

Structure Determination and Infrared Spectroscopy of $K(UO_2)(SO_4)(OH)(H_2O)$ and $K(UO_2)(SO_4)(OH)$

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Two potassium uranyl sulfate compounds were synthesized, and their crystal structures were determined by single-crystal X-ray diffraction. $K(UO_2)(SO_4)(OH)(H_2O)$ (*KUS1*) crystallizes in space group $P2_1/c$, $a = 8.0521(4)$ Å, $b = 7.9354(4)$ Å, $c = 11.3177(6)$ Å, $\beta = 107.6780(10)^\circ$, $V = 689.01(6)$ Å³, and $Z = 4$. $K(UO_2)(SO_4)(OH)$ (*KUS2*) is orthorhombic *Pbca*, $a = 8.4451(2)$ Å, $b = 10.8058(4)$ Å, $c = 13.5406(5)$ Å, $V = 1235.66(7)$ Å³, and $Z = 8$. Both structures were refined on the basis of F^2 for all unique data collected with Mo $K\alpha$ radiation and a CCD-based detector to agreement indices $R1 = 0.0251$ and 0.0206 calculated for 2856 and 2616 reflections for *KUS1* and *KUS2*, respectively. The structures contain vertex-sharing uranyl pentagonal bipyramids and sulfate tetrahedra linked into new chains and sheet topologies. Infrared spectroscopy provides additional information about the linkages between the sulfate and uranyl polyhedra, as well as the hydrogen bonding present in the structures. The U–O–S connectivity is examined in detail, and the local bond angle is impacted by the steric constraints of the crystal structure.

Introduction

Recent studies have revealed tremendous structural diversity in uranyl (UO_2)²⁺ compounds containing $X^{6+}O_4$ tetrahedra ($X = S, Se, Mo, Cr$).^{1–17} The most remarkable of these new structures are novel uranyl selenates with nanotubular structures.^{12,14} The structural hierarchy for inorganic uranyl compounds provided by Burns¹⁸ included 100 uranyl struc-

tures that also contain $X^{6+}O_4$ tetrahedra. In these, uranyl polyhedra are usually linked by the sharing of equatorial vertices of the uranyl bipyramids with the tetrahedra, and only four structures involve the sharing of an edge of a tetrahedron with a uranyl bipyramid. As for uranyl compounds in general, infinite sheets of polyhedra are generally dominant and occur in 50 of these structures. Chains of linked uranyl polyhedra and $X^{6+}O_4$ are also important, with 26 examples. The remaining structures contain isolated clusters¹⁶ and infinite frameworks.¹⁵

Uranyl sulfates are an important class of minerals^{19,20} that often form where sulfide minerals are oxidized in the

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presence of uranium.²¹ These minerals impact the environmental mobility of uranium in many abandoned uranium mine sites. Most uranyl sulfate minerals are members of the zippeite group, all of which contain topologically identical sheets composed of chains of edge-sharing uranyl pentagonal bipyramids that are linked by vertex-sharing with sulfate tetrahedra.²² These sheets are linked through bonds to interlayer cations and H₂O groups. An open sheet of uranyl pentagonal bipyramids and sulfate tetrahedra occurs in the mineral johannite,²³ and a complex chain containing clusters of six uranyl pentagonal bipyramids, as well as sulfate tetrahedra, is the basis of the structure of uranopilite.²⁴ In the zippeite and uranopilite structures, each sulfate tetrahedron bridges between four uranyl pentagonal bipyramids, whereas in the structure of johannite, each tetrahedron bridges between only three uranyl polyhedra. In synthetic uranyl sulfates, sulfate tetrahedra are either nonbridging or bridge between two or three uranyl polyhedra.¹⁸

Linkages of uranyl ions and sulfate tetrahedra can result in uncharged ion pairs in solution. Such complexes have been the subject of spectroscopic studies,^{25–27} most recently by synchrotron high-energy X-ray scattering from solutions.²⁸ Under the conditions of the latter study, sulfate was found to bind to the uranyl ion as a monodentate ligand.²⁸ The U–O–S bond angle of the complex appears nearly constant in solution, prompting Newufeind et al.²⁸ to conclude that an U–O–S angle of 143° is an intrinsic property of the uranyl–sulfate bond. Solid-state structures from the literature support this conclusion.²⁸ The extent to which the steric constraints in a crystal structure impact the U–O–S bond angle has not been fully explored.

