

## THE STRUCTURE OF COMPREIGNACITE, $K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$

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### ABSTRACT

The structure of compreignacite,  $K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$ ,  $Z = 2$ , orthorhombic,  $a$  14.8591(7),  $b$  7.1747(3),  $c$  12.1871(5) Å,  $V$  1299.3(2) Å<sup>3</sup>, space group  $Pnmm$ , has been solved by direct methods and refined by full-matrix least-squares techniques to an agreement factor ( $R$ ) of 3.2% and a goodness-of-fit ( $S$ ) of 1.05 using 1497 unique observed reflections ( $|F_o| \geq 4\sigma_F$ ) collected with MoK $\alpha$  X-radiation and a CCD (charge-coupled device) area detector. The structure contains two symmetrically distinct  $U^{6+}$  cations that are part of  $(UO_2)^{2+}$  uranyl ions ( $Ur$ ), both of which are in turn coordinated by two O atoms and three OH groups arranged at the equatorial corners of pentagonal bipyramids. The uranyl polyhedra share equatorial edges and corners to form sheets of polyhedra that are parallel to (100) at  $x = 1/4$  and  $3/4$ . The sheets are topologically identical to the sheets that occur in the structures of becquerelite, billietite, protasite, richetite, and  $\alpha$ - $U_3O_8$ . There is one symmetrically distinct partially occupied K position and three symmetrically distinct  $H_2O$  groups in the interlayer at  $x = 0$  and  $1/2$ . Each K cation is coordinated by four  $O_{Ur}$  atoms of the adjacent sheets of uranyl polyhedra, as well as three  $H_2O$  groups. Two of the symmetrically distinct  $H_2O$  groups in the structure are bonded to K, and the other is held in the structure only by H bonds. The K polyhedra share a face, forming a dimer with the composition  $K_2O_6(H_2O)_4$ . Additional linkages between the interlayer constituents and the sheets of uranyl polyhedra are provided by H bonds.

**Keywords:** compreignacite, uranyl mineral, uranium, structure determination, uranyl oxide hydrate.

### SOMMAIRE

La structure de la compreignacite,  $K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$ ,  $Z = 2$ , orthorhombique,  $a$  14.8591(7),  $b$  7.1747(3),  $c$  12.1871(5) Å,  $V$  1299.3(2) Å<sup>3</sup>, groupe spatial  $Pnmm$ , a été résolue par méthodes directes et affinée par moindres carrés sur matrice entière jusqu'à un résidu  $R$  de 3.2% et un indice de conformité  $S$  de 1.05 en utilisant 1497 réflexions uniques observées ( $|F_o| \geq 4\sigma_F$ ) prélevées avec rayonnement MoK et un détecteur de rayons X sur aire à charge couplée. La structure contient deux cations  $U^{6+}$  symétriquement distincts faisant partie d'ions uranyle  $(UO_2)^{2+}$  ( $Ur$ ); ceux-ci sont à leur tour coordonnés à deux atomes d'oxygène et trois groupes OH groupés agencés aux coins équatoriaux de bipyramides pentagonales. Les polyèdres contenant l'uranyle partagent des arêtes équatoriales et des coins pour donner des feuillets de polyèdres parallèles à (100) à  $x = 1/4$  et  $3/4$ . Ces feuillets sont topologiquement identiques à ceux des structures de becquerelite, billietite, protasite, richetite, et  $\alpha$ - $U_3O_8$ . Il y a une position symétriquement distincte qui est partiellement remplie par le K et trois sites distincts pour les groupes  $H_2O$  entre les feuillets, à  $x = 0$  et  $1/2$ . Chaque atome de K est coordonné à quatre atomes  $O_{Ur}$  faisant partie des feuillets adjacents de polyèdres d'uranyle, et à trois molécules de  $H_2O$ . Deux de celles-ci ont une liaison avec le potassium, et la troisième n'est maintenue dans la structure que par des liaisons hydrogène. Les polyèdres renfermant le K partagent une face, formant ainsi un dimère dont la composition est  $K_2O_6(H_2O)_4$ . Des liens additionnels impliquant les composants entre les feuillets et les polyèdres d'uranyle des feuillets sont assurés par des liaisons hydrogène.

