# U(VI) Uranyl Cation−Cation Interactions in Framework Germanates

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S *Supporting Information*

ABSTRACT: The isomorphous compounds $NH_4[(UO_6)_2(UO_2)_9(GeO_4)(GeO_3(OH))]$ (**1**), $K[(UO_6)_2(UO_2)_9(GeO_4)(GeO_3(OH))]$ (**2**), $Li_3O[(UO_6)_2(UO_2)_9(GeO_4)(GeO_3(OH))]$ (**3**), and $Ba[(UO_6)_2(UO_2)_9(GeO_4)_2]$ (**4**) were synthesized by hydrothermal reaction at 220 °C. The structures were determined using single crystal X-ray diffraction and refined to R_1 = 0.0349 (**1**), 0.0232 (**2**), 0.0236 (**3**), 0.0267 (**4**). Each are trigonal, $P\bar{3}1c$. **1**: a = 10.2525(5), c = 17.3972(13), V = 1583.69(16) Å^3, Z = 2; **2**: a = 10.226(4), c = 17.150(9), V = 1553.1(12) Å^3, Z = 2; **3**: a = 10.2668(5), c = 17.0558(11), V = 1556.94(15) Å^3, Z = 2; **4**: a = 10.2012(5), c = 17.1570(12), V = 1546.23(15) Å^3, Z = 2. There are three symmetrically independent U sites in each structure, two of which correspond to typical $(UO_2)^{2+}$ uranyl ions and the other of which is octahedrally coordinated by six O atoms. One of the uranyl ions donates a

cation−cation interaction, and accepts a different cation−cation interaction. The linkages between the U-centered polyhedra result in a relatively dense three-dimensional framework. Ge and low-valence sites are located within cavities in the framework of U-polyhedra. Chemical, thermal, and spectroscopic characterizations are provided.
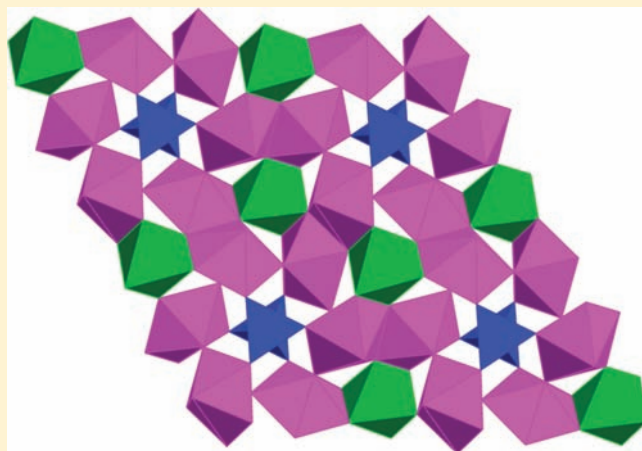
1. INTRODUCTION

The $(UO_2)^{2+}$ uranyl ion is central to the complex chemistry of U(VI).[1] Recent studies have provided unexpected results that challenge our understanding of this normally unreactive functional group.[2] Of particular interest in the current study is the occurrence of U(VI) uranyl cation−cation interactions.[3,4] First found in solutions containing uranyl and neptunyl,[5] a cation−cation interaction occurs where an O atom of one actinyl ion is also an equatorial ligand of a bipyramid about a second actinyl ion. Put another way, one actinyl ion coordinates one or two other actinyl ions. Such interactions provide novel linkages within structural units.

The U(VI) uranyl ion is normally present in structures coordinated by four, five, or six ligands arranged at the equatorial vertices of square, pentagonal, or hexagonal bipyramids, respectively. In inorganic extended solids, these bipyramids usually link with each other, or through other oxyanions, forming sheets and, to a lesser extent, chains of polyhedra.[6] Frameworks of uranyl polyhedra are relatively uncommon, and where they do occur sheet-like layering is often present. Cation−cation interactions only occur in 2% of U(VI) compounds.[6] They are much more common in Np(V) neptunyl compounds and U(V) compounds, both of which have been the focus of considerable recent attention.[7−10] Np(V) neptunyl cation−cation interactions result in a variety of framework structures, as well as a few sheets and chains.[8] The few inorganic U(VI)

compounds with cation−cation interactions all adopt framework structures, and creation of cation−cation interactions in U(VI) compounds may increase the dimensionality of the structures.

