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$Cs_3UGe_7O_{18}$: A Pentavalent Uranium Germanate Containing Four- and Six-Coordinate Germanium

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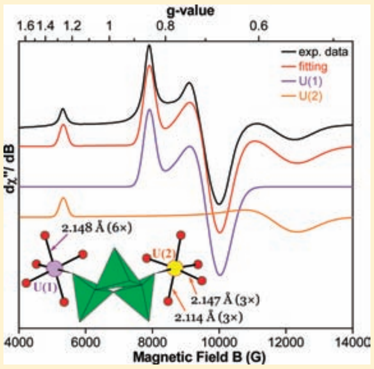
S Supporting Information

ABSTRACT: A pentavalent uranium germanate, $Cs_3UGe_7O_{18}$, was synthesized under high-temperature, high-pressure hydrothermal conditions at 585 °C and 160 MPa and structurally characterized by single-crystal X-ray diffraction and infrared spectroscopy. The valence state of uranium was confirmed by X-ray photoelectron spectroscopy and electron paramagnetic resonance. The room-temperature EPR spectrum can be simulated with two components using an axial model that are consistent with two distinct sites of uranium(V). In the structure of the title compound, each $^{[6]}GeO_6$ octahedron is bonded to six three-membered single-ring $^{[4]}Ge_3O_9{}^{6-}$ units to form germanate triple layers in the *ab* plane. Each layer contains nine-ring windows; however, these windows are blocked by adjacent layers. The triple layers are further connected by UO_6 octahedra to form a three-dimensional framework with intersecting six-ring channels along the $\langle 1\bar{1}0\rangle$ directions. The Cs^+ cation sites are fully occupied, ordered, and located in the cavities of the framework. Pentavalent uranium germanates or silicates are very rare, and only two uranium silicates and one germanate analogue have been published. However, all of them are iso-structural with those of the Nb or Ta analogues. In contrast, the title compound adopts a new structural type and contains both four- and six-coordinate germanium. Crystal data of $Cs_3UGe_7O_{18}$: trigonal, $P\bar{3}c1$ (No. 165), a = 12.5582(4) Å, c = 19.7870(6) Å, V = 2702.50(15) Å^3, Z = 6, D_{calc} = 5.283 g·cm^{-3}, μ(Mo Kα) = 26.528 mm^{-1}, R_1 = 0.0204, wR_2 = 0.0519 for 1958 reflections with $I > 2\sigma(I)$. GooF = 1.040, $\rho_{max,min}$ = 1.018, and −1.823 e·Å^{-3}.



INTRODUCTION

The structural chemistry of uranium compounds has been the focus of considerable research over several decades for emerging technologies of nuclear fuel processing, determination of speciation of actinoids in the environment, or for searching new radioactive waste forms.[1a] In its compounds, uranium may exhibit different oxidation states, namely +3, +4, +5, and +6, although +6 is the predominant one.[1b] Uranyl silicates have been found as minerals in the altered zones of many uranium deposits, and some synthetic examples have also been reported.[2,3] The U^{3+} ion is a powerful reducing agent, and no uranium(III) silicate or germanate has been reported. Uranium(IV) silicates and germanates exist. For instance, 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, $Cs_2USi_6O_{15}$,[5] and two synthetic uranium(IV) germanates, $UGeO_4$ and $Cs_4UGe_8O_{20}$,[6,7] were reported. The chemistry of uranium(V) is considerably less developed owing to the tendency of U^{5+} to either oxidize to U^{6+} or disproportionate to U^{4+} and U^{6+}.[8] The isolation of stable pentavalent uranium compounds is very challenging. Recently, two uranium(V) silicates, $K(UO)Si_2O_6$ and $K_3(U_3O_6)Si_2O_7$,[9] and a germanate analogue, $Rb_3(U_3O_6)Ge_2O_7$,[9b] have been synthesized; however, all of them are iso-structural with the Nb^{5+} or Ta^{5+} analogues. In addition, several interesting mixed-valence uranium silicates and germanates have also been synthesized by us.[10] All mixed-valence uranium silicates and germanates with the oxidation states of uranium from +4 to +6 have been observed. Herein, we report a new pentavalent uranium germanate, $Cs_3UGe_7O_{18}$ (denoted as **1**), which adopts a new structural type and contains four- and six-coordinate germanium.

