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Hydrothermal Synthesis

$A_3(U_2O_4)(Ge_2O_7)$ (A = Rb, Cs): Mixed-Valence Uranium(V,VI) Germanates**

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The crystal chemistry of uranium compounds and minerals has been extensively studied, not only because of their role as alteration products of uraninite (UO_{2+x}), the main ore mineral for uranium, under oxidizing conditions, but also because of their importance as corrosion products of the alteration of UO_2 in spent nuclear fuel.[1] Uranyl silicates are the most abundant group of uranium(VI) minerals, and one uranium(IV) silicate exists, namely coffinite ($USiO_4$), which is the most important ore mineral for uranium after uraninite. Recently, numerous synthetic uranyl silicates containing organic amines or alkali metals as countercations have been reported.[2,3] They were synthesized under either mild hydrothermal conditions at 180–245 °C or under high-temperature, high-pressure hydrothermal conditions at 550–600 °C.

We previously reported two uranium(V) silicates, $K(UO)Si_2O_6$[4] and $K_3(U_3O_6)(Si_2O_7)$,[5] and a uranium(V) germanate, $Rb_3(U_3O_6)(Ge_2O_7)$,[5] which are isostructural to the Nb^{5+} or Ta^{5+} analogues. The U^{5+} valence state is unstable in aqueous solution and exists as UO_2^+ in a narrow stability field. The isolation of stable UO_2^+ species is extremely challenging. Apart from its fundamental interest, this elusive species has important environment implications.[6]

Although a large number of uranyl silicates, two uranium(V) silicates, and one uranium(IV) silicate are known, no mixed-valence uranium silicates are known. For the germanate counterparts, only one uranium(V) and two uranium(VI) compounds have been structurally characterized.[5,7] Herein, we report the first mixed-valence uranium(V,VI) germanates, $Rb_3(U_2O_4)(Ge_2O_7)$ (**1**) and $Cs_3(U_2O_4)(Ge_2O_7)$ (**2**), which were synthesized by a high-temperature, high-pressure hydrothermal method.

The IR spectrum of **1** shows medium bands at 855, 820, and 788 cm^{-1}, which are assigned to the stretches of UO_6 groups (see Figure S1 in the Supporting Information). The strong, broad bands at 772 and 731 cm^{-1} are assigned to the asymmetric stretching vibrations of Ge–O bonds. The strong, broad band at 548 cm^{-1} and the medium band at 428 cm^{-1} are attributed to the symmetric stretching and bending vibrations of germanate groups. The IR spectrum of **2** shows bands at 851, 826, 789, 743, 722, 567, 533, and 413 cm^{-1} (Figure S1). The bands at 851, 826, and 789 cm^{-1} are assigned to the stretching modes of UO_6 groups, and the other bands are assigned to germanate groups.

Magnetic data were measured on a 40.6-mg powder sample of **1** between 5 and 300 K in a magnetic field of 0.2 T. The $\chi_M T$ value decreases rapidly with decreasing temperature in the range of 20 to 300 K, indicating that the main magnetic interactions between U^{5+} ions are antiferromagnetic (Figure S2). The effective magnetic moment μ_{eff} at 300 K is 1.59 μ_B per formula unit, which is consistent with observations that the values of μ_{eff} for uranium(V) compounds around room temperature are between 1.26 and 1.86 μ_B.[8] The reason for the ferromagnetic rise in $\chi_M T$ at 11 K is unclear to us. There may have been an impurity phase or phases present in the sample that impacted the measurements, although powder X-ray diffraction did not show any impurities. Measurements of magnetization versus applied field and of heat capacity versus temperature did not reveal a phase transition at 11 K.

Compounds **1** and **2** are isostructural. To our knowledge, no other uranium-bearing phases adopt an analogous structure. The structure is constructed from the following distinct structural elements: three UO_6 polyhedra, two GeO_4 tetrahedra, and three Rb^+ (in **1**) or Cs^+ (in **2**) ions (Figures 1 and 2). All the atoms are in general positions, except the U(1) and U(2) atoms, which are at inversion centers.

