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THE SHARING OF AN EDGE BETWEEN A URANYL PENTAGONAL BIPYRAMID AND SULFATE TETRAHEDRON IN THE STRUCTURE OF $KNa_5[(UO_2)(SO_4)_4](H_2O)$

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ABSTRACT

The new uranyl sulfate compound $KNa_5[(UO_2)(SO_4)_4](H_2O)$ has been synthesized and its structure has been determined. It is monoclinic, space group *C*2/*c*, *a* 16.917(1), *b* 5.5999(5), *c* 35.340(3) Å, β 90.437(2)°, *V* 3347.7(5) Å^3, *Z* = 8. The structure has been solved and refined on the basis of F^2 for all unique data collected with monochromatic Mo$K\alpha$ X-radiation and a CCD-based detector to an agreement factor *R*1 of 3.6%, calculated using 4981 unique observed reflections ($F_o \geq 4\sigma_F$). The structure contains an unusual uranyl sulfate cluster with composition $[(UO_2)(SO_4)_4]^{6-}$. The cluster is composed of a uranyl pentagonal bipyramid and four sulfate tetrahedra. Three sulfate tetrahedra are linked to the uranyl pentagonal bipyramid by the sharing of vertices, and the other shares an equatorial edge of the uranyl pentagonal bipyramid. The uranyl sulfate clusters are linked through bonds to K and Na cations, and by H bonding. The uranyl sulfate cluster, which was recently also found in two Na uranyl sulfates, is unusual in the sharing of an edge between a uranyl polyhedron and a $M^{6+}O_4$ tetrahedron.

Keywords: uranyl sulfate, uranium crystal chemistry, actinide sulfate.

SOMMAIRE

Nous avons synthésisé un nouveau composé sulfaté à uranyle, $KNa_5[(UO_2)(SO_4)_4](H_2O)$, et nous en avons déterminé la structure. Il s'agit d'une phase monoclinique, groupe spatial *C*2/*c*, *a* 16.917(1), *b* 5.5999(5), *c* 35.340(3) Å, β 90.437(2)°, *V* 3347.7(5) Å^3, *Z* = 8. La structure a été résolue et affinée en tenant compte des facteurs F^2 de toutes les données uniques en diffraction X, prélevées avec rayonnement monochromatique Mo$K\alpha$ et un détecteur à charges couplées, jusqu'à un facteur de concordance *R*1 de 3.6%, calculé avec 4981 réflexions uniques observées ($F_o \geq 4\sigma_F$). La structure contient un groupement de sulfate à uranyle inhabituel, ayant la composition $[(UO_2)(SO_4)_4]^{6-}$. Le groupement contient une bipyramide pentagonale à uranyle et quatre tétraèdres de sulfate. Trois de ces tétraèdres sont liés à une bipyramide pentagonale à uranyle par partage de coins, tandis que le quatrième partage une arête équatoriale d'une de ces bipyramides pentagonales. Les groupements de sulfate d'uranyle sont liés par liaisons avec les cations K et Na, et par liaisons hydrogène. Le groupement de sulfate d'uranyle, découvert récemment dans deux sulfates d'uranyle contenant le sodium, est inhabituel à cause du partage d'une arête entre un polyèdre à uranyle et un tétraèdre $M^{6+}O_4$.

(Traduit par la Rédaction)

Mots-clés: sulfate d'uranyle, cristallochimie de l'uranium, sulfate d'un actinide.

INTRODUCTION

Uranyl sulfate minerals are important constituents of many uranium deposits, although they typically are not abundant. Fifteen uranyl sulfates have been described as minerals (Mandarino 1999), but many uncertainties persist concerning their chemical compositions, structures and properties. Their fine grain-size and occurrence as admixtures of species make uranyl sulfates difficult to study. The structures are known for only four uranyl sulfate minerals; natural crystals were used to refine the structures of schröckingerite (Mereiter 1986), johannite (Mereiter 1982) and uranopilite (Burns 2001), whereas that of zippeite (Vochten *et al.* 1995) was reported on the basis of a synthetic crystal.

