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Article

Cation–Cation Interactions in $Sr_5(UO_2)_{20}(UO_6)_2O_{16}(OH)_6(H_2O)_6$ and $Cs(UO_2)_9U_3O_{16}(OH)_5$

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Two novel U^{6+} compounds, $Sr_5(UO_2)_{20}(UO_6)_2O_{16}(OH)_6(H_2O)_6$ (Sr*Fm*) and $Cs(UO_2)_9U_3O_{16}(OH)_5$ (Cs*Fm*), have been synthesized by mild hydrothermal reactions. The structures of Sr*Fm* (orthorhombic, $C222_1$, $a = 11.668(1)$, $b = 21.065(3)$, $c = 13.273$ Å, $V = 3532.5(1)$ Å^3, $Z = 2$) and Cs*Fm* (trigonal, $R\bar{3}c$, $a = 11.395(2)$, $c = 43.722(7)$ Å, $V = 4916.7(1)$ Å^3, $Z = 6$) are rare examples of uranyl compounds that contain cation–cation interactions where an O atom of one uranyl ion is directly linked to another uranyl ion. Both structures are complex frameworks. Sr*Fm* contains sheets of polyhedra that are linked through cation–cation interactions with uranyl ions located between the sheets. Cs*Fm* possesses an unusually complex framework of vertex- and edge-sharing U^{6+} polyhedra that incorporates cation–cation interactions.

1. Introduction

Hexavalent uranium is almost invariably present in solids and solutions as part of an approximately linear dioxo uranyl cation, $(UO_2)^{2+}$. In inorganic structures, the uranyl ion is usually coordinated by 4−6 ligands that are arranged at the equatorial vertexes of square, pentagonal, and hexagonal bipyramids.[1] In terms of the bond-valence model, the bonds within the uranyl ion correspond to approximately 1.7 valence units.[2] The bonding requirements of the O atoms of the uranyl ion are nearly met by the bonds to the U^{6+} cation alone, and these atoms seldom bond to other cations of higher valence.[2] In contrast to the O atoms of the uranyl ion, the bonds between the U^{6+} cation and the equatorial ligands are much weaker, with bond valences typically in the range of 0.4−0.7 valence units.[1] Linkage of uranyl polyhedra with other uranyl polyhedra and other polyhedra containing higher-valence cations is therefore common through the equatorial vertexes and often results in infinite chains or sheets.[1]

In the case of pentavalent actinide cations such as Np^{5+}, a dioxo cation also dominates the crystal chemistry.[3] However, the lower charge of the cation results in somewhat weaker bonds within the actinyl ion. The O atoms of these actinyl ions tend to form stronger bonds than those of $(UO_2)^{2+}$. This leads to a significant divergence of the structural topologies of compounds containing hexavalent and pentavalent actinides.[3] Much of this divergence arises from the possibility of direct linkage of an O atom of an actinyl ion to another actinyl ion, where the O atom of the first actinyl ion is a coordinating equatorial ligand of the second. First postulated from solution studies,[4] the direct linkage of two actinyl ions in this fashion has been designated a cation−cation interaction. These interactions are relatively common in the case of Np^{5+} structures and occur in about one-third of known structures.[3]

Cation−cation interactions are uncommon in uranyl structures. Burns[1] examined the hierarchical structural arrangements of 368 inorganic U^{6+} compounds. Of these, cation−cation interactions occur in only $(NH_4)_3(H_2O)_2[(UO_2)_{10}O_{10}OH](UO_4)(H_2O)_2$,[5] the uranyl peridates $(Li,Na,K,Rb,Cs)[(UO_2)_3(HIO_6)(OH)(O)(H_2O)]\cdot1.5H_2O$[6] and $(UO_2)Cl_2(H_2O)$,[7] and the isostructural compounds α-$(UO_2)(SeO_4)$,[8]

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Table 1. Crystallographic Data and Structure Refinement Information for Sr*Fm* and Cs*Fm*

