

Mixed-Valence Uranium(V,VI) and Uranyl Oxyhydroxides Synthesized under High-Temperature, High-Pressure Hydrothermal Conditions: $\text{Na}_5[\text{U}_5\text{O}_{16}(\text{OH})_2]$ and $\text{Na}_5[\text{U}_5\text{O}_{17}(\text{OH})]$

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Supporting Information

ABSTRACT: An unusual mixed-valence uranium(V,VI) oxyhydroxide, $\text{Na}_5[\text{U}_5\text{O}_{16}(\text{OH})_2]$, was synthesized via reduction of UO_2^{2+} with zinc under hydrothermal conditions at 570 °C and 150 MPa. Its structure consists of extended sheets of edge-sharing U^{VI} pentagonal bipyramids and U^{V} square bipyramids. The overall anion topology is the same as that of the uranyl mineral sayrite, but the squares are populated by $\text{U}^{\text{V}}(\text{OH})_2^{3+}$ ions. The valence state of uranium was confirmed by X-ray photoelectron spectroscopy. A hydrothermal reaction without zinc under the same reaction conditions yielded a uranyl oxyhydroxide, $\text{Na}_5[\text{U}_5\text{O}_{17}(\text{OH})]$, with a new sheet structure. The sheet anion topology, which is closely related to that of the mixed-valence compound, contains chains of edge-sharing pentagons as well as dimers of corner-sharing squares.

A large number of uranyl oxyhydroxide minerals with the general formula $\text{M}_x[(\text{UO}_2)_x\text{O}_y(\text{OH})_z](\text{H}_2\text{O})_m$ (M = divalent or monovalent cations) are known.^{1,2} They are typically the first minerals to form during the oxidation and corrosion of uraninite-bearing ore deposits. Continued alteration often results in other minerals such as uranyl silicates and phosphates. The specific uranyl compounds that precipitate are influenced by the cations and anions available in the aqueous solution. Uranyl oxyhydroxides have received much attention because they form in laboratory experiments on UO_2 in spent nuclear fuel if the conditions are oxidizing and the fuel is in contact with water.

The structures of most uranyl oxyhydroxides are based on sheets of uranyl bipyramids that are connected by sharing of their equatorial edges and corners. The uranyl ions are oriented roughly perpendicular to the sheet. Adjacent sheets are linked through interlayer cations and through hydrogen bonding. Burns et al. developed a method of deriving the anion topology of each sheet for classification and comparison of these sheet structures.^{2a,3} An understanding of the chemical and structural features of these compounds is important to studies of the alteration of UO_2 in spent nuclear fuel.

Although uranium reportedly has all valence states from 3+ to 6+, only the 4+ and 6+ states are important in minerals. The synthesis of U^{V} compounds is challenging because of the tendency of this species to either oxidize to U^{VI} or disproportionate to U^{IV} and U^{VI} . There are only two pentavalent uranium-

containing minerals: wyartite, $\text{Ca}[\text{U}^{\text{V}}(\text{U}^{\text{VI}}\text{O}_2)_2(\text{CO}_3)\text{O}_4(\text{OH})]\cdot\text{H}_2\text{O}$, and dehydrated wyartite.⁴ Recently, we have synthesized a good number of uranium(VI), -(V), and -(IV) silicates and germanates 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 During our continued exploratory synthesis of uranium compounds with novel structures and unusual valence states, we have synthesized a mixed-valence uranium(V,VI) oxyhydroxide and a uranyl oxyhydroxide. In this work, we report the synthesis, crystal structures, and X-ray photoelectron spectroscopy (XPS) of $\text{Na}_5[\text{U}_5\text{O}_{16}(\text{OH})_2]$ (**1**) and $\text{Na}_5[\text{U}_5\text{O}_{17}(\text{OH})]$ (**2**).

High-temperature, high-pressure hydrothermal synthesis was performed in gold ampules contained in an autoclave where the pressure was provided by water. Typically, a reaction mixture of 362 μL of 10 M NaOH(aq), 128.7 mg of Na_2MoO_4 , 45.8 mg of UO_3 , and 2.6 mg of zinc (molar ratio Na:U:Zn:Mo = 31:1:0.25:4) in a 5.8-cm-long gold ampule (inside diameter = 0.48 cm) was placed in an autoclave and counterpressured with water at a fill level of 55%. Zinc metal was included in the reaction mixture as a reducing agent. The autoclave was heated at 570 °C for 2 days, cooled to 350 °C at 5 °C·h⁻¹, and then quenched to room temperature by removing it from the furnace. The pressure at 570 °C was estimated to be 150 MPa according to the P - T diagram of pure water. Molybdate was added as a mineralizer. The product was filtered off, washed with water, rinsed with ethanol, and dried at ambient temperature. The reaction produced dark-green foliated crystals of **1** as the major phase together with some black block crystals of NaUO_3 . A qualitative energy-dispersive X-ray analysis of several dark-green crystals confirmed the presence of sodium and uranium and did not show any zinc and molybdenum. A suitable crystal was selected for single-crystal X-ray diffraction, from which the chemical formula was determined.⁷ The yield of **1** was about 50% based on uranium. A powder X-ray diffraction (PXRD) pattern of the dark-green crystalline product is shown in Figure S1 in the Supporting Information (SI). A hydrothermal reaction without zinc metal under the same reaction conditions produced orange foliated crystals of compound **2** in a yield of 66%. The orange color is typical for hexavalent uranium compounds. The product was pure, as indicated by PXRD (Figure S2 in the SI). Most

