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A Novel Uranyl Sulfate Cluster in the Structure of $Na_6(UO_2)(SO_4)_4(H_2O)_2$

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The sodium uranyl sulfate hydrate, $Na_6(UO_2)(SO_4)_4(H_2O)_2$, has been synthesized and the crystal structure has been determined by single-crystal X-ray diffraction. The structure crystallizes in space group $P\bar{1}$, $a = 5.5503(5)$, $b = 11.2456(9)$, and $c = 14.256(1)$ Å, $\alpha = 91.483(2)$, $\beta = 92.583(2)$, and $\gamma = 97.588(2)^\circ$, $V = 880.6(2)$ Å^3, $Z = 2$, and has been 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 ($R1$) of 3.38%, calculated using 5617 unique observed reflections ($|F_o| \geq 4\sigma_F$). The structure contains a novel uranyl sulfate cluster with composition $[(UO_2)(SO_4)_4]^{6-}$ that 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. This is the second structure known to involve the sharing of an edge of a uranyl polyhedron with a tetrahedron containing a hexavalent cation. The uranyl sulfate clusters are linked through bonds to Na cations, and by H bonding. © 2002 Elsevier Science

Key Words: **uranyl sulfate; uranium crystal chemistry; actinide sulfate.**

INTRODUCTION

Uranyl compounds are environmentally important because they form in the oxidized portions of U deposits, in mine and mill tailings derived from U mining, in soils contaminated with actinides, and as alteration products of nuclear waste (1–6). Uranyl sulfates are fairly widespread as mineral species, but most remain poorly understood; many uncertainties persist concerning their chemical compositions, structures, and properties. Admixtures of uranyl sulfate species consisting of fine-grained mats and coatings are typical in nature, making their detailed characterization difficult (2). We have undertaken a systematic study of the structures of natural and synthetic uranyl sulfates, and have grown crystals of a new sodium uranyl sulfate that contains a novel uranyl sulfate cluster.

EXPERIMENT

Crystal Synthesis

A uranyl sulfate solution was prepared by dissolving 5.78 g of UO_3 (Alfa Aesar) in a solution containing 40 mL of ultrapure water and 5.2 mL of concentrated sulfuric acid. Five milliliters of the solution was placed in a test tube, 0.65 g $ZnSO_4 \cdot 7H_2O$ (Sigma) 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. The products consisted of approximately 80% acicular light yellow crystals of $Na_6(UO_2)(SO_4)_4(H_2O)_2$ up to ~500 μm in length; the remaining product was fine-grained yellow powder.

Single-Crystal X-Ray Diffraction

An acicular single crystal of $Na_6(UO_2)(SO_4)_4(H_2O)_2$ with dimensions $420 \times 25 \times 20$ 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 3804 reflections using least-squares techniques. The data were reduced and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A semiempirical absorption correction was applied on the basis of equivalent reflections by modeling the crystal as an ellipsoid, which reduced R_{INT} of 1833 intense reflections from 6.0% to 3.9%. A total of 18,006 intensities was collected, of which 7122 were independent, with 5617 classed as observed reflections ($|F_o| \geq 4\sigma_F$).

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TABLE 1
Crystallographic Data and Details of the Structure Refinement of $Na_6(UO_2)(SO_4)_4(H_2O)_2$

a (Å)	5.5503(5)
b (Å)	11.2456(9)
c (Å)	14.256(1)
α (°)	91.483(2)
β (°)	92.583(2)
γ (°)	97.588(2)
V (Å^3)	880.6(2)
Space group	$P\bar{1}$
Z	2
Formula	$Na_6(UO_2)(SO_4)_4(H_2O)_2$
F (000)	772
μ (mm^{-1})	9.94
D_{calc} (g/cm^3)	3.123
Crystal size (μm)	420 × 25 × 20
Total ref.	18,006
Unique ref.	7122
R_{int} (%)	5.9
Unique $\|F_o\| \geq 4\sigma_F$	5617
Refinement method	Full-matrix least-squares on F^2
Parameters varied	283
$R1$ (%)	3.38
$wR2$ (%)	7.43
S	0.83
$w = 1/[\sigma^2(F_o^2) + (0.0219P)^2 + 0.68P], P = (\max(F_o^2, 0) + 2F_c^2)/3$	
Max., min. $\Delta\rho$, e.Å^{-3}	2.22, − 1.92