Both GeO_4 tetrahedra are slightly distorted, as indicated by the Ge–O bond lengths (1.724–1.776 Å, average 1.749 Å for **1**; 1.732–1.782 Å, average 1.751 Å for **2**) and O-Ge-O bond angles (106.6–112.7° for **1**; 106.1–113.6° for **2**). Every GeO_4 tetrahedron shares a corner with another GeO_4 tetrahedron to form a Ge_2O_7 dimer, with the bond angle at

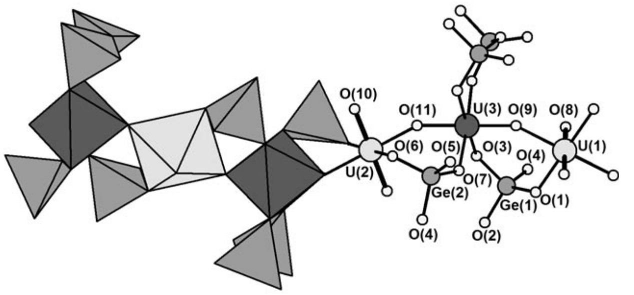

Figure 1. Section of the structure of **1** showing a 1D chain of corner-sharing $U(3)^{5+}O_6$ octahedra (dark gray) and $U r\phi_4$ ($U(1)^{6+}O_6$ and $U(2)^{6+}O_6$) tetragonal bipyramids (light gray). The UO_6 polyhedra also share corners with GeO_4 tetrahedra (medium gray).

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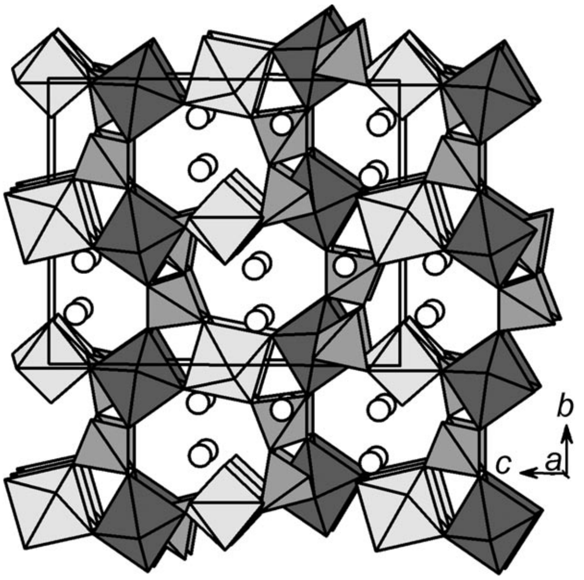

Figure 2. Structure of **1** viewed along the *a* axis. $U(3)^{5+}O_6$ octahedra are dark gray, $Ur\phi_4$ ($U(1)^{6+}O_6$ and $U(2)^{6+}O_6$) tetragonal bipyramids are light gray, GeO_4 tetrahedra are medium gray, and Rb^+ ions are open circles.

the bridging oxygen atom being 128.4(2)° for **1** and 129.7(2)° for **2**.

In the $U(1)O_6$ and $U(2)O_6$ tetragonal bipyramids (designated as $Ur\phi_4$), the U(1) and U(2) atoms have unsymmetrical oxygen coordination environments: two U=O bonds are short (1.830 and 1.840 Å for **1**; 1.836 and 1.818 Å for **2**), forming a linear uranyl (Ur) unit, which is typical for uranium(VI) compounds; and four U−O bonds in the plane normal to the O=U=O axis are longer (2.208–2.263 Å for **1**; 2.231–2.266 Å for **2**). The bond-valence sums at the U(1) and U(2) sites, calculated with the coordination-specific bond-valence parameters of Burns et al., are both 6.04 vu (vu = valence unit) for **1**, and are 5.98 and 6.13 vu for **2**, consistent with the occurrence of U^{6+} ions in these sites.[9]

