

High-Temperature, High-Pressure Hydrothermal Synthesis, Crystal Structure, and Solid-State NMR Spectroscopy of $\text{Cs}_2(\text{UO}_2)(\text{Si}_2\text{O}_6)$ and Variable-Temperature Powder X-ray Diffraction Study of the Hydrate Phase $\text{Cs}_2(\text{UO}_2)(\text{Si}_2\text{O}_6)\cdot 0.5\text{H}_2\text{O}$

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A new uranium(VI) silicate, $\text{Cs}_2(\text{UO}_2)(\text{Si}_2\text{O}_6)$, has been synthesized by a high-temperature, high-pressure hydrothermal method and characterized by single-crystal X-ray diffraction and solid-state NMR spectroscopy. It crystallizes in the orthorhombic space group *Ibca* (No. 73) with $a = 15.137(1) \text{ \AA}$, $b = 15.295(1) \text{ \AA}$, $c = 16.401(1) \text{ \AA}$, and $Z = 16$. Its structure consists of corrugated achtler single chains of silicate tetrahedra extending along the *c* axis linked together via corner-sharing by UO_6 tetragonal bipyramids to form a 3-D framework which delimits 8- and 6-ring channels. The Cs^+ cations are located in the channels or at sites between channels. The ^{29}Si and ^{133}Cs MAS NMR spectra are consistent with the crystal structure as determined from X-ray diffraction, and the resonances in the spectra are assigned. Variable-temperature in situ powder X-ray diffraction study of the hydrate $\text{Cs}_2(\text{UO}_2)(\text{Si}_2\text{O}_6)\cdot 0.5\text{H}_2\text{O}$ indicates that the framework structure is stable up to 800 °C and transforms to the structure of the title compound at 900 °C. A comparison of related uranyl silicate structures is made.

Introduction

Recently a large number of hydrothermally synthesized silicates of transition metals and main group elements have been reported.^{1–14} They show a rich structural chemistry, and

some of them show good thermal stability, absorption, and ion-exchange properties. Most of these compounds were synthesized with alkali metal cations in a Teflon-lined autoclave under mild hydrothermal conditions at 180–240 °C. We have also synthesized a number of new silicates of V, Nb, and In by high-temperature, high-pressure hydrothermal reactions at 500–600 °C in gold ampules.^{11–14} Compounds which are synthesized under high-*T*, high-*P* hydrothermal conditions generally have more compact structures as compared with those from mild hydrothermal reactions. The vanadium compounds appear to form the largest group among these synthetic silicates. The extremely rich structural chemistry of vanadium silicates is evidenced by at least seven different structures with the composition $\text{A}_2(\text{VO})\text{Si}_4\text{O}_{10}\cdot n\text{H}_2\text{O}$ ($\text{A} = \text{alkali- or alkaline-earth-metal}$

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- (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) Ferreira, A.; Lin, Z.; Rocha, J.; Morais, C. M.; Lopes, M.; Fernandez, C. *Inorg. Chem.* **2001**, *40*, 3330.

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

(12) Kao, H.-M.; Lii, K.-H. *Inorg. Chem.* **2002**, *41*, 5644.

(13) Hung, L.-I.; Wang, S.-L.; Kao, H.-M.; Lii, K.-H. *Inorg. Chem.* **2003**, *42*, 4057.

(14) Huang, L.-I.; Wang, S.-L.; Szu, S.-P.; Hsieh, C.-Y.; Kao, H.-M.; Lii, K.-H. *Chem. Mater.* **2004**, *16*, 1660.

cation, $n \geq 0$).^{2–5} Jacobson et al. reported that a series of uranium silicates (denoted as USH- n) have been developed by replacing the VO²⁺ cation in the vanadium(IV) silicates with UO₂²⁺ as the bridging metal species.^{15–17} A uranium silicate has also been synthesized by using an organic ammonium cation as a structure-directing agent.¹⁶ An interesting uranyl silicate was produced by vapor hydration experiments on a U-doped borosilicate glass at 200 °C.¹⁸ Structural study reveals the potential of this compound to incorporate radionuclides from nuclear-waste glasses. Many of these synthetic uranium silicates have new open-framework structures without mineral analogues. In this paper, we report the synthesis and structural characterization by single-crystal X-ray diffraction and ²⁹Si and ¹³³Cs MAS NMR spectroscopy of a new uranium silicate, Cs₂(UO₂)(Si₂O₆) (denoted as **1**), whose structure is analogous to that of Cs₂(UO₂)(Si₂O₆)·0.5H₂O (USH-5Cs).¹⁷ Both compounds contain 8-ring channels, although the anhydrous compound was prepared under high- T , high- P hydrothermal conditions. A temperature-dependent powder X-ray diffraction study of the hydrate has also been performed.

