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SYNTHESIS AND CRYSTAL STRUCTURE OF A NEW Pb URANYL OXIDE HYDRATE WITH A FRAMEWORK STRUCTURE THAT CONTAINS CHANNELS

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ABSTRACT

Using lead oxide, uranyl nitrate and ultrapure water, seven hydrothermal synthesis experiments were performed with Pb:U molar ratios ranging from 1:1 to 1:10. Reaction products were characterized by powder and single-crystal X-ray diffraction. Two novel Pb uranyl oxide hydrates were found, with structural formulae $Pb_2(H_2O)[(UO_2)_{10}UO_{12}(OH)_6(H_2O)_2]$ and $Pb_{0.5}[(UO_2)_4O_2(OH)_5](H_2O)_4$ (Pb-poor fourmarierite). The synthesis products are related to the Pb:U molar ratio of the solution, and indicate a trend from curite, $Pb_{3+x}(H_2O)_2[(UO_2)_4O_{4+x}(OH)_{3-x}]_2$, to $Pb_2(H_2O)[(UO_2)_{10}UO_{12}(OH)_6(H_2O)_2]$, then to $Pb_{0.5}[(UO_2)_4O_2(OH)_5](H_2O)_4$ with decreasing Pb in the solution. The structure of $Pb_2(H_2O)[(UO_2)_{10}UO_{12}(OH)_6(H_2O)_2]$, $Z = 4$, monoclinic, space group $C2/c$, a 13.281(5), b 10.223(4), c 26.10(1) Å, β 103.202(6)°, V 3450(2) Å^3, was solved by direct methods and refined on the basis of F^2 using 4065 unique reflections. The agreement index ($R1$) was 6.38%, calculated for 1306 unique observed reflections ($|F_o| \geq 4\sigma_F$). The structure contains complex chains of edge- and vertex-sharing uranyl pentagonal and square bipyramids, as well as distorted $U^{6+}O_6$ octahedra, along both the [110] and $[\bar{1}10]$ directions. The chains in the two orientations are linked at $z \approx 0.25$ and $z \approx 0.75$, forming a framework that contains elongate open channels. The Pb^{2+} cations occur in the channels between adjacent chains.

Keywords: Pb uranyl oxide hydrate, uranyl minerals, structure determination.

SOMMAIRE

Nous avons effectué sept expériences de synthèse hydrothermale en utilisant l'oxyde de plomb, le nitrate d'uranyle et de l'eau ultrapure, les mélanges ayant un rapport molaire Pb:U allant de 1:1 à 1:10. Nous avons caractérisé les produits de réaction par diffraction X sur poudre et sur cristal unique. Deux nouveaux oxydes d'uranyle hydratés de plomb ont été trouvés: $Pb_2(H_2O)[(UO_2)_{10}UO_{12}(OH)_6(H_2O)_2]$ et $Pb_{0.5}[(UO_2)_4O_2(OH)_5](H_2O)_4$ (fourmariérite déficitaire en Pb). Les produits de synthèse dépendent du rapport molaire Pb:U de la solution, et indiquent une évolution allant de curite, $Pb_{3+x}(H_2O)_2[(UO_2)_4O_{4+x}(OH)_{3-x}]_2$, à $Pb_2(H_2O)[(UO_2)_{10}UO_{12}(OH)_6(H_2O)_2]$, et ensuite à $Pb_{0.5}[(UO_2)_4O_2(OH)_5](H_2O)_4$ à mesure que diminue la teneur de la solution en Pb. La structure du composé $Pb_2(H_2O)[(UO_2)_{10}UO_{12}(OH)_6(H_2O)_2]$, $Z = 4$, monoclinique, groupe spatial $C2/c$, a 13.281(5), b 10.223(4), c 26.10(1) Å, β 103.202(6)°, V 3450(2) Å^3, a été résolue par méthodes directes et affinée en utilisant les facteurs F^2 dérivés de 4065 réflexions uniques. L'indice de concordance ($R1$) est 6.38%, calculé sur la base de 1306 réflexions uniques observées ($|F_o| \geq 4\sigma_F$). La structure contient des chaînes complexes de bipyramides à uranyle pentagonales et carrées, partageant coins et arêtes, de même que des octaèdres $U^{6+}O_6$ difformes le long des deux directions [110] et $[\bar{1}10]$. Les chaînes dans ces deux directions sont rattachées à $z \approx 0.25$ et $z \approx 0.75$, pour former une trame contenant des canaux ouverts allongés. Les cations Pb^{2+} sont logés dans les canaux entre chaînes adjacentes.

(Traduit par la Rédaction)

Mots-clés: oxyde à uranyle de plomb hydraté, minéraux à uranyle, détermination de la structure.

