The Canadian Mineralogist
Vol. 40, pp. 1579-1586 (2002)

A TOPOLOGICALLY NOVEL SHEET OF URANYL PENTAGONAL BIPYRAMIDS IN THE STRUCTURE OF $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$

PETER C. BURNS[§] AND KATHRYN M. DEELY

Department of Civil Engineering and Geological Sciences, University of Notre Dame, 156 Fitzpatrick Hall, Notre Dame, Indiana 46556–5602, U.S.A.

ABSTRACT

A new sodium uranyl oxide hydrate, $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$, has been synthesized by hydrothermal reaction. The structure, space group $P\bar{1}$, a 8.0746(9), b 8.4633(10), c 11.2181(13) Å, α 80.398(2), β 87.492(2), γ 71.308(2)°, V 715.97(14) 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 (R1) of 4.49%, calculated using 2915 unique observed reflections ($F_o \geq 4\sigma_F$). The structure contains four symmetrically distinct U^{6+} cations, each of which is strongly bonded to two atoms of O, giving $(UO_2)^{2+}$ uranyl ions. Each uranyl ion is coordinated by five anions. The resulting uranyl pentagonal bipyramids are linked by sharing vertices and edges, resulting in sheets with a previously unobserved topology. The single symmetrically distinct Na cation is located between the sheets, where it is coordinated by eight ligands, including two H_2O groups. The structure of $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$ is closely related to that of $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$, although the sheets in these two structures have different topologies.

Keywords: uranium, crystal chemistry, sodium uranium oxide hydrate.

SOMMAIRE

Nous avons synthétisé un nouveau composé, un oxyde de sodium et d'uranyle hydraté, $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$, par réaction hydrothermale. La structure, dans le groupe spatial $P\bar{1}$, a 8.0746(9), b 8.4633(10), c 11.2181(13) Å, α 80.398(2), β 87.492(2), γ 71.308(2)°, V 715.97(14) Å^3, $Z = 2$, a été résolue et affinée en utilisant les facteurs F^2 pour toutes les données uniques prélevées avec rayonnement X monochromatique Mo$K\alpha$ et un détecteur CCD jusqu'à un facteur de concordance (R1) de 4.49%, calculé en utilisant 2915 réflexions uniques observées ($|F_o| \geq 4\sigma_F$). La structure contient quatre cations U^{6+} symétriquement distincts, chacun d'eux fortement liés à deux atomes d'oxygène, pour donner des ions uranyles $(UO_2)^{2+}$. Chacun de ces ions est coordonné à cinq anions. Les bipyramides pentagonales uranylées qui en résultent sont liées par partage de coins et d'arêtes en feuillets qui ont une topologie non encore observée. Le seul cation Na, symétriquement distinct, est situé entre les feuillets, où il entre en coordinence avec huit ligands, y inclus deux groupes H_2O. La structure de $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$ ressemble étroitement à celle du composé $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$, quoique les feuillets dans ces deux structures possèdent des topologies distinctes.

(Traduit par la Rédaction)

Mots-clés: uranium, cristallochimie, oxyde hydraté de sodium et d'uranium.

INTRODUCTION

Uranyl oxide hydrates crystallize in a fascinating variety of structures, most of which are based upon sheets of uranyl polyhedra (Burns 1999a). They are common in the oxidized portions of U deposits (Frondel 1958), in soils contaminated by actinides (Buck *et al.* 1996), and are likely to be important phases where spent nuclear fuel is altered in a geological repository (Wronkiewicz *et al.* 1992, 1996, Finch & Ewing 1992, Pearcy *et al.* 1994, Finn *et al.* 1996, Finch *et al.* 1999).

We are interested in the topological variations of sheets of uranyl polyhedra that occur in uranyl oxide hydrates (Glatz *et al.* 2002, Burns & Li 2002, Li & Burns 2000a, b, c, 2001, Burns & Hill 2000a, b, Cahill & Burns 2000, Burns 1997, 1998a, b, 1999b, Burns & Hanchar 1999, Hill & Burns 1999). Such sheets are compared using the sheet anion-topology approach

§ *E-mail address*: pburns@nd.edu

(Burns *et al.* 1996), which considers the topological arrangement of anions that are bonded to at least two cations within the sheet of polyhedra. Miller *et al.* (1996), Burns & Hill (2000a) and Burns (1999a) showed that a small number of one-dimensional chains of polygons are needed to assemble the sheet anion-topologies that are the basis of the sheets found in uranyl oxide hydrates, and Burns (1997, 1999b) demonstrated that this approach reveals relationships between extraordinarily complex sheets, such as those found in vandendriesscheite and wölsendorfite, and much simpler sheets.

As part of our ongoing studies of the structures of uranyl oxide hydrates, and the phases that may form due to the alteration of nuclear waste in Yucca Mountain, we have synthesized the new phase $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$ and have determined its crystal structure.