Uranyl sulfates may significantly control the mobility of uranium in rocks and aquifers that contain sulfate. The alteration of nuclear waste could give rise to uranyl sulfates, owing to the presence of sulfur as an impurity in some of the steel alloys used in waste containers. As such, uranyl sulfates may affect the mobility of radionuclides in a geological repository by directly incorpo-

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rating them into their crystal structures. Thus, uranyl sulfates are of considerable importance from an environmental perspective.

Uranyl sulfates are also interesting from a crystal-chemical point of view, as they combine uranyl polyhedra with $M^{6+}O_4$ tetrahedra (M = S, Cr, Mo). Burns *et al.* (1997) noted that the sharing of vertices only between $Ur\phi_n$ polyhedra and $M^{6+}O_4$ tetrahedra dominates the structures of such compounds, and that edge-sharing between $Ur\phi_n$ polyhedra and $M^{6+}O_4$ tetrahedra is very unusual, with only one example known. Burns *et al.* (1997) proposed that the lack of this mode of polymerization is associated with repulsion between the U^{6+} and M^{6+} cations. In contrast, studies of uranyl sulfate complexes in solution indicate that bidentate coordination of sulfate to uranyl, characterized by a U–S distance of 3.11 Å, is common (Moll *et al.* 2000). Crystal-structure analyses of uranyl sulfate compounds have the potential of providing insight into complexes in solution from which the crystals grew. In order to gain a more detailed understanding of the mineralogy and geochemistry of uranyl sulfates, we have undertaken studies of minerals from several localities, and synthetic crystals grown under a range of conditions. The purpose of the current contribution is to report the synthesis and structure of the compound $KNa_5[(UO_2)(SO_4)_4](H_2O)$, and to discuss the crystal-chemical implications of its unusual structure.

EXPERIMENTAL

Crystal synthesis

A uranyl sulfate solution was prepared by dissolving 5.78 g UO_3 (Alfa Aesar) in a solution containing 40 mL ultrapure water and 5.2 mL concentrated sulfuric acid. Five mL of the solution was placed in a test tube, 0.306 g of $KHSO_4$ (Merck) was added, and the pH was adjusted to 4.0 using sodium hydroxide. The resulting solution was placed in a Fisher Scientific Isotemp oven at 70°C until evaporation was complete. Acicular light yellow crystals of $KNa_5[(UO_2)(SO_4)_4](H_2O)$ up to ~1 mm in length were recovered.

Single-crystal X-ray diffraction

An acicular single crystal of $KNa_5[(UO_2)(SO_4)_4](H_2O)$ with dimensions $240 \times 40 \times 30$ μm^3 was selected and mounted on a glass fiber, and diffraction data were collected using a Bruker APEX SMART CCD diffractometer with a crystal-to-detector distance of 4.7 cm and Mo$K\alpha$ X-radiation. A sphere of three-dimensional data was collected using frame widths of 0.3° in ω, with 20 seconds spent counting per frame. The unit-cell dimensions (Table 1) were refined from 946 reflections using least-squares techniques. The data were reduced and corrected for Lorentz, polarization and background effects using the Bruker program SAINT. A semi-empirical absorption correction was applied on the basis of equivalent reflections by modeling the crystal as an ellipsoid, which reduced R_{INT} of 2365 intense reflections from 6.1 to 4.2%. A total of 34,335 intensities was collected, of which 6972 were independent, with 4981 classed as observed reflections ($|F_o| \geq 4\sigma_F$).

STRUCTURE SOLUTION AND REFINEMENT

The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the crystal structure. Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from *International Tables for X-Ray Crystallography*, Vol. IV (Ibers & Hamilton 1974). The systematic absences of reflections observed are consistent with space groups *C*2/*c* and *Cc*. The structure was solved in space group *C*2/*c* by direct methods, which gave the positions of the U and S atoms. The Na, K and O atoms were located on difference-Fourier maps calculated following refinement of the model. The structure model included refined atom-coordinates, anisotropic displacement parameters for all atoms, and a weighting scheme of the structure factors. It was refined on the basis of F^2 for all unique reflections, and gave a final agreement index (R1) of 3.6%, calculated for the 4981 unique observed ($|F_o| \geq 4\sigma_F$) reflections. In the final cycle of refinement, the mean parameter shift/esd was 0.000. The final atomic coordinates and anisotropic displacement parameters are given in Table 2; selected interatomic distances and angles are presented in Table 3. A bond-valence analysis is presented in Table 4. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

