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Syntheses, Structures, and Characterization of Open-Framework Uranyl Germanates

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Three uranyl germanates, $Cs_2[(UO_2)(Ge_2O_6)](H_2O)$ (**1**), $Ag[(UO_2)_2(HGe_2O_7)](H_2O)$ (**2**), and $Ag_2[(UO_2)_3(GeO_4)_2](H_2O)_2$ (**3**) were synthesized under hydrothermal conditions, and their structures were determined by single crystal X-ray diffraction. Compound **1** crystallizes in space group $P2_1/n$, $a = 7.9159(2)$ Å, $b = 21.5949(5)$ Å, $c = 12.4659(3)$ Å, $\beta = 96.964(1)°$, $V = 2115.24(9)$ Å^3, $Z = 8$; **2** is orthorhombic $Ama2$, $a = 7.124(1)$ Å, $b = 10.771(2)$ Å, $c = 14.024(1)$ Å, $V = 1076.2(4)$ Å^3, $Z = 4$; **3** is orthorhombic $Pnma$, $a = 10.0462(6)$ Å, $b = 7.4699(5)$ Å, $c = 17.776(1)$ Å, $V = 1334.0(2)$ Å^3, $Z = 4$. These compounds are frameworks of uranyl square (**1**) or pentagonal (**2, 3**) bipyramids and four-membered rings of germanate tetrahedra (**1**), dimers of germanate tetrahedra (**2**), or chains of GeO_5 triangular bipyramids (**3**). There are channels through each of the frameworks that contain the low-valence cations and the H_2O groups. Compound **1** dehydrates upon heating, but the framework remains intact to at least 900 °C.

Introduction

Uranium is the fuel of commercial nuclear energy and is a problematic environmental contaminant at U mine and mill sites as well as various facilities involved in the cold-war era buildup of nuclear weapons. Hexavalent U, the water-soluble oxidation state, forms the linear $(UO_2)^{2+}$ uranyl ion in most solids and coordination complexes. The crystal chemistry of the uranyl ion is diverse, in part, because it commonly occurs in square, pentagonal, or hexagonal bipyramidal coordination.[1,2] In inorganic systems the equatorial ligands of these bipyramids are usually O, OH, or H_2O, and linkage of uranyl polyhedra with other uranyl polyhedra or other oxyanions is common. As only the equatorial ligands are usually involved in such linkages, sheets of polyhedra dominate. Only ~15% of inorganic uranyl compounds possess framework structures, although this class of compounds is expanding as new modes of polyhedral connectivity are identified.

Uranyl germanates are of particular interest to us because germanates are known to form a variety of framework structures in different chemical systems.[3−9] In contrast with Si, which is tetrahedrally coordinated in oxide structures other than under extremely high pressures, Ge exhibits GeO_4 tetrahedra, GeO_5 trigonal bipyramids, and GeO_6 octahedra owing to its larger atomic radius. Ge−O bond lengths are longer than Si−O bond lengths (1.76 versus 1.61 Å) and the Ge−O−Ge angles are typically more acute than Si−O−Si angles.[9] The flexible coordination geometries of Ge foster the formation of open-framework structures with extra-large pores, such as FDU-4[10] and ASU-16[11] that contain channels bounded by 24-membered rings. Six uranyl germanates, $(UO_2)_2(GeO_4)(H_2O)_2$,[12] $Cu(H_2O)_4(UO_2)_2(HGeO_4)_2(H_2O)_2$,[13] $Cs_6[(UO_2)_3(Ge_2O_7)_2]\cdot 4H_2O$,[14] $A_3(U_2O_4)(Ge_2O_7)$ (A = Rb, Cs),[15] and $Rb_3(U_3O_6)(Ge_2O_7)$[16] have been reported, and each exhibit framework structures.

In order to diversify the range of uranyl-based compounds that possess framework structures, we are exploring the synthesis of uranyl germanates under mild hydrothermal conditions. Here we report the synthesis, structures, and characterization of three novel uranyl germanate framework materials.