Experimental Section

Synthesis. High-temperature, high-pressure hydrothermal synthesis was performed 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.¹⁹ The degree of filling of the autoclave by water at room temperature was 50%. A reaction mixture of 174 μ L of CsOH(aq) (50 wt %), 35.8 mg of UO₃ (Cerac, 99.8%), and 30.1 mg of SiO₂ (Alfa Aesar, 99.995%) (molar ratio Cs:U:Si = 8:1:4) in a 2.4 cm long gold ampule (inside diameter = 0.48 cm) was heated at 550 °C for 3 d. The pressure 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 and quenched at room temperature by removing the autoclave from the furnace. The product was filtered off, washed with water, rinsed with ethanol, and dried at ambient temperature. The reaction produced 50.5 mg of yellow-green polygon crystals. A qualitative EDX analysis of several yellow-green crystals confirmed the presence of Cs, U, and Si. Powder X-ray data were collected on a Shimadzu XRD-6000 automated powder diffractometer with Cu K α radiation equipped with a scintillation detector. Data were collected in the range $5^\circ \leq 2\theta \leq 50^\circ$ using the θ – 2θ mode in a Bragg–Brentano geometry. The bulk product was a single phase of Cs₂(UO₂)(Si₂O₆), **1**, because its powder pattern was in good agreement with the calculated pattern based on the results from single-crystal X-ray diffraction. The program XPOW in the SHELXTL version 5.1 software package was used for XRPD simulation. The yield was 58.7% based on uranium. The sample was used for solid-state NMR spectroscopy.

The hydrated compound Cs₂(UO₂)(Si₂O₆)·0.5H₂O (USH-5Cs) was prepared by heating UO₂(CH₃COO)₂ (0.2121 g), tetramethyl orthosilicate (0.448 mL, 98%), CsOH(aq) (1.743 mL, 50 wt %),

Table 1. Crystallographic Data for Cs₂(UO₂)(Si₂O₆)

chem formula	Cs ₂ O ₈ Si ₂ U
$a/\text{\AA}$	15.137(1)
$b/\text{\AA}$	15.295(1)
$c/\text{\AA}$	16.401(1)
$V/\text{\AA}^3$	3797.2(8)
Z	16
fw	688.03
space group	<i>Ibca</i> (No. 73)
$T, ^\circ\text{C}$	23
$\lambda(\text{Mo K}\alpha), \text{\AA}$	0.710 73
$D_{\text{calc}}, \text{g}\cdot\text{cm}^{-3}$	4.814
$\mu(\text{Mo K}\alpha), \text{cm}^{-1}$	249.2
R_1^a	0.0355
wR_2^b	0.0829

^a $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2(F_c^2)]/3$, where $a = 0.0147$ and $b = 167.34$.

and water (3 mL) (molar ratio U:Si:Cs = 1:4:20) in a 23 mL Teflon-lined autoclave at 230 °C for 7 d followed by slow cooling at 10 °C h⁻¹ to room temperature. The product was monophasic as indicated by powder X-ray diffraction. The thermal stability of USH-5Cs was investigated using variable-temperature (30–900 °C under N₂) in situ powder X-ray diffraction.

