

$K_5(UO_2)_2[Si_4O_{12}(OH)]$: A Uranyl Silicate Containing Chains of Four Silicate Tetrahedra Linked by $SiO\cdots HOSi$ Hydrogen Bonds

Chih-Shan Chen,[†] Hsien-Ming Kao,[†] and Kwang-Hwa Lii^{*†‡}

Department of Chemistry, National Central University, Chungli, Taiwan 320, R.O.C.,
and Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan, R.O.C.

Received August 31, 2004

A new uranium(VI) silicate, $K_5(UO_2)_2[Si_4O_{12}(OH)]$, has been synthesized by a high-temperature, high-pressure hydrothermal method. It crystallizes in the orthorhombic space group *Pbcm* (No. 57) with $a = 13.1274(7)$ Å, $b = 12.2635(7)$ Å, $c = 22.233(1)$ Å, and $Z = 8$. Its structure consists of unbranched chains of four silicate tetrahedra extending along the *b* axis linked together via corner-sharing by UO_6 tetragonal bipyramids to form a 3-D framework, which delimits intersecting channels along the *c* and *b* axes to accommodate K^+ cations. A hydrogen atom is bonded to a terminal oxygen of a terminal silicate in the oligosilicate anion. Adjacent chains are linked along the *b* axis by hydrogen bonds. The sample shows a resonance at 14.7 ppm in the 1H MAS NMR spectrum, which is assigned to the $SiO\cdots HOSi$ hydrogen bond. A comparison of uranyl silicate structures is made.

Introduction

Recently much work has focused on the synthesis of new metal silicates with 3-D framework structures because some of these new materials possess a number of interesting characteristics as heterogeneous catalysts.¹ For example, the titanosilicate material named ETS-10 shows high cation exchange capacity, facile metal loading for bifunctionality, and very high basicity. In addition, ETS-10 offers the potential for photocatalysis and asymmetric synthesis. A good number of vanadium silicates have also been reported.^{2–5} Some of them show good thermal stability, absorption, and ion-exchange properties, suggesting their potential for applications as molecular sieves or in catalysis. Their structural chemistry is also interesting, as shown by a wide variety of structure types adopted by the compounds with the general formula $A_2(VO)Si_4O_{10}\cdot nH_2O$ ($A =$ alkali metals, $n \geq 0$). Other recent examples include titanium,^{6–8} niobium,^{9,10}

cerium,^{11,12} tin,¹³ and indium silicates.^{14,15} Most of these compounds were synthesized with alkali metal cations in a Teflon-lined autoclave under hydrothermal conditions at 180–240 °C. A series of uranium silicates have also been developed by replacing the VO_2^{2+} cation in the vanadium(IV) silicates with UO_2^{2+} as the bridging metal species.^{16–18} A niobium and a uranium silicate have been synthesized by using organic ammonium cations as structure-directing agents.^{9,17} We have also synthesized a number of new silicates of vanadium,¹⁹ niobium,¹⁰ and indium^{14,15} with alkali

* Author to whom correspondence should be addressed. E-mail: liikh@cc.ncu.edu.tw.

[†] National Central University.

[‡] Academia Sinica.

- (1) Rocha, J.; Anderson, M. W. *Eur. J. Inorg. Chem.* **2000**, 801 and references therein.
- (2) Wang, X.; Liu, L.; Jacobson, A. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2174.
- (3) Wang, X.; Liu, L.; Jacobson, A. J. *J. Am. Chem. Soc.* **2002**, *124*, 7812.
- (4) Huang, J.; Wang, X.; Liu, L.; Jacobson, A. J. *Solid State Sci.* **2002**, *4*, 1193.
- (5) Brandão, P.; Valente, A.; Philippou, A.; Ferreira, A.; Anderson, M. W.; Rocha, J. *Eur. J. Inorg. Chem.* **2003**, 1175.