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 (7). The structure was solved in space group $P\bar{1}$ by direct methods, which gave the positions of the U and S atoms. The Na and O atoms were located on difference Fourier maps calculated following refinement of the model. The structure model included refined atomic coordinates, anisotropic displacement parameters for all atoms, and a weighting scheme of the structure factors (Table 1). It was refined on the basis of F^2 for all unique reflections, and gave a final $R1$ of 3.38%, calculated for the 5617 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 given in Table 3. A bond-valence analysis is presented in Table 4.

RESULTS

Cation Polyhedra

The structure of $Na_6(UO_2)(SO_4)_4(H_2O)_2$ contains one symmetrically distinct U atom, and consideration of its coordination environment (Table 3) and the sum of bond valences incident upon the site (6.02 *vu*, Table 4) indicates it is occupied by U^{6+}. The U^{6+} cation is strongly bonded to two O atoms, forming an approximately linear $(UO_2)^{2+}$ uranyl ion (designated Ur) with a $\langle U\text{–}O_{Ur}\rangle$ bond length of 1.772 Å. The uranyl ion is coordinated by O atoms located at the equatorial vertices of a pentagonal bipyramid that is capped by the O_{Ur} atoms. The $\langle U\text{–}O_{eq}\rangle$ (eq: equatorial) bond length of 2.385 Å is in good agreement with the average bond length of 2.37(9) Å for uranyl polyhedra from numerous well-refined structures (8).

There are four unique S^{6+} cations in the structure, each of which is tetrahedrally coordinated by O atoms, with $\langle S\text{–}O\rangle$ bond lengths ranging from 1.466 to 1.475 Å. The structure contains seven symmetrically distinct Na cations, two of which [Na(6) and Na(7)] are located on centers of symmetry. The Na(1), Na(2), Na(3), and Na(6) cations are each coordinated by six ligands arranged at the vertices of distorted octahedra, with $\langle Na\text{–}\phi\rangle$ (ϕ: O, H_2O) bond lengths ranging from 2.419 to 2.477 Å. The Na(2)ϕ_6 and Na(3)ϕ_6 octahedra contain only O atoms, whereas the Na(1)ϕ_6 octahedron contains five O atoms and one H_2O group, and the Na(6)ϕ_6 octahedron has four O atoms and two H_2O groups. The Na(4) cation is coordinated by seven atoms of O. The Na(5) and Na(7) cations are each coordinated by eight ligands. The Na(5)ϕ_8 polyhedron contains seven O atoms and one H_2O group, whereas Na(7)ϕ_8 has six O atoms and two H_2O groups.

Structure Connectivity

The structure of $Na_6(UO_2)(SO_4)_4(H_2O)_2$ contains novel uranyl sulfate clusters with composition $[(UO_2)(SO_4)_4]^{6-}$

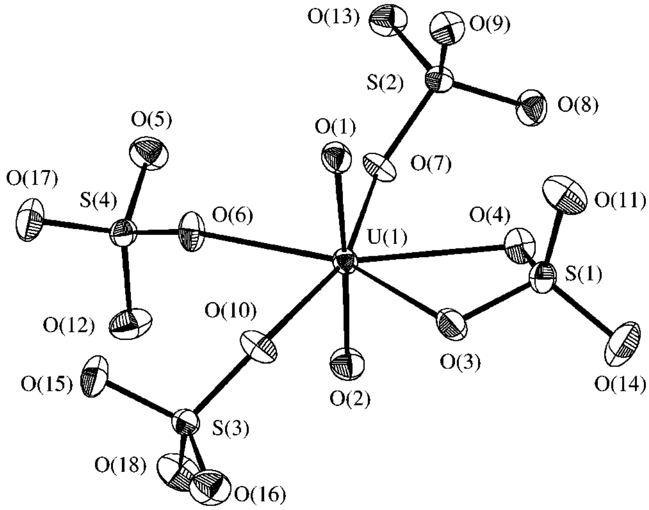

FIG. 1. The uranyl sulfate cluster in the structure of $Na_6(UO_2)(SO_4)_4(H_2O)_2$.