Here we present the structures and infrared spectra of two synthetic uranyl sulfates that contain a novel chain and sheet of uranyl and sulfate polyhedra. The extent to which topological aspects of the structure impact the observed U–O–S bond angle is examined using these structures, as well as others from the literature.

Experimental Methods

Crystal Synthesis. *KUS1* (K(UO₂)(SO₄)(OH)(H₂O)). The reagents (UO₂)(NO₃)₂(H₂O)₆ (MV Laboratories, Lot no. P705UA1), K₂SO₄ (Fisher Scientific, Lot no. 046809), KCl (Fisher Scientific, Lot no. 941604), and H₂SO₄ (Fisher Scientific, Lot no. 053911) were used as received. *KUS1* was synthesized by the reaction of 4 mL of a 2 M uranyl nitrate solution in water with 0.260 g of K₂SO₄ and 10 μL of a 3 M KCl solution in a 23 mL Teflon-lined

Table 1. Selected Crystallographic Data and Structure Refinement Parameters for *KUS1* and *KUS2*

	<i>KUS1</i>	<i>KUS2</i>
formula	K(UO ₂)(SO ₄)(OH)(H ₂ O)	K(UO ₂)(SO ₄)(OH)
fw	440.17	422.17
cryst syst	monoclinic, <i>P</i> 2 ₁ / <i>c</i>	orthorhombic, <i>Pbca</i>
<i>a</i> (Å)	8.0521(4)	8.4451(2)
<i>b</i> (Å)	7.9354(4)	10.8058(4)
<i>c</i> (Å)	11.3177(6)	13.5406(5)
β (deg)	107.6780(10)	
<i>V</i> (Å ³)	689.01(6)	1235.66(7)
<i>Z</i>	4	8
calcd density (mg/m ³)	4.244	4.539
abs coeff (mm ⁻¹)	24.466	27.263
<i>F</i> (000)	776	1472
θ range for data collection	2.6–34.46°	3.01–34.50°
limiting indices	–12 < <i>h</i> < 12, –12 < <i>k</i> < 12, –17 < <i>l</i> < 17	–13 < <i>h</i> < 13, –17 < <i>k</i> < 17, –21 < <i>l</i> < 21
reflns collected/ unique	13 557/2856 (<i>R</i> _{int} = 0.0369)	23 537/2616 (<i>R</i> _{int} = 0.0461)
refinement method	full-matrix least- squares on <i>F</i> ²	full-matrix least- squares on <i>F</i> ²
data/restraints/ params	2856/3/109	2616/1/95
GOF on <i>F</i> ²	1.184	1.147
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0251, w <i>R</i> 2 = 0.0601	<i>R</i> 1 = 0.0206, w <i>R</i> 2 = 0.0479
largest diff. peak and hole	1.980, –2.565 e.Å ⁻³	2.395, –2.165 e.Å ⁻³

Parr reaction vessel. The pH of the solution was adjusted from 4.45 to 4.04 by the addition of 340 μL of 1 M H₂SO₄. The reaction vessel was then heated in a mechanical convection oven at 150 °C for 72 h. Following cooling, the solution was allowed to evaporate for several months and crystals ranging from 600 μm to 1 mm were recovered.

***KUS2* (K(UO₂)(SO₄)(OH)).** Crystals were synthesized using mild hydrothermal conditions. A 7 mL Teflon cup with a screw-top lid was loaded with 0.131 g of K₂SO₄ and 2.00 mL of 0.20 M uranyl nitrate hexahydrate in water. The pH of the solution was adjusted to 2.03 using 30 μL of 2.0 M KOH. The sample vial was placed in a 125 mL Parr reaction vessel and was heated at 145 °C for 72 h in a gravity convection oven. The vessel was allowed to cool slowly to room temperature inside the oven to promote crystal growth. Crystals were obtained directly after the cooling process without evaporation. The product was washed with 3 mL of 18 MΩ ultrapure water and crystals ranging from 100 to 300 μm were recovered.

