

THE STRUCTURE OF A SYNTHETIC Cs URANYL OXIDE HYDRATE AND ITS RELATIONSHIP TO COMPREIGNACITE

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ABSTRACT

Cesium uranyl oxide hydrate (designated CsUOH), $\text{Cs}_3[(\text{UO}_2)_{12}\text{O}_7(\text{OH})_{13}](\text{H}_2\text{O})_3$, $Z = 3$, is a new phase. Its structure is rhombohedral, space group $R\bar{3}$, a 14.1241(6), c 22.4073(14) Å, V 3871.16(8) Å³; it refined to an agreement factor (R) of 5.1% for 3883 unique observed reflections ($|F_o| \geq 4\sigma_F$). It is related to the structure of compreignacite, $\text{K}_2[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2(\text{H}_2\text{O})_7$, but the phases are not isostructural. The structure of CsUOH contains sheets of pentagonal bipyramidal uranyl polyhedra that share equatorial edges and corners to form sheets that are parallel to (100). Cesium occurs in the interlayer at the center of an eight-coordinated distorted polyhedron. H_2O groups are also contained in the interlayer.

Keywords: uranyl, uranium, structure determination, compreignacite.

SOMMAIRE

Un oxyde à uranyle hydraté de césium (designé CsUOH), $\text{Cs}_3[(\text{UO}_2)_{12}\text{O}_7(\text{OH})_{13}](\text{H}_2\text{O})_3$, $Z = 3$, est une nouvelle phase. Sa structure est rhomboédrique, groupe spatial $R\bar{3}$, a 14.1241(6), c 22.4073(14) Å, V 3871.16(8) Å³; elle a été affinée jusqu'à un résidu R de 5.1% en utilisant 3883 réflexions uniques observées ($|F_o| \geq 4\sigma_F$). La structure montre certains points communs avec celle de la compreignacite, $\text{K}_2[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2(\text{H}_2\text{O})_7$, mais elles ne sont pas identiques. La structure de CsUOH contient des feuillets de polyèdres pentagonaux bipyramidaux d'uranyle qui partagent des arêtes équatoriales et des coins pour donner des couches parallèles à (100). Le césium se trouve dans la position inter-feuillet au centre d'un polyèdre difforme à coordinance huit. Des groupes H_2O sont aussi présents entre les feuillets.

(Traduit par la Rédaction)

Mots-clés: uranyle, uranium, détermination de la structure, compreignacite.

INTRODUCTION

Cesium is an electropositive, heavy alkali metal that occurs as twelve distinct isotopes, ranging from the stable form, ¹³³Cs, to the short-lived ¹²⁶Cs with a half-life of 1.6 minutes, to the long-lived ¹³⁵Cs with a half-life of 2.3×10^6 years. Owing to its potential mobility in geological fluids and to the existence of long-lived ¹³⁵Cs, the presence of Cs in spent nuclear fuel is cause for concern in the design of nuclear waste repositories, such as the proposed repository at Yucca Mountain, Nevada. Laboratory simulations indicate that spent nuclear fuel is unstable in water under oxidizing conditions, and elements such as Cs occur in the leachate collected during tests (Finn *et al.* 1996). In corrosion studies in the laboratory, yellowish white products of alteration began to form on the surface of the spent

nuclear fuel within two years, but the Cs contained in the leachate began to decrease over this same time period, indicating that Cs may be incorporated into the products of alteration, which are mainly uranyl phases (Finn *et al.* 1996).

Most products of alteration of spent fuel and UO_2 in laboratory simulations at 90°C are hydrated (Finn *et al.* 1996, Wronkiewicz *et al.* 1996). There are ~20 known phases that contain both Cs and U, but most are anhydrous and are thus unlikely to have formed in the studies of Finn *et al.* (1996). Compreignacite, $\text{K}_2[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2(\text{H}_2\text{O})_7$, possesses the structural and chemical attributes that could serve as a starting model for the incorporation of Cs into a uranyl oxide hydrate phase (Burns 1998a). The structure of compreignacite (Burns 1998a) contains sheets of uranyl polyhedra, linked by the sharing of equatorial edges and corners, that are