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INTRODUCTION

Pb uranyl oxide hydrates are important for understanding the interaction of groundwater with geologically old uranium deposits owing to the buildup of radiogenic lead (Frondel 1958, Finch & Ewing 1992). Seven Pb uranyl oxide hydrate minerals are known, and the structure of each has been determined [fourmarierite, Piret (1985); sayrite, Piret *et al.* (1983); curite, Taylor *et al.* (1981); masuyite, Burns & Hanchar (1999); vandendriesscheite, Burns (1997); richetite, Burns (1998), and wölsendorfite, Burns (1999a)]. All seven structures are based upon sheets of edge- and corner-sharing uranyl polyhedra, with Pb^{2+} cations and H_2O groups located in the interlayers. Despite the dominance of sheets in these minerals, they show considerable structural diversity. Six distinct sheet-topologies occur in Pb uranyl oxide hydrates, including the vandendriesscheite and wölsendorfite sheets, which are the most complex sheets of uranyl polyhedra known. The interlayers of Pb uranyl oxide hydrate minerals also are complex, and in some cases involve partially occupied sites (*e.g.,* richetite, vandendriesscheite and curite). In fourmarierite, the Pb content of the interlayer also varies significantly, with $OH^- \leftrightarrow O^{2-}$ substitution in the sheets of uranyl polyhedra providing for charge balance (Li & Burns 2000).

Continued alteration of geologically old uraninite results in a series of Pb uranyl oxide hydrates variable in their Pb:U ratio (Finch & Ewing 1992). These minerals are therefore ideal candidates for developing an understanding of the relationships between the structures and paragenesis of uranyl minerals. Moreover, many aspects of the crystal chemistry, stability, and alteration mechanisms of these minerals require further study.

The technique of hydrothermal synthesis has provided crystals of curite and its strontium analogue of a size and quality sufficient for single-crystal X-ray-diffraction studies (Mereiter 1979, Burns & Hill 2000). As part of our ongoing studies of Pb uranyl oxide hydrates, we have conducted hydrothermal syntheses in the system Pb–U–O–H, the Pb:U ratios being variable. Initial characterization using X-ray powder diffraction combined with single-crystal diffraction indicated two novel phases. Crystal-structure analysis of one of them has shown that it is a new Pb uranyl oxide hydrate with an unusual framework structure; the results of the structure determination are reported herein. An earlier study showed that the other phase is Pb-poor fourmarierite (Li & Burns 2000).

TABLE 1. CRYSTALLINE PHASES FORMED BY REACTION OF SOLUTIONS CONTAINING DIFFERENT Pb:U RATIOS

Experiment	Molar Pb:U ratio in solution	Precipitate*
1	1:1	yellow curite
2	1:2	yellow curite and minor orange *PbUOH*
3	1:3	orange *PbUOH* and minor yellow curite
4	1:4	orange *PbUOH*
5	1:6	orange *PbUOH* and minor unidentified yellow crystals
6	1:8	orange *PbUOH* and minor crystals of yellow Pb-poor fourmarierite
7	1:10	orange *PbUOH* and a few unidentified yellow crystals

* precipitates were examined both optically and by X-ray powder and single-crystal diffraction.

EXPERIMENTAL

Crystal synthesis

Crystals were synthesized using hydrothermal techniques. Seven experiments were conducted, each with 0.4 M uranyl nitrate solution and different amounts of PbO, with Pb:U molar ratios ranging from 1:1 to 1:10 (Table 1). The pH of each solution was adjusted to 3.2 using 1 M NaOH solution. Approximately 4 mL of reactants were transferred to 23 mL Teflon-lined Parr bombs that were placed in an oven and heated at 220°C for 10 to 14 days. Reaction products were recovered by filtration and were washed using ultrapure water, and dried at room temperature.

Characterization of precipitates

Precipitates were examined optically and by X-ray powder diffraction using a Rigaku Miniflex automated diffractometer. The products of synthesis contain at least three phases that could be distinguished optically. The X-ray powder diffractograms for the two most abundant crystalline phases in the products showed that one corresponds to curite, but the other could not be identified. A third phase that occurs in small quantities was shown to be Pb-poor fourmarierite by structure determination (Li & Burns 2000). The proportions of these phases were found to be sensitive to the Pb:U ratio of the experiments (Table 1). We noted what may be a fourth phase in the experiment that had a Pb:U molar ratio of 1:6, but were unable to isolate a sufficient quantity for identification using X-ray diffraction.

Single-crystal X-ray-diffraction studies

The new Pb uranyl oxide hydrate (hereafter designated *PbUOH*) occurs as platy orange crystals with maximum dimensions of 0.2 mm. A crystal from experiment 3 (Table 1) was chosen for further study using single-crystal X-ray diffraction. More than a hemisphere of three-dimensional data to 57°2θ was collected using Mo*K*α X-radiation and a Bruker CCD-based detector mounted on a three-circle diffractometer. Frame widths of 0.3° in ω were used, with 60 seconds spent counting per frame. The unit-cell dimensions (Table 2) were refined using 510 reflections and least-squares techniques.

