THE CRYSTAL STRUCTURE AND CRYSTAL CHEMISTRY
OF URANOSPHAERITE, Bi(UO$_2$)O$_2$OH

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Abstract

The crystal structure of uranosphaerite, Bi(UO$_2$)O$_2$OH, has been solved and refined using single-crystal X-ray-diffraction data collected from synthetic and natural crystals. The structure of natural uranosphaerite from the Clara barite and fluorite mine, Black Forest, Germany, was refined to an agreement index (R_1) of 2.86%, calculated for 1194 unique observed reflections ($|F_o| > 4\sigma_F$). Uranosphaerite is monoclinic, space group $P2_1/n$, a 7.559(2), b 7.811(2), c 7.693(2) Å, β 92.88(3)°, V 453.6(2) Å^3. Crystals of synthetic uranosphaerite were obtained by mild hydrothermal techniques; the structure was refined to an R_1 of 5.84%, calculated for 1590 unique observed reflections ($|F_o| > 4\sigma_F$). The synthetic crystal has slightly smaller unit-cell dimensions, a 7.540(3), b 7.801(3), c 7.674(3) Å, β 92.948(7)°, V 450.75(1) Å^3. The structure consists of one symmetrically distinct U^{6+} cation that is bonded to two atoms of oxygen, forming a nearly linear uranyl ion [(UO$_2$)$^{2+}$, designated *Ur*]. The uranyl ion is further coordinated by five O and OH anions, resulting in a pentagonal bipyramid capped by the oxygen atoms of the uranyl ion. The single symmetrically distinct Bi^{3+} cation in the structure is coordinated by four anions arranged at the base of a pyramid that is capped by Bi^{3+}, consistent with the presence of a lone pair of electrons on Bi^{3+}. The Bi^{3+} cation is weakly bonded to two additional O$_{Ur}$ atoms. *Ur*ϕ_5 (ϕ: O, OH) pentagonal bipyramids share an equatorial edge, giving a dimer. Pairs of Biϕ_4 polyhedra also share an edge, and the resulting dimers are linked to the dimers of uranyl polyhedra, forming a heteropolyhedral sheet that is parallel to (101). Adjacent sheets are linked by weak Bi–O bonds and by weak hydrogen bonds. The sheet is based upon the anion-topology of the francevillite sheet.

Keywords: uranosphaerite, crystal structure, uranyl oxide hydrate, uranium, crystal chemistry.

Sommaire

Nous avons résolu et affiné la structure cristalline de l'uranosphaerite, Bi(UO$_2$)O$_2$OH, en utilisant des données en diffraction X prélevées sur monocristaux naturels et synthétiques. La structure de l'uranosphaerite naturelle, déterminée sur un échantillon de la mine Clara, dans la Forêt Noire, en Allemagne, où l'on exploite la barite et la fluorite, a été affinée jusqu'à un résidu R_1 de 2.86%, calculé selon 1194 réflexions uniques observées ($|F_o| > 4\sigma_F$). L'uranosphaerite est monoclinique, groupe spatial $P2_1/n$, a 7.559(2), b 7.811(2), c 7.693(2) Å, β 92.88(3)°, V 453.6(2) Å^3. Nous avons synthétisé les cristaux d'uranosphaerite par techniques hydrothermales légères; sa structure a été affinée jusqu'à un résidu R_1 de 5.84%, calculé selon 1590 réflexions uniques observées ($|F_o| > 4\sigma_F$). Le cristal synthétique possède une maille élémentaire légèrement plus petite: a 7.540(3), b 7.801(3), c 7.674(3) Å, β 92.948(7)°, V 450.75(1) Å^3. La structure contient un cation U^{6+} symétriquement distinct lié à deux atomes d'oxygène, pour former un ion uranyle presque linéaire [(UO$_2$)$^{2+}$, symbole *Ur*]. L'ion uranyle est de plus coordonné à cinq anions O et OH, ce qui mène à une bipyramide pentagonale chapeautée par les atomes d'oxygène de l'ion uranyle. Le cation unique Bi^{3+}, symétriquement distinct dans cette structure, montre une coordinence à quatre anions disposés à la base d'une pyramide avec le Bi^{3+} au sommet, en concordance avec la présence d'une paire d'électrons isolée sur le cation Bi^{3+}. De plus, celui-ci est faiblement lié à deux atomes O$_{Ur}$. Les bipyramides pentagonales *Ur*ϕ_5 (ϕ: O, OH) partagent une arête équatoriale, pour donner un dimère. Des paires de polyèdres Biϕ_4 partagent aussi une arête, et les dimères qui en résultent sont liés aux dimères de polyèdres à uranyle pour former un feuillet hétéropolyédrique parallèle à (101). Les feuillets adjacents sont rattachés par de faibles liaisons Bi–O et hydrogène. Le feuillet est fondé sur la topologie anionique du feuillet de la francevillite.

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Mots-clés: uranosphaerite, structure cristalline, oxyde hydraté d'uranyle, uranium, cristallochimie.

