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REFINEMENT OF THE STRUCTURE OF BANDYLITE

YAPING LI AND PETER C. BURNS[§]

Department of Civil Engineering and Geological Sciences, 156 Fitzpatrick Hall, University of Notre Dame,
Notre Dame, Indiana 46556-0767, U.S.A.

ABSTRACT

The structure of bandylite, $Cu_2[B(OH)_4]_2Cl_2$, $Z = 1$, tetragonal, *a* 6.171(2), *c* 5.587(3) Å, *V* 212.7 Å^3, space group *P*4/*n*, has been refined by full-matrix least-squares techniques on the basis of F^2 using 263 unique reflections collected with Mo*K*a X-radiation and a CCD (charge-coupled device) area detector. The final agreement factor (*R*1) was 3.7% and the goodness-of-fit (*S*) was 0.90 for the 144 unique observed reflections ($|F_o| > 4s_F$). The structure consists of mixed-ligand Jahn–Teller-distorted $Cu(OH)_4Cl_2$ octahedra and $B(OH)_4$ tetrahedra that are linked by vertex sharing.

Keywords: bandylite, borate, Cu oxysalt.

SOMMAIRE

Nous avons affiné la structure de la bandylite, $Cu_2[B(OH)_4]_2Cl_2$, $Z = 1$, tétragonal, *a* 6.171(2), *c* 5.587(3) Å, *V* 212.7 Å^3, groupe spatial *P*4/*n*, par moindres carrés sur matrice entière sur la base de F^2 en utilisant 263 réflexions uniques prélevées avec rayonnement Mo*K*α et un détecteur à aire et à charges couplées (CCD). Le résidu *R*1 final est égal à 3.7%, et l'indice de concordance *S* est 0.90 pour 144 réflexions uniques observées ($|F_o| > 4\sigma_F$). La structure contient des octaèdres $Cu(OH)_4Cl_2$, à ligands mixtes, rendus difformes à cause de l'effet Jahn–Teller, et des tétraèdres $B(OH)_4$ articulés par partage de coins.

(Traduit par la Rédaction)

Mots-clés: bandylite, borate, oxysel de cuivre.

INTRODUCTION

Bandylite, $Cu_2[B(OH)_4]_2Cl_2$, is a rare Cu^{2+} borate that was first described from Mina Quetena, near Calama, Antofagasta, Chile by Palache & Foshag (1938). Its structure was determined and refined by Collin (1951) using X-ray-diffraction data derived from film techniques. A modern structure refinement for bandylite has not been reported. We have refined the structure of bandylite and report the results herein.

EXPERIMENTAL

A specimen containing superb crystals of bandylite was provided by Dr. Mark Feinglos. A crystal with approximate dimensions 0.12 × 0.06 × 0.02 mm was selected for study. The crystal was mounted on a Bruker PLATFORM 3-circle goniometer equipped with a 1K SMART CCD (charge-coupled device) detector with a crystal-to-detector distance of 5 cm.

The data were collected using Mo*K*α X-radiation. Preliminary examination of the diffraction pattern showed that the peak widths were ~2° in ω, possibly indicating that the crystal was slightly bent. Owing to the fairly large peak-widths, frame widths of 0.6° in ω were used for the collection of data, with 60 s used to acquire each frame. A sphere of three-dimensional data was acquired, and the data were analyzed to locate peaks for the determination of the unit-cell dimensions (Table 1), which were refined with 312 reflections using least-squares techniques. Data were collected for $3° \leq 2\theta \leq 56.6°$ in approximately 22 hours; comparison of the intensities of identical reflections collected at different times during the data collection showed no decay. The three-dimensional data were reduced and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A semi-empirical absorption-correction was done on the basis of 196 intense reflections with the crystal modeled as an ellipsoid, which reduced R_{INT} from 5.3 to 4.8%. A total of 1886 reflections were collected, of which there are 263 unique reflections with 144 classed as observed ($|F_o| \geq 4\sigma_F$).

