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A CRYSTAL-STRUCTURE REFINEMENT OF LIBETHENITE

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ABSTRACT

Three-dimensional single-crystal counter-diffractometer X-ray data and a least-squares method have been used to refine the crystal structure of libethenite, $Cu_2(OH)PO_4$, *a* 8.062(5), *b* 8.384(4), *c* 5.881(2)Å, space group *Pnnm*. The final *R* index is 3.1% for 945 observed reflections. Libethenite has copper in two coordinations and is isotypic with andalusite and the minerals of the olivenite group. Chains of edge-sharing $CuO_4(OH)_2$ octahedra extend parallel to the *c* axis and are linked by corner-sharing PO_4 tetrahedra to form channels in that direction. The octahedra, which are elongate due to the Jahn-Teller effect, share corners with pairs of edge-sharing $CuO_4(OH)$ trigonal bipyramids that occur in these channels. The position for the hydrogen atom, resulting in a bifurcated hydrogen bonding model, is proposed as x 0.43, y 0.73, z 0.

SOMMAIRE

La structure cristalline de la libéthénite $Cu_2(OH)PO_4$ a été affinée dans le groupe *Pnnm* et la maille *a* 8.062(5), *b* 8.384(4), *c* 5.881(2)Å, par la méthode des moindres carrés sur données tridimensionnelles obtenues aux rayons X sur diffractomètre à compteur. Le résidu final est $R=0.031$ pour les 945 réflexions observées. La structure contient le cuivre en deux coordinations; elle est isotype de celle de l'andalousite et des minéraux du groupe de l'olivénite. Des chaînes d'octaèdres $CuO_4(OH)_2$ à arêtes mises en commun s'allongent parallèlement à l'axe *c* et elles sont reliées par des tétraèdres PO_4 à sommets communs de façon à former des tunnels dans cette direction. Les octaèdres, allongés à cause de l'effet Jahn-Teller, ont des sommets communs avec des paires de bipyramides trigonales à arêtes partagées qui occupent les tunnels. L'atome d'hydrogène, placé en x 0.43, y 0.73, z 0, donne une liaison hydrogène bifurquée.

(Traduit par la Rédaction)

INTRODUCTION

The orthorhombic mineral libethenite, $Cu_2(PO_4)(OH)$, occurs in the oxidized zone of ore deposits associated with malachite, $Cu_2(CO_3)(OH)_2$, azurite, $Cu_3(CO_3)_2(OH)_2$, pyromorphite, $Pb_5(PO_4)_3Cl$ and limonite (Palache *et al.* 1951). The crystal structure was solved by Heritsch (1940) using intensities measured on two Weissenberg and two rotation photographs; a two-dimensional refinement was given by Walitzi (1963b) using Weissenberg data. The structure of libethenite has been refined here to improve its *R* index and to confirm its isotypy with andalusite and minerals of the olivenite group.

EXPERIMENTAL

The transparent, light green crystals used in this study are from Libethen, Hungary. Bergemann (1858) reports the following composition for crystals from Libethen: CuO 66.29, P_2O_5 26.46, As_2O_5 2.3 and H_2O 4.04 wt.%, total 99.09 wt.%. Precession and Weissenberg photographs display systematic absences $h0l$, $h+l=2n+1$; $0kl$, $k+l=2n+1$. As a piezoelectric effect has never been observed (Strunz 1936), libethenite is assumed to be centric, with the space group *Pnnm*. The cell parameters calculated from precession photographs agree well with those determined by a least-square refinement of 40 high-angle reflections measured on a single-crystal diffractometer. Cell parameters calculated from earlier precession photographs with different crystals agree with the values of Strunz (1936) and Walitzi (1963a), but the spots on these photographs are not uniform; the new values (Table 1) are thought to be more accurate. For the intensity-data collection, graphite-monochromatized Mo$K\alpha$ radiation (λ 0.71069Å) was used on a four-circle diffractometer (modified Picker unit at CANMET, Ottawa). The reflections within a 2θ angle of 75° were measured for two octants in the θ-2θ scan mode. The intensities of the 1131 reflections of one octant agreed well with the intensities of the reflections of the other octant. An absorption correction was applied assuming a spherical shape for the nearly equidimensional crystal (μ 11.391mm^{-1}; Gabe & O'Byrne 1970). The data were corrected for Lorentz, polarization and background effects and then reduced to structure factors, on a relative scale. A list of observed and calculated struc-