TABLE 2
Atomic Positions and Displacement Parameters (Å × 10^3) for $Na_6(UO_2)(SO_4)_4(H_2O)_2$

	x	y	z	U_{eq}[a]	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	0.74535(3)	0.29074(2)	0.24472(1)	13.55(5)	13.96(8)	12.41(8)	14.03(8)	– 0.43(6)	– 0.47(6)	1.08(6)
S(1)	0.7008(2)	0.5628(1)	0.25376(9)	17.8(2	20.5(6)	12.4(5)	20.6(6)	0.6(4)	1.1(5)	2.9(4)
S(2)	0.6897(2)	0.2861(1)	0.49165(8)	14.8(2)	14.8(5)	14.3(5)	14.9(5)	0.6(4)	0.3(4)	– 0.1(4)
S(3)	0.8448(2)	0.2086(1)	0.00639(8)	16.0(2)	18.0(5)	15.0(5)	14.9(5)	– 0.6(4)	– 0.9(4)	2.3(4)
S(4)	0.2274(2)	0.0317(1)	0.74657(9)	16.2(2)	18.1(6)	11.4(5)	18.9(6)	0.6(4)	– 2.8(4)	2.0(4)
Na(1)	0.1621(4)	0.2284(2)	0.5764(1)	23.2(4)	22(1)	23(1)	26(1)	2.7(8)	– 0.2(9)	4.8(8)
Na(2)	– 0.2338(4)	0.2297(2)	0.7518(2)	30.2(5)	21(1)	24(1)	47(1)	11(1)	9(1)	5.8(9)
Na(3)	0.7507(4)	0.5323(2)	0.5838(1)	26.9(5)	24(1)	24(1)	30(1)	– 6.6(9)	4.0(9)	– 4.6(9)
Na(4)	0.7208(4)	– 0.0356(2)	– 0.1039(2)	31.2(5)	38(1)	23(1)	33(1)	2.2(9)	– 9(1)	7(1)
Na(5)	0.3408(4)	0.2340(2)	– 0.0937(2)	31.1(5)	32(1)	33(1)	29(1)	6(1)	4(1)	6(1)
Na(6)	$\frac{1}{2}$	0	$\frac{1}{2}$	44(1)	29(2)	23(2)	77(3)	– 12(2)	– 17(2)	4(1)
Na(7)	0	$\frac{1}{2}$	0	63(1)	31(2)	25(2)	131(4)	– 1(2)	– 7(2)	6(2)
O(1)	0.0427(6)	0.3425(3)	0.2910(2)	20.6(7)	19(2)	18(2)	24(2)	– 3(1)	0(1)	0(1)
O(2)	0.4481(6)	0.2335(3)	0.1996(2)	22.5(8)	19(2)	22(2)	26(2)	– 2(1)	0(1)	– 1(1)
O(3)	0.7647(7)	0.4907(3)	0.1711(2)	22.4(8)	31(2)	18(2)	18(2)	– 2(1)	2(2)	4(1)
O(4)	0.6003(6)	0.4674(3)	0.3177(2)	20.7(7)	24(2)	15(2)	23(2)	2(1)	6(1)	1(1)
O(5)	0.2366(7)	0.0499(3)	0.6447(2)	27.7(8)	37(2)	26(2)	19(2)	5(2)	– 2(2)	1(2)
O(6)	0.1505(6)	– 0.0987(3)	0.7598(3)	22.8(8)	27(2)	11(2)	31(2)	1(1)	6(2)	2(1)
O(7)	0.6299(6)	0.2323(3)	0.3943(2)	20.5(7)	24(2)	21(2)	14(2)	– 5(1)	0(1)	– 2(1)
O(8)	0.4919(6)	0.3516(3)	0.5181(2)	22.7(8)	17(2)	22(2)	29(2)	– 5(2)	4(2)	5(1)
O(9)	0.9195(6)	0.3652(3)	0.4931(2)	20.5(7)	18(2)	17(2)	25(2)	2(1)	1(1)	– 4(1)
O(10)	0.8865(6)	0.2847(3)	0.0947(2)	23.4(8)	27(2)	24(2)	17(2)	– 6(1)	2(1)	– 5(2)
O(11)	0.9172(7)	0.6332(3)	0.2978(3)	29.6(9)	30(2)	27(2)	27(2)	– 4(2)	3(2)	– 11(2)
O(12)	0.4664(7)	0.0682(3)	0.7932(3)	28.0(9)	23(2)	26(2)	33(2)	9(2)	– 8(2)	– 3(2)
O(13)	0.7098(6)	0.1864(3)	0.5551(2)	23.2(8)	26(2)	20(2)	22(2)	7(1)	– 2(2)	0(1)
O(14)	0.5233(8)	0.6411(4)	0.2257(3)	37(1)	39(2)	31(2)	45(3)	9(2)	5(2)	20(2)
O(15)	0.0421(7)	0.1363(3)	0.0021(3)	30.5(9)	31(2)	29(2)	34(2)	– 1(2)	3(2)	16(2)
O(16)	0.8478(7)	0.2885(3)	– 0.0725(3)	29.5(9)	42(2)	26(2)	20(2)	7(2)	– 1(2)	5(2)
O(17)	0.0437(7)	0.0958(3)	0.7878(3)	30.0(9)	32(2)	23(2)	38(2)	– 3(2)	3(2)	12(2)
O(18)	0.6106(7)	0.1319(3)	0.0077(3)	29.9(9)	24(2)	30(2)	31(2)	– 5(2)	– 1(2)	– 11(2)
$H_2O(19)$	0.1755(7)	0.1001(3)	0.4365(3)	27.4(8)	26(2)	26(2)	29(2)	– 1(2)	– 3(2)	1(2)
$H_2O(20)$	0.3452(7)	0.4028(4)	0.0396(3)	35(1)	30(2)	33(2)	38(2)	7(2)	– 7(2)	– 2(2)