Single-Crystal X-ray Diffraction. A suitable yellow-green crystal of **1** having dimensions 0.12 × 0.20 × 0.22 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. Intensity data were collected at room temperature in 1271 frames with ω scans (width 0.30°/frame). The program SADABS was used for absorption correction ($T_{\text{min/max}} = 0.329/0.965$).²⁰ On the basis of reflection conditions, statistical analysis of the intensity distributions, and successful solution and refinement of the structure, the space group was determined to be *Ibca* (No. 73). The structure was solved by direct methods and difference Fourier syntheses. Four Cs sites were located and refined with full occupancy. The bond-valence parameters $R_{ij} = 2.074 \text{ \AA}$ and $b = 0.554 \text{ \AA}$ for ¹⁶U⁶⁺ polyhedra were used to calculate the bond-valence sum at each uranium site,²¹ and the values are U(1) = 6.15 and U(2) = 6.14 valence units, indicating that both uranium atoms are hexavalent, consistent with the color of the crystals. The final cycles of least-squares refinement including atomic coordinates, anisotropic thermal parameters for all non-hydrogen atoms converged at $R_1 = 0.0355$ and $wR_2 = 0.0829$. The largest residual electron densities in the final difference Fourier maps are near uranium atoms (2.53 e \AA^{-3} at 1.06 \AA from U(2); -1.16 e \AA^{-3} at 0.00 \AA from U(1)). For heavy atom compounds, it is normal to find ripples of up to $\pm 10\%$ of the atomic number of the heavy atom/ \AA^3 at a distance of 0.6–1.2 \AA from it.²² All calculations were performed using the SHELXTL version 5.1 software package.²³ The crystal data and structure refinement parameters are given in Table 1, and selected bond lengths, in Table 2.

Solid-State NMR Measurements. All NMR spectra were acquired on a Bruker AVANCE-400 spectrometer, operating at 79.46 and 52.49 MHz for ²⁹Si and ¹³³Cs nuclei, respectively. A Bruker probe equipped with 4 mm rotors was used. ²⁹Si and ¹³³Cs

- (15) Wang, X.; Huang, J.; Liu, L.; Jacobson, A. J. *J. Mater. Chem.* **2002**, *12*, 406.
 (16) Wang, X.; Huang, J.; Jacobson, A. J. *J. Am. Chem. Soc.* **2002**, *124*, 15190.
 (17) Huang, J.; Wang, X.; Jacobson, A. J. *J. Mater. Chem.* **2003**, *13*, 191.
 (18) Burns, P. C.; Olson, R. A.; Finch, R. J.; Hanchar, J. M.; Thibault, Y. *J. Nucl. Mater.* **2000**, *278*, 290.
 (19) Luth, W. C.; Tuttle, O. F. *Am. Mineral.* **1963**, *48*, 1401.

- (20) Sheldrick, G. M. *SADABS, Program for Siemens Area Detector Absorption Corrections*; University of Göttingen: Göttingen, Germany, 1997.
 (21) Burns, P. C.; Ewing, R. C.; Hawthorne, F. C. *Can. Mineral.* **1997**, *35*, 1551.
 (22) Massa, W. *Crystal Structure Determination*; Springer-Verlag: Berlin, 2000.
 (23) Sheldrick, G. M. *SHELXTL Programs*, version 5.1; Bruker AXS GmbH: Karlsruhe, Germany, 1998.

Table 2. Selected Bond Lengths (Å) for Cs₂(UO₂)(Si₂O₆)^a

U(1)–O(4)	2.249(6) (2×)	U(1)–O(7)	2.238(7) (2×)
U(1)–O(9)	1.812(7) (2×)	U(2)–O(3)	2.235(6) (2×)
U(2)–O(6)	2.239(6) (2×)	U(2)–O(8)	1.820(6) (2×)
Si(1)–O(1)	1.608(3)	Si(1)–O(2)	1.635(7)
Si(1)–O(3)	1.604(6)	Si(1)–O(4)	1.617(7)
Si(2)–O(2)	1.645(7)	Si(2)–O(5)	1.644(4)
Si(2)–O(6)	1.601(7)	Si(2)–O(7)	1.618(7)

^a Note: Cs–O distances are available from Supporting Information.

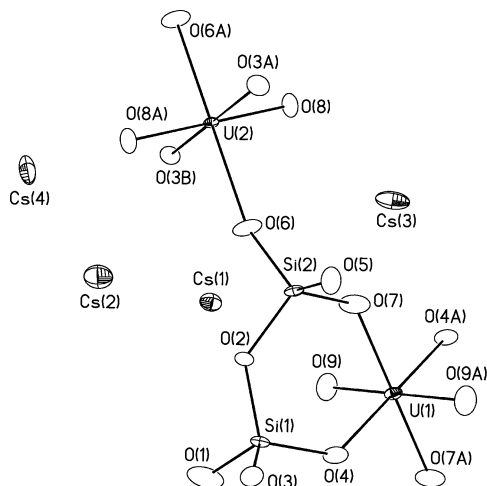


Figure 1. Building units of **1** showing the atom-labeling scheme. Thermal ellipsoids are shown at 50% probability.

