge_2O_7$ (A = Rb, Cs),[9] and a uranium(IV,V,VI) silicate, $Na_7U^{IV}O_2(U^{V}O)_2(U^{V/VI}O_2)_2Si_4O_{16}$,[10] in which three oxidation states of uranium coexist in one compound. Another mixed-valence uranium(V,VI) oxide, $[U^{V}(H_2O)_2(U^{VI}O_2)_2O_4(OH)](H_2O)_4$, has also been synthesized.[11] Two mixed-valence minerals of uranium(V,VI), wyartite, $CaU^{V}(UO_2)_2(CO_3)O_4(OH)(H_2O)_7$, and dehydrated wyartite have also been observed in nature.[12,13] Although one compound of uranium(IV,VI) phosphate, $U(UO_2)(PO_4)_2$,[14] and at least one uranium(IV,VI) mineral of ianthinite, $[U_2{}^{4+}(UO_2)_4O_6(OH)_4(H_2O)_4](H_2O)_5$,[15] have been observed, no uranium(IV,VI) silicate and germanate have been published in the literature so far. Herein, we report the first mixed-valence uranium(IV,VI) germanate, $Cs_8U(UO_2)_3(Ge_3O_9)_3\cdot 3H_2O$ (denoted as **1**), which was synthesized by a high-temperature, high-pressure hydrothermal method.

Compound **1** was synthesized by heating a mixture of 200 μL of CsOH (50 wt %), 200 μL of 10 M CsF(aq), 278 mg of CsCl, 93.5 mg of UO_3 (99.8%), 2.9 mg of Al (99.99%), and 239 mg of GeO_2 (99.99%) in the molar ratio Cs:U:Al:Ge = 14.6:1:0.333:7 in a 5.8-cm-long gold ampule with an inner diameter of 0.48 cm, which was contained in an autoclave and counterpressured with water at a fill level of 55%. The autoclave was heated at 585 °C for 4 days, cooled to 350 at 2 °C/h, and quenched to room temperature by removing it from the furnace. The pressure at 585 °C was estimated to be 160 MPa according to the $P-T$ diagram of pure water. The product contained light-brown polyhedral crystals as a major phase, some colorless crystals, and a white powder. The light-brown crystals were manually separated from the others and gave a pure phase, as indicated by powder X-ray diffraction (PXRD; Figure S1 in the Supporting Information, SI). The yield was 45% based on uranium. Energy-dispersive X-ray analysis of several light-brown crystals did not show any Al and F and confirmed the presence of Cs, U, and Ge. A suitable crystal was selected for single-crystal X-ray diffraction.[16] In the synthesis of **1**, Al metal was added as a reducing agent; upon synthesis under similar conditions without Al, two hexavalent uranium germanates, which are isostructural with USH-4Rb and USH-5A, were obtained.[3a]

The IR spectrum confirmed the presence of H_2O molecules and uranyl groups (Figure S2 in the SI). Thermogravimetric analysis (TGA) of **1** showed that the observed weight loss at 300 °C is 1.55%, which is close to the calculated value of 1.66% for three H_2O molecules per formula unit (Figure S3 in the SI).[3c,11] The thermal stability of **1** has been investigated by heating a sample in flowing N_2 for 30 min at certain temperatures, then cooling to room temperature, and measuring the PXRD patterns. The patterns (Figure S4 in the SI), together with X-ray data analysis of the dehydrated phase $Cs_8U(UO_2)_3(Ge_3O_9)_3$, which was collected at room temperature after heating a single crystal of **1** at 350 and 600 °C under N_2 (Tables S1−S3 in the SI), indicate that the framework structure is retained up to 800 °C and transforms to an unknown material at ~900 °C. To determine whether water can be adsorbed reversibly, a dehydrated crystal was immersed in water for 1 day and its X-ray diffraction data were measured. Crystal structure analysis did not reveal any H_2O molecules in the structural channels.

