

STUDIES OF THE TORBERNITE MINERALS (II): THE CRYSTAL STRUCTURE OF META-TORBERNITE¹

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ABSTRACT

The crystal structure of meta-torbernite, $\text{Cu}(\text{UO}_2\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, has been determined and refined by three-dimensional least-squares analysis. The structure consists of infinite $(\text{UO}_2\text{PO}_4)_n^{n-}$ sheets isostructural with those of meta-autunite(I) and abernathyite. Between the sheets lie squares of four water molecules. Two of the four squares per unit cell coordinate the two copper atoms. The other two squares do not coordinate a cation but are hydrogen bonded together in the same manner as those in the abernathyite structure. Each water molecule of the $\text{Cu}(\text{H}_2\text{O})_4$ squares is hydrogen bonded to a water molecule of an adjacent $(\text{H}_2\text{O})_4$ square and to a phosphate oxygen atom. Each water molecule of the $(\text{H}_2\text{O})_4$ squares is hydrogen bonded to two other water molecules within the square, to an adjacent $\text{Cu}(\text{H}_2\text{O})_4$ water molecule, and to a phosphate oxygen atom. The copper atoms are also bonded to two uranyl-oxygen atoms; thus the coordination polyhedra about the copper cations is in the form of an asymmetrical tetragonal dipyrmaid. X-ray powder data for meta-torbernite are given. Unit-cell data for meta-zeunerite, $\text{Cu}(\text{UO}_2\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, are also presented.

INTRODUCTION

In the first paper of this three-part series (Ross and Evans, 1964, hereafter referred to as Part I) the crystal structures of three members of the torbernite mineral group were given, namely those of abernathyite, $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$, and $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$. The present paper (Part II) presents the crystal structure of a fourth member of this group, meta-torbernite, $\text{Cu}(\text{UO}_2\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. A general discussion of the torbernite minerals was given in Part I. In Part III of this series (Ross and Evans, 1965) the crystal chemistry of the torbernite minerals will be discussed in detail.

CRYSTALLOGRAPHY OF META-TORBERNITE

A sample of meta-torbernite from Schneeberg, Germany, (U. S. National Museum No. 84318) was used in the crystal-structure study. The crystals are clear, transparent, and bright emerald green in color. The optical properties are: uniaxial negative, $\omega = 1.626 \pm 0.002$. The value of ϵ was not determined because of the small amount of material available. No birefringence is evident in the plane of the plate. Spectrographic analysis of this specimen (K. V. Hazel, analyst) showed $> 10\%$ U, 1-5% P,

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Cu, and 0.1–0.5% Mn. No other elements were detected. X-ray powder patterns (Daphne R. Ross, analyst) confirmed that the material is meta-torbernite.

X-ray single-crystal studies were made with the Buerger precession camera using zirconium-filtered molybdenum radiation. The space group was determined from the inspection of the $hk0$, $hk1$, $hk2$, $hk3$, $hk4$, $hk5$, $0kl$, and $1kl$ photographs. The condition limiting the possible reflections is:

$$hk0:h + k = 2n$$

The $hk1$, $hk3$, and $hk5$ photographs show distinct $4/m$ Laue symmetry. Thus the space group is $P4/n$ (No. 85). The $4/m$ Laue symmetry is not apparent in the $hk0$, $hk2$, $hk4$, $0kl$, and $1kl$ photographs, and if only these were used for the space group determination it would appear that meta-torbernite possesses $4/mmm$ Laue symmetry and belongs in space group $P4/nmm$ (No. 129). As will be discussed later, the strong pseudo-symmetry is due to the fact that the uranium, phosphorus, copper, and uranyl oxygen atoms occupy special positions compatible with the higher $4/mmm$ symmetry. All x-ray reflections are sharp, giving no indication of possible atomic disorder or mechanical distortion in the crystals. The unit-cell and optical data found for meta-torbernite in the present study, the unit-cell data found for this mineral by Donnay and Donnay (1955), and the data of Makarov and Tobelko (1960) are compared in Table 1. The unit-cell data for the present study were obtained from a least-squares refinement of the x-ray powder film data listed in Table 2 using a program written by Evans *et al.* (1963). Donnay and Donnay observed the $4/m$ Laue symmetry but did not observe the weak 003 and 005 reflections and thus assumed that meta-torbernite possessed a screw axis parallel to c . As a result they assigned the space group $P4_2/n$. Makarov and Tobelko did not observe the $4/m$ Laue symmetry and thus assigned the space group $P4/nmm$ to this mineral. The indexed x-ray powder data for meta-torbernite (U.S.N.M. specimen No. 84318) are given in Table 2.

CRYSTAL STRUCTURE DETERMINATION

A small tabular crystal measuring $0.02 \times 0.30 \times 0.42$ mm, mounted with the thin direction parallel to the precession axis, was used to collect the $hk0$, $hk1$, $hk2$, $hk3$, $hk4$, and $hk5$ intensity data. The thinness of the crystal in the c -direction minimizes the absorption error for these net planes (Donnay and Donnay, 1955). To collect the $0kl$, $1kl$, and $2kl$ data, a pyramidal-shaped crystal measuring $0.05 \times 0.06 \times 0.10$ mm was used. The $hk1$, $hk3$, and $hk5$ photographs were made with unfiltered molybdenum radiation; all others with zirconium-filtered molybdenum radi-

TABLE 1. X-RAY AND OPTICAL PROPERTIES OF META-TORBERNITE,
 $\text{Cu}(\text{UO}_2\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$

	Present study ¹	Donnay and Donnay, 1955	Makarov and Tobelko, 1960
System	Tetragonal	Tetragonal	Tetragonal
a (Å)	6.969 ± 0.001	6.98	6.95
c (Å)	17.306 ± 0.005	17.41	17.26
V (Å ³)	840.5	848.2	833.7
Z	2	2	2
Laue Group	$4/m$	$4/m$	$4/mmm$
Space Group	$P4/n$	$P4_2/n$	$P4/nmm$
Density, g/cm ³ (Obs)	—	3.40	3.79
Density, g/cm ³ (calc)	3.70	3.67	3.73
ϵ	—	—	—
ω	1.626	—	—
Forms	{100}, {001}	—	—
Locality	Schneeberg, Germany (U.S.N.M. 84318)	Cornwall, England	—

¹ The unit-cell edges were obtained from a least-squares refinement of the X-ray powder film data listed in Table 2. These values are in excellent agreement with the values $a = 6.963 \pm 0.007$ Å and $c = 17.297 \pm 0.018$ Å obtained from single-crystal patterns taken with a quartz-calibrated Buerger precession camera.

ation. Lorentz and polarization corrections were applied to the observed intensities by means of a computer program based on the relations given by Waser (1951). No absorption corrections were made.