	Sr*Fm*	Cs*Fm*
formula	$Sr_5(UO_2)_{20}(UO_6)_2O_{16}(OH)_6(H_2O)_6$	$Cs(UO_2)_9U_3O_{16}(OH)_5$
mol wt	6972.83	3618.27
cryst syst	orthorhombic	trigonal
space group	$C222_1$	$R\bar{3}c$
a (Å)	11.668(1)	11.395(2)
b (Å)	21.065(3)	
c (Å)	14.373(2)	43.722(7)
V (Å^3)	3532.5(8)	4916.7(14)
Z	2	6
D_{calcd} (g/cm^3)	6.542	7.332
μ (mm^{-1})	54.08	60.27
R1	0.0430	0.0308
wR2	0.1120	0.0457

β-$(UO_2)(SO_4)$,[8] and $(UO_2)(MoO_4)$.[9] We are interested in comparing and contrasting the topological aspects of structures containing hexavalent and pentavalent actinides, with specific focus on the importance of cation−cation interactions. Here we document two novel compounds that contain uranyl ions that are involved in cation−cation interactions.

2. Experimental Section

Synthesis. Yellow prismatic crystals of $Sr_5(UO_2)_{20}(UO_6)_2O_{16}(OH)_6(H_2O)_6$ (designated Sr*Fm*) were crystallized by the hydrothermal reaction of 1.67 g of UO_3, 2.38 g of $Sr(NO_3)_2$, 0.44 g of $CaCO_3$, and 4 mL of H_2O in a Teflon-lined Parr reaction vessel at 493 K for 30 days. The product was recovered by filtration and was washed with boiling H_2O. Crystals of Sr*Fm* with maximum dimensions of 10 mm were attained. The yield is estimated to be close to 100% on the basis of U. A synthesis conducted without $CaCO_3$ under otherwise identical conditions yielded only a fine-grained powder. Because Sr*Fm* contains no detectable Ca or CO_3, the role of $CaCO_3$ in the reaction is unclear.

Crystals of $Cs(UO_2)_9U_3O_{16}(OH)_5$ (designated Cs*Fm*) were synthesized by the hydrothermal reaction of 1.67 g of UO_3, 0.44 g of $CaCO_3$, 3.11 g of $CsNO_3$, and 4 mL of H_2O in a Teflon-lined Parr reaction vessel at 493 K for 30 days. Crystals were recovered by filtration and were washed with boiling H_2O. The yield is estimated at 40% on the basis of U. As in the case of Sr*Fm*, exclusion of $CaCO_3$ from the synthesis of Cs*Fm* eliminated single crystals from the reaction products.

X-ray Crystallography. A single crystal of each compound was mounted on a Bruker PLATFORM three-circle X-ray diffractometer equipped with a 4 K APEX CCD detector, graphite-monochromatized Mo Kα radiation, and a crystal-to-detector distance of 4.67 cm. A sphere of three-dimensional data was collected for each crystal using frame widths of 0.3° in ω and 10 s spent counting per frame. The Bruker SHELXTL, version 5, system of programs was used for the solution and refinement of the crystal structure. Intensity data was corrected for Lorentz, polarization, and background effects using the Bruker program SAINT.[10] Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from International Tables for Crystallography, Vol. IV.[11]

Semiempirical corrections for absorption were applied by modeling the crystals of Sr*Fm* and Cs*Fm* as ellipsoids, reducing R_{int} from 17.8 to 9.1% and from 10.5 to 4.1% for Sr*Fm* and Cs*Fm*, respectively. The structure of Sr*Fm* was solved and refined in space group $C222_1$. The positions of the U and Sr atoms were determined by direct methods, and the O atoms were located in subsequent difference Fourier maps calculated for the partial-structure models. The U and Sr atoms were refined anisotropically. Unusually large isotropic displacement parameters for the O(20) and O(21) sites, each of which was on a special position, were alleviated by displacing the corresponding sites from their special positions. The occupancies of the Sr(1) and Sr(2) sites were refined without constraint using the atomic scattering factor for Sr. The refined occupancies were 79.2(8)% and 82.4(7)% for Sr(1) and Sr(2), respectively. The Sr(1) site is on a 2-fold axis, whereas Sr(2) is on a general position, thus the refined occupancies correspond to 4.88 atoms per formula unit, in reasonable agreement with the expected value of 5. The refined Flack parameter for Sr*Fm* was 0.48(3), indicating the presence of racemic twining that was subsequently included in the refinement. The structure of Cs*Fm* was solved and refined in space group $R\bar{3}c$. The U atom positions were obtained from a direct methods solution, and the Cs and O positions were identified in difference Fourier maps calculated using the partial-structure models. All atoms were refined anisotropically. H atoms were not located in the difference Fourier map of either structure, as is typical for structures containing U. Crystallographic information for each compound is summarized in Table 1.