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Introduction

Uranyl oxide hydrate minerals are common constituents of oxidized portions of uranium deposits, and are important for understanding the genesis of such deposits, as well as the interaction of the deposits with the environment (Frondel 1958, Finch & Ewing 1992). Uranyl minerals form early during the corrosion of UO_2, and are likely to be important during alteration of nuclear waste under oxidizing conditions (Finn *et al.* 1996, Wronkiewicz *et al.* 1996, Finch *et al.* 1999), such as those expected in the proposed geological repository at Yucca Mountain, Nevada, U.S.A. Uranyl oxide hydrates are also present in soils contaminated by actinides, including the vadose zones of the Oak Ridge and Hanford sites in the U.S.A., where they exert an impact on the mobility of uranium (Roh *et al.* 2000, Yamakawa & Traina 2001).

Structures of most of the uranyl oxide hydrate minerals have been solved; the structures of schoepite (Finch *et al.* 1996), metaschoepite (Weller *et al.* 2000), masuyite (Burns & Hanchar 1999), billietite (Pagoaga *et al.* 1987), protasite (Pagoaga *et al.* 1987), becquerelite (Pagoago *et al.* 1987, Burns & Li 2002), compreignacite (Burns 1998a), curite (Mereiter 1979, Taylor *et al.* 1981, Li & Burns 2000a), fourmarierite (Piret 1985, Li & Burns 2000b), wölsendorfite (Burns 1999a), vandendriesscheite (Burns 1997), agrinierite (Cahill & Burns 1999), richetite (Burns 1998b), ianthinite (Burns *et al.* 1997b), and sayrite (Piret *et al.* 1983) have all been reported. The crystal structure of the rare U–Bi–O–H species uranosphaerite has remained unknown, probably owing to the difficulty in obtaining suitable single crystals.

Previous Work

Uranosphaerite is an inadequately defined mineral. It was first described by Weisbach (1873), with the approximate formula $Bi_2O_3 \cdot 2UO_3 \cdot 3H_2O$, from the Weisser Hirsch mine at Neustädtl, near Schneeberg, Saxony, Germany. At its type locality, it occurs as small globular yellowish orange aggregates of crystals, and is associated with various uranium and cobalt–nickel arsenates in veins of hydrothermal origin that contain oxidized uraninite, native bismuth, and cobalt–nickel arsenides (Weisbach 1873, Anthony *et al.* 1997). Berman (1957) found uranosphaerite associated with walpurgite, uranospinite, trögerite, zeunerite, erythrite, and "black cobalt oxide". He provided optical properties and an unindexed X-ray powder-diffraction pattern (see also Frondel *et al.* 1956 and ICDD–PDF 8–321), and concluded that it is probably orthorhombic. Protas (1959) synthesized well-developed platy crystals of synthetic uranosphaerite by hydrothermal reactions at 180°C and pH 2.5, and provided their optical properties, thermo-analytical behavior, and an X-ray powder-diffraction pattern. He proposed a primitive monoclinic unit-cell with *a* 7.65(4), *b* 7.78(4), *c* 7.53(4) Å, β 93(1)°, *V* 448 Å^3. Wet-chemical analyses gave the formula $UO_4Bi(OH)$. Protas (1959) reported that the much less well-formed crystals from the type locality give an X-ray powder-diffraction pattern identical to that of the synthetic material. He also noted that the natural material, in comparison to the synthetic crystals, shows slightly lower indices of refraction, a somewhat higher content of H_2O, as well as a minor amount of As.

Baptista *et al.* (1962) suggested a tetragonal cell for uranosphaerite, with *a* 7.404, *c* 6.939 Å, on the basis of studies of synthetic material. They obtained a slightly different content of H_2O from chemical analyses and gave the formula $Bi(OH)UO_4 \cdot nH_2O$. A second locality of uranosphaerite at Kerségalec-en-Lignol, Département du Morbihan, France, was briefly mentioned by Chervet (1960), who also reported an X-ray powder-diffraction pattern. Three additional occurrences in the Czech Republic have been briefly described (Sejkora *et al.* 1994, J. Sejkora, pers. commun., 2001). Recently, uranosphaerite was reported from the Clara barite and fluorite mine, Black Forest, Germany (Kolitsch 1997; unpubl. data). Specimens from this locality show crystal shapes consistent with monoclinic symmetry, and give X-ray powder-diffraction patterns that are, neglecting effects of preferred orientation parallel to (101), in relatively good agreement with data given previously (Berman 1957, Frondel *et al.* 1956, ICDD–PDF 8–321, Chervet 1960). Reflection splitting is evident in these powder patterns, indicating a symmetry lower than orthorhombic (Kolitsch 1998). Semiquantitative energy-dispersion (EDS) analyses yielded a Bi:U ratio of 1:1, and demonstrated the presence of trace amounts of Sb in the crystals (Kolitsch 1997).

Contradictory formulae and crystal-symmetry data for uranosphaerite are listed in recent mineral encyclopedias and similar works: Strunz (1982) gave $[UO_2|(OH)_2|BiOOH]$ and orthorhombic symmetry, Anthony *et al.* (1997), $Bi_2U_2O_9 \cdot 3H_2O$ and undetermined symmetry, Gaines *et al.* (1997), $Bi_2U_2O_9 \cdot 3H_2O$ and probable orthorhombic symmetry, Mandarino (1999), $Bi_2U_2O_9 \cdot 3H_2O$, and Strunz & Nickel (2001), $Bi_2[(UO_2)_2|O_5] \cdot 3H_2O$ and an orthorhombic cell with *a*, *b*, and *c* identical to the parameters reported by Protas (1959).

