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A NEW URANYL SULFATE CHAIN IN THE STRUCTURE OF URANOPILITE

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ABSTRACT

The structure of uranopilite, $[(UO_2)_6(SO_4)O_2(OH)_6(H_2O)_6](H_2O)_8$, space group $P\bar{1}$, *a* 8.896(2), *b* 14.029(3), *c* 14.339(3) Å, α 96.610(4), β 98.472(4), γ 99.802(4)°, *V* 1726.1(4) Å^3, $Z = 2$, 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 7.0%, calculated using 3907 unique observed reflections ($F_o \geq 4\sigma_F$). The structure contains six symmetrically distinct U^{6+} cations, each of which is part of an approximately linear $(UO_2)^{2+}$ uranyl ion (*Ur*). The uranyl ions are each coordinated by five ligands arranged at the equatorial vertices of $Ur\phi_5$ [ϕ: O^{2-}, $(OH)^-$, H_2O] pentagonal bipyramids that are capped by O_{Ur} atoms. The single symmetrically unique S^{6+} cation is coordinated by four O atoms in a tetrahedral arrangement. The $Ur\phi_5$ pentagonal bipyramids share vertices and edges, resulting in a cluster of composition $[(UO_2)_6O_6(OH)_6(H_2O)_6]^{6-}$. These clusters are linked through SO_4 tetrahedra, which share each of their vertices with different $Ur\phi_5$ pentagonal bipyramids, resulting in electroneutral uranyl sulfate chains of composition $[(UO_2)_6(SO_4)O_2(OH)_6(H_2O)_6]$ that extend along [100]. The uranyl sulfate chains are linked to form the extended structure by hydrogen bonds bridging directly between the chains and to interstitial H_2O groups. The uranyl sulfate chain in uranopilite is novel in minerals and synthetic compounds.

Keywords: uranopilite, uranyl sulfate, uranyl mineral.

SOMMAIRE

La structure de l'uranopilite, $[(UO_2)_6(SO_4)O_2(OH)_6(H_2O)_6](H_2O)_8$, groupe spatial $P\bar{1}$, *a* 8.896(2), *b* 14.029(3), *c* 14.339(3) Å, α 96.610(4), β 98.472(4), γ 99.802(4)°, *V* 1726.1(4) Å^3, $Z = 2$, a été résolue et affinée en utilisant les facteurs F^2 pour toutes les données prélevées avec rayonnement monochromatique Mo$K\alpha$ et un détecteur de type CCD, jusqu'à un résidu *R*1 de 7.0%, calculé en utilisant 3907 réflexions uniques observées ($F_o \geq 4\sigma_F$). La structure contient six cations U^{6+} symétriquement distincts, chacun faisant partie d'un groupe uranyle, $(UO_2)^{2+}$ (*Ur*) à peu près linéaire. Chaque ion uranyle est coordonné à cinq ligands disposés aux coins équatoriaux de bipyramides pentagonales $Ur\phi_5$ [ϕ: O^{2-}, $(OH)^-$, H_2O] ayant les atomes O_{Ur} à leur sommet. L'unique cation S^{6+} est coordonné à quatre atomes d'oxygène dans un agencement tétraédrique. Les bipyramides pentagonales $Ur\phi_5$ partagent coins et arêtes, pour donner un groupement de composition $[(UO_2)_6O_6(OH)_6(H_2O)_6]^{6-}$. Ces groupements sont liés par tétraèdres SO_4, qui partagent chacun de leur quatre coins avec différentes pyramides pentagonales $Ur\phi_5$, avec comme résultat des chaînes à sulfate électrostatiquement neutres, de composition $[(UO_2)_6(SO_4)O_2(OH)_6(H_2O)_6]$, allongées selon [100]. Les chaînes à uranyle et sulfate sont liées pour former la structure à longue échelle grâce à des liaisons hydrogène agissant comme ponts entre les chaînes et avec les groupes H_2O interstitiels. La chaîne à uranyle et sulfate dans l'uranopilite est unique parmi les minéraux et les composés synthétiques.

(Traduit par la Rédaction)

Mots-clés: uranopilite, sulfate d'uranyle, minéral d'uranyle.

INTRODUCTION

Uranyl sulfate minerals are fairly widespread, although they are not abundant. They typically occur close to actively oxidizing uraninite and sulfide minerals (Smith 1984). Fifteen uranyl sulfates are recognized as mineral species (Mandarino 1999), but most remain poorly understood; many uncertainties persist concerning their chemical compositions, structure and properties. Admixtures of uranyl sulfate species consisting of fine-grained mats and coatings are typical, making their detailed characterization difficult (Frondel 1958). The structures are known for only three uranyl sulfate minerals; the structures of schröckingerite (Mereiter 1986)

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and johannite (Mereiter 1982) were reported for natural crystals, and that of zippeite (Vochten *et al.* 1995) was reported for a synthetic crystal.

Uranopilite has been reported from more than a dozen localities, including the type locality at Johanngeorgenstadt, Saxony (Frondel 1958). Despite being recognized as a mineral since 1882, there is little crystallographic information available for uranopilite. Traill (1952) and Frondel (1952) provided powder-diffraction patterns for uranopilite, but were unable to determine the unit-cell dimensions, although rotation photographs for a bundle of elongate crystals produced a value of 8.91 Å for the lattice parameter along the axis of crystal elongation (Traill 1952). Frondel (1958) provided the most complete description of uranopilite, including several determinations of its chemical composition, and concluded that the most likely formula is $(UO_2)_6(SO_4)(OH)_{10}{\bullet}12(H_2O)$. The infrared spectra for uranopilite are reviewed by Čejka (1999).

