

# Revision of the crystal structure of ulrichite, $\text{CaCu}^{2+}(\text{UO}_2)(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$

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## ABSTRACT

The crystal structure of ulrichite,  $\text{CaCu}^{2+}(\text{UO}_2)(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  (space group  $P2_1/c$ ,  $a = 12.784(3)$ ,  $b = 6.996(1)$ ,  $c = 13.007(3)$  Å,  $\beta = 91.92(1)^\circ$ ,  $V = 1162.7(4)$  Å<sup>3</sup>,  $Z = 4$ ) was redetermined using X-ray diffraction data measured from a twinned crystal with Mo- $K\alpha$  radiation and a CCD area detector (2510 unique reflections with  $F_o > 4\sigma(F_o)$ ,  $R1 = 8.8\%$ ). Ulrichite crystallizes in space group  $P2_1/c$  rather than  $C2/m$  reported previously. The newly determined atomic positions give reasonable coordination polyhedra. One unique Ca atom is irregularly coordinated by eight O atoms ( $\langle \text{Ca-O} \rangle = 2.46$  Å). One unique U atom shows a [2+5] coordination with characteristic bond angles and lengths (1.806(11) Å, 1.842(12) Å and five bonds between 2.252(15) and 2.441(11) Å). Furthermore, the structure contains groups in which strongly elongated  $\text{CuO}_6$  ‘octahedra’ (also describable as  $\text{CuO}_4$  squares) are corner-linked to two  $\text{PO}_4$  tetrahedra via two opposite, equatorial O atoms. Edge- and corner-sharing  $\text{UO}_7$ ,  $\text{CaO}_8$  and  $\text{PO}_4$  polyhedra form heteropolyhedral sheets parallel to (001) that are linked to adjacent sheets via the  $\text{CuO}_6$  ‘octahedra’ and hydrogen bonds.

**KEYWORDS:** ulrichite, crystal structure, twinning, uranium, phosphates.

## Introduction

ULRICHITE,  $\text{CaCu}^{2+}(\text{UO}_2)(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ , is a very rare phosphate found as sprays of pale greenish acicular crystals in small miarolitic cavities of a granite at Lake Boga, near Swan Hill, Victoria, Australia (Birch *et al.*, 1988; Henry and Birch, 1988). It was said to have crystallized from late-stage hydrothermal solutions, and is associated with chalcociderite  $[\text{CuFe}_6^{3+}(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}]$ , turquoise  $[\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}]$ , cyrilovite  $[\text{NaFe}_3^{3+}(\text{PO}_4)_2(\text{OH})_4 \cdot 2\text{H}_2\text{O}]$ , libethenite  $[\text{Cu}_2^{2+}(\text{PO}_4)(\text{OH})]$ , pseudomalachite  $[\text{Cu}_5^{2+}(\text{PO}_4)_2(\text{OH})_4]$ , torbernite  $[\text{Cu}^{2+}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8-12\text{H}_2\text{O}]$ , saléeite  $[\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}]$ , fluorapatite  $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$  and an unidentified clay mineral. No other occurrences of ulrichite have been reported. Film methods and scanning electron microscopy performed by (Birch *et al.*, 1988) demonstrated that ulrichite is monoclinic,

with  $a = 12.79(3)$ ,  $b = 6.85(2)$ ,  $c = 13.02(3)$  Å,  $\beta = 91.03(7)^\circ$ ,  $V = 1140.3$  Å<sup>3</sup>,  $Z = 4$ , and space group  $C2/m$ . The mineral was commonly found to be twinned parallel to (100), and the crystal structure had been determined on a twinned crystal with film methods and Cu- $K\alpha$  radiation ( $R = 13\%$ ; Birch *et al.*, 1988). The bond lengths and angles given for the U–O, P–O and Cu–O polyhedra were, however, highly improbable (e.g. P–O 1.54–1.73 Å with  $\langle \text{P-O} \rangle = 1.608$  and 1.643 Å for two P atoms; Cu(1)–O = 1.72, 1.63 Å) and far from expected values (average P–O = 1.573 Å, Baur, 1981; average Cu–O in planar  $\text{CuO}_4 = 1.933$  Å, Lambert, 1988; see also Eby and Hawthorne, 1993; Hawthorne, 1998). This and the high  $R$  factor prompted us to conduct a redetermination of the crystal symmetry and structure, the results of which are presented here.

