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$K_3(U_3O_6)(Si_2O_7)$ and $Rb_3(U_3O_6)(Ge_2O_7)$: A Pentavalent-Uranium Silicate and Germanate

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A new uranium(V) silicate, $K_3(U_3O_6)(Si_2O_7)$, and the germanate analogue, $Rb_3(U_3O_6)(Ge_2O_7)$, have been synthesized under high-temperature, high-pressure hydrothermal conditions and characterized by single-crystal X-ray diffraction. Their structures contain uranate columns formed of triple octahedral chains of the α-UF_5 type linked by disilicate (or digermanate) units to form a 3-D framework structure. The valence state of uranium is confirmed by X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, and magnetic susceptibility.

Uranium exhibits oxidation states from +3 to +6, and most uranium compounds can be grouped into reduced species and oxidized ones. The former U occurs primarily as U^{4+}, and the latter U is fully oxidized U^{6+}. The U^{5+} valence state is considered unstable in aqueous solution and exists as UO_2^+ in a narrow stability field between pH 2 and 4, where the disproportionation reaction to give U^{4+} and UO_2^{2+} is negligibly slow.[1,2] The isolation of stable UO_2^+ species is extremely challenging. Apart from its fundamental interest, this elusive species has important environment implications.[3]

Uranyl silicates exist as minerals, and their structural chemistry has been extensively studied by Burns et al.[4] In the past decade, numerous uranyl silicates, which contain an organic amine[5] or alkali metals[6–10] as counter cations, had been synthesized under either mild hydrothermal or high-temperature, high-pressure hydrothermal conditions. In our previous work, we had reported the first uranium(V) silicate, $K(UO)Si_2O_6$,[10] and its structure consists of four-membered single rings of corner-sharing SiO_4 tetrahedra linked together via corner-sharing by 1-D $UO_{4/1}O_{2/2}$ chains to form a 3-D framework. This very interesting pentavalent-uranium silicate is actually isostructural with a niobium silicate, $K_2(NbO)_2Si_4O_{12}$, which was prepared while in search of a fast alkali-ion conductor.[11] Although a large number of uranium silicates have been synthesized, there are only two uranium germanates in the literature, and none contains pentavalent uranium.[12] Herein, we successfully synthesized a new uranium(V) silicate, $K_3(U_3O_6)(Si_2O_7)$ (denoted as **1**), and the germanate analogue, $Rb_3(U_3O_6)(Ge_2O_7)$ (denoted as **2**), which consist of uranate columns formed of triple octahedral chains linked by X_2O_7 groups (X = Si or Ge) to form a 3-D framework structure.

Dark-red needle crystals of **1** were synthesized by heating a mixture of 170 μL of 10 M $KOH_{(aq)}$, 340 μL of 10 M $KF_{(aq)}$, 97.2 mg of UO_3 (Cerac, 99.8%), and 40.9 mg of SiO_2 (Alfa Aesar, 99.995%; molar ratio K/U/Si/F = 15:1:2:10) in a 6.8-cm-long gold ampule (inside diameter = 0.48 cm) at 600 °C for 5 d. The pressure was estimated to be 170 MPa. The autoclave was then cooled to 350 at 5 °C/h and quenched at room temperature by removing the autoclave from the furnace. The bulk product was pure, as indicated by powder X-ray diffraction (Figure S1, Supporting Information). The yield was 56% on the basis of uranium. Dark-red

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needle crystals of **2** were synthesized as a minor product (only about 10%) by heating a mixture of 97 μL of $RbOH_{(aq)}$ (50 wt %), 164 μL of 10 M $RbF_{(aq)}$, 46.9 mg of UO_3, and 34.3 mg of GeO_2 (Cerac, 99.999%; molar ratio Rb/U/Ge/F = 15:1:2:10) in a 3.65-cm-long gold ampule under the same reaction conditions. The major product was an orange crystalline material which was not characterized because of poor crystal quality. A qualitative energy dispersive X-ray analysis of several dark red crystals confirmed the presence of K, U, and Si for **1** and Rb, U, and Ge for **2**. Suitable crystals were selected for single-crystal X-ray diffraction analysis, from which the chemical formulas were determined to be $K_3(U_3O_6)(Si_2O_7)$ and $Rb_3(U_3O_6)(Ge_2O_7)$.[13] An attempt to prepare the K analogue of **2** yielded brown, thin plate crystals, which have not been characterized because of poor crystal quality.