Two crystal structures were independently determined for uranosphaerite; a natural crystal was studied at Institut für Mineralogie und Kristallographie, Vienna, and a synthetic crystal was examined at the University of Notre Dame. The results of both structure determinations, leading to the correct symmetry and chemical formula of uranosphaerite, are reported herein, and details of the arrangements of atoms, including the polyhedron connectivity and the topology of the fundamental building-unit, are discussed.

EXPERIMENTAL METHODS

Synthesis of uranosphaerite

Crystals of synthetic uranosphaerite were obtained by mild hydrothermal techniques. Experiments were done at 90, 120, 150, 180, and 220°C. In each experiment, three crystals of calcite, totaling 0.51 g, were combined with 1.87 g $Bi(NO_3)_3(H_2O)_5$ (J.T. Baker) and 1.62 g UO_3 (98%, Alfa Aesar) in 4 mL of ultrapure water and placed in a 23 mL Teflon-lined Parr reaction vessel. The reaction vessels were heated for 10 days, then allowed to cool to room temperature. Reaction products were recovered by filtering and were rinsed using ultrapure water. All experiments yielded yellow to orange uranosphaerite, as confirmed by X-ray powder diffraction. The experiment at 180°C provided the maximum yield and the largest crystals, which attain 300 μm in length.

Single-crystal X-ray diffraction

Natural crystal: Crystallographic studies of several natural crystals of uranosphaerite were conducted to determine the correct Laue symmetry and to exclude the possibility of polymorphs. Three specimens are from the Clara barite and fluorite mine, Black Forest, Germany (one specimen is described in Kolitsch 1997, 1998), and the fourth specimen is from Měděnec, the Krušné hory Mountains, Czech Republic. Visually, all crystals and crystal aggregates are similar in appearance, with orange-brown to yellowish brown colors, curved crystal faces and morphologies consistent with monoclinic symmetry. Single-crystal studies, using a Nonius Kappa CCD four-circle X-ray diffractometer equipped with a 300 μm diameter capillary-optics collimator to provide increased resolution, showed that the mineral has a tendency to form crystals of poor quality with pervasive subparallel intergrowths; this observation is in agreement with the report by Protas (1959). Each crystal studied consistently and unambiguously showed the same primitive monoclinic cell, which is similar to that reported by Protas (1959) for synthetic crystals. A pseudo-tetragonal distribution of intensities was evident in patterns collected by exposure along *a* or *c*, which is consistent with the tetragonal cell suggested by Baptista *et al.* (1962).

After considerable effort, a crystal fragment with dimensions $50 \times 30 \times 30$ μm³ and reasonable quality was obtained from a specimen from the Clara mine. The chemical composition of immediately adjacent aggregates of crystals was characterized using semiquantitative energy-dispersion analyses done with a scanning electron microscope (SEM); these analyses gave an approximate Bi:U ratio of 43:57, and revealed no impurities. A sphere of intensity data up to 60° in 2θ was collected at room temperature using the Nonius Kappa CCD diffractometer, graphite-monochromatized MoKα

radiation, a crystal-to-detector distance of 3.6 cm, frame widths of 1.0°, and counting times per frame of 200 s. The data were processed with the Nonius program suite DENZO–SMN and corrected for Lorentz, polarization, background and absorption effects, the latter by the multi-scan method of Otwinowski & Minor (1997) (R_{int} = 2.54%). The unit cell (Table 1) was refined from 1410 reflections. Systematic extinctions and structure-factor statistics unambiguously indicated the centrosymmetric space group $P2_1/n$. The structure was solved by direct methods (SHELXS–97: Sheldrick 1997a) and subsequent Fourier and difference-Fourier syntheses. A full-matrix least-squares refinement was done with SHELXL–97 (Sheldrick 1997b).

Synthetic crystal: A synthetic single crystal of $Bi(UO_2)O_2OH$ grown at 180°C, with dimensions 100 × 100 × 100 μm³, was mounted on a tapered glass fiber. A sphere of diffraction data to 69° in 2θ was collected using a Bruker PLATFORM three-circle X-ray diffractometer equipped with a 4K APEX CCD detector with a crystal-to-detector distance of 4.67 cm. Data were collected at room temperature using graphite-monochromatized MoKα radiation, with frame widths of 0.3° in ω, and 10 s spent counting per frame. The unit cell (Table 1) was refined from 746 reflections using least-squares techniques. Intensity data were reduced and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A semi-empirical correction for absorption was applied by modeling the crystal as an ellipsoid and reduced R_{int} of 1088 reflections from 14.35% to 9.65%. A total of 9302 reflections were collected, of which 1894 were unique, and 1590 of the unique reflections were classed as

TABLE 1. CRYSTAL DATA AND REFINEMENT RESULTS FOR URANOSPHAERITE

	natural crystal	synthetic crystal
a (Å)	7.559(2)	7.540(3)
b (Å)	7.811(2)	7.801(3)
c (Å)	7.693(2)	7.674(3)
β (°)	92.88(3)	92.948(7)
V (Å³)	453.6(2)	450.75(1)
Space group	$P2_1/n$	$P2_1/n$
Z	4	4
Formula	$Bi(UO_2)O_2(OH)$	$Bi(UO_2)O_2(OH)$
$F(000)$	864	864
μ (mm^{-1})	74.30	74.78
D_{calc}* (g/cm³)	7.731	7.781
Crystal size (μm)	50 × 30 × 30	100 × 100 × 100
Radiation	MoKα	MoKα
Reflections collected	2651	9302
Independent reflections	1320	1894
Unique $|F_o| > 4\sigma_F$	1194	1590
Parameters varied	65	64
R_1 (%)	2.86	5.84
wR_2 (%)	7.59	14.48
S	1.066	1.056

* D_{meas} of synthetic crystals is 7.69(6) g/cm³ (Protas 1959).

