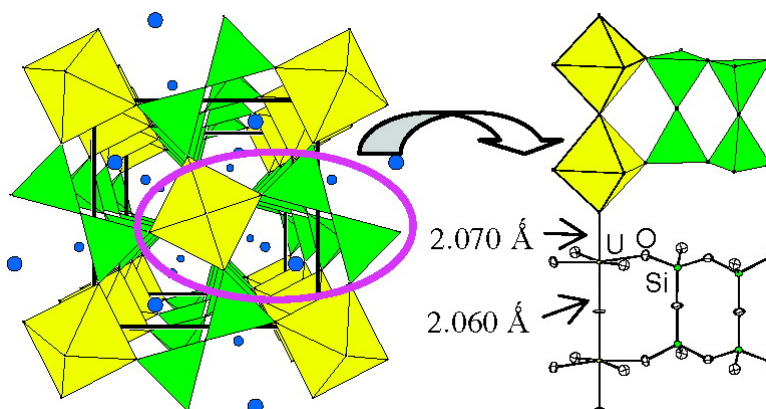


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K(UO)Si₂O₆: A Pentavalent–Uranium Silicate

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Uranyl silicates are known to exist as minerals; their structural chemistry has been extensively studied because an understanding of their structures may be a key to understanding the long-term performance of a geological repository for nuclear waste.^{1–3} A naturally occurring uranium(IV) silicate, coffinite (USiO₄), also exists.⁴ Recently, a number of synthetic uranyl silicates, including an organically templated uranyl silicate, have been reported, and all of them were synthesized in a Teflon-lined autoclave under hydrothermal conditions at 180–245 °C.^{5–7} To date, no silicates have been described that contain essential U⁵⁺. The U⁵⁺ valence state is considered unstable in aqueous solutions and exists as UO₂⁺ in a narrow stability range between pH 2 and 4, where the disproportionation reaction to give U⁴⁺ and uranyl cation, UO₂²⁺, is negligibly slow.^{8,9} U⁵⁺ can be stabilized with respect to disproportionation by complexing with F[–] as UF₆[–].

The synthesis of U(V) compounds is interesting and challenging because U⁵⁺ has the simplest 5f electron configuration [Rn]5f¹ and these compounds are useful for magnetic and spectroscopic studies to understand the behavior of the f electrons of actinide ions. In the literature, only one naturally occurring U⁵⁺-bearing carbonate, wyartite,¹⁰ was discovered, and several U(V) oxo compounds, such as AUO₃ (A = Na, K),¹¹ SrU₂O₆,¹² USbO₅,¹³ and UVO₅,¹⁴ were synthesized by solid-state reactions at high temperature and controlled oxygen fugacities. Until now, no U(V) compound has yet been prepared by hydrothermal synthesis. Following our previous work on the synthesis of several new uranyl silicates under high-temperature, high-pressure hydrothermal conditions (550 °C, 110 MPa), we report in this paper the first pentavalent–uranium silicate, K(UO)Si₂O₆ (denoted as **1**).

Compound **1** was synthesized by heating a mixture of 100 μL of 10 M KOH_(aq), 200 μL of 10 M KF_(aq), 62.9 mg of UO₃ (Cerac, 99.8%), and 52.9 mg of SiO₂ (Alfa Aesar, 99.995%) (molar ratio K:U:Si:F = 15:1:4:10) in a 4.2 cm long gold ampule (inside diameter = 0.48 cm) at 600 °C for 2 days. The pressure was estimated to be 170 MPa. The autoclave was then cooled to 350 °C at 5 °C/h and quenched at room temperature by removing the autoclave from the furnace. The product contained brown square tablets of **1** along with some colorless crystals. A suitable crystal was selected for single-crystal X-ray diffraction analysis¹⁵ from which the chemical formula was determined to be K(UO)Si₂O₆. The brown crystals were manually separated from the colorless crystals, giving a pure sample as indicated by powder X-ray diffraction (Figure S1). The yield of **1** was approximately 64% based on uranium. A qualitative EDX analysis of several brown crystals confirmed the presence of K, U, and Si.

The IR spectrum of **1** shows a strong, broad band with maximum at 941 cm^{–1}, which can be assigned to the stretching modes of the UO₂⁺ group (Figure S2). The bands in the regions of 1000–1200

and 450–700 cm^{–1} are due to stretching and bending vibrations of the silicate groups, respectively. Magnetic data were measured on a powder sample of 40.4 mg 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 dominating magnetic interactions between U atoms are antiferromagnetic (Figure S3). The magnetic susceptibilities follow the Curie–Weiss law at high temperature. Below 50 K, there is a phase transition into a paramagnetic state, which follows Curie's law. The phase transition is still under investigation. The μ_{eff} at 300 K is 1.32 μ_B /mol, which is consistent with the observations that the values of μ_{eff} for U(V) compounds around room temperature are between 1.26 and 1.86 μ_B .¹⁶ The XPS 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 (BE) of all the peaks were referenced to the C 1s peak (BE = 284.5 eV). The U 4f XPS spectrum of **1** is shown in Figure S4. The U 4f_{7/2} peak is located at 380.7 eV (fwhm = 2.47 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.¹⁷

The structure of **1** is constructed from the following distinct structural elements: 1 UO₆ octahedron, 1 SiO₄ tetrahedron, and 1 K site. The U atom sits on a 4-fold axis, Si lies in a mirror plane, and K has a local symmetry of C_{2v}. The UO₆ octahedron contains four longer (2.164(2) Å) and two shorter (2.060(2) and 2.070(2) Å) bonds. Therefore, **1** is not a uranyl compound. 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 for all types of U⁶⁺ coordination polyhedra from Burns et al., is 5.16 v.u., in accordance with the occurrence of U⁵⁺ in this site.¹⁸ The U⁵⁺ cations in those U(V) oxo compounds and wyartite occur either in octahedral coordination or in a pentagonal bipyramidal coordination that contain a linear or near-linear UO₂⁺ ion with a U–O bond length of ~2.10 Å. In contrast, the uranyl ion contains two strongly bonded O atoms with U⁶⁺–O bond lengths of ~1.8 Å. Therefore, the bond-valence sum and polyhedral geometry both indicate that the U atom in **1** is pentavalent.