The infrared spectrum of **1** shows strong, broad bands with maxima at 891 and 909 cm^{-1}, which can be assigned to the stretching modes of the UO_2^+ group (Figure S2, Supporting Information). The lower frequency of the stretching modes in **1** in comparison with another U(V) silicate, $K(UO)Si_2O_6$,[10] indicates weaker U−O bonds. The bands in the regions of 1000−1200 cm^{-1} and 450−700 cm^{-1} are due to stretching and bending vibrations of the silicate groups, respectively. The IR spectrum of **2** shows bands at 963, 862, 758, 625, and 546 cm^{-1}. The band at 758 cm^{-1} is assigned to the UO_2^+ group and the other bands to the germanate groups (Figure S2, Supporting Information). The room-temperature Raman spectrum of **1** shows lines at 888, 924, and 972 cm^{-1}, likely corresponding to stretching vibrations of UO_2^+ groups, and the lines at 232 and 361 cm^{-1} are tentatively assigned to deformation modes (Figure S3, Supporting Information). The lines around 570 cm^{-1} are common for potassium silicates. Similar to many other pentavalent actinide compounds, compound **1** is easily modified by laser beam, as indicated by a prominent band at 770 cm^{-1}; thus, the use of low power is necessary to record an undisturbed spectrum. Magnetic data were measured on a 50.6 mg powder sample of **1** between 2 and 300 K in a magnetic field of 0.2 T. The $\chi_M T$ value decreases rapidly upon cooling, indicating that the magnetic interactions between U atoms are antiferromagnetic (Figure S4, Supporting Information). The magnetic susceptibilities do not follow the Curie−Weiss law. The μ_{eff} (effective magnetic moment) at 300 K is 2.20 μ_B/mol or 1.27 μ_B per U, which is consistent with the observations that the values of μ_{eff} for uranium(V) compounds around room temperature are between 1.26 and 1.86 μ_B.[14] The XPS (X-ray photoelectron spectroscopy) spectrum of **1** shows peaks of K, U, Si, O, and C. Slight carbon contamination is present on the sample surface, originating from hydrocarbons. The spectrum does not reveal the presence of F. Binding energies (BEs) of all of the peaks were referenced to the C 1s peak (BE = 284.5 eV). The U 4f XPS spectrum of **1** is shown in Figure S5, Supporting Information. The U $4f_{7/2}$ peak is located at 380.5 eV (fwhm = 2.83 eV), which is in agreement with the observations that the BE values of U(VI) $4f_{7/2}$ and U(V) $4f_{7/2}$ in several alkali and alkaline earth uranates are at 381.3 ± 0.13 and 380.42 ± 0.05 eV, respectively.[15] An X-ray absorption spectroscopy (XAS) study of compound **1** was performed at the beamline STM of synchrotron source at RRC Kurchatov Institute, Moscow, in transmission modes at 293 K. Experimental extended X-ray absorption fine structure (EXAFS) spectra were fitted in R space using an IFEFFIT package[16] with FEFF8 amplitude and phase functions based on crystallographic parameters (for details on data acquisition and processing, see the Supporting Information). The XAS results for **1** are shown in Figure S6, Supporting Information. The shape of the U L_{III}-edge X-ray absorption near edge structure (XANES), namely, a slightly asymmetric white line with a shoulder at the low-energy side, and the position of the multiple-scattering peak gives strong evidence that the dominant charge state of the uranium in **1** is U^{5+}.[17] Parameters of the local environment of the U atom obtained from the EXAFS fitting procedure are fully consistent with the crystallographic data except for a slightly broader distribution of the U−O bond lengths within the first coordination sphere.

Compounds **1** and **2** are isostructural. The structure is constructed from the following distinct structural elements: one UO_6 octahedron, one SiO_4 (or GeO_4) tetrahedron, and one K (or Rb) site. The U atom sits on a 2-fold axis; Si (or Ge) sits on a 3-fold axis, and K (or Rb) lies in a mirror plane. The UO_6 octahedron is quite regular with d(U−O) = 2.087(1) Å (2×), 2.119(4) Å (2×), and 2.190(8) Å (2×) for **1** and 2.1077(4) Å (2×), 2.123(3) Å (2×), and 2.194(7) Å (2×) for **2**. The sum of bond-valences incident at the U site, calculated by using the bond-valence parameters $R_{ij} = 2.051$ Å and $b = 0.519$ Å from Burns et al.,[4a] is 5.15 v.u. for **1** and 5.04 v.u. for **2**, in accord with the occurrence of U^{5+} in this site. The U^{5+} cations in those U(V) oxo compounds and the mineral wyartite[18] occur either in an octahedral coordination or in a pentagonal bipyramidal coordination that contains a linear or near-linear UO_2^+ ion with a U−O bond length of ~2.10 Å. In contrast, the uranyl ion (UO_2^{2+}) contains two strongly bonded oxygen atoms with U−O bond lengths of ~1.8 Å. Therefore, the bond-valence sum, polyhedral

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(13) Crystallographic data for **1**: hexagonal, space group $P\bar{6}2c$, $M_r = 1095.57$, $a = 9.5389(5)$ Å, $c = 8.3389(9)$ Å, $V = 657.11(9)$ Å^3, $Z = 2$, $d_{cal} = 5.537$ g cm^{-3}, μ(Mo Kα) = 380.74 cm^{-1}. A total of 4174 reflections were measured on a Siemens SMART/CCD single-crystal diffractometer at 293 K, which gave 584 independent reflections with $R_{int} = 0.0627$. An absorption correction was made by using the SADABS program. Final refinement converged at R1 = 0.0247 and wR2 = 0.0564 for 509 reflections with $I > 2\sigma(I)$ and 38 parameters. The Flack parameter is 0.0053. Crystallographic data for **2**: The same as those for **1** except $M_r = 1323.68$, $a = 9.8014(3)$ Å, $c = 8.4198(4)$ Å, $V = 700.50(5)$ Å^3, $Z = 2$, $d_{cal} = 6.276$ g cm^{-3}, μ(Mo Kα) = 492.17 cm^{-1}, 4980 reflections measured, and 625 independent reflections with $R_{int} = 0.0523$. Final refinement converged at R1 = 0.0214 and wR2 = 0.0532 for 582 reflections with $I > 2\sigma(I)$ and 38 parameters. The Flack parameter is −0.0536.