EXPERIMENTAL SECTION

Synthesis. High-temperature, high-pressure hydrothermal synthesis was performed using a Tem-Pres autoclave where the pressure was provided by water. A reaction mixture of 76.7 μL of 10 M CsF(aq), 67.1 mg of CsI, 43.5 mg of CsCl, 33.0 mg of UO_3, 1.0 mg of Al, and 120.5 mg of GeO_2 (the molar ratio of Cs/U/Al/Ge = 11.1:1:0.333:10) was sealed in a 2.1-cm-long gold ampule (inner diameter = 0.48 cm) and placed inside an autoclave and counter-pressured with water at a fill level of 55%. Aluminum metal was included in the reaction mixture as a reducing agent. The autoclave was heated at 585 °C for 2 days, cooled to 350 at 2 °C/h, and then rapidly cooled to room temperature by removing the autoclave from the furnace. The pressure at 585 °C was estimated to be 160 MPa according to the P−T phase diagram of pure water. The product was filtered, washed with water, rinsed with ethanol, and dried under

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ambient conditions. The reaction produced pale cyan plate crystals of **1** as the major phase together with some colorless prismatic crystals of GeO_2 (rutile form)[11] and some unidentified white powder. A qualitative energy-dispersive X-ray analysis of several pale cyan crystals did not show any aluminum or fluorine and confirmed the presence of cesium, uranium, and germanium. The pale cyan crystals were manually separated from the others, giving a pure sample as indicated by powder X-ray diffraction (Figure S1 in the Supporting Information). The yield of **1** was 71.6% based on UO_3. In this synthesis, although halide ions were not incorporated into the structure, they are necessary for the formation of **1**. Under similar conditions, with one or a mixture of two of the above halides, the synthesis of **1** was unsuccessful.

Single-Crystal X-Ray Diffraction. A suitable pale cyan plate crystal of **1** having dimensions 0.1 × 0.1 × 0.02 mm was selected for indexing and intensity data collection on a Bruker Kappa Apex II CCD diffractometer equipped with a normal focus, 3 kW sealed tube X-ray source. Intensity data were collected at 296 K over 1319 frames with φ and ω scans (width 0.5°/ frame) and an exposure time of 30 s/frame. APEX II software was used for preliminary determination of the unit cell. A determination of integrated intensities and unit cell refinement were performed using SAINT program.[12] The SADABS program was used for absorption correction (T_{min}/T_{max} = 0.4515/0.7457).[13] On the basis of reflection conditions and successful solution and refinement of the structure, the space group was determined to be $P\bar{3}c1$ (No. 165) with lattice constants of a = 12.5582(4) Å and c = 19.7870(6) Å. The structure was solved by direct methods and successive difference Fourier syntheses. Two Cs atom sites were located and refined with full occupancy. The final cycles of least-squares refinement including atomic coordinates and anisotropic thermal parameters for all atoms converged at R_1 = 0.0204 and wR_2 = 0.0519 for 1958 reflections with $I > 2\sigma(I)$, GoF = 1.040, and $\rho_{max,min}$ = 1.018 and −1.823 e·Å^{-3}. All calculations were performed using the *SHELXTL*, version 6.14 software package.[14] The crystallographic data are given in Table 1 and selected bond distances in Table 2.

Table 1. Crystallographic Data for $Cs_3UGe_7O_{18}$

chemical formula	$Cs_3Ge_7O_{18}U$
fw	1432.89
cryst syst	trigonal
space group	$P\bar{3}c1$ (No. 165)
a/Å	12.5582(4)
c/Å	19.7870(6)
V/Å^3	2702.5(2)
Z	6
T, °C	23
λ(Mo Kα), Å	0.71073
D_{calcd}, g·cm^{-3}	5.283
μ(Mo Kα), mm^{-1}	26.528
$R_1{}^a$	0.0204
$wR_2{}^b$	0.0519

$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^bwR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\mathrm{Max}(F_o^2,0) + 2(F_c)^2]/3$, where a = 0.0262 and b = 0.956.