TABLE 1. CRYSTALLOGRAPHIC DATA AND DETAILS OF THE STRUCTURE REFINEMENT FOR $KNa_5[(UO_2)(SO_4)_4](H_2O)$

a (Å)	16.917(1)
b (Å)	5.5999(5)
c (Å)	35.340(3)
β (°)	90.437(2)
V (Å^3)	3347.7(5)
Space group	*C*2/*c*
Z	8
Formula	$KNa_5[(UO_2)(SO_4)_4](H_2O)$
F (000)	3072
μ (mm^{-1})	10.7
D_{calc} (g/cm^3)	3.279
Crystal size (μm^3)	240 x 40 x 30
Total ref.	34,335
Unique ref.	6972
R_{int} (%)	7.7
Unique $\lvert F_o \rvert \geq 4\sigma_F$	4981
Refinement method	Full-matrix least-squares on F^2
Parameters varied	275
R1 (%)	3.6
wR2 (%)	5.6
S	0.93
Max., min. $\Delta\rho$, e.Å^{-3}	2.12, -1.99

TABLE 2. ATOM POSITIONS AND DISPLACEMENT PARAMETERS FOR $KNa_5[(UO_2)(SO_4)_4](H_2O)$

	x	y	z	U_{eq}[a]	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	0.0647(1)	0.8543(1)	0.1305(1)	0.016(1)	0.018(1)	0.015(1)	0.014(1)	0.000(1)	0.001(1)	0.002(1)
S(1)	-0.0406(1)	0.0541(2)	0.1942(1)	0.015(1)	0.016(1)	0.014(1)	0.015(1)	-0.002(1)	0.001(1)	0.002(1)
S(2)	0.1984(1)	0.5947(2)	0.2005(1)	0.016(1)	0.017(1)	0.013(1)	0.017(1)	0.000(1)	-0.002(1)	0.002(1)
S(3)	0.1933(1)	0.7487(2)	0.0523(1)	0.017(1)	0.019(1)	0.016(1)	0.017(1)	-0.001(1)	0.004(1)	0.003(1)
S(4)	0.4475(1)	0.2307(2)	0.0481(1)	0.019(1)	0.024(1)	0.016(1)	0.017(1)	-0.002(1)	-0.004(1)	0.003(1)
K(1)	0.2912(1)	0.4352(3)	0.1183(1)	0.058(1)	0.076(1)	0.064(1)	0.033(1)	0.019(1)	0.011(1)	0.033(1)
Na(1)	¼	¼	0	0.026(1)	0.027(2)	0.018(1)	0.034(2)	-0.005(1)	0.010(1)	0.002(1)
Na(2)	0.1505(1)	0.1040(3)	0.2363(1)	0.024(1)	0.023(1)	0.021(1)	0.026(1)	-0.002(1)	-0.001(1)	-0.002(1)
Na(3)	0	0.5794(4)	¼	0.025(1)	0.021(1)	0.019(1)	0.034(2)	0	-0.005(1)	0
Na(4)	0.0754(1)	0.2841(3)	0.0505(1)	0.028(1)	0.026(1)	0.024(1)	0.034(1)	0.000(1)	0.003(1)	0.007(1)
Na(5)	0.3320(1)	0.0635(3)	0.1992(1)	0.031(1)	0.025(1)	0.020(1)	0.047(1)	0.004(1)	-0.003(1)	0.001(1)
Na(6)	0.3883(1)	0.7097(3)	0.0239(1)	0.029(1)	0.033(1)	0.023(1)	0.029(1)	0.000(1)	-0.006(1)	-0.003(1)
O(1)	0.1107(2)	0.1286(5)	0.1179(1)	0.023(1)	0.028(2)	0.017(2)	0.024(2)	0.001(1)	0.003(1)	-0.004(1)
O(2)	-0.0799(2)	0.8675(5)	0.2161(1)	0.021(1)	0.026(2)	0.017(2)	0.021(2)	0.002(1)	0.004(1)	-0.002(1)
O(3)	0.1433(2)	0.6697(5)	0.0848(1)	0.023(1)	0.035(2)	0.014(2)	0.019(2)	0.002(1)	0.011(1)	0.006(1)
O(4)	0.0461(2)	0.0109(5)	0.1948(1)	0.019(1)	0.013(2)	0.026(2)	0.020(2)	-0.006(1)	-0.001(1)	0.002(1)
O(5)	0.0194(2)	0.5831(5)	0.1421(1)	0.022(1)	0.024(2)	0.016(2)	0.026(2)	0.001(1)	0.003(1)	-0.001(1)