Background Information

To date, clarkeite, with ideal end-member formula $Na[(UO_2)O(OH)](H_2O)_{0-1}$, is the only uranyl oxide hydrate mineral known to contain essential Na (Finch & Ewing 1997). Li & Burns (2001) reported the structure of $Na_2[(UO_2)_3O_3(OH)_2]$ (grown hydrothermally at 230°C), the only Na uranyl oxide hydrate for which a single-crystal determination of the structure exists. It contains α-U_3O_8-type sheets of uranyl pentagonal bipyramids, with Na located in the interlayer. There is evidence that Na uranyl oxide hydrates may be important phases formed during the alteration of nuclear waste in a geological repository. In experiments intended to provide insight into the behavior of spent nuclear fuel in Yucca Mountain, Finch *et al.* (1999) subjected spent nuclear fuel to oxidative corrosion in dripping groundwater at 90°C. The experiments used two pressurized-water-reactor fuels, ATM103 and ATM106, which have burn-ups of ~30 MWd/kg-U and ~45 MWd/kg-U, respectively (Finch *et al.* 1999). The groundwater used in their experiments (EJ–13) was from well J–13 at the Yucca Mountain site, and was reacted with crushed Tonopah Springs tuff at 90°C for 80 days. The water contains Na and Si concentrations of 46.5 and 34.4 μg/mL, respectively (Wronkiewicz *et al.* 1992). Tests involving weekly injection of 0.15 mL of EJ–13 water onto the spent fuel resulted in the formation of a uranyl compound containing Na after 4.1 and 5.2 years (Finch *et al.* 1999). Owing to insufficient quantities of material, the uranyl phase could not be fully characterized, and it was tentatively designated the Na analogue of compreignacite (Finch *et al.* 1999), which is a K uranyl oxide hydrate (Burns 1998c).

TABLE 1. CRYSTALLOGRAPHIC DATA AND REFINEMENT RESULTS FOR $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$

a (Å)	8.0746(9)	Radiation	Mo$K\alpha$
b (Å)	8.4633(10)	$2\theta_{max}$(°)	69.0
c (Å)	11.2181(13)	Total reflections	14,664
α (°)	80.398(2)	Unique reflections	5847
β (°)	87.492(2)	Data with $\|F_o\| > 4\sigma F_o$	2915
γ (°)	71.308(2)	$R1$ (%)	4.49
V (Å^3)	715.97(14)	$wR2$ (%)	11.80
Space group	$P\bar{1}$	S	0.83
$F(000)$	1048		
μ(mm^{-1})	45.22		
D_{calc} (g/cm^3)	5.827		

h, k, l ranges: $-12 \rightarrow 12$, $-13 \rightarrow 13$, $-17 \rightarrow 17$

Unit cell contents 2 $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$

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

$wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

$w = 1/[\sigma^2(F_o^2) + (0.029 \times P)^2]$, $P = (\max(F_o^2, 0) + 2 \times F_c^2)/3$

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

Experimental

Hydrothermal synthesis of $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$

Synthesis of $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$ was achieved in a 23 mL Teflon-lined stainless steel Parr vessel. The reactants were a mixture of 0.313 g uranyl acetate (Alfa), 0.03g $Na_2(CO_3)$ (Fisher), and 4 mL of ultrapure H_2O. The reactants were combined at room temperature; the reaction vessel was heated to 150°C for 5 days, and then cooled to room temperature. The product consisted of yellow tabular crystals ranging to ~50 μm in maximum dimension.

Single-crystal X-ray diffraction

A tabular crystal of $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$ that showed sharp extinction between crossed polarizers and uniform optical properties was mounted on a Bruker PLATFORM three-circle goniometer equipped with an APEX SMART CCD (charge-coupled device) detector with a crystal-to-detector distance of 4.5 cm. A sphere of data to 69° 2θ was collected using monochromatic Mo$K\alpha$ X-radiation and frame widths of 0.3° in ω, with 60 s used to collect each frame. The three-dimensional data were analyzed to locate reflections for the determination of the unit-cell dimensions (Table 1), which were refined using least-squares techniques. The data were integrated using the Bruker program SAINT, and were corrected for Lorentz, polarization, and background effects. A semi-empirical absorption-correction was done with the crystal modeled as an ellipsoid, and lowered R_{INT} of 844 reflections from 11.16 to 6.85%. A total of 14,664 reflections was collected, of which there were 5847 unique reflections, with 2915 classed as observed ($F_o \geq 4\sigma_F$).