X-Ray Photoelectron Spectroscopy (XPS). The XPS data on the crystals of **1** were recorded on a PHI Quantera SXM spectrometer using monochromatic Al Kα (1486.6 eV) X-ray radiation at room temperature. The anode was operated at 24.2 W with a typical spot size of 100 μm. In order to remove surface contaminants on the crystals, the samples were etched using a 1 KV Ar$^+$ ion beam for 20 s before measurement. The binding energy scale was referenced to adventitious C1s at 285.0 eV. The U 4f data were analyzed with MultiPak software using the iterated Shirley background and the asymmetric peak profile for both primary and satellite peaks.

Electron Paramagnetic Resonance (EPR). The EPR spectrum on a powder sample of **1** was recorded in the X-band at room temperature using a Bruker ELEXSYS E580 spectrometer. The spectral simulations and nonlinear least-squares fitting were performed using MATLAB with the EasySpin toolbox.[15] The Nelder-Mead simplex algorithm was used for numerical optimizations. In the least-squares fitting, two spectral components were required to achieve a good quality of theoretical fit to the experimental spectrum. An axial model was used for g values of both components.

Table 2. Selected Bond Lengths (Å) for $Cs_3UGe_7O_{18}{}^a$

U(1)−O(6)	2.148(3) (6×)	Ge(1)−O(1)	1.888(3) (6×)
U(2)−O(8)	2.147(3) (3×)	Ge(2)−O(2)	1.902(3) (3×)
U(2)−O(9)	2.114(3) (3×)	Ge(2)−O(3)	1.858(3) (3×)
Ge(3)−O(1)	1.720(3)	Ge(3)−O(4)	1.770(3)
Ge(3)−O(5)	1.778(3)	Ge(3)−O(6)	1.758(3)
Ge(4)−O(3)	1.706(3)	Ge(4)−O(5)	1.766(3)
Ge(4)−O(7)	1.769(3)	Ge(4)−O(8)	1.748(3)
Ge(5)−O(2)	1.712(3)	Ge(5)−O(4)	1.771(3)
Ge(5)−O(7)	1.748(3)	Ge(5)−O(9)	1.753(3)

^{a}Note: Cs−O distances are available from the Supporting Information.

RESULTS AND DISCUSSION

Structural Description. The structure of **1** consists of the following distinct structural elements: two UO_6 octahedra, two GeO_6 octahedra, three GeO_4 tetrahedra, and two Cs sites. U(1) is at the 2b special position with a local symmetry of S_6. U(2) and Ge(2) are at the 4d position with C_3 symmetry. Ge(1) is at the 2a position with D_3 symmetry, Cs(1) is at the 6f position with C_2 symmetry. All of the other atoms are in general positions. The U(1)O_6 octahedron is regular with six equal U−O bond lengths of 2.148(3) Å, and the U(2)O_6 octahedron is slightly distorted with U−O bond lengths of 2.114(3) Å (3×) and 2.147(3) Å (3×). These values are close to the predicted U^{5+}−O bond length of 2.11 Å according to the effective ionic radius for a six-coordinate U^{5+} ion.[16] The bond-valence sums at the U(1) and U(2) sites, calculated with the parameters R_{ij} = 2.051 Å and b = 0.519 Å are 4.97 and 5.15 valence units, respectively, which are consistent with the presence of U^{5+} ions in these sites.[17a]

Ge(1) and Ge(2) atoms are each bonded to six O atoms to form GeO_6 octahedra. The Ge(1)O_6 octahedron is regular with six equal Ge(1)−O bond lengths of 1.888(3) Å, whereas the Ge(2)O_6 octahedron is slightly distorted with the bond lengths of 1.858(3) Å (3×) and 1.902(3) Å (3×). The other Ge atoms are four-coordinate in tetrahedral geometry. The Ge−O bond lengths and O−Ge−O bond angles are within normal ranges. The bond-valence sums at Ge sites are in the range of 3.91−4.20 v.u., which are in agreement with the valence state of the Ge atoms.[17b] 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(4), O(5), and O(7) being 130.39(17), 124.55(16), and 127.69(17)°, respectively (Figure 1). Each $^{[6]}GeO_6$ octahedron is bonded to six $Ge_3O_9{}^{6-}$ units such that germanate triple layers in the ab plane are formed (Figure S3). Each of the triple layers contains nine-ring windows, but the windows are blocked by adjacent layers. The triple layers are connected by UO_6 octahedra to form a three-dimensional framework with intersecting six-ring channels along the $\langle 1\bar{1}0\rangle$ directions (Figure S4). The Cs sites are ordered, fully occupied, and located in the intersections of the channels. The structure can also be described in terms of close-packed columns. Each column consists of a core of alternating UO_6 and GeO_6 octahedra along the 3-fold axes (Figure 2).