We are interested in the role of U(VI) uranyl cation−cation interactions in the structural topologies and properties of actinide materials. On the basis of the handful of known structures, inclusion of cation−cation interactions results in unique structure connectivities. Here, we examine the uranyl-germanate system because, by analogy with uranyl silicates, uranyl germanates are expected to present considerable structural diversity. The structures of nine U germanate compounds are already known and present the expected complexity.[11] One contains U(V), two are mixed-valence U(V)−U(VI) compounds, and in six all of the U is U(VI). With the exception of one that contains structural sheets, each has a complex framework structure.

Here we report four uranyl germanates that were obtained under mild hydrothermal conditions: $NH_4[(UO_6)_2(UO_2)_9(GeO_4)(GeO_3(OH))]$ (**1**), $K[(UO_6)_2(UO_2)_9(GeO_4)(GeO_3(OH))]$ (**2**), $Li_3O[(UO_6)_2(UO_2)_9(GeO_4)(GeO_3(OH))]$ (**3**),

and $Ba[(UO_6)_2(UO_2)_9(GeO_4)_2]$ (**4**). Each presents a complex framework that includes cation–cation interactions.

2. EXPERIMENTAL SECTION

Synthesis. Crystals of compounds **1**–**4** were synthesized by heating solutions consisting of aqueous uranyl nitrate, GeO_2, and the corresponding base. *Caution! Although depleted uranium was used in these studies, standard precautions for handling radioactive materials should be followed.* Solutions were heated at 220 °C in 23 mL Teflon-lined stainless steel reaction vessels placed in preheated mechanical convection ovens. Products were recovered by filtration and in each case consisted of deep red-orange stacks of pseudo-hexagonal platy crystals ranging in diameter to 500 μm, as well as a fine-grained yellow powder consisting of $UO_3(H_2O)_{0.8}$ and $(UO_2)_2(GeO_4) \cdot 2H_2O$, verified by powder X-ray diffraction. Optimization of solution pH and Ge:U ratios provided an increased yield of crystals relative to the microcrystalline phases, but a pure yield was not obtained. **1**: 0.675 mL of 2 M aqueous uranyl acetate, 0.675 mL of an aqueous-powder slurry containing 0.010 g of GeO_2 powder, 0.413 mL of 4.24 M aqueous NH_4OH. **2**: 1.35 mL of 2 M aqueous uranyl nitrate, 1.35 mL of an aqueous-powder slurry contqaining 0.020 g of GeO_2 powder, 0.825 mL of 4.24 M aqueous KOH. **3**: 1.35 mL of 1 M aqueous uranyl nitrate, 1.35 mL of an aqueous-powder slurry containing 0.020 g of GeO_2 powder, 0.825 mL of 4.24 M aqueous LiOH. **4**: 0.675 mL of 0.2 M aqueous uranyl nitrate, 0.675 mL of an aqueous-powder slurry containing 0.010 g of GeO_2 powder, 0.413 mL of 0.25 M aqueous $Ba(OH)_2$.

Single Crystal X-ray Diffraction. Crystals were examined under cross-polarized light, and suitable single crystals of each compound that showed no twinning were selected. These were mounted on a glass fiber for single crystal X-ray diffraction studies using a Bruker three-circle single-crystal X-ray diffractometer equipped with an APEX II CCD detector and Mo Kα radiation. A sphere of three-dimensional diffraction data was collected at room temperature for each crystal using frame widths of 0.5° in ω. Data were integrated and corrected for background, Lorentz, and polarization effects using the APEX II software, and were corrected for absorption empirically using SADABS. Additional data was collected for a crystal of each compound at 110 K. The crystallographic parameters and refined structure parameters reported in the tables are from the room-temperature data.

Structures were solved and refined using SHELXTL[12] on the basis of F^2. Systematic absences of reflections indicated that a c glide is the only translational symmetry operator present. Structures were solved and refined in space groups $P\bar{3}1c$, $C2/c$, Cc, and $P1$, although the unit cell is metrically trigonal. Merging R factors for all of the data sets ranged from 4.7 to 9.9%, being fairly high because the crystals diffract weakly because of their size. Merging R factors for the monoclinic space groups were only slightly lower than those of $P\bar{3}1c$. As discussed below, each structure model included positional disorder of some sites. Such disorder was required even in the lower symmetry space groups, including $P1$, so $P\bar{3}1c$ was selected for final refinements. The final refinement in each case included all atomic positional coordinates, anisotropic displacement parameters for U sites, and a mixture of anisotropic and isotropic displacement parameters for the remaining atoms as the data permitted. Refined anisotropic displacement parameters for the Ge sites in compounds **1**–**3** were highly elongated, and a split-site model was subsequently adopted. The corresponding Ge(1) and Ge(2) sites refined to a separation of ~0.7 Å, only one of which is occupied locally. Data was recollected at 110 K for each compound. However, this did not alleviate the disorder evidenced by the elongated displacement parameters. Selected crystallographic information is given in Table 1, and interatomic separations are provided in Table 2. Full details of the structures are provided in the Supporting Information.