Single-Crystal X-ray Diffraction. Single crystals of *KUS1* and *KUS2* were mounted on tapered glass fibers for X-ray diffraction analysis. A sphere of data was collected for each compound at room temperature using a Bruker three-circle X-ray diffractometer equipped with a APEX CCD detector. The data was 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-square techniques using the Bruker SMART software,²⁹ and the SAINT software³⁰ was used for data integration inducing Lorentz and polarization corrections. Semiempirical absorption corrections were applied using the program SADABS. Selected data collection parameters and crystallographic information are provided in Table 1.

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Table 2. Selected Bond Lengths [Å] and Angles [deg] for *KUS1*

U(1)–O(5)	1.774(3)	K(1)–O(5)	2.720(3)
U(1)–O(4)	1.787(3)	K(1)–O(3) ^b	2.753(3)
U(1)–O(2) ^a	2.295(3)	K(1)–O(7) ^a	2.807(4)
U(1)–O(2)	2.350(3)	K(1)–O(4) ^c	2.878(3)
U(1)–O(1)	2.398(3)	K(1)–O(3) ^d	2.884(4)
U(1)–O(6) ^a	2.416(3)	K(1)–O(4) ^e	2.923(4)
U(1)–O(8)	2.491(4)		
		O(5)–U(1)–O(4)	176.5(2)
S(1)–O(7)	1.460(4)		
S(1)–O(3)	1.463(3)		
S(1)–O(6)	1.485(3)		
S(1)–O(1)	1.499(3)		

^a Symmetry transformations used to generate equivalent atoms: $-x + 1, y + 1/2, -z + 1/2$. ^b $x + 1, -y + 1/2, z + 1/2$. ^c $-x + 1, y - 1/2, -z + 1/2$. ^d $-x + 1, -y + 1, -z$. ^e $x + 1, y, z$.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for *KUS2*

U(1)–O(6)	1.762(2)	K(1)–O(7) ^e	2.701(3)
U(1)–O(2)	1.782(2)	K(1)–O(3) ^d	2.703(3)
U(1)–O(1) ^a	2.350(2)	K(1)–O(7)	2.736(3)
U(1)–O(1)	2.356(2)	K(1)–O(4) ^e	2.813(2)
U(1)–O(5) ^a	2.404(3)	K(1)–O(5) ^e	2.987(3)
U(1)–O(3)	2.408(2)	K(1)–O(6) ^a	3.064(3)
U(1)–O(4) ^b	2.436(2)	K(1)–O(2)	3.071(3)
		K(1)–O(1) ^f	3.088(2)
S(1)–O(7)	1.438(3)		
S(1)–O(5)	1.470(3)	O(6)–U(1)–O(2)	178.3(1)
S(1)–O(3)	1.471(2)		
S(1)–O(4)	1.485(2)		

^a Symmetry transformations used to generate equivalent atoms: $x + 1/2, -y + 3/2, -z + 1$. ^b $x, -y + 3/2, z - 1/2$. ^c $x + 1/2, y, -z + 3/2$. ^d $x + 1/2, y, -z + 3/2$. ^e $-x + 1/2, y - 1/2, z$. ^f $-x, -y + 1, -z + 1$.

The structures of *KUS1* and *KUS2* were solved using direct methods and refined on the basis of F^2 for all unique data using the Bruker SHELXTL version 5 system of programs.³¹ Atomic scattering factors for each atom were taken from the International Tables for X-ray Crystallography.³² The U and K atoms were located in direct-methods solutions and the S and O atoms were identified in the difference Fourier maps calculated following refinement of the partial-structure models. *KUS1* crystallizes in the monoclinic space group $P2_1/c$, and *KUS2* crystallizes in the orthorhombic space group $Pbca$. The models for both structures include anisotropic displacement parameters for U, K, S, and O atoms. H atom positions were located in the difference Fourier maps and were refined with the soft constraint that O–H bonds be ~ 0.96 Å. The atomic positional parameters are in the Supporting Information, and the selected interatomic distances are in Tables 2 and 3 for *KUS1* and *KUS2*, respectively. Additional details of the crystal structure analysis can be found in the Supporting Information.

Infrared Spectroscopy. Infrared spectra were obtained for single crystals of *KUS1* and *KUS2* 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 3600 cm^{-1} with an aperture of 100 μm . Infrared spectra of *KUS1* and *KUS2* are shown in Figures 1 and 2, respectively.