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crystals of **2** in the reaction product were twinned. Many were selected and checked for reflection profiles before a satisfactory one was obtained.⁷

The U 4f XPS spectrum of **1** is fitted with two components of U^{5+} and U^{6+} . The spectrum and fitting parameters are given in Figure S3 and Table S1 in the SI. Argon-ion sputtering was not applied. The binding energies (BEs) of all peaks were referenced to the adventitious C 1s at 285 eV. The BEs of U^{5+} were at 380.2 eV (U 4f_{7/2}) and 391.4 eV (U 4f_{5/2}), which are comparable to 380.2 and 391.1 eV of U^{5+} in Cs₃UGe₇O₁₈.^{5c} The BEs of U^{6+} were at 381.1 eV (U 4f_{7/2}) and 392.0 eV (U 4f_{5/2}), which are also comparable with those of U^{6+} compounds. For uranium, both U 4f core-level peaks show shakeup satellites at higher BEs with 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 of the satellites from the main peaks for **1** were 8.3 and 8.2 eV for the U^{5+} component and 4.4, 4.3, 10.0, and 10.0 eV for the U^{6+} component. The spectrum indicates the presence of U^{5+} and U^{6+} with a main peak area ratio of 4.00 for U^{6+}/U^{5+} 4f_{7/2} and 4.02 for U^{6+}/U^{5+} 4f_{5/2}. These values are consistent with the results from structure analysis.

The overall structure of **1** is layered with sheets of uranium oxyhydroxide, separated by Na⁺ cations. The structure is formed from the following units: five Na atoms, two UO₇ pentagonal bipyramids, and one UO₄(OH)₂ tetragonal bipyramid. Na(5), U(1), U(2), and all O atoms are in general positions. Na(5) is disordered over two sites, each with an occupancy factor of 0.5. All of the other Na atoms sit on 2-fold axes. U(3) is at an inversion center. U(1) and U(2) are seven-coordinate in a pentagonal-bipyramidal geometry with two shorter axial U–O distances [U(1)–O = 1.834 and 1.825 Å and ∠O–U(1)–O = 179.4°; U(2)–O = 1.846 and 1.854 Å and ∠O–U(2)–O = 179.5°] and five longer equatorial U–O bonds [U(1)–O = 2.205–2.507 Å; U(2)–O = 2.191–2.673 Å]. A pentagonal arrangement of equatorial anions is the most common mode of accommodation of U^{6+} in solids.³ In contrast to U^{6+} –O polyhedra, which contain two strongly bonded uranyl O atoms, the U(3)O₄(OH)₂ octahedron is considerably more regular with $d[U(3)–O] = 2.070–2.204$ Å, close to the predicted U^{5+} –O bond length of 2.14 Å.⁹ The mean U(3)–O bond length of 2.139 Å is comparable to those of 2.131, 2.148, and 2.130 Å for the U^{5+} –O octahedra in K₂UOSi₂O₆ and Cs₃UGe₇O₁₈.^{5b,c} The bond-valence sum 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.,¹⁰ were 6.10, 6.05, and 5.10 vu (valence unit), respectively, thus indicating the presence of U^{6+} , U^{6+} , and U^{5+} ions at these sites. To balance the charge, it needs two protons per formula unit. The bond-valence sum incident upon the O(9) site, which is bonded to U^{5+} in the axial positions, is 1.25 vu, a value expected for (OH)[–]. The bond-valence sums for all of the other O atoms are in the range 1.82–2.25 vu.