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topologically identical to those found in the minerals becquerelite, $\text{Ca}[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2(\text{H}_2\text{O})_8$ (Pagoaga *et al.* 1987), billietite, $\text{Ba}[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2(\text{H}_2\text{O})_4$ (Pagoaga *et al.* 1987), protasite, $\text{Ba}[(\text{UO}_2)_3\text{O}_3(\text{OH})_2](\text{H}_2\text{O})_3$ (Pagoaga *et al.* 1987), richetite, $\text{M}_x\text{Pb}_{8.57}[(\text{UO}_2)\text{O}_{18}(\text{OH})_{12}]_2(\text{H}_2\text{O})_{41}$ (Burns 1998b) and the inorganic phase $\alpha\text{-U}_3\text{O}_8$ (Loopstra 1977). Potassium occurs solely as an interlayer constituent in the structure of compreignacite, as in other uranyl phases that contain low-valence cations only in the interlayer. We have obtained a synthetic Cs uranyl oxide hydrate phase that is structurally related to compreignacite, and which may be involved in the retention of Cs during the alteration of nuclear waste.

EXPERIMENTAL

Synthesis of crystals

Crystals of the Cs uranyl oxide hydrate (hereafter designated CsUOH) were synthesized from an aqueous solution of 0.1 M uranyl acetate hydrate (Alfa Aesar) and 50 mM CsOH (Aldrich 50 wt. %). The reactants were dissolved in ultrapure water and placed in a Teflon-lined Parr bomb that was heated to 185°C for 24 hours. The resulting product was washed and filtered, yielding orange-yellow hexagonal plates up to 0.12 mm in diameter and 0.01 mm in thickness. Optical examination showed that nearly all of the crystals are twinned.

X-ray diffraction

A crystal was selected and 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. Burns (1998c) discussed the application of CCD detectors to the analysis of crystal structures.

The data were collected using monochromatic $\text{MoK}\alpha$ X-radiation and frame widths of 0.3° in ω , with 20 s used to acquire each frame. More than a hemisphere of three-dimensional data was collected, and the data were analyzed to locate peaks for the determination of the unit-cell dimensions (Table 1), which were refined with 5185 reflections using least-squares techniques. Data were collected for $3^\circ \leq 2\theta \leq 56.6^\circ$ in ~ 9 hours; comparison of the intensities of equivalent reflections

TABLE 1. MISCELLANEOUS INFORMATION FOR CsUOH

a (Å)	14.1241(6)	Crystal size (mm)	0.05 x 0.05 x 0.1
c (Å)	22.4073(14)	Total ref.	7964
V (Å ³)	3871.16 (8)	Unique ref.	3883
Space group	$R\bar{3}$	R_{int}	5.1
$F(000)$	4213.0	Unique $ F_o \geq 4\sigma_F$	3733
μ (mm ⁻¹)	34.70	Final R	4.1
D_{calc} (g/cm ³)	3.454	S	1.04
Unit cell contents: $\text{Cs}_9[(\text{UO}_2)_{12}\text{O}_7(\text{OH})_{13}]_3(\text{H}_2\text{O})_9$			
$R = \Sigma(F_o - F_c)/\Sigma F_o $			
$S = [\Sigma w(F_o - F_c)^2/(m-n)]^{1/2}$, for m observations and n parameters			

collected at different times during the data collection showed no decay. The three-dimensional data were reduced and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. An empirical absorption-correction was done by modeling the crystal as a {001} plate, and reduced R_{INT} of 2273 intense reflections from 14.9 to 4.4%. Reflections with a plate-glancing angle less than 0.5° were discarded. A total of 7964 reflections was collected, of which there were 3883 unique reflections ($R_{INT} = 5.1\%$) with 3733 classed as observed ($|F_o| \geq 4\sigma_F$).

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from *International Tables for X-Ray Crystallography, Vol. IV* (Ibers & Hamilton 1974). The Bruker SHELXTL Version 5 system of programs was used for the refinement of the crystal structure.