The assumption was made at first that the structure of the $(\text{UO}_2\text{PO}_4)_n^{n-}$ sheets of meta-torbernite is identical to that of the $(\text{UO}_2\text{AsO}_4)_n^{n-}$ sheets of abernathyite (Part I). The four uranium atoms were placed tentatively in two $2c$ positions; two U at $z = 0.051$, and two U at $z = 0.551$ cycles of space group $P4/n$. The four phosphorus atoms were placed in positions $2b$ and $2a$. The 16 water molecules and the 16 phosphate oxygen atoms were placed in four eight-fold positions ($8g$) at coordinates equivalent to those given the water molecules and arsenate oxygens in abernathyite. The two copper atoms were placed in position $2c$ at $z = 0.815$. This positioning permits each copper atom to be coordinated by four water molecules so as to form square planar $\text{Cu}(\text{H}_2\text{O})_4$ groups. Thus, with the exception of copper, the tentative structure was given atomic coordinates identical to those of abernathyite.

Instead of first preparing Fourier projections, as was done with the previous compounds (Part I), it was decided to subject the proposed

TABLE 2. X-RAY POWDER DATA FOR META-TORBERNITE¹

I ²	d(meas.)	d(calc.) ³	hkl	I ²	d(meas.)	d(calc.) ³	hkl
		17.31	001	2	1.940	1.937	217
20	8.71*	8.65	002			1.929	305
8	6.48	6.46	101			1.923	009
5	5.75	5.77	003			1.921	321
15	5.44*	5.43	102	9	1.888*	1.886	322
15	4.93*	4.93	110			1.873	226
4	4.70	4.74	111			1.859	315
		4.44	103			1.854	109
13	4.31*	4.33	004	10	1.838*	1.839	208
		4.28	112			1.833	323
		3.747	113	10	1.809*	1.809	306
20	3.678*	3.676	104			1.791	119
16	3.480*	3.484	200	9	1.778	1.777	218
		3.461	005	12	1.766*	1.765	324
		3.416	201			1.751	316
		3.251	114	10	1.743*	1.742	400
16	3.232*	3.232	202	8	1.732		
		3.100	105	10	1.710*	1.708	402
8	3.063	3.067	211	5	1.658*	1.659	412
3	2.979	2.982	203	5	1.642		
14	2.931*	2.932	212	10	1.634*	1.633	11,1,0
		2.884	006	6	1.616		
2	2.840	2.832	115	9	1.605*	1.606	326
		2.742	213	7	1.585	1.583	308
8	2.714*	2.714	204	10	1.575*	1.574	414
14	2.667*	2.665	106	10	1.560	1.558	420
14	2.529*	2.529	214	12	1.544*	1.544	318
9	2.488*	2.489	116	6	1.535		
		2.472	007	6	1.459*	1.458	416
12	2.462*	2.464	220	6	1.443		
		2.456	205	11	1.414		
		2.439	221	8	1.386		
13	2.368*	2.370	222	6	1.376		
		2.330	107	11	1.361		
		2.316	215	3	1.351*	1.350	512
2	2.304	2.302	301	5	1.333		

¹ CuK α radiation, Ni filter ($\lambda=1.5418$ Å). Camera diameter: 114.59 mm. Lower limit 2θ measurable: approximately 8° (11.0 Å).

² Intensities were measured with a calibrated intensity strip.

³ d-spacings were calculated from the following unit-cell data: tetragonal, $P4/n$, $a=6.969$ Å, $c=17.306$ Å. These unit cell data were obtained by least-squares refinement of the observed d-spacings marked with an asterisk in the table above. All calculated spacings ≥ 1.750 Å permitted by the space group are listed. Calculated spacings less than 1.750 Å are listed only if uniquely indexed to an observed reflection.

TABLE 2—(continued)

I ²	d(meas.)	c(calc.) ³	hkl	I ²	d(meas.)	c(calc.) ³	hkl
		2.266	223	9	1.327		
10	2.241*	2.244	302	9	1.309		
		2.222	206	5	1.280		
		2.210	117	7	1.264		
14	2.201*	2.204	310	7	1.255		
		2.186	311	5	1.241		
14	2.161*	2.163	008	7	1.227		
		2.155	303	8	1.218		
		2.141	224	8	1.207		
12	2.137*	2.136	312	7	1.191		
14	2.115*	2.111	216	6	1.182		
11	2.065*	2.066	108	5	1.172		
		2.059	313	9	1.158		
14	2.045*	2.047	304	8	1.150		
		2.016	207	5	1.138		
		2.007	225				
14	1.981*	1.981	118				
		1.964	314				

structure directly to full-matrix least-squares analysis. The $0kl$ data, consisting of 126 non-zero terms, were subjected to four cycles of refinement using an overall temperature factor. The reliability factor,

$$R = \frac{\sum | |F_o| - |F_c| |}{\sum |F_o|},$$

dropped from 30.0 to 8.3% during this refinement. There were some large shifts in the positions of the oxygen atoms and small shifts in the heavy atom positions. Interatomic distances calculated from these new atomic positions seemed plausible and with the low R-factor it appeared that most of the atoms had been correctly positioned.

A heavy-atom subtraction map, projected on (100), was then prepared by subtracting the calculated contributions of the copper, uranium, and phosphorus atoms to the structure factors from the observed structure factors. This subtraction map showed clearly all the oxygen atoms in the structure.

It appeared at this point that meta-torbernite has essentially the same structure as abernathyite with the following exceptions: (1) the center of two of the four squares of water molecules are occupied by copper; (2) no atoms substitute for H_2O ; (3) the 16 water molecules and 16 phosphate oxygens lie in four eight-fold positions instead of two sixteen-fold positions, which permits a different configuration of water molecules in the two $Cu(H_2O)_4$ squares than is found in the two $(H_2O)_4$ squares.