The $U(3)O_6$ polyhedron is considerably more regular with U−O distances between 2.009 and 2.230 Å for **1**, and between 1.991 and 2.243 Å for **2**. The bond-valence sum at the U(3) site, calculated by using the bond-valence parameters $R_{ij} = 2.051$ Å and $b = 0.519$ Å of Burns et al., is 5.02 vu for **1** and 5.01 vu for **2**, in accordance with the occurrence of U^{5+} ions in this site.[9] The U^{5+} ions in uranium(V) oxo compounds and in the mixed-valence uranium(V,VI) mineral wyartite[10] ($CaU^{5+}(U^{6+}O_2)_2(CO_3)O_4(OH)(H_2O)_7$) occur in a coordination environment, either octahedral or pentagonal bipyramidal, that contains a linear or near-linear UO_2^+ ion with U−O bond lengths of approximately 2.10 Å. Therefore, the bond-valence sum and polyhedral geometry of the U(3) atom both indicate a valence of 5+.

The $Ur\phi_4$ tetragonal bipyramids have four equatorial oxygen atoms (ϕ, O_{eq}) that are shared with two GeO_4 tetrahedra and two $U(3)O_6$ octahedra, and two apical uranyl oxygen atoms (O_{Ur}) that are unshared. Every $U(3)O_6$ octahedron shares four oxygen atoms with one Ge_2O_7 group and two GeO_4 tetrahedra belonging to two different Ge_2O_7 groups. The two remaining oxygen atoms of each $U(3)O_6$ octahedron act as common vertices with two $Ur\phi_4$ tetragonal bipyramids to form a 1D chain along the *c* axis (Figure 1). Adjacent chains are linked together through corner-sharing by Ge_2O_7 groups to form a 3D framework that delimits one type of 7-ring channels along the *a* axis (Figure 2). All the rubidium (in **1**) or cesium sites (in **2**) are ordered and fully occupied.

According to Burns, each O_{Ur} atom receives 1.65 vu from the bond to the U^{6+} ion at the center of the $Ur\phi_4$ tetragonal bipyramid, whereas each O_{eq} atom receives 0.64 vu.[1a] The bonding requirements of the equatorial anions are only partially met by the bond to the U^{6+} ion, and it is necessary for them to form additional strong bonds to other cations in the structure. Therefore, it is uncommon for $Ur\phi_4$ tetragonal bipyramids to share vertices to form a 1D chain, because the bond valence of the bridging O_{eq} atom is only 1.28 vu, if steric hindrance prevents sharing of the bridging atom with other cations. The $U(3)^{5+}O_6$ octahedron is considerably more regular and does not contain very short U−O bonds. Thus, the bridging oxygen atom shared by a $U(3)O_6$ octahedron and a $Ur\phi_4$ tetragonal bipyramid receives more bond valence from the U^{5+} ion, favoring the formation of a 1D chain, as observed in the title compounds (Figure 1).

In summary, we have successfully synthesized two uranium(V,VI) germanates under high-temperature, high-pressure hydrothermal conditions. Their 3D framework is uniquely characterized by UO_6 polyhedra that share common corners to give infinite $-U^{6+}-O-U^{5+}-O-U^{6+}-$ chains. There are a few mixed-valence uranium(IV,VI) minerals, such as ianthinite ($[U^{4+}_2(U^{6+}O_2)_4O_6(OH)_4(H_2O)_4]\cdot 5H_2O$),[11] and at least one mixed-valence uranium(V,VI) mineral, wyartite.[10] However, no mixed-valence uranium silicates or germanates had previously been described.

The synthesis of the title compounds requires partial reduction of uranium in solution. Under the high-temperature, high-pressure hydrothermal conditions, gold is soluble in concentrated aqueous solutions of alkali metal hydroxides, and forms a monovalent Au(OH)(aq) complex and H_2 gas,[12] leading to partial reduction of uranium in solution. The U^{5+} valence state is unstable owing to its high tendency to undergo disproportionation to U^{4+} and U^{6+} ions; however, the solution complex $UO_2^+{:}UO_2^{2+}$ disproportionates at a much slower rate than UO_2^+ alone. Thus, the UO_2^+ species in solution is stabilized in the presence of the UO_2^{2+} species, owing to the formation of the $UO_2^+{:}UO_2^{2+}$ complex.[13] The pH value of the reaction mixture is very critical to the outcome of the synthesis. For example, a uranium(VI) compound is obtained if more alkali metal hydroxide is used in the reaction mixture. More examples are required to better understand the conditions of formation of these very interesting silicates and germanates containing U^{5+} ions. Further research on this theme is in progress.