TABLE 2. CRYSTALLOGRAPHIC DATA AND REFINEMENT RESULTS FOR $Pb_2(H_2O)[(UO_2)_{10}UO_{12}(OH)_6(H_2O)_2]$

a (Å)	13.281(5)	Crystal size(mm)	0.04×0.04×0.01
b (Å)	10.223(4)	Radiation	Mo$K\alpha$
c (Å)	26.10(1)	$2\theta_{max}$(°)	56.76
β (°)	103.202(6)	Total reflections	9213
V (Å^3)	3450(2)	Unique reflections	4065
Space group	$C2/c$	Data with $\|Fo\|>4\sigma\|Fo\|$	1306
F(000)	6064	$R1$(%)	6.38
μ(mm^{-1})	61.3	S	0.68
D_{calc} (g/cm^3)	7.125		

Unit cell contents 4 $Pb_2(H_2O)[(UO_2)_{10}UO_{12}(OH)_6(H_2O)_2]$

$R1 = \Sigma(|F_o| - |F_c|)/ \Sigma |F_o| \times 100$

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

The intensity data were integrated and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A semi-empirical absorption-correction was based on equivalent reflections with the crystal modeled as a (001) plate. Reflections with a plate-glancing angle of less than 3% were discarded from the data set, reducing $R_{azimuthal}$ from 11.2% to 3.3%. A total of 9213 reflections were collected; merging of equivalent reflections gave 4065 unique reflections, of which 1306 were classified as observed ($F_o \geq 4\sigma_F$).

Structure solution and refinement

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 refinement of the crystal structure.

Systematic extinctions of reflections indicated space groups $C2/c$ or Cc. The structure was successfully solved in $C2/c$. The positions of heavy atoms were obtained from a direct-methods solution, and anions were located in difference-Fourier maps calculated following refinement of the model. During the course of refinement, we noted that the displacement parameter for the $H_2O(2)$ position was unusually high, suggesting that the site is not fully occupied. The occupancy factor refined to 0.45(8) and was subsequently fixed at 0.5. Refinement of the occupancy factor for the Pb site gave 1.009(7), indicating that it is fully occupied by Pb. The final cycle of refinement included all atomic-positional parameters, anisotropic-displacement parameters for U and Pb atoms, isotropic-displacement parameters for anions, and a weighting scheme of the structure factors. The displacement parameters for O(1), O(2) and O(13) refined to physically unrealistic (small) values, and were fixed during the final cycles of refinement. The refinement, which was done on the basis of F^2 for all unique reflections, converged to an agreement index ($R1$) of 6.38%, calculated for the 1306 unique observed reflections ($F_o > 4\sigma_F$). The maximum electron-density peaks in the final difference-Fourier maps were 3.76 e/Å^3 and –3.44 e/Å^3. The structure was also solved and refined in space group Cc, but no improvement over the refinement in $C2/c$ resulted. Final positional parameters and equivalent isotropic-displacement parameters are given in Table 3, anisotropic-displacement parameters for the U and Pb atoms are given in Table 4, selected interatomic distances and angles are in Table 5, and bond-valence sums at the cation and anion sites are in Table 6. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

DESCRIPTION OF THE STRUCTURE

Cation polyhedra

The structure of *PbUOH* contains six symmetrically unique U^{6+} cations. The U(1), U(3), U(4), U(5) and U(6) cations are part of approximately linear $(UO_2)^{2+}$ uranyl ions (designated *Ur*). Of these, all but the U(3) uranyl

TABLE 3. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC-DISPLACEMENT PARAMETERS FOR $Pb_2(H_2O)[(UO_2)_{10}UO_{12}(OH)_6(H_2O)_2]$

	x	y	z	$U(eq)$
U(1)	0.2350(1)	0.4222(2)	0.4726(1)	0.0084(4)
U(2)	0	0.6390(2)	¼	0.0072(6)
U(3)	0.5091(1)	0.3390(2)	0.5306(1)	0.0081(4)
U(4)	-0.0560(1)	0.4531(2)	0.3567(1)	0.0079(4)
U(5)	0.2090(1)	0.7269(2)	0.3559(1)	0.0070(4)
U(6)	0.2288(1)	0.9133(2)	0.2340(1)	0.0097(4)
Pb(1)	0.1709(2)	0.1434(2)	0.3728(1)	0.0208(5)
O(1)	0.115(2)	0.767(2)	0.262(1)	0.01*
O(2)	0.262(2)	0.579(3)	0.336(1)	0.01*
O(3)	0.032(2)	0.316(2)	0.346(1)	0.0039(66)
O(4)	0.212(2)	0.488(2)	0.535(1)	0.0062(69)
O(5)	0.604(2)	0.502(3)	0.515(1)	0.0253(87)
O(6)	0.343(2)	0.273(3)	0.524(1)	0.0225(81)
O(7)	0.151(2)	0.874(3)	0.380(1)	0.0172(77)
O(8)	0.049(2)	0.620(3)	0.331(1)	0.0146(75)
O(9)	0.252(2)	0.357(3)	0.410(1)	0.0111(70)
O(10)	0.497(2)	0.413(3)	0.593(1)	0.0165(76)
O(11)	0.288(2)	0.790(2)	0.201(1)	0.0041(64)
O(12)	-0.139(2)	0.587(3)	0.371(1)	0.0130(72)
O(13)	0.107(2)	0.503(2)	0.237(1)	0.01*
O(14)	0.168(2)	0.037(3)	0.262(1)	0.0115(72)
O(15)	0.526(2)	0.253(3)	0.473(1)	0.0221(84)
O(16)	-0.195(2)	0.342(3)	0.314(1)	0.0201(84)
OH(1)	0.213(2)	0.640(3)	0.436(1)	0.0169(76)
OH(2)	0.052(2)	0.472(3)	0.440(1)	0.0119(72)
OH(3)	-0.131(2)	0.309(2)	0.415(1)	0.0117(73)
$H_2O(1)$	0.081(2)	0.880(3)	0.156(1)	0.0256(87)
$H_2O(2)$	-0.005(7)	0.085(9)	0.203(3)	0.0836(300)