Bond Valence Analysis. The bond valence sums were calculated for $\text{U}^{6+}-\text{O}$,³³ K^+-O ,³⁴ and $\text{S}^{6+}-\text{O}^{34}$ interactions. The bond valence

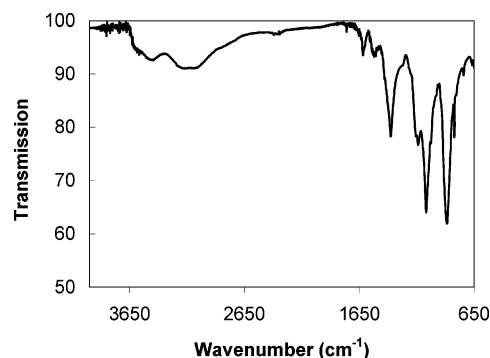


Figure 1. Infrared spectrum of *KUS1* (see Supporting Information for spectrum with peaks labeled).

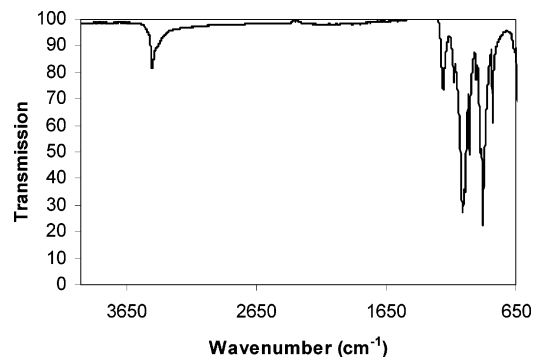


Figure 2. Infrared spectrum of *KUS2* (see Supporting Information for spectrum with peaks labeled).

Table 4. Bond Valence Sums for *KUS1*

	U1	S1	K1	Σ	
O1	0.49	1.48		1.97	OH
O2	0.61			1.15	
	0.54				
O3		1.63	0.19	1.81	H ₂ O
O4	1.66		0.13	1.79	
			0.12		
O5	1.70		0.20	1.90	
O6	0.48	1.53		2.01	
O7		1.65	0.16	1.81	
O8	0.41			0.41	
Σ	5.89	6.29	0.80		

Table 5. Bond Valence Sums for *KUS2*

	U1	S1	K1	Σ	
O1	0.56			1.11	OH
	0.55				
O2	1.68		0.08	1.76	
O3	0.49	1.62	0.22	2.32	
O4	0.47	1.55	0.16	2.18	
O5	0.50	1.63	0.10	2.23	
O6	1.75		0.08	1.83	
O7		1.75	0.22	2.17	
Σ	5.99	6.55	1.06		

sums are listed in Tables 4 and 5 for *KUS1* and *KUS2*, respectively. The calculated sums are in agreement with the expected values for U^{6+} , K^+ , and S^{6+} .

Results

Structural Description. *KUS1* and *KUS2* both contain one symmetrically independent U^{6+} cation that is strongly bonded to two O atoms, giving the nearly linear uranyl cation $(\text{UO}_2)^{2+}$. The bond lengths of the uranyl cation are 1.774(3) and 1.787(3) Å for *KUS1* and 1.760(2) and 1.780(2) Å for