O(6)	0.2423(2)	0.3830(6)	0.1894(1)	0.032(1)	0.032(2)	0.026(2)	0.038(2)	-0.006(2)	-0.001(2)	0.016(2)
O(7)	-0.0608(2)	0.2872(5)	0.2092(1)	0.022(1)	0.027(2)	0.014(2)	0.024(2)	-0.008(1)	0.003(1)	0.003(1)
O(8)	0.1670(2)	0.9805(5)	0.0382(1)	0.023(1)	0.031(2)	0.013(2)	0.025(2)	0.003(1)	0.008(2)	0.005(1)
O(9)	-0.0613(2)	0.0317(5)	0.1533(1)	0.019(1)	0.019(2)	0.024(2)	0.015(2)	-0.003(1)	-0.001(1)	0.006(1)
O(10)	0.4566(2)	-0.0125(5)	0.0625(1)	0.022(1)	0.028(2)	0.013(2)	0.024(2)	0.000(1)	-0.002(1)	0.002(1)
O(11)	0.1826(2)	0.5672(5)	0.0230(1)	0.024(1)	0.031(2)	0.020(2)	0.020(2)	-0.006(1)	0.002(1)	0.005(1)
O(12)	0.3643(2)	0.2993(6)	0.0461(1)	0.035(1)	0.024(2)	0.024(2)	0.056(3)	-0.001(2)	-0.013(2)	0.008(2)
O(13)	0.4871(2)	0.4027(5)	0.0754(1)	0.023(1)	0.032(2)	0.013(2)	0.024(2)	-0.003(1)	-0.009(1)	0.002(1)
O(14)	0.1292(2)	0.5256(5)	0.2223(1)	0.025(1)	0.022(2)	0.023(2)	0.031(2)	0.007(2)	0.005(2)	-0.003(1)
O(15)	0.1746(2)	0.7283(6)	0.1657(1)	0.026(1)	0.023(2)	0.034(2)	0.021(2)	0.007(2)	-0.002(1)	0.003(2)
O(16)	0.2475(2)	0.7587(5)	0.2229(1)	0.026(1)	0.029(2)	0.020(2)	0.028(2)	0.000(1)	-0.007(2)	-0.007(1)
O(17)	0.2751(2)	0.7595(6)	0.0653(1)	0.033(1)	0.019(2)	0.033(2)	0.047(2)	-0.004(2)	-0.005(2)	0.003(2)
O(18)	0.4841(2)	0.2590(6)	0.0113(1)	0.037(1)	0.055(3)	0.034(2)	0.021(2)	-0.003(2)	0.008(2)	-0.012(2)
OW19	-0.1564(2)	0.4891(7)	0.1311(1)	0.046(1)	0.039(2)	0.055(3)	0.044(3)	-0.009(2)	0.009(2)	-0.005(2)

[a] $U_{eq} = \frac{1}{3}\Sigma U_{ij} a_{i*} b_{j*} a_i b_j$. The anisotropic displacement factors take the form $-2\pi[h^2 a^* U_{11} + \ldots 2hka^* b^* U_{12}]$.

RESULTS

Cation polyhedra

The structure of $KNa_5[(UO_2)(SO_4)_4](H_2O)$ contains a symmetrically unique U site. Consideration of the geometry of the coordination polyhedron (Table 3) and the sum of bond-valences incident upon the site (5.99 valence units, *vu*, Table 4) indicates that the uranium is hexavalent. The U^{6+} cation is strongly bonded to two atoms of O, forming an approximately linear $(UO_2)^{2+}$ uranyl ion (designated *Ur*) with a $\langle U–O_{Ur} \rangle$ bond-length of 1.765 Å. The uranyl ion is coordinated by five atoms of O arranged at the equatorial vertices of a pentagonal bipyramid that is capped by the O_{Ur} atoms. The $\langle U–O_{eq} \rangle$ bond-length of 2.396 Å is in good agreement with 2.37(9) Å, the average value obtained for uranyl pentagonal bipyramids in many well-refined structures (Burns *et al.* 1997).