* displacement parameter fixed during refinement

TABLE 4. ANISOTROPIC-DISPLACEMENT PARAMETERS FOR $Pb_2(H_2O)[(UO_2)_{10}UO_{12}(OH)_6(H_2O)_2]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	0.0070(9)	0.0076(9)	0.0097(11)	0.0013(9)	-0.0001(8)	-0.0025(8)
U(2)	0.0030(12)	0.0054(12)	0.0132(16)	0	0.0015(11)	0
U(3)	0.0071(9)	0.0088(9)	0.0083(11)	0.0002(8)	0.0015(8)	0.0008(8)
U(4)	0.0067(9)	0.0076(9)	0.0094(11)	0.0018(8)	0.0021(8)	-0.0003(7)
U(5)	0.0056(9)	0.0057(8)	0.0094(11)	0.0007(9)	0.0014(8)	0.0002(7)
U(6)	0.0087(9)	0.0073(9)	0.0131(11)	0.0007(9)	0.0024(8)	-0.0031(8)
Pb(1)	0.0190(11)	0.0134(10)	0.0299(14)	0.0000(10)	0.0055(10)	0.0021(9)

TABLE 5. SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR $Pb_2(H_2O)[(UO_2)_{10}UO_{12}(OH)_6(H_2O)_2]$

U(1)-O(9)	1.83(3)	U(2)-O(1)	1.98(3)	U(3)-O(15)	1.80(3)
U(1)-O(4)	1.84(3)	U(2)-O(1)c	1.98(3)	U(3)-O(10)	1.84(3)
U(1)-O(5)a	2.23(3)	U(2)-O(8)c	2.07(3)	U(3)-O(5)	2.17(3)
U(1)-O(6)b	2.26(3)	U(2)-O(8)	2.07(3)	U(3)-O(6)	2.27(3)
U(1)-O(6)	2.31(3)	U(2)-O(13)c	2.08(2)	U(3)-O(5)a	2.35(3)
U(1)-OH(1)	2.41(3)	U(2)-O(13)	2.08(2)	U(3)-OH(3)b	2.42(3)
U(1)-OH(2)	2.44(3)	<U(2)-ϕ>	2.04	<U(3)-O$_{Ur}$>	1.82
<U(1)-O$_{Ur}$>	1.83			O(15)-U(3)-O(10)	175(1)
O(4)-U(1)-O(9)	178(1)			<U(3)-ϕ_{eq}>	2.30
<U(1)-ϕ_{eq}>	2.33				
U(4)-O(12)	1.85(3)	U(5)-O(2)	1.80(3)	U(6)-O(14)i	1.75(3)
U(4)-O(3)	1.88(2)	U(5)-O(7)	1.86(3)	U(6)-O(11)	1.81(2)
U(4)-O(16)	2.23(3)	U(5)-O(16)d	2.19(3)	U(6)-O(16)d	2.23(3)
U(4)-OH(2)	2.33(3)	U(5)-OH(1)	2.27(3)	U(6)-O(13)e	2.32(3)
U(4)-O(8)	2.39(3)	U(5)-O(8)	2.35(3)	U(6)-O(1)	2.37(3)
U(4)-O(13)c	2.44(3)	U(5)-OH(3)d	2.47(3)	U(6)-H_2O(1)	2.50(3)
U(4)-OH(3)	2.47(3)	U(5)-O(1)	2.51(3)	U(6)-O(2)e	2.51(3)
<U(4)-O$_{Ur}$>	1.86	<U(5)-O$_{Ur}$>	1.83	<U(6)-O$_{Ur}$>	1.78
O(12)-U(4)-O(3)	177(1)	O(2)-U(5)-O(7)	176(1)	O(14)-U(6)-O(11)	177(1)
<U(4)-ϕ_{eq}>	2.37	<U(5)-ϕ_{cq}>	2.36	<U(6)-ϕ_{eq}>	2.39
Pb(1)-O(3)	2.54(2)				
Pb(1)-O(9)	2.53(3)				
Pb(1)-O(12)f	2.60(3)				
Pb(1)-H_2O(2)c	2.67(9)				
Pb(1)-O(11)g	2.59(2)				
Pb(1)-O(10)b	2.65(3)				
Pb(1)-O(7)h	2.77(3)				
Pb(1)-O(6)b	2.87(4)				
Pb(1)-O(4)b	2.89(3)				
Pb(1)-O(14)	3.07(3)				
<Pb(1)-ϕ>	2.72				

a: -x+1, -y+1, -z+1; b: -x+1/2, -y+1/2, -z+1; c: -x, y, z+1/2; d: x+1/2, y+1/2, z; e: -x+1/2, y+1/2, -z+1/2; f: x+1/2, y-1/2, z; g: -x+1/2, y-1/2, -z+1/2; h: x, y-1, z; i: x, y+1, z