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(1) Burns, P. C. *Can. Mineral.* **2005**, *43*, 1839.
(2) Burns, P. C.; Ewing, R. C.; Hawthorne, F. C. *Can. Mineral.* **1997**, *35*, 1551.
(3) Beitone, L.; Loiseau, T.; Ferey, G. *Inorg. Chem.* **2002**, *41*, 3962.
(4) Bu, X.; Feng, P.; Stucky, G. D. *Chem. Mater.* **2000**, *12*, 1505.
(5) Cascales, C.; Gutierrez-Puebla, E.; Monge, M. A.; Ruiz-Valero, C. *Angew. Chem., Int. Ed.* **1998**, *37*, 129.
(6) Conradsson, T.; Zou, X.; Dadachov, M. S. *Inorg. Chem.* **2000**, *39*, 1716.
(7) Li, H.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, *120*, 10569.
(8) Medina, M. E.; Iglesia, M.; Monge, M. A.; Gutierrez-Puebla, E. *Chem. Commun.* **2001**, 2548.
(9) O'Keeffe, M.; Yaghi, O. M. *Chem.—Eur. J.* **1999**, *5*, 2796.
(10) Zhou, Y.; Zhu, H.; Chen, Z.; Chen, M.; Xu, Y.; Zhang, H.; Zhao, D. *Angew. Chem., Int. Ed.* **2001**, *40*, 2166.
(11) Plevert, J.; Gentz, T. M.; Laine, A.; Li, H.; Young, V. G.; Yaghi, O. M.; O'Keeffe, M. *J. Am. Chem. Soc.* **2001**, *123*, 12706.
(12) Legros, J. P.; Jeannin, Y. *Acta Crystallogr.* **1975**, *B31*, 1140.
(13) Legros, J. P.; Jeannin, Y. *Acta Crystallogr.* **1975**, *B31*, 1133.
(14) Lin, C.-H; Chiang, R.-K.; Lii, K.-H. *J. Am. Chem. Soc.* **2009**, *131*, 2068.
(15) Lin, C.-H.; Lii, K.-H. *Angew. Chem., Int. Ed.* **2008**, *47*, 8711.
(16) Lin, C.-H.; Chen, C. S.; Shiryaev, A. A.; Zubavichuv, Y. V.; Lii, K.-H. *Inorg. Chem.* **2008**, *47*, 4445.

Experimental Section

Synthesis. $UO_2(NO_3)_2 \cdot 6H_2O$ (MV Laboratories, lot no. P705-UA1), $UO_2(C_2H_3O_2) \cdot 2H_2O$ (MV Laboratories, lot no. P705UA1), GeO_2 (99.9%, Aldrich), CsOH (99.9%, Aldrich), and $AgNO_3$ (99%, Aldrich) were used as received without further purification. Distilled and Millipore filtered water with a resistance of 18.2 MΩ cm was used in all reactions. ***Caution***! *While the $UO_2(NO_3)_2 \cdot 6H_2O$ and $UO_2(C_2H_3O_2) \cdot 2H_2O$ used here contain depleted U, standard precautions for handling radioactive materials should be followed.*

$Cs_2[(UO_2)(Ge_2O_6)](H_2O)$ (**1**) was synthesized by loading 1.65 mL of a 4.24 M aqueous CsOH solution (7 mmol), 0.108 g $UO_2(C_2H_3O_2) \cdot 2H_2O$ (0.29 mmol), 0.443 g GeO_2 (4.24 mmol), and 2.7 mL of deionized water into a 23 mL Teflon-lined Parr reaction vessel that was sealed and heated at 220 °C for 7 days. After cooling, the product was washed with deionized water and allowed to dry in air. The synthesis gave a pure product of **1** consisting of bright-yellow needle-shaped crystals with a yield of 62.5% based on U. Energy dispersive analysis provided a Cs:U:Ge ratio of 2:1:2 (39:20:41%).

$Ag[(UO_2)_2(HGe_2O_7)](H_2O)$ (**2**) and $Ag_2[(UO_2)_3(GeO_4)_2](H_2O)_2$ (**3**) were synthesized by reacting 0.086 g $UO_2(NO_3)_2 \cdot 6H_2O$ (0.25 mmol), 0.043 g $AgNO_3$ (0.25 mmol), 0.105 or 0.026 g GeO_2 (1 or 0.25 mmol), and 2 mL of distilled water under hydrothermal conditions at 220 °C for 9 days. After slowly cooling to room temperature, small yellow needle-shaped crystals of **2** or **3**, as minor products, were found together with abundant yellow powder. Yields were not determined due to the difficulty of isolating crystals of **2** or **3**. Attempts to increase the yield and purity of **2** and **3** by adjusting the reaction temperature, heating time, ratios of reactants, and solution pH did not succeed in producing a superior product. Energy dispersive spectral analyses provided Ag:U:Ge ratios of 1:2:2 (18:42:40%) and 2:3:2 (28:43:29%) for **2** and **3**, respectively.

Crystallographic Studies. Single crystals of **1**−**3** were selected using a polarized-light stereomicroscope and were mounted on tapered glass fibers with epoxy for X-ray diffraction analysis. A sphere of diffraction data was collected for each compound at 110 K using a Bruker three-circle X-ray diffractometer equipped with an APEX CCD detector. The data were collected using monochromatic Mo Kα radiation with a frame width of 0.3° in ω and a counting time per frame of 10 s. Unit-cell parameters were refined by least-squares techniques using the Bruker SMART software.[17] The SAINT software[18] was used for data integration including Lorentz, background, and polarization corrections. Empirical absorption corrections were applied using the program SADABS. The SHELXTL version 5 series of programs was used for the solution and refinement of the crystal structures. Selected data collection parameters and crystallographic information are listed in Table 1. Selected bond distances of each compound are listed in Tables 2−4. In the case of compound **2**, the structure is reported in space group *Ama*2. The structure is approximately compatible with *Cmcm*, but refinement in this space group resulted in significantly poorer agreement indices and required treatment of the Ag atoms as disordered sites.