Next, the least-squares refinement was continued using three-dimen-

sional data. The classes of data used in this refinement are given in Table 3. For this least-squares analysis the following atomic scattering factors were used: U^0 from Thomas and Umeda (1957) reduced uniformly by 5.6 electrons for anomalous dispersion, O^0 from Berghuis and others (1955), and P^0 and Cu^0 from *Internationale Tabellen* (1935). After four cycles of three-dimensional least-squares refinement were completed using an overall temperature factor it was found that the hkl data with l odd would not refine below an R factor of 43%. Since only the copper atoms, the phosphate oxygen atoms, and the water molecules contribute appreciably to these structure factors, it was apparent that there was a

TABLE 3. INTENSITY DATA USED FOR FINAL LEAST-SQUARES ANALYSIS OF META-TORBERNITE

hkl	F > 0	F = 0
<i>hk0</i>	35	1
<i>hk1</i>	57	9
<i>hk2</i>	79	3
<i>hk3</i>	35	11
<i>hk4</i>	59	27
<i>hk5</i>	29	9
<i>0kl</i> ¹	100	63
<i>1kl</i> ¹	158	179
<i>2kl</i> ¹	120	193
	672	495

¹ Redundant reflections not included.

significant error in the positioning of one or more of these atoms. It was observed that the water molecule O_7 was positioned with an x coordinate of 0.160 cycle. With this parameter, hydrogen-bonding of the O_7 water molecules to the O_5 phosphate oxygen atoms is not possible. Since in tetragonal structures there is often an ambiguous solution to the x or y parameters if two-dimensional data are used, it was thought that the x parameter of O_7 should be 0.340, not 0.160 cycle. To test this new model, three-dimensional least-squares analysis was carried out using only the *hk1*, *hk3*, and *hk5* data. With this new parameter the refinement of these data proceeded smoothly, the R-factor dropping from 43% to 19% in nine cycles.

Least-squares analysis was then continued with the full three-dimensional data for seven more cycles starting with the coordinates and individual temperature factors given by the 9th cycle of the previous refinement. The refinement then proceeded satisfactorily to completion.

The final reliability factor is 9.7% for the complete set of non-zero three-dimensional data consisting of 672 terms. The final R-factor for the $hk1$, $hk3$, and $hk5$ data is 16.0%. The higher R-factor for these data is to be expected because the structure factors of these reflections are very small. Table 4 gives the final atomic parameters for the meta-torbernite structure as given by the last cycle of refinement. Table 5 gives the bond distances and bond angles and their standard errors.

As mentioned previously, and also as discussed in connection with the abernathyite structure problem, many tetragonal structures give ambiguous solutions to the x or y parameters of certain equivalent positions if only two-dimensional data are used. The meta-torbernite structure offers a similar problem. Here Fourier projections on (100) cannot distinguish between the positions x and $(\frac{3}{2}) - x$ for atoms O_5 and O_6 , and the positions x and $(\frac{1}{2}) - x$ for atoms O_7 and O_8 . The low R-factor of 16.0% for the $hk1$, $hk3$, and $hk5$ data seemed to indicate that the final model, with hydrogen bonds between O_8 and O_7 , O_8 and O_6 , O_7 and O_7 , and O_7 and O_5 , is the correct one. Although the procedure described above was expected to give the correct structure model it was thought that an independent test of all the possible models should be made, in view of the possibility of a false minimum in the refinement procedure. The sixteen possible models were tested by taking the parameters given by the last cycle of three-dimensional refinement and calculating the R-factor of the $hk1$, $hk3$, and $hk5$ structure factors. The various models were formed by taking the various combinations of

O_5 at $x=0.7834$ or 0.7166 (aA),
 O_6 at $x=0.7038$ or 0.7962 (bB),
 O_7 at $x=0.3476$ or 0.1524 (cC), and
 O_8 at $x=0.2225$ or 0.2775 cycles (dD).

Table 7 gives the various models, the R-factors obtained, and the H-bonds formed by the particular model. As can be seen, the model (abcd) gives by far the lowest reliability factor. A shift of the x parameter of O_8 by 0.055 cycles raises the R-factor to 23%—a significant increase for such a small displacement of one atom. The other models give even higher R-factors. Four models permit hydrogen bonds between all water molecules and phosphate oxygen atoms but only one, (abcd), gives a low R-factor of 16.0%. This test clearly shows that the model (abcd) given by the three-dimensional refinement is the correct one.

As an additional test to see if the three-dimensional least-squares refinement truly proceeded to convergence, the correlation matrix was examined for large coefficients indicative of interactions between the positional parameters (Geller, 1961). The standard errors of the inter-

TABLE 4. FINAL ATOMIC PARAMETERS AND STANDARD ERRORS FOR META-TORBERNITE, $\text{Cu}(\text{UO}_2\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}^1$

Atom	Position	Parameters ²	Standard Error ³
O ₁	2c	$x = \frac{1}{4}$	—
		$y = \frac{1}{4}$	—
		$z = 0.1564$	0.0045
		$B = 1.58$	0.95
O ₂	2c	$x = \frac{1}{4}$	—
		$y = \frac{1}{4}$	—
		$z = 0.6563$	0.0043
		$B = 1.22$	0.84
O ₃	2c	$x = \frac{1}{4}$	—
		$y = \frac{1}{4}$	—
		$z = 0.9488$	0.0037
		$B = 0.67$	0.75
O ₄	2c	$x = \frac{1}{4}$	—
		$y = \frac{1}{4}$	—
		$z = 0.4403$	0.0041
		$B = 1.54$	1.07
O ₅	8g	$x = 0.7834$	0.0036
		$y = 0.0802$	0.0035
		$z = 0.4466$	0.0019
		$B = 1.59$	0.42
O ₆	8g	$x = 0.7038$	0.0029
		$y = 0.0818$	0.0026
		$z = 0.9486$	0.0014
		$B = 0.40$	0.28
O ₇ (H ₂ O)	8g	$x = 0.3476$	0.0039
		$y = 0.9814$	0.0039
		$z = 0.3105$	0.0024
		$B = 2.74$	0.52
O ₈ (H ₂ O)	8g	$x = 0.2225$	0.0038
		$y = 0.9768$	0.0039
		$z = 0.8095$	0.0024
		$B = 2.62$	0.52
P ₁	2a	$x = \frac{1}{4}$	—
		$y = \frac{3}{4}$	—
		$z = 0$	—
		$B = 0.136$	0.196
P ₂	2b	$x = \frac{1}{4}$	—
		$y = \frac{3}{4}$	—

¹ Space group $P4/n$ (No. 85b), origin at $\bar{1}$. A complete list of the observed and calculated structure factors for meta-torbernite may be found in Ross (1962) or may be obtained by writing the authors.