A projection of the structure of **1** along the *c* axis (Figure 1) shows U–O polyhedra connected to form sheets parallel to (100), with the Na⁺ being located between the sheets. The O=U=O and HO–U–OH groups are oriented approximately perpendicular to the sheet. As shown in Figure 2, each sheet results from the sharing of equatorial edges between UO₇ and UO₄(OH)₂ polyhedra. The U(2)O₇ polyhedra share edges to form PaCl₅-type chains with the composition UO_{2/1}O_{4/2}O_{1/1} (i.e., UO₃).¹¹ U(1)O₇ polyhedra share an edge to form dimers that are linked together by the sharing of edges with UO₄(OH)₂ polyhedra, forming chains parallel to the *c* axis that are two UO₇

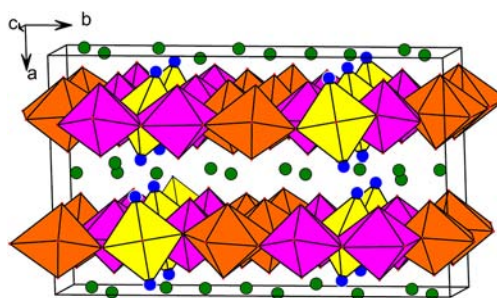


Figure 1. Structure of **1** viewed along the *c* axis. The purple, orange, and yellow polyhedra are U(1)^{VI}O₇, U(2)^{VI}O₇ pentagonal bipyramids, and U^VO₄(OH)₂ octahedra, respectively. Green and blue circles are Na atoms and OH groups, respectively.

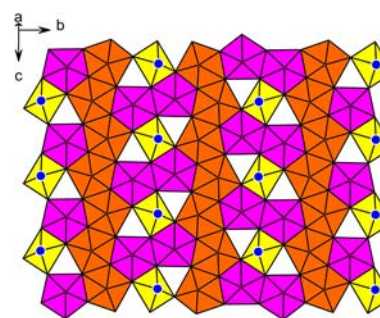


Figure 2. Section of a sheet in **1**. Blue circles are OH groups.

polyhedra wide; these chains are connected to PaCl₅-type chains by the sharing of edges between U(1)O₇ and U(2)O₇ polyhedra. The resulting sheets have an anion topology composed of triangles, squares, and pentagons. Every pentagon and square of the anion topology are populated by UO₂²⁺ and U(OH)₂³⁺ units, respectively. The anion topology of **1** also occurs in the structure of the uranyl mineral sayrite, Pb[(UO₂)₅O₆(OH)₂]₂·4H₂O,¹² as well as the synthetic phase K₂[(UO₂)₅O₈](UO₂)₂,^{3,13} where the interlayer contains uranyl ions. This complex anion topology contains both up (**U**) and down (**D**) arrowhead chains and **P** and **R** chains, oriented vertically in Figure 2, giving the repeat sequence **RUPURDPDRUPU**... In the structure of **1**, adjacent sheets are linked through bonds from the O atoms to the Na⁺ cations, which are located halfway between the sheets. The coordination number for Na(5) is 5, and that for the other Na atoms is 8. Hydrogen bonding also exists between the O(9)H groups from adjacent sheets, as indicated from the short O(9)⋯O(9) distance of 2.65 Å.

Compound **2** also adopts a sheet structure with the Na⁺ cations between adjacent sheets. The structure consists of the following units: five Na atoms, three UO₇ pentagonal bipyramids, and two UO₆ tetragonal bipyramids. Each U atom is strongly bonded to two O atoms, forming an O=U=O unit. Bond-valence-sum calculation indicates that all of the U atoms are hexavalent. The O atom O(5), which bridges U(1)O₇ and U(2)O₇, is also bonded to a H atom, such that one of the uranyl ions in the **P** chains in the structure of **1** is bonded to four equatorial O atoms to form a UO₆ tetragonal bipyramid (Figure 3). The bond-valence sums for all of the other O atoms are close to 2. Each sheet contains wavy chains of edge-sharing pentagons, which are connected by dimers of corner-sharing squares. To our knowledge, this sheet anion topology is only known from **2**.

Recently, Cahill and co-workers reported the synthesis of a dark-red mixed-valent uranium(V)/uranium(VI) oxide,

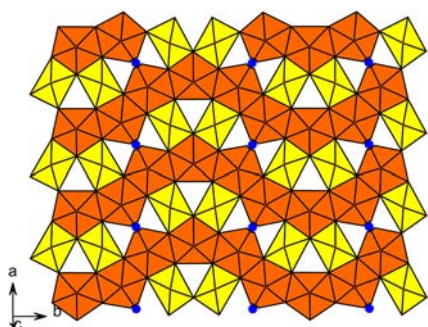


Figure 3. Section of a sheet in **2**. The orange and yellow polyhedra are $U^{VI}O_7$ pentagonal bipyramids and $U^{VI}O_6$ square bipyramids, respectively. Blue circles are OH groups.