The valence states of uranium in **1** were analyzed by X-ray photoelectron spectroscopy (XPS). The U 4f XPS spectrum is shown in Figure 1, which is fitted with two components of U^{4+} and U^{6+}. The fitting parameters of XPS data analysis are given in Table S4 in the SI. The binding energies (BEs) of all of the peaks were referenced to the adventitious C 1s at 284.1 eV. The BEs of U^{4+} were at 379.44 eV (U $4f_{7/2}$) and 390.40 eV (U $4f_{5/2}$), which are comparable with those of U^{4+} in $U(C_2O_4)_2\cdot 6H_2O$, as the

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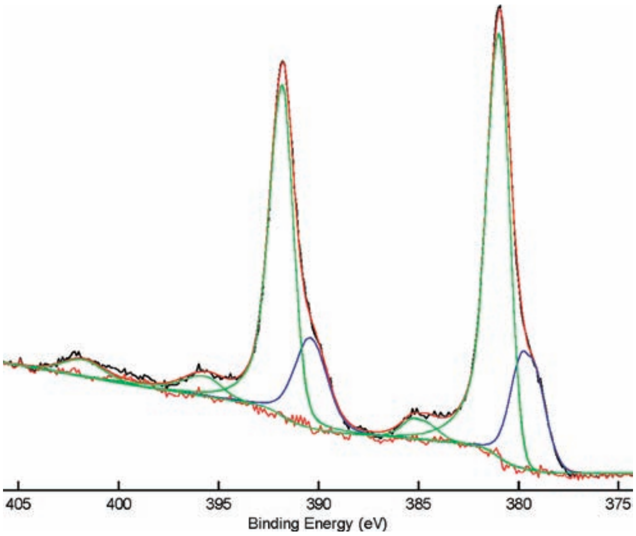

Figure 1. U 4f XPS spectrum of **1**. The spectrum is modeled with two components (black —, data; red —, fit envelope; blue —, U^{IV}; green —, U^{VI}; red · · ·, deviation).

U^{4+} reference material (Figure S6 and Table S5 in the SI) or the U^{4+} in $Na_7U^{IV}O_2(U^{V}O)_2(U^{V/VI}O_2)_2Si_4O_{16}$[10] and in UO_2.[17] The BEs of U^{6+} were at 380.96 eV (U $4f_{7/2}$), the shake-up satellite peak at 384.90 eV, and 391.80 eV (U $4f_{5/2}$), accompanied with the satellite peaks at 395.69 and 401.76 eV. These values are also comparable with those of U^{6+} compounds.[18] The XPS spectrum of **1** indicates the presence of two different oxidation states of uranium with the primary peak area ratio of 2.88:1 for U^{VI}/U^{IV} $4f_{7/2}$ and that of 3.04:1 for U^{VI}/U^{IV} $4f_{5/2}$. These values are consistent with the U^{VI}/U^{IV} ratio of 3:1 according to the results from crystal structure analysis.

The structure of **1** is constructed by the following structural elements: two Cs cations, one on a 3-fold axis and the other in a general position; one $U(1)O_6$ octahedron on a 3-fold inversion axis; one $U(2)O_6$ tetragonal bipyramid at an inversion center; three GeO_4 tetrahedra on a mirror plane. Every GeO_4 tetrahedron shares two corners with two other tetrahedra to form a three-membered single-ring $Ge_3O_9{}^{6-}$ anion, with the Ge−O−Ge bond angles at the bridging O atoms of O(1), O(3), and O(5) being 132.2, 130.0, and 130.3°, respectively. Each GeO_4 has two longer and two shorter bonds corresponding to Ge−O−Ge and Ge−O−U linkages, respectively.

The $U(1)O_6$ octahedron is regular with a U−O distance of 2.206 Å (6×), close to the predicted U^{4+}−O bond length of 2.25 Å according to the effective ionic radius for a six-coordinate U^{4+} ion.[19] The bond-valence sum at the U(1) site, calculated with the parameters R_{ij} = 2.075 Å and b = 0.37 Å, is 4.21 valence units, consistent with the presence of a U^{4+} ion in this site.[20a] U(2) is bonded to six O atoms in the geometry of a tetragonal bipyramid with two shorter U−O bonds of 1.812 Å (2×) in the uranyl unit, $UO_2{}^{2+}$, and four longer U−O bonds in the equatorial plane with bond lengths of 2.237 Å (2×) and 2.231 Å (2×). This coordination geometry is typical for uranium(VI) compounds. The bond-valence sum at the U(2) site, calculated with the parameters R_{ij} = 2.051 Å and b = 0.519 Å is 5.98 valence units.[20b] The four equatorial O atoms are shared with four different GeO_4 tetrahedra, and two apical uranyl O atoms are unshared.

