A new polymorph of $Cu_3B_2O_6$

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A new polymorph of nonacopper(II) bis(orthoborate) bis-(hexaoxodiborate), $Cu_9(BO_3)_2(B_2O_6)_2$, or $Cu_3B_2O_6$ with $Z' = 3$, has a pseudo-layered monoclinic structure containing BO_3 triangles and B_2O_6 units consisting of corner-sharing BO_3 triangles and BO_4 tetrahedra. The compound was obtained during an investigation of the Li–Cu–B–O system. In contrast to the triclinic form of $Cu_3B_2O_6$, the layers are linked to one another by BO_4 tetrahedra.

Comment

The copper(II) boron oxides CuB_2O_4 and $Cu_3B_2O_6$ attract great interest owing to the combination of their structural and unusual physical properties (Sakurai *et al.*, 2002; Saito *et al.*, 2008; Martinez-Ripoll *et al.*, 1971; Behm, 1982). The noncentrosymmetric ($I\bar{4}2d$) canted antiferromagnet CuB_2O_4 becomes chiral by application of a static magnetic field (Saito *et al.*, 2008). Its crystal structure consists exclusively of BO_4 tetrahedra and CuO_4 squares. Antiferromagnetic triclinic $Cu_3B_2O_6$ can be considered as a two-dimensional spin system because of the pronounced layered character of the crystal structure (Sakurai *et al.*, 2002). Recently, a high-pressure modification of CuB_4O_7 (Knyrim *et al.*, 2008) with Cu^{II}, isotypic with β-ZnB_4O_7, has been reported, showing BO_4 tetrahedra and CuO_5 square pyramids. The common feature of all these systems is Jahn–Teller distortion of the Cu coordination polyhedra, due to the electronic configuration of the d^9 ion, which can lead to anisotropic character of the crystal structure.

During an investigation of the Li–Cu–B–O system we prepared a new polymorphic modification of $Cu_3B_2O_6$. A monoclinic crystal structure of $Cu_3B_2O_6$ with $Z' = 3$ was obtained, which can be considered as pseudo-layered with much shorter distances between neighbouring layers (1.506 Å; Fig. 1) than in the triclinic polymorph with $Z' = 5$ (2.7 Å; Behm, 1982). The monoclinic structure contains six-layer packing; the layers are parallel to the [402] plane and offset with respect to one another.
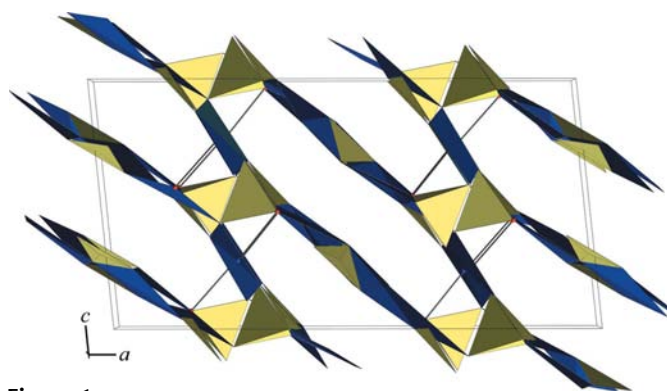

Figure 1
The structure of the new $Cu_3B_2O_6$ pseudo-layered monoclinic modification. Solid lines show the closest interlayer Cu—O bonds.

Figure 2
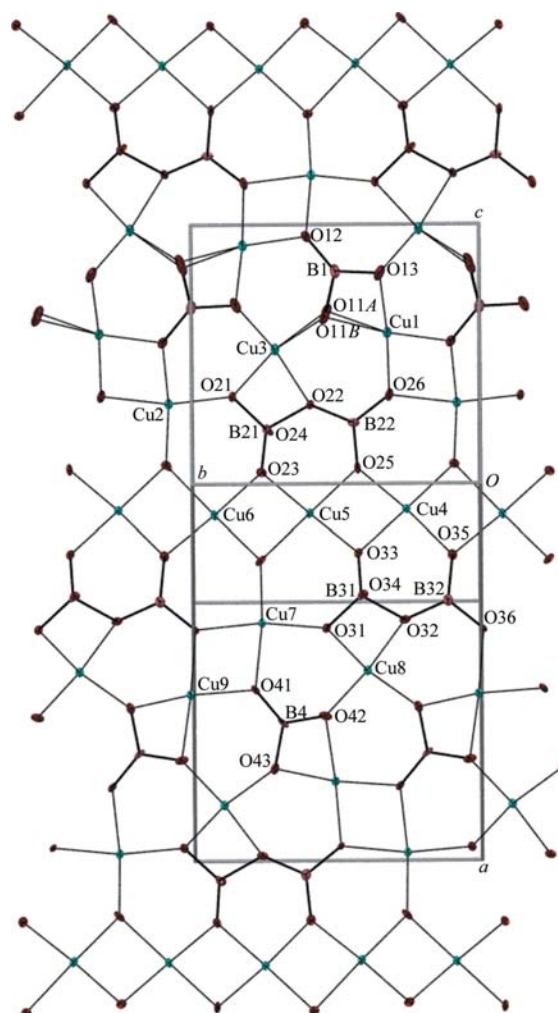The pseudo-layer packing of $Cu_3B_2O_6$. Each layer consists of isolated CuO_4 squares, Cu_2O_6 dimers of edge-sharing CuO_4 squares, infinite CuO_2 chains, and BO_3 and corner-sharing B_2O_5 units. B—O bonds are shown with thicker lines. Displacement ellipsoids are plotted at the 70% probability level.