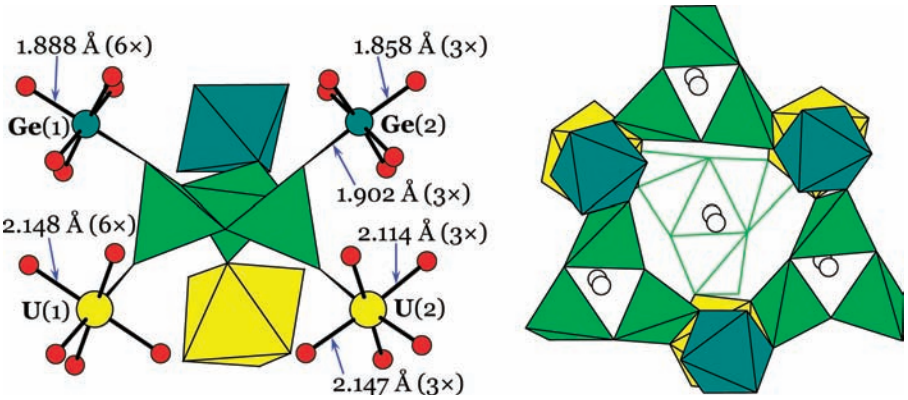

Figure 1. Section of the structure of **1** showing the connectivity between UO_6 and GeO_6 octahedra and a $Ge_3O_9^{6-}$ unit (left) and a polyhedral plot viewed along the *c* axis (right). The yellow, blue-green, red, and open circles are U, Ge, O, and Cs atoms, respectively. The UO_6, GeO_6, and GeO_4 polyhedra are shown in yellow, blue-green, and green, respectively.

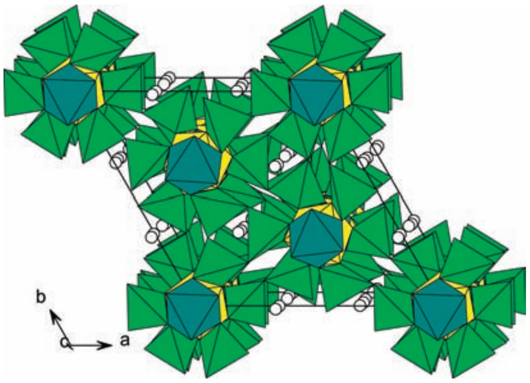

Figure 2. The structure of **1** viewed along the *c* axis.

XPS Analysis. The valence state of uranium in **1** was analyzed by X-ray photoelectron spectroscopy. The U 4f XPS spectrum is shown in Figure 3, which is fitted with one component of U^{5+} together with its satellites. The fitting parameters of the XPS data are given in Table S2. The BEs of the primary peaks were at 380.19 eV (U $4f_{7/2}$) and 391.07 eV (U $4f_{5/2}$), which are comparable to those of U^{5+} in $Ba_2U_2O_7$ or KUO_3.[18] For uranium, both 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+}.[19] The BEs of the satellites in **1** were at 388.16 and 399.11 eV, from which the separations of satellites from the main peaks were 7.97 and 8.04 eV, respectively, which are in typical range for U^{5+}. Therefore, the XPS spectrum confirms the presence of U^{5+} in **1**.