The application of CCD-based (charge-coupled device) detectors of X-rays to mineral-structure analysis (Burns 1998) has provided many new insights into the extraordinarily complex structures of uranyl minerals. As part of our continuing studies of uranyl minerals, CCD-based diffractometry has been applied to determine the structural details of uranopilite.

EXPERIMENTAL

Over the course of several years, many specimens of uranopilite were examined in the search for crystals of suitable size and quality for single-crystal X-ray-diffraction analysis. In many cases, the largest crystals present on a specimen are ~5–10 μm in maximum dimension. Several specimens were obtained that contain crystals of uranopilite with maximum dimensions of ~100 μm, but X-ray-diffraction analysis revealed detrimental features such as streaking and excessive peak-widths. A crystal obtained from specimen 89612 of the Harvard Museum, from Joachimsthal, Bohemia, provided sharp diffraction-peaks, and ultimately provided the data for the solution and refinement of the structure.

TABLE 1. CRYSTALLOGRAPHIC DATA FOR URANOPILITE

a (Å)	8.896(2)	Crystal size (μm)	10 x 20 x 140
b (Å)	14.029(3)	Radiation	Mo$K\alpha$
c (Å)	14.339(3)	Total Ref.	20,997
α (°)	96.610(4)	Unique Ref.	8066
β (°)	98.472(4)	Unique $\lvert F_o \rvert \geq 4\sigma_F$	3907
γ (°)	99.802(4)	$wR2$	17.2
V (Å^3)	1726.1(4)	$R1$	7.0
Space group	$P\bar{1}$	S	0.92
F_{000}	1812	$\Delta\rho_{min}$, $\Delta\rho_{max}$ (eÅ^{-3})	-2.5. 3.4
μ (cm^{-1})	282.2		
D_{calc} (g/cm^3)	4.045		

Unit-cell contents: $2\{[(UO_2)_6(SO_4)O_2(OH)_6(H_2O)_6](H_2O)_8\}$

$R1 = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$S = [\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, for m observations and n parameters

Collection of X-ray data

The crystal of uranopilite selected for study is a thin blade with dimensions 10 × 20 × 140 μm. Data were collected using a Bruker three-circle diffractometer equipped with a SMART CCD detector located 5 cm from the crystal. A sphere of data was collected using monochromatic Mo$K\alpha$ X-radiation and frame widths of 0.3° in ω, with 60 s spent counting per frame. Analysis of several hundred frames of data provided the positions of 950 reflections, but it was impossible to index these reflections on the basis of a single-crystal orientation. Analysis of the peak positions revealed that indexing required two identical triclinic unit-cells (Table 1) related by a 9.1° rotation. The crystal therefore corresponds to two microcrystals, but they are too small to be separated. Examination of the diffraction pattern indicated that only ~5% of the reflections of the two reciprocal lattices overlapped. The intensities of reflections corresponding to the larger of the two crystal components were extracted and corrected for Lorentz, polarization and background effects using the Bruker program SAINT. A correction for absorption was done by Gaussian quadrature integration using the measured dimensions of the crystal faces. A total of 20,997 intensities was measured, and merging of equivalent reflections gave 8273 unique reflections, with 4113 classed as observed ($F_o \geq 4\sigma_F$).

Solution and refinement of the 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 Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the structure.

The structure was solved by direct methods in space group $P1$. The initial model included the positions of the U and S atoms; the positions of the anions were obtained from difference-Fourier maps calculated following refinement of the model. Refinement of the structure, done on the basis of all unique F^2, included all atomic positional parameters, anisotropic-displacement parameters for the U and S atoms, and isotopic-displacement parameters for the anions. The refinement converged to an agreement index ($R1$) of 9.2%, calculated for the 4113 unique observed ($F_o \geq 4\sigma_F$) reflections. A listing of the most disparate calculated and observed structure-factors revealed that these involved observed structure-factors that were much larger than those calculated, a feature attributed to overlap of reciprocal lattices corresponding to the two microcrystals. Removal of the 205 reflections most affected by overlap, corresponding to 5.0% of the total observed reflections, substantially improved the refinement, and lowered $R1$ to 7.0%, which was calculated using the remaining 3907 unique observed ($F_o \geq 4\sigma_F$) reflections.