TABLE 2. ATOM COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS FOR URANOSPHAERITE

	x	y	z	$*U_{eq}$	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
				natural uranosphaerite						
U	0.15866(4)	0.99182(4)	0.31567(4)	0.0135(1)	0.0139(2)	0.0169(2)	0.0100(2)	-0.0002(1)	0.0050(1)	0.000(1)
Bi	0.11052(4)	0.60575(4)	0.66482(4)	0.0162(1)	0.0164(2)	0.0197(2)	0.0129(2)	0.0001(1)	0.0036(1)	0.0004(1)
O(1)	0.177(1)	0.6024(9)	0.0500(9)	0.025(2)	0.027(4)	0.029(4)	0.019(3)	-0.001(3)	0.001(3)	0.001(3)
O(2)	-0.0077(9)	0.8842(9)	0.1786(9)	0.026(2)	0.019(3)	0.037(4)	0.021(3)	-0.011(3)	0.002(3)	-0.002(3)
O(3)	0.0710(9)	0.8511(9)	0.5586(9)	0.023(1)	0.028(3)	0.021(3)	0.020(3)	0.007(3)	0.014(3)	0.008(3)
O(4)	-0.1460(9)	0.5069(8)	0.5907(9)	0.019(1)	0.014(3)	0.022(4)	0.022(3)	-0.008(2)	0.008(2)	-0.004(2)
OH(5)	-0.1196(8)	0.7422(8)	0.8413(7)	0.017(1)	0.023(3)	0.016(3)	0.011(3)	0.001(2)	0.005(2)	0.001(2)
				synthetic uranosphaerite						
U	0.15796(6)	-0.00914(6)	0.31531(6)	0.0215(2)	0.0211(2)	0.0234(3)	0.0204(2)	-0.0002(1)	0.0052(2)	-0.0003(1)
Bi	0.10974(6)	0.60517(7)	0.66556(6)	0.0231(2)	0.0228(2)	0.0245(3)	0.0223(2)	0.0004(2)	0.0045(2)	0.0004(2)
O(1)	0.184(2)	0.603(2)	0.050(2)	0.032(2)	0.034(6)	0.039(6)	0.025(5)	0.007(4)	0.001(4)	0.005(4)
O(2)	-0.008(2)	0.883(2)	0.179(2)	0.032(2)	0.029(5)	0.040(6)	0.028(5)	-0.004(4)	0.001(4)	0.004(4)
O(3)	0.070(1)	0.850(1)	0.563(1)	0.027(2)	0.029(5)	0.020(4)	0.032(5)	0.005(4)	0.014(4)	0.001(4)
O(4)	-0.150(2)	0.507(1)	0.590(2)	0.030(2)	0.026(5)	0.038(6)	0.028(5)	-0.011(4)	0.009(4)	-0.013(4)
OH(5)	-0.119(1)	0.741(1)	0.840(1)	0.026(2)	0.031(5)	0.029(5)	0.018(4)	0.000(3)	0.004(3)	-0.002(4)

$$U = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})] \times 10^4 \, \text{Å}^2$$
$$*U_{eq} = (1/3) \Sigma\Sigma \, U_{ij}a_i^*a_j^*a_ia_j$$

observed ($|F_o| \geq 4\sigma_F$). The Bruker SHELXTL Version 5 system of programs was used for the solution and refinement of the crystal structure in space group $P2_1/n$.

Scattering curves for neutral atoms and anomalous-dispersion corrections for both refinements were taken from International Tables for Crystallography, Vol. IV (Ibers & Hamilton 1974). The final structure-models included refined coordinates of the atoms, anisotropic displacement parameters for all detected atoms (H atoms could not be located), and a weighting scheme of the structure factors. The structures were refined on the basis of F^2 for all unique reflections to final agreement indices (R_1) of 2.86% (natural crystal) and 5.84% (synthetic crystal), which were calculated for the 1194 (natural) and 1590 (synthetic) unique observed reflections ($|F_o| > 4\sigma_F$). Final coordinates and displacement parameters of the atoms are given in Table 2. Selected interatomic distances and angles are listed in Table 3. A bond-valence analysis is presented in Table 4. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

RESULTS AND DISCUSSION

The structure solutions of both natural and synthetic uranosphaerite provide the formula $Bi(UO_2)O_2OH$, thus confirming the chemical-analytical results of Protas (1959). The two refinements provided essentially the