$[U^V(H_2O)_2(U^{VI}O_2)_2O_4(OH)] \cdot 4H_2O$, under mild hydrothermal conditions in the water/acetonitrile solvent system.¹⁴ Its structure consists of sheets of edge- and corner-shared U^{VI} pentagonal bipyramids that are further connected by edge-sharing to U^V square bipyramids. The sheet anion topology is similar to the mineral ianthinite, $[U^{IV}_2(U^{VI}O_2)_4O_6(OH)_4(H_2O)_4] \cdot SH_2O$, which consists of U^{IV} and U^{VI} .¹⁵ Ianthinite is unstable in air at ambient conditions and oxidizes to the uranyl mineral schoepite or metaschoepite.¹⁶ The color of partly oxidized ianthinite varies from reddish-purple to amber-brown or green. Accordingly, $[U^V(H_2O)_2(U^{VI}O_2)_2O_4(OH)] \cdot 4H_2O$ may form because of incomplete oxidation of ianthinite. The synthesis of **1** also has implications for uranium chemistry. Its sheet anion topology is the same as that of the uranyl mineral sayrite, but the squares are populated by $U^V(OH)_2^{3+}$ ions. This mixed-valence compound is a possible intermediate phase of alteration products of uraninite. Compound **2** might form initially under hydrothermal conditions and, in the presence of reducing agent **2**, is reduced to **1** with concomitant loss of the proton from the bridging OH group and protonation of two uranyl O atoms to form the $U^V(OH)_2^{3+}$ unit.

Under oxidizing conditions, UO_2 dissolves in an aqueous solution by oxidation to uranyl ions. In an alkali/alkaline-earth-rich environment, uranyl oxyhydroxides can form.¹⁷ We have reported a mixed-valence uranium(V,VI) oxyhydroxide synthesized through the partial reduction of UO_2^{2+} cation by zinc metal in concentrated $NaOH(aq)$. Its sheet structure has the same anion topology as that of sayrite and the valence state of uranium was confirmed by XPS. A uranyl oxyhydroxide with a new anion topology was also synthesized, and its sheet structure is closely related to that of the mixed-valence compound. This work also shows that the high-temperature, high-pressure hydrothermal method provides a route to the synthesis of uranium oxyhydroxides and stabilization of pentavalent uranium without the need for the incorporation of carbonate and silicate ligands. Further research on this theme is in progress.

■ ASSOCIATED CONTENT

📄 Supporting Information

X-ray crystallographic data in CIF format, PXRD patterns, and the U 4f 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.

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- (7) Crystal data of **1**: A total of 14727 reflections of a dark-green foliated crystal with dimensions of $0.01 \times 0.10 \times 0.22$ mm³, monoclinic, $C2/c$ (No. 15), $a = 12.2675(4)$ Å, $b = 19.7275(6)$ Å, $c = 6.8643(6)$ Å, $\beta = 101.414(1)^\circ$, $V = 1628.36(16)$ Å³, $Z = 4$, $\rho_{\text{calc}} = 6.507$ g·cm⁻³, and $\mu(\text{Mo K}\alpha) = 49.78$ mm⁻¹, were measured on a Kappa Apex II diffractometer at 296 K, which gave 1723 independent reflections [$I_o > 2\sigma(I_o)$] with $R(\text{int}) = 0.0375$. An empirical absorption correction based on the symmetry equivalent was applied with $T_{\text{min}}/T_{\text{max}} = 0.384/0.746$. The final cycles of refinement converged at $R1 = 0.0327$, $wR2 = 0.0985$, and $\text{GOF} = 1.186$ with 136 parameters, $\rho_{\text{max/min}} = +3.13/-3.95$ e·Å⁻³. The H atoms could not be located from the difference Fourier maps. Crystal data of **2**: 4068 reflections, an orange foliated crystal with dimensions $0.01 \times 0.07 \times 0.11$ mm³, monoclinic, $P2_1/c$ (No. 14), $a = 6.9369(4)$ Å, $b = 19.844(1)$ Å, $c = 12.7132(9)$ Å, $\beta = 111.116(4)^\circ$, $V = 1632.54(18)$ Å³, $Z = 4$, $\rho_{\text{calc}} = 6.486$ g·cm⁻³, $\mu(\text{Mo K}\alpha) = 49.66$ mm⁻¹, 296 K, 2263 independent reflections [$I_o > 2\sigma(I_o)$] with $R(\text{int}) = 0.103$, $T_{\text{min}}/T_{\text{max}} = 0.310/0.746$, $R1 = 0.0617$, $wR2 = 0.1526$, and $\text{GOF} = 1.043$ with 164 parameters, $\rho_{\text{max/min}} = +5.40/-3.51$ e·Å⁻³. The H atom could not be located.
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