Solution and refinement of the structure

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 Crystallog-*

raphy, Vol. IV (Ibers & Hamilton 1974). The structure was solved in space group $P\bar{1}$ by direct methods, which gave the positions of the U atoms. The Na and O atoms were located on difference-Fourier maps calculated following refinement of the model. Refinement was done on the basis of F^2 for all 5847 unique reflections. Refinement of all atom-position parameters, allowing for anisotropic displacement of the U and Na atoms and isotropic displacement of the anions, and inclusion of a weighting scheme of the structure factors, gave an agreement index ($R1$) of 4.49%, calculated for the 2915 unique observed reflections. In the final cycle of refinement, the mean parameter shift/esd was 0.000. The final coordinates of the atoms and anisotropic-displacement parameters are listed in Tables 2 and 3, selected interatomic distances are in Table 4, and a bond-valence analysis is given 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.

Description of the Structure of $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$

The structure of $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$ is shown projected along [010] in Figure 1. Consistent with other uranyl oxide hydrates, the structure is based upon a sheet of uranyl polyhedra, with low-valence cations and H_2O groups located between the sheets.

Cation polyhedra

The structure of $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$ contains four symmetrically distinct U sites, and consideration of their polyhedron geometries (Table 4) and bond-valence sums (Table 5) indicates that each contains U^{6+}. Each U^{6+} cation is strongly bonded to two atoms of O, forming approximately linear $(UO_2)^{2+}$ uranyl ions with U–O_{Ur} (*Ur*: uranyl ion) bond-lengths of ~1.8 Å, as is almost invariably observed in uranyl compounds (Burns *et al.* 1997). Each uranyl ion is coordinated by five ligands arranged at the equatorial vertices of pentagonal bipyramids, with <U–ϕ_{eq}> (ϕ: unspecified ligand) ranging from 2.36 to 2.42 Å, which is consistent with 2.37(9) Å, the average U–ϕ_{eq} for pentagonal bipyramids from a large number of well-refined structures (Burns *et al.* 1997). The equatorial ligands of the U(1) and U(3) pentagonal bipyramids are two O atoms and three OH groups, whereas the U(2) and U(4) polyhedra each involve one O atom and four OH groups.

The single symmetrically unique Na cation is located between the sheets of uranyl polyhedra, where it is coordinated by six O_{Ur} atoms and two H_2O groups. The <Na–ϕ> bond-length is 2.565 Å, and the sum of bond valences at the site is 1.08 valence units (*vu*).

Sheets of uranyl polyhedra

The uranyl pentagonal bipyramids in the structure of $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$ share equatorial vertices

TABLE 2. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC-DISPLACEMENT PARAMETERS (Å²) FOR $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$

	x	y	z	*U_{eq}
U(1)	0.9616(1)	0.8725(1)	0.1450(1)	0.011(1)
U(2)	0.6822(1)	0.6054(1)	0.4211(1)	0.012(1)
U(3)	0.6741(1)	1.0695(1)	0.4169(1)	0.011(1)
U(4)	0.9414(1)	1.3401(1)	0.1365(1)	0.011(1)
Na(1)	0.4220(10)	0.9835(9)	0.1418(7)	0.028(2)
O(1)	0.8098(17)	0.0313(16)	0.5488(12)	0.025(3)
O(2)	0.7466(16)	0.8969(15)	0.0941(11)	0.022(3)
O(3)	0.8151(16)	0.5090(14)	0.5537(10)	0.019(2)
O(4)	0.1682(16)	0.2344(15)	0.1565(11)	0.023(3)
O(5)	0.1780(15)	0.8387(14)	0.1955(10)	0.018(2)
O(6)	0.7079(16)	0.4508(15)	0.1091(11)	0.020(3)
O(7)	0.5562(17)	0.6982(16)	0.2796(12)	0.025(3)
O(8)	0.5559(16)	0.1065(15)	0.2702(11)	0.023(3)
O(9)	0.9207(15)	0.1362(14)	0.0436(10)	0.018(2)
O(10)	0.5823(16)	0.8508(15)	0.4847(11)	0.021(3)
OH(11)	0.0351(15)	0.5887(14)	0.0874(10)	0.017(2)
OH(12)	0.5669(14)	0.3783(13)	0.4201(10)	0.015(2)
OH(13)	0.9045(14)	0.1086(13)	0.2826(10)	0.013(2)
OH(14)	0.9155(16)	0.4389(14)	0.3138(11)	0.020(3)
OH(15)	0.8736(14)	0.7839(13)	0.3473(10)	0.013(2)
OW(16)	0.4816(17)	0.7854(16)	0.0005(12)	0.028(3)
OW(17)	0.3677(17)	0.4705(16)	0.1890(12)	0.027(3)

*$U_{eq} = \frac{1}{3}\Sigma\Sigma U_{ij} a_i^* a_j^* a_i a_j$

TABLE 3. ANISOTROPIC-DISPLACEMENT PARAMETERS (Å²) FOR $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$

	*U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	0.015(1)	0.010(1)	0.010(1)	-0.002(1)	0.004(1)	-0.003(1)
U(2)	0.013(1)	0.011(1)	0.011(1)	-0.003(1)	0.002(1)	-0.003(1)
U(3)	0.013(1)	0.012(1)	0.011(1)	-0.003(1)	0.003(1)	-0.005(1)
U(4)	0.014(1)	0.009(1)	0.011(1)	-0.003(1)	0.004(1)	-0.003(1)
Na(1)	0.021(4)	0.029(4)	0.034(5)	-0.011(3)	-0.005(3)	-0.001(3)