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN THE CRYSTAL STRUCTURE OF URANOSPHAERITE

natural crystal		synthetic crystal	
U-O(1)a	1.795(7)	U-O(1)a	1.77(1)
U-O(2)	1.807(7)	U-O(2)	1.80(1)
U-O(3)	2.294(6)	U-O(4)b	2.31(1)
U-O(4)b	2.331(7)	U-O(3)	2.33(1)
U-O(3)c	2.372(6)	U-O(3)	2.35(1)
U-OH(5)c	2.414(6)	U-OH(5)c	2.42(1)
U-OH(5)b	2.481(6)	U-OH(5)b	2.47(1)
<O(1)-U-O(2)>	179.0(3)	<O(1)-U-O(2)>	178.0(5)
Bi-O(3)	2.099(7)	Bi-O(3)	2.08(1)
Bi-O(4)	2.138(7)	Bi-O(4)	2.16(1)
Bi-O(4)d	2.182(7)	Bi-O(4)	2.18(1)
Bi-OH(5)e	2.499(6)	Bi-OH(5)e	2.47(1)
Bi-O(2)e	2.884(7)	Bi-O(2)e	2.88(1)
Bi-O(1)	2.981(7)	Bi-O(1)	2.97(1)

a = -x + 1/2, y + 1/2, -z + 3/2; b = x + 1/2, -y + 3/2, z - 1/2; c = -x, -y + 2, -z + 1;
d = -x, -y + 1, -z + 1; e = x + 1/2, -y + 3/2, z + 1/2.

same results within error, although the synthetic crystal has slightly smaller unit-cell dimensions. Anisotropic displacement parameters and U_{eq} values for the heavy atoms in both structures are different (Table 2), possibly reflecting the different methods of absorption correction employed.

Cation polyhedra

The structure of uranosphaerite contains one symmetrically distinct U^{6+} cation, one Bi^{3+} cation, and five O^{2-} anions, of which O(5) is an OH group. All atoms are on general positions in space group $P2_1/n$. The U^{6+} cation is strongly bonded to two oxygen atoms, O(1) and O(2), forming an approximately linear uranyl ion $[(UO_2)^{2+}$, designated *Ur*], with U–O_{Ur} bonds close to 1.80 Å. The uranyl ion is coordinated by five anions arranged at the equatorial vertices of a pentagonal bipyramid that is capped by the oxygen atoms of the uranyl ion. The average U^{6+}–ϕ_{eq} (ϕ: O^{2-}, OH^-; eq: equatorial) bond-length is 2.38(11) Å (Table 3), which may be compared to 2.37(9) Å, the average for uranyl pentagonal bipyramids from numerous well-refined structures (Burns *et al.* 1997a).

The unique Bi^{3+} cation is strongly bonded to four anions, with Bi–ϕ bond lengths ranging from 2.08 to 2.50 Å. The anions are arranged at the base of a flattened pyramid that is capped by the Bi^{3+} cation, consistent with the presence of a stereochemically active lone-pair of electrons on Bi^{3+} that extend away from the four anions. The Bi^{3+} cation is also weakly bonded to O(1) and O(2), with bond distances of 2.97/2.98 and 2.88 Å, respectively (Table 3, Fig. 1), which corresponds to 0.11/0.12 and 0.09 valence units, respectively (Table 4).

Structural connectivity

The structure of uranosphaerite contains $Ur\phi_5$ pentagonal bipyramids that share an equatorial edge, resulting in dimers of polyhedra. Pairs of $Bi\phi_4$ polyhedra also form dimers by sharing an edge. The sharing of edges between dimers of $Ur\phi_5$ pentagonal bipyramids and dimers of $Bi\phi_4$ polyhedra results in a sheet parallel to (101) (Fig. 2). Each dimer of $Ur\phi_5$ pentagonal bipyramids shares four equatorial edges with four different dimers of $Bi\phi_4$ polyhedra; each dimer of $Bi\phi_4$ polyhedra shares four edges with four dimers of $Ur\phi_5$ pentagonal bipyramids (Fig. 2). Adjacent sheets (Fig. 3) are linked by weak Bi–O bonds and by weak hydrogen bonding, with OH(5)-acceptor distances greater than 2.9 Å. The presence of sheets parallel to (101) and the weak intersheet linkages are consistent with the tabular {101} habit and {101} cleavage observed in synthetic crystals (Protas 1959).

The anion topology of the uranosphaerite sheet, obtained by using the procedure of Burns *et al.* (1996), is shown in Figure 4. This sheet anion-topology was previously designated the francevillite anion-topology by Burns *et al.* (1996), although considerable distortion of the topology occurs in the case of uranosphaerite. The francevillite anion-topology is the basis of sheets that occur in francevillite, curienite, and sengierite, as well as various anhydrous carnotite-type structures (Burns 1999b).

TABLE 4. BOND-VALENCE (*vu*) ANALYSIS FOR THE STRUCTURE OF URANOSPHAERITE

	U	Bi	Σ
natural uranosphaerite			
O(1)	1.630	0.090	1.72
O(2)	1.590	0.117	1.71
O(3)	0.607 + 0.521	0.900	2.03
O(4)	0.565	0.810 + 0.718	2.09
OH(5)	0.480 + 0.420	0.306	1.21
Σ	5.81	2.94	
synthetic uranosphaerite			
O(1)	1.707	0.086	1.79
O(2)	1.628	0.109	1.74
O(3)	0.571 + 0.543	0.951	2.07
O(4)	0.585	0.773 + 0.721	2.08
OH(5)	0.478 + 0.249	0.327	1.23
Σ	5.94	2.97	