(Traduit par la Rédaction)

**Mots-clés:** compreignacite, minéral d'uranyle, uranium, détermination de la structure, oxyde hydraté d'uranyle.

### INTRODUCTION

Uranyl ( $U^{6+}$ ) minerals are major constituents of the oxidized portions of U deposits, both as primary minerals and as the products of alteration of uraninite (Fron del 1958, Finch & Ewing 1992, Percy *et al.* 1994). Uranyl minerals have recently received substantial attention, owing to their significance to environmental issues (*e.g.*, Burns 1997, 1998a, Burns *et al.* 1997a, b, c, Finch *et al.*

1992, 1996, Finch & Ewing 1992, Miller *et al.* 1996, Murakami *et al.* 1997, Sowder *et al.* 1996, Vochten *et al.* 1995). They are important for understanding water-rock interactions in U deposits, are products of the oxidation of U mine and mill tailings, and are prominent alteration-induced phases in laboratory experiments on  $UO_2$  as well as spent nuclear fuel subjected to dissolution under oxidizing conditions (*e.g.*, Wadsten 1977, Wang & Katayama 1982, Wilson 1990, Wronkiewicz

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*et al.* 1992, 1996, Forsyth & Werme 1992, Johnson & Werme 1994, Finn *et al.* 1996).

Compreignacite is a rare K uranyl oxide hydrate that was first described by Protas (1964) from a locality near Compreignac, Haute-Vienne, France. More recently, a second occurrence of compreignacite was reported from Cornwall, England (Elton *et al.* 1994). The rarity of compreignacite in Nature belies its possible importance to environmental issues. Wronkiewicz *et al.* (1996) identified compreignacite on samples of  $\text{UO}_2$  treated in unsaturated drip tests designed to model the behavior of spent nuclear fuel in a geological repository. The alteration of spent fuel pellets under oxidizing conditions also results in a variety of uranyl phases, and experiments suggest that radionuclides such as  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  are being retained to some extent with the products of alteration (Finn *et al.* 1996). Thus, it is possible that compreignacite is a key phase in determining the future mobility of radionuclides such as  $^{137}\text{Cs}$  and  $^{135}\text{Cs}$  under repository conditions, owing to the possibility of  $\text{Cs}^+ \leftrightarrow \text{K}^+$  substitution in its structure.

Granger & Protas (1965) conducted a study of the structure of compreignacite using X-ray diffraction. Their single-crystal investigation provided the space group  $Pnmm$  and the positions of the U and K, but not of the anions. In the current study, a CCD-based detector mounted on an automated single-crystal diffractometer has been used to collect X-ray-diffraction data, resulting in the successful elucidation of the entire structure.

#### EXPERIMENTAL

A specimen containing superb crystals of compreignacite from the type locality at the Margnac deposit, Haute-Vienne, France was provided by Mr. Forrest Cureton. The specimen contains hundreds of crystals of compreignacite, many of which are plates that exhibit a pseudohexagonal outline, with maximum diameters of about 0.1 mm. Optical studies of several crystals that were removed from the specimen showed that most crystals exhibit twinning. A small twin-free crystal, with approximate dimensions  $0.05 \times 0.04 \times 0.005$  mm, was selected for study. The crystal was mounted on a Siemens PLATFORM 3-circle goniometer equipped with a 1K SMART CCD (charge-coupled device) detector with a crystal-to-detector distance of 5 cm. Burns (1998b) discussed the application of CCD detectors to the analysis of mineral structures.