## X-ray data collection

The unit cells of ~20 acicular crystals, taken from different specimens in the collection of the first author, were determined using a Nonius

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KappaCCD diffractometer equipped with a 300  $\mu\text{m}$  capillary-optics collimator providing increased resolution. All crystals gave sharp reflection spots and a monoclinic unit cell similar to the one reported previously (Birch *et al.*, 1988), but with a distinctly larger value for  $b$  ( $\sim 6.99 \text{ \AA}$  vs.  $6.85 \text{ \AA}$ ) and without any evidence of  $C$ -centring. All investigated crystals turned out to be twinned simply in an identical manner; no polysynthetic twinning was observed. The twin plane is parallel to their elongation axis,  $b$ , in agreement with the observations of Birch *et al.* (1988). Further splitting of crystals parallel to their elongation was tried but did not yield suitable crystal fragments because of a distinct cleavage perpendicular to the elongation. Optical studies demonstrated that the twinning is recognized only from very small deviations of the extinction positions of the twin individuals. The

volume ratio of the two twin components is always close to 1:1, in agreement with the intensity distribution on the recorded CCD frames (suggesting growth twins). The crystals, which show almost straight extinction, have a negative elongation, contradicting the data given in Birch *et al.* (1988). Detailed single-crystal studies of two twins revealed that the twinning is parallel to (001), contradicting the data in the original publication.

A tiny acicular twinned crystal with the approximate dimensions  $0.08 \times 0.03 \times 0.03 \text{ mm}$  was chosen to collect intensity data (see Table 1 for further details). The measured intensity data were processed using the Nonius program suite DENZO-SMN and corrected for Lorentz and polarization effects. A multi-scan empirical absorption correction was applied via the scaling process. Normalized structure factor statistics and

TABLE 1. Crystal data, data collection information and refinement details for ulrichite.

Formula	$\text{CaCu}^{2+}(\text{UO}_2)(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$
Space group	$P2_1/c$
$a, b, c$ ( $\text{\AA}$ )	12.784(3), 6.996(1), 13.007(3)
$\beta$ ( $^\circ$ ), $V$ ( $\text{\AA}^3$ )	91.92(1), 1162.7(4)
$Z, F(000)$	4, 1164
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	3.631
$\mu$ ( $\text{mm}^{-1}$ )	16.53
Data collection:	
Diffractometer	Nonius KappaCCD system
$\lambda$ ( $\text{\AA}$ ), $T$ (K)	0.71073, 293
Crystal-detector dist. (mm)	28
Rotation axis	$\varphi, \omega$
Rotation width ( $^\circ$ )/frame	2.0
Total no. of frames	284
Coll. time per frame (s)	175
$2\theta_{\text{max}}$	57.44
$h, k, l$ ranges	$-17 \rightarrow 17, -9 \rightarrow 9, -17 \rightarrow 17$
Total reflections measured	5452
Unique reflections	2840 ( $R_{\text{int}}$ 3.17%)
Refinement:	
Refinement on	$F^2$
'Observed' refls.	2510 [ $F_o > 4\sigma(F_o)$ ]
$R1(F)$ , $wR2(F^2)$ *	8.82%, 23.43%
Extinct. factor	0.0007(4)
No. of refined parameters	106
GOF	1.073
$(\Delta/\sigma)_{\text{max}}$	0.000
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}}$ ( $\text{e/\AA}^3$ )	$-4.38, 16.95$

\*  $w = 1/[\sigma^2(F_o^2) + (0.15P)^2 + 63.00P]$ ;  $P = ([\text{max of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$

