SYNTHESIS AND STRUCTURE OF A NEW Ca URANYL OXIDE HYDRATE, Ca[(UO₂)₄O₃(OH)₄](H₂O)₂, AND ITS RELATIONSHIP TO BECQUERELITE

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ABSTRACT

A new Ca uranyl oxide hydrate, $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$, has been synthesized by hydrothermal reaction of a solution of 0.03 M UO_3 with calcite crystals. Fifteen hydrothermal synthesis experiments at 140, 180 and 220°C, with starting solution pH in the range 2 to 6, resulted in $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$. The structure, space group $P\bar{1}$, *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)°, *V* 649.6(2) Å³, $Z = 2$, 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 3.47%, calculated using 2523 unique observed reflections ($F_o \geq 4\sigma_F$). The structure contains four symmetrically distinct U^{6+} cations, each of which is part of a nearly linear $(UO_2)^{2+}$ uranyl ion. Three of the uranyl ions are coordinated by five ligands arranged at the equatorial vertices of pentagonal bipyramids, and the other is coordinated by four ligands at the equatorial vertices of a square bipyramid. Polymerization of the uranyl polyhedra by the sharing of vertices and edges results in a novel sheet. The single unique Ca^{2+} cation is located in the interlayer, together with two H_2O groups, one of which is bonded to the Ca^{2+} cation, whereas the other is held in the structure by hydrogen bonding only. The phase $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$ contains more Ca than becquerelite, $Ca[(UO_2)_6O_4(OH)_6](H_2O)_8$, and polymerization of Ca polyhedra occurs in the interlayer, whereas in becquerelite, the Ca polyhedra do not share polyhedron elements.

Keywords: uranium crystal chemistry, calcium uranium oxide hydrate, uranyl oxide hydrate, becquerelite.

SOMMAIRE

Nous avons synthétisé un nouvel oxyde uranylé hydraté de calcium, $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$, par réaction hydrothermale d'une solution de 0.03 M UO_3 avec des cristaux de calcite. Quinze expériences de synthèse hydrothermale à 140, 180 et 220°C, ayant un pH initial de la solution dans l'intervalle de 2 à 6, ont produit le composé $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$. La structure, répondant au groupe spatial $P\bar{1}$, *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)°, *V* 649.6(2) Å³, $Z = 2$, a été résolue et affinée en utilisant les facteurs F^2 de toutes les données uniques prélevées en diffraction X, avec rayonnement monochromatique Mo$K\alpha$ et un détecteur à charges couplées, jusqu'à un facteur de concordance R1 de 3.47%, calculé avec 2523 réflexions uniques observées ($F_o \geq 4\sigma_F$). La structure contient quatre cations U^{6+} symétriquement distincts, chacun faisant partie d'un ion uranyle $(UO_2)^{2+}$ presque linéaire. Trois des ions uranyle sont rattachés à cinq ligands aux coins équatoriaux de bipyramides pentagonales, et l'autre montre une coordinence avec quatre ligands aux coins équatoriaux d'une bipyramide carrée. La polymérisation des polyèdres à uranyle, par partage des coins et des arêtes, mène à un feuillet nouveau. Le seul cation Ca^{2+} est situé dans l'interfeuillet, avec deux groupes H_2O, dont un est lié au cation Ca^{2+}, et l'autre n'est rattaché que par liaisons hydrogène. La phase $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$ contient plus de Ca que la becquerelite, $Ca[(UO_2)_6O_4(OH)_6](H_2O)_8$, et la polymérisation des polyèdres Ca se déroule dans l'interfeuillet, tandis que dans la becquerelite, les polyèdres Ca ne partagent pas les éléments des polyèdres.

(Traduit par la Rédaction)

Mots-clés: cristallochimie de l'uranium, oxyde de calcium et d'uranium hydraté, oxyde uranylé hydraté, becquerelite.

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INTRODUCTION

Uranyl oxide hydrates are significant constituents of the oxidized portions of U deposits (Frondel 1958); they impact upon release rates of U and Pb from radioactive mine and mill tailings, are common in soils contaminated by actinides (Buck *et al.* 1996), and are likely to be important in the phases of alteration of nuclear waste in a geological repository (Wronkiewicz *et al.* 1992, 1996, Finch & Ewing 1992, Pearcy *et al.* 1994, Finn *et al.* 1996, Finch *et al.* 1999). As part of our ongoing research concerning the mineralogy and crystal chemistry of uranium, we have for several years been utilizing hydrothermal techniques of synthesis to obtain crystals of a size and quality that are suitable for analysis by single-crystal X-ray diffraction. In 1998, we first noted a novel Ca uranyl oxide hydrate in some of our products of synthesis intended to produce Ca uranyl selenites, and have since found the same phase in many experiments involving the system Ca–U–O–H. Techniques have been developed that produce excellent single crystals of this phase, and the structure has been determined.