The data were collected using monochromatic  $\text{MoK}\alpha$  X-radiation and frame widths of  $0.2^\circ$  in  $\omega$ , with 30 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. These were refined (Table 1) with 4547 reflections using least-squares techniques. Data were collected for  $3^\circ \leq 2\theta \leq 56.6^\circ$  in approximately 19 hours; comparison of the intensities of equivalent reflections collected at different times during the data

TABLE 1. MISCELLANEOUS INFORMATION CONCERNING COMPREIGNACITE

$a$ (Å)	14.8591(7)	Crystal size (mm)	0.05x0.04 x0.005
$b$ (Å)	7.1747(3)	Total ref.	8023
$c$ (Å)	12.1871(5)	Unique ref.	1687
$V$ (Å <sup>3</sup> )	1299.3(2)	$R_{int}$ (%)	4.7
Space group	$Pnmm$	Unique $ F_o  \geq 4\sigma_F$	1497
$F(000)$	1684	Final $R$ (%)	3.2
$\mu$ (mm <sup>-1</sup> )	37.7	$S$	1.05
$D_{calc}$ (g/cm <sup>3</sup> )	5.088		
Unit-cell contents:	$2[\text{K}_2(\text{UO}_2)_2\text{O}_2(\text{OH})_2(\text{H}_2\text{O})_2]$		
$R = \sum( F_o  -  F_c ) / \sum  F_o $			
$S = [\sum w( F_o  -  F_c )^2 / (m - n)]^{1/2}$	for $m$ observations and $n$ parameters		

collection showed no significant decay. The three-dimensional data were reduced and corrected for Lorentz, polarization, and background effects using the Siemens program SAINT. An empirical absorption-correction was done based upon 1978 intense reflections. The crystal was modeled as a (100) plate; reflections with a plate-glancing angle of less than  $1^\circ$  were discarded from the data set, which lowered the  $R_{azimuthal}$  from 10.7 to 3.8%. A total of 8023 reflections were collected, of which there were 1687 unique reflections ( $R_{INT} = 4.7\%$ ), with 1497 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 Siemens SHELXTL Version 5 system of programs was used for the determination and refinement of the crystal structure.

Systematic absences and reflection statistics indicated the space group  $Pnmm$ , as did the work of Granger & Protas (1965), with verification provided by the successful solution and refinement of the structure. The positions of the two symmetrically distinct U atoms were obtained from a direct-methods solution. Refinement of the U atom positions, together with isotropic-displacement parameters, gave an agreement factor ( $R$ ) of 11.6%. The positions of the K atom and the anions were obtained from difference-Fourier maps. The K site and one of the  $\text{H}_2\text{O}$  sites were determined to be partially occupied (see below), and their occupancy parameters were refined. A model that included refined positional parameters and isotropic-displacement parameters gave an  $R$  of 5.0%. Conversion of the displacement parameters to an anisotropic form for all atoms, together with the inclusion of a refinable weighting-scheme of the structure factors and a correction for isotropic extinction, resulted in a final  $R$  of 3.2% for 1497 observed reflections ( $|F_o| \geq 4\sigma_F$ ) and a goodness-of-fit ( $S$ ) of 1.05. In the final cycle of refinement, the average parameter shift/esd was 0.000, and the maximum peaks in the final difference-Fourier maps were 2.18 and  $-2.20$  e/Å<sup>3</sup>. The final atomic-position parameters and anisotropic-displacement parameters are given

TABLE 2. FINAL ATOMIC PARAMETERS FOR COMPREGNACITE

	x	y	z	*U <sub>m</sub>	**U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
U(1)	0.73021(3)	0.04748(6)	0	11(1)	143(2)	111(2)	80(2)	-6(1)	0	0
U(2)	0.75811(2)	-0.00872(4)	-0.30983(3)	109(1)	161(2)	73(2)	94(2)	4(1)	2(1)	-6(1)
K <sup>+</sup>	0.0034(3)	-0.144(1)	-0.1270(5)	358(23)	303(27)	518(47)	255(27)	-9(21)	-5(19)	-2(26)
OH(1)	0.7959(7)	-0.058(1)	-½	195(19)	361(58)	138(40)	87(38)	16(38)	0	0
O(2)	0.6091(6)	0.082(1)	0	182(18)	241(49)	166(44)	140(41)	52(36)	0	0
OH(3)	0.7048(4)	-0.1859(8)	-0.1382(5)	131(11)	148(30)	126(25)	118(27)	25(21)	42(23)	-8(22)
O(4)	0.8754(5)	-0.0372(9)	-0.2775(6)	220(14)	278(40)	170(30)	213(33)	46(26)	-26(30)	-35(36)
O(5)	0.6420(5)	0.0233(9)	-0.3480(5)	217(14)	267(37)	228(32)	157(35)	49(26)	-38(28)	0(26)
O(6)	0.7475(4)	0.1813(9)	-0.1616(5)	176(14)	328(39)	85(26)	117(29)	2(22)	26(25)	-21(24)
O(7)	0.8483(7)	-0.012(1)	0	255(23)	233(56)	386(60)	147(46)	-42(41)	0	0
H <sub>2</sub> O(8)	0.5195(5)	-0.201(1)	-0.1622(8)	374(20)	245(40)	316(42)	362(56)	1(31)	0(39)	-166(40)
H <sub>2</sub> O(9)	0	0	½	438(47)	619(137)	355(98)	339(99)	-77(78)	0	0
H <sub>2</sub> O(10) <sup>a</sup>	0.006(1)	-0.257(3)	-0.090(2)	336(68)	230(96)	175(108)	604(147)	4(58)	-40(77)	79(97)