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TABLE 1. MISCELLANEOUS INFORMATION

UNIT-CELL DIMENSIONS OF LIBETHENITE

a (Å)	b (Å)	c (Å)	
8.10	8.45	5.91	Strunz (1936)†
8.11	8.47	5.92	Walitzi (1963a)
8.061	8.388	5.882	This study, precession
8.062	8.384	5.881	This study, diffractometer
± .005	.004	.002	

FINAL R FACTORS

All 1131 reflections:	weighted R	0.055
	unweighted R	0.047
945 unrejected reflections:	weighted R	0.032
	unweighted R	0.031

$$R_w = [\Sigma w(|F_{obs}| - |F_{calc}|)^2/\Sigma w|F_{obs}|^2]^{\frac{1}{2}},\ w = 1$$

$$R = \Sigma(|F_{obs}| - |F_{calc}|)/\Sigma|F_{obs}|)$$

MISCELLANEOUS

Space group	$Pnnm$	Crystal size	0.0053 mm³
Cell volume	397.5 Å³	μ	11.391 mm⁻¹
Z	4	Radiation	Mo$K\alpha$
D_{calc}	3.972 g/cm³	Monochromator	C

† converted from kX units

ture factors is available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

REFINEMENT

The refinement process was carried out on the Burroughs B6700 at the Queen's University Computing Centre. The atomic X-ray scattering factors for Cu^{2+}, P, O^- and H^- were taken from Volume IV of the International Tables for X-ray Crystallography.

Walitzi (1963b) chose the position 2b (0,0,½) as the origin, whereas in this work 2a (0,0,0) is used. The positional parameters given by Walitzi (1963b) were used as input to the least-squares program RFINE (Finger 1969) taking into account the typographical error in Walitzi's paper for Cu(1). Its coordinates are given as x 0, y 0.5, z 0.25 instead of x 0, y 0, z 0.25. Several cycles of coordinate and anisotropic temperature-factor refinement with incorrect dispersion corrections (those for Cu$K\alpha$) led to an R of 6.3%. Three additional cycles using 945 reflections and the correct dispersion corrections (those for Mo$K\alpha$) in the refinement procedure (Table 1) lowered R to 3.1%. Reflections with net intensity $I<1.65\sigma(I)$ were classed as unobserved; 173 reflections were rejected. Thirteen additional reflections having ΔF greater than 5.0 were excluded from the final stages of the refinement process because no correction for extinction had been included. The standard deviation of an observation of unit weight for F_{obs} was 1.02 for the final cycle. The introduction of 2.3 wt. % As_2O_3, which Bergemann reported in the chemical analysis, did not improve the results of the refinement. At this stage, a difference map showed a small peak on the 2-fold axis in the expected position of the H atom. Introduction of the H position into the refinement did not reduce the R index, but the peak on the difference map disappeared. The hydrogen position is thus regarded as tentative and no errors are reported. All atomic parameters and anisotropic temperature factors are given in Table 2.

DISCUSSION OF THE STRUCTURE

The three important features of the libethenite structure are the anion polyhedra around Cu(1), Cu(2) and P. They are linked by either edge- or corner-sharing and run parallel to the c axis, producing a strong chain character. Cu(1) is octahedrally surrounded by six oxygen atoms (Table 3, Fig. 1). Four of the oxygen atoms occur at distances of less than 2.0Å; the O(1)

TABLE 2. ATOMIC POSITIONS AND ANISOTROPIC TEMPERATURE-FACTOR COEFFICIENTS ($\beta_{ij}\times10^5$Å²)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	0	0	0.24926(7)†	327(5)	379(4)	238(8)	-166(4)	0	0
Cu(2)	0.13828(6)	0.62472(6)	0	191(5)	345(5)	949(11)	21(4)	0	0
P	0.23270(10)	0.24835(11)	0	171(9)	185(8)	322(16)	-23(7)	0	0
O(1)	0.34057(26)	0.26073(25)	0.21117(33)	564(25)	471(23)	490(42)	-253(20)	-285(26)	182(26)
O(2)	0.13289(33)	0.08893(31)	0	309(28)	257(26)	266(47)	-127(23)	0	0
O(3)	0.10212(36)	0.38378(36)	0	206(30)	236(28)	2464(112)	8(26)	0	0
O(4)≡OH	0.37622(32)	0.60288(30)	0	205(27)	256(27)	493(51)	7(22)	0	0
H	0.426	0.726	0	B = 1.792 Å²					