## CRYSTAL STRUCTURE OF ULRICHITE

TABLE 2. Atomic coordinates and displacement parameters for ulrichite.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}/U_{iso}$
U	0.31584(4)	-0.52226(9)	0.74637(5)	0.0152(3)
Ca	0.1659(3)	-0.0204(4)	0.7589(3)	0.0159(7)
Cu(1)	0.0	0.5	0.5	0.0193(6)
Cu(2)	0.5	0.5	0.0	0.0248(7)
P(1)	0.0761(3)	-0.5135(6)	0.7481(4)	0.0168(9)
P(2)	0.5948(3)	-0.5121(6)	0.7735(4)	0.0190(9)
O(1)	0.1532(9)	-0.3469(17)	0.7475(8)	0.019(2)
O(2)	0.8516(9)	-0.1885(16)	0.7464(8)	0.017(2)
O(3)	0.0011(10)	-0.5124(15)	0.6531(10)	0.017(2)
O(4)	0.0028(10)	0.4925(15)	0.8395(9)	0.016(2)
O(5)	0.6571(10)	-0.694(2)	0.7607(9)	0.027(3)
O(6)	0.4887(12)	-0.5259(18)	0.7185(11)	0.027(3)
O(7)	0.6596(10)	-0.3531(19)	0.7260(9)	0.025(3)
O(8)	0.5859(13)	-0.467(2)	0.8889(12)	0.035(3)
Ow(9)	0.0374(10)	-0.7651(19)	0.5003(9)	0.026(3)
Ow(10)	0.1903(13)	-0.107(3)	0.9463(12)	0.044(4)
Ow(11)	0.4938(12)	-0.785(3)	0.9826(12)	0.046(4)
O(12)	0.3260(9)	-0.5106(14)	0.8851(9)	0.012(2)
Ow(13)	0.2033(14)	-0.010(2)	0.5718(13)	0.035(4)
O(14)	0.3076(9)	-0.5450(16)	0.6053(9)	0.017(2)

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
U	0.0137(4)	0.0118(4)	0.0202(4)	-0.00005(19)	0.0001(2)	0.00012(17)
Ca	0.0131(14)	0.0035(13)	0.031(2)	-0.0007(10)	-0.0020(12)	0.0001(9)
Cu(1)	0.0238(16)	0.0164(13)	0.0177(15)	-0.0003(10)	-0.0011(11)	0.0011(9)
Cu(2)	0.0276(18)	0.0201(15)	0.0269(18)	0.0008(11)	0.0062(13)	0.0019(10)
P(1)	0.0097(19)	0.0129(18)	0.028(2)	-0.0011(14)	-0.0041(16)	-0.0019(12)
P(2)	0.0090(19)	0.0132(18)	0.035(3)	0.0005(15)	0.0023(17)	0.0014(12)

Note: Oxygens of water molecules are designated as Ow

systematic absences indicated the centrosymmetric space group  $P2_1/c$  ( $R_{int} = 2.7\%$  for 4475 reflections). The refined unit-cell parameters are  $a = 12.784(3)$ ,  $b = 6.996(1)$ ,  $c = 13.007(3)$  Å,  $\beta = 91.92(1)^\circ$ ,  $V = 1162.7(4)$  Å<sup>3</sup>. The two more or less equally strongly scattering twin components showed only a very small angular difference between their orientations, resulting in complete overlap of their reflections at low and medium-low spectral resolution. Thus, although only the reflections of one twin component were chosen for integration, the reflection overlap led to imprecise intensities in the resolution range mentioned. To obtain a somewhat better separation of the overlapped spots, an attempt was made to collect intensity data from two other, larger

twins at an increased crystal-detector distance (42 mm). However, this did not lead to improved refinements, regardless of the processing variables chosen or the refinement strategies applied.

### Structure solution and refinement

Crystal structure determination and refinement were performed using SHELXS-97 (Sheldrick, 1997a) and SHELXL-97 (Sheldrick, 1997b), respectively. For the calculations, 2840 unique reflections including 2118 'observed' reflections with  $F_o > 4\sigma(F_o)$  were used (Table 1). As expected, it was impossible to locate H atoms. The final structure model, with anisotropic displacement parameters for all cations, led to

TABLE 3. Selected interatomic distances (Å) and suggested hydrogen bonds for the coordination polyhedra in ulrichite.