TABLE 6. BOND VALENCE (*vu*) ANALYSIS* FOR $Pb_2(H_2O)[(UO_2)_{10}UO_{12}(OH)_6(H_2O)_2]$

	U(1)	U(2)	U(3)	U(4)	U(5)	U(6)	Pb(1)	Σ
O(1)		1.19×2↓			0.40	0.53		2.12
O(2)					1.63	0.40		2.03
O(3)				1.37			0.32	1.69
O(4)	1.48						0.12	1.60
O(5)	0.69		0.83, 0.61					2.13
O(6)	0.65, 0.60		0.70					2.08
O(7)					1.43		0.17	1.60
O(8)		1.00×2↓		0.50	0.55			2.05
O(9)	1.53						0.32	1.85
O(10)			1.52				0.23	1.75
O(11)						1.58	0.28	1.86
O(12)				1.47			0.27	1.74
O(13)		1.00×2↓		0.46		0.58		2.04
O(14)						1.77	0.07	1.84
O(15)			1.64					1.64
O(16)				0.69	0.75	0.69		2.13
OH(1)	0.49				0.64			1.13
OH(2)	0.46			0.57				1.03
OH(3)			0.53	0.43	0.43			1.39
H_2O(1)						0.41		0.41
H_2O(2)							0.22	0.22
Σ#	5.90	6.38	5.83	5.49	5.83	5.96	2.02	

* bond-valence parameters for U^{6+} from Burns *et al.* (1997a) and for Pb^{2+} from Brese & O'Keeffe (1991). # bond-valence contributions into Pb^{2+} from Pb-ϕ bonds have been scaled by occupancy of the H_2O(2) site.

ion are coordinated by five anions arranged at the equatorial positions of pentagonal bipyramids that are capped by the O_{Ur} atoms. The U(3) uranyl ion is coordinated by four anions arranged at the equatorial corners of a square bipyramid. The <U–5ϕ_{eq}> (ϕ: unspecified ligand, eq: equatorial) bond lengths range from 2.33 to 2.39 Å, and the <U–4ϕ_{eq}> bond length is 2.30 Å. These values are in the range observed for uranyl polyhedra in well-refined structures (Burns *et al.* 1997a). The coordination polyhedron about the U(2) cation is unusual in that it does not involve a uranyl ion. The U(2) cation is coordinated by six anions in a distorted octahedral arrangement (Fig. 1), with bond lengths ranging from 1.98 to 2.08 Å and a mean bond-length of 2.04 Å (Table 5). Similar coordination geometries have been reported for several synthetic uranyl compounds (Burns *et al.* 1997a).

The structure contains a single unique Pb^{2+} cation that is coordinated by nine atoms of O and one H_2O group, with a mean <Pb–ϕ> bond-length of 2.72 Å (Fig. 2, Table 5). There are two distinct H_2O groups in the structure; H_2O(1) is bonded to U(6), with a bond length of 2.48 Å. The H_2O(2) site, which is only partially occupied, is bonded to the Pb^{2+} cation.

Structural connectivity

Projection of the structure of *PbUOH* onto (100) shows that it is composed of a framework of vertex- and edge-sharing uranium polyhedra (Fig. 3), in contrast to the structures of other Pb uranyl oxide hydrates that are based upon sheets of polyhedra. The details of the structural connectivity are best illustrated by projection along [110] and $[\bar{1}10]$, as shown in Figure 4. The basic structural unit of *PbUOH* is a complex chain of edge- and vertex-sharing uranyl pentagonal and square bipyramids, and distorted UO_6 octahedra. The chains of uranium polyhedra are six polyhedra wide, as shown in Figure 5a. The chains are aligned parallel with the [110] and $[\bar{1}10]$ directions, and are laterally stacked and connected through a net of corner-sharing $U(2)O_6$–$U(6)\phi_7$ polyhedra (Fig. 6) at $z \approx 0.25$ and $z \approx 0.75$ (Figs. 4a, b), forming a framework of uranium polyhedra with elongate open channels 3.9 × 8.1 Å in diameter (Fig. 4), as

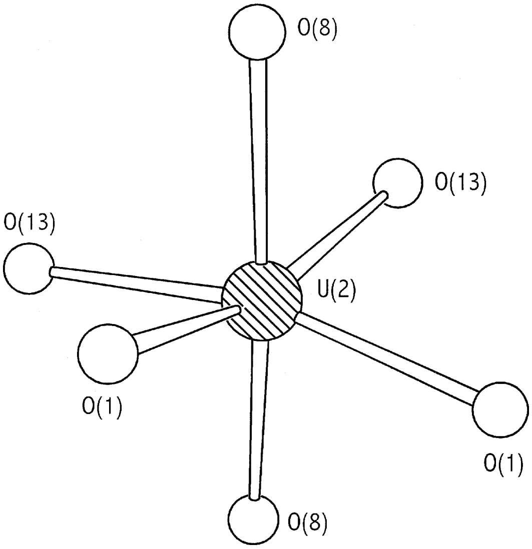

FIG. 1. The distorted octahedral coordination about the U(2) cation in the structure of *PbUOH*.