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

(Fig. 1). Four sulfate tetrahedra are linked to the uranyl pentagonal bipyramid, the S(2), S(3), and S(4) tetrahedra by sharing tetrahedral vertices with equatorial vertices of the bipyramid, and the S(1) tetrahedron by sharing an equatorial edge of the bipyramid. Edge-sharing between the $S(1)O_4$ tetrahedron and the UrO_5 bipyramid results in a short S(1)–U separation of 3.101(1) Å, which can be compared to the S(2), S(3), and S(4) separations from the U cation, which range from 3.55 to 3.65 Å. The bond angles of the $S(1)O_4$ tetrahedron are also more distorted than those of the other tetrahedra because of repulsion between the S^{6+} and U^{6+} cations, and range from 102.2(2) to 112.6(2)° (Table 3).

The uranyl sulfate clusters are oriented approximately parallel to (100) (Fig. 2), and are linked into a three-dimensional structure by bonds to Na cations and by H bonding. The H_2O (19) and H_2O (20) groups are each bonded to two Na cations only.

DISCUSSION

Uranyl sulfate minerals and synthetic compounds show a myriad of structural varieties. Burns *et al.* (9) developed a hierarchy of structures for inorganic uranyl compounds on the basis of polymerization of polyhedra of higher bond valence to form clusters, chains, sheets, and frameworks. The structures of 16 uranyl sulfates are now known; three [including $Na_6(UO_2)(SO_4)_4(H_2O)_2$] contain isolated clusters of polyhedra of higher bond valence, five contain chains, seven contain sheets, and one involves a framework of uranyl and sulfate polyhedra.

