Structure of Ba₂Cu(BO₃)₂

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Abstract. Dibarium copper orthoborate, $M_r =$ 455·82, orthorhombic, *Pnma*, $a = 8\cdot023$ (1), $b = 11\cdot290$ (1), $c = 13\cdot889$ (1) Å, $V = 1258\cdot1$ (3) Å³, $Z = 8$, $D_x = 4\cdot81$ g cm⁻³, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 157\cdot21$ cm⁻¹, $F(000) = 1592$, $T = 298$ K, $R = 0\cdot020$ and $wR = 0\cdot031$ for 2069 averaged observed reflections. The structure features discrete units of formula $Cu_2(BO_3)_4$ that are interconnected by three crystallographically independent Ba atoms. The copper borate unit is composed of two highly distorted O square planes occupied by the Cu atoms that are bridged by two triangular BO_3 groups. One edge of each CuO_4 group is shared with an additional BO_3 group, resulting in the acute O—Cu—O angles 71·8 (1) and 72·3 (2)°.

Introduction. As part of our program in the synthesis and characterization of new solid-state borates, we recently synthesized the polymorphic compound $Sr_2Cu(BO_3)_2$ (Smith & Keszler, 1989) which undergoes a first-order phase transition from a low-temperature form to a high-temperature form at 1073 K. The high-temperature β form exhibits larger coordination numbers for the Sr atoms and a substantial rearrangement of the copper borate network relative to that of the low-temperature α form.

From an analysis of the phase system BaO–CuO–B_2O_3 we have determined that the Ba analog $Ba_2Cu(BO_3)_2$ crystallizes in one form only, isostructural to β-$Sr_2Cu(BO_3)_2$. Herein, we describe the crystal structure of this new compound.

Experimental. Powder samples of the title compound were prepared by grinding stoichiometric ratios of $Ba(NO_3)_2$ (reagent grade, Mallinckrodt), $Cu(NO_3)_2.2\frac{1}{2}H_2O$ (reagent grade, Mallinckrodt), and B_2O_3 (99·99%, Morton Thiokol) under hexane followed by heating at 1173 K for 18 h; the heating was interrupted several times to grind the sample. Crystals were grown from a melt composed of 50 mol% $LiBO_2$ and 50 mol% $Ba_2Cu(BO_3)_2$. A crystal with dimensions $0\cdot22 \times 0\cdot08 \times 0\cdot04$ mm was selected for data collection. Unit-cell parameters were derived from a least-squares analysis of the angle settings of 25 reflections in the range $30 \le 2\theta \le$ 45° that were automatically centered on a Rigaku AFC6R diffractometer. Intensity data were collected with the ω–2θ scan technique; intensities of three standard reflections monitored throughout data collection exhibited an average fluctuation of 2·3%. From 4064 reflections measured to $[(\sin\theta)_{max}]/\lambda = 1\cdot28$ Å⁻¹ in the index range $-12 \le h \le 12$, $0 \le k \le 17$, $0 \le l \le 21$, 2069 unique data with $F_o^2 \ge 3\sigma(F_o^2)$ were obtained.

All calculations were performed on a MicroVAXII computer with programs from the *TEXRAY* crystallographic software package (Molecular Structure Corporation, 1985). Because unit-cell dimensions and systematic absences of reflections indicated that the compound was isostructural to β-$Sr_2Cu(BO_3)_2$, the coordinates for this structure were used as a trial solution. Following refinement with isotropic thermal parameters, the data were corrected for absorption with the computer program *DIFABS* (Walker & Stuart, 1983) and subsequently averaged ($R_{int} = 0\cdot024$). Final refinement on F_o for those data having $F_o^2 \ge 3\sigma(F_o^2)$ with 113 variables and 2069 observations resulted in $R = 0\cdot020$, $\Delta/\sigma = 0\cdot06$, and $wR = 0\cdot031$ where the weights are derived from counting statistics and a value of $p = 0\cdot05$. The isotropic extinction parameter is $4\cdot5 \times 10^{-7}$ (Zachariasen, 1968) and $S = 0\cdot92$. A maximum peak of 0·77 e Å⁻³ was observed in the final difference electron density map, corresponding to 0·40% of a Ba atom. Atomic scattering factors are from *International Tables for X-ray Crystallography* (1974). Final atomic coordinates of the compound are given in Table 1.*