IR Spectra. An IR spectrum was obtained for each compound using a SensIR Technology IlluminatIR FT-IR microspectrometer equipped with a diamond ATR objective. Each spectrum was taken from 650 to 4000 cm^{-1} with a beam aperture of 100 μm for crystals that were stored in a desiccator for 24 h prior to analysis. Infrared spectra are provided in the Supporting Information.

UV–vis–NIR. Absorption data were acquired for each compound using a Craic Technologies UV–vis–NIR microspectrophotometer. Each spectrum was taken from 250 to 1500 nm. Absorption spectra are provided in the Supporting Information.

Electron Microprobe Analysis. Elemental analyses were done for single crystals of each compound using a Cameca SX50 electron microprobe. Standards were natural paracelsian (Ba), Ge metal, UO_2 (Oak Ridge), and microcline (K). Quantitative wavelength dispersive analyses were done for U, Ge, K, and Ba. Qualitative wavelength dispersive scans confirmed the presence of N in **1**, and did not reveal the presence of F in any case (which could have been derived from the Teflon-lined vessels). Oxide abundances are averages of three to five spots analyzed, with the expected value from the structure determination in parentheses (wt %): **1**: UO_3 = 93.6 (93.0), GeO_2 = 5.65 (6.19); **2**: UO_3 = 93.1 (92.2), K_2O = 1.36 (1.38), GeO_2 = 5.57 (6.13); **3**: UO_3 = 93.3 (93.1), GeO_2 = 5.70 (6.19); **4**: UO_3 = 89.9 (89.4), BaO = 4.22 (4.36), GeO_2 = 5.58 (5.94).

Thermogravimetric Analysis. Thermogravimetric measurement was done for compound **2** using a Netzsch TG209 F1 Iris thermal analyzer. The sample was loaded into an Al_2O_3 crucible and heated from 20 to 900 °C at a rate of 5 °C/min under flowing nitrogen gas. Data are shown in the Supporting Information.

3. RESULTS

Crystals of compounds **1** through **4** were readily attained under mild hydrothermal conditions at 220 °C. Structure analysis, spectroscopic studies, and chemical analysis support the assigned compositions of each compound. Thermogravimetric analysis of **2** indicated only less than 0.3 wt % loss through heating to 900 °C, and powder X-ray diffraction indicated that there was no structural change upon heating to 900 °C.

The structures of compounds **1** through **4** were refined in space group $P\bar{3}1c$. Each presents essentially identical frameworks of U polyhedra. In each the U(2) and U(3) cations are present as typical $(UO_2)^{2+}$ uranyl ions with bond lengths ranging from 1.748(10) to 1.843(8) Å over the four compounds. The U(2)–O(5) bonds are the longest, and range from 1.822(7) to 1.843(8) Å, whereas the others are no longer than 1.790(8) Å. Each of the uranyl ions are coordinated by five O atoms that are arranged at the equatorial vertices of pentagonal bipyramids, with the bipyramids capped by the O atoms of the uranyl ions. Bond-valence sums at the U(2) and U(3) sites, calculated using coordination-specific parameters,[13] range from 5.91 to 6.03 vu, consistent with the formal valence of U(VI).

The U(1) cation in each structure is coordinated by six O atoms, all of which also belong to uranyl bipyramids, that are in a distorted octahedral arrangement. There are two distinct U(1)–O bond lengths in each structure. The U(1)–O(3) bond lengths range from 2.037(6) to 2.060(9) Å over the four structures, whereas the range for the U(1)–O(4) bonds is from 2.095(6) to 2.118(6) Å. Although unusual, U(VI) cations in distorted octahedral coordination similar to those found here have been reported in several structures.[6,13] Bond-valence sums at the U(1) site, calculated using coordination-specific parameters,[13] range from 5.89 to 6.10 vu in compounds **1** to **4**, consistent with the expected formal valence.