[§] *E-mail address*: pburns@nd.edu

TABLE 1. MISCELLANEOUS INFORMATION FOR BANDYLITE

a (Å)	6.171(2)	Crystal size (mm)	0.12 x 0.06
c (Å)	5.587(3)		x 0.02
V (Å^3)	212.7	Total ref.	1886
Space group	$P4/n$	Unique ref.	263
$F(000)$	174	Unique $\|F_o\| \geq 4\sigma_F$	144
μ (mm^{-1})	5.64	Final R	3.7
D_{calc}	2.776	S	0.90

Unit cell contents: $Cu_2[B(OH)_4]_2Cl_2$

$R1 = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$S = [\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{½}$, for m observations and n parameters

STRUCTURE 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 Bruker SHELXTL Version 5 system of programs was used for the refinement of the crystal structure.

Reflection statistics and systematic absences indicated space groups $P4/n$ and $P4/nmm$. Refinement of the structure was conducted in both space groups, proceeding from the structure model given by Collin (1951). In space group $P4/nmm$, refinement of a model that included anisotropic-displacement parameters for all atoms converged to an agreement index ($R1$) of 9.0% calculated for the 144 observed reflections ($|F_o| \geq 4\sigma_F$). Inspection of the structure revealed that the U_{11} displacement parameter for the O atom was unrealistically large, with a value of 0.19(2). In addition, the <B–O> bond length was found to be 1.44 Å, which is significantly smaller than normal. Refinement in space group $P4/n$ resulted in a substantial improvement in $R1$, and it was possible to locate the H atom in difference-Fourier maps. The resulting anisotropic displacement parameters were found to be reasonable, with the <B–O> bond length equal to 1.477 Å, a typical value for borate tetrahedra. The refinement was done on the basis of F^2 using all 263 unique reflections, and included all atomic positional parameters with allowance for anisotropic displacement for all atoms except H, and a weighting scheme of the structure factors. The refinement converged to a final agreement index ($R1$) of 3.6 % calculated for the 144 unique observed reflections (the $R1$ was 9.0% for all 263 unique reflections) and a goodness-of-fit (S) of 0.90. An isotropic correction for extinction was tried, but did not lead to an improvement of the refinement. Final atomic parameters are listed in Table 2. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

RESULTS

The current study confirms the structure of bandylite presented by Collin (1951), although the precision of this refinement is much higher owing to the use of a modern detector of X-rays.

The single symmetrically distinct B atom is tetrahedrally coordinated by OH groups at a distance of 1.477(4) Å. The tetrahedron bond-angles range from 108.5(3) to 109.9(2)°, with a <O–B–O> angle of 109.47°.

The Cu^{2+} cation is coordinated by four OH groups and two Cl atoms, arranged such that the OH groups are located at the equatorial corners of a (4 + 2)-distorted octahedron. The Cu–OH bond length is 1.966(3) Å. There are two distinct Cu–Cl bond-lengths, 2.732(4) and 2.854(4) Å. Burns & Hawthorne (1995) observed that this is the most common type of mixed-ligand $Cu^{2+}\Phi_6$ octahedron (Φ: O, OH, H_2O and at least one Cl), and that it occurs in 12 mineral structures, including bandylite. Note that the mixed-ligand $Cu^{2+}\Phi_6$ octahedron is strongly distorted owing to the Jahn–Teller effect. Expected Cu–OH and Cu–Cl bond-lengths in the absence of a distortion are 2.11 and 2.40 Å, respectively, on the basis of sums of ionic radii (Shannon 1976, Whittaker & Muntus 1970). The Jahn–Teller distortion is responsible for a shortening of the equatorial Cu–OH bonds by 0.14 Å, and a lengthening of the apical Cu–Cl bonds by ~0.4 Å.

The H atom refined to a position 0.86(5) Å from the O position, and the H bond is accepted by a Cl atom with a H...Cl bond length of 2.39(5) Å and a O–H...Cl bond angle of 153.9°. Each Cl atom is bonded to two Cu^{2+} cations and accepts four H bonds.