The structure contains four symmetrically distinct S^{6+} cations, each of which is tetrahedrally coordinated by O atoms. The $\langle S–O \rangle$ bond-lengths range from 1.468 to 1.473 Å, values that are typical of sulfate in solids (Hawthorne *et al.* 2000). There are seven low-valence cation sites in the structure, one of which contains dominantly K, whereas the others contain Na. Refinement of the site occupancies of these sites indicated that Na(1) to Na(6) are 100% occupied by Na, whereas the K(1) site contains 69(1)% K and 31(1)% Na. Substitution of Na for K in this site is reflected by the relatively large displacement-parameters for the site, which suggest that Na assumes a slightly different position than K. The K(1) site is coordinated by eight ligands, two of which are H_2O groups, with a $\langle K(1)–\phi \rangle$ (ϕ: O, H_2O) bond length of 2.892 Å. The Na sites are coordinated by either six or seven ligands. The Na(5) coordination polyhedron contains the single symmetrically distinct H_2O group in the structure. The $\langle Na–\phi \rangle$ bond lengths, which range from 2.415 to 2.542 Å, are significantly shorter than the average bond-length for the K(1) polyhedron.

Structure connectivity

Projection of the structure along [010] reveals that it contains finite clusters of uranyl pentagonal bipyramids and sulfate tetrahedra, with K and Na cations located between the clusters (Fig. 1). The details of the uranyl sulfate cluster are shown in Figure 2. It involves the linkage of four sulfate tetrahedra to the equatorial vertices of the uranyl pentagonal bipyramid, three by the sharing of vertices only, and one by the sharing of an edge. The U(1)–S(1) separation is only 3.090(1) Å as a consequence of the sharing of polyhedron edges. The uranyl sulfate clusters are linked by bonding to K and Na cations, as well as by hydrogen bonding associated with the single symmetrically distinct H_2O group, which is bonded to one Na and one K cation.

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR $KNa_5[(UO_2)(SO_4)_4](H_2O)$