The U(1), U(2), and U(3) polyhedra share edges and vertices, resulting in a complex and rather dense framework (Figure 1). Consider first the U(2) pentagonal bipyramids that occur in layers perpendicular to [001] at $c = 0$ and 1/2. One of these layers

Table 1. Selected Crystallographic Parameters for Compounds 1−4

	1	2	3	4
structure formula	$NH_4[(UO_6)_2(UO_2)_9$ $(GeO_4)(GeO_3(OH))]$	$K[(UO_6)_2(UO_2)_9$ $(GeO_4)(GeO_3(OH))]$	$Li_3O[(UO_6)_2(UO_2)_9$ $(GeO_4)(GeO_3(OH))]$	$Ba[(UO_6)_2(UO_2)_9$ $(GeO_4)_2]$
formula weight	3385.52	3410.61	3408.33	3508.85
temperature (K)	296(2)	296(2)	296(2)	296(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
crystal system	trigonal	trigonal	trigonal	trigonal
space group	$P\bar{3}1c$ (No. 163)	$P\bar{3}1c$ (No. 163)	$P\bar{3}1c$ (No. 163)	$P\bar{3}1c$ (No. 163)
a (Å)	10.2525(5)	10.226(4)	10.2668(5)	10.2012(5)
b (Å)	10.2525(5)	10.226(4)	10.2668(5)	10.2012(5)
c (Å)	17.3972(13)	17.150(9)	17.0558(11)	17.1570(12)
volume (Å³)	1583.69(16)	1553.1(12)	1556.94(15)	1546.23(15)
Z	2	2	2	2
density (g/cm³)	7.100	7.293	7.270	7.537
μ (mm⁻¹)	58.0	59.3	59.0	60.7
$F(000)$	2774	2798	2794	2872
crystal size (mm)	0.029 × 0.012 × 0.005	0.035 × 0.017 × 0.006	0.045 × 0.034 × 0.007	0.066 × 0.038 × 0.005
theta range for data collection (deg)	2.29 to 27.56	2.30 to 27.69	2.29 to 27.57	2.31 to 27.58
limiting indices	$-13 \le h \le 13$ $-13 \le k \le 13$ $-22 \le l \le 22$	$-13 \le h \le 13$ $-13 \le k \le 13$ $-22 \le l \le 22$	$-12 \le h \le 13$ $-13 \le k \le 13$ $-21 \le l \le 22$	$-13 \le h \le 13$ $-13 \le k \le 13$ $-22 \le l \le 22$
reflections collected/unique	17559/1237 [R(int) = 0.0843]	17590/1229 [R(int) = 0.0781]	16252/1211 [R(int) = 0.0606]	17102/1197 [R(int) = 0.0740]
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	1237/0/83	1229/0/83	1211/1/86	1197/0/78
goodness-of-fit on F^2	1.199	1.006	1.201	1.140
final R indices [$I > 2\sigma(I)$]	R1 = 0.0349 wR2 = 0.0960	R1 = 0.0232 wR2 = 0.0561	R1 = 0.0236 wR2 = 0.0521	R1 = 0.0267 wR2 = 0.0750
R indices (all data)	R1 = 0.0383, wR2 = 0.0977	R1 = 0.0307, wR2 = 0.0593	R1 = 0.0287, wR2 = 0.0536	R1 = 0.0313, wR2 = 0.0772
largest diff. peak and hole (Å)	3.207 and −2.570	1.446 and −2.943	1.133 and −4.073	2.065 and −3.585

is shown in Figure 1b. Each U(2) pentagonal bipyramid shares an equatorial edge defined by O(4) atoms with an adjacent U(2) bipyramid, resulting in dimers that are canted about the −3 symmetry axis. These dimers are linked through cation−cation interactions, such that each U(2) uranyl ion donates one cation− cation interaction that is accepted by a U(2) uranyl ion of an adjacent dimer. Each dimer therefore is linked to two others by cation−cation interactions, which results in the layer of U(2) bipyramids that is perpendicular to [001].

The U(1) distorted octahedron is within the layer of U(2) bipyramids, where it is located on the −3 axis. Three of the octahedral edges are also equatorial edges of adjacent U(2) bipyramids.

The U(3) cations are located between the U(1)−U(2) layers (Figure 1a), where the pentagonal bipyramids are arranged about the −3 axis such that they occur in trimers with the bipyramids sharing the O(8) vertex. Each U(3) bipyramid shares two of its equatorial edges with U(2) bipyramids, one of which is from each adjacent U(1)−U(2) layer.