*The anisotropic displacement factors take the form $-2\pi^2[h^2a^{*2}U_{11} + \ldots 2hka^*b^*U_{12}]$

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$

U(1)-O(5)a	1.78(1)	U(2)-O(3)	1.79(1)	U(3)-O(1)b	1.80(1)
U(1)-O(2)	1.79(1)	U(2)-O(7)	1.84(1)	U(3)-O(8)b	1.87(1)
U(1)-O(9)b	2.26(1)	U(2)-O(10)	2.20(1)	U(3)-O(10)	2.22(1)
U(1)-O(9)c	2.28(1)	U(2)-OH(14)	2.38(1)	U(3)-O(10)e	2.26(1)
U(1)-OH(15)	2.42(1)	U(2)-OH(12)	2.39(1)	U(3)-OH(13)b	2.41(1)
U(1)-OH(11)a	2.47(1)	U(2)-OH(15)	2.51(1)	U(3)-OH(12)b	2.48(1)
U(1)-OH(13)b	2.64(1)	U(2)-OH(12)d	2.61(1)	U(3)-OH(15)	2.66(1)
O(2)-U(1)-O(5)	177.2(5)	O(3)-U(2)-O(7)	176.7(5)	O(1)-U(3)-O(8)	173.7(5)
<U(1)-O_{Ur}>	1.784	<U(2)-O_{Ur}>	1.815	<U(3)-O_{Ur}>	1.835
<U(1)-ϕ_{eq}>	2.414	<U(2)-ϕ_{eq}>	2.419	<U(3)-ϕ_{eq}>	2.406
U(4)-O(4)f	1.77(1)	Na(1)-O(8)h	2.38(1)	a = x−1,y,z; b = x,y+1,z; c =	
U(4)-O(6)h	1.83(1)	Na(1)-OW(16)	2.42(1)	-x+2,-y+1,-z; d = -x+1,-	
U(4)-O(9)h	2.21(1)	Na(1)-O(4)h	2.46(1)	y+1,-z+1; e = -x+1,-y+2,-	
U(4)-OH(14)b	2.26(1)	Na(1)-O(2)	2.54(1)	z+1; f = x+1,y−1,z; g =	
U(4)-OH(13)b	2.42(1)	Na(1)-O(7)	2.57(1)	-x+1,-y+2,-z	
U(4)-OH(11)f	2.43(1)	Na(1)-OW(16)g	2.61(1)		
U(4)-OH(11)g	2.50(1)	Na(1)-O(5)	2.63(1)		
O(4)-U(4)-O(6)	177.7(5)	Na(1)-O(2)g	2.90(1)		
<U(4)-O_{Ur}>	1.799	<Na(1)-ϕ>	2.565		
<U(4)-ϕ_{eq}>	2.364				

TABLE 5. BOND VALENCE (*vu*) ANALYSIS* FOR $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$

	U(1)	U(2)	U(3)	U(4)	Na(1)	Σ
O(1)			1.61			1.61
O(2)	1.65				0.05 0.13	1.83
O(3)		1.65				1.65
O(4)				1.70	0.17	1.89
O(5)	1.68				0.10	1.78
O(6)				1.52		1.52
O(7)		1.49			0.12	1.61
O(8)			1.41		0.21	1.62
O(9)	0.66 0.63			0.72		2.01
O(10)		0.74	0.72 0.65			2.11
OH(11)	0.43			0.41 0.47		1.31
OH(12)		0.33 0.51	0.42			1.26
OH(13)	0.31		0.49	0.48		1.28
OH(14)		0.52		0.66		1.18
OH(15)	0.48	0.40	0.30			1.18
OW(16)					0.11 0.19	0.30
OW(17)						0.00
Σ	5.84	5.64	5.60	5.98	1.08	

*bond-valence parameters for U^{6+} are from Burns *et al.* (1997) and for Na^{+} are from Brese & O'Keeffe (1991). The bond-valence sums do not include contributions from H atoms.

and edges, resulting in the novel sheet of uranyl polyhedra shown in Figure 2. The corresponding sheet anion-topology, derived using the method of Burns *et al.* (1996), is presented in Figure 3b. Nodes in the anion topology corresponding to OH groups are shown as open circles. Although the sheet anion-topology is topologically fairly simple, with only pentagons and triangles, it has not been previously observed in any structure of a uranyl compound.

Following the procedure developed by Miller *et al.* (1996) and Burns (1999a), the sheet anion-topology can be constructed as a stacking sequence of chains. Only the arrowhead (**U** and **D**) and **P** chains are required, and the sequence is **UDPUDP**… (Fig. 3a).