The magnetic moment of the compound was measured at 295 K by the Gouy method. Measurements were made at a field strength of 5 kG ($\hat{=} 0\cdot5$ T), using an Alpha Model AL 7500 water-cooled magnet with 10 cm pole faces and a 4 cm air gap. The Gouy tube was calibrated with the standard $HgCo(SCN)_4$. Diamagnetic corrections to molar

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52232 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters for* $Ba_2Cu(BO_3)_2$

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Ba(1)	0	0	0	0·86 (1)
Ba(2)	0·37931 (4)	$\frac{1}{4}$	0·95179 (2)	0·75 (1)
Ba(3)	0·16013 (2)	0·01993 (2)	0·71717 (1)	0·69 (1)
Cu(1)	0·30766 (8)	$\frac{1}{4}$	0·57279 (5)	0·87 (2)
Cu(2)	0·03874 (8)	$\frac{1}{4}$	0·30007 (4)	0·80 (2)
B(1)	0·0634 (7)	$\frac{1}{4}$	0·1290 (4)	0·9 (2)
B(2)	0·4896 (6)	$\frac{1}{4}$	0·7078 (4)	0·6 (2)
B(3)	0·1337 (5)	0·4281 (3)	0·4365 (3)	0·7 (1)
O(1)	0·0762 (5)	$\frac{1}{4}$	0·7093 (3)	1·0 (1)
O(2)	0·0676 (5)	$\frac{1}{4}$	0·0336 (3)	1·2 (1)
O(3)	0·4386 (3)	0·1461 (2)	0·6615 (2)	0·9 (1)
O(4)	0·2993 (3)	0·4740 (2)	0·8936 (2)	1·1 (1)
O(5)	0·0603 (4)	0·1472 (2)	0·1864 (2)	1·3 (1)
O(6)	0·4981 (3)	0·1304 (2)	0·1055 (2)	1·0 (1)
O(7)	0·1932 (3)	0·1125 (2)	0·5235 (2)	1·0 (1)

Table 2. *Selected bond distances* (Å) *and bond angles* (°) *for* $Ba_2Cu(BO_3)_2$

Cu(1)—O(3)	2·000 (2) × 2	O(3)—Cu(1)—O(3)	71·8 (1)
Cu(1)—O(7)	1·929 (3) × 2	O(7)—Cu(1)—O(7)	107·2 (2)
		O(3)—Cu(1)—O(7)	89·8 (1)
Cu(2)—O(5)	1·967 (3) × 2	O(5)—Cu(2)—O(5)	72·3 (2)
Cu(2)—O(6)	1·911 (3) × 2	O(6)—Cu(2)—O(6)	89·9 (2)
		O(5)—Cu(2)—O(6)	98·6 (1)
B(1)—O(2)	1·325 (7)	O(2)—B(1)—O(5)	124·5 (2)
B(1)—O(5)	1·409 (4) × 2	O(5)—B(1)—O(5)	111·0 (4)
B(2)—O(1)	1·345 (6)	O(1)—B(2)—O(3)	123·0 (2)
B(2)—O(3)	1·399 (4) × 2	O(3)—B(2)—O(3)	114·0 (4)
B(3)—O(4)	1·366 (4)	O(4)—B(3)—O(6)	120·4 (3)
B(3)—O(6)	1·400 (4)	O(6)—B(3)—O(7)	118·5 (3)
B(3)—O(7)	1·378 (4)	O(7)—B(3)—O(4)	121·1 (3)

susceptibilities were made from reported values (Mulay & Boudreaux, 1976).