Bond-valence parameters for U^{6+} from Burns *et al.* (1997a), and for Bi^{3+}, from Brese & O'Keeffe (1991).
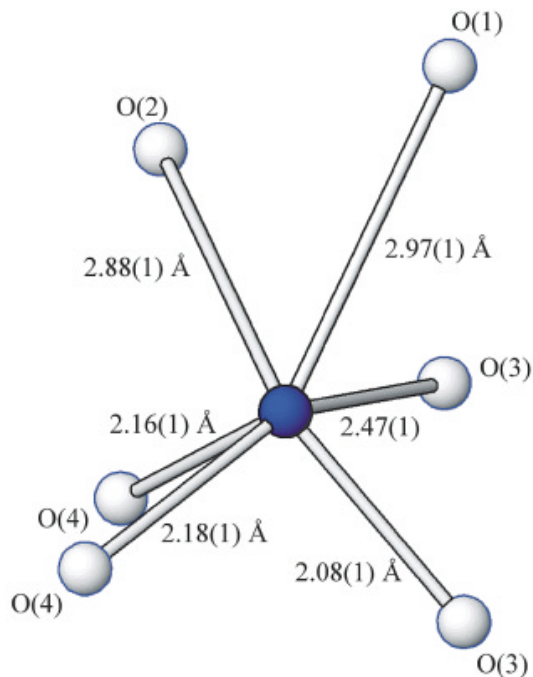

FIG. 1. Coordination around Bi in the structure of uranosphaerite. Bond distances indicated are for the synthetic crystal.
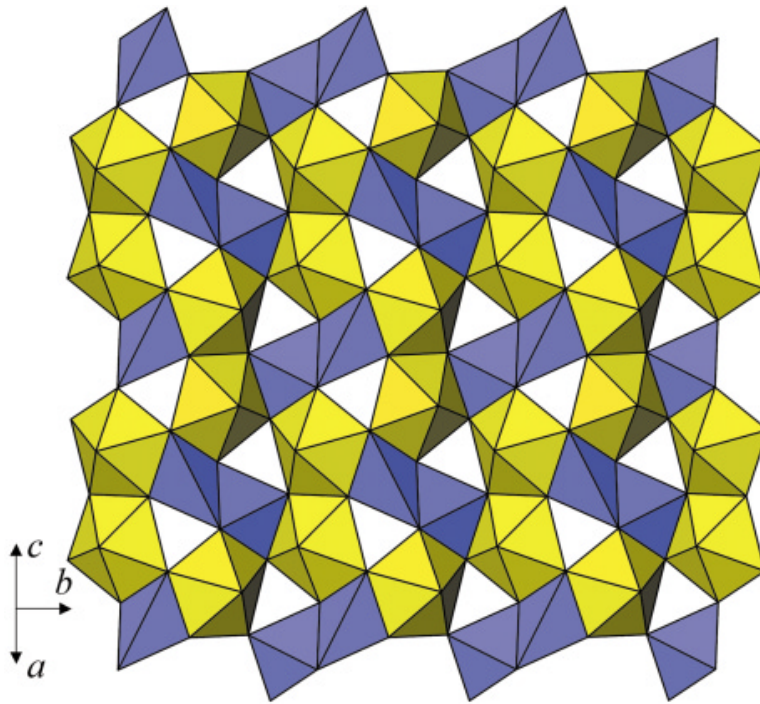
FIG. 2.   Two-dimensional sheets formed by the sharing of edges between dimers of uranyl
         pentagonal bipyramids and dimers of $B\phi_4$ polyhedra in the structure of uranosphaerite
         projected onto (101). $Ur\phi_5$ and $Bi\phi_4$ polyhedra are shown in yellow and blue, respec-
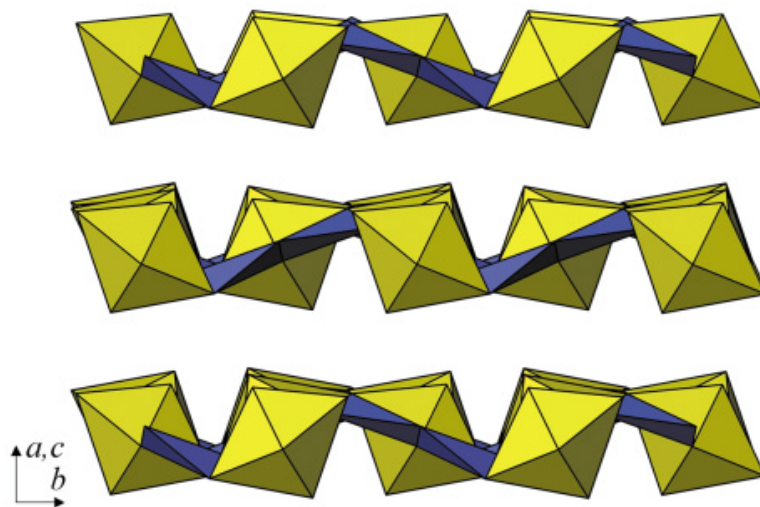   tively.

FIG. 3. _ Adjacent heteropolyhedral sheets in the structure of uranosphaerite projected down
         [10$\bar{1}$]. The sheets are connected by weak Bi–O bonds and weak hydrogen bonding (not
         shown). $Ur\phi_5$ and $Bi\phi_4$ polyhedra are shown in yellow and blue, respectively.