Infrared Spectroscopy. Infrared spectra were obtained for single crystals of **1**−**3** using a SensIR technology IlluminatIR FT-IR microspectrometer. A single crystal of each compound was placed on a glass slide, and the spectrum was collected with a diamond ATR objective. Each spectrum was taken from 650 to 4000 cm^{-1} with a beam aperture of 100 μm. Infrared spectra are shown in Figure S1 (see Supporting Information).

Thermal Gravimetric Analysis (TGA). A TGA measurement was conducted using a Netzsch TG209 F1 Iris thermal analyzer for 28 mg of powdered **1** in an Al_2O_3 crucible that was heated from 20 to 900 °C at a rate of 5 °C/min under flowing nitrogen gas. The data are shown in Figure 1.

Powder X-ray Diffraction. Powder X-ray diffraction patterns of **1** and its residue after heating to 900 °C were collected using a Scintag $\theta-\theta$ diffractometer equipped with a solid-state point detector at room temperature over the angular range 5−90° (2θ, Cu Kα) with a step width of 0.05° and a fixed counting time of 1 s/step. The experimentally derived diffraction patterns are compared with a pattern calculated for the single-crystal structure in Figure 2.

Table 1. Crystallographic Data for **1**−**3**

formula	**1**	**2**	**3**
formula mass	793.03	921.11	1331.01
crystal system	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/n$	*Ama*2	*Pnma*
a (Å)	7.9159(2)	7.124(1)	10.0462(6)
b (Å)	21.5949(5)	10.771(2)	7.4699(5)
c (Å)	12.4659(3)	14.024(3)	17.776(1)
β (°)	96.964(1)		
V (Å^3)	2115.24(9)	1076.2(4)	1334.01(15)
Z	8	4	4
λ (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	27.727	37.358	43.688
2θ (°) maximun	25.25	33.67	28.27
ρ_{calcd} (g cm^{-3})	4.980	5.685	6.627
GOF	0.863	1.033	0.997
$R(F)$ for ${F_o}^2 > 2\sigma({F_o}^2)^a$	0.0360	0.0260	0.0206
$2\sigma({F_o}^2)^a$ $2\sigma({F_o}^2)^a$			
$R_w({F_o}^2)^b$	0.0694	0.0495	0.0449

^{a} $R(F) = \sum\|F_o|-|F_c\|/\sum|F_o|$. ^{b} $R_w(F_o^2) = [\sum[w(F_o^2-F_c^2)^2]/\sum wF_o^4]^{1/2}$.

Table 2. Selected Bond Lengths (Å) for **1**

distances (Å)			
U(1)−O(1)	1.820(8)	Ge(1)−O(4)	1.718(8)
U(1)−O(2)	1.828(7)	Ge(1)−O(8)	1.741(8)
U(1)−O(3)	2.204(8)	Ge(1)−O(13)	1.751(7)
U(1)−O(4)	2.231(9)	Ge(1)−O(14)	1.737(8)
U(1)−O(5)	2.264(8)	Ge(2)−O(6)	1.732(8)
U(1)−O(6)	2.223(8)	Ge(2)−O(9)	1.739(8)
U(2)−O(7) × 2	1.817(7)	Ge(2)−O(14)	1.757(8)
U(2)−O(8) × 2	2.219(8)	Ge(2)−O(15)	1.779(7)
U(2)−O(9) × 2	2.256(8)	Ge(3)−O(3)	1.748(8)
U(3)−O(10) × 2	1.809(8)	Ge(3)−O(12)	1.708(8)
U(3)−O(11) × 2	2.243(7)	Ge(3)−O(15)	1.762(7)
U(3)−O(12) × 2	2.239(8)	Ge(3)−O(16)	1.757(8)
		Ge(4)−O(5)	1.730(8)
		Ge(4)−O(11)	1.732(8)
		Ge(4)−O(13)	1.784(7)
		Ge(4)−O(16)	1.761(8)

Table 3. Selected Bond Lengths (Å) for **2**

distances (Å)			
U(1)−O(1)	1.799(9)	Ge(1)−O(3) × 2	1.754(6)
U(1)−O(2)	1.769(9)	Ge(1)−O(5)	1.735(8)
U(1)−O(3) × 2	2.287(6)	Ge(1)−O(9)	1.771(9)
U(1)−O(4) × 2	2.459(6)	Ge(2)−O(4) × 2	1.723(6)
U(1)−O(5)	2.354(9)	Ge(2)−O(8)	1.777(9)
U(2)−O(3) × 2	2.450(6)	Ge(2)−O(9)	1.761(9)
U(2)−O(4) × 2	2.312(5)		
U(2)−O(6)	1.796(9)	Ag(1)−O(1) × 2	2.500(7)
U(2)−O(7)	1.780(9)	Ag(1)−O(6) × 2	2.655(8)
U(2)−O(8)	2.348(9)	Ag(1)−O(10) × 2	2.397(8)

Bond-Valence Analysis. Bond-valence sums were calculated for $U^{6+}-O$,[2] $Ge^{4+}-O$,[19] $Cs^{+}-O$,[19] and $Ag^{+}-O$[19] interactions and are listed in Tables S1−S3 (see Supporting Information). The calculated sums are in agreement with theoretical valences.