- (6) Nyman, M.; Bonhomme, F.; Teter, D. M.; Maxwell, R. S.; Bu, B. X.; Wang, L. M.; Ewing, R. C.; Nenoff, T. M. *Chem. Mater.* **2000**, *12*, 3449.
- (7) Nyman, M.; Bonhomme, F.; Maxwell, R. S.; Nenoff, T. M. *Chem. Mater.* **2001**, *13*, 4603.
- (8) Kuznicki, S. M.; Bell, V. A.; Nair, S.; Hillhouse, H. W.; Jacobinas, R. M.; Braunbarth, C. M.; Toby, B. H.; Tsapatsis, M. *Nature* **2001**, *412*, 720.
- (9) Francis, R. J.; Jacobson, A. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2879.
- (10) Kao, H.-M.; Lii, K.-H. *Inorg. Chem.* **2002**, *41*, 5644.
- (11) Rocha, J.; Ferreira, P.; Carlos, L. D.; Ferreira, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3276.
- (12) Jeong, H.-K.; Chandrasekaran, A.; Tsapatsis, M. *Chem. Commun.* **2002**, 2398.
- (13) Ferreira, A.; Lin, Z.; Rocha, J.; Morais, C. M.; Lopes, M.; Fernandez, C. *Inorg. Chem.* **2001**, *40*, 3330.
- (14) Hung, L.-I.; Wang, S.-L.; Kao, H.-M.; Lii, K.-H. *Inorg. Chem.* **2003**, *42*, 4057.
- (15) Huang, L.-I.; Wang, S.-L.; Szu, S.-P.; Hsieh, C.-Y.; Kao, H.-M.; Lii, K.-H. *Chem. Mater.* **2004**, *16*, 1660.
- (16) Wang, X.; Huang, J.; Liu, L.; Jacobson, A. J. *J. Mater. Chem.* **2002**, *12*, 406.
- (17) Wang, X.; Huang, J.; Jacobson, A. J. *J. Am. Chem. Soc.* **2002**, *124*, 15190.
- (18) Huang, J.; Wang, X.; Jacobson, A. J. *J. Mater. Chem.* **2003**, *13*, 191.

metal cations by high-temperature, high-pressure hydrothermal reactions (500–600 °C, ~110–160 MPa) in gold ampules. Their structures, solid-state NMR spectroscopy, and ionic conductivity have been studied. Although these silicates were prepared under much higher temperature and pressure hydrothermal conditions, many of them adopt open-framework structures. For example, the anhydrous vanadium silicate $\text{Cs}_2\text{VOSi}_6\text{O}_{14}$,²⁰ which was prepared at 500 °C and ~110 MPa, adopts a considerably different structure from the hydrous compound $\text{Cs}_2\text{VOSi}_6\text{O}_{14}\cdot 3\text{H}_2\text{O}$,³ which was prepared at 240 °C, but both of them contain 8-ring channels. The high-temperature/high-pressure synthetic route facilitates crystal growth of refractory silicate systems and may produce new compounds that are distinct from those by typical mild or moderate-condition hydrothermal method. We have extended the exploratory synthetic and structural studies to the class of uranium silicates because framework structures containing U(VI) combined with silicate or other anions are structurally quite diverse. This work describes the synthesis and structural characterization by single-crystal X-ray diffraction and ^1H MAS NMR spectroscopy of a new uranyl silicate, $\text{K}_5(\text{UO}_2)_2[\text{Si}_4\text{O}_{12}(\text{OH})]$.

Experimental Section

Synthesis and Initial Characterization. The hydrothermal reactions were carried out under autogenous pressure in gold ampules contained in a Leco Tem-Pres autoclave where pressure was provided by water. The apparatus is an externally heated cold-seal pressure vessel for use to 10 000 bar and 750 °C.²¹ The degree of filling of the autoclave by water at room temperature was 50%. A reaction mixture of 0.36 mL of 10 M $\text{KOH}_{(\text{aq})}$, 0.1144 g of UO_3 (Cerac, 99.8%), and 0.0721 g of SiO_2 (Alfa Aesar, 99.995%) (molar ratio K:U:Si = 10:1:4) in a 5.5 cm long gold ampule (inside diameter 4.85 mm) was heated at 550 °C for 3 d. The pressure inside the autoclave was estimated to be 110 MPa according to the pressure–temperature diagram of pure water. The autoclave was then cooled to 300 °C at 5 °C/h followed by fast cooling to room temperature by removing the autoclave from the tube furnace. The product was filtered off, washed with water, rinsed with ethanol, and dried at ambient temperature. The reaction produced 0.147 g of yellow prismatic crystals. A qualitative EDX analysis of several yellow crystals showed the presence of K, U, and Si. A crystal was selected for structure determination by single-crystal X-ray diffraction. Powder X-ray data were collected on a Shimadzu XRD-6000 automated powder diffractometer with $\text{Cu K}\alpha$ radiation equipped with a scintillation detector. Data were collected in the range $5^\circ \leq 2\theta \leq 50^\circ$ using θ – 2θ mode in a Bragg–Brentano geometry. The bulk product was a single phase of $\text{K}_5(\text{UO}_2)_2[\text{Si}_4\text{O}_{12}(\text{OH})]$, **1**, because its powder pattern is in good agreement with the calculated pattern based on the results from single-crystal X-ray diffraction (Figure 1). The program XPOW in the SHELXTL Version 5.1 software package was used for XRPD simulation. The yield was 70% based on uranium. The sample was used for solid-state NMR spectroscopy.