Ca—O(1)	2.294(12)	U—O(12)	1.806(11)
—O(2)	2.333(12)	—O(14)	1.842(12)
—O(3)	2.457(14)	—O(6)	2.252(15)
—O(4)	2.473(13)	—O(5)	2.325(14)
—Ow(13)	2.497(17)	—O(7)	2.362(13)
—O(7)	2.520(13)	—O(1)	2.414(12)
—Ow(10)	2.520(16)	—O(2)	2.441(11)
—O(5)	2.587(14)	<U—O>	1.82 [2] + 2.36 [5]
<Ca—O>	2.46		
Cu(1)—Ow(9)	1.915(13) × 2	P(1)—O(1)	1.526(12)
—O(3)	1.992(13) × 2	—O(2)	1.534(12)
—Ow(10)	2.661(17) × 2	—O(3)	1.539(13)
<Cu(1)—O>	1.95 [4] + 2.66 [2]	—O(4)	1.539(13)
		<P(1)—O>	1.53
Cu(2)—O(8)	1.859(16) × 2	P(2)—O(5)	1.514(14)
—Ow(11)	2.005(19) × 2	—O(6)	1.515(16)
—O(12)	2.639(11) × 2	—O(7)	1.530(13)
<Cu(2)—O>	1.93 [4] + 2.64 [2]	—O(8)	1.542(17)
		<P(2)—O>	1.53
Possible hydrogen bonds			
Ow(9)···O(4)	2.75(2)	Ow(11)···Ow(11)*	3.05(4)
Ow(9)···O(4)	2.65(2)	Ow(13)···O(8)	2.74(2)
Ow(10)···O(14)	2.73(2)	Ow(13)···O(9)	2.86(2)
Ow(10)···O(3)	2.81(2)		

\* Distances to other possible acceptors are all >3.11 Å

the discrepancy factors  $R1 = 8.8\%$  and  $wR2 = 23.4\%$  for a total of 106 refined parameters. Final anisotropic displacement parameters are all well behaved. The relatively high final  $R$  values are due to the presence of twinning. Refinement involving possible twin operators did not change the discrepancy factors by any significant amount. The final discrepancy factors were obtained after removal from the dataset of ~50 reflections, whose measured intensities had been most strongly affected by the twinning. This removal resulted in only very minor shifts in the positional parameters. We note that for all of the removed 'most disagreeable' reflections,  $F_o$  is much greater than  $F_c$ , a typical feature of non-merohedral twinning (e.g. Herbst-Irmer and Sheldrick, 1998). Manual removal of selected  $hkl$  classes resulted in only marginally lower discrepancy factors. Minimum and maximum peaks in the final difference-Fourier maps were  $-4.38$  and  $16.95 \text{ e}/\text{\AA}^3$ , respectively. These residua are discussed in more detail below. The final atomic

positions and displacement parameters are given in Table 2, selected bond lengths and possible hydrogen bonds in Table 3, and a bond-valence analysis is presented in Table 4. Observed and calculated structure factors (Table 5) have been deposited with the Principal Editor of *Mineralogical Magazine*, and are available upon request.

## Description of the structure

### Cation coordination and general topology

Based on the previous faulty structure determination (Birch *et al.*, 1988), ulrichite has been classified by Burns *et al.* (1996) as a member of sheet-structure  $\text{U}^{6+}$ -compounds, whose anion topologies in a 2-dimensional net projected normal to the sheet are based on triangles, squares and pentagons (see reference for more details). Similar anion topologies are encountered in  $\text{U}^{6+}$  silicate minerals such as  $\alpha$ - and  $\beta$ -uranophane, cuprosklodowskite and kasolite.

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TABLE 4. Bond-valence analysis for ulrichite.

	U	Ca	Cu(1)	Cu(2)	P(1)	P(2)	Sum
O(1)	0.497	0.413			1.231		2.14
O(2)	0.472	0.372			1.208		2.05
O(3)		0.266	0.428 ↓ × 2		1.192		1.89
O(4)		0.255			1.192		1.45
O(5)	0.590	0.187				1.275	2.05
O(6)	0.679					1.272	1.95
O(7)	0.549	0.224				1.221	1.99
O(8)				0.615 ↓ × 2		1.182	1.80
Ow(9)			0.528 ↓ × 2				0.53
Ow(10)		0.224	0.007 ↓ × 2				0.23
Ow(11)				0.414 ↓ × 2			0.41
O(12)	1.602			0.075 ↓ × 2			1.68*
Ow(13)		0.239					0.24
O(14)	1.496						1.50*
Sum	5.89	2.18	2.05	2.21	4.82	4.95	