TABLE 2. ATOMIC COORDINATES AND ISOTROPIC-DISPLACEMENT PARAMETERS FOR URANOPILITE

	x	y	z	$*U_{eq}$
U(1)	0.4048(1)	0.29632(8)	0.17773(8)	0.0208(3)
U(2)	0.0749(1)	0.08489(8)	0.23090(8)	0.0212(3)
U(3)	0.4729(1)	0.02304(8)	0.31677(8)	0.0208(3)
U(4)	0.4121(1)	0.56611(7)	0.17472(8)	0.0216(3)
U(5)	0.0512(1)	0.40617(8)	0.22362(8)	0.0212(3)
U(6)	0.0993(1)	-0.15307(8)	0.32936(8)	0.0224(3)
S(1)	0.7523(8)	0.2046(5)	0.2428(5)	0.024(2)
O(1)	0.450(2)	0.331(1)	0.310(1)	0.024(4)
O(2)	0.365(2)	0.263(1)	0.053(1)	0.024(4)
O(3)	0.119(2)	0.150(1)	0.353(1)	0.035(5)
O(4)	0.029(2)	0.025(1)	0.109(1)	0.027(5)
O(5)	0.456(3)	0.084(2)	0.433(2)	0.051(6)
O(6)	0.509(2)	-0.037(1)	0.207(1)	0.035(5)
O(7)	0.474(2)	0.578(1)	0.301(1)	0.031(5)
O(8)	0.357(2)	0.561(1)	0.048(1)	0.027(5)
O(9)	-0.059(2)	0.386(1)	0.112(1)	0.034(5)
O(10)	0.150(2)	0.432(1)	0.346(1)	0.032(5)
O(11)	0.115(2)	-0.105(1)	0.450(1)	0.036(5)
O(12)	0.068(3)	-0.218(2)	0.212(2)	0.052(6)
O(13)	0.662(2)	0.171(1)	0.318(1)	0.022(4)
O(14)	0.641(2)	0.234(1)	0.168(1)	0.022(4)
O(15)	0.273(2)	0.421(1)	0.169(1)	0.024(4)
O(16)	0.219(2)	-0.023(1)	0.285(1)	0.031(5)
O(17)	0.875(2)	0.294(1)	0.286(1)	0.042(6)
O(18)	0.820(2)	0.126(1)	0.203(1)	0.031(5)
OH(19)	0.121(2)	0.242(1)	0.181(1)	0.029(5)
OH(20)	0.577(2)	0.446(1)	0.154(1)	0.021(4)
OH(21)	-0.085(2)	-0.052(1)	0.275(1)	0.025(4)
OH(22)	0.349(2)	0.131(1)	0.208(1)	0.025(4)
OH(23)	0.378(2)	-0.138(1)	0.354(1)	0.024(4)
OH(24)	0.154(2)	0.571(1)	0.209(1)	0.024(4)
H_2O(25)	0.675(2)	0.658(1)	0.162(1)	0.034(5)
H_2O(26)	0.415(2)	0.738(1)	0.199(1)	0.027(4)
H_2O(27)	-0.153(2)	-0.253(1)	0.342(1)	0.037(5)
H_2O(28)	0.716(2)	-0.019(1)	0.390(1)	0.027(5)
H_2O(29)	-0.147(2)	0.497(1)	0.273(1)	0.032(5)
H_2O(30)	0.153(3)	-0.313(2)	0.380(2)	0.051(6)
H_2O(31)	-0.300(2)	-0.153(1)	0.127(1)	0.036(5)
H_2O(32)	0.340(3)	0.012(2)	0.024(2)	0.067(8)
H_2O(33)	-0.001(3)	-0.194(2)	0.014(2)	0.055(7)
H_2O(34)	0.889(3)	0.598(2)	0.064(2)	0.068(8)
H_2O(35)	0.310(3)	0.802(2)	0.029(2)	0.052(6)
H_2O(36)	0.386(4)	-0.324(3)	0.507(3)	0.12(1)
H_2O(37)	-0.293(4)	-0.284(2)	0.488(2)	0.11(1)
H_2O(38)	0.098(4)	0.443(3)	0.543(2)	0.11(1)

*isotropic U in the case of the O atoms

TABLE 3. ANISOTROPIC-DISPLACEMENT PARAMETERS FOR URANOPILITE

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	0.0147(5)	0.0216(6)	0.0292(7)	0.0067(5)	0.0060(5)	0.0078(4)
U(2)	0.0149(5)	0.0231(6)	0.0276(7)	0.0069(5)	0.0039(5)	0.0065(4)
U(3)	0.0143(5)	0.0227(6)	0.0271(6)	0.0057(5)	0.0053(4)	0.0055(4)
U(4)	0.0163(5)	0.0201(6)	0.0294(7)	0.0050(5)	0.0047(5)	0.0047(4)
U(5)	0.0142(5)	0.0228(6)	0.0280(6)	0.0049(5)	0.0053(4)	0.0052(4)
U(6)	0.0180(6)	0.0225(6)	0.0272(6)	0.0063(5)	0.0043(5)	0.0033(4)
S(1)	0.011(3)	0.030(4)	0.034(4)	0.011(3)	0.001(3)	0.006(3)