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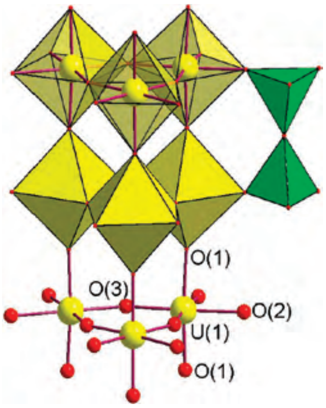

Figure 1. Section of the structure of **1** showing a uranate column formed of corner-sharing UO_6 octahedra.

geometry, and asymmetry of the white line in the XAS spectrum indicate that the U atom in **1** (or **2**) is pentavalent.

Every UO_6 octahedron has two equatorial silicate (or germanate) oxygen atoms, two equatorial oxygen atoms which share corners with neighboring UO_6 octahedra, and two axial oxygen atoms that act as common vertices to other octahedra to form a 1-D chain along the *c* axis, corresponding to the Niggli formula $UO_{2/2}O_{2/2}O_{2/1}$. The three parallel strings of α-UF_5 type are joined via common corners to form a uranate column with the composition $(UO_{2/2}O_{2/2}O_{2/1})_3$ (Figure 1). Such a structure gives rise to numerous collinear multiple scattering paths for photoelectrons. This structure is reminiscent of that of hexagonal tungsten bronze. The main difference between the two structures is that the octahedral columns in **1** are separated by silicate groups. The observed Si−O bond lengths (1.602 Å (3×), 1.607 Å, average 1.603 Å) and O−Si−O bond angles (108.8−110.2°) for **1** are typical values and are within the normal range.[19] The GeO_4 tetrahedron for **2** also has a regular environment, as indicated by the Ge−O bond lengths (1.731 Å (3×) and 1.716 Å) and O−Ge−O bond angles (108.3−110.6°). Every SiO_4 (or GeO_4) tetrahedron shares a corner with another tetrahedron to form a disilicate unit, with the bond angle at the bridging oxygen being equal to 180°. The structure consists of octahedral columns connected by disilicate (or digermanate) groups via corner-sharing to form a 3-D framework that delimits one type of five-ring channels along the *c* axis (Figure 2). The K (or Rb) atom is located in the channel and is probably immobile, as indicated by regular K−O (or Rb−O) bond lengths and nearly isotropic thermal parameters.

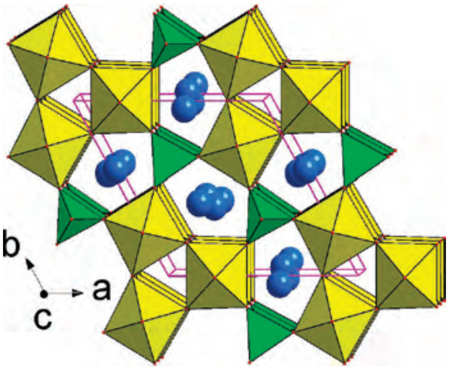

Figure 2. Structure of **1** viewed along the *c* axis. The yellow and green polyhedra are UO_6 octahedra and SiO_4 tetrahedra, respectively. Blue circles are potassium atoms.

Actinyl(V) cations are known to participate in cation−cation interactions (CCIs), whereby the two AnO_2^+ units coordinate one another.[20] CCIs are much more common for Np(V) relative to U(VI). However, the direct sharing of an O atom between two NpO_2^+ cations would be very unlikely due to the strong Np^{5+}−O bond (1.83 Å) as compared to U^{5+}−O. It appears that such a connection as observed in the uranate column in **1** can only occur in U(V) compounds. In the literature, several niobium and tantalum compounds, $A_3M_6Si_4O_{26}$ (M = Nb, A = Ba; M = Ta, A = Sr, Ba)[21] and $K_3M_3O_6Si_2O_7$ (M = Nb or Ta),[22] which contain the same kind of octahedral column, are isostructural with the title compounds. Although the ionic radius for six-coordinate U^{5+} (0.78 Å) is larger than those for Nb^{5+} (0.64 Å) and Ta^{5+} (0.64 Å), all U^{5+} silicates or germanates which have been synthesized until now are isostructrural to the Nb^{5+} or Ta^{5+} analogs. Therefore, known niobium or tantalum silicates can be synthesis guidances for new pentavalent-uranium compounds. It is anticipated that more examples in this interesting class of compounds will be synthesized.

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Supporting Information Available: X-ray crystallographic data in CIF format, X-ray powder patterns, IR and Raman spectra, magnetic data, XPS spectrum, and XAS data and fitting are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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