U(1)-O(5)	1.751(3)		Na(4)-O(8)c	2.344(3)
U(1)-O(1)a	1.780(3)		Na(4)-O(10)b	2.352(4)
U(1)-O(3)	2.340(3)		Na(4)-O(18)f	2.411(4)
U(1)-O(15)	2.339(3)		Na(4)-O(11)	2.602(4)
U(1)-O(13)b	2.353(3)		Na(4)-O(1)	2.602(4)
U(1)-O(4)a	2.460(3)		Na(4)-O(3)	2.725(4)
U(1)-O(9)a	2.490(3)		Na(4)-O(13)k	2.755(4)
<U(1)-O_{Ur}>	1.765		<Na(4)-O>	2.542
<U(1)-O_{eq}>	2.396			
O(5)-U(1)-O(1)a	179.1(1)		Na(5)-O(2)d	2.337(4)
			Na(5)-O(6)	2.369(4)
S(1)-O(7)	1.451(3)		Na(5)-O(16)c	2.383(4)
S(1)-O(2)c	1.463(3)		Na(5)-O(7)d	2.408(3)
S(1)-O(4)	1.487(3)		Na(5)-OW19d	2.450(4)
S(1)-O(9)	1.489(3)		Na(5)-O(14)h	2.855(4)
<S(1)-O>	1.472		<Na(5)-O>	2.467
S(2)-O(6)	1.455(3)		Na(6)-O(10)a	2.364(3)
S(2)-O(14)	1.457(3)		Na(6)-O(11)g	2.391(4)
S(2)-O(16)	1.466(3)		Na(6)-O(17)	2.434(4)
S(2)-O(15)	1.493(3)		Na(6)-O(12)	2.463(4)
<S(2)-O>	1.468		Na(6)-O(18)l	2.506(4)
			Na(6)-O(8)g	2.607(4)
S(3)-O(17)	1.455(3)		Na(6)-O(13)	3.003(3)
S(3)-O(8)	1.459(3)		<Na(6)-O>	2.538
S(3)-O(11)	1.462(3)			
S(3)-O(3)	1.498(3)		O(7)-S(1)-O(2)c	109.9(2)
<S(3)-O>	1.468		O(7)-S(1)-O(4)	112.0(2)
			O(2)c-S(1)-O(4)	109.1(2)
S(4)-O(18)	1.455(4)		O(7)-S(1)-O(9)	112.1(2)
S(4)-O(10)	1.461(3)		O(2)c-S(1)-O(9)	110.5(2)
S(4)-O(12)	1.461(3)		O(4)-S(1)-O(9)	103.0(2)
S(4)-O(13)	1.516(3)		<O-S(1)-O>	109.4
<S(4)-O>	1.473			
			O(6)-S(2)-O(14)	109.9(2)
K(1)-O(17)	2.623(4)		O(6)-S(2)-O(16)	111.5(2)
K(1)-O(6)	2.667(4)		O(14)-S(2)-O(16)	109.6(2)
K(1)-OW19d	2.688(4)		O(6)-S(2)-O(15)	108.7(2)
K(1)-O(9)e	2.828(3)		O(14)-S(2)-O(15)	110.8(2)
K(1)-O(12)	2.945(4)		O(16)-S(2)-O(15)	106.2(2)
K(1)-O(3)	3.057(3)		<O-S(2)-O>	109.4
K(1)-O(15)	3.072(4)			
K(1)-OW19e	3.257(4)		O(17)-S(3)-O(8)	111.0(2)
<K(1)-O>	2.892		O(17)-S(3)-O(11)	111.4(2)
			O(8)-S(3)-O(11)	109.8(2)
Na(1)-O(11),f	2.265(3)	x2	O(17)-S(3)-O(3)	108.2(2)
Na(1)-O(8)c,g	2.470(3)	x2	O(8)-S(3)-O(3)	110.6(2)
Na(1)-O(12)f	2.534(3)	x2	O(11)-S(3)-O(3)	105.6(2)
<Na(1)-O>	2.423		<O-S(3)-O>	109.4
Na(2)-O(4)	2.346(3)		O(18)-S(4)-O(10)	111.6(2)
Na(2)-O(16)h	2.401(4)		O(18)-S(4)-O(12)	110.1(2)
Na(2)-O(14)	2.439(4)		O(10)-S(4)-O(12)	111.1(2)
Na(2)-O(2)i	2.457(3)		O(18)-S(4)-O(13)	108.1(2)
Na(2)-O(16)c	2.582(4)		O(10)-S(4)-O(13)	109.1(2)
Na(2)-O(7)j	2.666(4)		O(12)-S(4)-O(13)	106.6(2)
Na(2)-O(6)	2.765(4)		<O-S(4)-O>	109.4
<Na(2)-O>	2.522			
Na(3)-O(7),j	2.407(3)	x2		
Na(3)-O(2),j	2.417(3)	x2		
Na(3)-O(14),j	2.421(3)	x2		
<Na(3)-O>	2.415			

a = x, y+1, z; b = x-1/2, y+1/2, z; c = x, y-1, z; d = x+1/2, y-1/2, z; e = x+1/2, y+1/2, z; f = -x+1/2, -y+1/2, -z; g = -x+1/2, -y+3/2, -z; h = -x+1/2, y-1/2, -z+1/2; i = -x, y-1, -z+1/2; j = -x, y, -z+1/2; k = x-1/2, y-1/2, z; l = -x+1, -y+1, -z

DISCUSSION

Burns *et al.* (1996) developed a structural hierarchy of uranyl minerals and inorganic compounds that is based upon the polymerization of polyhedra of higher bond-valence. The uranyl sulfate cluster found in $KNa_5[(UO_2)(SO_4)_4](H_2O)$ places this compound in the class of structures that are based upon finite clusters of polyhedra of higher bond-valence. There are relatively few structures in this class, as there is a strong tendency for uranyl compounds to adopt structures based upon sheets of polyhedra, owing to the strongly asymmetric distribution of bond valences within uranyl polyhedra (Burns *et al.* 1997). The uranyl sulfate cluster in $KNa_5[(UO_2)(SO_4)_4](H_2O)$ is remarkable in that it involves the sharing of an equatorial edge of the uranyl pentagonal bipyramid with a sulfate tetrahedron. Until recently, the only known structure that involved the sharing of an edge of *any* tetrahedron containing a hexavalent cation with a uranyl polyhedron was $K_4[(UO_2)(SO_4)_3]$ (Mikhailov *et al.* 1977) (Fig. 3).