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF URANOPILITE

U(1)-O(2)	1.76(2)	U(2)-O(4)	1.81(2)
U(1)-O(1)	1.87(2)	U(2)-O(3)	1.83(2)
U(1)-O(15)	2.27(2)	U(2)-O(16)	2.27(2)
U(1)-OH(22)	2.39(2)	U(2)-OH(19)	2.39(2)
U(1)-O(14)	2.42(2)	U(2)-OH(21)	2.40(2)
U(1)-OH(20)	2.47(2)	U(2)-O(18)a	2.42(2)
U(1)-OH(19)	2.52(2)	U(2)-OH(22)	2.49(2)
<U(1)-O_{Ur}>	1.81	<U(2)-O_{Ur}>	1.82
<U(1)-ϕ_{eq}>	2.41	<U(2)-ϕ_{eq}>	2.39
U(3)-O(6)	1.79(2)	U(4)-O(7)	1.79(2)
U(3)-O(5)	1.82(2)	U(4)-O(8)	1.80(2)
U(3)-O(16)	2.20(2)	U(4)-O(15)	2.18(2)
U(3)-OH(23)	2.42(2)	U(4)-H_2O(26)	2.39(2)
U(3)-O(13)	2.43(2)	U(4)-OH(24)	2.43(2)
U(3)-H_2O(28)	2.46(2)	U(4)-OH(20)	2.43(2)
U(3)-OH(22)	2.56(2)	U(4)-H_2O(25)	2.52(2)
<U(3)-O_{Ur}>	1.80	<U(4)-O_{Ur}>	1.79
<U(3)-ϕ_{eq}>	2.41	<U(4)-ϕ_{eq}>	2.39
U(5)-O(9)	1.72(2)	U(6)-O(11)	1.76(2)
U(5)-O(10)	1.81(2)	U(6)-O(12)	1.77(2)
U(5)-O(15)	2.22(2)	U(6)-O(16)	2.16(2)
U(5)-O(17)a	2.37(2)	U(6)-OH(23)	2.42(2)
U(5)-OH(24)	2.38(2)	U(6)-OH(21)	2.44(2)
U(5)-H_2O(29)	2.48(2)	U(6)-H_2O(27)	2.48(2)
U(5)-OH(19)	2.51(2)	U(6)-H_2O(30)	2.54(2)
<U(5)-O_{Ur}>	1.76	<U(6)-O_{Ur}>	1.76
<U(5)-ϕ_{eq}>	2.39	<U(6)-ϕ_{eq}>	2.41
S(1)-O(18)	1.45(2)		
S(1)-O(14)	1.49(2)		
S(1)-O(13)	1.50(2)		
S(1)-O(17)	1.52(2)		
<S(1)-O>	1.49		

a = x-1, y, z

The final atomic positional parameters and equivalent isotopic-displacement parameters are listed in Table 2, anisotropic-displacement parameters for the cations are in Table 3, selected interatomic distances are in Table 4, and a bond-valence analysis is presented in Table 5. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

RESULTS

Cation coordination polyhedra

The structure of uranopilite contains six symmetrically distinct U atoms. Consideration of the bond-valence sums incident upon each site (Table 5), as well as of the nature of coordination polyhedra about the cations, indicates that each site is occupied by a U^{6+} cation. Each U^{6+} cation is strongly bonded to two atoms of O, resulting in approximately linear $(UO_2)^{2+}$ uranyl ions (*Ur*), as is typical for U^{6+} minerals. The mean U^{6+}–O bond lengths within the uranyl ions range from 1.76 to 1.82 Å, in agreement with the mean of 1.79(4) Å obtained from many well-refined structures (Burns *et al.* 1997). Each uranyl ion is coordinated by five additional

TABLE 5. BOND-VALENCE* (*vu*) ANALYSIS FOR URANOPILITE

	U(1)	U(2)	U(3)	U(4)	U(5)	U(6)	S(1)	Σ	H	Σ
O(1)	1.41							1.41	0.18	1.59
O(2)	1.75							1.75	0.19	1.94
O(3)		1.52						1.52	0.17	1.69
O(4)		1.59						1.59	0.10	1.69
O(5)			1.55					1.55	0.11	1.64
O(6)			1.65					1.65	0.30	1.95
O(7)				1.65				1.65		1.65
O(8)				1.62				1.62	0.26	1.86
O(9)					1.89			1.89		1.89
O(10)					1.59			1.59	0.14	1.75
O(11)						1.75		1.75	0.19	1.94
O(12)						1.71		1.71	0.16	1.87
O(13)			0.47				1.40	1.87		
O(14)	0.48						1.44	1.92	0.15	2.08
O(15)	0.64			0.77	0.71			2.12		
O(16)		0.64	0.74			0.80		2.18		
O(17)					0.53		1.32	1.85		
O(18)		0.48					1.60	2.08		
OH(19)	0.39	0.51			0.40			1.30	0.82	2.12
OH(20)	0.43			0.47				0.90	1.10	2.00
OH(21)		0.50				0.46		0.96	1.04	2.00
OH(22)	0.51	0.42	0.36					1.29	0.86	2.15
OH(23)			0.48			0.48		0.96	1.09	2.05
OH(24)				0.47	0.52			0.99	1.07	2.06
H_2O(25)				0.39				0.39	1.74	2.13
H_2O(26)				0.51				0.51	1.61	2.12
H_2O(27)						0.43		0.43	1.56	1.99
H_2O(28)			0.44					0.44	1.55	1.99
H_2O(29)					0.43			0.43	1.51	1.94
H_2O(30)						0.38		0.38	1.64	2.02
H_2O(31)								0	2.06	2.06
H_2O(32)								0	2.06	2.06
H_2O(33)								0	1.93	1.93
H_2O(34)								0	2.09	2.09
H_2O(35)								0	2.10	2.10
H_2O(36)								0	1.95	1.95
H_2O(37)								0	2.14	2.14
H_2O(38)								0	2.13	2.13
Σ	5.61	5.66	5.69	5.88	6.07	6.01	5.76			

*values calculated using the parameters for U^{6+} from Burns *et al.* (1997), S^{6+} from Brese & O'Keeffe (1991), and H···O from Ferraris & Ivaldi (1988)