\*U<sub>m</sub> = U<sub>m</sub> Å<sup>2</sup> × 10<sup>4</sup>\*\*U<sub>11</sub> = U<sub>11</sub> Å<sup>2</sup> × 10<sup>4</sup><sup>a</sup>the site-occupancy factor for K is 0.51(1) and H<sub>2</sub>O(10) is 0.46(4).

in Table 2, selected interatomic distances and angles are given in Table 3, and a bond-valence analysis is provided in Table 4. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

## RESULTS

All of the known structures of uranyl oxide hydrate minerals are based upon sheets of uranyl polyhedra, with low-valence cations and H<sub>2</sub>O groups located in the interlayer positions (Burns *et al.* 1996). The structure of compregnacite is consistent with this trend; sheets of uranyl polyhedra that are parallel to (100) occur at  $x \approx \frac{1}{4}$  and  $\frac{3}{4}$ , and the K cations and H<sub>2</sub>O groups are located in the interlayer.

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR COMPREGNACITE

U(1)-O(7)	1.81(1)	K-O(4)d	2.753(9)
U(1)-O(2)	1.82(1)	K-H <sub>2</sub> O(10)a	2.77(2)
U(1)-O(6)a	2.206(6) x2	K-H <sub>2</sub> O(8)e	2.81(1)
U(1)-OH(3)a	2.405(6) x2	K-O(4)f	2.882(9)
U(1)-OH(1)b	2.856(9)	K-H <sub>2</sub> O(10)g	2.92(2)
<U(1)-O <sub>eq</sub> >	1.81	K-O(7)h	2.91(1)
<U(1)-φ <sub>eq</sub> >	2.416	K-O(7)d	2.93(1)
		<K-φ>	2.85
U(2)-O(4)	1.798(7)		
U(2)-O(5)	1.802(7)	O(4)-U(2)-O(5)	177.5(3)
U(2)-O(6)e	2.252(6)	O(4)-U(2)-O(6)e	87.5(3)
U(2)-O(6)	2.269(6)	O(4)-U(2)-O(6)	87.8(3)
U(2)-OH(1)	2.411(3)	O(4)-U(2)-OH(1)	88.2(3)
U(2)-OH(3)b	2.463(5)	O(4)-U(2)-OH(3)b	86.9(2)
U(2)-OH(3)	2.573(6)	O(4)-U(2)-OH(3)	93.7(3)
<U(2)-O <sub>eq</sub> >	1.800	O(5)-U(2)-O(6)	92.9(2)
<U(2)-φ <sub>eq</sub> >	2.394	O(5)-U(2)-O(6)	93.6(3)
		O(5)-U(2)-OH(1)	89.6(3)
		O(5)-U(2)-OH(3)b	91.6(2)
O(7)-U(1)-O(2)	174.3(4)	O(5)-U(2)-OH(3)	88.8(2)
O(7)-U(1)-O(6)a	89.4(2) x2	O(6)e-U(2)-O(6)	135.5(2)
O(7)-U(1)-OH(3)a	89.3(3) x2	O(6)e-U(2)-OH(1)	73.4(2)
O(7)-U(1)-OH(1)b	111.4(4)	O(6)e-U(2)-OH(3)b	153.7(2)
O(2)-U(1)-O(6)a	93.2(2) x2	O(6)e-U(2)-OH(3)	68.0(2)
O(2)-U(1)-OH(3)a	86.6(2) x2	O(6)-U(2)-OH(1)	150.4(3)
O(2)-U(1)-OH(1)b	74.3(3)	O(6)-U(2)-OH(3)	69.8(2)
O(6)-U(1)-O(6)a	126.4(3)	O(6)-U(2)-OH(3)	68.2(2)
O(6)a-U(1)-OH(3)a	161.2(2) x2	OH(1)-U(2)-OH(3)	141.3(2)
O(6)a-U(1)-OH(1)b	72.3(2) x2	OH(3)b-U(2)-OH(3)	137.9(2)
O(6)a-U(1)-OH(1)b	65.4(2) x2		
OH(3)-U(1)-OH(3)a	88.9(3)		
OH(3)a-U(1)-OH(1)b	132.0(1) x2		