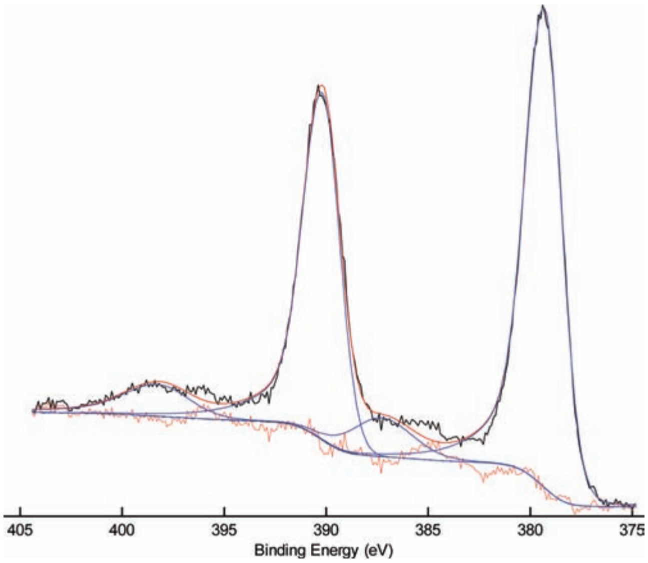

Figure 3. The U 4f spectrum and the fitting curves of **1**. The black, red, and blue curves are the data, fit envelope, and main peaks accompanied with satellites, respectively. The red dotted curve is the deviation.

Sputtering of the samples before XPS measurement is known to reduce the oxidation states of metals.[18] The XPS spectrum of **1** also shows that a little bit of U(V) near the surface of the crystals of **1** is reduced to U(IV) during the sputtering, as indicated by the presence of very weak additional satellites (not modeled) at lower BEs than those of the U(V) satellites.

EPR Analysis. The X-band electron paramagnetic resonance spectrum of **1**, recorded in powder form at room temperature, is shown in Figure 4. The spectrum can be simulated with two components using the axial model that are consistent with two distinct sites of uranium(V) in **1**, as indicated from single-

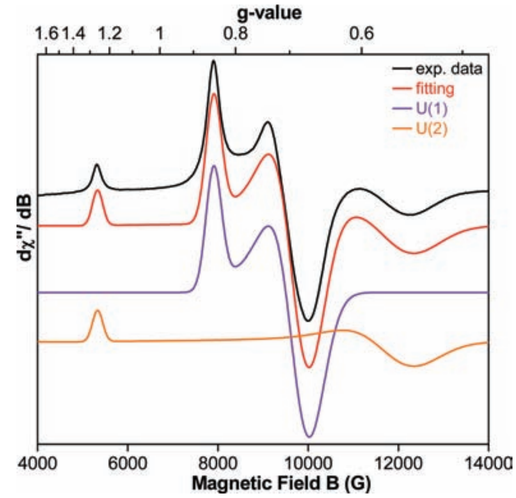

Figure 4. The X-band EPR spectrum of **1** recorded at room temperature. The spectrum is simulated with two components of uranium(V).

crystal X-ray diffraction. The best-fit values for ($g\perp$, $g\|$) are (0.683, 0.846) and (0.560, 1.254) for U(1) and U(2), respectively. These g values are comparable to those of U(V) in several UF_6M (M = Li, Na, Cs, NO) and those in UOF_5^{2-}, UBr_6^-, and $UOBr_5^{2-}$ complexes or in Na_3UF_8.[20] Therefore, EPR measurement results confirmed the presence of two distinct U(V) sites in **1**.

In summary, we have successfully synthesized a pentavalent uranium germanate with a new structural type under high-temperature, high-pressure hydrothermal conditions. The electroneutrality principle, polyhedral geometry, bond-valence sums, and the XPS and EPR measurements confirm that **1** is a pentavalent uranium compound. The structures of previously reported uranium(V) silicates and germanates contain strings of UO_6 octahedra sharing *trans* corners. In contrast, the structure of **1** contains discrete UO_6 octahedra which are coordinated by $Ge_3O_9^{6-}$ anions. Germanium can exhibit different coordination numbers and geometries such as the GeO_4 tetrahedron, GeO_5 trigonal bipyramid, and GeO_6 octahedron. Recently, we reported a uranium(IV) germanate containing four- and five-coordinate germanium.[7] Compound **1** is the first uranium germanate that contains four- and six-coordinate germanium. The high-temperature, high-pressure hydrothermal method has been successfully used in the synthesis of uranium silicates and germanates with an unusual oxidation state and interesting crystal structures. Further research on this interesting class of compounds is in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The X-ray crystallographic data of **1** in CIF format and PXRD patterns, an infrared spectrum, 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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