Comparison with other uranyl oxide hydrates

The structures of richetite, masuyite, agrinierite, compreignacite, schoepite, metaschoepite, four-marierite, becquerelite, curite, billietite, protasite, wölsendorfite, vandendriesscheite, ianthinite, and sayrite each contain sheets of uranyl polyhedra, with H_2O groups, and in some cases mono- and divalent cations, located between the sheets. The structure of uranosphaerite is unusual amongst uranyl oxide hydrates because its sheets contain cation polyhedra ($Bi\phi_4$) other than uranyl polyhedra. Vandenbrandeite, $CuUO_2$ $(OH)_4$ (Rosenzweig & Ryan 1977), is the only other uranyl oxide hydrate mineral known to contain non-uranyl polyhedra in sheets with the uranyl polyhedra (Fig. 5). The vandenbrandeite sheet contains dimers of edge-sharing $Ur\phi_5$ pentagonal bipyramids, as well as dimers of $Cu\phi_5$ square pyramids formed by the sharing of equatorial edges. The apical ligands of adjacent $Cu\phi_5$ pyramids within each dimer point in opposite directions. Sheets are linked directly through the apical ligands of the $Cu\phi_5$ square pyramids, which are O_{Ur} atoms of adjacent sheets. Other than the sharing of an equatorial edge between two uranyl pentagonal bipyramids within
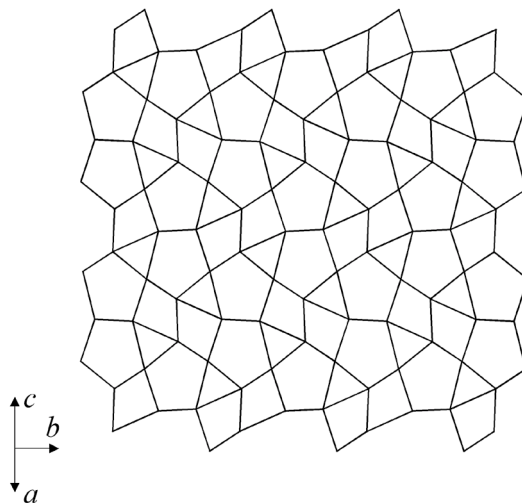

FIG. 4. Anion topology of uranosphaerite, obtained by using the procedures of Burns *et al.* (1996).
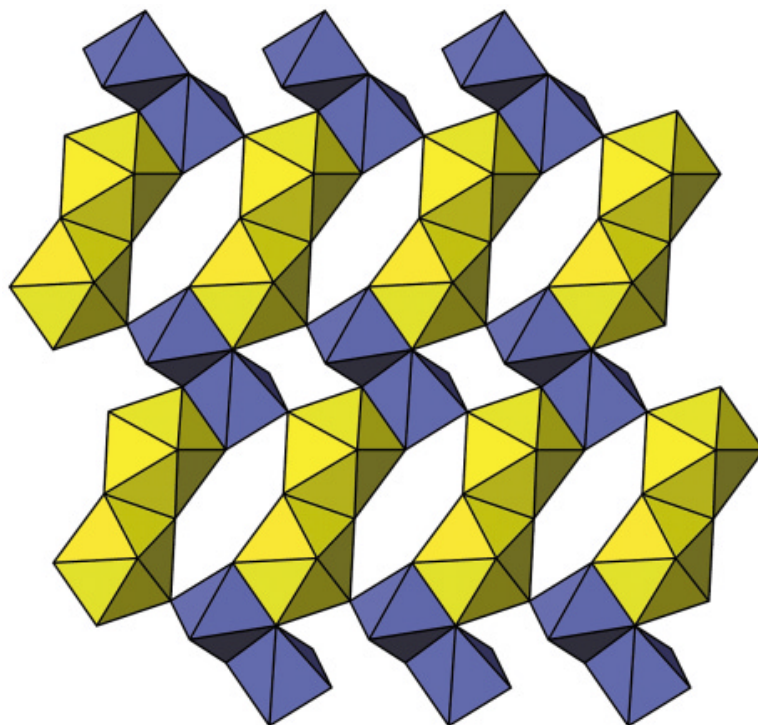

FIG. 5. Projection of the structure of vandenbrandeite along [110]. The $Ur\phi_5$ and $Cu\phi_5$ polyhedra are shown in yellow and blue, respectively.

the dimer, there are no direct linkages between the uranyl polyhedra in the vandenbrandeite sheet (Fig. 5). In the uranosphaerite sheet, in contrast, the uranyl pentagonal bipyramids of each dimer share vertices with four other uranyl pentagonal bipyramids of adjacent dimers (Fig. 2). Thus, the uranosphaerite sheet and other sheets based upon the francevillite anion-topology involve a more dense packing of anions than does the vandenbrandeite sheet.

REFERENCES

ANTHONY, J.W., BIDEAUX, R.A., BLADH, K.W. & NICHOLS, M.C. (1997): *Handbook of Mineralogy*. III. *Halides, Hydroxides, Oxides*. Mineral Data Publishing, Tucson, Arizona.

BAPTISTA, A., BAPTISTA, N.R. & DE OLIVEIRA, O.E. (1962): A contribution to the study of the mineral uranosphrite. *Anais Acad. Brasil. Cienc.* **34**, 45-49.

BERMAN, R. (1957): Studies of uranium minerals. XXIII. Torbernite, zeunerite, and uranospherite. *Am. Mineral.* **42**, 905-908.

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

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 uranyl oxide hydrate. *Can. Mineral.* **36**, 187-199.

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

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

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

_____, FINCH, R.J., HAWTHORNE, F.C., MILLER, M.L. & EWING, R.C. (1997b): The crystal structure of ianthinite, $[U^{4+}_2(UO_2)_4O_6(OH)_4(H_2O)_4](H_2O)_5$: a possible phase for Pu^{4+} incorporation during the oxidation of spent nuclear fuel. *J. Nucl. Mater.* **249**, 199-206.