The chain-stacking sequences corresponding to sheets of uranyl polyhedra found in uranyl oxide hydrates are described by Burns & Hill (2000a). In addition, a new sheet anion-topology was recently described from the structure of $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$ by Glatz *et al.* (2002). Miller *et al.* (1996) noted that **P** chains are invariably adjacent to either **U** or **D** chains in such topologies, and the chains on either side of the **P** chain invariably have the same orientation, although it was unclear to them why the **UPU** and **DPD** sequences dominate, as the sequence **DPU** involves the same degree of structural misfit. Burns & Hill (2000a) reported the sheet anion-topology in the structure of $K_5[(UO_2)_{10}O_8(OH)_9](H_2O)$, which contains the first example of the **UPD** sequence. The structure of $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$ provides the second example of an anion topology with the sequence **UPD**.

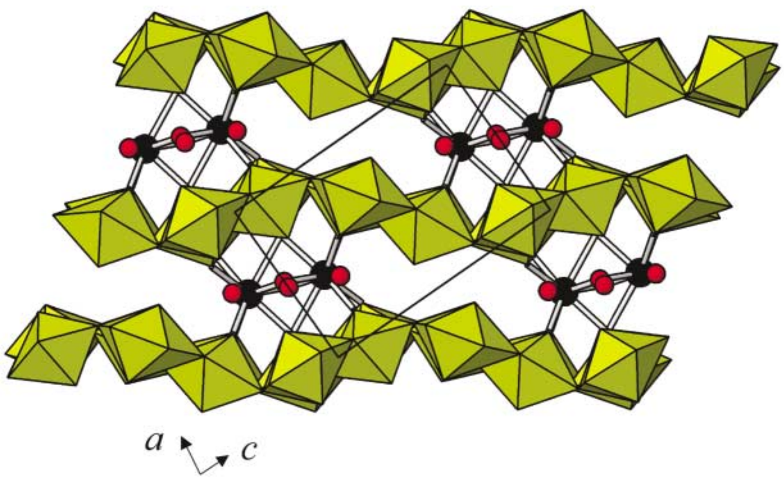

FIG. 1. Polyhedral representation of the structure of $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$ projected along [010]. The uranyl polyhedra are shown in green, Na cations in black, and O atoms of the H_2O groups are shown in red.

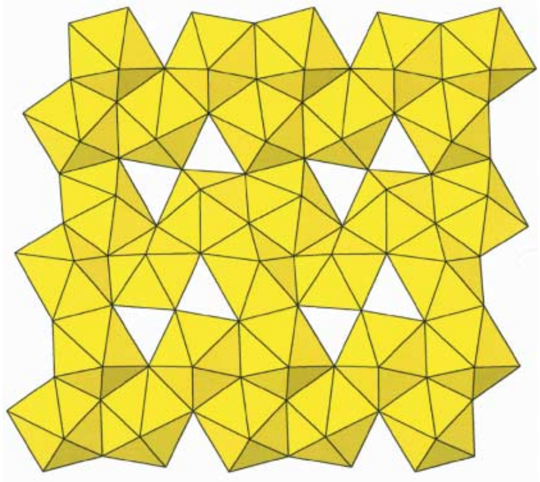

FIG. 2. Polyhedral representation of the sheet of uranyl polyhedra in the structure of $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$.

Interlayer constituents

The interlayer of $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$ contains dimers of face-sharing $Na\phi_8$ polyhedra. One interlayer H_2O group is bonded to two Na cations, whereas the other is held in the structure by H bonding only.

Hydrogen bonding

The X-ray data did not provide sufficient resolution to reveal the positions of the H atoms, as is typical in the case of uranyl compounds. However, it is possible to propose a network of H bonding on the basis of crystal-chemical arguments. Possible H bonds are listed in Table 6. There are five symmetrically distinct OH groups located at equatorial positions of uranyl polyhedra within the sheets. Bonds donated by OH(11) and OH(12) are both accepted by OW(17), which is located