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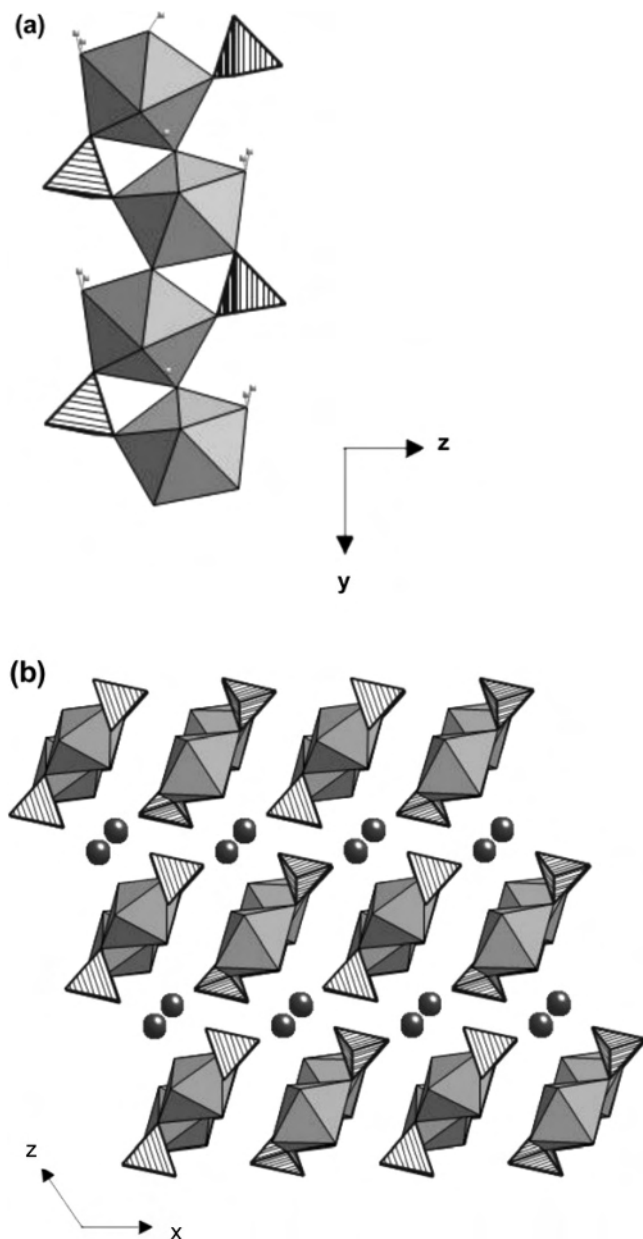


Figure 3. Polyhedral representation of *KUS1*. (a) The chain of vertex-sharing uranyl pentagonal bipyramids and sulfate tetrahedra projected along the [100] direction. (b) The K cations are located between the uranyl sulfate chains, as indicated by black circles.

KUS2. The $(\text{UO}_2)^{2+}$ cation in each structure is coordinated by five additional O, OH, or H_2O ligands that are arranged at the equatorial vertices of pentagonal bipyramids that are capped by the uranyl ion O atoms. The $\text{U}^{6+}-\text{O}_{\text{eq}}$ (eq: equatorial) bond lengths range from 2.350(3) to 2.491(4) Å in these structures. One symmetrically distinct S^{6+} cation is present in each structure in tetrahedral coordination, with $\text{S}^{6+}-\text{O}$ bond lengths ranging from 1.460(4) to 1.499(3) Å.

The structures of *KUS1* and *KUS2* are based upon similar linkages between the uranyl polyhedra and sulfate tetrahedra. In both structures, each uranyl pentagonal bipyramid shares two equatorial vertices with two adjacent bipyramids, creating a chain of uranyl polyhedra that extends in the [010] direction in *KUS1* (Figure 3a). The shared equatorial vertex in each case corresponds to the single hydroxyl group. The