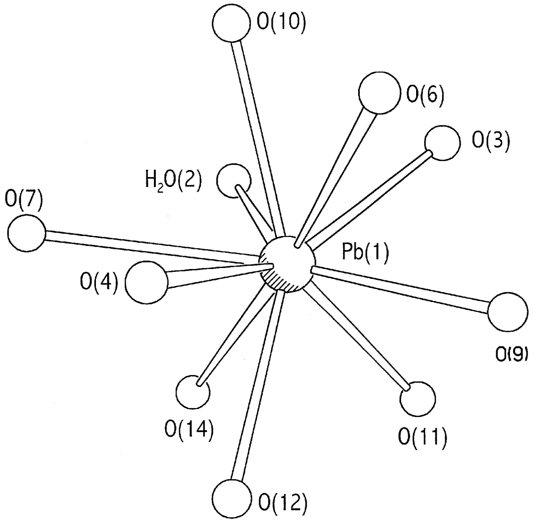

FIG. 2. The coordination environment about the Pb^{2+} cation in the structure of *PbUOH*.

measured from the centers of the oxygen atoms defining the channel edge.

The complex chain of uranium polyhedra shown in Figure 5a contains three individual chains of edge-sharing uranium polyhedra. The ratio of $Ur\phi_4$: $Ur\phi_5$ polyhedra in the central chain is 1:1, and the ratio of UO_6 : $Ur\phi_5$ in the chains on either side is 1:3 (Fig. 5a). Sharing of polyhedron edges occurs in these chains, and they are connected to form the complex chain by vertex-sharing only. The complex chain of polyhedra contains topological elements in common with the sheet found in curite, as shown in Figure 5.

The Pb^{2+} cations are located in both ends of the elongate channels that pass through the framework of uranium polyhedra (Fig. 4). This configuration is somewhat similar to the arrangement in curite, where Pb^{2+} cations are located between sheets containing similar structural elements.

Structural formula

The structure solution indicates that there are five U^{6+} and one Pb^{2+} cations in general positions of space group $C2/c$, and one U^{6+} cation on Wyckoff position 4*e*, giving a total of 44 U^{6+} and 8 Pb^{2+} cations per unit cell. There are 164 O atoms in the unit cell, and the bond-valence analysis (Table 6) indicates that these correspond to 128 atoms of O, 24 $(OH)^-$ groups and 12 H_2O groups. The structural formula is $Pb_2(H_2O)[(UO_2)_{10}UO_{12}(OH)_6(H_2O)_2]$, $Z = 4$, with the composition of the uranium polyhedral framework enclosed in square braces.

DISCUSSION

The structure of *PbUOH* is composed of a framework of uranium polyhedra that share vertices and edges, whereas all other known structures of Pb uranyl oxide hydrates contain sheets of uranyl polyhedra. The uneven distribution of bond-valences within uranyl polyhedra favors polymerization in two dimensions, and usually results in sheets of polyhedra (Burns 1999b). However, in *PbUOH* the U(2) cation does not involve a uranyl ion, thus the distribution of bond-valences in the $U(2)O_6$ octahedron is more uniform than is the case in uranyl polyhedra, with each anion receiving ~1.0 *vu* (valence unit) from the bond to the central U^{6+} cation. This polyhedron may be compared to a uranyl polyhe-

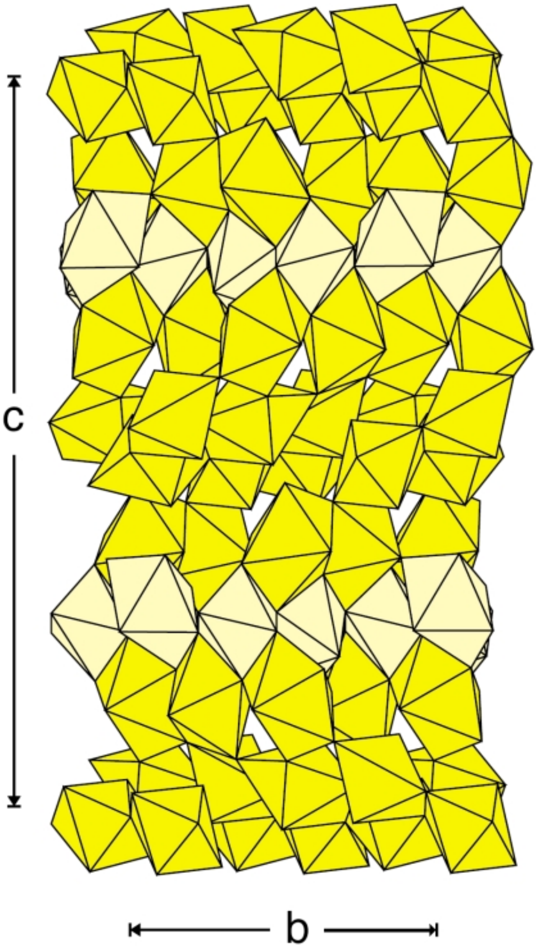

FIG. 3. The structure of *PbUOH* projected onto (100). Only uranium polyhedra are shown. The $U(2)O_6$ and $U(6)\phi_7$ polyhedra are shown in light yellow, the others are colored dark yellow.