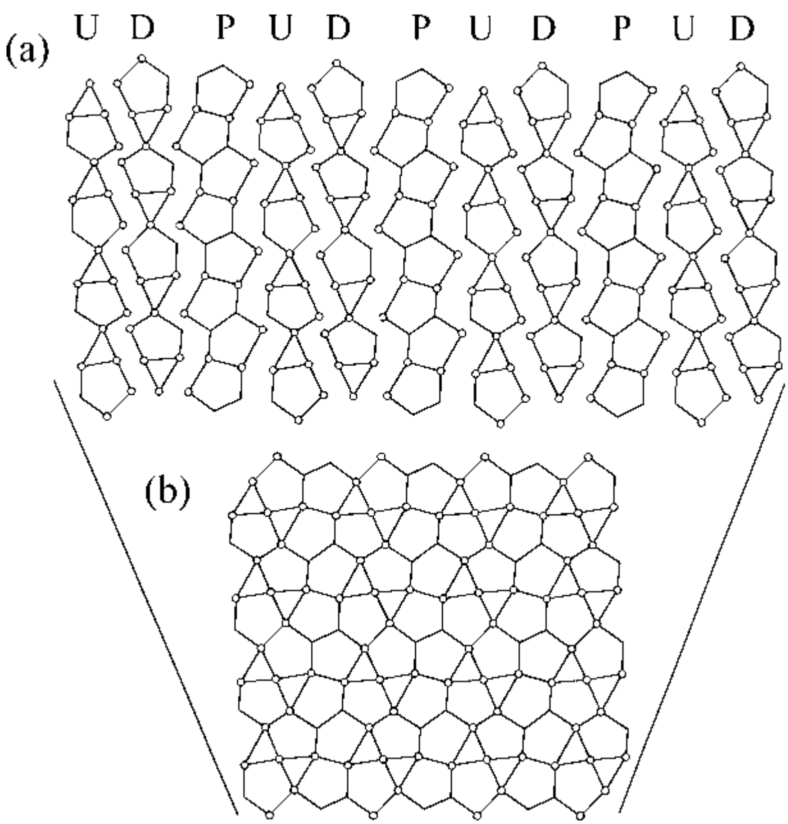

FIG. 3. The sheet anion-topology of the sheet in the structure of $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$, derived using the method of Burns *et al.* (1996). The positions of the OH groups are indicated by circles. (a) Development of the anion topology as a stacking sequence of chains. (b) The sheet anion-topology.

in the interlayer. Bonds donated by OH(13), OH(14) and OH(15) are accepted by the O(1), O(3) and O(3) atoms, respectively, each of which are O_{Ur} atoms located in adjacent sheets. The O atom of the OW(17) H_2O group accepts bonds from OH(11) and OH(12), but there is ambiguity as to which anions accept the two H bonds donated by OW(17). Any of the O(4), O(5), O(6) and O(8) O_{Ur} atoms are potential acceptors, and are located between 2.81 and 3.01 Å from OW(17) (Table 6).

TABLE 6. POSSIBLE HYDROGEN BONDS IN THE STRUCTURE OF $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$

OH(11) → OW(17)	2.77(2)
OH(12) → OW(17)	2.97(2)
OH(13) → O(1)a	2.86(2)
OH(14) → O(3)b	2.87(2)
OH(15) → O(3)b	3.00(2)
OW(16) → O(6)	2.93(2)
OW(16) → O(2)c	2.79(2)
OW(16) → O(2)	2.90(2)
OW(16) → O(8)d	3.02(2)
OW(17) → O(4)	3.01(2)
OW(17) → O(5)	3.01(2)
OW(17) → O(6)	2.81(2)
OW(17) → O(8)	2.97(2)

a = 2-x, -y, 1-z; b = 2-x, 1-y, 1-z; c = 1-x, 2-y, -z; d = 1-x, 1-y, -z

OW(16), which is shared between two $Na\phi_8$ polyhedra, probably donates a H bond that is accepted by O(6). The other H bond associated with the OW(16) group is probably accepted by O(2), which is located 2.79 Å away, but this H bond is located along the edge of the $Na\phi_8$ polyhedron.

Structural formula

All atoms in the structure are located on general positions in space group $P\bar{1}$. It is straightforward to distinguish which O atoms correspond to OH and H_2O on the basis of the bond-valence analysis (Table 5). The resulting formula is $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$, with a *Z* of 2, and a calculated density of 5.827 g/cm^3.

Discussion

The structure of $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$ is closely related to that of $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$, which was recently reported by Glatz *et al.* (2002). The latter crystallizes in space group $P\bar{1}$ with the unit-cell parameters *a* 8.0556(8), *b* 8.4214(8), *c* 10.958(1) Å, α 78.878(2), β 87.922(2), γ 72.277(2)°. The two structures have similar formulae; that of $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$ may be obtained from $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$ by the replacement Ca + O → Na + OH. The connectivities of the interlayers of the two structures, including the H bonding, are similar. The primary difference between the structures lies in the topology of the sheet of uranyl polyhedra.

The sheet in the structure of $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$ contains three uranyl pentagonal bipyramids and one uranyl square bipyramid, and involves a novel arrangement of these polyhedra (Fig. 4). The U(3) square bipyramid contains only four equatorial ligands; if this were a pentagonal bipyramid, the sheet would be topologically identical to that shown in Figure 2. The OH(4) atom is located 3.17(2) Å from U(3), a separation that is too great to be considered a significant bond. Displacement of this anion ~0.6 Å toward U(3) would result in a pentagonal bipyramid, and a sheet topologically identical to that found in $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$.

The sheet of uranyl polyhedra in synthetic Pb-poor fourmarierite, $Pb_{0.5}[(UO_2)_4O_2(OH)_5](H_2O)_4$ (Li & Burns 2000c), is chemically identical to that in $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$. The structure of $Pb_{0.5}[(UO_2)_4O_2(OH)_5](H_2O)_4$ contains fourmarierite-type sheets of uranyl pentagonal bipyramids, rather than the topology observed in $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$.