EXPERIMENTAL

Hydrothermal synthesis of $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$

The first synthesis of $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$ was achieved by combining 1 mL of 0.1 M $Ca(NO_3)_2$ •$4H_2O$ (Fisher Scientific), 2 mL of 0.09 M SeO_2 (Aldrich), and 3 mL of 0.1 M $UO_2(NO_3)_2$•$6H_2O$ (Alfa Aesar). The pH of the resulting solution was adjusted to ~5 using dilute $Ca(OH)_2$ (Fisher Scientific). The reactants were heated in a 23 mL Teflon-lined Parr bomb at 200°C for 24 h. The product contained yellow slender acicular needles up to ~100 μm in length, and a fine-grained orange matrix. Single-crystal X-ray analysis indicated that the crystals are twinned, and a satisfactory refinement of the structure could not be achieved.

High-quality crystals of $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$ were obtained by hydrothermal reaction of a solution containing UO_3 and macroscopic crystals of calcite. Hydrothermal experiments were conducted using 23 mL Teflon-lined Parr bombs. Each reaction vessel contained 4 mL of ~0.03 M UO_3 solution, as well as two or three crystals of calcite totaling ~0.25 g. The pH of the solutions was adjusted using hydrochloric acid or ammonium hydroxide. Experiments with pH values adjusted to 2, 4 and 6 were heated at each of 140, 180 and 220°C for both 3 and 7 days. Measurement of solution pH following reaction indicated that each had changed to ~5. The products were analyzed using X-ray powder and single-crystal diffraction. The relative proportions of phases were estimated on the basis of optical examination of products and peak heights in powder-diffraction patterns. Results are presented in Table 1.

Single-crystal X-ray diffraction

The crystal of $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$ selected for the structural study is from synthesis experiment 3D–220–2 (Table 1). The acicular yellow crystal shows sharp extinction between crossed polarizers and uniform optical properties. It was mounted on a Bruker PLATFORM three-circle goniometer equipped with a 1K SMART CCD (charge-coupled device) detector, with a crystal-to-detector distance of 5 cm. A sphere of data to

TABLE 1. RESULTS OF HYDROTHERMAL SYNTHESIS EXPERIMENTS

T (°C)	3 Day Experiments		
	Starting pH = 2	Starting pH = 4	Starting pH = 6
140	ID = 3D-140-2 85% becquerelite 15% *FGY*	ID = 3D-140-4 10% becquerelite 90% *FGY*	ID = 3D-140-6 10% becquerelite 90% *FGY*
180	ID = 3D-180-2 25% becquerelite 50% *FGY* 25% $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$	ID = 3D-180-4 100% $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$	ID = 3D-180-6 100% $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$
220	ID = 3D-220-2 100% $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$	ID = 3D-220-4 100% $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$	ID = 3D-220-6 100% $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$
	7 Day Experiments		
	Starting pH = 2	Starting pH = 4	Starting pH = 6
140	ID = 7D-140-2 15% becquerelite 75% *FGY* 10% $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$	ID = 7D-140-4 20% *FGY* 80% $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$	ID = 7D-140-6 50% *FGY* 50% $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$
180	ID = 7D-180-2 100% $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$	ID = 7D-180-4 100% $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$	ID = 7D-180-6 100% $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$
220	ID = 7D-220-2 100% $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$	ID = 7D-220-4 100% $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$	ID = 7D-220-6 100% $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$

$56.6°$ 2θ was collected using monochromatic $MoK\alpha$ X-radiation and frame widths of $0.3°$ in ω, with 120 s spent collecting each frame. The three-dimensional data were analyzed to locate reflections for the determination of the unit-cell dimensions (Table 2), which were refined with 3647 reflections using least-squares techniques. The data were integrated using the Bruker program SAINT, and corrected for Lorentz, polarization, and background effects. A semi-empirical absorption-correction was done using the program SADABS (G. Sheldrick, unpubl. computer program). A total of 8474 reflections was collected, of which there were 3330 unique reflections ($R_{INT} = 7.1\%$), with 2523 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 Crystallography*, 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 cations. The Ca 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 unique reflections. Refinement of all atom-position parameters, allowing for isotropic displacement of the atoms, gave an agreement index ($R1$) of 4.1%. Conversion of all atomic displacement parameters to an anisotropic form, refinement of atom-position parameters, and inclusion of a weighting scheme of the structure factors improved $R1$ to 3.47%, calculated for the 2523 unique observed reflections ($|F_o| \geq 4\sigma_F$). In the final cycle of refinement, the mean parameter shift/esd was 0.000. The final atom-coordinates and anisotropic-displacement parameters are listed in Tables 3 and 4, selected interatomic distances are in Table 5, and a bond-valence analysis is given 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.