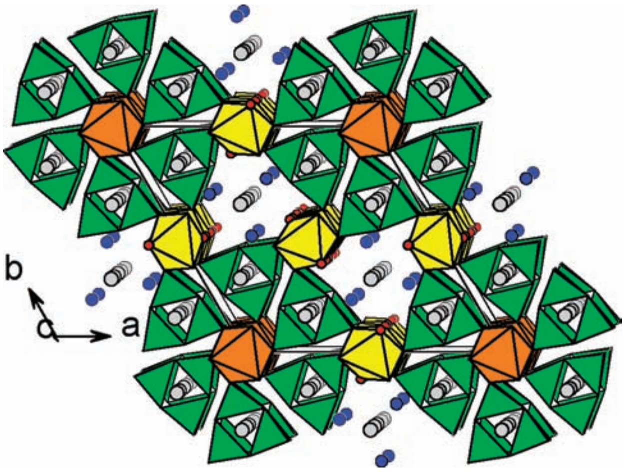

Figure 2. Structure of **1** viewed along the [001] direction. The orange, yellow, and green polyhedra are $U(1)O_6$ octahedra, $U(2)O_6$ tetragonal bipyramids, and GeO_4 tetrahedra, respectively. Color code: gray circles, Cs atoms; blue circles, water oxygen atoms. H atoms are omitted for clarity.

The structure contains two types of infinite columns parallel to the *c* axis formed of discrete $U(1)O_6$ and $U(2)O_6$ units, respectively, which are packed in a closest-packing arrangement (Figure 2). Along the *a* or *b* axis, layers of $U(2)O_6$ alternate with layers of mixed $U(1)O_6$ and $U(2)O_6$. Each $U(1)O_6$ in a column is connected to six $U(2)O_6$ units in neighboring columns by six different $Ge_3O_9{}^{6-}$ anions, and each $U(2)O_6$ is connected with two $U(1)O_6$ and four $U(2)O_6$ units by four different $Ge_3O_9{}^{6-}$ anions, such that a three-dimensional framework is formed. One type of 9-ring channel, which is formed by the edges of three $U(2)O_6$ units and six GeO_4 tetrahedra, is observed along the *c* axis. The shortest O···O distance across the 9-ring window is 5.95 Å. Cs(1) and three H_2O molecules are located in the channels and Cs(2) at the site between two $Ge_3O_9{}^{6-}$ anions. Among the known microporous framework structures of metal silicates and germanates, channels bound by odd-membered rings are rare, with the exception of more frequent 5-rings. Several zeotype materials and metal silicates have been known to possess 9-ring channels. One uranium silicate, $K_5(UO_2)_2[Si_4O_{12}(OH)]$, contains 9-ring channels, which are formed of two UO_6 tetragonal bipyramids and seven SiO_4 tetrahedra.[3b] The 9-ring channels in $Na_3TbSi_3O_9 \cdot 3H_2O$ consist of four TbO_6 octahedra and five SiO_4 tetrahedra.[21] Compound **1** is the first microporous uranium germanate containing 9-ring channels.

In summary, we have successfully synthesized a mixed-valence uranium(IV,VI) germanate under high-temperature, high-pressure hydrothermal conditions. Previously, a mixed-valence uranium(IV,V) silicate and two uranium(V,VI) germanates with infinite chains of corner-sharing UO_6 polyhedra have been reported.[8,9] In contrast, the structure of **1** is composed of discrete $U^{IV}O_6$ octahedra connected with $U^{VI}O_6$ tetragonal bipyramids via $Ge_3O_9{}^{6-}$ anions. After the synthesis of **1**, all mixed-valence uranium silicates or germanates with the oxidation states of uranium from 4 to 6 have been observed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic data in CIF format, PXRD patterns, a TGA curve, a IR spectrum, the XPS fitting parameters, and crystal data of a dehydrated phase of $Cs_8U(UO_2)_3(Ge_3O_9)_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Crystal data for **1**: A light-brown crystal with dimensions 0.12 × 0.1 × 0.1 mm^3, hexagonal, $P6_3/m$ (No. 176), a = 14.8850(7) Å, c = 11.0320(6) Å, V = 2116.81(18) Å^3, Z = 2, ρ_{calcd} = 5.100 g/cm^3; μ(Mo Kα) = 28.404 mm^{-1}. A total of 9906 reflections were measured on a CCD diffractometer at 296 K, which gave 1860 independent reflections with R(int) = 0.0328. An empirical absorption corrections based on symmetry equivalents were made ($T_{\min}/T_{\max}$ = 0.533/0.746). Final cycles of refinement converged at R1 = 0.0249, wR2 = 0.0801, and GOF = 1.108.

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