a = x, y, -z, b = -x+½, y+½, -z-½, c = -x+½, y-½, -z-½, d = x-1, y, z, e = x-½, y-½, -z-½, f = -x+1, -y, z, g = -x, -y, z, h = -x+1, -y, -z.

## Sheets of uranyl polyhedra

The structure contains two symmetrically distinct U positions. The bond-valence sums (Table 4) and polyhedron geometries (Table 3) are consistent with both of these sites containing U<sup>6+</sup>. Both of the U<sup>6+</sup> cations are part of approximately linear (UO<sub>2</sub>)<sup>2+</sup> uranyl ions (designated *Ur*) with U<sup>6+</sup>-O<sub>Ur</sub> bond-lengths of ~1.8 Å, as is almost invariably found for U<sup>6+</sup> in minerals and inorganic crystals (Burns *et al.* 1997a). Each U<sup>6+</sup> cation is also coordinated by two O atoms and three OH groups in a roughly coplanar arrangement about the uranyl ion, resulting in *Ur*φ<sub>5</sub> (φ: unspecified anion) pentagonal bipyramids. As first noted by Evans (1963), the pentagonal bipyramid is the most common coordination observed for U<sup>6+</sup>, although both square and hexagonal bipyramids also occur. The <<sup>171</sup>U<sup>6+</sup>-φ<sub>eq</sub>> (φ<sub>eq</sub>: equatorial φ) bond-lengths are 2.416 and 2.394 Å for the U(1) and U(2) sites, respectively, in good agreement with the average <sup>171</sup>U<sup>6+</sup>-φ<sub>eq</sub> of 2.37(9) Å for well-refined structures (Burns *et al.* 1997a).

The *Ur*φ<sub>5</sub> pentagonal bipyramids link by sharing equatorial edges and corners to form sheets (Fig. 1a), with the uranyl ions oriented approximately perpendicular to the sheet. This sheet is known from other structures, and is commonly referred to as an α-U<sub>3</sub>O<sub>8</sub>-type sheet. The corresponding sheet anion-topology

TABLE 4. BOND-VALENCE\* (v<sub>B</sub>) ANALYSIS FOR COMPREGNACITE

	U(1)	U(2)	K	Σ
OH(1)	0.20	0.49 <sup>±1</sup>		1.18
O(2)	1.56			1.56
OH(3)	0.49 <sup>±2</sup>	0.44, 0.36		1.29
O(4)		1.62	0.19, 0.13	1.94
O(5)		1.61		1.61
O(6)	0.73 <sup>±2</sup>	0.67, 0.64		2.04
O(7)	1.60		0.12, 0.11	1.83
H <sub>2</sub> O(8)			0.16	0.16
H <sub>2</sub> O(9)				0
H <sub>2</sub> O(10)			0.12, 0.18	0.30
Σ	5.80	5.83	1.01	

\*Bond-valence parameters for U<sup>6+</sup> from Burns *et al.* (1997a) and for K from Brese & O'Keefe (1991)