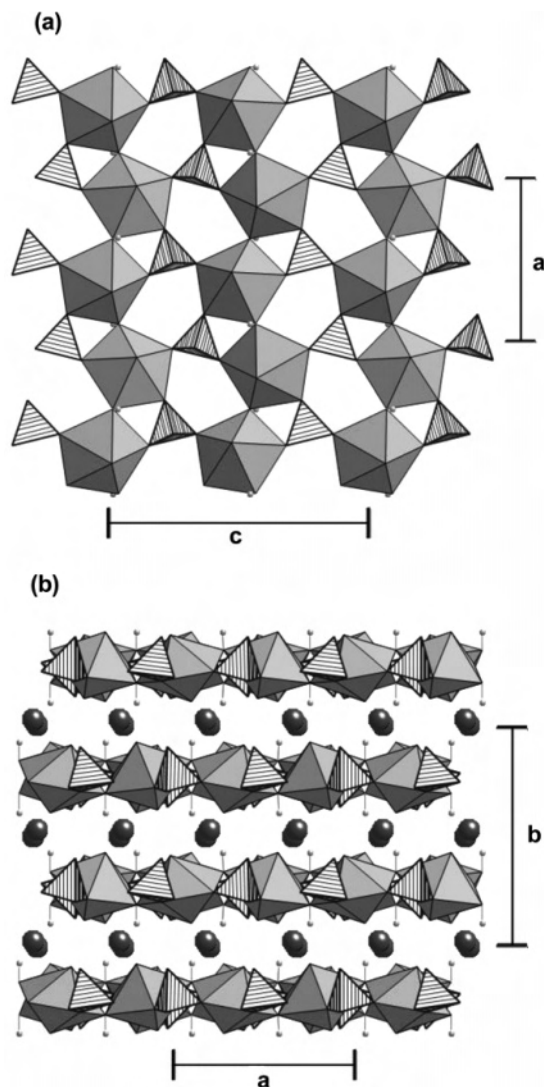


Figure 4. Polyhedral representation of *KUS2*. (a) The chains of uranyl and sulfate polyhedra observed in *KUS1* are linked into sheets in *KUS2* through vertex-sharing with the neighboring sulfate tetrahedral with (b) K cations positioned between the sheets.

H bonds in the OH groups [O(2) and O(1)] extend to the oxygen acceptors of the uranyl ion oxygen atoms [O(5) and O(2)] with oxygen acceptor lengths of 1.92 and 1.98 Å for *KUS1* and *KUS2*, respectively. The sulfate tetrahedra decorate the outside of the chain with bridging bidentate linkages between the uranyl pentagonal bipyramids. The orientations of the sulfate tetrahedra alternate on either side of the chain, with the apex of the sulfate tetrahedra pointing up on one side and down on the other.

In the structure of *KUS1*, the edges of the chain are terminated by a H_2O ligand on the nonbridging vertex of each uranyl polyhedron. The H bonds from the H_2O group [O(8)] extend to oxygen acceptors on the sulfate tetrahedra [O(7)] and the uranyl ion O atoms on the uranyl polyhedra [O(4)]. The oxygen acceptor lengths are 2.23 Å for H(1)–O(8) and 2.41 Å for H(2)–O(4). There is no H_2O group in *KUS2*, and the corresponding polyhedral vertex is shared with a sulfate tetrahedron of a neighboring chain, resulting in a two-dimensional uranyl sheet (Figure 4a). The orientations

of the sulfate tetrahedra continue to alternate up, down, up, down along the chain length in the sheet, as observed in *KUS1*.

The uranyl sulfate chains and sheets in *KUS1* and *KUS2* are linked through bonds to interstitial K^+ cations and by H bonds. *KUS1* contains one unique K^+ atom in octahedral coordination, with bond lengths ranging from 2.720(3) to 2.923(4) Å (Figure 3b). The one symmetrically independent K^+ atom in *KUS2* is located between the sheets of uranyl and sulfate polyhedra (Figure 4b). The K^+ cation is coordinated by seven O atoms with bond lengths ranging from 2.692(3) to 3.062(3) Å.

IR Spectroscopy. The dominate peak in the infrared spectra of *KUS1* and *KUS2* is located at 881 and 887 cm^{-1} , respectively. These peaks are assigned to the UO_2 antisymmetric stretching vibration, ν_3 , that is generally observed as a intense peak within the 850–1000 cm^{-1} region.³⁵ The IR-active region for the SO_4 tetrahedron is located between 1018 and 1160 cm^{-1} .³⁵ In both structures, the sulfate tetrahedra are in a bridged configuration with the uranyl polyhedra. This bonding arrangement lowers the tetrahedral symmetry of the sulfate polyhedra from T_d to C_{2v} . Lowering the symmetry results in activation of the symmetric stretching vibrations of the sulfate tetrahedra and causes in peak splitting.³⁵ The SO_4 region of the spectrum exhibits peaks at 1125 and 1058 cm^{-1} for *KUS1* and 1106, 1054, and 1024 cm^{-1} for *KUS2*. The sharp peaks at 1362 and 1201 cm^{-1} has been assigned to stretching vibrations of the hydroxyl group in *KUS1* and *KUS2*, respectively. H_2O groups positioned at the equatorial vertices of the uranyl polyhedra in the structure of *KUS1* are verified in the infrared spectrum. The H_2O group is indicated by a diffuse band from 3650 to 2650 cm^{-1} and a sharp bending mode peak at 1605 cm^{-1} .³⁵ The spectrum presents two distinct bands from 3650 to 3400 and 3400 to 2650 cm^{-1} . The diffuse band below 3400 cm^{-1} corresponds to OH groups or a strongly polarized H_2O group with strong H bonds, while the band from 3650 to 3400 cm^{-1} corresponds to H bonds that have been weakly polarized by the K^+ cations. Peaks corresponding to molecular H_2O are absent from the *KUS2* spectrum, which is corroborated by the bond valence analysis.