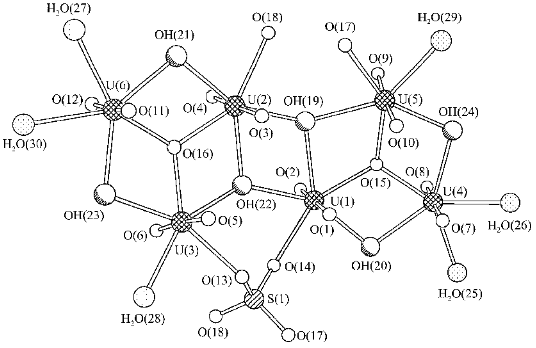

FIG. 1. The $[(UO_2)_6O_4(OH)_6(SO_4)(H_2O)_6]^{4-}$ cluster of polyhedra of higher bond-valence in the structure of uranopilite.

ligands arranged at the equatorial corners of *Ur*ϕ_5 [ϕ: O^{2-}, $(OH)^-$, H_2O] pentagonal bipyramids that are capped by O_{Ur} atoms. The equatorial ligands coordinating each of the U(1) and U(2) sites are two atoms of O and three $(OH)^-$ groups. In the case of the U(3) and U(5) sites, the equatorial ligands in each polyhedron correspond to two atoms of O, two $(OH)^-$ groups, and one H_2O group. The equatorial ligands coordinating each of the U(4) and U(6) cations correspond to one atom of O, two $(OH)^-$ groups, and two H_2O groups. The mean $\langle U^{6+}–\phi \rangle$ bond lengths for the equatorial ligands in the *Ur*ϕ_5 polyhedra range from 2.39 to 2.41 Å, in agreement with the value of 2.37(9) Å obtained from numerous well-refined structures containing *Ur*ϕ_5 pentagonal bipyramids (Burns *et al.* 1997).

The structure of uranopilite contains a single symmetrically distinct S^{6+} cation in the usual tetrahedral coordination, with a <S–O> bond-length of 1.49 Å.

Connectivity of coordination polyhedra of higher bond-valence

The local connectivity of the *Ur*ϕ_5 and SO_4 polyhedra is shown in Figure 1. The basic structural unit is a cluster that contains all six symmetrically distinct *Ur*ϕ_5 pentagonal bipyramids, as well as the SO_4 tetrahedron. The *Ur*(2)ϕ_5, *Ur*(3)ϕ_5, and *Ur*(6)ϕ_5 pentagonal bipyramids share O(16), and the sharing of equatorial edges between polyhedra results in a trimer of polyhedra with the composition $[(UO_2)_3O_2(OH)_4(H_2O)_3]^{2-}$. A topologically and compositionally identical trimer is formed by the *Ur*(1)ϕ_5, *Ur*(4)ϕ_5, and *Ur*(5)ϕ_5 pentagonal bipyramids, which share O(15). The trimers are linked by the sharing of an equatorial edge between the *Ur*(1)ϕ_5 and *Ur*(2)ϕ_5 polyhedra, resulting in a cluster with composition $[(UO_2)_6O_6(OH)_6(H_2O)_6]^{6-}$. The SO_4 tetrahedron is attached to the cluster by sharing one vertex with each of two *Ur*ϕ_5 pentagonal bipyramids, resulting in a cluster with composition $[(UO_2)_6O_4(OH)_6(SO_4)(H_2O)_6]^{4-}$, which contains all cation polyhedra of the asymmetric unit.

The $[(UO_2)_6O_4(OH)_6(SO_4)(H_2O)_6]^{4-}$ clusters are linked to form infinite electroneutral chains extending along [100] with composition $[(UO_2)_6(SO_4)O_2(OH)_6(H_2O)_6]$ (Fig. 2). The linkages involve the SO_4 tetrahedron, which shares all four of its vertices with four distinct uranyl polyhedra; the sharing of edges between uranyl polyhedra and SO_4 tetrahedra does not occur. The uranyl sulfate chains are linked to form the extended structure only by hydrogen bonding. Adjacent chains are approximately coplanar and parallel to (001), and are linked by hydrogen bonding along the [100] and [010] directions, forming a sheet (Fig. 2). Linkages between the chains along the [001] direction involve both hydrogen bonds that bridge directly between the chains, and those that bridge to interstitial H_2O groups (Fig. 3).

The distribution of anions within the uranyl sulfate chain is worthy of further consideration. The O_{Ur} atoms are not shared within the chain, as expected given that their bond-valence requirements are largely met by the uranyl-ion bond. The O(15) and O(16) atoms are bonded to three U^{6+} cations, with mean bond-lengths of 2.22 and 2.21 Å, respectively, which give bond-valence sums