The U-centered polyhedra are linked to create a complex frame-work that contains cavities. Low-valence cations occur in one of these cavities. In the NH₄ (1), K (2) and Ba (4) compounds, the coor-dination environment about the low-valence cation is octahedral, with the vertices corresponding to symmetrically equivalent O atoms that are part of the uranyl ion associated with the U(2) cation. The interatomic distances are 2.809(7) and 2.773(8) Å for the K and Ba cations, respectively. Li is incompatible with this site owing to its small

size. Instead, in the Li compound, a Li₃O group resides in a cavity, with each Li coordinated by five O atoms in a distorted trigonal bipyramidal arrangement with bond distances ranging from 1.75(5) to 2.306(7) Å. In all cases (especially the Li compound (3)), large and elongated displacement parameters indicate positional disorder of the low-valence cation and to a smaller extent the associated O atoms.

The Ge atoms occur in cavities within the framework of U polyhedra that are elongated in the [001] direction (Figure 1b). The details of the coordination environments about the Ge sites are quite complex. In the NH₄ (1), K (2), and Li (3) compounds the electron density associated with the Ge sites is strongly elongated in the [001] direction. The site was subsequently split and refined as the Ge(1) and Ge(2) sites that refined to a separation of ~0.7 Å, each set at half occupancy. The coordina-tion environment about these cations may be loosely defined as trigonal bipyramidal. The equatorial O atoms are the symme-trically equivalent O(1) atoms. The apexes of the bipyramid are defined by the O(6) and O(8) atoms, each of which exhibit displacement parameters that are elongated in the [001] direc-tion, which is also parallel to the corresponding Ge−O bonds. The O(8) anion is bonded to three U(3) cations, whereas O(6) is shared between two Ge atoms only. If the true coordination environment about the Ge cations is trigonal bipyramidal, there is an infinite chain of these sites extending along [001] and the O(6) site is occupied by OH. A similar chain was recently reported in the structure of $Ag_2[(UO_2)_3(GeO_4)_2](H_2O)_2$.[14]

Table 2. Selected Interatomic Distances (Å) for Compounds 1−4[a]