Various views of the structure are presented in Figure 1. The structure consists of layers of $Cu^{2+}\Phi_6$ octahedra and BO_4 tetrahedra that are parallel to (001),

TABLE 2. FINAL ATOMIC PARAMETERS FOR BANDYLITE

	x	y	z	$*U_{eq}$	$*U_{11}$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	0	½	0.6317(4)	139(5)	86(5)	86(5)	245(10)	0	0	0
Cl	0	½	0.1427(6)	187(7)	182(10)	182(10)	195(19)	0	0	0
B	0	0	½	166(31)	52(39)	52(39)	396(86)	0	0	0
O	0.3134(5)	0.5540(5)	0.6543(8)	122(9)	78(18)	102(18)	186(26)	–8(14)	–26(19)	–32(19)
H	0.155(9)	0.150(9)	0.753(9)	200						

** $Uij = U_{ij}$ Å$^2 \times 10^4$

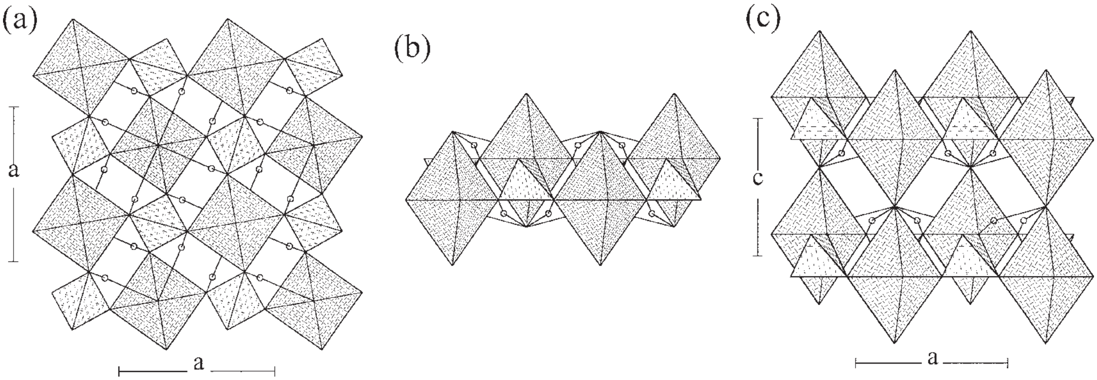

FIG. 1. Polyhedral representations of the structure of bandylite (a) projected along [001], (b) layer projected along [010], and (c) projected along [010]. $B(OH)_4$ tetrahedra are shaded with crosses, and $Cu(OH)_4Cl_2$ octahedra are shaded with a herring-bone pattern. H atoms are represented by open circles, with lines illustrating the H bonds.

arranged such that each tetrahedron shares all of its vertices with $Cu^{2+}\Phi_6$ octahedra (Fig. 1a). H bonds extend from the shared vertices to Cl atoms located at the apical positions of adjacent $Cu^{2+}\Phi_6$ octahedra. Only one half of the Cl atoms receive H bonds from within the layer; the remaining receive H bonds from an adjacent symmetrically identical layer (Fig. 1b). Adjacent layers are linked by the sharing of Cl atoms at the apical positions of $Cu^{2+}\Phi_6$ octahedra, and by H bonds (Fig. 1c). The $B(OH)_4$ tetrahedra are not polymerized, thus representation of the fundamental building block in bandylite is 1□:□ (Burns *et al.* 1995).

The structure of bandylite is confirmed to be in space group *P*4/*n*, as earlier reported by Collin (1951). The structure approximately conforms to space group *P*4/*nmm*, as can be seen in Figure 1a. Relatively small rotations of the BO_4 tetrahedra would bring the structure into conformation with *P*4/*nmm*, but would diminish the strength of the H bonds donated by the hydroxyl groups of the borate tetrahedra, and accepted by the Cl anions in the apical positions of the $Cu^{2+}\Phi_6$ octahedra.

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