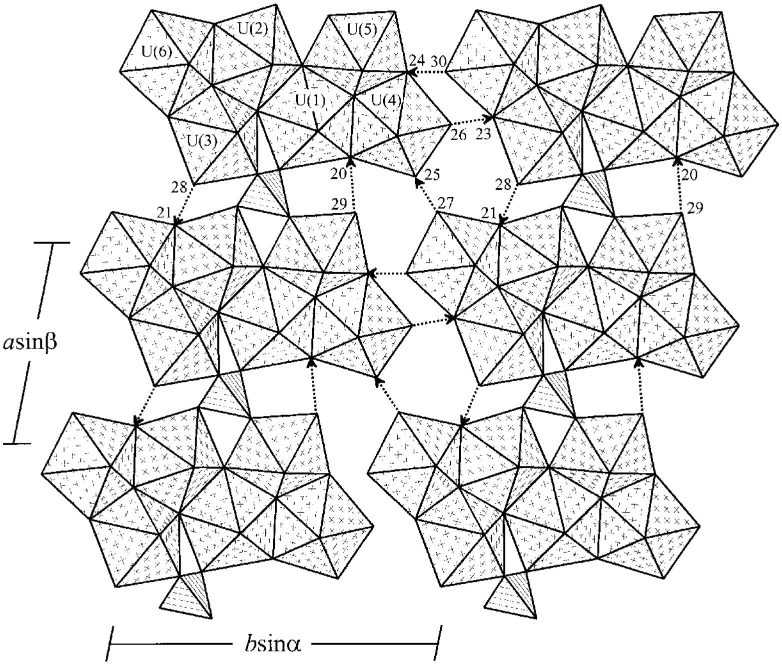

FIG. 2. Representation of the structure of uranopilite as polyhedra projected along [001]. Note the uranyl sulfate chain of composition $[(UO_2)_6(SO_4)O_2(OH)_6(H_2O)_6]$ that extends along [100]. Proposed hydrogen bonds are shown as dotted lines, with arrows designating the acceptor anions. The numbers correspond to anion designations given in Table 2. Interstitial H_2O groups have been omitted. The $Ur\phi_5$ pentagonal bipyramids and SO_4 tetrahedra are shown shaded with crosses and parallel lines, respectively.

incident at the O atoms of 2.12 and 2.18 *vu* (valence units), respectively. The O(13), O(14), O(17) and O(18) atoms constitute the tetrahedron about S^{6+}, and each is also the equatorial vertex of a $Ur\phi_5$ pentagonal bipyramid. The O atoms of the OH(19) and OH(22) groups are bonded to three U^{6+} cations, with mean bond-lengths of 2.47 and 2.48 Å, respectively, giving bond-valence sums at the O atoms, attributable to the bonds to U^{6+}, of 1.30 and 1.29 *vu*, respectively. The O atoms of the OH(20), OH(21), OH(23) and OH(24) groups are each bonded to two U^{6+} cations. These bonds give bond-valence sums incident upon the O atoms that range from 0.90 to 0.99 *vu*. The O atoms of the $H_2O(25)$ through $H_2O(30)$ groups occur at the corners of the clusters of uranyl polyhedra, and are bonded to one U^{6+} cation. The bond valences associated with these bonds range from 0.38 to 0.51 *vu*.

Hydrogen bonding in uranopilite

As is the case for most uranyl minerals, hydrogen bonding is of fundamental importance to the stability of the structure of uranopilite. Unfortunately, the X-ray-diffraction data are insufficient to provide the positions of H atoms in uranopilite, as is typically the case for uranyl minerals. However, most aspects of the hydrogen bonding can be established on the basis of crystal-chemical arguments. Proposed hydrogen bonds are listed in Table 6, and are in part illustrated in Figure 2. Contributions to the bond-valence sums arising from H atoms (Ferraris & Ivaldi 1988) are given in Table 5.

The O atoms of the OH(19) and OH(22) groups are each bonded to three U^{6+} cations, which contribute ~1.3 *vu* to the bond-valence requirements of the O atoms. The O atoms of the OH(19) and OH(22) groups each donate a hydrogen bond that is accepted by an interstitial H_2O group (Fig. 3).

The O atoms of each of the OH(20), OH(21), OH(23) and OH(24) groups are bonded to two U^{6+} cations, which contribute ~0.9 to 1.0 *vu* toward satisfaction of the bonding requirements of the O atoms. The OH(20) and OH(23) O atoms donate hydrogen bonds that are accepted by O_{Ur} atoms of adjacent uranyl sulfate chains, thereby providing direct linkage between adjacent chains along [001]. The OH(21) and OH(24) O atoms donate hydrogen bonds that are accepted by interstitial