Systematic absences of reflections were found to be consistent with space groups $R\bar{3}$ and $R\bar{3}$, and assigning phases to a set of normalized structure-factors gave a mean value $|E^2 - 1|$ of 0.745, consistent with space group $R\bar{3}$. The initial structure-model was derived from a direct-methods solution, and included the positional parameters and isotropic-displacement parameters of the U and Cs atoms. This model refined to an agreement index (R) of 17.6%. Difference-Fourier maps calculated at this stage failed to reveal any additional atoms. Inspection of the calculated and observed structure-factors revealed that many F_{obs} are much greater than F_{calc} , as is commonly the case if a crystal is twinned. A model providing for the twin operation $[010, 100, 00\bar{1}]$ was incorporated using the method of Jameson (1982)

TABLE 2. FINAL ATOMIC PARAMETERS FOR CsUOH

	x	y	z	$*U_{eq}$
U(1)	0.47576(8)	0.33444(8)	-0.02919(5)	122(2)
U(2)	0.35595(9)	0.0247(1)	-0.00859(5)	133(2)
U(3)	0.35652(9)	0.52352(8)	0.00675(4)	123(2)
U(4)	0.17139(9)	0.15090(8)	0.01209(4)	112(2)
Cs	0.5303(2)	0.4590(2)	0.16350(9)	342(6)
O(1)	0.361(2)	0.493(2)	0.0822(9)	238(41)
O(2)	0.348(2)	0.547(2)	-0.0692(9)	219(41)
O(3)	0.220(2)	0.188(2)	0.086(1)	271(44)
O(4)	0.119(2)	0.118(2)	-0.0600(9)	232(39)
O(5)	0.455(2)	0.339(2)	0.8915(9)	236(40)
O(6)	0.311(2)	-0.020(1)	-0.0844(8)	208(38)
O(7)	1/3	2/3	0.030(1)	154(66)
O(8)	0.395(1)	0.068(1)	0.0670(9)	167(37)
O(9)	0.498(2)	0.504(2)	-0.018(1)	270(50)
O(10)	0.507(2)	0.331(2)	0.046(1)	395(62)
O(11)	0.324(1)	0.159(1)	-0.0213(8)	144(38)
OH(12)	0	0	0.046(1)	43(51)
OH(13)	0.164(1)	0.460(1)	0.0242(7)	91(34)
OH(14)	0.032(1)	0.206(1)	0.0270(8)	116(36)
OH(15)	0.527(1)	0.198(1)	-0.0523(9)	144(35)
OH(16)	0.287(2)	0.331(2)	-0.0219(9)	216(43)
H ₂ O(17)	0.346(2)	0.221(2)	0.1918(9)	281(46)

$$*U_{eq} = U_{eq} \lambda^2 \times 10^4$$

and Herbst-Irmer & Sheldrick (1998), and resulted in a substantial improvement of the refinement, with an R of 8.2%. Difference-Fourier maps calculated at this stage revealed the positions of 17 anions, and refinement of a model that permitted isotropic displacement of all atoms resulted in an R of 6.0%. Refinement after conversion of the displacement parameters of the cations to an anisotropic form gave an R of 4.1% for the 3733 observed unique reflections ($|F_o| \geq 4\sigma_F$) and a goodness-of-fit (S) of 1.04. A model that included anisotropic-displacement parameters for the anions was tried, but resulted in non-positive-definite parameters for several anions. In the final cycle of refinement, the mean parameter shift/esd was 0.000, and the maximum peaks in the final difference-Fourier maps were 2.68 and $-2.94 e/\text{\AA}^3$. The final model was checked for a missed element of symmetry using the computer program MISSYM (Le Page 1987), but none was found. The final atomic-positional parameters are in Table 2, anisotropic-displacement parameters are in Table 3, selected interatomic distances and angles are in Table 4, and a bond-valence analysis is provided in Table 5. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

RESULTS

The structure determination has demonstrated that the crystals are not isostructural with any known uranyl oxide hydrate. The structure is shown projected along [100] in Figure 1a. As is the case for other uranyl oxide hydrates, the structure contains sheets of uranyl polyhedra, with low-valence cations and H_2O groups in the interlayer.

The structural formula for CsUOH is $\text{Cs}_3[(\text{UO}_2)_{12}\text{O}_7(\text{OH})_{13}](\text{H}_2\text{O})_3$, with $Z = 3$. Constituents comprising the sheets of uranyl polyhedra are enclosed in square braces in the formula. Delineation of $(\text{OH})^-$ and H_2O groups was accomplished through bond-valence analysis (Table 5). The calculated density for CsUOH is 3.454 g/cm^3 .