Fluorescence Spectroscopy. Fluorescence data were acquired for compound **1** for a single crystal using a Craic Technologies UV−vis-NIR microspectrophotometer with a fluorescence attachment. Excitation was achieved using 365 nm light from a mercury lamp. The fluorescence spectrum is provided in the Figure 3. Compounds **2** and **3** did not give fluorescence spectra.

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(17) Bruker, A. X. S. *SMART*; Bruker AXS: Madison, WI, 1998.
(18) Bruker, A. X. S. *SAINT*; Bruker AXS: Madison, WI, 1998.
(19) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192.

Table 4. Selected Bond Distances (Å) for **3**

distances (Å)			
U(1)−O(1)	1.799(6)	Ge(1)−O(3)	1.763(4)
U(1)−O(2)	1.805(6)	Ge(1)−O(4)	2.001(2)
U(1)−O(3) × 4	2.326(4)	Ge(1)−O(7)	1.783(4)
U(1)−O(4)	2.488(6)	Ge(1)−O(8)	1.781(4)
U(2)−O(5)	1.802(6)	Ge(1)−O(9)	1.878(2)
U(2)−O(6)	1.811(6)		
U(2)−O(7) × 2	2.310(4)		
U(2)−O(8) × 2	2.406(4)	Ag(1)−O(1)	2.675(5)
U(2)−O(9)	2.311(6)	Ag(1)−O(2)	2.715(4)
U(3)−O(4)	2.586(6)	Ag(1)−O(5)	2.715(5)
U(3)−O(7) × 2	2.314(4)	Ag(1)−O(6)	2.482(4)
U(3)−O(8) × 2	2.283(4)	Ag(1)−O(10)	2.929(7)
U(3)−O(10)	1.797(6)	Ag(1)−O(11)	2.527(4)
U(3)−O(11)	1.809(6)	Ag(1)−O(12)	2.371(5)

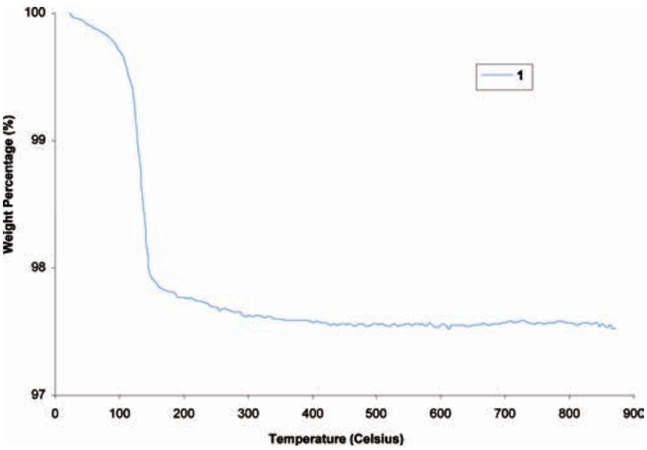

Figure 1. Thermal gravimetric analysis profile for **1**.

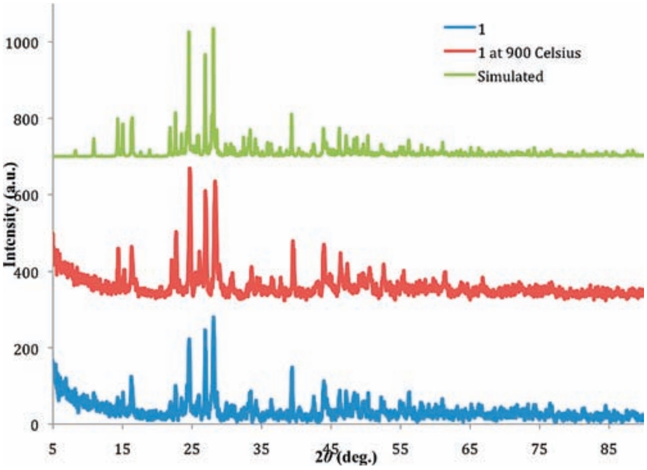

Figure 2. Powder X-ray diffraction patterns for **1**, its TGA residue, and the simulated pattern from the single-crystal structure.