RESULTS OF HYDROTHERMAL SYNTHESIS EXPERIMENTS

Three phases were found in the products of the hydrothermal synthesis (Table 1). In addition to becquerelite and $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$, a fine-grained yellow compound, designated *FGY*, was noted in the products of several experiments, but this phase could

TABLE 2. CRYSTALLOGRAPHIC DATA AND REFINEMENT RESULTS FOR $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$

a (Å)	8.0556(8)	Radiation	$MoK\alpha$
b (Å)	8.4212(8)	$2\theta_{max}(°)$	56.55
c (Å)	10.958(1)	Total reflections	8474
α (°)	78.878(2)	Unique reflections	3330
β (°)	87.922(2)	Data with $|F_o|>4\sigma|F_o|$	2523
γ (°)	72.277(2)	$R1$ (%)	3.47
V (Å³)	694.6(2)	$wR2$ (%)	8.37
Space group	$P\bar{1}$	S	0.97
$F(000)$	1064		
$\mu(mm^{-1})$	46.95		
D_{calc} (g/cm³)	6.083		

h, k, l ranges: $-10\rightarrow10, -11\rightarrow11, -14\rightarrow14$
Unit cell contents 2 $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$
$R1 = \Sigma(|F_o|-|F_c|)/\Sigma|F_o| \times 100$
$wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$
$w = 1/[\sigma^2(F_O^2) + (0.0401 \times P)^2], P = (max(F_O^2,0) + 2 \times F_c^2)/3$
$S = [\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, for m observations and n parameters

TABLE 3. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC-DISPLACEMENT PARAMETERS (Å²) FOR $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$

	x	y	z	$^aU(eq)$
U(1)	0.44695(6)	0.40453(5)	0.85968(4)	0.0125(1)
U(2)	0.46623(6)	-0.05465(5)	0.84821(4)	0.0118(1)
U(3)	0.16021(6)	0.30513(5)	0.57354(4)	0.0137(1)
U(4)	0.17971(6)	-0.19134(5)	0.57226(4)	0.0128(1)
Ca(1)	-0.0729(4)	0.0618(3)	0.8156(3)	0.0260(6)
O(1)	0.083(1)	0.584(1)	0.5531(8)	0.019(2)
O(2)	0.420(1)	0.157(1)	0.9551(8)	0.017(2)
O(3)	0.032(1)	0.289(1)	0.7168(8)	0.019(2)
O(4)	0.689(1)	-0.061(1)	0.8039(8)	0.018(2)
O(5)	0.078(1)	0.096(1)	0.536(1)	0.029(2)
O(6)	0.243(1)	-0.048(1)	0.8834(9)	0.021(2)
O(7)	0.292(1)	-0.197(1)	0.4251(8)	0.020(1)
O(8)	0.680(1)	0.301(1)	0.8412(8)	0.019(2)
O(9)	0.061(1)	-0.177(1)	0.7201(9)	0.023(2)
O(10)	0.222(1)	0.505(1)	0.8825(9)	0.024(2)
O(11)	0.309(1)	0.304(1)	0.4440(9)	0.026(2)
OH(1)	0.535(1)	0.6332(9)	0.9090(8)	0.014(2)
OH(2)	0.405(1)	0.2309(9)	0.7105(8)	0.014(2)
OH(3)	0.416(1)	0.5744(9)	0.6674(8)	0.018(2)
OH(4)	0.395(1)	-0.078(1)	0.6497(9)	0.025(2)
$H_2O(1)$	-0.019(1)	-0.186(1)	0.9958(9)	0.027(2)
$H_2O(2)$	0.854(1)	-0.427(1)	0.828(1)	0.031(2)