Discussion

The structures of *KUS1* and *KUS2* possess unique structural units composed of uranyl pentagonal bipyramids and sulfate tetrahedra. Six uranyl sulfate compounds have structures based upon infinite chains of polyhedra. Four of these have polyhedra that are linked through vertex-sharing between uranyl polyhedra and sulfate tetrahedra. The structure of $\text{Mn}[(\text{UO}_2)(\text{SO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_4$ contains uranyl pentagonal bipyramids that share four equatorial vertices with sulfate tetrahedra, giving a chain of bridged uranyl polyhedra. An additional sulfate tetrahedron is shared with the fifth equatorial vertex of the uranyl polyhedron, decorating the

outside of the chain.³⁶ The sulfate tetrahedra in $[(\text{UO}_2)(\text{SO}_4)(\text{H}_2\text{O})_2](\text{H}_2\text{O})_{1.5}$, $[(\text{UO}_2)(\text{SO}_4)(\text{H}_2\text{O})_2](\text{H}_2\text{O})_{0.5}$, and $[(\text{UO}_2)(\text{SO}_4)(\text{H}_2\text{O})_2]_2(\text{H}_2\text{O})_3$ also bridge between the uranyl polyhedra, with each pentagonal bipyramid sharing three equatorial vertices with a sulfate tetrahedron.^{37–39}

In uranyl structures in which the structural units are chains, it is rare to have the direct sharing of uranyl polyhedral elements. Only one uranyl sulfate compound other than those studied here contains infinite chains with direct linkages between uranyl polyhedra. The mineral uranopilite, $[(\text{UO}_2)_6(\text{SO}_4)\text{O}_2(\text{OH})_6(\text{H}_2\text{O})_6]$, is composed of edge-sharing uranyl pentagonal bipyramids that forming six-member clusters.²⁴ These clusters are linked into chains by sharing vertices with sulfate tetrahedra. Other examples of infinite chains with direct linkages between uranyl polyhedra include those in the isostructural compounds $\text{Na}_4[(\text{UO}_2)\text{O}_3]$,⁴⁰ $\text{Ca}_2[(\text{UO}_2)\text{O}_3]$, $\text{Sr}_2[(\text{UO}_2)\text{O}_3]$,⁴¹ and $\text{Li}_4[(\text{UO}_2)\text{O}_3]$.⁴² These compounds contain uranyl square bipyramids that are linked into infinite chains through the sharing of two equatorial vertices. No additional linkages are found within the chain, and the structure is held together through bonding to lower-valence cations positioned between the chains.

KUS2 contains a novel uranyl sulfate sheet topology that is most closely related to the sheet in $(\text{NH}_4)(\text{UO}_2)\text{F}(\text{SeO}_4)(\text{H}_2\text{O})$.⁴³ Both structures contain uranyl pentagonal bipyramids that are linked into infinite chains by the sharing of a single vertex between neighboring uranyl polyhedra. The shared vertex in $(\text{NH}_4)(\text{UO}_2)\text{F}(\text{SeO}_4)(\text{H}_2\text{O})$ is an F atom, which is a rare connectivity between uranyl polyhedra. Both chains are linked into a two-dimensional sheet through the sharing of vertices between uranyl polyhedra and sulfate or selenate tetrahedra. The chains of uranyl polyhedra in $(\text{NH}_4)(\text{UO}_2)\text{F}(\text{SeO}_4)(\text{H}_2\text{O})$ are offset relative to the uranyl sulfate chains in *KUS2*, resulting in a new topology. These structures contain the only sheets with U^{6+} and XO_4 with direct linkages through sharing of vertices between uranyl polyhedra.