MAS (magic angle spinning) NMR spectra were recorded with an excitation pulse of 30 and 15°, a spinning rate of 5 and 10 kHz, and a recycle delay of 60 and 1 s, respectively. The chemical shifts were externally referenced to tetramethylsilane (TMS) for ²⁹Si NMR and aqueous CsCl solution for ¹³³Cs NMR, both at 0 ppm.

Results and Discussion

Structure. As shown in Figure 1, the structure of **1** is constructed from the following structural elements: 2 SiO₄ tetrahedra, 2 UO₆ tetragonal bipyramids, and 4 Cs sites. Both Si atoms are at general positions, but all U and Cs atoms are at special positions. U(1) and U(2) are located at inversion centers, and all Cs atoms sit on 2-fold axes. The observed Si–O bond lengths (1.601–1.645 Å, average 1.623 Å) and O–Si–O bond angles (106.6–114.1°) are typical values and are within the normal range.²⁴ The SiO₄ tetrahedra share corners with other tetrahedra to form an achter single chain, namely a single chain with a period of eight tetrahedra. All oxygen atoms in the chain are either bridging oxygen atoms O_{br} linking two Si atoms or terminal atoms O_{term} which coordinate to U atoms. The Si–O_{br}–Si angles are 167.3, 133.0, and 135.2° for O(1), O(2), and O(5), respectively. All UO₆ tetragonal bipyramids have unsymmetrical oxygen coordination such that two U–O bonds are short (1.812 and 1.820 Å), forming the linear uranyl unit O=U=O²⁺, as is typical for U⁶⁺ in crystal structures, with other longer U–O bonds (2.235–2.249 Å) in the plane normal to this UO₂ axis. Uranyl ions occur in three coordination polyhedra in crystal structures: tetragonal bipyramidal, pentagonal bipyramidal,

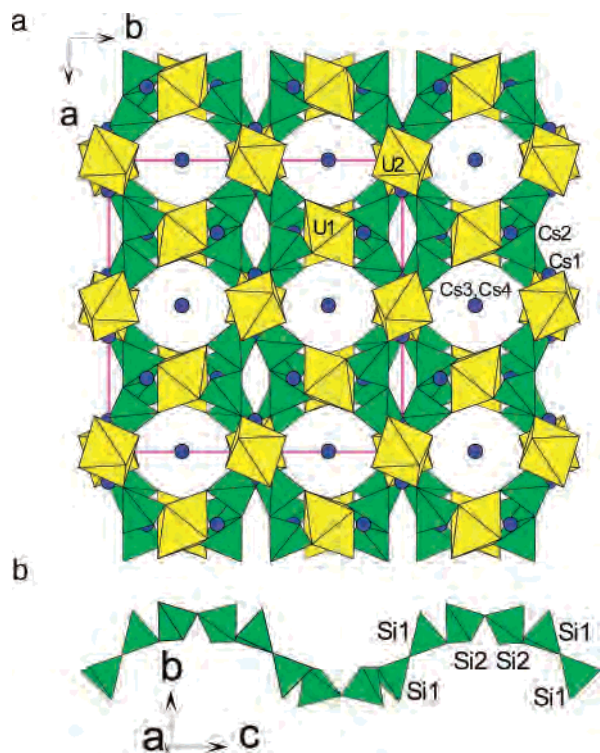


Figure 2. (a) Structure of **1** viewed along the *c*-axis. The yellow and green polyhedra are UO₆ octahedra and SiO₄ tetrahedra, respectively. Blue circles are Cs atoms. (b) Section of a silicate chain in **1**.

and hexagonal bipyramidal, with uranyl pentagonal bipyramids being the most common. All Cs sites are fully occupied. The coordination number of the Cs atom was determined on the basis of the maximum cation–anion distance by Donnay and Allmann.²⁵ A limit of 3.70 Å was set for Cs–O interactions, which gives the following coordination numbers: Cs(1), CN = 9 + 1, the first number referring to the number of neighboring atoms at the shorter distance; Cs(2), CN = 9; Cs(3), CN = 6; Cs(4), CN = 6 + 2; mean bond lengths of 3.285, 3.308, 3.108, and 3.200 Å, respectively.