$^aU_{eq} = 1/3\Sigma U_{ij}a_i \cdot b_j \cdot a_i b_j$

TABLE 4. ANISOTROPIC-DISPLACEMENT PARAMETERS (Å²) FOR $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$

	$^aU_{11}$	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	0.0137(2)	0.0103(2)	0.0131(2)	-0.0016(2)	-0.0001(2)	-0.0034(2)
U(2)	0.0128(2)	0.0108(2)	0.0120(2)	-0.0019(2)	0.0003(2)	-0.0040(2)
U(3)	0.0141(2)	0.0145(2)	0.0130(2)	-0.0016(2)	0.0005(2)	-0.0058(2)
U(4)	0.0143(2)	0.0103(2)	0.0139(2)	-0.0024(2)	0.0005(2)	-0.0038(2)
Ca(1)	0.015(1)	0.016(1)	0.048(2)	-0.009(1)	0.004(1)	-0.005(1)
O(1)	0.030(5)	0.010(4)	0.018(5)	-0.001(3)	0.000(4)	-0.011(4)
O(2)	0.027(5)	0.011(4)	0.011(4)	-0.001(3)	-0.003(4)	-0.005(4)
O(3)	0.019(5)	0.026(4)	0.011(4)	0.001(3)	0.004(4)	-0.007(4)
O(4)	0.017(5)	0.017(4)	0.017(5)	0.000(3)	0.000(4)	-0.006(4)
O(5)	0.022(5)	0.012(4)	0.052(7)	-0.005(4)	-0.010(5)	-0.002(4)
O(6)	0.021(5)	0.013(4)	0.030(5)	-0.002(4)	-0.003(4)	-0.008(4)
O(7)	0.032(5)	0.023(4)	0.009(4)	-0.005(3)	0.006(4)	-0.013(4)
O(8)	0.017(5)	0.015(4)	0.021(5)	-0.002(3)	-0.004(4)	-0.001(4)
O(9)	0.028(5)	0.023(5)	0.022(5)	-0.009(4)	0.011(4)	-0.012(4)
O(10)	0.024(5)	0.017(4)	0.026(5)	-0.002(4)	0.003(4)	-0.001(4)
O(11)	0.009(4)	0.039(5)	0.025(5)	-0.002(4)	0.001(4)	-0.004(4)
OH(1)	0.024(5)	0.008(4)	0.010(4)	0.002(3)	0.000(3)	-0.007(3)
OH(2)	0.018(4)	0.014(4)	0.012(4)	-0.001(3)	-0.010(3)	-0.010(3)
OH(3)	0.015(4)	0.012(4)	0.018(5)	0.009(3)	0.001(4)	0.001(3)
OH(4)	0.026(5)	0.032(5)	0.020(5)	-0.010(4)	0.004(4)	-0.011(4)
$H_2O(1)$	0.025(5)	0.039(5)	0.021(5)	-0.009(4)	0.002(4)	-0.013(4)
$H_2O(2)$	0.027(6)	0.030(5)	0.036(6)	-0.009(4)	0.005(5)	-0.006(4)

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

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES(Å) FOR Ca[(UO₂)₄O₃(OH)₄](H₂O)₂

U(1)-O(10)	1.785(9)	U(2)-O(6)	1.815(9)	U(3)-O(11)	1.826(9)
U(1)-O(8)	1.833(9)	U(2)-O(4)	1.828(8)	U(3)-O(3)	1.852(8)
U(1)-O(2)	2.213(7)	U(2)-O(2)	2.250(8)	U(3)-O(5)	2.170(9)
U(1)-OH(3)	2.281(8)	U(2)-O(2)b	2.276(8)	U(3)-O(1)	2.207(8)
U(1)-OH(1)	2.402(7)	U(2)-OH(4)	2.329(8)	U(3)-O(1)d	2.285(9)
U(1)-OH(2)	2.486(8)	U(2)-OH(1)c	2.475(7)	U(3)-OH(2)	2.377(8)
U(1)-OH(1)a	2.497(8)	U(2)-OH(2)	2.497(7)	<U(3)-O$_{Ur}$>	1.839
<U(1)-O$_{Ur}$>	1.809	<U(2)-O$_{Ur}$>	1.822	O(3)-U(3)-O(11)	172.9(4)
O(8)-U(1)-O(10)	178.3(4)	O(4)-U(2)-O(6)	176.8(4)	<U(3)-ϕ_{eq}>	2.260
<U(1)-ϕ_{eq}>	2.376	<U(2)-ϕ_{eq}>	2.365		
U(4)-O(7)	1.823(8)	Ca(1)-O(3)	2.381(8)		
U(4)-O(9)	1.857(9)	Ca(1)-O(9)	2.389(9)		
U(4)-O(5)	2.265(8)	Ca(1)-O(8)f	2.419(9)	a: -x+1, -y+1,-z+2; b: -x+1,
U(4)-O(5)e	2.27(1)	Ca(1)-O(4)f	2.461(9)	-y,-z+2; c: x, y-1, z; d: -x,
U(4)-O(1)c	2.300(8)	Ca(1)-O(6)	2.512(9)	-y+1, -z+1; e: -x, -y, -z+1; f:
U(4)-OH(3)c	2.379(8)	Ca(1)-H₂O(1)	2.52(1)	x-1, y, z; g: -x, -y, -z+2; h: x,
U(4)-OH(4)	2.465(9)	Ca(1)-H₂O(1)g	2.71(1)	y+1, z; i: x+1, y, z
<U(4)-O$_{Ur}$>	1.840	Ca(1)-O(7)e	3.05(1)		
O(9)-U(4)-O(7)	177.8(4)	<Ca(1)-ϕ>	2.56		
<U(4)-ϕ_{eq}>	2.34				