_____ & 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.

_____ & 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. (1999): The structure of agrinierite: a Sr-containing uranyl oxide hydrate mineral. *Am. Mineral.* **85**, 1294-1297.

CHERVET, J. (1960): Les minéraux secondaires. *In* Les minerais uranifères français I (M. Roubault, ed.). Institut National des Sciences et Techniques Nucléaires, et Presses Universitaires de France, Paris, France.

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. *Mater. Res. Soc., Symp. Proc.* **556**, 431-438.

_____, COOPER, M.A. & HAWTHORNE, F.C. (1996): The crystal structure of schoepite, $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$. *Can. Mineral.* **34**, 1071-1088.

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

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. *Radiochimica Acta* **74**, 65-71.

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

_____, RISKA, D. & FRONDEL, J.W. (1956): X-ray powder data for uranium and thorium minerals. *U.S. Geol. Surv., Bull.* **1036**, 91-153.

GAINES, R.V., SKINNER, H.C.W., FOORD, E.E., MASON, B. & ROSENZWEIG, A. (1997): *Dana's New Mineralogy* (8th ed.). John Wiley & Sons, Inc., New York, N.Y.

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

KOLITSCH, U. (1997): Uranosphärit und weitere neue Mineralfunde von der Grube Clara im Schwarzwald. *Mineralien-Welt* **8**(3), 18-26.

_____ (1998): Röntgenographische Untersuchungen an Uranosphärit von der Grube Clara im Schwarzwald. *Aufschluss* **49**, 172-176.

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

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

MANDARINO, J.A. (1999): *Fleischer's Glossary of Mineral Species 1999*. The Mineralogical Record Inc., Tucson, Arizona.

MEREITER, K. (1979): Crystal structure of curite, $Pb_{6.56}(H_2O, OH)_4[(UO_2)_8O_8(OH)_6]_2$. *Tschermaks Mineral. Petrogr. Mitt.* **26**, 279-292.

OTWINOWSKI, Z. & MINOR, W. (1997): Processing of X-ray diffraction data collected in oscillation mode. *Methods in Enzymology* **276**, 307-326.

PAGOAGA, M.K., APPLEMAN, D.E. & STEWART, J.M. (1987): Crystal structures and crystal chemistry of the uranyl oxide hydrates becquerelite, billietite, and protasite. *Am. Mineral.* **72**, 1230-1238.

PIRET, P. (1985): Structure cristalline de la fourmariérite $Pb(UO_2)_4O_3(OH)_4 \cdot 4H_2O$. *Bull. Minéral.* **108**, 659-665.

_____, DELIENS, M., PIRET-MEUNIER, J. & GERMAIN, G. (1983): La sayrite, $Pb_2[(UO_2)_5O_6(OH)_2 \cdot 4H_2O$, nouveau minéral; propriétés et structure cristalline. *Bull. Minéral.* **106**, 299-304.

PROTAS, J. (1959): Contribution à l'étude des oxydes d'uranium hydratés. *Bull. Soc. Fr. Minéral. Cristallogr.* **82**, 239-272.

ROH, Y., LEE, S.R., CHOI, S.K., ELLES, M.P. & LEE, S.Y. (2000): Physiochemical and mineralogical characterization of uranium-contaminated soils. *Soil and Sediment Contamination* **9**, 463-486.

ROSENZWEIG, A. & RYAN, R.R. (1977): Vandenbrandeite $CuUO_2(OH)_4$. *Crystal Struct. Commun.* **6**, 53-56.

SEJKORA, J., VESELOVSKÝ, F. & ŠREIN, V. (1994): The supergene mineralization of uranium occurrence Ryzoviste near Harrachov (Krkonose Mts., Czech Republic). *Acta Musei Nationalis Pragae, Ser. B, Historia Naturalis* **50**, 55-91.

SHELDRICK, G.M. (1997a): SHELXS–97, a program for the solution of crystal structures. University of Göttingen, Göttingen, Germany.

_____ (1997b): SHELXL–97, a program for crystal structure refinement. University of Göttingen, Göttingen, Germany.

STRUNZ, H. (1982): *Mineralogische Tabellen* (8th ed.). Akad. Verlagsgesellschaft Geest & Portig K.-G., Leipzig, Germany.

_____ & NICKEL, E.H. (2001): *Strunz Mineralogical Tables*. E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, Germany.

TAYLOR, J.C., STUART, W.I. & MUMME, I.A. (1981): The crystal structure of curite. *J. Inorg. Nucl. Chem.* **43**, 2419-2423.

WEISBACH, A. (1873): Neue Uranerze von Neustädtel bei Schneeberg. *Neues Jahrb. Mineral., Geol., Palaeontol.*, 314-317.

WELLER, M.T., LIGHT, M.E. & GELBRICH, T. (2000): Structure of uranium(VI) oxide dihydrate, $UO_3 \cdot 2H_2O$; synthetic meta-schoepite $(UO_2)_4O(OH)_6 \cdot 5H_2O$. *Acta Crystallogr.* **B56**, 577-583.

WRONKIEWICZ, D.J., BATES, J.K., 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.

YAMAKAWA, I. & TRAINA, S.J. (2001): Precipitation processes of uranium in highly alkaline solutions: possible chemical reactions occurring in the Hanford vadose zone. *American Chemical Society, 222nd National Meet.* (*Chicago*), GEOC-055 (abstr.).