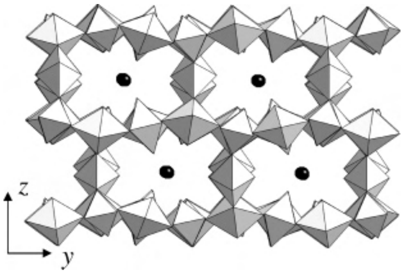

Figure 1. Polyhedral representation of the structure of Sr*Fm* projected along [100]. The β-U_3O_8-type sheets are horizontal in the figure. The locations of Sr atoms are given by black spheres.

Thermograviometric Analysis. Aliquots of Sr*Fm* (64.74 mg) and Cs*Fm* (44.84 mg) were powdered and pressed into pellets. The mass loss of each sample was recorded in a Netzsch TG209 thermal analysis system as a function of temperature, with a heating rate of 5 K per minute from 298 to 800 K. The sample chamber was continually flushed with nitrogen during each data collection.

Elemental Analysis. Energy dispersive spectra were collected for single crystals of Sr*Fm* and Cs*Fm* using a LEO EVO-50XVP variable-pressure/high-humidity scanning electron microscope. The spectra were qualitatively consistent with the reported structural formulas, and Ca was not detected in either compound.

3. Results and Discussion

Crystal Structure of Sr*Fm*. The structure of Sr*Fm* is closely related to that of $(NH_4)_3(H_2O)_2[(UO_2)_{10}O_{10}OH](UO_4)(H_2O)_2$.[5] The coordination polyhedra about the U^{6+} cations are almost identical, apart from relatively minor variations in bond lengths and angles, and the U^{6+} polyhedra are linked into topologically identical frameworks in these two structures (Figure 1). In both cases, channels through the framework are occupied: in Sr*Fm*, by Sr and H_2O that is bonded to the Sr and, in the NH_4 compound, by NH_4 groups and H_2O groups that are held in the structure by H bonding only. The structure of Sr*Fm* is orthorhombic, whereas that

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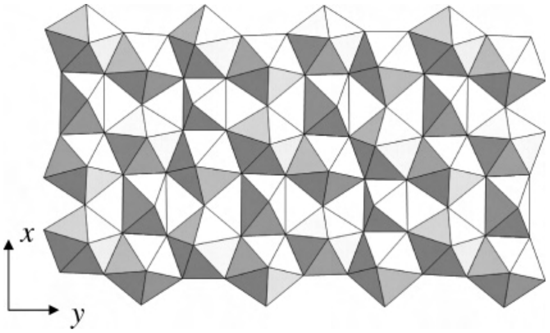

Figure 2. Polyhedral representation of the sheet of uranyl polyhedra in the structure of Sr*Fm*.

of the NH_4 compound is monoclinic, space group *C*2/*c*. The change in symmetry arises from the distribution of the constituents in the channels. In Sr*Fm*, the Sr is located at the center of the channel, whereas in the NH_4 compound the NH_4 groups are displaced ~1 Å from the center.