TABLE 6. BOND VALENCE (vu) ANALYSIS* FOR Ca[(UO₂)₄O₃(OH)₄](H₂O)₂

	U(1)	U(2)	U(3)	U(4)	Ca(1)	H	Σ
O(1)			0.79, 0.68	0.61			2.08
O(2)	0.72	0.67, 0.64					2.02
O(3)			1.49		0.33		1.82
O(4)		1.53			0.26	0.15	1.94
O(5)			0.84	0.65, 0.64			2.13
O(6)		1.57			0.23	0.36	2.16
O(7)				1.55	0.05	0.20	1.80
O(8)	1.52				0.30		1.81
O(9)				1.45	0.32		1.77
O(10)	1.66					0.15	1.81
O(11)			1.57			0.33	1.90
OH(1)	0.50, 0.41	0.43				0.73	2.07
OH(2)	0.42	0.41	0.58			0.80	2.21
OH(3)	0.63			0.52		0.84	1.99
OH(4)		0.57		0.44		0.83	1.84
H₂O(1)					0.22, 0.14	1.63	1.99
H₂O(2)						1.97	1.97
Σ	5.86	5.82	5.95	5.85	1.84		

*bond-valence parameters for U^{6+} from Burns *et al.* (1997), for Ca^{2+} from Brese & O'Keeffe (1991), and for H bonds from Ferraris & Ivaldi (1988).

not be identified using X-ray powder diffraction. Single-crystal studies were precluded by the lack of crystals exceeding a few μm in maximum dimension. Microchemical analyses provided by Galbraith Laboratories, Inc. indicated that the phase contains 4.04% Ca, 74.35% U, 0.79% H, and no detectable C. This is consistent with the formula Ca(UO₂)₃O₄(H₂O)₄.

The hydrothermal synthesis procedure involving a solution of UO₃ and calcite crystals produces superb crystals of becquerelite and Ca[(UO₂)₄O₃(OH)₄](H₂O)₂, with crystal dimensions as large as 0.5 mm. This is in contrast to earlier approaches to synthesis, which gave crystals of becquerelite that typically do not exceed ~20 μm in maximum dimension. Growth of large crystals of Ca uranyl oxide hydrates in our experiments is presumably facilitated by the relatively slow dissolution of calcite, which promotes nucleation and growth of a small number of crystals, as compared to many hydrothermal synthesis experiments that involve bulk precipitation from saturated solutions.

Becquerelite was found to be present in the products of all three three-day runs at 140°C, as well as the experiment at 180°C that had a starting solution pH of 2. The *FGY* phase also occurs in each of the products of these runs, and it dominates the 140°C experiments with starting pH values of 4 and 6. The products of the three-day experiments at 180°C with starting solution pH values of 4 and 6, as well as all three three-day experiments at 220°C, contain only Ca[(UO₂)₄O₃(OH)₄](H₂O)₂. Of these, the largest crystals were obtained in the experiments with low starting pH of the solution.

The only seven-day experiment that produced a product with detectable becquerelite was the run held at 140°C, with a starting pH of 2. All experiments heated to 140°C for seven days produced the phase *FGY*, although less of this occurs in the products than in the corresponding three-day experiments. Notably, Ca[(UO₂)₄O₃(OH)₄](H₂O)₂ was observed in all of the seven-day experiments, and was the only detectable product from the experiments conducted at 180° and 220°C.

Taken together, the hydrothermal experiments may indicate the paragenetic sequence becquerelite → *FGY* → Ca[(UO₂)₄O₃(OH)₄](H₂O)₂. The formation of Ca[(UO₂)₄O₃(OH)₄](H₂O)₂ is favored by increasing time and temperature, and the formation of large crystals is favored by a starting solution pH of ~2, although the phase also forms in solutions with starting pH values of 4 and 6.

Description of the Structure
of $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$

Almost all uranyl oxide hydrates involve sheets of uranyl polyhedra, with low-valence cations and H_2O groups located in interlayer sites (Burns *et al.* 1996, Burns 1999). The structure of $Ca[(UO_2)_4O_3(OH)_4]$ $(H_2O)_2$ is no exception; it involves sheets of uranyl polyhedra that are parallel to $(\bar{1}01)$, and Ca cations and H_2O groups are located in sites between the sheets (Fig. 1).