† Standard deviations are given in parentheses

TABLE 3. SELECTED INTERATOMIC DISTANCES AND ANGLES

Cu(1)-O(1)	2.3938(9)Å	×2	Cu(2)-O(1)	2.0529(7)Å	×2
Cu(1)-O(2)	1.9628(5)	×2	Cu(2)-O(3)	2.0410(1)	
Cu(1)-O(4)	1.9785(22)	×2	Cu(2)-O(3)	1.9394(14)	
			Cu(2)-O(4)	1.9270(43)	
Mean	2.1117 Å		Mean	2.0026 Å	
P-O(1)	1.5200(5)Å	×2			
P-O(2)	1.5602(5)				
P-O(3)	1.5484(1)				
Mean	1.5371 Å				
Cu(1) octahedron					
O(1)-O(1)*	4.765 Å		O(1)-Cu(1)-O(1)*	168.84(2)°	
O(1)-O(2)	3.167	×2	O(1)-Cu(1)-O(2)	92.72(4)	×2
O(1)-O(2)	3.241	×2	O(1)-Cu(1)-O(2)	95.61(4)	×2
O(1)-O(4)	2.840	×2	O(1)-Cu(1)-O(4)	80.39(11)	×2
O(1)-O(4)	3.139	×2	O(1)-Cu(1)-O(4)	91.26(9)	×2
O(2)-O(2)	^{s}2.610		O(2)-Cu(1)-O(2)	83.36(2)	
O(2)-O(4)	2.944	×2	O(2)-Cu(1)-O(4)	96.65(8)	×2
O(2)-O(4)*	3.939	×2	O(2)-Cu(1)-O(4)*	176.00(8)	×2
O(4)-O(4)	^{s}2.638		O(4)-Cu(1)-O(4)	83.62(14)	
Mean	2.992 Å		Mean	90.02°	
Cu(2) trigonal bipyramid					
O(1)-O(1)	3.397 Å		O(1)-Cu(2)-O(1)	111.66(3)°	
O(1)-O(3)	2.966	×2	O(1)-Cu(2)-O(3)	95.94(1)	×2
O(1)-O(3)	3.618	×2	O(1)-Cu(2)-O(3)	124.17(1)	×2
O(1)-O(4)	2.773	×2	O(1)-Cu(2)-O(4)	88.29(1)	×2
O(3)-O(3)	^{s}2.551		O(3)-Cu(2)-O(3)	79.68(1)	
O(3)-O(4)	2.874		O(3)-Cu(2)-O(4)	92.76(1)	
O(3)-O(4)*	3.858		O(3)-Cu(2)-O(4)*	172.44(1)	
Mean	3.179 Å		Mean	101.10°	
P tetrahedron					
O(1)-O(1)	2.484 Å		O(1)-P-O(1)	109.61(4)°	
O(1)-O(2)	2.534	×2	O(1)-P-O(2)	110.71(2)	×2
O(1)-O(3)	2.510	×2	O(1)-P-O(3)	109.82(4)	×2
O(2)-O(3)	2.485		O(2)-P-O(3)	106.12(9)	
Mean	2.509 Å		Mean	109.30°	
Bifurcated hydrogen bonds					
O(1)-O(1)	2.484 Å		O(1)-H-O(1)	66.75°	
O(1)-O(4)	2.840	×2	O(1)-H-O(4)	110.38	×2