Results

Structure Descriptions. The structure of **1** contains three crystallographically unique U^{6+} cations that are present as approximately linear $(UO_2)^{2+}$ uranyl ions, with $U-O_{Ur}$ (Ur: uranyl) bond lengths ranging from 1.809(8) to 1.828(7) Å. Each of the uranyl ions is coordinated by four ligands that are arranged at the equatorial positions of square bipyramids that are capped by the O atoms of the uranyl ions. The equatorial ligands are all O atoms of germanate tetrahedra, and equatorial bond lengths ($U-O_{eq}$) (eq: equatorial) vary from 2.204(8) to 2.264(8) Å. These U−O bond distances are consistent with the average $U-O_{Ur}$ and $U-O_{eq}$ bond lengths of 1.82(5) and 2.26(6) Å for 54 uranyl square bipyramids in 47 well-refined structures.[1] The four symmetrically distinct Ge^{4+} cations are tetrahedrally coordinated by O atoms, with Ge−O bond distances ranging from 1.708(8) to 1.784(7) Å.

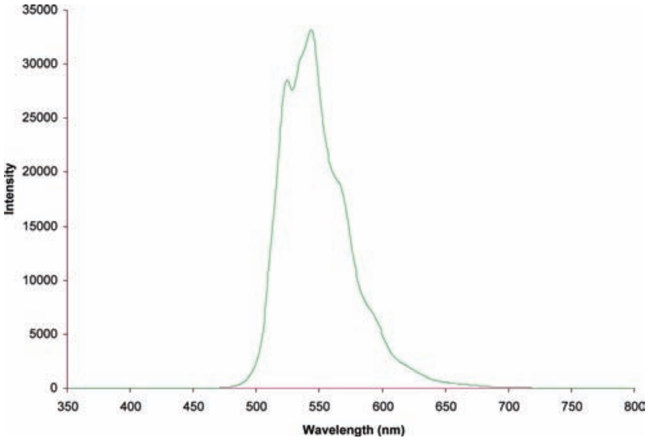

Figure 3. Fluorescence spectrum of **1**.

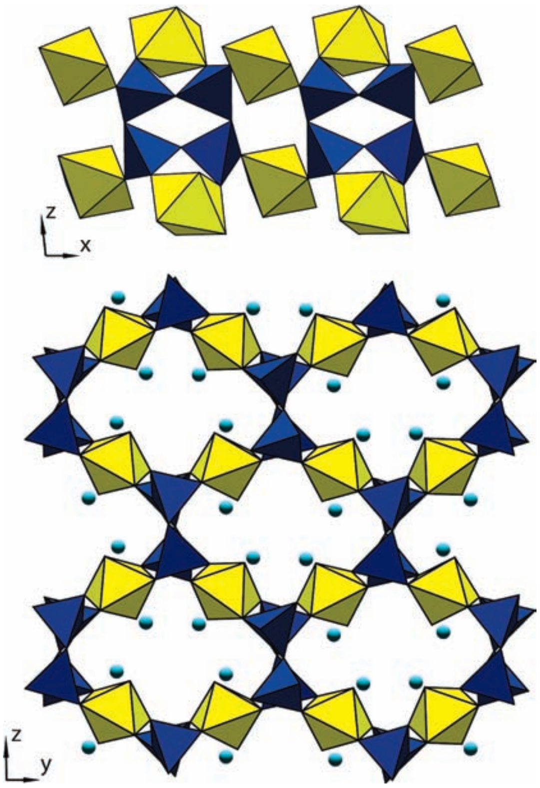

Figure 4. The structure of **1**: (top) one-dimensional chain of Ge_4O_{10} rings bridged through uranyl square bipyramids, and (bottom) three-dimensional $[(UO_2)(Ge_2O_6)]^{2-}$ framework with channels extending along [100]. Uranyl and germanate are shown as yellow and blue polyhedra, respectively. Pink balls represent Cs cations, and water molecules are omitted for clarity.

In the structure of **1**, four GeO_4 tetrahedra share bridging O atoms to create a four-membered Ge_4O_{10} ring (Figure 4). Within this ring, Ge−O−Ge angles of the bridges range from 126.0(4)° to 132.3(5)°, consistent with the average Ge−O−Ge angle of 130°.[9] Each Ge_4O_{10} ring is bridged along [100] through two uranyl square bipyramids that share an equatorial vertex with each of two adjacent Ge_4O_{10} rings. This linkage creates a chain that extends along [100]. The chain is decorated on each side by additional uranyl square bipyramids that share equatorial vertices with two GeO_4 tetrahedra that are adjacent in the Ge_4O_{10} ring. As a result, each GeO_4 tetrahedron in the ring shares two of its vertices with other tetrahedra, and the other two with square bipyramids. Each square bipyramid shares all four of its equatorial vertices with Ge_4O_{10} rings, resulting in a framework with composition $[(UO_2)(Ge_2O_6)]^{2-}$ (Figure 4). Cs^+ cations and H_2O molecules are located in channels that are bounded by 10-membered rings consisting of 4 uranyl bipyramids and 6 germanate tetrahedra. Channels extend along [100] with dimensions of 5.2 by 5.4 Å, as measured from the centers of O atoms on either side.