Cation polyhedra

The structure of $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$ contains four symmetrically distinct U sites, and the coordination polyhedra (Table 5) and bond-valence sums (Table 6) are consistent with these sites being occupied by U^{6+}. In each case, the U^{6+} cation is part of an approximately linear $(UO_2)^{2+}$ uranyl ion (designated *Ur*). The U(1), U(2) and U(4) uranyl ions are coordinated by five anions arranged at the equatorial vertices of pentagonal bipyramids capped by the O_{Ur} atoms. The equatorial ligands of these polyhedra correspond to one atom of O and four $(OH)^-$ groups, two atoms of O and three $(OH)^-$ groups, and three atoms of O and two $(OH)^-$ groups, in the U(1), U(2) and U(4) polyhedra, respectively. The $<U–\phi_{eq}>$ bond lengths [ϕ: O, $(OH)^-$, eq: equatorial ϕ] range from 2.34 to 2.38 Å for these polyhedra, which is consistent with the average of 2.37(9) Å calculated for uranyl pentagonal bipyramids in numerous well-refined structures (Burns *et al.* 1997).

The U(3) uranyl ion is coordinated by three atoms of O and one $(OH)^-$ group that are arranged at the equatorial vertices of a highly distorted square bipyramid capped by the O_{Ur} atoms. The $<U(3)–\phi_{eq}>$ bond length is 2.26 Å, which is in accord with the average value of 2.28(5) Å for uranyl square bipyramids in well-refined structures (Burns *et al.* 1997). Similarly distorted uranyl square bipyramids occur in the structures of curite (Mereiter 1979, Li & Burns 2000a), the synthetic Sr analogue of curite (Burns & Hill 2000a), $K_5[(UO_2)_{10}O_8$ $(OH)_9](H_2O)$ (Burns & Hill 2000b), and $Pb_2(H_2O)$ $[(UO_2)_{10}UO_{12}(OH)_6(H_2O)_2]$ (Li & Burns 2000b).

The structure contains a single symmetrically distinct Ca^{2+} cation. It is bonded to five O_{Ur} atoms, with bond lengths in the range 2.38 to 2.51 Å, and two H_2O groups, with bond lengths of 2.52 and 2.71 Å. An additional O_{Ur} atom [O(7)] is located 3.05(1) Å from the Ca^{2+} cation; assuming that this is a bond, O(7) contributes 0.05 *vu* (valence units) toward the bond-valence requirements of the Ca^{2+} cation, which total 1.84 *vu* (Table 6).

Sheets of uranyl polyhedra

The uranyl polyhedra in the structure of $Ca[(UO_2)_4O_3$ $(OH)_4](H_2O)_2$ share equatorial vertices and edges, resulting in novel sheets of polyhedra that are parallel to

$(\bar{1}01)$ (Fig. 2). The sheet contains two distinct chains of uranyl polyhedra that share edges that extend along [010]. Both chains are two polyhedra wide, and adjacent chains of polyhedra are linked only by the sharing of equatorial vertices. One chain contains the U(1) and U(2) pentagonal bipyramids, whereas the other contains the U(4) pentagonal bipyramid and the distorted U(3) square bipyramid.

The $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$ sheet anion-topology, obtained using the method proposed by Burns *et al.* (1996), is shown in Figure 3a. The anion topology contains pentagons, squares and triangles, and is unique amongst uranyl minerals and compounds. Miller *et al.* (1996), Burns (1999), and Burns & Hill (2000b) developed the description of sheet anion-topologies as chain-stacking sequences. The only chain required to generate the $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$ anion-topology is shown in Figure 3b. This is a new type of chain, although it is similar to the chain designated U^m that is required to produce the curite anion-topology (Burns 1999), which is obtained from the **U** chain by replacing every second pentagon and triangle with a square. In the case of the $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$ anion-topology, the chain required is obtained from the U chain by replacing every fourth pentagon and triangle with a square (Fig. 3b). These chains are stacked pointing in alternating directions to produce the anion topology.

Interlayer constituents

The structure contains a single symmetrically distinct $Ca\phi_8$ polyhedron in the interlayer, which contains six O_{Ur} atoms and two H_2O groups. The $Ca\phi_8$ polyhedra share the $H_2O(1)–H_2O(1)$ edge, resulting in a dimer. The interlayer also contains one symmetrically distinct H_2O group that is held in the structure by hydrogen bonding only.