* value excluded from the average ^{s} shared edge
Standard deviations are given in parentheses

atoms are 2.394Å from the central Cu atom and form the top and bottom of the octahedron. Chains of these strongly elongate and distorted octahedra run parallel to the *c* axis, alternately sharing O(2)–O(2) and O(4)–O(4) octahedral edges (Fig. 2). The linkage between these chains is formed by nearly regular PO_4 tetrahedra. This arrangement results in Cu(2) atoms lying in channels that run parallel to the *c* axis. The Cu(2) atoms are five-coordinated with the oxygen atoms around them forming trigonal bipyramids. These unusual trigonal bipyramidal coordination polyhedra occur because the axial bonds of the Cu(1) octahedra are elongate due to the Jahn-Teller effect, very common for octahedral arrangements around copper atoms. The octahedra occur in layers at $z{\sim}\frac{1}{4}$ and $z{\sim}\frac{3}{4}$, and the linking phosphate tetrahedra and trigonal bipyramids around copper lie at $z=0$ and $z=\frac{1}{2}$. Two of the edge-sharing trigonal bipyramids within the channels provide the linkage between the phosphate levels at $z=0$ and $z=\frac{1}{2}$ (Fig. 2). The O(3)–O(3) edge is extremely contracted (2.55Å) in order to reduce the Cu(2)–Cu(2) repulsive interaction (*cf.*, Hawthorne 1976).

Due to the low residual of 3.1% in the present work, it is possible to propose a hydrogen-atom position. Refining the coordinates of a peak on the difference map as a hydrogen-atom position did not improve the *R* index, but the peak on the difference map was smoothed. Other possible positions are excluded by geometrical restrictions. This model involves a bifurcated hydrogen bond from octahedral to phosphate oxygens (*cf.*, Moore & Araki 1974). The hydrogen atom, being on a two-fold rotor, is 1.11Å away from O(4) and 2.26Å from each of the O(1) atoms.

The relationship between the usual orientation of the olivenite group of minerals and the orientation of libethenite used in this study is given by $[t_{ij}]$, the relevant transformation matrix:

$$[t_{ij}] = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Although the *a* axis would become longer than *b*, the structures have to be called isotypes. With

TABLE 4. MAGNITUDES AND ORIENTATIONS OF THE PRINCIPAL AXES OF THE THERMAL ELLIPSOIDS IN LIBETHENITE

Atom	Axis	RMS displacement	Angle (in degrees) to +*a*	+*b*	+*c*	Equivalent isotropic B
Cu(1)						0.748 Å^2
	1	0.065 Å	90	90	0	
	2	0.079	142	128	90	
	3	0.134	52	142	90	
Cu(2)						0.927
	1	0.079	7	97	90	
	2	0.111	97	173	90	
	3	0.129	90	90	0	
P						0.470
	1	0.072	29	61	90	
	2	0.075	90	90	180	
	3	0.084	119	29	90	
O(1)						1.156
	1	0.071	64	91	26	
	2	0.096	56	38	105	
	3	0.172	135	53	69	
O(2)						0.631
	1	0.068	90	90	0	
	2	0.073	132	138	90	
	3	0.119	42	132	90	
O(3)						1.536
	1	0.082	9	99	90	
	2	0.092	99	171	90	
	3	0.208	90	90	0	
O(4)						0.645
	1	0.082	6	96	90	
	2	0.093	90	90	180	
	3	0.096	84	6	90	

Equivalent isotropic B = $\frac{4}{3}\sum_{i}\sum_{j}\beta_{ij}(a_i\cdot a_j)$ (Hamilton 1959)