There are two and three distinct U^{6+} cations in the structures of **2** and **3**, respectively. All of the U^{6+} cations are present as uranyl ions in pentagonal bipyramidal coordination environments. The $U-O_{Ur}$ and $U-O_{eq}$ bond lengths range from 1.769(9) to 1.811(6) Å and 2.287(6) to 2.586(6) Å in these two compounds, respectively. These values are consistent with the range of bond lengths in uranyl pentagonal bipyramids in 143 structures, for which the averages are 1.79(3) and 2.4(1) Å, respectively.[1]

In the structure of **2**, two distinct GeO_4 tetrahedra are linked through a bridging O atom, giving a Ge_2O_7 dimer. Within this dimer, Ge−O bond lengths range from 1.723(6) to 1.777(9) Å, and the Ge−O−Ge angle is 127.4(3)°. Based on the bond-valence analysis given in Table S2 (see Supporting Information), either of the O5 or O8 atoms are protonated locally but not both within a given dimer, and the dimer composition is $(HGe_2O_7)^{5-}$.

In the structure of **2**, uranyl pentagonal bipyramids are connected by sharing two equatorial edges with adjacent bipyramids, giving a chain of bipyramids extending along [100] that is one bipyramid wide (Figure 5). These chains are linked into a three-dimensional framework through the HGe_2O_7 dimers, both through the sharing of polyhedral edges and vertices. The framework has a composition of $[(UO_2)_2(HGe_2O_7)]^-$, and channels extend along [100] (Figure 5). These channels are bounded by 10-membered rings consisting of 4 uranyl pentagonal bipyramids and 6 germanate tetrahedra. The channel dimensions are 5.3 by 5.3 Å, as measured from the centers of bounding O atoms. Ag^+ ions and water molecules are in these channels (Figure 5).

In contrast to the structures of compounds **1** and **2** that contain GeO_4 tetrahedra, the Ge^{4+} cations in compound **3** are in distorted triangular bipyramidal coordination environments. Within the triangular bipyramid there are three short Ge−O bonds [1.763(4), 1.781(4), and 1.783(2) Å], one intermediate bond [1.878(2) Å], and one long bond [2.001(2) Å]. These GeO_5 polyhedra are linked to each other by vertex sharing and form a novel germanate chain that extends along [010] (Figure 6). Within the chain, the Ge−O−Ge angle is 150.3(3)°. Chains of uranyl pentagonal bipyramids that are analogous to those in compound **2** are linked to the germanate chains such that each pentagonal bipyramid shares two of its equatorial edges with the GeO_5 polyhedra. The resulting framework has composition $[(UO_2)_3(GeO_4)_2]^{2-}$ (Figure 6). Ag^+ cations and water molecules are in channels surrounded by 12-membered rings consisting of 6 uranyl pentagonal bipyramids and 6 GeO_5 polyhedra. These channels have dimensions of 5.3 by 9.1 Å, as measured between the centers of bounding O atoms, and extend along [010].

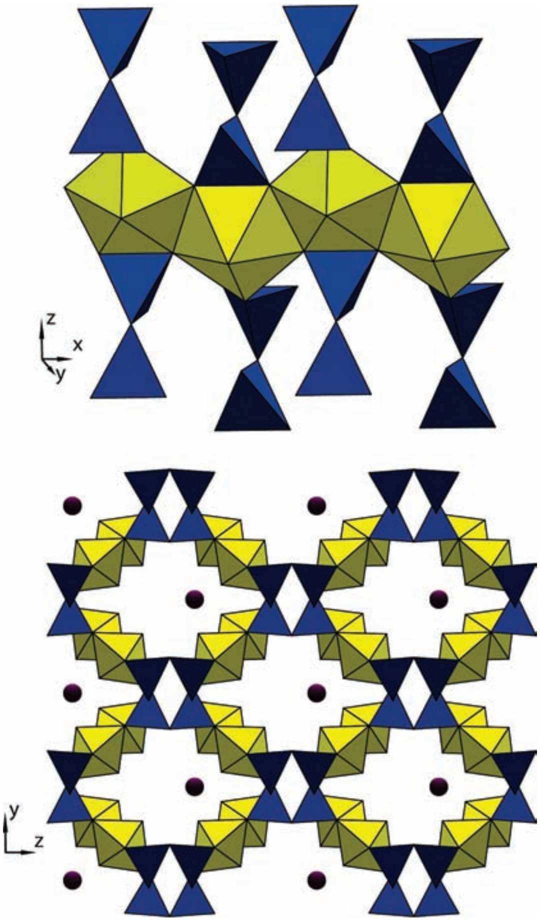

Figure 5. The structure of **2**: (top) chain of Ge_2O_7 dimers bridged by uranyl pentagonal bipyramds, and (bottom) three-dimensional $[(UO_2)_2(HGe_2O_7)]^-$ framework with channels extending along [100]. Uranyl and germanate are shown as yellow and blue polyhedra, respectively. Purple balls represent Ag cations, and water molecules are omitted for clarity.