Note: The bond-valence parameters used are from Brese and O'Keeffe (1991), those used for U ( $U^{6+}$ ) are from Burns *et al.* (1997)

\* See text for discussion

The present structure determination confirms this assignment, although the determination of the correct space-group symmetry now allows a scientifically sound discussion. In the case of ulrichite the triangles in the 2-D net represent ( $PO_4$ ) and the pentagons represent  $UO_5$  and  $CaO_8$  polyhedra; the  $Cu^{2+}$  assumes the role of an interlayer cation, rather than being part of the sheet as in vandenbrandeite [ $Cu^{2+}(UO_2)(OH)_4$ ].

The asymmetric unit of ulrichite contains 1 U, 1 Ca, 2 P, 2 Cu atoms (each on a special position), 14 O and 8 H atoms. All O atoms are bound to one or more of the metal cations. The heteropolyhedral sheet in ulrichite is composed of  $UO_7$  pentagonal dipyramids, irregular  $CaO_8$  polyhedra and  $PO_4$  tetrahedra (Fig. 1), and is parallel to (001). The  $P(1)O_4$  tetrahedron shares an edge with the  $UO_7$  polyhedron, whereas the  $P(2)O_4$  tetrahedron shares an edge with the  $CaO_8$  polyhedron. Rows of  $UO_7$  and  $CaO_8$  polyhedra are both aligned parallel to [010]. The two non-equivalent Cu atoms represent the only atoms situated on special positions within the structure. Each has four close and two very remote O ligands with

Cu–O distances in the range 1.915(13) to 2.005(19) and 2.639(11) to 2.661(17), respectively (Table 3). Thus, they basically form  $CuO_4$  squares. Topologically, the Cu–O polyhedra can also be described as strongly elongated  $CuO_6$  'octahedra' showing the typical Jahn-Teller [4+2] distortion (e.g. Eby and Hawthorne, 1993). The two elongate  $CuO_6$  'octahedra' are each corner-linked to two equivalent  $PO_4$  tetrahedra via two opposite, equatorial O atoms, thus forming mixed tetrahedral-octahedral trimers (Fig. 2). The trimer P–Cu–P axes are linear, but P–O–Cu angles are 141.8(8) and 142.7(10)°. The  $P(2)O_4$  tetrahedron exhibits a stronger distortion than the  $P(1)O_4$  tetrahedron (range of P–O distances 1.514(14)–1.542(17) and 1.526(12)–1.539(13) Å, respectively). The two Cu atoms take the role of an interlayer cation which connects the sheets mainly via the corner-linkage to the  $PO_4$  tetrahedra (Fig. 2). Additional interlayer connection is achieved through hydrogen bonds (see further discussion below).

The unique Ca atom is coordinated to 8 O atoms and has Ca–O distances ranging from

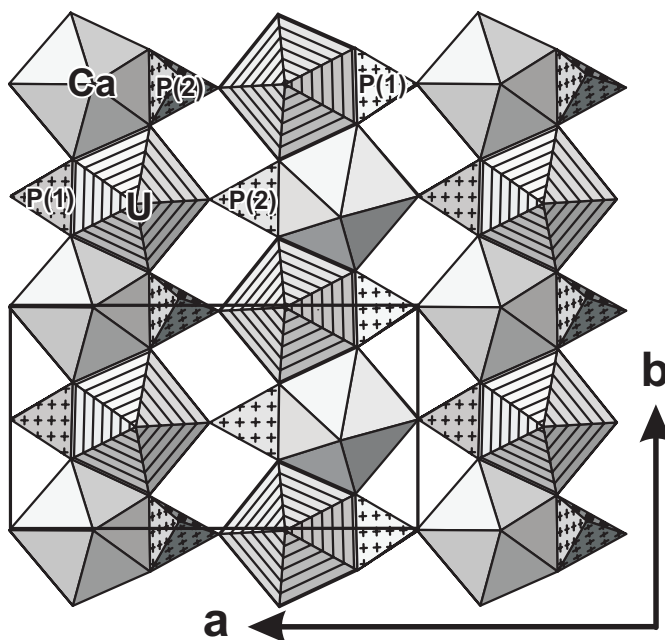


FIG. 1. The heteropolyhedral sheet with composition  $\{(\text{UO}_7)[\text{CaO}_7(\text{OH}_2)](\text{PO}_4)_2\}$  in the structure of ulrichite in a view down  $[001]$  (the Cu atoms have been omitted for clarity). The  $\text{UO}_7$  polyhedra are shown striped,  $\text{CaO}_7(\text{OH}_2)$  polyhedra are not marked and the  $\text{PO}_4$  tetrahedra are shown with crosses. The unit cell is also indicated. All drawings were done using ATOMS (Shape Software, 1999).