The structure of Sr*Fm* contains seven symmetrically unique U^{6+} cations. U(1) is coordinated by four O atoms and two OH groups in a highly distorted octahedral arrangement. The O atoms are at 1.986(10) and 2.013(10) Å, and the OH groups are at 2.252(14) Å. The U(1) cation is not part of a dioxo cation, and its coordination polyhedron is similar to the U(2) site in the analogous NH_4 compound, except that the apical ligands of the distorted octahedron correspond to H_2O groups at 2.37(4) Å in the latter. In Sr*Fm*, each OH group of the U(1) polyhedron is also bonded to two Sr cations located in the channels. The U(2), U(3), U(5), U(6), and U(7) cations are each part of dioxo cations and are coordinated by an additional five equatorial ligands, giving pentagonal bipyramids. The U(4) dioxo cation is coordinated by four equatorial ligands, giving a square bipyramid. The uranyl ion bond lengths range from 1.76 to 1.84 Å where they are terminal, which compare well with the average of 1.793(35) Å calculated for many well-refined structures containing uranyl pentagonal bipyramids.[1] Three O atoms of uranyl ions [O(5), O(8), O(10)] are involved in cation−cation interactions, and their corresponding bond lengths are longer, ranging from 1.87 to 1.97 Å. The symmetrically independent Sr(1) and Sr(2) sites are partially occupied and are coordinated by eight and nine ligands, respectively.

The U(2), U(3), U(5), and U(6) pentagonal bipyramids share equatorial edges, resulting in chains that are one polyhedron wide. Adjacent chains are linked by the sharing of vertexes of every third bipyramid along the chain length and by sharing edges with U(4) square bipyramids and U(1) octahedra that are located between the chains of pentagonal bipyramids (Figure 2). The resulting sheet is topologically identical to that found in β-U_3O_8, as well as several minerals and synthetic compounds.[1]

Each U(7) pentagonal bipyramid shares an edge with a symmetrically identical bipyramid, and the resulting dimers are located between the β-U_3O_8-type sheets (Figure 1). Linkages of the U(7) dimers to the sheets on both sides results in a framework of U^{6+} polyhedra. The remarkable aspect of this is the nature of the linkages between the U(7) polyhedra and the sheets (Figure 3). The U(7) pentagonal bipyramids share an O(5)−O(5) edge, and the O(5) atom is also part of the U(2) uranyl ion. This linkage constitutes a double cation−cation interaction, as the O atom of a uranyl ion is actually the equatorial vertex of two uranyl pentagonal bipyramids. This extraordinary configuration is permitted by the very long U(2)−O(5) bond length of 1.967(9) Å. The bond-valence sum at the O(5) site is 2.08 valence units.[2] Two of the other U(7) equatorial ligands are O(10), which is part of the U(4) uranyl ion, and O(8), which belongs to the U(5) uranyl ion: thus, both of these also correspond to cation−cation interactions. The U(4)−O(10) and U(5)−O(8) uranyl ion bond lengths are both 1.87(1) Å and reflect lengthening associated with the cation−cation interactions. The O(4) atom is the remaining equatorial vertex of the U(7) pentagonal bipyramid, and it is also an equatorial ligand of the U(2) and U(5) pentagonal bipyramids. The U(7) pentagonal bipyramid is involved in four cation−cation interactions, which is unprecedented in uranyl compounds.

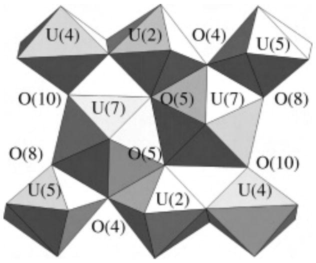

Figure 3. Local environment about the U(7) polyhedron in the structure of Sr*Fm*.

Crystal Structure of Cs*Fm*. The crystal structure of Cs*Fm* contains four symmetrically independent U^{6+} cations and one Cs cation. The U(1) and U(2) cations both belong to dioxo uranyl ions, and each is coordinated by five ligands at the equatorial vertexes of pentagonal bipyramids. The U(3) cation is coordinated by six atoms of O, three each at 2.037(5) and 2.101(5) Å, and the bond-valence sum at this site is 5.74 valence units.[2] U(4) is coordinated by six O(6) at 2.107(6) Å, giving a bond-valence sum at the U site of 5.31 valence units.[2] The O(6) atoms are each bonded to one U(4) cation at 2.107(6) Å and one U(2) cation at 2.376(6) Å, and the corresponding bond-valence sum at the O site is 1.41 valence units.[2] This is about 0.2 valence units higher than expected for an OH group, and charge balance requirements are consistent with the O(6) site containing both OH and O, such that 5/6 of the sites contain OH. In the event that the site is occupied locally by O rather than OH, the atom could be displaced toward U(4), thereby increasing the bond-valence sum at that site.