² Atomic coordinates in cycles, the temperature factor B in \AA^2 .

³ The standard errors of the atomic parameters which are refined by the method of least squares are evaluated with the relationships given by Clark *et al.* (1962, p. 213).

TABLE 4—(continued)

Atom	Position	Parameters ²	Standard Error ³
Cu	2c	$z = \frac{1}{2}$	—
		$B = 0.133$	0.195
		$x = \frac{1}{4}$	—
		$y = \frac{1}{4}$	—
U ₁	2c	$z = 0.8099$	0.0007
		$B = 1.058$	0.151
		$x = \frac{1}{4}$	—
		$y = \frac{1}{4}$	—
U ₂	2c	$z = 0.0510$	0.0002
		$B = 0.7571$	0.0476
		$x = \frac{1}{4}$	—
		$y = \frac{1}{4}$	—
		$z = 0.5524$	0.0002
		$B = 0.6269$	0.0443

atomic distances were computed both with and without the terms involving correlations between positional parameters. In no case was there a significant difference between the two values thus obtained for each standard error. This shows that there is no significant interaction between positional parameters. The possibility of large correlations between temperature and positional parameters was not investigated directly, but the apparent convergence of all parameters makes such correlations unlikely.

DESCRIPTION OF THE META-TORBERNITE STRUCTURE

The structural scheme of meta-torbernite, projected on (100) and (001), is shown in Fig. 1 and 2, respectively. If we compare these figures to those of abernathyite (Figs. 4 and 5 of Part I) we see that the two structures are quite similar.

The most interesting feature of this structure is the copper coordination and the associated hydrogen-bonding. The two copper atoms in the unit cell lie at the center of squares of four water molecules, one at $\frac{1}{4}, \frac{1}{4}, 0.810$, and one at $\frac{3}{4}, \frac{3}{4}, 0.190$ cycles. The distance between the copper atom and each water molecule of the square is 1.91 Å. This unusually short distance indicates a rather strong covalent copper-oxygen bond. The water molecules here must be highly polarized with a rather large positive charge directed away from the copper atom. Short copper-water bonds have been discovered in the compounds $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ (Geller and Bond, 1958), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Peterson and Levy, 1957) and $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$

TABLE 5. BOND DISTANCES AND BOND ANGLES IN META-TORBERNITE

Bond ¹	Multiplicity	Length (angle) ²	Standard Error ³
I. Uranyl ions			
U ₁₋₁ -O ₁₋₁	2	1.82 Å	0.08 Å
U ₁₋₁ -O ₃₋₁	2	1.77 Å	0.07 Å
O ₁₋₁ -O ₃₋₁	2	3.59 Å	0.15 Å
O ₃₋₁ -U ₁₋₁ -O ₁₋₁	2	180°	0
U ₂₋₁ -O ₂₋₁	2	1.80 Å	0.07 Å
U ₂₋₁ -O ₄₋₁	2	1.94 Å	0.07 Å
O ₂₋₁ -O ₄₋₁	2	3.74 Å	0.14 Å
O ₄₋₁ -U ₂₋₁ -O ₂₋₁	2	180°	0
II. PO₄ ions			
P ₁₋₂ -O ₆₋₁	8	1.51 Å	0.02 Å
O ₆₋₁ -P ₁₋₂ -O ₆₋₃	4	107.6°	1.7°
O ₆₋₁ -P ₁₋₂ -O ₆₋₆	8	110.4°	0.9°
O ₆₋₁ -O ₆₋₆	8	2.47 Å	0.04 Å
O ₆₋₁ -O ₆₋₃	4	2.43 Å	0.04 Å
P ₂₋₂ -O ₅₋₁	8	1.52 Å	0.03 Å
O ₅₋₁ -P ₂₋₂ -O ₅₋₃	4	105.1°	2.2°
O ₅₋₁ -P ₂₋₂ -O ₅₋₆	8	111.7°	1.2°
O ₅₋₁ -O ₅₋₆	8	2.51 Å	0.06 Å
O ₅₋₁ -O ₅₋₃	4	2.41 Å	0.04 Å
III. UO₂-PO₄ environment			
U ₁₋₁ -O ₆₋₆	2	2.33 Å	0.02 Å
O ₆₋₆ -U ₁₋₁ -O ₁₋₁	2	89.8°	0.6°
U ₂₋₁ -O ₅₋₆	2	2.31 Å	0.03 Å
O ₅₋₆ -U ₂₋₁ -O ₂₋₁	2	89.6°	0.8°
O ₆₋₆ -O ₁₋₁	8	2.96 Å	0.05 Å
O ₆₋₆ -O ₃₋₁	8	2.93 Å	0.05 Å
O ₆₋₁ -O ₃₋₁	8	3.37 Å	0.02 Å
O ₆₋₆ -O ₆₋₄	4	3.30 Å	0.03 Å
O ₆₋₆ -O ₆₋₅	4	3.54 Å	0.04 Å
O ₅₋₆ -O ₂₋₁	8	2.92 Å	0.05 Å
O ₅₋₆ -O ₄₋₁	8	3.03 Å	0.05 Å
O ₅₋₃ -O ₄₋₁	8	3.46 Å	0.03 Å
O ₅₋₆ -O ₅₋₄	4	3.27 Å	0.03 Å

¹ Atomic positions are given in Table 6.

² All interatomic distances less than 3.70 Å are listed.

³ The standard errors of the interatomic distances were calculated with a computer program written by D. S. Handwerker which is based on relationships given by Busing and Levy (1959, p. 4, 5).

⁴ Hydrogen bonds.