2.294(12) to 2.587(14) Å. The average bond length, 2.46 Å, agrees reasonably well with the usually encountered value of  $\sim 2.50$  Å (Baur, 1981). The unique U atom shows a  $[2+5]$  coordination (pentagonal bipyramid) with characteristic bond lengths and angles (Table 3; Fig. 3) similar to other bipyramidal uranyl-containing minerals (e.g. shröckingerite-related phases, Li *et al.*, 2001). The  $(\text{UO}_2)^{2+}$  (uranyl) group is almost linear (angle  $\text{O}(12)\text{—U—O}(14) = 177.5(5)^\circ$ ) and extends parallel to the  $c$  axis. The observed U environment is in very good agreement with the results for  $[2+5]$ -coordinated  $\text{U}^{6+}$  cations obtained in a recent survey on the crystal chemistry of hexavalent uranium by Burns *et al.* (1996, 1997). The improved bond-valence parameters for  $\text{U}^{6+}$  cations (Burns *et al.*, 1997) were used to compute reliable bond-valence sums for the U atom (Table 4). The value obtained, 5.89 v.u. (valence units), is in good accord with the formal valence. If the parameters of Brese and O’Keeffe (1991) or Brown (1996) are used, one obtains the less precise values 6.31 and 6.85 v.u., respectively. The ‘disadvantage’ of using the

revised parameters of Burns *et al.* (1997) is that the two O atoms very closely bonded to U, O(12) and O(14), then seem to have unrealistically low values, 1.68 and 1.50 v.u., whereas use of the Brese and O’Keeffe (1991) parameters would give 2.14 and 1.88 v.u. However, as discussed in the following section, probable hydrogen bonding would increase the bond-valence sum of O(14).

The consistent twinning of ulrichite is explained by its pseudo-orthorhombic symmetry ( $\beta = 91.9^\circ$ ), two very similar lattice parameters  $a$  and  $c$ , and its topology. The views of the structure along  $[001]$  and  $[010]$  (Figs. 1, 2) reveal at least one possible location of a mirror plane either parallel to (100) or (001). The effects of the twinning are evident from the maximum positive peaks in the final difference-Fourier maps: there are two distinct peaks with 16.95 and 14.86  $e/\text{Å}^3$ , followed by peaks near Ca and O atoms, with decreasing densities between 7 and 3  $e/\text{Å}^3$ . The two distinct peaks are located in the space about halfway between the U atom and its two nearest O neighbours, i.e. parallel to the  $c$  axis. These peaks are pseudo-peaks attributable to the twinning

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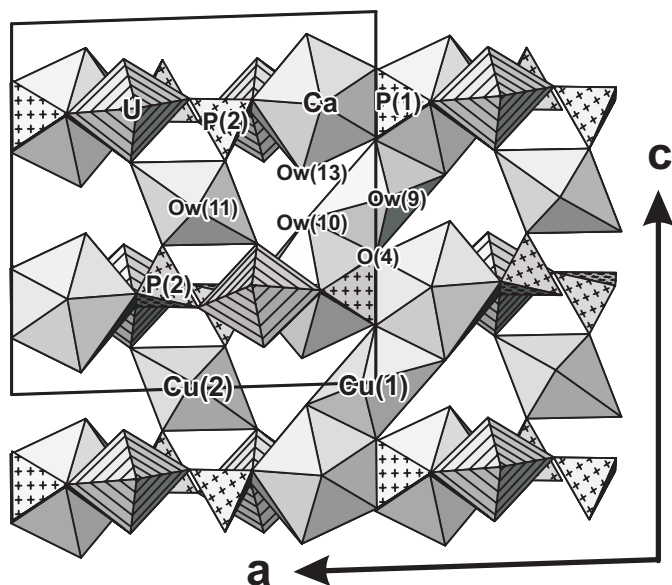


FIG. 2. The structure of ulrichite projected along [010], showing the linkage between the heteropolyhedral sheets via the elongated  $\text{CuO}_6$  'octahedra'. The positions of the O atoms belonging to the four water molecules and of O(4) are indicated. Designations as in Fig. 1.