Crystals of $\text{Na}_2(\text{UO}_2)\text{SiO}_4$,²² $\text{Rb}_2(\text{UO}_2)(\text{Si}_2\text{O}_6)$, and $\text{Cs}_2(\text{UO}_2)(\text{Si}_2\text{O}_6)$ have also been obtained from hydrothermal reactions of

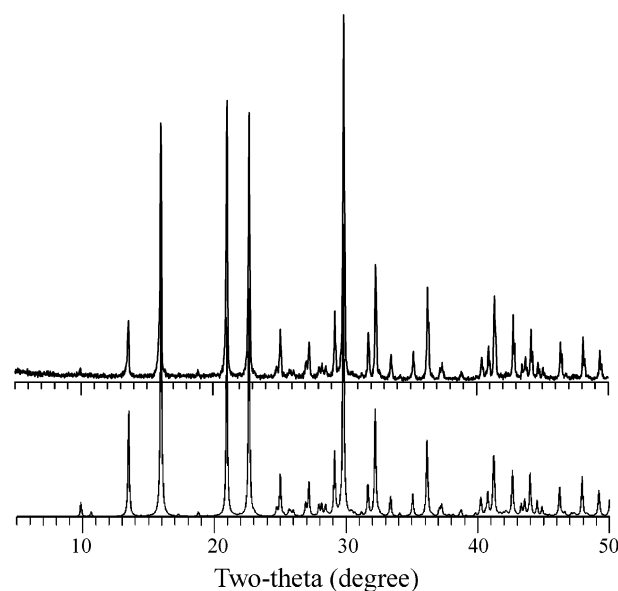


Figure 1. Experimental X-ray powder pattern (top) and simulated powder pattern based on the results from single-crystal X-ray diffraction (bottom) for **1**.

$\text{AOH}_{(\text{aq})}$ (A = Na, Rb, Cs), UO_3 , and SiO_2 under analogous conditions (A:U:Si = 10:1:4; 550 °C, 110 MPa). The latter two are new compounds. Their framework structures are similar to those of previously reported $\text{M}_2(\text{UO}_2)(\text{Si}_2\text{O}_6)\cdot 0.5\text{H}_2\text{O}$ (M = Rb, Cs)¹⁸ but have a different space group. Crystal data for $\text{Cs}_2(\text{UO}_2)(\text{Si}_2\text{O}_6)$: orthorhombic, *Ibca*, $a = 15.137(1)$, $b = 15.295(1)$, $c = 16.401(1)$ Å, $R_1 = 0.0355$, and $wR_2 = 0.0829$.

A reaction mixture of 0.212 g of $\text{UO}_2(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$, 0.448 mL of tetraethyl orthosilicate, 1 mL of 10 M KOH , and 3 mL of H_2O (molar ratio K:U:Si = 10:1:4) was heated in a 23-mL Teflon-lined acid digestion bomb at 230 °C for 7 d followed by slow cooling to room temperature. Based on visual microscopic examination and powder X-ray diffraction, the major product was an unidentified microcrystalline yellow solid.

Single-Crystal X-ray Diffraction. A small yellow crystal of **1** having dimensions $0.12 \times 0.06 \times 0.04$ mm was selected for indexing and intensity data collection on a Siemens SMART CCD diffractometer equipped with a normal focus, 3-kW sealed tube X-ray source. Most crystals in the reaction product were twinned. A number of crystals were selected and checked for reflection profiles before a satisfactory one was obtained. Intensity data were collected at room temperature in 1271 frames with ω scans (width 0.30° per frame). The program SADABS was used for the absorption correction ($T_{\text{min/max}} = 0.585/0.984$).²³ On the basis of reflection conditions, statistical analysis of the intensity distributions and successful solution and refinement of the structures, the space group was determined to be *Pbcm* (No. 57). The structure was solved by direct methods and difference Fourier syntheses. Seven K sites were located and refined with full occupancy. U(1) and U(2) lie in mirror planes, U(3) sits on 2-fold axes, and U(4) is located at inversion centers. The bond valence parameters $R_{ij} = 2.074$ Å and $b = 0.554$ Å for $^{60}\text{U}^{6+}$ polyhedra were used to calculate the bond valence sums at each uranium site and the values are U(1) = 6.20, U(2) = 6.12, U(3) = 6.10, and U(4) = 5.98 valence units,

(19) Li, C.-Y.; Hsieh, C.-Y.; Lin, H.-M.; Kao, H.-M.; Lii, K.-H. *Inorg. Chem.* **2002**, *41*, 4206.

(20) Hung, L.-I.; Wang, S.-L.; Lii, K.-H. Unpublished research.

(21) Luth, W. C.; Tuttle, O. F. *Am Mineral.* **1963**, *48*, 1401.