Sheets of uranyl polyhedra

The structure contains four symmetrically unique U cations, each of which is part of an approximately lin-

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR CsUOH

U(1)-O(10)	1.75(3)	U(4)-O(4)	1.74(2)
U(1)-O(5)a	1.81(2)	U(4)-O(3)	1.77(2)
U(1)-O(9)	2.27(2)	U(4)-O(11)	2.23(2)
U(1)-O(11)	2.33(2)	U(4)-OH(16)	2.36(2)
U(1)-OH(15)	2.43(2)	U(4)-OH(12)	2.415(9)
U(1)-OH(15)b	2.51(2)	U(4)-OH(14)	2.48(2)
U(1)-OH(16)	2.65(2)	U(4)-OH(14)d	2.63(2)
<U(1)-O ₁₀ >	1.78	<U(4)-O ₁₁ >	1.75
O(10)-U(1)-O(5)a	175(1)	O(4)-U(4)-O(3)	176.6(9)
<U(1)-φ _{eq} >	2.44	<U(4)-φ _{eq} >	2.42
U(2)-O(8)	1.79(2)	Cs-O(8)b	2.98(2)
U(2)-O(6)	1.81(2)	Cs-O(4)f	3.11(2)
U(2)-O(11)	2.18(2)	Cs-O(10)	3.11(3)
U(2)-O(9)c	2.24(2)	Cs-H ₂ O(17)	3.12(2)
U(2)-OH(14)d	2.41(2)	Cs-O(5)g	3.12(2)
U(2)-OH(13)d	2.48(2)	Cs-O(1)	3.23(2)
U(2)-OH(15)	2.62(2)	Cs-O(6)f	3.25(2)
<U(2)-O ₁₁ >	1.80	Cs-O(11)f	3.42(2)
O(8)-U(2)-O(6)	177.5(9)	<Cs-φ>	3.17
<U(2)-φ _{eq} >	2.39		
U(3)-O(2)	1.75(2)		
U(3)-O(1)	1.75(2)	a = x, y, z-1; b = y-x+1, 1-x, z; c = 1-y, x-y, z; d = y-x, -x, z; e = 1-y, x-y+1, z; f = 2/3-y, x-y+1/3, z+1/3; g = 2/3, y, x-y+1/3, z-2/3.	
U(3)-O(9)	2.22(2)		
U(3)-O(7)	2.267(8)		
U(3)-OH(13)	2.43(2)		
U(3)-OH(16)	2.47(2)		
U(3)-OH(13)e	2.60(2)		
<U(3)-O ₁₁ >	1.75		
O(2)-U(2)-O(1)	177.0(8)		
<U(3)-φ _{eq} >	2.40		

ear $(\text{UO}_2)^{2+}$ uranyl ion (designated U_r), with $\text{U}^{6+}-\text{O}_{U_r}$ bond-lengths of $\sim 1.8 \text{ \AA}$, as is typically observed (Burns *et al.* 1997). The presence of uranyl ions and the bond-valence sums at the U sites (Table 5) demonstrate that all U in the structure is U^{6+} .

TABLE 5. BOND-VALENCE* ANALYSIS (ν_u) FOR CsUOH

	U(1)	U(2)	U(3)	U(4)	Cs(1)	Σ
O(1)			1.77		0.11	1.88
O(2)			1.79			1.79
O(3)				1.71		1.71
O(4)				1.82	0.15	1.97
O(5)	1.59				0.15	1.74
O(6)		1.57			0.11	1.68
O(7)			0.65 ^{x3→}			1.95
O(8)		1.64			0.22	1.86
O(9)	0.65	0.69	0.71			2.05
O(10)	1.78				0.15	1.93
O(11)	0.57	0.77		0.69	0.07	2.10
OH(12)				0.48 ^{x3→}		1.44
OH(13)		0.43	0.47, 0.34			1.24
OH(14)		0.49		0.43, 0.32		1.24
OH(15)	0.51, 0.47	0.32				1.30
OH(16)	0.30		0.43	0.54		1.27
H ₂ O(17)					0.15	0.15
	5.76	5.91	6.16	6.00	1.12	

*Bond-valence parameters for U^{6+} from Burns *et al.* (1997) and for Cs from Bressé & O'Keeffe (1991)