The 3-D framework of **1** consists of discrete UO₆ tetragonal bipyramids and corrugated achter single chains of SiO₄ tetrahedra extending parallel to the *c*-axis (Figure 2). Each of the UO₆ tetragonal bipyramids shares its four equatorial vertexes with four silicate tetrahedra, two in each adjacent silicate chain to form the framework. Uranyl ions are oriented subperpendicular to the chains and do not link to the silicate tetrahedra. Eight-membered ring channels and two smaller six-membered ring channels are formed along [001], [010], and [100] directions. Cs(3) and Cs(4) are located in the center of 8-ring channels, whereas Cs(1) and Cs(2) are on the edge of 6-ring channels. The structure of **1** is closely related to that of USH-5Cs, but they crystallize in different space groups (*Ibca* vs *Pbca*). In the structure of the former all Cs atoms and one silicate oxygen atom, O(2), sit on 2-fold axes, and both uranium atoms are at inversion centers. In contrast, all atoms in the latter are at general positions. The SiO₄ tetrahedra in each single chain in **1** have a UDDUDUUD orientation, where U refers to a terminal oxygen corner

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

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

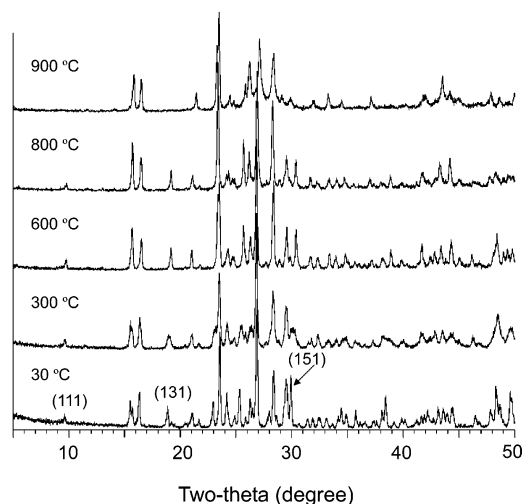


Figure 3. Variable-temperature X-ray powder patterns for the hydrate Cs₂(UO₂)(Si₂O₆)·0.5H₂O.

pointing up and D down, while in USH-5Cs they have a UUUUUDD orientation. The 8-ring channels along [001] in **1** are more rounded than those in USH-5Cs. Cs(3) and Cs(4) are located at the center of the 8-ring channel. Cs(1) and Cs(2) are at sites between 8-ring channels. In the structure of USH-5Cs one Cs atom is located at the center of the 8-ring channel, another Cs atom and the lattice water molecule are near the wall of the channel, and the other two Cs atoms are at sites between the channels. It is very likely that on dehydration the Cs atom near the wall shifts to the center of the channel. The high-temperature/high-pressure synthetic route facilitates crystal growth of dehydrated phase and may produce new compounds which are distinct from those by typical mild or moderate-condition hydrothermal methods. For example, the anhydrous vanadium silicate Cs₂-VOSi₆O₁₄,²⁶ which was prepared at 500 °C and ~110 MPa, adopts a structure considerably different from that of the hydrous compound Cs₂VOSi₆O₁₄·3H₂O,³ which was prepared at 240 °C, but both of them contain 8-ring channels.

X-ray Phase Study. A combination of variable-temperature in situ powder X-ray diffraction (Figure 3) and TGA studies of USH-5Cs show that the dehydration is the first event on heating and is completed at about 600 °C, the framework structure retains up to 800 °C, and the transformation from USH-5Cs to **1** occurs at about 900 °C. On cooling, the structural change from **1** to USH-5Cs does not occur. The unit cell of USH-5Cs shrinks on dehydration, and some reflections shift to higher 2θ angles. Some of the reflections in the USH-5Cs powder pattern disappear to give the powder pattern of **1**. Such a transition is because of the lattice type change from primitive to body centered. For example, (111), (131), and (151) reflections disappear at 900 °C. This study shows that the framework structure of the hydrate has a good thermal stability.