Hydrogen bonding

As is typical in the case of uranyl compounds, the X-ray-diffraction data did not provide sufficient resolution for the determination of the positions of hydrogen atoms. However, most aspects of the hydrogen bonding can be established on the basis of crystal-chemical arguments. Proposed hydrogen bonds are listed in Table 7. Contributions to the bond-valence sums arising from H atoms (Ferraris & Ivaldi 1988) are given in Table 6. The OH(1) through OH(4) hydroxyl groups are each located at equatorial vertices of uranyl polyhedra. The OH(1) oxygen atom donates a bond that is accepted by the oxygen atom of the $H_2O(2)$ group, which is located in the interlayer, where it is held in the structure by hydrogen bonding only. Each of the OH(2), OH(3) and OH(4) oxygen atoms donate hydrogen bonds that are accepted by O_{Ur} atoms of adjacent sheets (Table 7), thus they provide direct linkages between sheets. The $H_2O(1)$ oxygen atom is located in the interlayer, where it is
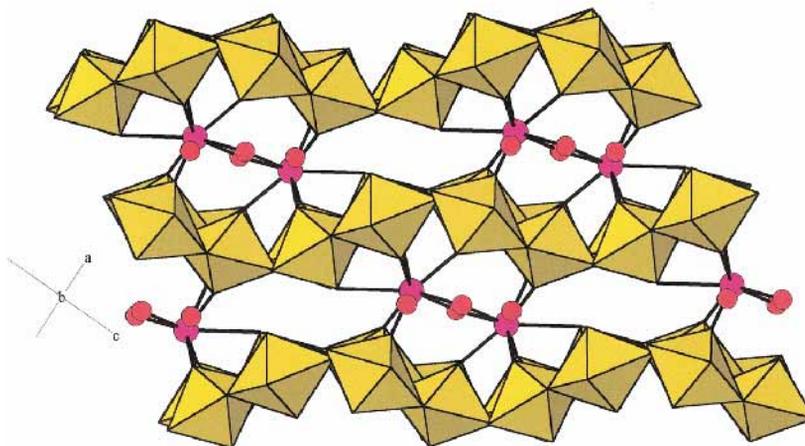
FIG. 1.   The structure of $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$ projected along [010]. Uranyl
          polyhedra are shown in yellow, Ca cations are shown as blue circles, and oxygen atoms
   are illustrated as red circles.
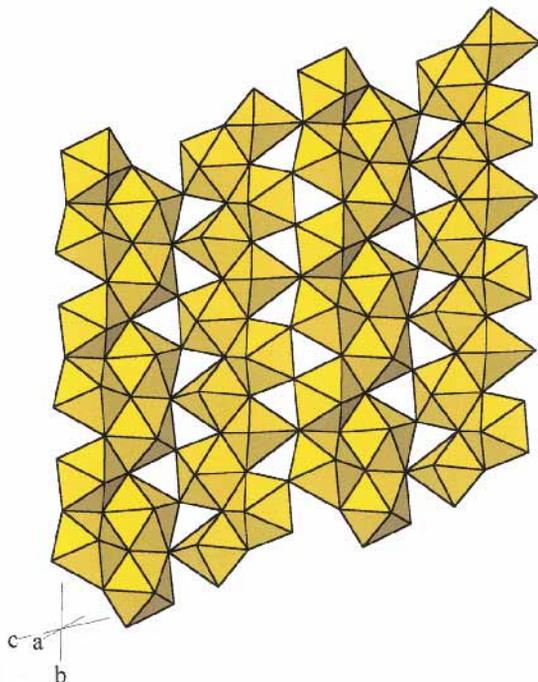
FIG. 2.   The sheet of uranyl polyhedra in the structure of
$Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$ projected along [$\bar{1}$01].

bonded to the Ca cation. It donates two hydrogen bonds
that are accepted by symmetrically equivalent O_{Ur}
[O(6)] atoms located in adjacent sheets on either side.
The oxygen atom of the $H_2O(2)$ group, in addition to
accepting a hydrogen bond donated by the OH(1) group,
donates two hydrogen bonds that are accepted by the
O(4) and O(10) atoms, which are O_{Ur} atoms of the adja-
cent sheets on either side.

Structural formula

The structural formula is $Ca[(UO_2)_4O_3(OH)_4]$
$(H_2O)_2$, Z = 2. Constituents comprising the sheets of
uranyl polyhedra are enclosed in square braces in the
formula. Delineation of $(OH)^-$ and H_2O groups was ac-
complished through analysis of the bond valences inci-
dent upon each O atom (Table 6). The calculated density
is 6.083 g/cm^3.