Spectroscopy, Thermal Analysis. The infrared spectra of **1**−**3** are similar (see Figure S1, Supporting Information). Several sharp bands occurring in the range of 800−950 cm^{-1} (812 and 884 cm^{-1} in **1**, 834 and 898 cm^{-1} in **2**, and 812, 857, and 936 cm^{-1} in **3**) are assigned as asymmetric stretches of the uranyl units.[20] Strong bands at 731 and 768 cm^{-1} in **1**, 709 and 781 cm^{-1} in **2**, and 686 and 758 cm^{-1} in **3** are attributed to the asymmetric stretching vibrations of Ge−O bonds.[21] A broad band in the range of 3000−3500 cm^{-1} and several weak bands centered at 1600 cm^{-1} are associated with O−H vibrations of the water molecules.

The fluorescence spectrum of **1** exhibits several characteristic peaks related to coupling between charge-transfer transitions and uranyl-stretching and -bending modes.[22] One band at 520 nm and four bands at 534, 545, 570, and 598 nm correspond to electronic transmissions $S_{11} \rightarrow S_{00}$ and $S_{10} \rightarrow S_{0v}$ with $v = 0-4$, respectively. Compared to the spectrum of $UO_2(NO_3)_2 \cdot 6H_2O$, **1** displays a red shift of about

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(20) Cejka, J. *Rev. Mineral.* **1999**, *38*, 521.

(21) Paquesledent, M. T. *Spectrochim. Acta* **1976**, *A32*, 383.

(22) Denning, R. G.; Norris, J. O. W.; Short, I. G.; Snellgrove, T. R.; Woodwark, D. R. Lanthanide and Actinide Chemistry and Spectroscopy, *ACS Symposium Series 131*; Edelstein, N. M., Ed; American Chemical Society: Washington, DC, 1980; Chapter *15*.

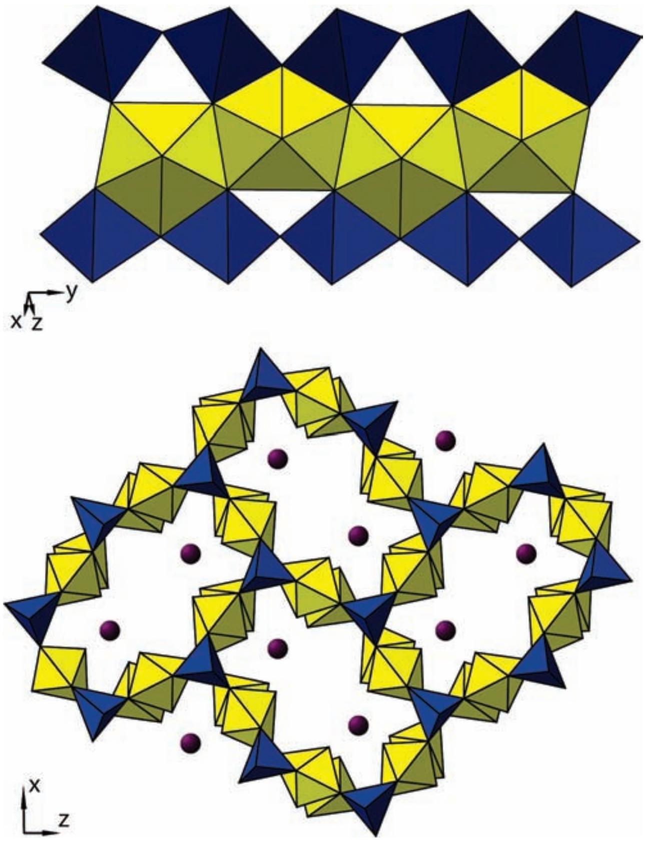

Figure 6. The structure of **3**: (top) edge-sharing uranyl chain linked to chains of GeO_5 triangular bipyramids, and (bottom) three-dimensional $[(UO_2)_3(GeO_4)_2]^{2-}$ framework with channels extending along [010]. Legend as in Figure 5.

30 nm that may be due to the difference in coordination environments about the U cations, the hydration level, and the crystal packing.[23] No significant fluorescence signals were observed for **2** and **3**, presumably owing to quenching associated with the Ag^+ cations.[24]

The thermal data collected for **1** reveals a simple one-step 2.42% weight loss over the temperature range 80−200 °C (Figure 1). This weight loss corresponds to the exit of the H_2O groups located within the channels of the framework structure and is in good agreement with the 2.27% expected weight loss based on the crystallographically derived formula. Following dehydration, the uranyl germanate framework persists at least to 900 °C. The powder diffraction pattern of the residue after heating to 900 °C is very similar to that of the unheated sample, indicating the uranyl germanate framework remained intact (Figure 2).