Discussion. A drawing of the contents of the unit cell is shown in Fig. 1 and selected interatomic distances and angles are listed in Table 2. The compound is isostructural to the high-temperature form of the orthoborate $Sr_2Cu(BO_3)_2$. The volume of the unit cell is approximately 13% larger than that of the Sr analog, reflecting the larger crystal radius of the Ba atom.

The primary structural feature is the discrete unit $Cu_2(BO_3)_4$ illustrated in Fig. 2. It consists of two highly distorted O square planes that are occupied by Cu atoms. These planes are bridged by sharing O vertices with two BO_3 triangles centered by atom B(3). At each end of the unit a CuO_4 group shares an edge with a triangular BO_3 group. Such an edge-shared BO_3 group is quite unusual in the structural chemistry of borates; it forces, in the present material, the acute angles 71·8 (1) and 72·3 (2)° for the interactions O(3)—Cu(1)—O(3) and O(5)—Cu(2)—O(5), respectively. The unit exhibits mirror symmetry with the atoms Cu(1), Cu(2), B(1), B(2), O(1), and

O(2) occupying positions on the mirror plane at $y = \frac{1}{4}$. Also, as seen in Fig. 2, when viewed along the direction [010] a substantial deviation from planarity is observed with a signficant bend at atom O(6).

The average Cu(1)—O and Cu(2)—O distances, 1·96 (2) and 1·94 (2) Å, are comparable to that, 1·95 (1) Å, reported for the compound $3CuO.B_2O_3$ (Behm, 1982). Perturbations in the planarity of the CuO_4 groups are evidenced by the angles O(3)—Cu(1)—O(7), 160·2 (1)°, and O(5)—Cu(2)—O(6), 169·5 (1)°. Dissimilar deviations from a square
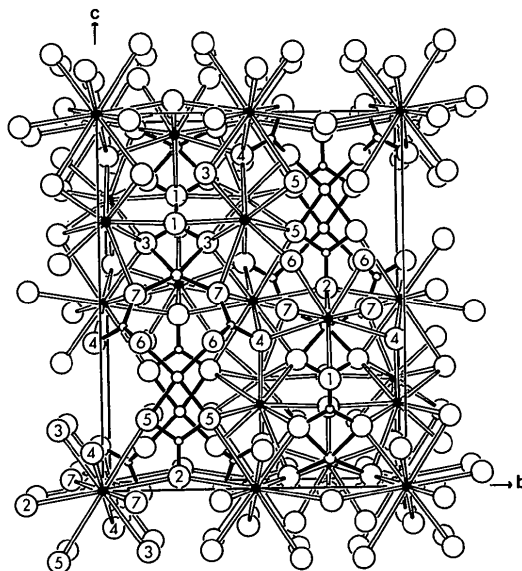

Fig. 1. Labeled sketch of the unit cell. Small shaded spheres represent Ba atoms, largest open spheres represent O atoms, and smallest open spheres represent B atoms; Cu—O and B—O bonds are shaded, here and in Fig. 2.
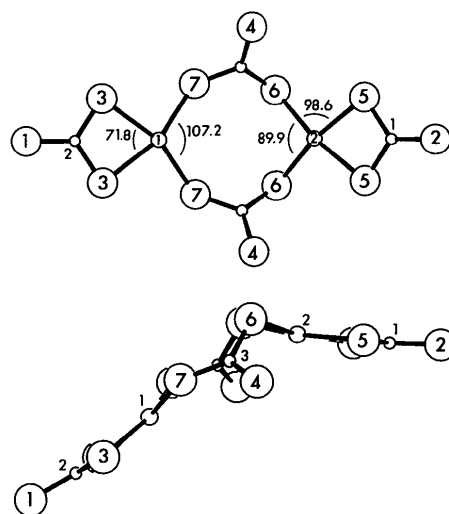