The U^{6+} polyhedra in the structure of Cs*Fm* are linked into an extraordinarily complex three-dimensional framework (Figure 4). Consider first a slice of the structure taken parallel to (001) at a height of 0.3 of *c* (Figure 5). Here, the U(1) pentagonal bipyramids and U(3) octahedra are linked into 12-membered rings by sharing vertexes. Each U(3) octahedron is at the intersection of three such rings, and each U(3) octahedron shares vertexes with three U(1) pentagonal bipyramids. Each U(1) pentagonal bipyramid is linked to two

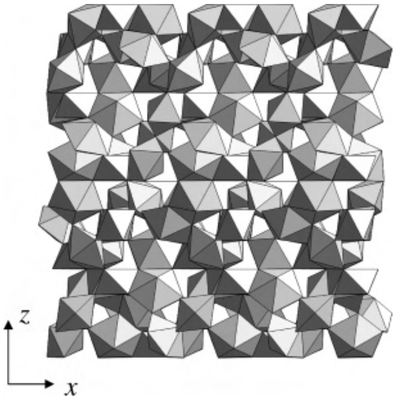

Figure 4. Polyhedral representation of the structure of Cs*Fm* projected along [010].

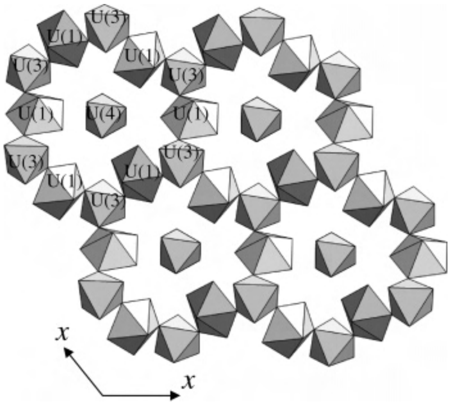

Figure 5. Slice of the structure of Cs*Fm* at $c \approx 0.3$. The U(2) polyhedra are omitted.

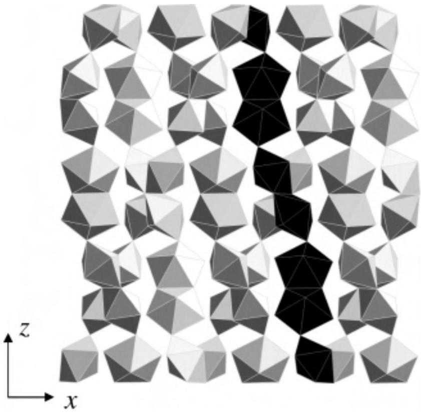

Figure 6. U(2) polyhedra in the structure of Cs*Fm*. One chain of polyhedra is shown in black.

U(3) octahedra. The U(4) octahedron is located at the center of the 12-membered rings, but it does not share vertexes with either the U(1) or U(3) polyhedra.

Each U(2) pentagonal bipyramid shares an edge with a symmetrically identical U(2) bipyramid, resulting in dimers. Each dimer is linked to two other U(2) dimers by vertex sharing, giving an infinite chain of U(2) dimers. The chains of U(2) bipyramids are distributed about the *c* axis with an inclination of ~20°, as shown in Figure 6. The chains of U(2) bipyramid dimers penetrate and connect to the layers of U(1), U(3), and U(4) polyhedra shown in Figure 5, resulting in a framework of polyhedra. Each U(2) pentagonal bipyramid shares one of its equatorial edges with a U(1) pentagonal bipyramid and another equatorial edge with a U(3) octahedron. It also shares an equatorial vertex with the U(4) octahedron, and each vertex of the U(4) octahedron is shared with a different U(2) pentagonal bipyramid. The O(2) atom of the U(2) uranyl ion is also an equatorial ligand of a U(1) uranyl pentagonal bipyramid; thus this is a cation−cation interaction.