DISCUSSION

Five Ca uranyl oxide hydrate minerals are known:
becquerelite, $Ca[(UO_2)_6O_4(OH)_6](H_2O)_8$ (Pagoaga *et al.*
1987), agrinierite, $K_2(Ca_{0.65}Sr_{0.35})[(UO_2)_3O_3(OH)_2]_2$
$(H_2O)_5$ (Cahill & Burns 2000), rameauite, $K_2CaU_6O_{20}$
•$9H_2O$ (Cesbron *et al.* 1972), calciouranoite, (Ca,Ba,Pb)
U_2O_7•$5H_2O$ (Rogova *et al.* 1974a), and metacalcio-
uranoite, (Ca,Na,Pb)U_2O_7•$2H_2O$ (Rogova *et al.* 1974b).
Of these, only the structures of becquerelite and
agrinierite are known, and both are based upon α–U_3O_8-
type sheets of uranyl pentagonal bipyramids, with low-
valence cations and H_2O groups in the interlayers. The
new compound $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$ is chemi-
cally most closely related to becquerelite, although it

(a)   (b)
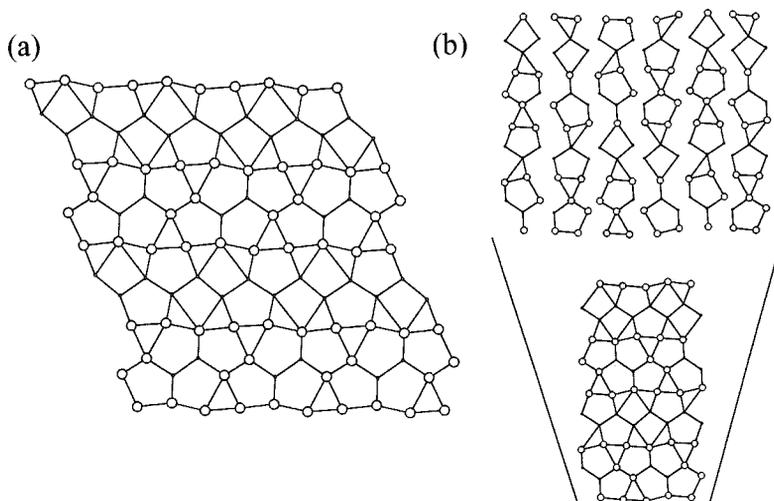
FIG. 3.   The $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$ sheet anion-topology developed using the proce-
dure of Burns *et al.* (1996). (a) The anion topology corresponding to the sheet shown in
Figure 2. (b) Development of the anion topology as a chain-stacking sequence.

contains a Ca:U ratio of 1:4, as compared to 1:6 in
becquerelite. Note that calciouranoite, which is reported
to be amorphous (Rogova *et al.* 1974a), and metacal-
ciouranoite have Ca:U ratios of 1:2; thus $Ca[(UO_2)_4O_3$
$(OH)_4](H_2O)_2$ is compositionally intermediate between
these minerals and becquerelite. As such, it seems pos-
sible that $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$ may occur in na-
ture, and possibly also as a result of the alteration of
nuclear waste in a geological repository.

The interlayer of $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$ con-
tains more Ca than that of becquerelite, and in
$Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$ polymerization of the $Ca\phi_8$
polyhedra occurs to form dimers, whereas in becquere-
lite the $Ca\phi_7$ polyhedra do not share polyhedron ele-
ments with each other. There is also significantly more
H_2O hydrogen bonded into the interlayer in becque-
relite.

The structures of nineteen uranyl oxide hydrates are
now known. With the exception of $Pb_2(H_2O)[(UO_2)_{10}$
$UO_{12}(OH)_6(H_2O)_2]$, which possesses a framework of
polyhedra of higher bond-valence (Li & Burns 2000b),
each of these structures involves a sheet formed by the
sharing of equatorial vertices and edges of uranyl poly-
hedra, with H_2O or low-valence cations (or both) located
in the interlayer. The α–U_3O_8-type sheet is the most
common, and occurs in nine phases, seven of which are
minerals. Four different distributions of $(OH)^-$ groups
have been found in this sheet; the chemical flexibility
of this topology may account for its dominance by pro-
viding compatibility with a broader range of interlayer
constituents and distributions. The remaining seven
types of sheet have so far only been found in one or two
structures each, perhaps indicating that their topologies
are compatible with fewer configurations of the
interlayer and a more restricted range of cation sizes.

TABLE 7. PROPOSED HYDROGEN BONDS
IN THE STRUCTURE OF
$Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$

		A–D–A(°)
OH(1)→H₂O(2)a	2.62(1)	
OH(2)→O(7)b	2.77(1)	
OH(3)→O(11)c	2.86(1)	
OH(4)→O(11)a	2.85(1)	
H₂O(1)→O(6)	2.84(1)	
H₂O(1)→O(6)d	2.75(1)	108.7(4)
H₂O(2)→O(4)	2.92(1)	
H₂O(2)→O(10)e	2.90(1)	107.5(4)

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

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