Fig. 2. Sketches of the $Cu_2(BO_3)_4$ unit. Top: view along [100]. Angles in °. Bottom: view along direction orthogonal to mirror plane at $y = \frac{1}{4}$.
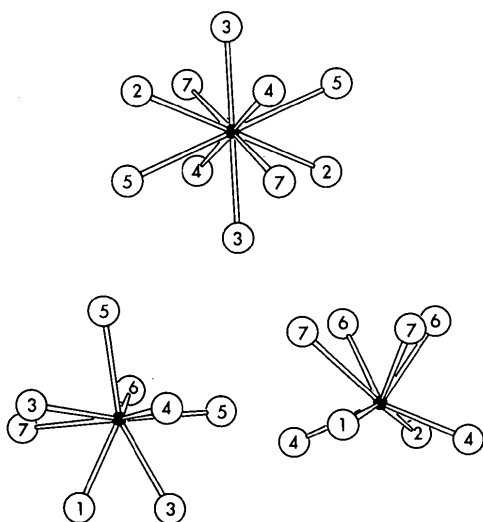
Fig. 3. Sketches of Ba environments [clockwise from top: environments for atoms Ba(1), Ba(2), and Ba(3)].

Ba(1) binds to ten O atoms placed at the vertices of a distorted bicapped cube. Atoms Ba(2) and Ba(3) each coordinate to eight O atoms placed at the vertices of a distorted square antiprism and an irregular dodecahedron, respectively. The mean Ba—O distances are 2·90 (4), 2·79 (4), and 2·81 (5) Å for the interactions Ba(1)—O, Ba(2)—O, and Ba(3)—O, respectively. These values compare well to the values 2·90 Å for a ten-coordinate Ba atom and 2·80 Å for an eight-coordinate Ba atom calculated from crystal radii (Shannon & Prewitt, 1969).

The effective magnetic moment for the compound at 295 K is 1·74 (2) BM (1 BM ≃ 9·274 × $10^{-24}JT^{-1}$). This is a typical value for a d^9, Cu^{2+} compound with primarily spin-only contributions to the magnetic moment.

geometry are noted from the angles O(6)—Cu(2)—O(6), 89·9 (2)°, and O(7)—Cu(2)—O(7), 107·2 (2)°. These angles are consistent with the chemical inequivalence of the atoms O(6) and O(7); atom O(6) binds to four nearest cations while atom O(7) binds to five cations.

The mean B—O bond length, 1·38 (1) Å, agrees with the expected value, 1·375 Å (Wells, 1975). Substantial reductions below the ideal trigonal angle, 120°, are observed for the interactions O(5)—B(1)—O(5), 111·0 (4)°, and O(3)—B(2)—O(3), 114·0 (4)°, that are involved in edge-sharing with the CuO₄ group.

The environments of the three crystallographically inequivalent Ba atoms are depicted in Fig. 3. Atom

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Synthèse et Structure du Borouranate de Lithium LiBUO₅

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Abstract. $M_r = 335·78$, monoclinic, $P2_1/c$, $a = 5·767$ (2), $b = 10·574$ (3), $c = 6·835$ (2) Å, $\beta = 105·04$ (3)°, $V = 402·52$ (3·62) Å³, $Z = 4$, $D_x = 5·45$ Mg m⁻³, $\lambda(Cu \, K\alpha) = 1·5418$ Å, $\mu = 121$ mm⁻¹, $F(000) = 560$, $T = 290$ K, $R = 0·062$, $wR = 0·073$ for 639 reflexions with $I \geq 3\sigma(I)$. The atomic arrangement is the same as for orthorhombic NaBUO₅ except for the environment of the alkali-metal ion: the Li⁺ ions are located in tetrahedra whereas the Na⁺ ions are surrounded by octahedra. This induces