(22) $\text{Na}_2(\text{UO}_2)\text{SiO}_4$: Shashkin, D. P.; Lure, E. A.; Belov, N. V. *Kristallogr.* **1974**, *19*, 958. $\text{M}_2(\text{UO}_2)(\text{Si}_2\text{O}_6)$ (M = Rb, Cs): Chen, C.-S.; Lii, K.-H. Unpublished research.

(23) Sheldrick, G. M. SADABS, Program for Siemens Area Detector Absorption Corrections, University of Göttingen, Germany, 1997.

Table 1. Crystallographic Data for $K_5(UO_2)_2[Si_4O_{12}(OH)]$

chemical formula	$HK_5O_{17}Si_4U_2$
$a/\text{\AA}$	13.1274(7)
$b/\text{\AA}$	12.2635(7)
$c/\text{\AA}$	22.233(1)
$V/\text{\AA}^3$	3579.2(6)
Z	8
formula weight	1056.93
space group	<i>Pbcm</i> (No. 57)
$T, ^\circ\text{C}$	23
$\lambda(\text{Mo K}\alpha), \text{\AA}$	0.710 73
$D_{\text{calc}}, \text{g}\cdot\text{cm}^{-3}$	3.923
$\mu(\text{Mo K}\alpha), \text{cm}^{-1}$	195.9
R_1^a	0.0331
wR_2^b	0.0914

^a $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\text{Max}(F_o, 0) + 2(F_c)^2]/3$, where $a = 0.0518$ and $b = 0$.

indicating that all uranium ions are hexavalent.²⁴ The bond valence sums for all oxygen atoms were also calculated and the results indicate that two of the oxygen atoms are considerably undersaturated, and all the other oxygen atoms have bond valence sums close to 2.²⁵ To balance charge, one hydrogen atom must be included in the formula. Valence sums of 1.56 and 1.41 were calculated for O(1) and O(11), respectively. The value for O(11) suggests that the oxygen is associated with a hydrogen atom. The value for O(1) and the short O(1)⋯O(11) distance of 2.471 Å indicate the presence of the H-bonded pair O(11)–H⋯O(1). The H atom was located from difference Fourier maps and refined with fixed isotropic thermal parameter. The final cycles of least-squares refinement including atomic coordinates, anisotropic thermal parameters for all non-hydrogen atoms converged at $R_1 = 0.0331$, and $wR_2 = 0.0914$. The largest residual electron densities in the final difference Fourier maps are near uranium atoms (5.24 eÅ⁻³ at 0.72 Å from U(1); -2.28 eÅ⁻³ at 0.87 Å from U(4)). For heavy atom compounds, it is normal to find ripples of up to ±10% of the atomic number of the heavy atom per Å³ at a distance of 0.6–1.2 Å from it.²⁶ At this point profile analysis of many reflections was performed. A few reflections showed broad profiles, which could be the reason for large residual electron densities. All calculations were performed using SHELXTL Version 5.1 software package.²⁷ The crystal data and structure refinement parameters are given in Table 1 and selected bond distances in Table 2.

Solid-State NMR Measurements. ¹H MAS (magic angle spinning) NMR spectrum was acquired on a Bruker AVANCE-400 spectrometer equipped with a double-tuned 4-mm MAS probe by using a spin-echo pulse sequence with a $\pi/2$ pulse width of 4 μs and a repetition time of 4 s. ¹H chemical shifts were externally referenced to tetramethylsilane (TMS) at 0 ppm.

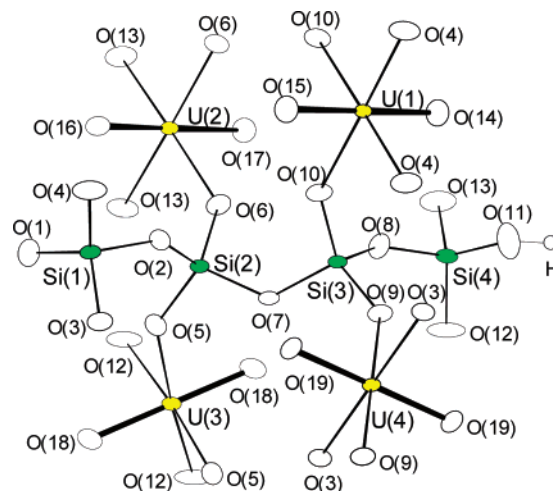
Results and Discussion

Structure. As shown in Figure 2, the structure of **1** is constructed from the following structural elements: 4 SiO₄ tetrahedra, 4 UO₆ tetragonal bipyramids, and 7 K sites. All Si atoms are at general positions, but all four U atoms at special positions. U(1) and U(2) lie in mirror planes (4*d*), U(3) sits on 2-fold axes (4*c*), and U(4) is located at inversion