Of the three structures that contain isolated clusters, schröckingerite, $NaCa_3[(UO_2)(CO_3)_3](SO_4)F(H_2O)_{10}$ (10), contains uranyl tricarbonate clusters; the sulfate tetrahedra occur isolated in the structure and are held in place by bonds to low-valence cations only. Thus, the only known structures that contain uranyl sulfate clusters are $K_4[(UO_2)$

TABLE 3
Selected Interatomic Distances (Å) and Angles (°) for $Na_6(UO_2)(SO_4)_4(H_2O)_2$

U–O(1)a	1.768(3)
U–O(2)	1.776(3)
U–O(6)b	2.308(3)
U–O(10)	2.313(3)
U–O(7)	2.340(3)
U–O(4)	2.464(3)
U–O(3)	2.498(3)
⟨U–O_{Ur}⟩	1.772
⟨U–O_{eq}⟩	2.385
O(1)–U–O(2)	177.9(2)
S(1)–O(11)	1.456(4)
S(1)–O(14)	1.456(4)
S(1)–O(3)	1.496(4)
S(1)–O(4)	1.493(3)
⟨S(1)–O⟩	1.475
S(2)–O(9)	1.455(3)
S(2)–O(8)	1.458(3)
S(2)–O(13)	1.472(3)
S(2)–O(7)	1.504(3)
⟨S(2)–)⟩	1.472
S(3)–O(16)	1.457(4)
S(3)–O(15)a	1.450(4)
S(3)–O(18)	1.463(4)
S(3)–O(10)	1.496(3)
⟨S(3)–O⟩	1.466
S(4)–O(17)	1.460(4)
S(4)–O(12)	1.460(4)
S(4)–O(5)	1.475(4)
S(4)–O(6)	1.492(3)
⟨S(4)–O⟩	1.472
Na(1)–O(5)	2.330(4)
Na(1)–O(8)	2.343(4)
Na(1)–O(11)c	2.437(4)
Na(1)–H_2O(19)	2.441(4)
Na(1)–O(9)d	2.468(4)
Na(1)–O(13)d	2.496(4)
⟨Na(1)–φ⟩	2.419
Na(2)–O(14)e	2.330(4)
Na(2)–O(11)c	2.327(4)
Na(2)–O(17)	2.342(4)
Na(2)–O(12)d	2.401(4)
Na(2)–O(16)f	2.578(4)
Na(2)–O(13)d	2.829(4)
⟨Na(2)–O⟩	2.468
Na(3)–O(9)g	2.360(4)
Na(3)–O(1)c	2.395(4)
Na(3)–O(4)c	2.452(4)
Na(3)–O(8)c	2.452(4)
Na(3)–O(8)	2.466(4)
Na(3)–O(9)	2.555(4)
⟨Na(3)–O⟩	2.447
Na(4)–O(15)h	2.329(4)
Na(4)–O(12)i	2.418(4)
Na(4)–O(18)h	2.493(4)
Na(4)–O(18)	2.586(4)
Na(4)–O(2)h	2.621(4)
Na(4)–O(17)j	2.728(5)
Na(4)–O(15)a	2.810(5)
⟨Na(4)–O⟩	2.569
Na(5)–O(15)	2.370(4)
Na(5)–O(18)	2.448(5)
Na(5)–O(14)k	2.464(5)
Na(5)–O(12)i	2.618(5)
Na(5)–O(17)i	2.631(5)
Na(5)–H_2O(20)	2.647(5)
Na(5)–O(16)	2.801(5)
Na(5)–O(16)d	2.909(5)
⟨Na(5)–φ⟩	2.611
Na(6)–O(13),b	2.357(4) × 2
Na(6)–H_2O(19),b	2.403(4) × 2
Na(6)–O(5),b	2.671(4) × 2
⟨Na(6)–φ⟩	2.477
Na(7)–H_2O(20),1	2.381(4) × 2
Na(7)–O(16)d,k	2.589(4) × 2
Na(7)–O(10)d,k	2.815(4) × 2
Na(7)–O(3)d,k	2.815(3) × 2
⟨Na(7)–φ⟩	2.650
O(11)–S(1)–O(14)	110.1(2)
O(11)–S(1)–O(3)	110.8(2)
O(11)–S(1)–O(4)	110.3(2)
O(14)–S(1)–O(3)	110.6(2)
O(14)–S(1)–O(4)	112.6(2)
O(3)–S(1)–O(4)	102.2(2)
O(9)–S(2)–O(8)	111.0(2)
O(9)–S(2)–O(13)	110.0(2)
O(9)–S(2)–O(7)	109.7(2)
O(8)–S(2)–O(13)	110.3(2)
O(8)–S(2)–O(7)	108.3(2)
O(13)–S(2)–O(7)	107.4(2)
O(16)–S(3)–O(15)a	110.4(2)
O(16)–S(3)–O(18)	110.6(2)
O(16)–S(3)–O(10)	107.8(2)
O(15)a–S(3)–O(18)	110.5(2)
O(15)a–S(3)–O(10)	107.5(2)
O(18)–S(3)–O(10)	109.8(2)
O(17)–S(4)–O(12)	110.9(2)
O(17)–S(4)–O(5)	111.3(2)
O(17)–S(4)–O(6)	106.8(2)
O(12)–S(4)–O(5)	110.5(2)
O(12)–S(4)–O(6)	109.8(2)
O(17)–S(4)–O(6)	107.4(2)