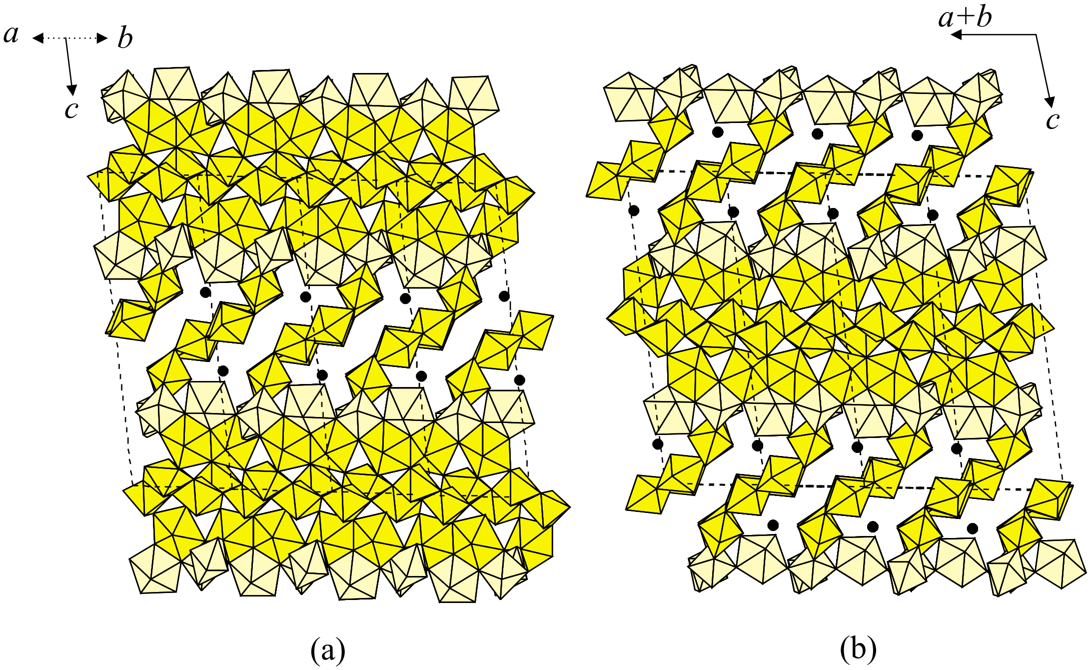

FIG. 4. The structure of *PbUOH* (a) viewed along [110], (b) viewed along [$\bar{1}$10]. Legend as in Figure 3; black circles represent Pb cations.

dron, in which the O atoms that are part of the uranyl ion receive ~1.7 *vu* from their bonds to the U^{6+} cation, whereas the equatorial anions of the polyhedra only receive ~0.5 *vu* from the bond to the U^{6+} cation at the center of the polyhedron. In the case of a uranyl polyhedron, polymerization with other uranium polyhedra may only occur through non-uranyl ion oxygen atoms because the bonding requirements of the O_{Ur} atoms are close to being met by the uranyl bond. In *PbUOH*, all six vertices of the $U(2)O_6$ polyhedron are shared with other U^{6+} cations, permitting the $U(2)O_6$ polyhedron, which is located along the edges of the complex chain (Fig. 5a), to be shared between two chains that are oriented in opposing directions, resulting in a framework of polyhedra.

Crystals of *PbUOH* occur together with curite and Pb-poor fourmarierite in the synthesis products obtained from our experiments. Thus it is apparent that *PbUOH* grows under conditions that are similar to some of the Pb uranyl oxide hydrate minerals. Crystals formed in our experiments have variable Pb:U ratios, and their abundances correlate with the Pb:U ratio of the solution from which they were synthesized (Table 1). The structure of *PbUOH* is related to that of curite, and it coexists with curite in some of our experiments, suggesting they have overlapping fields of stability. It is therefore possible that *PbUOH* will be found as a mineral.

The presence of a U^{6+} cation in approximately octahedral coordination in the structure of *PbUOH*, in opposition with the observation that U^{6+} in mineral structures invariably occurs as part of a uranyl ion (Burns 1999b), suggests that *PbUOH* may be a metastable phase. If this is the case, it may still occur in natural systems and be an important phase in the sequence that forms as Pb uranyl oxide hydrates are progressively altered, but it may not be stable enough to persist for a geologically long time.

Our findings may have some interesting implications for the disposal of nuclear waste in a geological repository. Laboratory simulations have shown that alteration of UO_2 under moist oxidizing conditions similar to those in the proposed repository at Yucca Mountain promotes the formation of a suite of uranyl phases, most of which have structures that are based upon sheets of polyhedra (Wronkiewicz *et al.* 1992, 1996). It is likely that these uranyl phases will incorporate various radionuclides into their structures (Burns *et al.* 1997b, Burns 1999c, Chen *et al.* 1999, 2000). Rates of release of radionuclides may depend to a large extent on the stabilities of the uranyl phases. With continued alteration, a sequence of uranyl phases will form, and radionuclides contained within early-formed structures may be released upon alteration, or they may be incorporated into the later-formed structures. *PbUOH* shows that frameworks of uranium poly-