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $K_5(UO_2)_2[Si_4O_{12}(OH)]^a$

Bond Lengths			
U(1)–O(4)	2.207(5) (2×)	U(1)–O(10)	2.266(4) (2×)
U(1)–O(14)	1.803(7)	U(1)–O(15)	1.824(7)
U(2)–O(6)	2.265(4) (2×)	U(2)–O(13)	2.207(5) (2×)
U(2)–O(16)	1.821(7)	U(2)–O(17)	1.834(6)
U(3)–O(5)	2.255(4) (2×)	U(3)–O(12)	2.221(5) (2×)
U(3)–O(18)	1.828(5) (2×)		
U(4)–O(3)	2.247(4) (2×)	U(4)–O(9)	2.266(4) (2×)
U(4)–O(19)	1.832(4) (2×)		
Si(1)–O(1)	1.609(5)	Si(1)–O(2)	1.651(5)
Si(1)–O(3)	1.612(5)	Si(1)–O(4)	1.629(5)
Si(2)–O(2)	1.651(5)	Si(2)–O(5)	1.612(5)
Si(2)–O(6)	1.609(5)	Si(2)–O(7)	1.654(5)
Si(3)–O(7)	1.656(5)	Si(3)–O(8)	1.639(5)
Si(3)–O(9)	1.598(5)	Si(3)–O(10)	1.618(5)
Si(4)–O(8)	1.648(5)	Si(4)–O(11)	1.612(6)
Si(4)–O(12)	1.615(5)	Si(4)–O(13)	1.619(5)
O(11)–H	0.884	O(1)⋯H	1.589
Bond Angles			
O(14)–U(1)–O(15)	177.9(3)	O(16)–U(2)–O(17)	177.4(3)
O(18)–U(1)–O(18)	179.9(3)	O(19)–U(4)–O(19)	180.0(3)
Si(1)–O(2)–Si(2)	140.4(4)	Si(2)–O(7)–Si(3)	130.8(3)
Si(3)–O(8)–Si(4)	148.7(3)	O(11)–H–O(1)	175.4

^a K–O distances are available from Supporting Information.

**Figure 2.** Structural building units of **1** showing atom labeling scheme. U=O bonds are shown in thick lines. Thermal ellipsoids are shown at 50% probability.

centers (4*a*). The observed Si–O bond lengths (1.598–1.656 Å, average 1.627 Å) and O–Si–O bond angles (118.1–102.3°) are typical values and are within the normal range.²⁸ The SiO₄ tetrahedra share corners with other tetrahedra to form chains of four tetrahedra. All oxygen atoms in this oligosilicate anion except O(1) and O(11) are either bridging oxygen atoms O_{br} linking two Si atoms or terminal atoms O_{term} that coordinate to U atoms. The Si–O_{br}–Si angles are 140.4, 130.8, and 148.7° for O(2), O(7), and O(8), respectively, which are within the range of Si–O_{br}–Si angles for two-coordinate oxygen (130–180°) observed in silicates containing [Si₂O₇] groups,²⁸ comparable with the angles (128.4, 137.7, and 146.5°) in Ag₁₀Si₄O₁₃,²⁹ and greater than those (124.5, 126.2, and 125.1°) in Na₄S₂Si₄O₁₃.³⁰ O(11) is a hydroxo oxygen, whereas O(1) receives hydrogen bond

(24) Burns, P. C.; Ewing, R. C.; Hawthorne, F. C. *Can. Mineral.* **1997**, *35*, 1551.

(25) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

(26) Massa, W. *Crystal Structure Determination*; Springer-Verlag: Berlin, 2000.

(27) Sheldrick, G. M. *SHELXTL Programs*, version 5.1; Bruker AXS GmbH: Karlsruhe, Germany, 1998.

(28) Liebau, F. *Structural Chemistry of Silicates: Structure, Bonding and Classification*; Springer-Verlag: Berlin, 1985.

(29) Jansen, M.; Keller, H.-L. *Angew. Chem.* **1979**, *91*, 500.