TABLE 3. ANISOTROPIC-DISPLACEMENT PARAMETERS FOR CsUOH

	*U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
U(1)	102(5)	68(4)	188(4)	36(3)	13(4)	-13(4)
U(2)	85(5)	97(5)	231(4)	57(5)	-24(5)	-12(5)
U(3)	82(5)	95(4)	199(5)	48(3)	3(5)	5(4)
U(4)	76(4)	85(5)	164(5)	33(4)	-2(4)	-2(4)
Cs	430(12)	350(10)	214(9)	171(9)	65(9)	41(8)

*U_{ij} = U_{ij} Å² × 10⁴

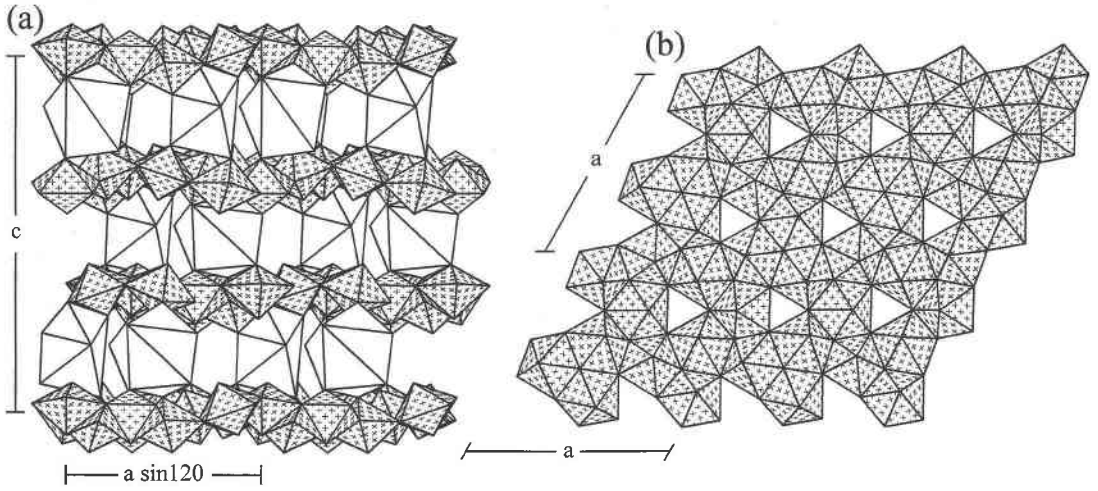


FIG. 1. Polyhedral representation of the structure of CsUOH. (a) The structure projected along [100]; (b) the sheet of uranyl polyhedra projected along [001]. The uranyl polyhedra are shown shaded with crosses, and the Cs polyhedra are unshaded.