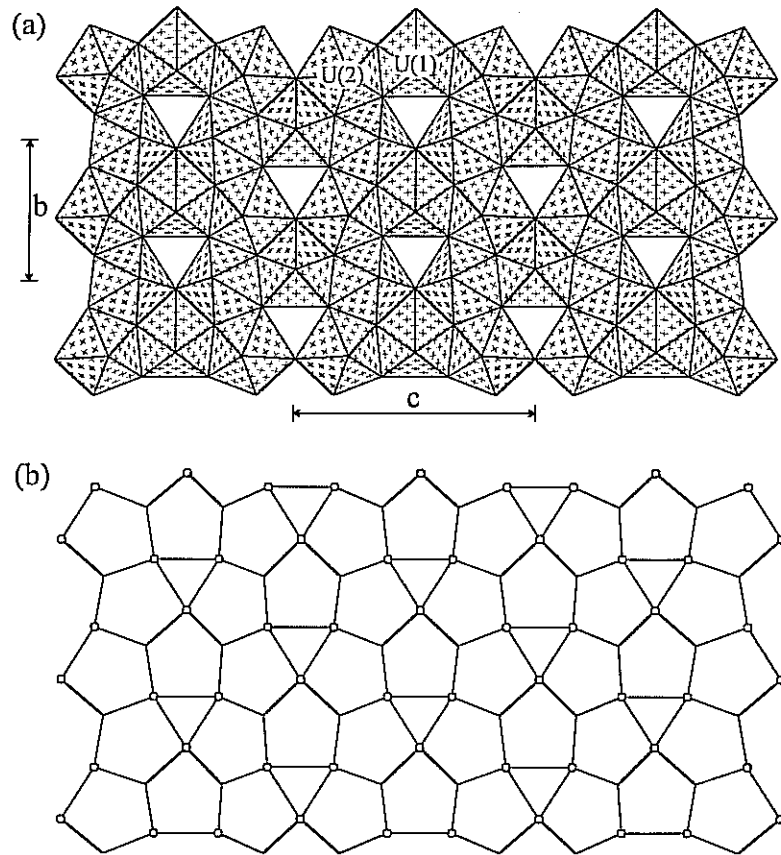


FIG. 1. The sheet of uranyl polyhedra that occurs in the structure of compreignacite at  $x = 3/4$ , projected onto (100). (a) Polyhedron representation, with the  $Ur\phi_5$  pentagonal bipyramids shaded with crosses. (b) The sheet anion-topology, derived using the method of Burns *et al.* (1996), with OH groups represented by open circles.

(Fig. 1b), derived using the method of Burns *et al.* (1996), is identical to the protasite anion-topology used by Burns *et al.* (1996) for classification purposes. The sheet in the structure of compreignacite is topologically identical to the sheets that occur in the structures of becquerelite,  $Ca[(UO_2)_3O_2(OH)_3]_2(H_2O)_8$  (Pagoaga *et al.* 1987), protasite,  $Ba[(UO_2)_3O_3(OH)_2](H_2O)_3$  (Pagoaga *et al.* 1987), billietite,  $Ba[(UO_2)_3O_2(OH)_3]_2(H_2O)_4$  (Pagoaga *et al.* 1987), richetite,  $M_3Pb_{8.57}[(UO_2)_{18}O_{18}(OH)_{12}]_2(H_2O)_{41}$  (Burns 1998a), and  $\alpha$ - $U_3O_8$  (Loopstra 1977). The distribution and quantity of OH groups contained in sheets of this topology are variable (Burns 1998a), with identical distributions in the becquerelite and billietite sheets, but different arrangements in both the protasite and richetite sheets. The distribution of anions in the compreignacite anion-topology (Fig. 1b) is identical to that in becquerelite and billietite.