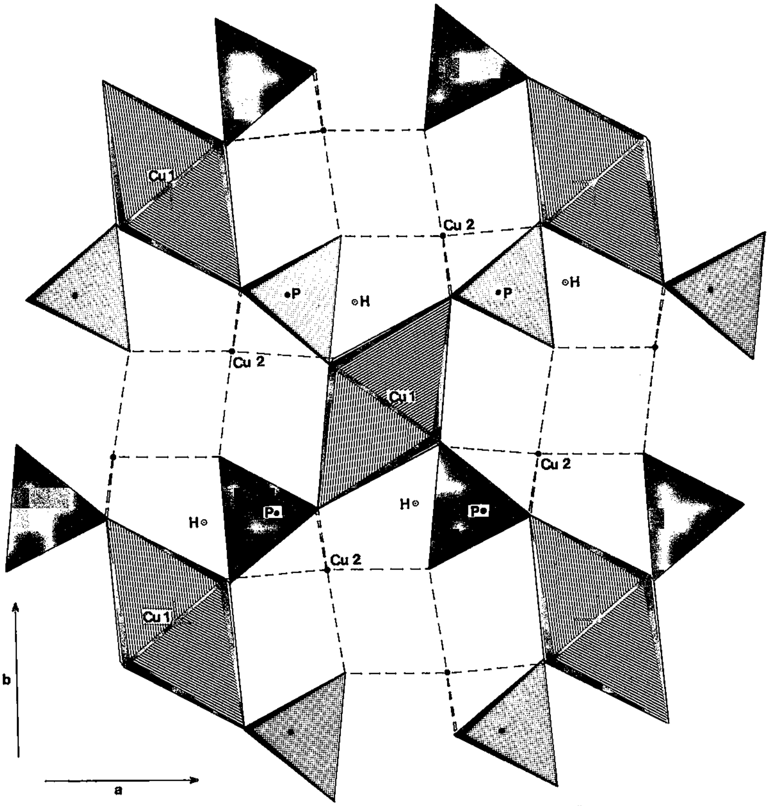

FIG. 1. The crystal structure of libethenite projected down the *c* axis.

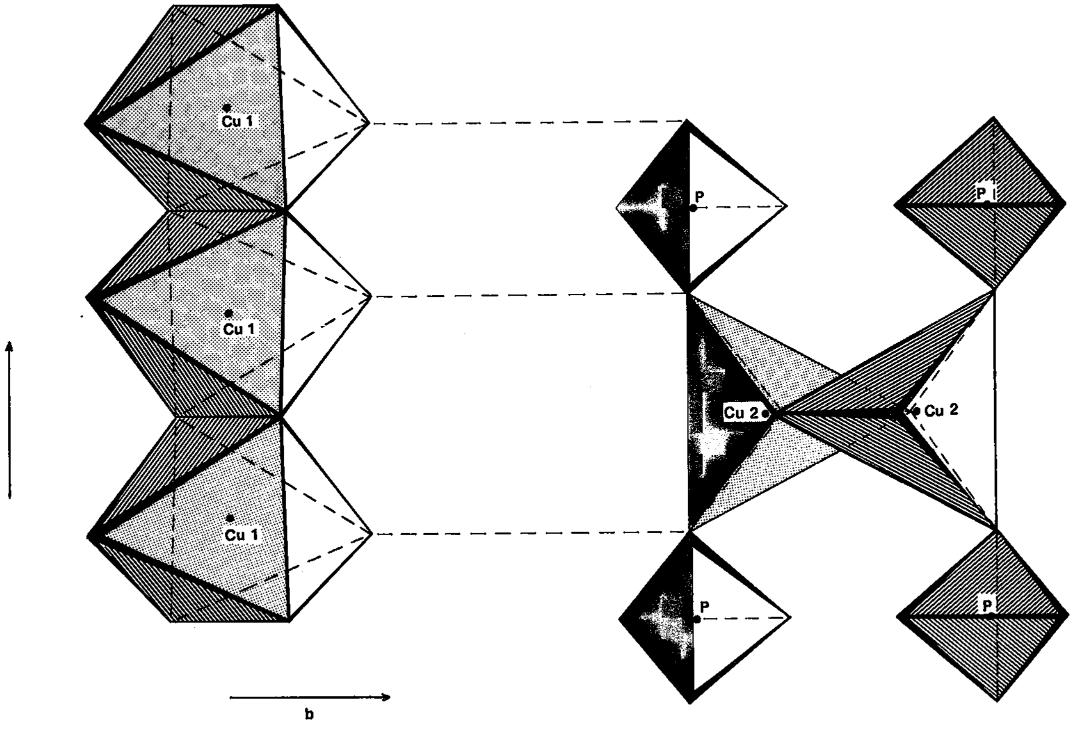

FIG. 2. A section of the crystal structure of libethenite projected down the *a* axis.

respect to the isotypy, the hydrogen atom position should be comparable as well. Hawthorne (1976) did not report any hydrogen-atom position in adamite but he proposes hydrogen bonding between O(4) and O(1) with an H–O(1) distance of 2.27Å (in the nomenclature of this paper).

Table 4 presents the ellipsoids of thermal vibration for each atom. Except for the O(1) atom, all atoms lie on special positions with one vibration axis parallel to the *c* axis and the remaining two constrained to the *a-b* plane (*cf.*, Hawthorne 1976).

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