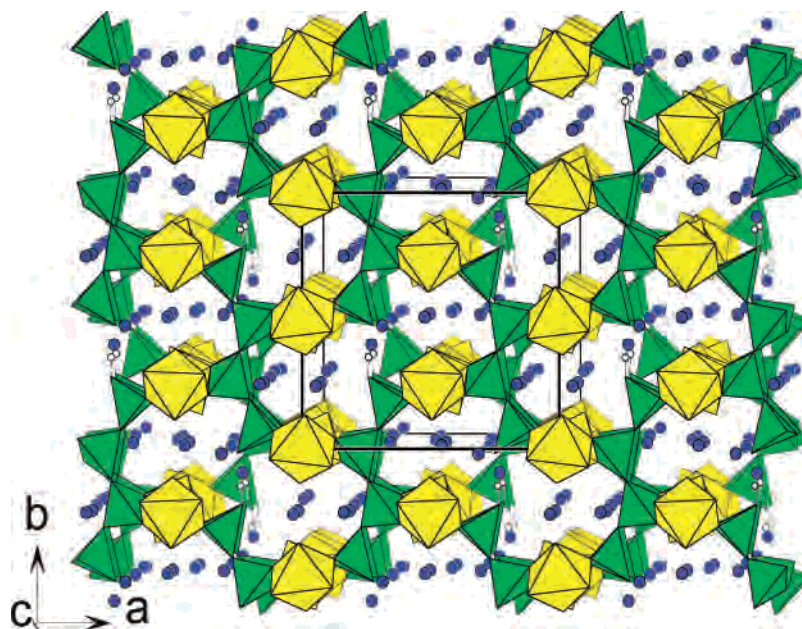


Figure 3. Structure of **1** viewed along the *c* axis. The yellow and green polyhedra are UO_6 tetragonal bipyramids and SiO_4 tetrahedra, respectively. Blue circles are potassium atoms. Small open circles are H atoms.

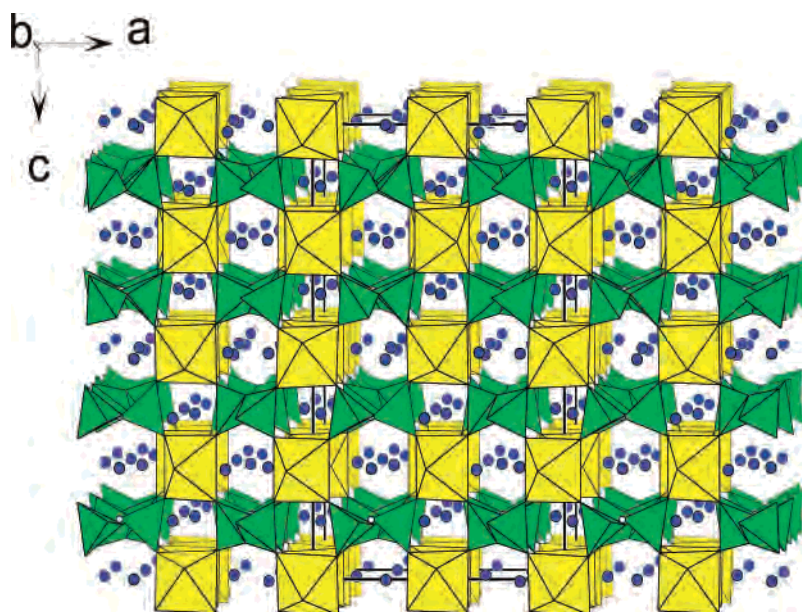


Figure 4. Structure of **1** viewed along the *b* axis.

from O(11)H in a neighboring chain ($\text{O}(11)\text{--H}\cdots\text{O}(1)$, $d(\text{O}(11)\text{--H}) = 0.884 \text{ \AA}$, $d(\text{O}(1)\cdots\text{H}) = 1.589 \text{ \AA}$, $\angle\text{O--H}\cdots\text{O} = 175.4^\circ$). All UO_6 polyhedra have unsymmetrical oxygen coordination such that two U--O bonds are short ($1.803\text{--}1.834 \text{ \AA}$), forming the linear uranyl unit $\text{O}=\text{U}=\text{O}^{2+}$, with other longer U--O bonds ($2.207\text{--}2.266 \text{ \AA}$) in the plane normal to this UO_2 axis. All K sites are ordered and fully occupied. K(1), K(3), and K(7) have a local symmetry of C_s , K(2) has C_2 symmetry, and all the other K atoms are at general positions. Based on the maximum cation–anion distance by Donnay and Allmann,³¹ a limit of 3.35 \AA was set for K–O interactions, which gives the following coordi-

inations: K(3), 6-coordinate; K(6), 7-coordinate; K(2) and K(7), 8-coordinate; K(1), K(3), and K(4), 9-coordinate. The atomic displacement factors for all of the K atoms are regular and normal, indicating that they are not loosely bound in the structural channels.