#### Interlayer constituents

The interlayer occurs at  $x = 0$  and  $1/2$  and contains both K cations and  $H_2O$  groups. Figure 2 shows the distribution of these constituents in relation to the sheet of uranyl polyhedra. There is one symmetrically distinct K site in the structure, and the refined site-occupancy factor is 0.51(1). For each K position, there are three nearby symmetrically related K sites, designated  $Ka$ ,  $Kb$  and  $Kc$ , at distances 2.07(1), 3.09(1) and 3.74(1) Å, respectively (Fig. 3). Of these four sites, only two are occupied locally, corresponding to a K - K separation of 3.74(1) Å (Fig. 2b, 3). The K cation is coordinated by seven anions; three are  $H_2O$  groups contained in the interlayer, and four are  $O_{Ur}$  atoms that are part of the two adjacent sheets of uranyl polyhedra. Locally, the occupancy of either the K-Kc or Ka-Kb pairs occurs, and in either case results in the sharing of polyhedral

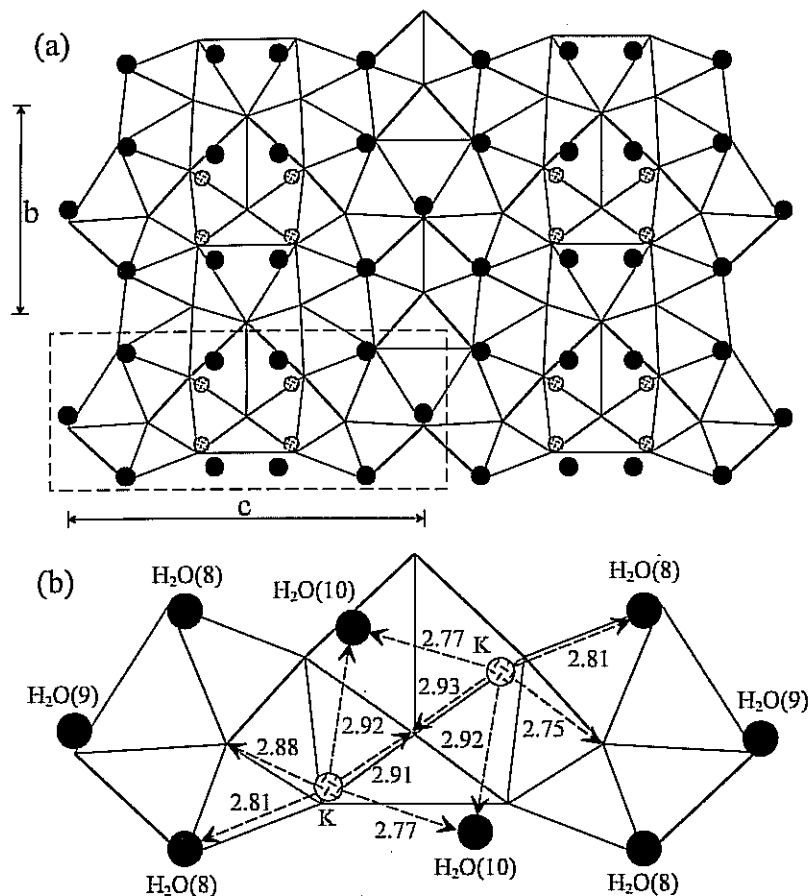


FIG. 2. The distribution of interlayer constituents at  $x = \frac{1}{2}$  shown in relation to the sheet of uranyl polyhedra at  $x = \frac{3}{4}$ . The projection is onto (100). The  $UO_2$  polyhedra are unshaded, the K cations are shown as circles shaded with a herring-bone pattern, and the  $H_2O$  groups are represented by solid black circles. (a) The long-range distribution. (b) An enlargement of the area enclosed in the broken lines in part (a), showing one of the two possible local arrangements of K and  $H_2O(10)$  sites, with corresponding bonds (Å).

faces between  $KO_4(H_2O)_3$  polyhedra, resulting in a dimer of composition  $K_2O_6(H_2O)_4$  (Fig. 3). The  $\langle K-\phi \rangle$  bond-length is 2.85 Å, and the calculated sum of bond valences at the site is 1.01 *vu* (valence units), both of which are consistent with the site containing only K.

The interlayer contains three symmetrically distinct  $H_2O$  groups. The  $H_2O(8)$  and  $H_2O(10)$  groups are bonded to K, whereas the  $H_2O(9)$  group is held in the structure only by H bonds. The refined site-occupancy factor for the  $H_2O(10)$  site is 0.46(4), and it is located 0.92(2) Å from a K site. It is not possible for both of these sites to be occupied locally, explaining why the  $H_2O(10)$  site is only partially occupied. The possible local arrangements of K and  $H_2O(10)$  sites are given in Figure 3.