Every UO₆ octahedron has four equatorial silicate oxygen atoms and two axial oxygen atoms that act as common vertices to other octahedra to form a 1-D straight chain along the *c*-axis, corresponding to the Niggli formula UO_{4/1}O_{2/2} (Figure 1). The bond angles at the bridging atoms are 180°. This type of straight chain has been observed in many compounds, such as BiF₅, UF₅, and WOCl₄.¹⁹ The observed Si–O bond lengths (1.604 (3×), 1.632, average 1.611 Å) and O–Si–O bond angles (107.4–111.6°) are typical values and are within the normal range.²⁰ The structure consists of four-membered single rings of corner-sharing SiO₄ tetrahedra linked together via corner-sharing 1-D UO_{4/1}O_{2/2} chains to form a 3-D framework that delimits one type of five ring channels along the *c*-axis (Figure 2). The K atom is located in the channel

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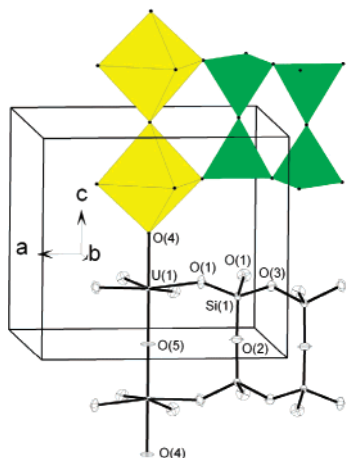


Figure 1. Section of the structure of **1** showing the connection between the four-membered SiO_4 tetrahedral rings and a $\text{UO}_{4/1}\text{O}_{2/2}$ straight chain.

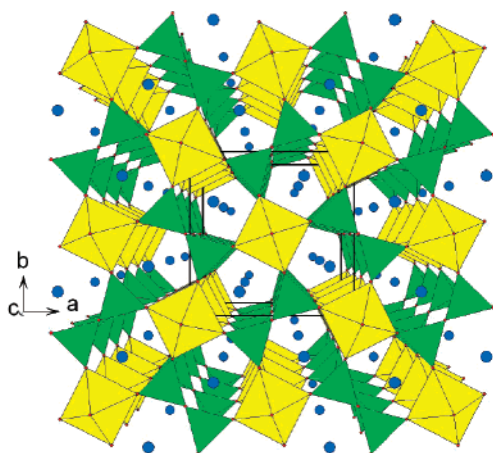


Figure 2. Structure of **1** viewed along the c -axis. The yellow and green polyhedra are UO_6 octahedra and SiO_4 tetrahedra, respectively. Blue circles are potassium atoms.

and is probably immobile, as indicated by regular K–O bond lengths and nearly isotropic thermal parameters.

The structure of **1** exhibits a most unusual connection in actinides. In contrast to the coordination chemistry of actinyl(VI) cations, actinyl(V) cations are known to participate in cation–cation interactions (CCIs), whereby the oxo atoms of the AnO_2^+ units coordinate one another.²¹ CCIs are much more common for Np^{5+} relative to U^{5+} . However, the direct sharing of an O atom between two NpO_2^+ ions would be very unlikely due to the stronger Np^{5+} –O bond (1.83 Å) as compared to U^{5+} –O. It appears that such a connection could only occur in U(V) compounds, such as **1**, AUO_3 ($A = \text{Na}, \text{K}$) and UVO_5 .

In summary, we have successfully synthesized the first U(V) silicate, compound **1**, which is also the first U(V) compound synthesized by hydrothermal method. Its 3-D framework is uniquely characterized by four-membered single rings of corner-sharing SiO_4 tetrahedra and strings of $\text{U}^{\text{V}}\text{O}_6$ octahedra sharing opposite corners to give infinite $-\text{U}-\text{O}-\text{U}-\text{O}-$ chains. XPS spectrum and magnetic susceptibilities were measured to identify the valence state of uranium. The major difference between the synthesis conditions for **1** and those for other silicates of U(VI) recently reported by us is that a large amount of KF is included in the reaction mixture.^{22,23} The synthesis requires partial reduction of uranium in solution. The brown color is common to U(V) compounds, and it is noteworthy that UO_3 was the only source of U in the reaction mixture. The most likely reducing agent is water itself. Reduction of U(VI) to

U(IV) has been observed in the preparation of organically templated U(IV) fluorides.²⁴ Aliphatic amines are apparently the reducing agents. The high concentration of F^- ion may stabilize UO_2^{2+} in solution and promote precipitation of a U^{5+} -bearing silicate, such as **1**. We have also synthesized another U(V) silicate, $\text{K}_3(\text{U}_3\text{O}_6)\text{Si}_2\text{O}_7$, as a major product using a smaller amount of SiO_2 ($\text{K}:\text{U}:\text{Si}:\text{F} = 15:1:2:10$) under analogous reaction conditions.²⁵ The structure consists of three parallel strings of BiF_5 -type, which are joined via common corners to form a uranate column with the composition $(\text{UO}_{2/2}\text{O}_{2/2}\text{O}_{2/1})_3$. The columns are connected by disilicate groups via corner-sharing to form a 3-D framework. The successful use of high concentration of F^- ion in the synthesis of these two U(V) silicates suggests further opportunities for synthesizing more examples in this interesting class of compounds in a systematic way.

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

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