We have recently found uranyl sulfate clusters that are topologically identical to that in $KNa_5[(UO_2)(SO_4)_4](H_2O)$ in the structures of $Na_6[(UO_2)(SO_4)_4](H_2O)_2$ (Hayden & Burns 2002) and $Na_{10}[(UO_2)(SO_4)_4](SO_4)_2(H_2O)_3$ (Burns & Hayden 2002). All three of these compounds were grown under similar conditions, specifically by the evaporation of uranyl sulfate solutions in air at 70°C. The rapid growth of mm-sized crystals of these compounds is in contrast to our findings for most other uranyl sulfates, such as zippeite and related compounds, for which it is difficult to grow crystals larger than a few tens of μm in maximum dimension (unpublished results). The existence of clusters involving the sharing of an edge between a uranyl pentagonal bipyramid and a sulfate tetrahedron in these structures, with U–S separations of ~3.1 Å, is consistent with the presence of uranyl sulfate complexes in solution with bidentate coordination of sulfate to uranyl, characterized by a U–S distance of 3.11 Å, as reported by Moll *et al.* (2000). These clusters are apparently stable, despite the relatively short U–S distance. The absence in minerals of any clusters involving the sharing of an edge of a uranyl polyhedron with any tetrahedron containing a hexavalent cation is interesting, and could conceivably reflect the lower stability of such clusters, as compared to the sheets of polyhedra, which are prevalent.

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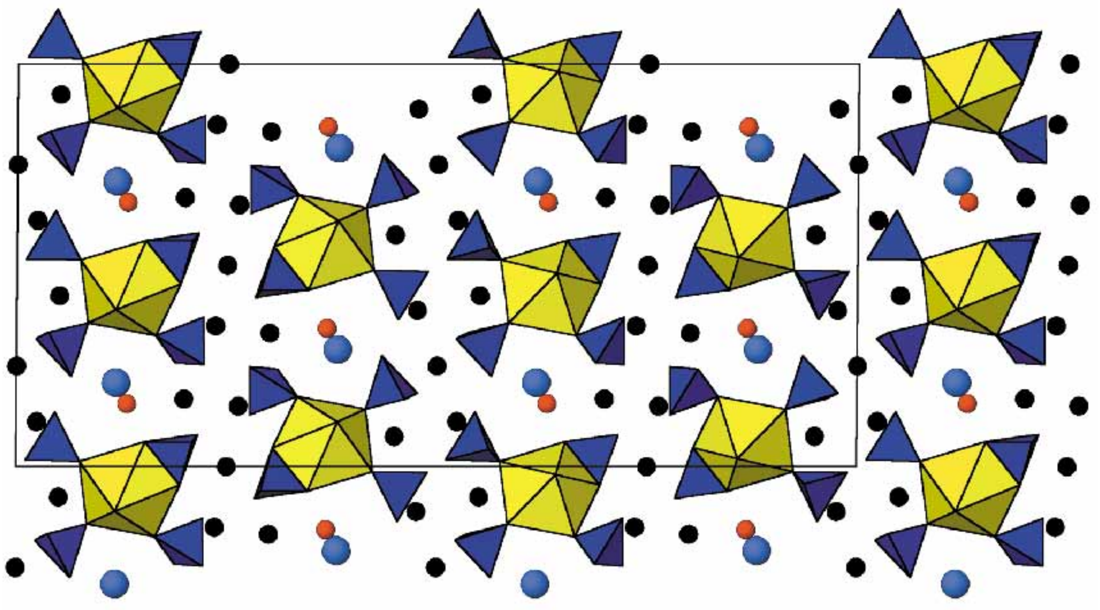

FIG. 1. Polyhedral representation of the structure of $KNa_5[(UO_2)(SO_4)_4](H_2O)$ projected along [010]. Uranyl pentagonal bipyramids and sulfate tetrahedra are colored yellow and blue, respectively. Na and K cations are shown as black and blue balls, respectively, and the O atoms of the H_2O group are shown as red balls.