1		2		3		4	
U(1)−O(3)	2.060(9)	U(1)−O(3)	2.037(6)	U(1)−O(3)[a]	2.053(6)	U(1)−O(3)[cc]	2.041(7)
U(1)−O(3)[a]	2.060(9)	U(1)−O(3)[a]	2.037(6)	U(1)−O(3)[b]	2.053(6)	U(1)−O(3)[dd]	2.041(7)
U(1)−O(3)[b]	2.060(9)	U(1)−O(3)[b]	2.037(6)	U(1)−O(3)	2.053(6)	U(1)−O(3)	2.041(7)
U(1)−O(4)	2.096(8)	U(1)−O(4)[b]	2.095(6)	U(1)−O(4)[b]	2.118(6)	U(1)−O(4)	2.109(7)
U(1)−O(4)[b]	2.096(8)	U(1)−O(4)[a]	2.095(6)	U(1)−O(4)	2.118(6)	U(1)−O(4)[cc]	2.109(7)
U(1)−O(4)[a]	2.096(8)	U(1)−O(4)	2.095(6)	U(1)−O(4)[a]	2.118(6)	U(1)−O(4)[dd]	2.109(7)
U(2)−O(2)	1.763(10)	U(2)−O(2)	1.760(7)	U(2)−O(2)	1.772(6)	U(2)−O(2)	1.790(7)
U(2)−O(5)[c]	1.828(10)	U(2)−O(5)[c]	1.822(7)	U(2)−O(5)[c]	1.833(6)	U(2)−O(5)	1.843(7)
U(2)−O(1)[d]	2.277(9)	U(2)−O(1)[d]	2.263(6)	U(2)−O(1)[d]	2.255(6)	U(2)−O(1)[j]	2.238(7)
U(2)−O(4)[e]	2.324(8)	U(2)−O(4)[e]	2.294(6)	U(2)−O(4)[e]	2.305(6)	U(2)−O(4)[l]	2.299(7)
U(2)−O(4)[f]	2.339(8)	U(2)−O(4)[s]	2.333(6)	U(2)−O(4)[f]	2.327(6)	U(2)−O(4)[dd]	2.329(7)
U(2)−O(5)[e]	2.428(9)	U(2)−O(5)[e]	2.430(6)	U(2)−O(5)[e]	2.418(6)	U(2)−O(5)[l]	2.416(7)
U(2)−O(3)[c]	2.492(9)	U(2)−O(3)[c]	2.479(7)	U(2)−O(3)[c]	2.472(6)	U(2)−O(3)	2.484(7)
U(3)−O(7)	1.748(10)	U(3)−O(7)[f]	1.751(7)	U(3)−O(7)	1.773(6)	U(3)−O(7)[ee]	1.771(7)
U(3)−O(7)[g]	1.748(10)	U(3)−O(7)	1.751(7)	U(3)−O(7)[g]	1.773(6)	U(3)−O(7)	1.771(7)
U(3)−O(3)[g]	2.364(9)	U(3)−O(3)[f]	2.374(6)	U(3)−O(1)[z]	2.373(6)	U(3)−O(1)[ff]	2.383(8)
U(3)−O(3)	2.364(9)	U(3)−O(3)	2.374(6)	U(3)−O(1)[a]	2.373(6)	U(3)−O(1)[j]	2.383(8)
U(3)−O(1)[h]	2.417(10)	U(3)−O(1)[g]	2.396(6)	U(3)−O(3)	2.396(6)	U(3)−O(3)	2.396(7)
U(3)−O(1)[a]	2.417(10)	U(3)−O(1)[a]	2.396(6)	U(3)−O(3)[g]	2.396(6)	U(3)−O(3)[ee]	2.396(7)
U(3)−O(8)[i]	2.5689(6)	U(3)−O(8)[x]	2.5150(11)	U(3)−O(8)[h]	2.4539(4)	U(3)−O(8)	2.4387(5)
Ge(1)−O(6)	1.735(5)	Ge(1)−O(6)	1.744(7)	Ge(1)−O(1)[i]	1.743(6)	Ge(1)−O(6)	1.711(8)
Ge(1)−O(1)[l]	1.777(9)	Ge(1)−O(1)[a]	1.750(7)	Ge(1)−O(1)[j]	1.743(6)	Ge(1)−O(1)[ll]	1.711(7)
Ge(1)−O(1)[m]	1.777(9)	Ge(1)−O(1)[a]	1.750(7)	Ge(1)−O(1)[k]	1.743(6)	Ge(1)−O(1)[j]	1.711(7)
Ge(1)−O(1)[n]	1.777(9)	Ge(1)−O(1)[a]	1.750(7)	Ge(1)−O(6)	1.747(3)	Ge(1)−O(1)	1.939(15)
Ge(2)−O(1)[l]	1.709(9)	Ge(2)−O(1)[a]	1.694(6)	Ge(2)−O(1)[a]	1.718(6)		
Ge(2)−O(1)[m]	1.710(9)	Ge(2)−O(1)[a]	1.694(6)	Ge(2)−O(1)[a]	1.718(6)		
Ge(2)−O(1)[n]	1.710(9)	Ge(2)−O(1)[a]	1.694(6)	Ge(2)−O(1)[a]	1.718(6)		
Ge(2)−O(8)[o]	1.881(7)	Ge(2)−O(8)[a]	1.93(2)	Ge(2)−O(8)[a]	1.767(11)		

[a] Symmetry transformations used to generate equivalent atoms: a: $x-1$, y, z; b: x+1, y, z; c: $-x$, $-y+1$, $-z+1$; d: $-y+1$, $x-y+1$, z; e: $-x+y$, $-x$, z; f: $x-y+1$, x, $-z+1$; g: $-y+1$, $-x$, $-z+3/2$; h: $-x+1$, $-y$, $-z+1$; i: $-y$, $x-y-1$, z; j: $-y+1$, $x-y$, z; k: $-x+y+1$, $-z+1$; l: $-x+y+1$, $-x+1$, z; m: $x-y-1$, $x-1$, $-z+1$; n: $-x$, $-y$, $-z$; o: y+1, x+1, z+1/2; p: $-x$, $-y$, $-z+1$; q: y, x, z+1/2; r: y+1, x, z+1/2; s: $-x+y$, $-x+1$, z; t: y-1, x-1, z$-1/2$; u: $x-y$, $-y+1$, z$-1/2$; v: x, x$-y$, $-z+3/2$; w: $-x+1$, $-x+y$, z$-1/2$; x: $-x+1$, $-x+1$, $-z+3/2$; y: $-y$, x$-y$, z; z: $-x+y$, y, $-z+3/2$; aa: x, x$-y+1$, $-z+3/2$; bb: $-y$, $-x+1$, $-z+3/2$; cc: $-x+2$, $-y+1$, $-z+1$; dd: $-y+1$, x$-y-1$, z; ee: x$-y$, x-1, $-z+1$; ff: $-y+1$, $-x+1$, $-z+1/2$; gg: $-x+y+2$, $-x+1$, z; hh: $-x+2$, $-y$, $-z+1$; ii: x, x$-y-1$, $-z+1/2$; jj: $-y+2$, x$-y$, z; kk: $-x+y+2$, $-x+2$, z; ll: $-y+2$, $-x+2$, $-z+1/2$; mm: $-x+y+2$, y, $-z+1/2$; nn: x, x$-y$, $-z+1/2$; oo: y+1, $-x+y+1$, $-z+1$.