Discussion

The compounds **1**−**3** have novel framework structures consisting of uranyl square and pentagonal bipyramids as well as GeO_4 tetrahedra or GeO_5 triangular bipyramids. Polymerization of germanate polyhedra in these structures gives four-membered rings (**1**), dimers (**2**) and infinite chains (**3**).

The uranyl germanate framework found in **1** is topologically identical to that of the uranyl silicate $RbNa[(UO_2)(Si_2O_6)](H_2O)$,[25] but **1** is the first uranyl compound with a four-membered ring of germanate tetrahedra. This framework is stable to at least 900 °C in the case of the germanate compound, in contrast to the silicate compound which collapses at about 700 °C.[14]

The compounds $A_3(U_2O_4)(Ge_2O_7)$ (A = Rb, Cs)[15] have the same U:Ge ratio as **2**, but their frameworks are distinct. In $A_3(U_2O_4)(Ge_2O_7)$, the U cations are in square bipyramids, but two of these contain U(VI), and the other is U(V). The square bipyramids share two equatorial vertices, giving a chain that extends along [001]. Adjacent chains are connected through the Ge_2O_7 dimers into a framework that contains channels bounded by seven-membered rings of polyhedra.

Although GeO_5 polyhedra have been reported in transition-metal, lanthanide, and organically templated germanates, **3** is the first uranyl compound with GeO_5 polyhedra. The chain of GeO_5 polyhedra in **3** appears to be unique in germanates. The compounds **3** and $Cs_6[(UO_2)_3(Ge_2O_7)_2]\cdot 4H_2O$[14] both have framework structures with channels that are bounded by 12 uranyl and germanate polyhedra. In the latter compound, the channels have more equal dimensions of 7 Å^2. $Cs_6[(UO_2)_3(Ge_2O_7)_2]\cdot 4H_2O$ contains only U(VI) in square bipyramids. The $U(1)O_6$ bipyramids are connected by Ge_2O_7 dimers into sheets that are linked into a framework through $U(2)O_6$ polyhedra. The compound $Rb_3(U_3O_6)(Ge_2O_7)$[16] contains only U(V) in square bipyramids. Three parallel chains of U bipyramids, which are connected by corner sharing of O atoms along [001], are joined through shared equatorial O atoms, resulting in a triangular column. These columns are further linked into a framework by the Ge_2O_7 dimers. This framework contains two channels that are bounded either by three bipyramids and two tetrahedra or just by three bipyramids.

Uranyl silicate minerals are often found in the oxidized areas of U ore deposits. Many of these belong to the uranophane group, all members of which contain uranyl silicate sheets with low-valence cations located in the interlayer regions.[1] Uranyl pentagonal bipyramids share equatorial edges, giving chains that are one polyhedron wide. These chains are linked into a sheet by sharing equatorial edges or vertices with SiO_4 tetrahedra, such that each tetrahedron is three-connected within the sheet. The remaining vertex of each silicate tetrahedron is directed into the interlayer, where it coordinates interlayer cations.

The uranyl silicate mineral haiweeite ($Ca[(UO_2)_2Si_5O_{12}(OH)_2](H_2O)_3$)[26] has sheets that are more complex than those in the uranophane group. These contain double-wide crankshaft-like chains of silicate tetrahedra that link chains of uranyl pentagonal bipyramids. Weeksite ($K_{1.26}Ba_{0.25}Ca_{0.12}[(UO_2)_2(Si_5O_{13})]H_2O$)[27] contains the same uranyl silicate sheets as haiweeite, but here tetrahedra of adjacent sheets are linked, resulting in a framework. Soddyite ($(UO_2)_2(SiO_4)(H_2O)_2$)[28] is a framework consisting of edge-sharing uranyl pentagonal bipyramids that are cross-linked by sharing equatorial edges with silicate tetrahedra. The resulting framework is identical to that found in the Ge analogue.[12]

It is apparent that the structures of uranyl germanates tend toward frameworks, whereas those of uranyl silicates in

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(23) Valeur, B. Molecular Fluorescence, 1st ed.; Wiley-VCH: Weiheim, Germany, 2002.

(24) Yokoyama, Y; Moriyasu, M.; Ikeda, S. *J. Inorg. Nucl. Chem.* **1977**, *39*, 2211.

(25) Wang, X.; Huang, J.; Liu, L.; Jacobson, A. J. *J. Mater. Chem.* **2002**, *12*, 406.

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

(27) Jackson, J. M.; Burns, P. C. *Can. Mineral.* **2001**, *39*, 187.

(28) Demartin, F.; Gramaccioli, C. M.; Pilati, T. *Acta Crystallogr.* **1992**, *C48*, 1.

nature are most commonly built from uranyl silicate sheets. However, hydrothermal syntheses giving uranyl silicates framework structures that display similar connectivies to uranyl germanates have been reported in some cases.[23]

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Supporting Information Available: Crystallographic information files, crystallographic tables, bond-valence analyses, and infrared spectra.This material is available free of charge via the Internet at http://pubs.acs.org.