TABLE 5—(continued)

Bond ¹	Multiplicity	Length (angle) ²	Standard Error ³
O ₃₋₁ -P ₁₋₃	4	3.59 Å	0.01 Å
O ₄₋₁ -P ₂₋₂	4	3.63 Å	0.01 Å
IV. Cu environment			
Cu ₁ -O ₈₋₃	8	1.91 Å	0.03 Å
O ₈₋₃ -Cu ₁ -O ₈₋₁	4	179.6°	2.6°
O ₈₋₃ -Cu ₁ -O ₈₋₅	8	90.0°	0.0°
Cu ₁ -O ₈₋₁	2	2.40 Å	0.07 Å
Cu ₁ -O ₂₋₁	2	2.66 Å	0.07 Å
Cu ₂ -O ₇₋₅	2	3.84 Å	0.03 Å
V. H ₂ O environment			
O ₇₋₆ -O ₇₋₄	8	2.81 Å ⁴	0.04 Å
O ₇₋₆ -O ₈₋₃	8	2.67 Å ⁴	0.05 Å
O ₇₋₆ -O ₅₋₄	8	2.77 Å ⁴	0.05 Å
O ₇₋₄ -O ₇₋₆ -O ₇₋₂	8	90°	0°
O ₇₋₄ -O ₇₋₆ -O ₈₋₃	8	109.8°	1.1°
O ₇₋₂ -O ₇₋₆ -O ₈₋₃	8	122.0°	1.1°
O ₇₋₄ -O ₇₋₆ -O ₅₋₄	8	112.0°	1.0°
O ₇₋₂ -O ₇₋₆ -O ₅₋₄	8	112.0°	1.0°
O ₈₋₃ -O ₇₋₆ -O ₅₋₄	8	109.5°	1.3°
O ₈₋₃ -O ₈₋₅	8	2.70 Å	0.04 Å
O ₈₋₃ -O ₆₋₅	8	2.89 Å ⁴	0.05 Å
O ₈₋₅ -O ₈₋₃ -O ₈₋₇	8	90°	0°
O ₈₋₅ -O ₈₋₃ -O ₇₋₆	8	85.7°	1.1°
O ₈₋₇ -O ₈₋₃ -O ₇₋₆	8	128.7°	0.9°
O ₈₋₅ -O ₈₋₃ -O ₆₋₅	8	97.1°	1.0°
O ₈₋₇ -O ₈₋₃ -O ₆₋₅	8	122.6°	0.8°
O ₇₋₆ -O ₈₋₃ -O ₆₋₅	8	108.7°	1.2°
O ₈₋₁ -O ₈₋₃	8	3.18 Å	0.04 Å
O ₈₋₁ -P ₁₋₃	8	3.66 Å	0.03 Å
O ₇₋₁ -O ₇₋₃	8	3.50 Å	0.04 Å
O ₇₋₁ -O ₈₋₂	8	3.65 Å	0.05 Å
O ₇₋₁ -O ₂₋₈	8	3.56 Å	0.04 Å
O ₇₋₃ -O ₁₋₁	8	3.33 Å	0.07 Å
O ₇₋₃ -O ₄₋₁	8	3.00 Å	0.06 Å
O ₇₋₆ -O ₂₋₁	8	3.28 Å	0.04 Å
O ₇₋₆ -O ₅₋₂	8	3.52 Å	0.04 Å
O ₈₋₃ -O ₃₋₁	8	3.08 Å	0.06 Å
O ₈₋₃ -O ₂₋₁	8	3.27 Å	0.07 Å
O ₈₋₃ -O ₁₋₂	8	3.70 Å	0.03 Å
O ₈₋₃ -O ₆₋₇	8	3.36 Å	0.04 Å

TABLE 6. ATOMIC POSITIONS¹ FOR ATOMS LISTED IN TABLE 5

Atom	Position	Atom	Position
U ₁₋₁	x, y, z	O ₆₋₄	$x - \frac{1}{2}, \frac{1}{2} + y, 1 - z$
U ₂₋₁	x, y, z	O ₆₋₅	$\frac{1}{2} - y, x, z - 1$
P ₁₋₂	$\frac{1}{2} + x, y - \frac{1}{2}, z$	O ₆₋₆	$\frac{1}{2} + y, 1 - x, 1 - z$
P ₁₋₃	$x, y, 1 + z$	O ₆₋₇	$y, \frac{3}{2} - x, z$
P ₂₋₂	$\frac{1}{2} + x, y - \frac{1}{2}, z$	O ₇₋₁	x, y, z
Cu ₁	x, y, z	O ₇₋₂	$1 - x, 2 - y, 1 - z$
O ₁₋₁	x, y, z	O ₇₋₃	$\frac{1}{2} + x, \frac{3}{2} - y, z$
O ₂₋₁	x, y, z	O ₇₋₄	$\frac{1}{2} + x, y - \frac{1}{2}, 1 - z$
O ₃₋₁	$x, y, z - 1$	O ₇₋₆	$y - \frac{1}{2}, 1 - x, 1 - z$
O ₄₋₁	x, y, z	O ₈₋₁	$x, y - 1, z$
O ₁₋₂	$\frac{1}{2} + x, \frac{1}{2} + y, 1 - z$	O ₈₋₂	$1 - x, 2 - y, 1 - z$
O ₅₋₁	x, y, z	O ₈₋₃	$\frac{1}{2} - x, \frac{3}{2} - y, z$
O ₅₋₂	$1 - x, 1 - y, 1 - z$	O ₈₋₅	$\frac{3}{2} - y, x, z$
O ₅₋₃	$\frac{3}{2} - x, \frac{1}{2} - y, z$	O ₈₋₇	$y - 1, \frac{1}{2} - x, z$
O ₅₋₄	$x - \frac{1}{2}, \frac{1}{2} + y, 1 - z$	O ₈₋₈	$1 - y, 1 - x, 1 - z$
O ₅₋₆	$\frac{1}{2} + y, 1 - x, 1 - z$	O' ₈₋₁	x, y, z
O ₆₋₁	x, y, z		
O ₆₋₃	$\frac{3}{2} - x, \frac{1}{2} - y, z$		

¹ The equivalent positions are taken from *International Tables*, 1952, p. 175, Space group $P4/n$, No. 85b.