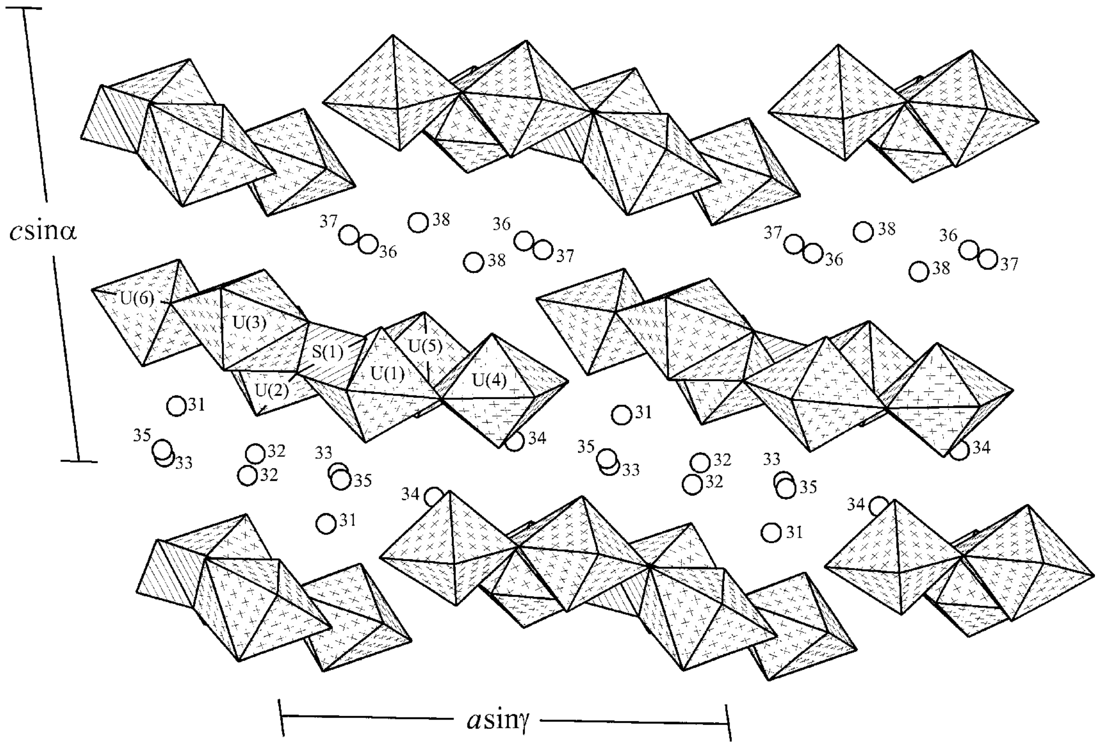

FIG. 3. Representation of the structure of uranopilite as polyhedra projected along [010]. Interstitial H_2O groups are shown as circles, with numerical labels corresponding to atom designations in Table 2. The $Ur\phi_5$ pentagonal bipyramids and SO_4 tetrahedra are shown shaded with crosses and parallel lines, respectively.

H_2O groups. The O atoms of each of the OH(20), OH(21), OH(23) and OH(24) groups also accept a hydrogen bond, each of which is donated by the O atom of a H_2O group of an adjacent uranyl sulfate chain, providing direct linkage of the chains in the [100] and [010] directions (Fig. 2).

The O atoms of the H_2O groups numbered 25 to 30 are bonded to single U^{6+} cations and occur along the edges of the uranyl sulfate chains (Fig. 1). The O atoms of each of these H_2O groups donate two hydrogen bonds. The hydrogen bonds are accepted by O atoms corresponding to an O_{Ur} atom, four $(OH)^-$ groups, one H_2O group that is bonded to U^{6+}, and six interstitial H_2O groups. The O atom of the $H_2O(30)$ group also accepts a hydrogen bond donated by an interstitial H_2O group.

The structure contains eight interstitial H_2O groups (numbered 31 to 38) that are held in place by hydrogen bonding. With the exception of the $H_2O(36)$ O atom, which probably accepts only one hydrogen bond, each of the O atoms contained within the interstitial H_2O groups are tetrahedrally coordinated by H atoms. In addition to donating two hydrogen bonds, each of these O atoms also accepts two hydrogen bonds that are donated by the O atoms of $(OH)^-$ groups, H_2O groups bonded to U^{6+} cations, and other interstitial H_2O groups.

TABLE 6. PROPOSED HYDROGEN BONDS IN THE STRUCTURE OF URANOPILITE

OH(19)→H_2O(33)a	2.81(3)		OH(22)→H_2O(32)	2.94(3)	
OH(20)→O(8)b	3.03(2)		OH(23)→O(5)	3.11(3)	
OH(21)→H_2O(31)	2.72(3)		OH(24)→H_2O(34)c	3.02(3)	
		A-D-A(°)			A-D-A(°)
H_2O(25)→H_2O(31)d	2.74(3)		H_2O(32)→O(4)	3.20(3)	
H_2O(25)→H_2O(34)	2.71(3)	100.7(9)	H_2O(32)→O(6)	3.03(3)	93.6(9)
H_2O(26)→OH(23)e	2.76(3)		H_2O(33)→O(12)	2.89(3)	
H_2O(26)→H_2O(35)	2.78(3)	111.1(8)	H_2O(33)→H_2O(35)j	2.75(3)	80.4(9)
H_2O(27)→H_2O(25)f	2.83(3)		H_2O(34)→O(8)b	2.97(3)	
H_2O(27)→H_2O(37)	2.62(4)	115(1)	H_2O(34)→H_2O(33)d	3.11(3)	128(1)
H_2O(28)→O(11)g	2.78(3)		H_2O(35)→O(14)b	2.93(3)	
H_2O(28)→OH(21)h	2.64(3)	106.6(9)	H_2O(35)→H_2O(32)c	2.92(4)	92.0(9)
H_2O(29)→OH(20)c	2.71(3)		H_2O(36)→O(1)g	2.82(4)	
H_2O(29)→H_2O(38)i	2.62(4)	128(1)	H_2O(36)→H_2O(37)h	2.88(5)	75(1)
H_2O(30)→OH(24)j	2.78(3)		H_2O(37)→O(3)k	2.85(4)	
H_2O(30)→H_2O(36)	2.59(4)	111(1)	H_2O(37)→H_2O(38)k	3.09(5)	105(1)
H_2O(31)→O(2)a	2.78(3)		H_2O(38)→O(10)	2.92(4)	
H_2O(31)→O(6)c	2.82(3)	126.4(9)	H_2O(38)→H_2O(30)k	3.05(4)	127(1)

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

The hydrogen bonds donated by the O atoms of the eight interstitial H_2O groups are accepted by O atoms consisting of nine O_{Ur} atoms, one O atom that is shared between a $Ur\phi_5$ pentagonal bipyramid and a SO_4 tetrahedron, one H_2O group that is bonded to a U^{6+} cation, and five interstitial H_2O groups.