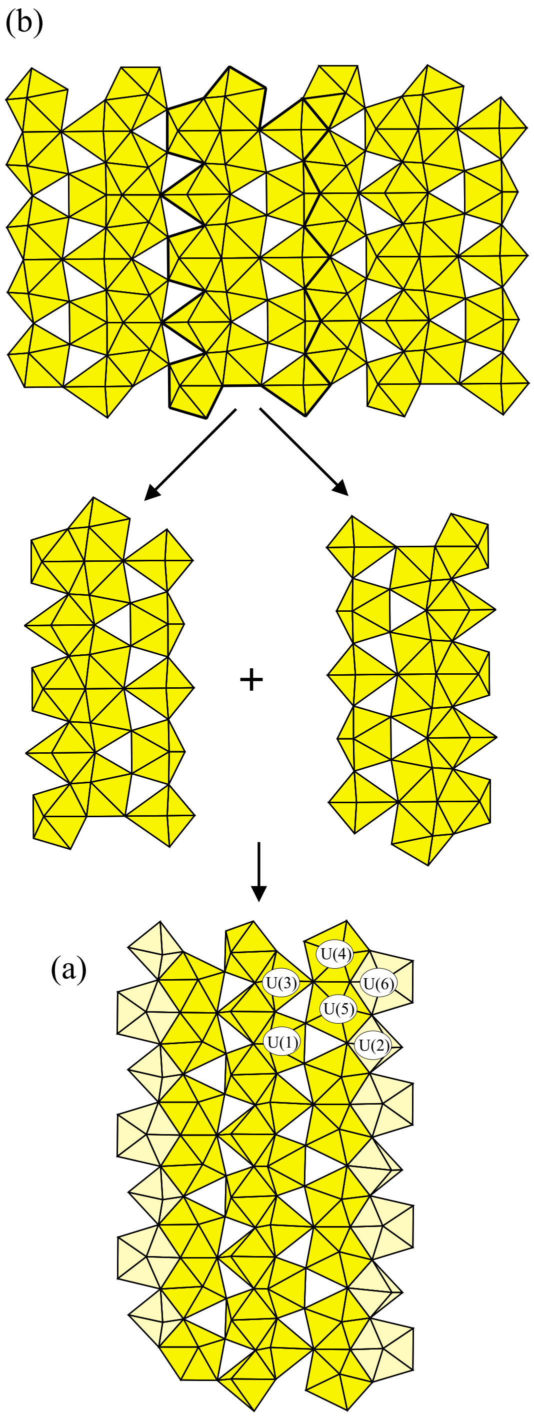

FIG. 5. a. The complex chain of uranyl polyhedra in *PbUOH*. b. Sheet of uranyl polyhedra in the structure of curite, with components that occur in *PbUOH* delineated by heavy lines.

hedra can contain structural fragments known from sheets in other phases, provided that octahedrally coordinated U^{6+} is involved. It is possible that such phases will occur as intermediates during the alteration of early-formed uranyl phases in a geological repository, and thus they may have an impact upon the ultimate release of radionuclides.

During the time this manuscript was progressing through the review process, we obtained the Ca analogue of *PbUOH* by methods of hydrothermal synthesis similar to those reported for *PbUOH*. A structural analysis ($R1$ = 4.3%) showed that the Ca phase, with lattice parameters a 13.314(2), b 10.086(1), c 26.113(3) Å, β 103.229(3)°, is isostructural with *PbUOH*.

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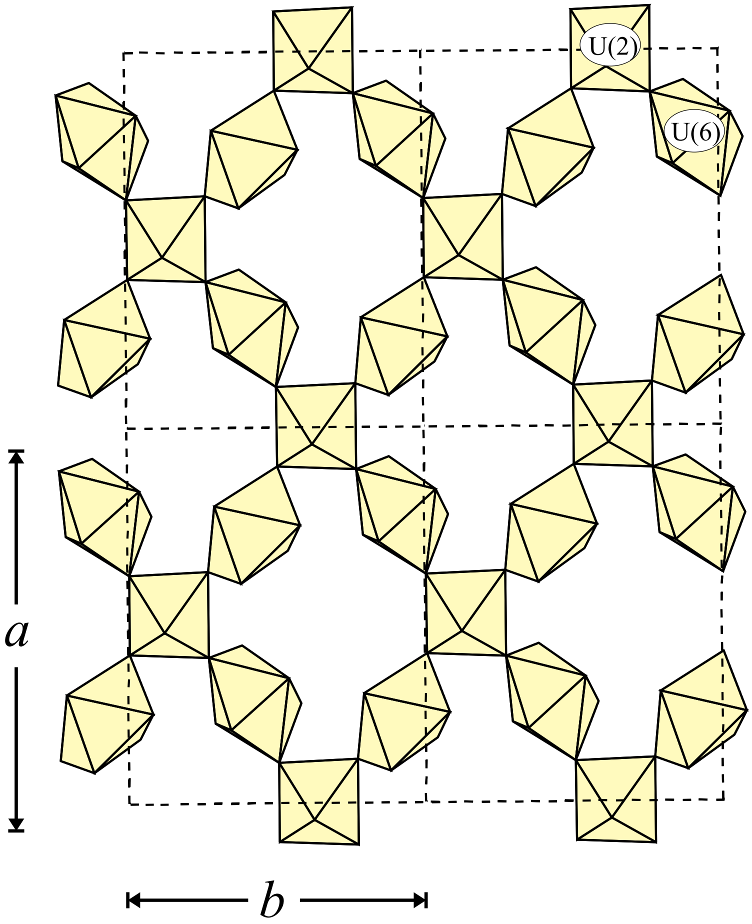

FIG. 6. Net of corner sharing U(2)O_6–U(6)ϕ_7 polyhedra at $z \approx 0.25$ and $z \approx 0.75$ in the structure of *PbUOH*.

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