TABLE 7. TEST OF THE POSSIBLE STRUCTURE MODELS FOR META-TORBERNITE USING $hk1$, $hk3$, AND $hk5$ DATA

Model	R-factor	H-bonds formed ¹
abcd	16.0%	O ₇ -O ₇ , O ₇ -O ₈ , O ₇ -O ₅ , O ₈ -O ₆
ABCD	50.9	O ₇ -O ₇ , O ₇ -O ₈ , O ₇ -O ₅ , O ₈ -O ₆
aBcd	34.0	O ₇ -O ₇ , O ₇ -O ₃ , O ₇ -O ₅
AbCD	43.3	O ₇ -O ₇ , O ₇ -O ₈ , O ₇ -O ₅
Abcd	29.9	O ₇ -O ₇ , O ₇ -O ₈ , O ₈ -O ₆
aBCD	44.5	O ₇ -O ₇ , O ₇ -O ₈ , O ₈ -O ₆
ABcd	37.2	O ₇ -O ₇ , O ₇ -O ₈
abCD	37.4	O ₇ -O ₇ , O ₇ -O ₈
abcD	23.1	O ₇ -O ₇ , O ₇ -O' ₈ , O ₇ -O ₅
ABCd	42.3	O ₇ -O ₇ , O ₇ -O' ₈ , O ₇ -O ₅
abCd	29.3	O ₇ -O ₇ , O ₇ -O' ₈ , O ₈ -O ₆
ABcD	44.5	O ₇ -O ₇ , O ₇ -O' ₈ , O ₈ -O ₆
aBcD	37.0	O ₇ -O ₇ , O ₇ -O' ₈ , O ₇ -O ₅ , O ₈ -O ₆
AbCd	35.2	O ₇ -O ₇ , O ₇ -O' ₈ , O ₇ -O ₅ , O ₈ -O ₆
aBCd	36.2	O ₇ -O ₇ , O ₇ -O' ₈
AbcD	33.8	O ₇ -O ₇ , O ₇ -O' ₈

¹ The bond lengths for the various possible hydrogen bonds are as follows: O₇-O₇ (2.81 Å), O₇-O₈ (2.67 Å), O₇-O'₈ (2.89 Å), O₇-O₅ (2.77 Å), and O₈-O₆ (2.89 Å). The values of the interatomic distances for O₇-O₈, O₇-O'₈, O₇-O₅, and O₈-O₆ in the unbonded settings are 3.38, 3.56, 3.30 and 3.22 Å respectively.

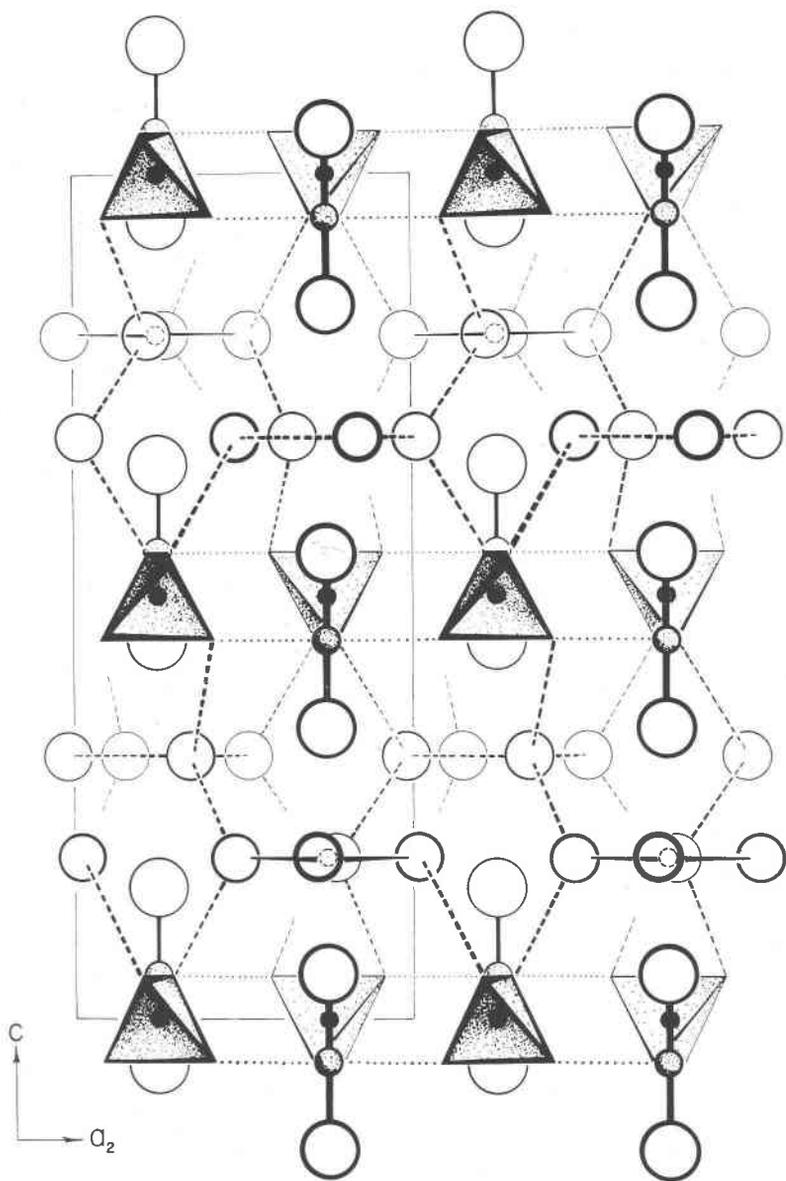


FIG. 1. Projection of the meta-torbernite structure on (100). The dotted lines indicate the uranium-phosphate oxygen bonds, the dashed lines indicate hydrogen bonds, and the solid lines indicate copper-water bonds. Large open circles, uranyl oxygens; smaller open circles, water molecules; small stippled circles, uranium atoms; small solid circles, phosphorus atoms; and small dashed circles, copper atoms.

(Gattow, 1958). In the very precisely determined $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ structures, copper-water bonds were found to be 1.93 and 1.925 Å respectively. A $\text{Cu-H}_2\text{O}$ bond of 1.94 Å was found in $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$.