Formula of uranopilite

The currently accepted formula for uranopilite is $(UO_2)_6(SO_4)(OH)_{10}$•$12H_2O$ (Frondel 1958), which was determined on the basis of chemical analysis. The structure determination indicates that all atoms are on general positions in space group $P1$, and analysis of the bond-valence sums incident upon the O atom positions readily permits the distinction of O^{2-}, $(OH)^-$ and H_2O (Table 6). Of the fourteen symmetrically distinct H_2O groups, six are bonded to U^{6+} cations and are thus part of the structural unit, whereas the remaining eight H_2O groups are held in the structure only by hydrogen bonding. The structural formula for uranopilite may be written as $[(UO_2)_6(SO_4)O_2(OH)_6(H_2O)_6](H_2O)_8$, $Z = 2$, which gives a calculated density of 4.045 g/cm^3. The constituents of the uranyl sulfate chains are contained within square braces. Note that this formula is identical to that given by Frondel (1958) except in the distribution of H between hydroxyl and H_2O groups.

Comparison to related structures

The structure of uranopilite is unique amongst minerals and synthetic uranyl phases. Of the four known structures of uranyl sulfate minerals, only uranopilite is based upon chains of polyhedra of higher bond-valence. The structures of zippeite (Vochten *et al.* 1995) and johannite (Mereiter 1982) contain uranyl sulfate sheets, with low-valence cations and H_2O groups located in the interlayers. The zippeite sheet contains zig-zag chains of edge-sharing $Ur\phi_5$ pentagonal bipyramids cross-linked by vertex-sharing with SO_4 tetrahedra (Fig. 4a). The johannite sheet involves edge-sharing dimers of $Ur\phi_5$ pentagonal bipyramids linked by sharing equatorial vertices with SO_4 tetrahedra (Fig. 4b), and is based upon the phosphuranylite sheet anion-topology (Burns *et al.* 1996, Burns 1999). The structure of schröckingerite (Mereiter 1986) contains isolated uranyl tricarbonate clusters and SO_4 tetrahedra linked through bonds to low-valence cations and by hydrogen bonding.

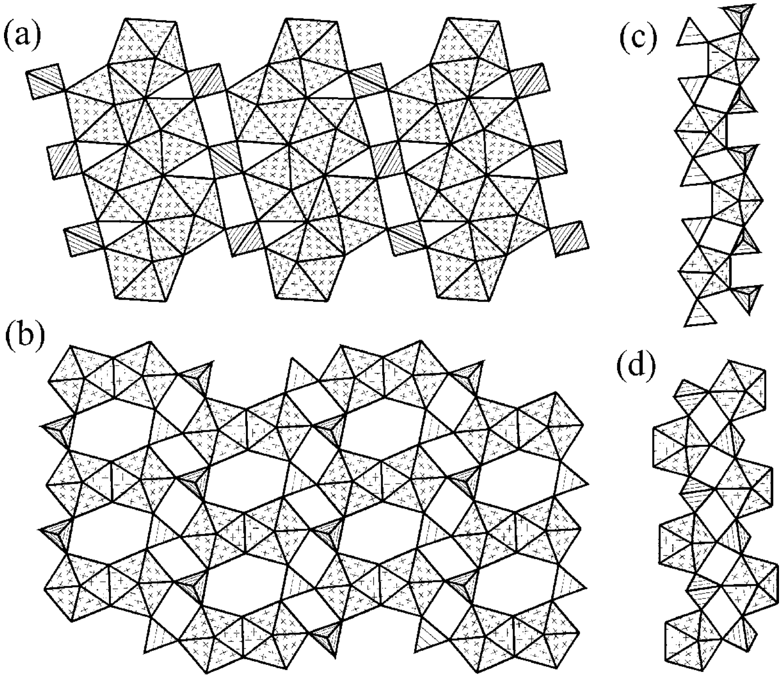

FIG. 4. Polyhedral representations of the structural units in (a) zippeite, (b) johannite, (c) $Mn[(UO_2)(SO_4)_2(H_2O)](H_2O)_4$, (d) $[(UO_2)(SO_4)(H_2O)_2](H_2O)_{1.5}$, $[(UO_2)(SO_4)(H_2O)_2](H_2O)_{0.5}$ and $[(UO_2)(SO_4)(H_2O)_2]_2(H_2O)_{3.0}$. Uranyl pentagonal bipyramids and SO_4 tetrahedra are shown shaded with crosses and parallel lines, respectively.

Burns *et al.* (1996) reviewed the structures of synthetic uranyl sulfates. These phases exhibit considerable structural diversity, and involve sheets (six examples), chains (four examples), isolated clusters (one example) and frameworks (one example) of polyhedra of higher bond-valence. Two distinct uranyl sulfate chains have been found in synthetic phases. The structure of $Mn[(UO_2)(SO_4)_2(H_2O)](H_2O)_4$ (Tabachenko *et al.* 1979) contains the chain shown in Figure 4c, and the structures of $[(UO_2)(SO_4)(H_2O)_2](H_2O)_{1.5}$ (Brandenburg & Loopstra 1973), $[(UO_2)(SO_4)(H_2O)_2](H_2O)_{0.5}$ (van der Putten & Loopstra 1974) and $[(UO_2)(SO_4)(H_2O)_2]_2(H_2O)_{3.0}$ (Zalkin *et al.* 1978) contain the uranyl sulfate chain shown in Figure 4d. Both of these chains involve only vertex-sharing between uranyl and sulfate polyhedra, and are much simpler than the chain found in the structure of uranopilite.

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