Additional linkages between the interlayer  $H_2O$  groups and the sheets of uranyl polyhedra are provided by H bonds. As is normally the case for U minerals, it was not possible to obtain the H atom positions from the X-ray data.

#### Structural formula

The formula for compreignacite provided by Granger & Protas (1965) is  $K_2O \cdot 6UO_3 \cdot 11H_2O$ ; by analogy with becquerelite, this formula may be rewritten as  $K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_8$  (Finch & Ewing 1992). The bond-valence analysis (Table 4) permits the recognition of O, OH, and  $H_2O$  anions. The O(2) and O(5) positions have valence sums of  $\sim 1.6$  *vu*, indicating that

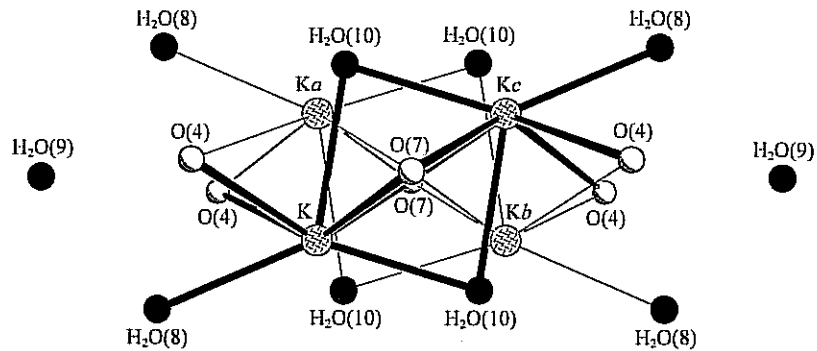


FIG. 3. A projection onto (100) that shows the disordered  $K_2O_6(H_2O)_4$  dimer. Possible local arrangements correspond to the occupancy of both the K and Kc sites, with the corresponding bonds shown by heavy lines, or the occupancy of the Ka and Kb sites, with the corresponding bonds shown by light lines. Legend as in Figure 2, except that the O atoms are shown as circles with shading in the lower left portions.

these anions likely accept H bonds. The presence of OH groups at either of these positions can be ruled out because the bond-valence sums are too high, and because each is part of a uranyl ion. The solution of the structure indicates that the formula for the crystal studied is  $K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$ . This formula differs from the previously accepted formula only in the quantity of  $H_2O$  contained in the interlayer. The new formula gives a calculated density of  $5.088 \text{ g/cm}^3$ , which is in good agreement with the measured density of  $5.03(5) \text{ g/cm}^3$  (Protas 1964).

#### DISCUSSION

The structure of compreignacite is significant in that it is the first structure that contains an  $\alpha\text{-}U_3O_8$ -type sheet and monovalent cations in the interlayer. With the exception of  $\alpha\text{-}U_3O_8$ , which has no interlayer in its structure, each of the other phases that contain the  $\alpha\text{-}U_3O_8$ -type sheet has divalent cations in the interlayer: protasite and billietite have Ba, becquerelite has Ca, and richetite has Pb. It is apparent that the  $\alpha\text{-}U_3O_8$ -type sheet is compatible with a variety of interlayer cations, both in terms of size and valence.

Burns *et al.* (1997b) suggested that the alteration phases that form in a repository, most of which will be uranyl minerals, may retard the migration of radionuclides by directly incorporating them in their crystal structures. The structure of compreignacite appears to be ideally suited to the incorporation of Cs. The sums of effective ionic radii for  $Cs^+$  and  $O^{2-}$  (Shannon 1976) give a predicted Cs–O bond-length of  $3.10 \text{ \AA}$ , which is 9% larger than the mean bond-length of the K site in the interlayer of compreignacite. Thus, it seems reasonable

to predict that substantial amounts of Cs can be incorporated into the structure of compreignacite in place of K in the interlayer, although this requires confirmation by experiment.

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