²⁹Si and ¹³³Cs MAS NMR. The ²⁹Si MAS NMR spectrum of USH-5Cs displays one resonance with its maximum intensity at -81.3 ppm. Although there are 4 unique Si(2Si, 2U) sites in the framework, all Si environments are too

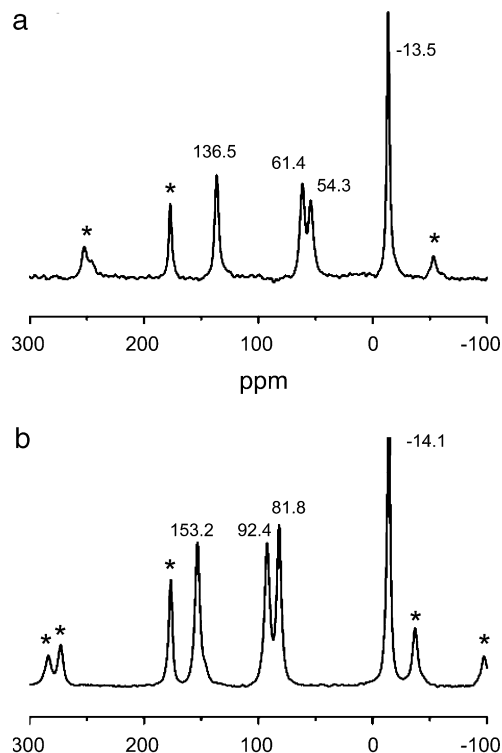


Figure 4. ¹³³Cs MAS NMR spectra of (a) **1** and (b) USH-5Cs, acquired at a spinning speed of 10 kHz. Asterisks denote spinning sidebands.

similar to discriminate, so the resonance can be ascribed to overlapping peaks. In contrast to USH-5Cs, the ²⁹Si MAS NMR spectrum of **1** shows two resonances at -81.2 and -87.8 ppm with nearly identical intensities, corresponding to two distinct silicon sites as determined by X-ray diffraction. It has been reported that the ²⁹Si chemical shift depends on the average value of the four Si-O-T bond angles (three Si-O-Si angles and one Si-O-U angle for each silicon atom) and shifts upfield with increasing Si-O-T bond angle.²⁷ The average Si-O-T bond angles in **1** are 143.8 and 140.4° for Si(1) and Si(2), respectively. The resonances at -87.8 ppm are therefore assigned to Si(1), and the other resonance is assigned to Si(2). The ¹³³Cs MAS NMR spectrum of **1** displays four sharp isotropic peaks at 136.5, 61.4, 54.3, and -13.5 ppm (Figure 4a). The sidebands were determined by varying the spinning speed. The four peaks correspond to four unique Cs sites as determined from X-ray diffraction. ¹³³Cs nuclei in inorganic cesium compounds show a moderate chemical shift range of about 300 ppm. The assignment of the isotropic peaks in the ¹³³Cs MAS NMR spectrum is based on the bond valence sum (BVS) calculation results. The valence of the Cs atom is equal to the sum of the bond valences between Cs and coordinating O atoms. Valence is defined as the number of electrons that take part in bonding. The electron density about the Cs atom is expected to increase with decreasing BVS, and the resonance signal should lie at a higher magnetic field. The BVS decreases in the following order with the BVS values in parentheses: Cs(4) (1.14) > Cs(1) (1.03) > Cs(3) (1.01) > Cs(2) (0.93). Consequently, the four peaks at 136.5, 61.4,

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

(27) Radeaglia, R.; Engelhardt, G. *Chem. Phys. Lett.* **1985**, *114*, 28.

54.3, and -13.5 ppm can be assigned to Cs(4), Cs(1), Cs(3), and Cs(2), respectively. The ^{133}Cs MAS NMR spectrum of USH-5Cs is analogous to that of **1** and shows four resonances at 153.2, 92.4, 81.8, and -14.1 ppm (Figure 4b), which correspond to four symmetry-independent Cs cation sites.