Compound **1** adopts a new structural type. Its structure consists of unbranched chains of four silicate tetrahedra extending along the *b* axis linked together via corner-sharing by UO_6 tetragonal bipyramids to form a 3-D framework which delimits intersecting channels along the *c* and *b* axes (Figures 3 and 4). Each UO_6 tetragonal bipyramid has two apical uranyl oxygen atom corners and four equatorial oxygen atoms that are shared with four silicate tetrahedra. Adjacent chains are linked along the *b* axis by hydrogen bonds (Figure 5). The K^+ cations are located at the

(30) Maksimov, B. A.; Mel'nikov, O. K.; Zhdanova, T. A.; Ilyukhin, V. V.; Belov, N. V. *Sov. Phys. Dokl.* **1980**, *25*, 143.

(31) Donnay, G.; Allmann, R. *Am. Mineral.* **1970**, *55*, 1003.

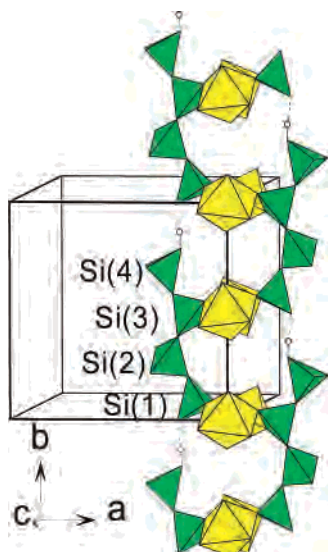


Figure 5. Chains of silicate tetrahedra in **1** linked along the *b* axis by $\text{SiO}\cdots\text{HOSi}$ hydrogen bonds.

intersections of these channels. An 8-ring channel and a 9-ring channel are observed parallel to the *c* axis. The 6-ring channels and 4-ring channels are observed along the *b* axis. The K^+ cations fill the channels and are located at the intersections.

Recently a few synthetic uranium silicates have been reported.^{16–18,32} All of them were synthesized in a Teflon-lined autoclave under hydrothermal conditions at 180–245 °C. Their structures contain four-membered rings, single chains, double chains, single layers, and double layers of silicate tetrahedra. Compound **1** is the first uranium silicate that contains chains of four silicate tetrahedra. Although unbranched chains of four tetrahedra have been observed in the synthetic compounds such as $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ and $\text{Na}_4\text{Sc}_2\text{Si}_4\text{O}_{13}$,^{29,30} compound **1** is the first example of metal silicate that contains chains of four tetrahedra linked by $\text{SiO}\cdots\text{HOSi}$ hydrogen bonds. The hydrogen bonds between SiO^- groups and SiOH were found in a number of as-synthesized high-silica zeolites and are identified by a very characteristic ^1H NMR line at 10.2 ppm.³³ Because of this, we conducted a ^1H MAS NMR study of **1** in order to confirm the presence of $\text{SiO}\cdots\text{HOSi}$ hydrogen bond as derived from single-crystal X-ray diffraction.

^1H MAS NMR Spectroscopy. The ^1H MAS NMR spectrum of **1** shows a sharp resonance at 14.7 ppm, which is assigned to $\text{SiO}\cdots\text{HOSi}$ hydrogen bond (Figure 6). The ^1H chemical shifts of oxygen-bound hydrogen depend linearly on the $\text{O}-\text{H}\cdots\text{O}$ distance, an index of the hydrogen-bond strength. From the correlation $\delta/\text{ppm} = 79.05 - 0.255 d(\text{O}-\text{H}\cdots\text{O})/\text{pm}$ published in the literature,³⁴ a 14.7 ppm resonance translates into an $\text{O}\cdots\text{O}$ distance of 2.52 Å, which is close to the distance of 2.47 Å as determined from single-crystal X-ray diffraction. The two broad resonances at 4.1

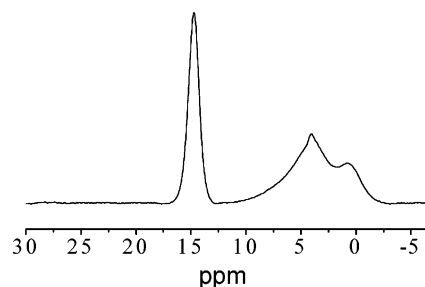


Figure 6. ^1H MAS NMR spectrum of **1** acquired at a spinning speed of 12 kHz.

and 0.8 ppm can be ascribed to absorbed water and assigned to clustered water molecules forming hydrogen bonds and isolated water molecules, respectively.