Uranyl compounds containing XO_4 ($\text{X} = \text{S}, \text{Cr}, \text{Se}, \text{Mo}$) are uniquely topologically diverse.⁴⁴ The flexibility of the $\text{U}-\text{O}-\text{X}$ angle is associated with the complexity of the structural linkages. Krivovichev (2004)⁴⁴ analyzed the bond lengths and angles of over 65 uranyl sulfate, chromate, and molybdate compounds. The $\text{U}-\text{O}-\text{S}$ bond angles for uranyl sulfates tends to vary from 127.7° to 175.4°, with a majority of the angles occurring between 130° and 150°. The $\text{U}-\text{O}-\text{Mo}$ bond angles in uranyl molybdates vary from 120° to 177° but display a broader distribution. A majority of uranyl molybdates have $\text{U}-\text{O}-\text{Mo}$ bond angles that vary from 120°

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Table 6. Comparison of the Number of Sulfate Tetrahedra Vertices Shared to Neighboring Uranyl Polyhedra Related to the U–O–S Bond Angle^a

no. of vertices	average	range	between 130–150°	refs
1	139.3	123.7–153.8	5 out of 6	47–52
2	141.2	123.6–160.0	12 out of 13	36, 38, 50, 53–60
3	143.8	129.6–162.3	3 out of 9	23, 37, 45, 50, 61–63
4	128.2	119.8–140.5	1 out of 11	22, 24, 64

^a The average bond angle and range of angles are listed, as well as the number of structures that contain U–O–S bond angles between 130° and 150°.

to ~165°; thus, the uranyl molybdate moiety can be considered more flexible. The relationship between flexibility and structural diversity is demonstrated by the existence of more than 10 types of three-dimensional framework structures for uranyl molybdates, compared to one known purely inorganic uranyl sulfate framework, β -(UO₂)(SO₄).⁴⁵

The hypothesis that the U–O–S angle of 143° is an intrinsic property of the uranyl sulfate bond is substantiated by observation in both aqueous solutions and in the solid state but is not consistent with all bond angles observed in uranyl sulfate structures.²⁸ The variation of U–O–S bond angles for uranyl sulfates sorted on the basis of the number of vertices shared to uranyl polyhedra for known uranyl sulfate solids is summarized in Table 6. The average U–O–S bond angles are consistent with the idea of an intrinsic angle, where as many as three of the sulfate vertices are shared with uranyl polyhedra. However, where all sulfate vertices are linked to uranyl polyhedra the bond angle noticeably decreases. As observed by Krivovichev (2004), the range of bond angles are similar, but the number of structures that have angles deviating from the 130–150° majority increases with the number of shared tetrahedral vertices.

The deviations of the U–O–S bond angle from the average value, especially where all tetrahedral vertices are shared, is most likely caused by steric constraints of the structure. Bond strengths within the uranyl polyhedra favor two-dimensional polymerization and sheet structures.¹⁸ If all sulfate tetrahedral vertices are to be shared with uranyl polyhedra arranged in a two-dimensional sheet or chain, then the U–O–S bond angles must be significantly distorted to accommodate the rigid O–S–O angles within the tetrahedron. The compound may tolerate the distortions of the U–O–S angle if the energetics of the sheet are favored over the energetics of the local environment. The coordination geometry of the uranyl sulfate complex in solution is influenced primarily by the local environment, as the overall energetics of an extended structure are not relevant. The occurrence of decreased bond angles where the sulfate

tetrahedron are linked through four vertices underscores the possible effect that the overall structural connectivity has on the local environment.

Smaller U–O–S angles may cause strain within the lattice, thus the stability of uranyl sulfate structures with four-connected tetrahedron is of interest. However, the structures of both uranopilite and the zippeite group contain such linkages. These uranyl sulfate minerals are widespread and have existed for thousands of years within geologic systems.⁴⁶ In contrast, a majority of the compounds with one, two, or three vertex linkages are synthetic, and are not known to form or endure under natural conditions. Therefore, the decreased U–O–S bond angles may cause additional stress within the lattice, but ultimately, the overall structural energies may be the overarching factor determining formation and stability of uranyl sulfate compounds.

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Supporting Information Available: Crystallographic information files (CIF) for (K(UO₂)(SO₄)(OH)(H₂O)) and K(UO₂)(SO₄)(OH). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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