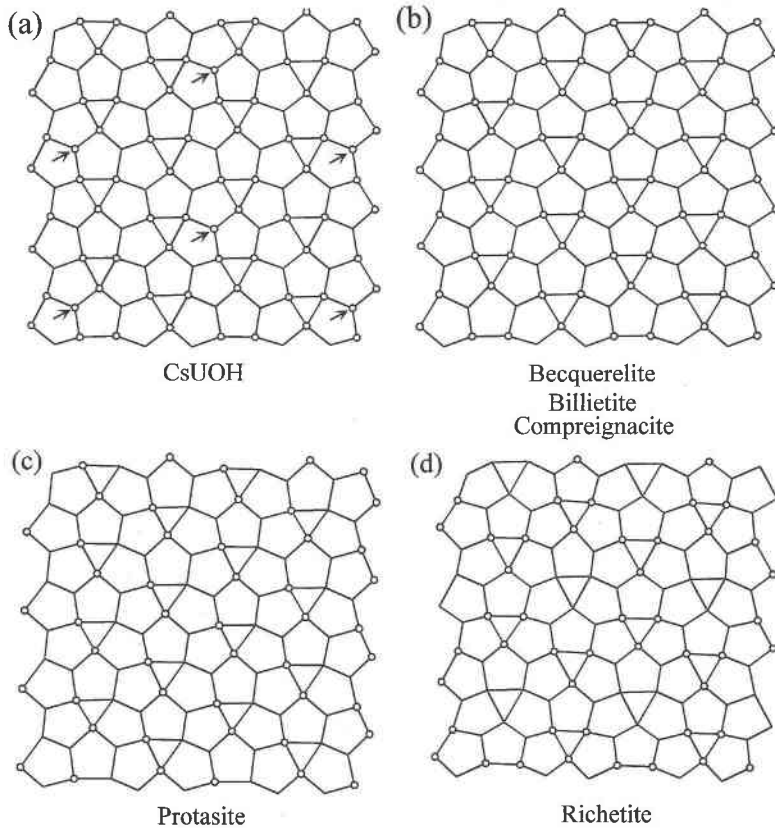


FIG. 2. Sheet anion-topologies of α - U_3O_8 -type sheets found in various phases, derived using the method of Burns *et al.* (1996). The position of the $(OH)^-$ groups are shown by circles. The arrows are explained in the text.

All the uranyl ions are coordinated by five additional anions arranged at the equatorial positions of pentagonal bipyramids, with the O_{Ur} atoms at the apices of the bipyramids. The equatorial anions of the U(1), U(2) and U(3) polyhedra consist of two O atoms and three $(OH)^-$ groups, with $\langle U^{6+}-\phi_{eq} \rangle$ (ϕ : unspecified anion; ϕ_{eq} : equatorial ϕ) bond-lengths of 2.44, 2.39, and 2.40 Å, respectively. The equatorial anions of the U(4) polyhedron consist of one O atom and four $(OH)^-$ groups, with a $\langle U^{6+}-\phi_{eq} \rangle$ bond-length of 2.42 Å. These polyhedron geometries are consistent with those found in well-refined structures, for which the overall mean $\langle U^{6+}-\phi_{eq} \rangle$ bond-length for pentagonal bipyramids is 2.37(9) Å (Burns *et al.* 1997).

The $Ur\phi_5$ pentagonal bipyramids link by sharing equatorial edges and corners to form sheets that are parallel to (001) (Fig. 1), with the uranyl ions extending roughly perpendicular to the sheets. This sheet is well-known from uranyl minerals, and is often referred to as the α - U_3O_8 -type or protasite-type sheet (Burns *et al.* 1996). The sheet anion-topology of the CsUOH sheet, derived using the method of Burns *et al.* (1996), is shown in Figure 2a.

Interlayer constituents

The interlayer of CsUOH contains Cs and H_2O groups. There is one symmetrically distinct Cs site, and the refined site-occupancy (1.00) and bond-valence sum (1.11 *vu*) are consistent with the presence of Cs only. The Cs cation is coordinated by eight anions that form a distorted polyhedron. This polyhedron occupies nearly three times the volume of the uranyl polyhedra that comprise the uranyl sheets; it contains seven O atoms and one H_2O group. The Cs- ϕ bonds range from 2.98 to 3.42 Å, with a $\langle Cs-\phi \rangle$ of 3.17 Å.

DISCUSSION

Although the sheets of uranyl polyhedra contained in the structure of CsUOH and compreignacite are topologically identical, there are several differences in the structures. In compreignacite, the X:U (X: monovalent cation) ratio is 1:3, whereas in CsUOH it is 1:4. Neither structure contains charged species in the interlayer other than the monovalent cation, thus the X:U ratio is related to the valence of the sheet of uranyl polyhedra.

The sheets in CsUOH contain more $(OH)^-$ groups than those in compreignacite, as is apparent by inspection of the sheet anion-topologies provided in Figure 2, in which the locations of the $(OH)^-$ groups are shown by circles. The anion topologies are identical except in the positions of the $(OH)^-$ groups; each contains only triangles and pentagons. Consider first the anion topology that corresponds to the compreignacite sheet (Fig. 2b). All corners of each triangle correspond to $(OH)^-$ groups, and there are no other $(OH)^-$ groups in

the topology. In contrast, the CsUOH topology (Fig. 2a) has $(OH)^-$ groups at the corners of each triangle, as well as an additional $(OH)^-$ group that is indicated in Figure 2a by arrows.

Several structures contain α - U_3O_8 -type sheets, but the distribution of $(OH)^-$ groups in the anion topology of CsUOH is distinct (Fig. 2). With the discovery of the structure of CsUOH, four unique distributions of $(OH)^-$ within otherwise identical sheet anion-topologies are now known, providing the basis for six structures. The compliant nature of the α - U_3O_8 -type sheet that permits the different distributions of anions is structurally significant because it permits the sheet to be compatible with various configurations of the interlayer.

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