Related Structures. The structural chemistry of uranyl silicates have been extensively studied by Burns et al.³⁵ There is a structural trend in these compounds that is related to the U/Si ratio. With increasing Si relative to U, there is increasing polymerization of silicate tetrahedra and a decreasing tendency for edge-sharing between uranyl polyhedra and silicate tetrahedra. For example, soddyite is a uranyl silicate with a U/Si ratio of 2:1. All U in the structure is in pentagonal bipyramidal coordination, with uranyl polyhedra linked by sharing edges to form chains, which in turn linked into a framework by sharing edges with silicate tetrahedra. α -Uranophane and sklodovskite have a U/Si ratio of 1:1 and involve sheets of uranyl and silica polyhedra. The U in these two structures is in pentagonal bipyramidal coordination, with the uranyl polyhedra sharing edges to form chains. The chains are cross-linked by sharing edges and vertexes with silica tetrahedra, forming uranyl silicate sheets. Those with U/Si ratios 2:1 and 1:1 do not involve polymerization of the silica tetrahedra. Several synthetic uranyl silicates have a U/Si ratio of 1:2. The 3-D framework structures of $\text{RbNa}(\text{UO}_2)(\text{Si}_2\text{O}_6)\cdot\text{H}_2\text{O}$ and $\text{Rb}_2(\text{UO}_2)(\text{Si}_2\text{O}_6)\cdot\text{H}_2\text{O}$ contain discrete UO_6 polyhedra connected by individual 4 rings of silicate tetrahedra.^{16,18} In contrast, the frameworks of $\text{A}_2(\text{UO}_2)(\text{Si}_2\text{O}_6)\cdot 0.5\text{H}_2\text{O}$ ($\text{A} = \text{Rb}, \text{Cs}$) are composed of discrete UO_6 units and single chains of silicate tetrahedra.¹⁸ The framework of the title compound, which also has a U/Si ratio of 1:2, contains discrete UO_6 polyhedra connected by chains of four silicate tetrahedra. The structure of haiweeite with a U/Si ratio of 1:2.5 involves sheets of uranyl and silicate polyhedra.³⁶ The U in this structure is in tetragonal bipyramidal coordination, with the uranyl polyhedra sharing edges to form chains. Silicate tetrahedra share edges with uranyl polyhedra. Adjacent chains are linked through additional silicate tetrahedra. The silicate tetrahedra form a crankshaft-like chain that involves 4-rings. Two synthetic uranyl silicates with a U/Si ratio of 1:4 have been reported. The structure of $\text{KNa}_3(\text{UO}_2)_2(\text{Si}_4\text{O}_{10})_2(\text{H}_2\text{O})_4$ contains vertex-sharing silica tetrahedra arranged in four and eight-membered rings that are linked to give sheets.³⁷ The sheets are cross-linked by vertex-

(32) Burns, P. C.; Olson, R. A.; Finch, R. J.; Hanchar, J. M.; Thibault, Y. *J. Nucl. Mater.* **2000**, 278, 290.

(33) Koller, H.; Lobo, R. F.; Burkett, S. L.; Davis, M. E. *J. Phys. Chem.* **1995**, 99, 12588.

(34) Eckert, H.; Yesinowski, J. P.; Silver, L. A.; Stolper, E. M. *J. Phys. Chem.* **1988**, 92, 2055.

(35) Burns, P. C.; Miller, M. L.; Ewing, R. C. *Can. Mineral.* **1996**, 34, 845 and references therein.

(36) Burns, P. C. *Can. Mineral.* **2001**, 39, 1153.

(37) Burns, P. C.; Olson, R. A.; Finch, R. J.; Hanchar, J. M.; Thibault, Y. *J. Nucl. Mater.* **2000**, 278, 290.

sharing with UO_6 tetragonal bipyramids. The structure of $\text{Rb}_4(\text{UO}_2)_2(\text{Si}_8\text{O}_{20})$ consists of UO_6 units connected by double chains of silicate tetrahedra.¹⁸ Those with U/Si ratios of 1:2, 1:2.5, and 1:4 contain rings, chains and sheets of vertex-sharing silica tetrahedra.

In summary, we have synthesized a new uranium(VI) silicate by high-temperature, high-pressure hydrothermal method and characterized its structure by single-crystal X-ray diffraction. The structure contains chains of four silicate tetrahedra linked by UO_6 tetragonal bipyramids to form a 3-D framework containing intersecting channels where the K^+ cations are located. A hydrogen atom is bonded to a terminal oxygen of a terminal silicate in the oligosilicate anion. Adjacent chains are linked by hydrogen bonds. This

is the first example of metal silicate that contains chains of four tetrahedra linked by $\text{SiO}\cdots\text{HOSi}$ hydrogen bonds. The compound shows a resonance at 14.7 ppm in the ^1H MAS NMR spectrum, which is assigned to $\text{SiO}\cdots\text{HOSi}$ hydrogen bond.

Acknowledgment. The authors thank the National Science Council for support and Ms. R.-R. Wu at National Cheng Kung University for NMR measurements.

Supporting Information Available: Crystallographic data for $\text{K}_5(\text{UO}_2)_2[\text{Si}_4\text{O}_{12}(\text{OH})]$ in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC0487880