The copper atom in meta-torbernite is also bonded to two uranyl oxygens O_2 and O_3 at 2.66 and 2.40 Å respectively. The next nearest atom to Cu is O_7 at 3.84 Å. The copper atom is within 0.007 Å of being exactly in the plane of the four O_8 water molecules. The $\text{O}_8\text{-Cu-O}_8$ angles are 179.6° and 90.0° . The planar coordination of copper with four bonds of 1.9 to 2.0 Å and two additional bonds of greater length to form an asymmetrical tetragonal dipyramid has been found in a large number of crystal structures: $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, and $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ are examples.

Eight additional water molecules form squares at $\frac{1}{4}$, $\frac{1}{4}$, 0.311 and $\frac{3}{4}$, $\frac{3}{4}$, 0.689 cycles. The H_2O molecules of these squares do not coordinate a cation. They are, however, hydrogen-bonded together as in abernathyite. The $\text{O}_7\text{-O}_7$ bond distance within these squares is 2.81 Å. The O_7 water

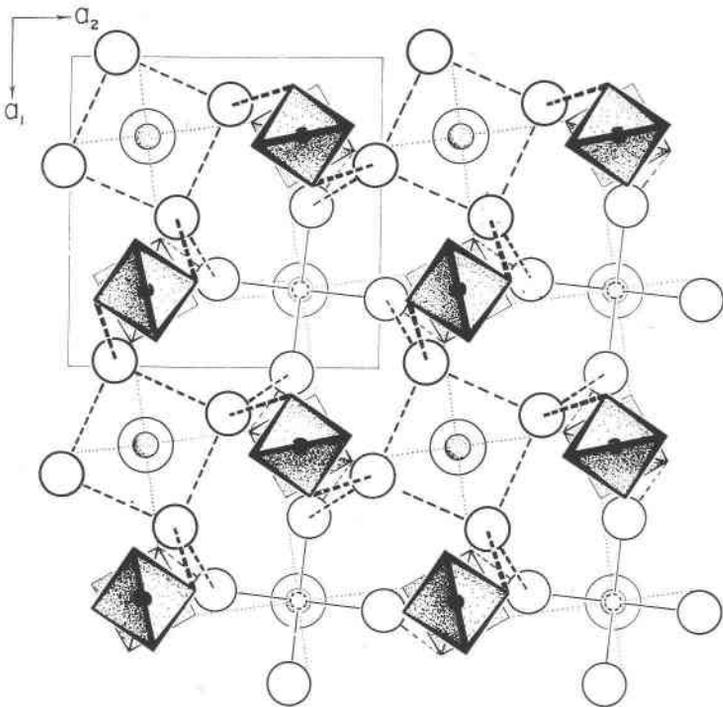


FIG. 2. Projection of the meta-torbernite structure on (001). The designation of the various bonds and atoms is the same as that given in Figure 1. Only the uranyl ions at ± 0.0510 cycles are shown.

molecules are also hydrogen-bonded to a phosphate oxygen O_5 (2.77 Å) and to an adjacent O_8 water molecule (2.67 Å). The O_8 water molecules of the $Cu(H_2O)_4$ squares are each hydrogen-bonded to an O_7 water molecule and to an O_6 phosphate oxygen atom (2.89 Å). Within the $Cu(H_2O)_4$ square the O_8 - O_8 distance is 2.70 Å. This short distance is not caused by hydrogen bonding but is the result of the close attraction of the H_2O molecules to the copper atom. The hydrogen bonds between O_7 and O_7 , O_7 and O_8 , O_7 and O_5 , and O_8 and O_6 account for all of the 32 protons in the unit cell. The next nearest atom to the O_7 water molecule is O_4 at 3.00 Å. The next nearest atom to the O_8 water molecule is O_3 at 3.08 Å. Thus, no hydrogen bonding between water molecules and uranyl oxygen atoms is indicated. About the O_7 water molecules lie two O_7 water molecules, one O_8 water molecule and one O_5 oxygen, in a distorted tetrahedral arrangement. The tetrahedral angles are 90° , 109.8° , 122.0° , 112.0° , 112.0° , and 109.5° . The average tetrahedral angle is 109.2° . About the O_8 water molecules lie two O_8 water molecules, an O_7 water molecule, an O_6 oxygen, and a copper atom. The water molecules and oxygen atoms are grouped about O_8 in a highly distorted tetrahedral arrangement. This distortion is due to the fact that O_8 is bonded only to the copper atom, the O_7 water molecule, and the O_6 oxygen. The O_6 - O_8 - O_7 , Cu - O_8 - O_7 , and Cu - O_8 - O_6 angles are 108.7° , 113.0° , and 117.7° , respectively.

The distribution of the positive charge on the copper atoms to the negatively charged $(UO_2PO_4)_n^{n-}$ sheets is accomplished through the copper-uranyl oxygen bonds (Cu - O_2 , Cu - O_3) and through the various hydrogen bonds. The $(UO_2PO_4)_n^{n-}$ sheet at $z=0$ contains the O_3 uranyl oxygen atoms and the O_6 phosphate oxygen atoms, whereas the sheet at $z=\frac{1}{2}$ contains the O_2 uranyl oxygen atoms and the O_5 phosphate oxygen atoms. Since the Cu - O_3 bond is shorter (2.40 Å) than the Cu - O_2 bond (2.66 Å) it is to be expected that a greater charge will be distributed through the uranyl oxygens to the sheet which lies at $z=0$. Each sheet must receive an equal charge; thus a greater positive charge must be transmitted through the hydrogen bonds to the sheet at $z=\frac{1}{2}$. This appears to be so, for the O_7 - O_5 H-bond (2.77 Å) is shorter than the O_8 - O_6 H-bond (2.89 Å).