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

$(SO_4)_3]$ (11) and $Na_6(UO_2)(SO_4)_4(H_2O)_2$. The uranyl sulfate cluster in $K_4[(UO_2)(SO_4)_3]$ (11) is shown in Fig. 3, and may be compared to that found in $Na_6(UO_2)(SO_4)_4(H_2O)_2$ (Fig. 1). Both clusters involve the sharing of an equatorial edge of a uranyl pentagonal bipyramid with a sulfate tetrahedron. This mode of polymerization is very unusual in uranyl sulfates; these are the only two uranyl sulfate structures know with this connectivity. In fact, these are the only two structures known that involve the sharing of an edge of a uranyl polyhedron with a tetrahedron containing a hexavalent cation, although almost 40 structures of uranyl compounds are known that contain S^{6+}, Cr^{6+}, and Mo^{6+} in tetrahedral coordination. This configuration presumably is unusual because the sharing of a polyhedral edge leads to increased repulsion between the U^{6+} and S^{6+} cations.

Safe disposal of nuclear waste in a geological repository requires a detailed knowledge of the long-term behavior of waste forms under repository conditions. Studies of natural analogues (12) and laboratory simulations (4, 5) indicate that spent nuclear fuel is unstable under the moist oxidizing conditions expected in the proposed repository at Yucca Mountain. Once containers are breached, alteration of the spent fuel is likely to be rapid, and will result in the

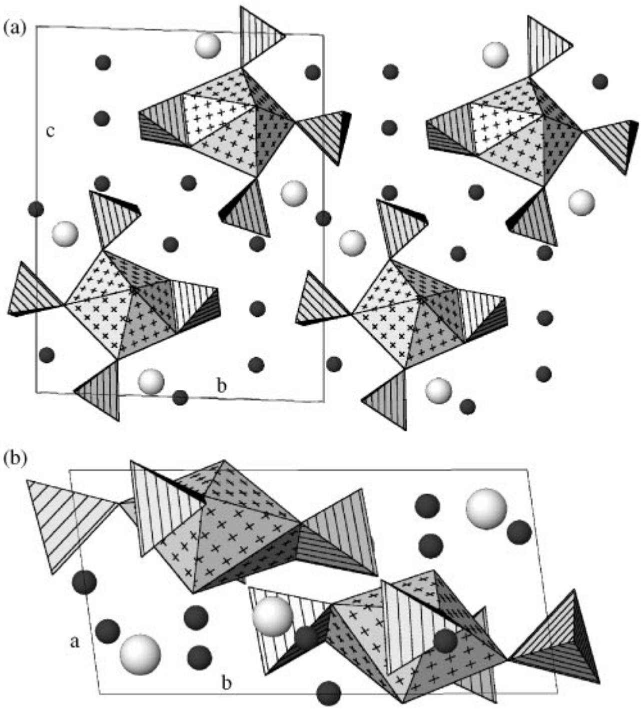

FIG. 2. Polyhedral representations of the structure of $Na_6(UO_2)(SO_4)_4(H_2O)_2$. Uranyl polyhedra and sulfate tetrahedra are shaded with crosses and parallel lines, respectively. Na cations are shown as solid balls, and H_2O groups are illustrated using large white circles.