Experimental Section

Compound **1** was synthesized by heating a mixture of RbOH(aq) (50 wt %, 239 μL), UO_3 (82.9 mg), and GeO_2 (121.3 mg; Rb/U/Ge molar ratio 7:1:4) in a gold ampoule (length 4.8 cm, inner diameter 0.48 cm) in an autoclave at 585 °C for 2 days. The autoclave was then cooled to 350 °C at 5 °C h^{-1} and quenched at room temperature by removing the autoclave from the furnace. Dark brown prismatic crystals of **1** were obtained as the major product, along with a yellow material of low crystal quality.

Dark brown prismatic crystals of **2** were synthesized as a major product by heating a mixture of CsOH(aq) (50 wt %, 257 µL), UO_3 (60.4 mg), and GeO_2 (88.3 mg; Cs/U/Ge molar ratio 7:1:4) in a gold ampoule (length 4.35 cm, inner diameter 0.48 cm) under the same reaction conditions. Yellow crystals of a new uranyl germanate, $Cs_6[(UO_2)_3(Ge_2O_7)_2]\cdot 4H_2O$, with a 3D framework structure containing 12-ring channels were synthesized as a minor product of the reaction.[14]

The dark brown crystals of **1** and **2** could be easily manually separated from the yellow crystalline material, giving a pure sample, as indicated by powder X-ray diffraction (Figures S3 and S4). Qualitative EDX analysis of several dark brown crystals confirmed the presence of rubidium, uranium, and germanium in **1**, and of cesium, uranium, and germanium in **2**. Suitable crystals of **1** and **2** were selected for single-crystal X-ray diffraction analysis, from which the chemical formulas were determined to be $Rb_3(U_2O_4)(Ge_2O_7)$ for **1** and $Cs_3(U_2O_4)(Ge_2O_7)$ for **2**.[15]

In the synthesis of the uranium(V) silicates and germanate, KF was added in the reaction mixture as a mineralizer,[4,5] whereas the F^- ion was not present in the synthesis of the title compounds. An attempt to synthesize the silicate analogues of **1** and **2** under the same reaction conditions produced the uranyl silicates $Rb_2(UO_2)(Si_2O_6)$ and $Cs_2(UO_2)(Si_2O_6)$, respectively, as the major products.[3b]

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[14] Crystal data for $Cs_6[(UO_2)_3(Ge_2O_7)_2]\cdot 4H_2O$: monoclinic, $P2_1/n$, $M_r = 2185.92$, $a = 7.6417(4)$, $b = 10.3281(6)$, $c = 18.854(1)$ Å, $\beta = 92.941(2)°$, $V = 1486.1(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 4.885$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 275.99$ cm^{-1}, $R1 = 0.0197$, $wR2 = 0.0410$.

[15] Crystal data for **1**: monoclinic, $P2_1/n$, $M_r = 1053.65$, $a = 6.9755(5)$, $b = 12.2284(8)$, $c = 15.399(1)$ Å, $\beta = 100.560(1)°$, $V = 1291.3(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 5.420$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 408.95$ cm^{-1}, 9379 reflections measured on a CCD diffractometer at 293 K, 3198 independent reflections with $R_{int} = 0.0318$, $R1 = 0.0248$ and $wR2 = 0.0621$ for 2954 reflections with $I > 2\sigma(I)$ and 167 parameters. Crystal data for **2**: monoclinic, $P2_1/n$, $M_r = 1195.97$, $a = 7.1054(3)$, $b = 12.5728(5)$, $c = 15.5611(6)$ Å, $\beta = 101.312(2)°$, $V = 1363.14(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 5.828$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 359.93$ cm^{-1}, 12059 reflections measured on a CCD diffractometer at 293 K, 3416 independent reflections with $R_{int} = 0.0266$, $R1 = 0.0239$ and $wR2 = 0.0524$ for 3278 reflections with $I > 2\sigma(I)$ and 167 parameters. Further details on the crystal structure investigation 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 numbers CSD-419783 (**1**) and CSD-419784 (**2**).