The sheet anion-topology of $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$ is rather closely related to the α-U_3O_8 sheet anion-topology shown in Figure 5. The uranyl oxide hydrates becquerelite, billietite, compreignacite, masuyite, richetite, and agrinierite, as well as two synthetic uranyl oxide hydrate compounds, contain sheets that are based upon this anion topology. Note that it contains chains of pentagons and triangles that are topologically identical to those in the $Na[(UO_2)_4O_2(OH)_5](H_2O)_2$ anion topology; it differs from the anion topology shown in Figure 3b only in the orientation of the arrowhead chains, which are all pointed in the same direction, resulting in the stacking sequence **PDPDPD**… An appreciation of the differences in free energy between sheets of uranyl pentagonal bipyramids based upon these two anion topologies will require further study.

Acknowledgements

This research was supported by the Environmental Management Science Program of the Office of Science, U.S. Department of Energy, grant DE–FG07–97ER 14820. We thank Drs. S.V. Krivovichev and M. Schindler for their helpful reviews, and Drs. E. Sokolova and R.F. Martin for editorial work.

References

Brese, N.E. & O'Keeffe, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.* **B47**, 192-197.

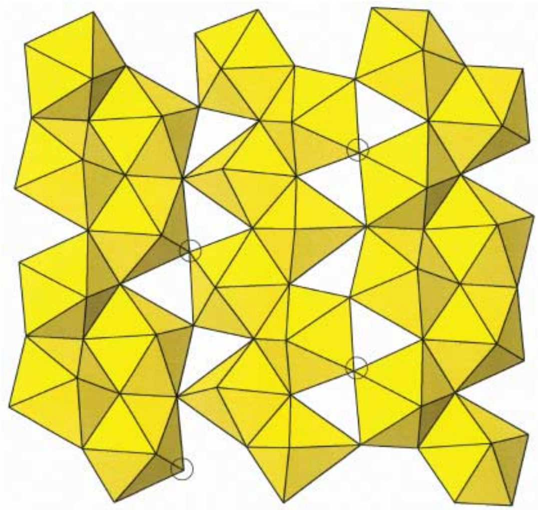

FIG. 4. The sheet of uranyl polyhedra in the structure of $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$ projected along [$\bar{1}$01]. The OH(4) positions are indicated by circles.

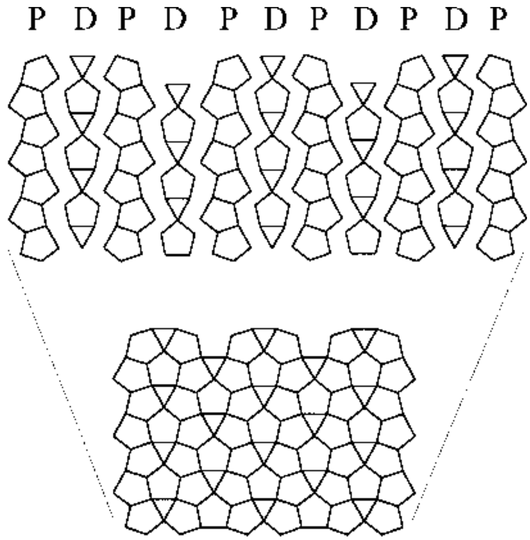

FIG. 5. The α-U_3O_8 sheet anion-topology (from Burns 1999a).

BUCK, E.C., BROWN, N.R. & DIETZ, N.L. (1996): Contaminant uranium phases and leaching at the Fernald site in Ohio. *Env. Sci. Technol.* **30**, 81-88.

BURNS, P.C. (1997): A new uranyl oxide hydrate sheet in the structure of vandendriesscheite: implications for mineral paragenesis and the corrosion of spent nuclear fuel. *Am. Mineral.* **82**, 1176-1186.

________ (1998a): The structure of compreignacite, $K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$. *Can. Mineral.* **36**, 1061-1067.

________ (1998b): The structure of richetite, a rare lead uranyl oxide hydrate. *Can. Mineral.* **36**, 187-199.

________ (1998c): The structure of boltwoodite and implications of solid-solution toward sodium boltwoodite. *Can. Mineral.* **36**, 1069-1075.

________ (1999a): The crystal chemistry of uranium. *In* Uranium: Mineralogy, Geochemistry and the Environment (P.C. Burns & R. Finch, eds.). *Rev. Mineral.* **38**, 23-90.

________ (1999b): A new sheet complex of uranyl polyhedra in the structure of wölsendorfite. *Am. Mineral.* **84**, 1661-1673.

________, EWING, R.C. & HAWTHORNE, F.C. (1997): The crystal chemistry of hexavalent uranium: polyhedron geometries, bond-valence parameters, and polymerization of polyhedra. *Can. Mineral.* **35**, 1551-1570.