TABLE 4
Bond Valence Analysis[a] (*vu*) for $Na_6(UO_2)(SO_4)_4(H_2O)_2$

	U	S(1)	S(2)	S(3)	S(4)	Na(1)	Na(2)	Na(3)	Na(4)	Na(5)	Na(6)	Na(7)	$\sum$
O(1)	1.72							0.20					1.92
O(2)	1.69								0.11				1.80
O(3)	0.41	1.41										$0.06^{x2}\downarrow$	1.88
O(4)	0.44	1.42						0.17					2.03
O(5)					1.50	0.24					$0.09^{x2}\downarrow$		1.83
O(6)	0.60				1.43								2.03
O(7)	0.56		1.38										1.94
O(8)			1.57			0.23		0.17, 0.17					2.14
O(9)			1.58			0.16		0.22, 0.13					2.09
O(10)	0.59			1.41								$0.06^{x2}\downarrow$	2.06
O(11)		1.57				0.18	0.24						1.99
O(12)					1.56		0.20		0.19	0.11			2.06
O(13)			1.51			0.15	0.06				$0.22^{x2}\downarrow$		1.94
O(14)		1.57					0.24			0.17			1.98
O(15)				1.60					0.24, 0.07	0.21			2.12
O(16)				1.57			0.12			0.07, 0.05		$0.12^{x2}\downarrow$	1.93
O(17)					1.56		0.23		0.08	0.11			1.98
O(18)				1.55					0.15, 0.12	0.17			1.99
$H_2O(19)$						0.18					$0.20^{x2}\downarrow$		0.38
$H_2O(20)$										0.10		$0.21^{x2}\downarrow$	0.31
$\sum$	6.02	5.99	6.04	6.13	6.04	1.14	1.09	1.06	0.96	0.99	1.03	0.91	

[a] Bond-valence parameters for U^{6+}–O from (8), and for S^{6+}–O and Na^{+}–O from (13).

formation of significant quantities of uranyl compounds. $Na_6(UO_2)(SO_4)_4(H_2O)_2$ may be a significant component of the alteration products of spent fuel under these conditions, owing to the presence of sulfur as an impurity in the steel used in the construction of the waste canisters.

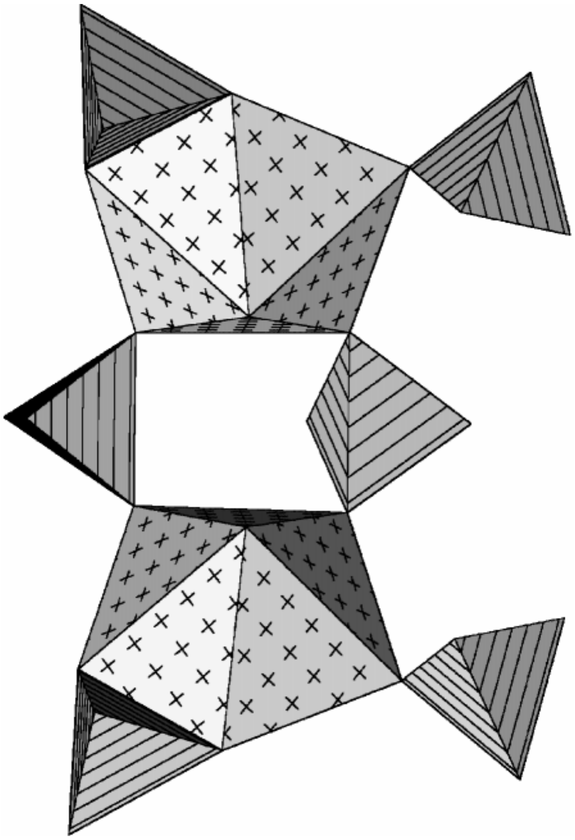

FIG. 3. The uranyl sulfate cluster in the structure of $K_4[(UO_2)(SO_4)_3]$. Uranyl polyhedra and sulfate tetrahedra are shaded with crosses and parallel lines, respectively.

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