However, the elongated displacement parameters of the Ge, O(6), and O(7) sites indicate in general an incompatibility with the extended framework of U-centered polyhedra. It appears that the Ge coordination polyhedra may best be regarded as transitional between tetrahedral and trigonal bipyramidal, and that local configurations differ considerably within the structure.

In the case of the Ba structure (4), splitting the Ge site over two positions did not significantly improve the refinement. Instead, the single Ge site is coordinated by four O atoms with bond distances in the range of 1.741(3) to 1.752(7) Å. The O(6) site bridges between Ge tetrahedra with a Ge−O−Ge bond angle of 180°. None of the O sites are protonated, consistent with incorporation of Ba in place of a monovalent cation in the corresponding structures of the NH$_4$ (1) and K (2) compounds.

4. DISCUSSION

The four uranyl germanates reported herein have complex framework structures that present several unusual characteristics. Foremost among these are the cation−cation interactions involving the U(2) uranyl ion, as this type of linkage occurs in only ~2% of U(VI) structures. The bonds within the U^{6+} uranyl ion are very strong, and correspond to about 1.7 valence units in the bond-valence formalism.[13] The linkages between the U^{6+} cation and equatorial ligands of its bipyramids are much weaker, about 0.5 valence units.[13] In U^{6+} compounds, cation−cation interactions are uncommon because mild overbonding occurs at the uranyl-ion O atom that also coordinates another uranyl ion. Where the actinyl ion contains a pentavalent cation (U^{5+} or Np^{5+}), the bonds are somewhat weaker. In these cases overbonding at the shared O atom is not significant, as demonstrated by the abundance of cation−cation interactions in compounds containing Np^{5+}.[8]
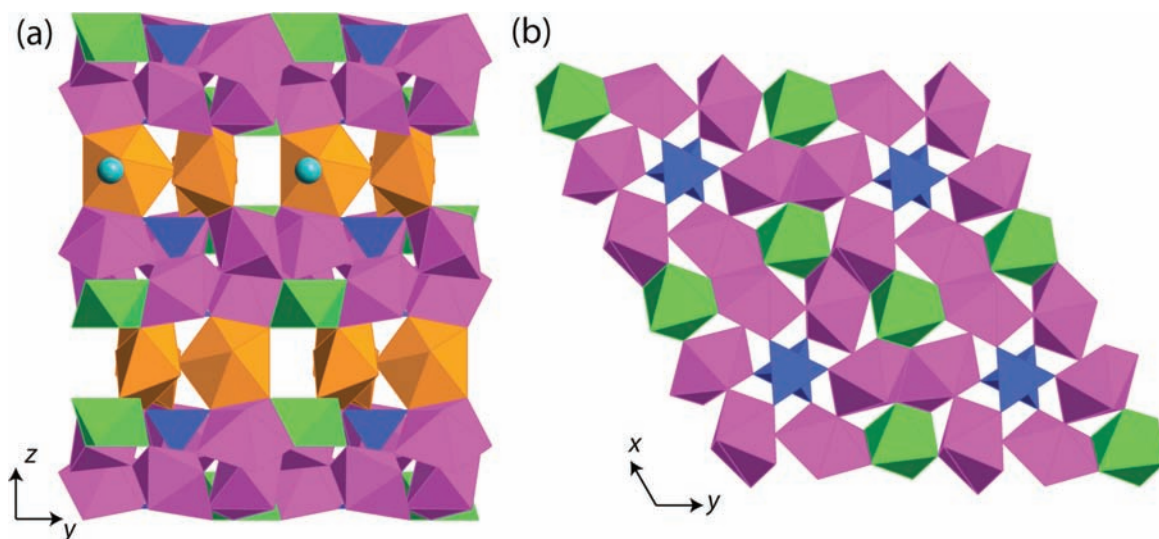
Figure 1. Polyhedral representations of the crystal structure of **4**. (a) Projected along [100]; (b) a slice of the structure at $c = 1/2$ projected along [001], showing the U(2), U(3), and Ge polyhedra only. U(1), U(2), and U(3) polyhedra are colored green, magenta, and orange, respectively. Ge polyhedra are shown in blue. The Ba position is indicated by a cyan sphere.