________ & HANCHAR, J.M. (1999): The structure of masuyite, $Pb[(UO_2)_3O_3(OH)_2](H_2O)_3$, and its relationship to protasite. *Can. Mineral.* **37**, 1483-1491.

________ & HILL, F.C. (2000a): A new uranyl sheet in $K_5[(UO_2)_{10}O_8(OH)_9](H_2O)$: new insight into sheet anion-topologies. *Can. Mineral.* **38**, 163-174.

________ & ________ (2000b): Implications of the synthesis and structure of the Sr analogue of curite. *Can. Mineral.* **38**, 175-182.

________ & LI, YAPING (2002): The structures of becquerelite and Sr-exchanged becquerelite. *Am. Mineral.* **87**, 550-557.

________, MILLER, M.L. & EWING, R.C. (1996): U^{6+} minerals and inorganic phases: a comparison and hierarchy of crystal structures. *Can. Mineral.* **34**, 845-880.

CAHILL, C.L. & BURNS, P.C. (2000): The structure of agrinierite: a Sr-containing uranyl oxide hydrate mineral. *Am. Mineral.* **85**, 1294-1297.

FINCH, R.J., BUCK, E.C., FINN, P.A. & BATES, J.K. (1999): Oxidative corrosion of spent UO_2 fuel in vapor and dripping groundwater at 90°C. *In* Scientific Basis for Nuclear Waste Management XXII (D.J. Wronkiewicz & J.H. Lee, eds.). *Mater. Res. Soc., Symp. Proc.* **556**, 431-438.

________ & EWING, R.C. (1992): The corrosion of uraninite under oxidizing conditions. *J. Nucl. Mater.* **190**, 133-156.

________ & ________ (1997): Clarkeite: new chemical and structural data. *Am. Mineral.* **82**, 607-619.

FINN, P.A., HOH, J.C., WOLF, S.F., SLATER, S.A. & BATES, J.K. (1996): The release of uranium, plutonium, cesium, strontium, technetium and iodine from spent fuel under unsaturated conditions. *Radiochim. Acta* **74**, 65-71.

FRONDEL, C. (1958): Systematic mineralogy of uranium and thorium. *U.S. Geol. Surv., Bull.* **1064**.

GLATZ, R.E., LI, YAPING, HUGHES, K.-A., CAHILL, C.L. & BURNS, P.C. (2002): Synthesis and structure of a new Ca uranyl oxide hydrate, $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$, and its relationship to becquerelite. *Can. Mineral.* **40**, 217-224.

HILL, F.C. & BURNS, P.C. (1999): Structure of a synthetic Cs uranyl oxide hydrate and its relationship to compreignacite. *Can. Mineral.* **37**, 1283-1288.

IBERS, J.A. & HAMILTON, W.C., eds. (1974): *International Tables for X-ray Crystallography* **IV**. The Kynoch Press, Birmingham, U.K.

LI, YAPING & BURNS, P.C. (2000a): Investigations of crystal-chemical variation in lead uranyl oxide hydrates. I. Curite. *Can. Mineral.* **38**, 727-735.

________ & ________ (2000b): Synthesis and crystal structure of a new Pb uranyl oxide hydrate with a framework structure that contains channels. *Can. Mineral.* **38**, 1433-1441.

________ & ________ (2000c): Investigations of crystal-chemical variation in lead uranyl oxide hydrates. II. Fourmarierite. *Can. Mineral.* **38**, 737-749.

________ & ________ (2001): The structures of two sodium uranyl compounds relevant to nuclear waste disposal. *J. Nucl. Mater.* **299**, 219-226.

MILLER, M.L., FINCH, R.J., BURNS, P.C. & EWING, R.C. (1996): Description and classification of uranium oxide hydrate sheet topologies. *J. Mater. Res.* **11**, 3048-3056.

PEARCY, E.C., PRIKRYL, J.D., MURPHY, W.M. & LESLIE, B.W. (1994): Alteration of uraninite from the Nopal I deposit, Peña Blanca District, Chihuahua, Mexico, compared to degradation of spent nuclear fuel in the proposed U.S. high-level nuclear waste repository at Yucca Mountain, Nevada. *Appl. Geochem.* **9**, 713-732.

WRONKIEWICZ, D.J., BATES, J.K., GERDING, T.J., VELECKIS, E. & TANI, B.S. (1992): Uranium release and secondary phase formation during unsaturated testing of UO_2 at 90°C. *J. Nucl. Mater.* **190**, 107-127.

________, ________, WOLF, S.F. & BUCK, E.C. (1996): Ten-year results from unsaturated drip tests with UO_2 at 90°C: implications for the corrosion of spent nuclear fuel. *J. Nucl. Mater.* **238**, 78-95.

Received June 22, 2002, revised manuscript accepted October 7, 2002.