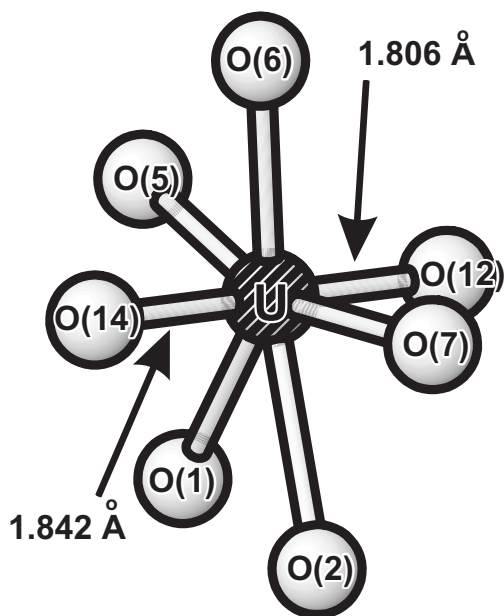


FIG. 3. View of the bonds in the pentagonal-dipyramidal coordination polyhedra about  $\text{U}^{6+}$  in the structure of ulrichite. There are two short U–O bonds (indicated) and five longer equatorial bonds, giving rise to a characteristic [2+5] coordination. The  $(\text{UO}_2)^{2+}$  (uranyl) cation is almost linear.

parallel to (001), which leads to small relative shifts of the U (and Ca) atoms in the two twin individuals along the  $c$  axis. The twin plane was also confirmed to be parallel to (001) by a trial removal of all  $hk0$  reflections from the dataset during the refinement. This lowered the  $R$  value by 0.6%, whereas a removal of all  $0kl$  reflections did not lead to a decrease of the  $R$  value.

*Hydrogen bonding*

Bond-valence calculations (Brown and Altermatt, 1985; Brese and O'Keeffe, 1991; Brown, 1996) and stereochemical considerations were used to identify the water molecules in the structure. The computed valence units (Table 4) demonstrate that O(4) is fairly undersaturated (1.45 v.u.), and Ow(9), Ow(10), Ow(11) and Ow(13) represent water molecules (0.53, 0.23, 0.41, 0.24 v.u., respectively). The latter assignment is also in agreement with the comparatively higher displacement parameters of the O atoms belonging to the water molecules (O(8) being an exception, however). The O(8) atom also appears to be slightly undersaturated (1.80 v.u.). Both O(4) and O(8) belong to different  $\text{PO}_4$  tetrahedra and each shows the longest distance to the respective central P atom (Table 3).



Thus, the H-bearing components in the structure are  $\text{CaO}_7(\text{OH}_2)$ ,  $\text{Cu(1)O}_2(\text{OH}_2)_4$  and  $\text{Cu(2)O}_4(\text{OH}_2)_2$  polyhedra, and the composition of the heteropolyhedral sheet parallel to (001) is  $\{(\text{UO}_7)[\text{CaO}_7(\text{OH}_2)](\text{PO}_4)_2\}$ . All water molecules and the hydroxyl group are situated more or less in the space between adjacent sheets (Fig. 2). Based on  $\text{O}\cdots\text{O}$  distances, the following oxygen atoms are plausible candidates for being the acceptor atom of a hydrogen bond: O(3), O(4), O(8), Ow(9), O(14) and possibly Ow(11) (all accepting from the four water molecules). The bonds to the strongly and slightly undersaturated O(4) and O(8) atoms, respectively, would provide the necessary increase of their respective bond valence. The suggested hydrogen bonds, listed in Table 3, would represent medium-strong to weak links, as the  $\text{O}\cdots\text{O}$  distances range from 2.65(2) to 3.05(4) Å. Consequently, these bonds provide additional linkage between the sheets via the involved polyhedra.

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