Cation—cation interactions in actinyl compounds have profound impacts on structure connectivity. Where uranyl bipyramids containing U^{6+} cations link to other uranyl bipyramids or various oxyanions in the absence of cation—cation interactions, connections are limited to the equatorial ligands of the bipyramids. The result is dominance of sheet structures, and to a lesser extent structures that contain infinite chains.[6] Where cation—cation interactions occur, uranyl bipyramids form linkages through both the apical and the equatorial vertices, which favors formation of three-dimensional topologies such as observed in the current study.

The distorted octahedral coordination polyhedron about the U(1) cation is also uncommon, as no uranyl ion is present. These polyhedral geometries and their connectivity result in an unusually dense framework structure. For example, the density of the K compound (**2**) is 7.29 g/cm^3. Compare this to the density of soddyite, $(UO_2)_2(SiO_4)(H_2O)_2$, a framework uranyl silicate hydrate, which is 5.09 g/cm^3.[15] The framework structure of K_5-$(UO_2)_2[Si_4O_{12}(OH)]$, which lacks cation—cation interactions, has a density of only 3.92 g/cm^3.[16] Another compound that also lacks cation—cation interactions, $KNa_3(UO_2)_2(Si_4O_{10})_2(H_2O)_4$, has a density of 3.34 g/cm^3.[17] In contrast, the compounds $Sr_5(UO_2)_{20^-}$ $(UO_6)_2O_{16}(OH)_6(H_2O)_6$ and $Cs(UO_2)_9U_3O_{16}(OH)_5$, both of which contain cation—cation interactions, have densities of 6.54 and 7.33 g/cm^3, respectively.[4] In a framework structure, cation—cation interactions between uranyl ions permit an overall closer packing of uranium in the structure, and thus a higher density is attainable.

The Ge cations, as well as the low-valence cations, are located in cavities within the framework of uranyl polyhedra. In all cases elongated anisotropic displacement parameters, and in three structures split Ge sites as well, indicate positional disorder and are consistent with the relatively poor fit of these cations within the available sites. Additional diffraction data collected for each compound at 110 K reduced the overall size of the displacement parameters, but did not impact their relative anisotropy. We also examined several plausible twin models to explain the elongated displacement parameters. The twin models did not produce superior refinements, leading us to conclude that local disorder is the cause of the elongated displacement parameters.

Of the more than 360 reported U(VI) minerals and inorganic compounds,[6] there are only 8 U(VI) germanate compounds and 18 similarly complex U(VI) silicate compounds. The previously reported U(VI) germanate compounds have shown a propensity for open ring- or channel-bearing framework structures,[14] whereas the four new framework germanate compounds presented here demonstrate a highly complex framework dominated by U polyhedra. The divergence of these structures further emphasizes the importance of cation—cation interactions in structure topologies.

Unlike U(VI) compounds, Np(V) compounds commonly have cation—cation interactions. This has led to the development of a system to categorize Np(V) cation—cation interactions that are a through h based on the local configuration of the ions.[9] The uranyl germanate frameworks contain a c-type interaction where each uranyl ion participates in two cation—cation interactions. Each uranyl ion donates a cation—cation interaction that is accepted by a symmetrically identical uranyl ion. In other words, each uranyl ion donates one cation—cation interaction and accepts another from a symmetrically identical uranyl ion. This type of configuration exists in ~20% of both Np(V) and U(VI) cation—cation interaction compounds. The most common configuration for Np(V) compounds was designated h, and is where the neptunyl ion participates in four cation—cation interactions. Specifically, the Np(V) neptunyl ion donates two cation—cation interactions (one through each O atom), and accepts two cation—cation interactions donated by other neptunyl ions. The most common configuration for U(VI) cation—cation interactions is type a, in which the uranyl ion donates a single cation—cation interaction.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Crystallographic data (CIF), infrared spectra, UV—vis spectra for each compound, TGA data for compound 2, thermal ellipsoid illustration for 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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