

Crystal structure of copper bis(uranyl phosphate) octahydrate (metatorbernite), $\text{Cu}(\text{UO}_2\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})$

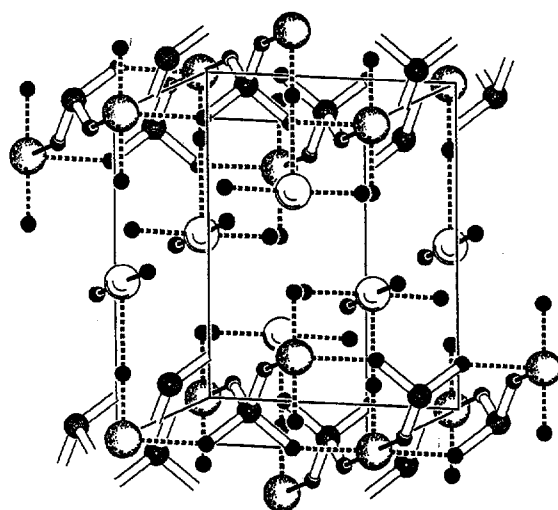
N. J. Calos

The University of Queensland, Centre for Microscopy and Microanalysis, Brisbane, Queensland 4072, Australia

and C. H. L. Kennard

The University of Queensland, Department of Chemistry, Brisbane, Queensland 4072, Australia

Received October 12, 1995, transferred to the 1st update of database ICSD in 1997, CSD-No. 402298



Projection down the a -axis; large clear circles represent Cu^{2+} ion, small black circles H_2O oxygen with tetrahedral P of PO_4^{3-} ions as concentric circles, and large shaded circles represent U atoms.

$\text{CuH}_{16}\text{O}_{20}\text{P}_2\text{U}_2$, tetragonal, $P4/nmm$ (No. 129), $a = 6.950(1) \text{ \AA}$, $c = 8.638(4) \text{ \AA}$, $V = 417.2 \text{ \AA}^3$, $Z = 1$, $R(F) = 0.092$, $R_w(F) = 0.214$.

Table 1. Parameters used for the X-ray data collection

Crystal:	fluorescent green orthogonal plate, size 0.125 x 0.075 x 0.13 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 \AA)
μ :	209.00 cm^{-1}
Diffractometer:	Enraf-Nonius CAD4
Scan mode:	ω
$T_{\text{measurement}}$:	293 K
$2\theta_{\text{max}}$:	50°
$N(hkl)_{\text{unique}}$:	250
Criterion for I_0 :	$I_0 > 2 \sigma(I_0)$
$N(\text{param})_{\text{refined}}$:	20
Program:	SHELXL-93

Source of material: The title compound (mineral name: metatorbernite) is a natural product from Sonora, Mexico. The structure was first solved by Makarov and Tobelko (see ref. 1) in the space group $P4/nmm$, using the centrosymmetric setting, with cell dimensions $a = 6.95 \text{ \AA}$, $c = 17.26 \text{ \AA}$. Ross et al. (see ref. 2, Schneeberg specimen) found a lower symmetry cell but with the same volume and space group $P4/n$, $a = 6.969 \text{ \AA}$, $c = 17.306 \text{ \AA}$, with the P atoms located at the 4 site, and Cu and U on the 4-fold axis. Stergiou et al. (see ref. 3) later confirmed this structure using single crystal diffraction. The present work indicates a higher symmetry for the P site ($42m$) which is verified from infrared spectroscopy, by the absence of a symmetric PO_4 deformation absorption at 405 cm^{-1} , as well as statistical occupancy of the Cu site ($4mm$). A high symmetry structure may constitute polytypism in the lamellar uranyl phosphate. In order to overcome any problem of identification, we propose calling the structures in refs. 2 and 3 the α -form and the current structure the β -form.

The two marginally differently types of uranyl and phosphate ions of Ross et al. (see ref. 2) are each reduced to one within this higher symmetry. The uranyl phosphate groups form extended two dimensional structures (lamellae), separated by the Cu^{2+} with its aquation shell (four water molecules with a distance of 1.92 \AA). Except for Cu half occupancies, the Schneeberg specimen is isostructural with the Sonora torbernite. Ross et al. (see ref. 2) found that there is statistical occupancy of copper occurring with higher symmetry when the heavy atoms dominate the scattering. A breakdown of the symmetry in $P4/nmm$ is then due to those lighter atoms. The point group $4/m$ is best observed with hkl , $l = 2n+1$ reflections, with contributions from the phosphate, water and copper. As no reflections of this type were observed, a smaller and more symmetric cell may be justified with disordered Cu occupancy. Perfect cleavage occurs about the $\{100\}$ and $\{001\}$ planes.

Table 2. Final atomic coordinates and displacement parameters (in \AA^2)

Atom	Site	x	y	z	U_{iso}
O(1)	2c	1/4	1/4	-0.104(2)	0.02(1)
O(2)	2c	1/4	1/4	0.315(2)	0.02(1)
O(3)	8i	1/4	-0.081(5)	0.108(4)	0.043(8)
O(4)	8i	0.527(9)	1/4	-0.388(5)	0.09(2)

Table 3. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
U	2c		1/4	1/4	0.1050(3)	0.004(1)	<i>U</i> ₁₁	0.027(2)	0	0	0
Cu	2c	0.5	1/4	1/4	-0.390(3)	0.010(5)	<i>U</i> ₁₁	0.06(1)	0	0	0
P	2a		1/4	3/4	0	0.014(5)	<i>U</i> ₁₁	0.008(8)	0	0	0

References

1. Makarov, E. S.; Tobelko, K. I.: Crystal Structure of metatorbernite. Dokl. Akad. Nauk. SSSR **131** (1960) 87-89.
2. Ross, M.; Evans, Jr. H. T.; Appleman, D. E.: Studies of the torbernite minerals(II): the crystal structure of metatorbernite. Amer. Miner. **49** (1964) 1603-1621.
3. Stergiou, A. C.; Rentzeperis, P. J.; Sklavounos, S.: Refinement of the crystal structure of metatorbernite. Z. Kristallogr. **205** (1993) 1-7.