The intensities of the ^{133}Cs resonances displayed by both **1** and USH-5Cs do not agree with what is expected from the crystal structure. Since ^{133}Cs is an $I = 7/2$ nucleus, a smaller pulse flip angle was also used to obtain quantitative spectra. However, the spectra are the same even with an angle less than 8° . If the rising time of the pulse is considered, a 15° pulse, as described in the Experimental Section, is actually shorter than expected. The differences in intensity could result from two factors, namely chemical shift anisotropy (CSA) and quadrupolar interactions of ^{133}Cs spins. We have also recorded ^{133}Cs MAS NMR spectra at a higher magnetic field (500 MHz for ^1H spins) and at a much faster spinning speed (26 kHz) on a Varian/Chemagnetics Infinityplus NMR spectrometer using a 2.5 mm Chemagnetics double-tuned probe (see Supporting Information). The relative spectral intensities of these four Cs sites are nearly the same as those obtained at a lower magnetic field strength, indicating that CSA is not the major factor for the differences in intensity. A close examination of the spectra recorded at 9.39 T shows that the fwhh (full width at half-height) of the peak for Cs(2) (at -13.5 ppm) is 162 Hz which is significantly smaller as compared with other peaks (fwhh = 218–268 Hz). In addition the change in the isotropic shift for Cs(2) at a higher magnetic field is 4.6 ppm which is smaller than the changes for other peaks (5.4–6.5 ppm). Given that the second-order quadrupolar interaction is inversely proportional to the magnetic field strength, both the smaller line width and smaller change in the isotropic shift of Cs(2) indicate that the quadrupolar interaction for Cs(2) is smaller than those for other Cs sites, although the quadrupolar interactions for all of these Cs sites are small. The peak intensities can still be different because of a significant contribution of satellite transitions (particularly the $|1/2\rangle$ to $|3/2\rangle$ and $|-1/2\rangle$ to $|-3/2\rangle$) to the isotropic resonance. Since the quadrupolar interaction for Cs(2) is the smallest, the peak at -13.5 ppm has a larger contribution from satellite transitions and thus is more intense than others.

Related Structures. The structural chemistry of uranyl silicates has been extensively studied by Burns et al.²⁸ 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. Several uranyl silicate minerals with U:Si ratios 2:1 and 1:1 are known. The U atoms in these minerals are in pentagonal bipyramidal coordination, with the uranyl polyhedra sharing edges to form chains. But these structures do not involve polymerization of silicate 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.^{15,17} In contrast, the frameworks of $\text{A}_2(\text{UO}_2)(\text{Si}_2\text{O}_6)\cdot 0.5\text{H}_2\text{O}$ (A = Rb, Cs) and the title compound are composed of discrete UO_6 units and single chains of silicate tetrahedra.¹⁷ Interestingly, the structure of $\text{K}_5(\text{UO}_2)_2[\text{Si}_4\text{O}_{12}(\text{OH})]$ contains discrete UO_6 polyhedra connected by oligosilicate anions of four silicate tetrahedra.²⁹ A few uranyl silicates with U:Si ratios of 1:2.5 and 1:4 have also been reported, and their structures contain chains and sheets of vertex-sharing silica tetrahedra.^{17,18,30}

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 and solid-state NMR spectroscopy. Its structure consists of corrugated single chains of SiO_4 tetrahedra linked by UO_6 tetragonal bipyramids to form a 3-D framework containing 8- and 6-ring channels. The ^{29}Si and ^{133}Cs MAS NMR spectra are consistent with the crystal structure as determined from X-ray diffraction, and the resonances in the NMR spectra are assigned. The structure is analogous to that of hydrate phase $\text{Cs}_2(\text{UO}_2)(\text{Si}_2\text{O}_6)\cdot 0.5\text{H}_2\text{O}$, which was prepared under mild hydrothermal conditions. Variable-temperature in situ powder X-ray diffraction shows that the framework structure of the hydrate phase retains up to 800°C and transforms to the structure of the title compound at about 900°C . The high-temperature/high-pressure hydrothermal method facilitates crystal growth of dehydrated phase.

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Supporting Information Available: Crystallographic data for $\text{Cs}_2(\text{UO}_2)(\text{Si}_2\text{O}_6)$ in CIF format, X-ray powder patterns, and ^{133}Cs NMR spectra measured at 11.7 T and a spinning speed of 26 kHz. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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

(29) Chen, C.-S.; Kao, H.-M.; Lii, K.-H. *Inorg. Chem.* **2005**, *44*, 935.

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