The hydrogen bonding between the water molecules and the phosphate oxygen atoms causes a clockwise 15° rotation of the tetrahedra at $z=0$ and a counter-clockwise 11° rotation of the tetrahedra at $z=\frac{1}{2}$ as viewed down the c -axis. The system of hydrogen bonding is shown as dashed lines in Figs. 1 and 2. A similar rotation of tetrahedra was found in the abernathyite structure. The two types of tetrahedra in meta-torbernite are rotated through slightly different angles because of the requirements of

hydrogen-bonding to the two different types of water molecules, O_7 and O_8 . The P_1-O_6 and the P_2-O_5 bond lengths of 1.51 and 1.52 Å, respectively, compare very favorably with other determinations of this interatomic distance. The PO_4 tetrahedra are distorted with the horizontal edges somewhat shortened (2.41, 2.43 Å) and the other edges somewhat lengthened (2.51, 2.47 Å). The average $O_5-P_2-O_5$ angle is 108.4° and the average $O_6-P_1-O_6$ angle is 109.0° . The phosphate oxygen-uranium interatomic distances are 2.33 and 2.31 Å, in close agreement with the value of 2.35 Å found for the arsenate oxygen-uranium bond in abernathyite. The U_1 and U_2 atoms are not significantly displaced from the plane of the four phosphate oxygen atoms. The average uranium-uranyl oxygen bond distance is 1.83 Å. Since these bonds have a large standard error associated with them (0.07–0.08 Å), the variation of these interatomic distances cannot be considered significant. The value of 1.94 Å obtained for U_2-O_4 is anomalously large.

The asymmetrical environment of the UO_2^{2+} ions found in abernathyite is retained in meta-torbernite. O_1 is adjacent to four O_6 atoms at 2.96 Å, and eight water molecules (four at 3.33 Å, and four at 3.70 Å). O_2 is associated with the copper atom at 2.66 Å, with four phosphate oxygens at 2.92 Å, and with eight H_2O molecules (four at 3.27 and four at 3.28 Å). O_3 is associated with the copper atom at 2.40 Å, with four water molecules at 3.08 Å, and with eight phosphate oxygen atoms (four at 2.93 Å and four at 3.37 Å). The O_4 atoms are adjacent to four water molecules (3.00 Å), and to eight phosphate oxygen atoms (four at 3.03 Å and four at 3.46 Å).

Makarov and Tobelko (1960) examined the crystal structure of meta-torbernite with $0kl$ intensity data gathered by Weissenberg techniques. These workers confirm the sheet structure proposed by Beintema (1938) for these compounds. They also propose that the copper atoms are coordinated in a square-planar arrangement by four water molecules. The placement of the uranium and phosphorus atoms is essentially the same as that found in the present study. However, the details of their structure cannot be considered correct for, by not examining the $hk1$ reciprocal lattice plane, they mistakenly assumed that $4/mmm$ Laue symmetry exists and they thus assigned the mineral to space group $P4/nmm$ instead of $P4/n$. This error forced them to propose a false statistical distribution of the two copper atoms over four sites and also made it impossible to obtain correct positions for the phosphate oxygen atoms and the water molecules. Ross (1963) discusses the problems encountered in determining the true symmetries of the torbernite minerals and gives examples of how serious errors can be made in deducing the positions of the light atoms when the correct symmetry is not found. In the case of meta-

torbernite the uranium, phosphorus, copper, and uranyl oxygen atoms occupy positions compatible with the higher $4/mmm$ Laue symmetry. The contributions of these atoms to the structure factors so dominate the hkl reflections when $l = 2n$ that the true $4/m$ Laue symmetry is completely obscured. Only by carefully examining the reflections where l is odd, to which only the copper atoms, the phosphate oxygen atoms and the water molecules appreciably contribute, can the true symmetry be observed.

META-ZEUNERITE

The structure of the arsenate analogue of meta-torbernite, meta-zeunerite, $\text{Cu}(\text{UO}_2\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, has been reported by Hanic (1960). He

TABLE 8. UNIT-CELL DATA AND PROPERTIES FOR META-ZEUNERITE,
 $\text{Cu}(\text{UO}_2\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$

	Present study	Hanic (1960)
System	Tetragonal	Tetragonal
a (Å)	7.12	7.10 ₅
c (Å)	17.45	17.70 ₄
Laue Group	$4/m$ (probable)	$4/mmm$
Space Group	$P4/n$ (probable)	$P4_2/nmc$
V (Å ³)	884.6	893.7
Z	2	2
Density (calc.) g/cm ³	3.85	3.81
ϵ	1.635 ± 0.005	—
ω	1.650 ± 0.005	—
Forms	{100}, {001}	—
Locality	Majuba Hill, Nevada (U.S.N.M. R8738)	Rotava, Czechoslovakia (Nat. Museum No. 30365)

proposes a structure which differs significantly from that of meta-torbernite, reported here. The unit-cell data measured by Hanic are given in Table 8. The choice of space group $P4_2/nmc$ forces Hanic to distribute two copper atoms over four positions ($4d$), and two sets of eight water molecules over two 16-fold positions ($16h$). He confirms Beintema's proposed structure for the $(\text{UO}_2\text{XO}_4)_n^{n-}$ layer and also finds the copper atoms coordinated by four water molecules in a square-planar arrangement. Hanic also states that hydrogen-bonds are formed between the water molecules and the uranyl oxygen atoms. He gives values of 1.94 and 1.78 Å for the uranium-uranyl oxygen bonds; 2.55 and 2.58 Å for the copper-uranyl oxygen bonds; 2.18 Å for the uranium-arsenate oxygen distance; 2.14 Å for the copper-water bond; and 1.77 Å for the arsenic-arsenate oxygen bond.

It is strongly suspected that meta-zeunerite is isostructural with meta-torbernite and that the details of Hanic's structure are incorrect. In order to check the crystallography found by Hanic, a number of so-called meta-zeunerites were examined. Only one sample, that from Majuba Hill, Nevada, appeared to contain significant amounts of arsenic. Semiquantitative *x*-ray fluorescence analysis (F. J. Flanagan, analyst) showed major amounts of uranium, copper and arsenic to be present. There is probably a minor amount of phosphorus substituting for arsenic in this sample. We did not have enough material to confirm this analytically.

The unit-cell data as determined by the precession technique are compared to Hanic's data in Table 8. The crystals examined are dull-green in color and showed cracks which may be evidence of an earlier dehydration. The condition limiting the possible reflections is:

$$hk0: h + k = 2n$$

The *hk1* photographs show evidence for $4/m$ Laue symmetry; thus the probable space group is $P4/n$ —the same as that found for metatorbernite. The present study suggests that meta-zeunerite is isostructural with meta-torbernite, although until crystals of higher quality than those obtained for this study are found the question will remain in doubt.

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