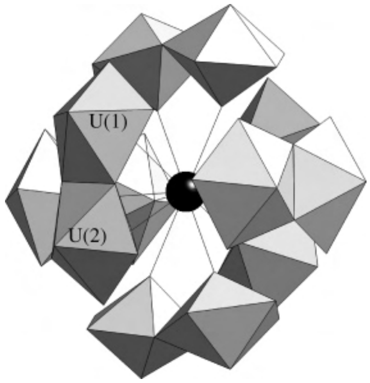

Figure 7. Coordination environment about Cs in Cs*Fm*.

Relatively large voids in the framework contain the Cs cation (Figure 7). The void is defined by dimers of edge-sharing U(1) and U(2) pentagonal bipyramids, and the Cs cation is coordinated by the O atoms of twelve different uranyl ions, with Cs−O bond lengths of 3.251(5) and 3.259(5) Å.

Thermograviometric Analysis. The measured mass loss for Sr*Fm* was 2.23%, in good agreement with the structure determination which indicates Sr*Fm* contains 2.32% H_2O. Dehydration of Sr*Fm* proceeds in one step between 450 and 650 K.

The measured mass loss for Cs*Fm* was 1.24%. This is consistent with the structure containing five OH groups per formula unit, which would be expected to result in a weight loss of 1.20%. Dehydroxylation proceeds in one stage above 400 K.

Discussion. The structures of most uranyl oxide hydrates are dominated by sheets of uranyl polyhedra, with uranyl ions oriented approximately perpendicular to the plane of the sheet.[1] In these structures, relatively weak interactions occur between the O atoms of the uranyl ions and lower-valence cations and H_2O groups located in the interlayer regions. The structure of Sr*Fm* and its NH_4 analogue are the only examples of uranyl oxide hydrates that contain well-defined sheets of uranyl polyhedra similar to other known structures, but with adjacent sheets linked through uranyl ions located in the interlayers. The occurrence of cation−cation interactions between the sheets and interlayer uranyl ions facilitates this unusual connectivity. The structure of Sr*Fm* is closely related to several other uranyl oxide hydrates with sheet structures, but the addition of cation−cation interactions provides for the three-dimensional linkages of the U^{6+} polyhedra.

Unlike the structure of Sr*Fm*, the structure of Cs*Fm* has little in common with any known U^{6+} compound. Here the typical uranyl pentagonal bipyramids are combined with the less-common distorted octahedra containing U^{6+}, and linkage into a complex framework is facilitated by cation−cation interactions. It is interesting to note that $Pb_2(H_2O)[(UO_2)_{10}UO_{12}(OH)_6(H_2O)_2]$ also has a framework of U^{6+} polyhedra, including distorted octahedra, but in this case, no cation−cation interactions are present, and the structure is built from slabs of a well-known sheet of uranyl polyhedra.[12]

In general, the structures of Sr*Fm* and Cs*Fm* illustrate important structural roles of cation−cation interactions in uranyl compounds. In Sr*Fm*, structural units that are known from structures without cation−cation interactions are combined with cation−cation interactions to produce an unusual framework structure. In the case of Cs*Fm*, cation−cation interactions facilitate formation of an entirely unique structure. These two structures serve to illustrate the importance of cation−cation interactions in creating new topologies in U^{6+} compounds.

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Supporting Information Available: Crystallographic data (CIF), atomic coordinates with anisotropic displacement parameters, and selected bond lengths and angles for $Sr_5(UO_2)_{20}(UO_6)_2O_{16}(OH)_6(H_2O)_6$ and $Cs(UO_2)_9U_3O_{16}(OH)_5$. This material is available free of charge via the Internet at http://pubs.acs.org.

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