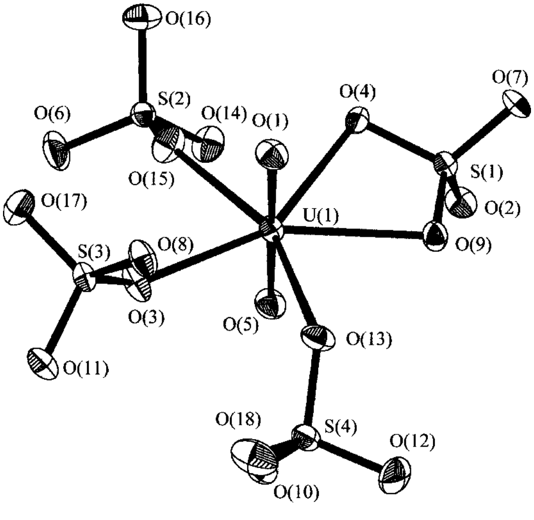

FIG. 2. The uranyl sulfate cluster of composition $[(UO_2)(SO_4)_4]^{6-}$ in the structure of $KNa_5[(UO_2)(SO_4)_4](H_2O)$.

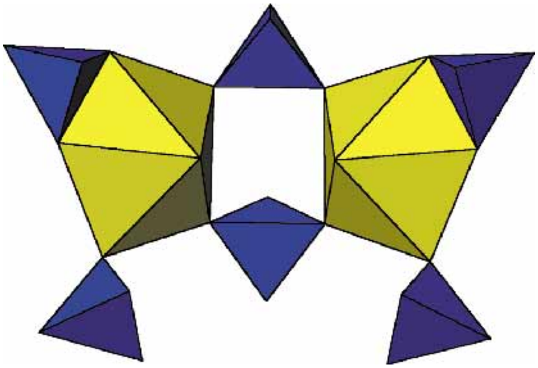

FIG. 3. The uranyl sulfate cluster of composition $[(UO_2)(SO_4)_3]_2^{8-}$ in the structure of $K_4[(UO_2)(SO_4)_3]$. Legend as in Figure 1.

TABLE 4. BOND-VALENCE ANALYSIS* (*vu*) FOR $KNa_5[(UO_2)(SO_4)_4](H_2O)$

	U(1)	S(1)	S(2)	S(3)	S(4)	K(1)	Na(1)	Na(2)	Na(3)	Na(4)	Na(5)	Na(6)	Σ
O(1)	1.68									0.11			1.79
O(2)		1.55						0.17	$0.19^{\times 2\downarrow}$		0.23		2.14
O(3)	0.56			1.41		0.08				0.08			2.13
O(4)	0.44	1.45						0.23					2.12
O(5)	1.78												1.78
O(6)			1.58			0.23		0.07			0.21		2.09
O(7)		1.60						0.10	$0.19^{\times 2\downarrow}$		0.19		2.08
O(8)				1.56			$0.16^{\times 2\downarrow}$			0.23		0.11	2.06
O(9)	0.42	1.44				0.15							2.01
O(10)					1.55					0.22		0.22	1.99
O(11)				1.55			$0.28^{\times 2\downarrow}$			0.11		0.20	2.14
O(12)					1.55	0.11	$0.14^{\times 2\downarrow}$					0.17	1.97
O(13)	0.55				1.34					0.07		0.04	2.00
O(14)			1.57					0.18	$0.18^{\times 2\downarrow}$		0.06		1.99
O(15)	0.56		1.42			0.08							2.06
O(16)			1.53					0.32			0.21		2.06
O(17)				1.58		0.26						0.18	2.02
O(18)					1.58					0.19		0.15	1.92
OW(19)						0.27					0.17		0.44
Σ	5.99	6.04	6.10	6.10	6.02	1.18	1.16	1.07	1.12	1.01	1.07	1.07	

* bond-valence parameters for U^{6+}-O from Burns *et al.* (1997), for S^{6+}-O and Na^{+}-O from Brese & O'Keeffe (1991)

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