There are isolated BO_3 triangles and B_2O_6 units, consisting of corner-shared BO_3 triangles and BO_4 tetrahedra, in the structure, giving the formula $Cu_9(BO_3)_2(B_2O_6)_2$, while the other polymorph has only $B_2O_5^{4-}$ and BO_3^{3-} species and a

separate O^{2-} anion, resulting in the composition $Cu_{15}[(B_2O_5)_2$-$(BO_3)_6O_2]$. The shortest distance between neighbouring layers is 1.506 Å for the B—O bond in the BO_4 tetrahedra (Fig. 1). The average B—O length is 1.366 (7) Å in the triangles and 1.483 (6) Å in the tetrahedra. This form of borate anion is quite unusual, but a report on the presence of tetrahedrally and triangularly bonded B atoms in one formation already exists (Rowsell *et al.*, 2002). Almost all of the Cu atoms have nearly planar square coordination environments, with one or two longer contacts to O atoms from neighbouring layers, forming distorted square-pyramidal or octahedral coordination environments. Atoms Cu1 and Cu2 are exceptions, having no additional contacts shorter than 3.1 Å. Each layer contains CuO_4 squares and Cu_2O_6 dimers sharing corners, and BO_3 triangles and B_2O_5 units, which are surrounded on both sides by infinite CuO_2 chains from edge-sharing CuO_4 squares (Fig. 2). The CuO_2 chains extend parallel to the *b* axis. The Cu—O bond lengths in the layer vary from 1.868 (3) to 2.088 (4) Å and those between neighbouring layers vary from 2.333 (3) to 2.738 (3) Å, forming CuO_5 and CuO_6 polyhedra.

It has already been shown (Behm, 1982; Pardo *et al.*, 1974) that $M_3B_2O_6$ borates (with M^{2+} = Mg, Ni and Co) crystallize in a completely different structure type, with only isolated BO_3 triangles and practically undistorted MO_6 octahedra, which form a three-dimensional network. The peculiarity of the $Cu_3B_2O_6$ structures is probably based on the ability of Cu^{2+} to adopt different coordination environments as a result of Jahn–Teller distortion.

Experimental

Single crystals of a new monoclinic polymorph of $Cu_3B_2O_6$ were obtained by melting a mixture of $LiBO_2$ and CuO at 1273 K in air and then cooling the mixture slowly to room temperature. All attempts to obtain the monoclinic form by quenching a stoichiometric mixture of CuO and B_2O_3 from 1273 K in air led to the formation of the triclinic form of $Cu_3B_2O_6$. High-temperature powder X-ray diffraction data of triclinic $Cu_3B_2O_6$ from room temperature up to 1073 K yielded no phase transformation.

Crystal data

$Cu_9(BO_3)_2(B_2O_6)_2$	$V = 1385.4$ (3) Å^3
$M_r = 924.81$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 17.820$ (2) Å	$\mu = 13.64$ mm^{-1}
$b = 8.5232$ (12) Å	$T = 296$ K
$c = 9.1706$ (12) Å	$0.20 \times 0.20 \times 0.15$ mm
$\beta = 95.913$ (6)°	

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer	9748 measured reflections
	3410 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)	2542 reflections with $I > 2\sigma(I)$
$T_{min} = 0.101$, $T_{max} = 0.153$	$R_{int} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$	301 parameters
$wR(F^2) = 0.063$	$\Delta\rho_{max} = 1.11$ e Å^{-3}
$S = 0.96$	$\Delta\rho_{min} = -0.91$ e Å^{-3}
3410 reflections	

Table 1
Selected bond lengths (Å).

Cu1—O11A	1.956 (5)	Cu7—O41	1.995 (3)
Cu1—O11B	1.92 (2)	Cu8—O31	1.910 (3)
Cu1—O12^i	1.906 (3)	Cu8—O32	1.996 (3)
Cu1—O13	1.896 (4)	Cu8—O42	1.898 (3)
Cu1—O26	1.924 (4)	Cu8—O43^{vii}	1.885 (3)
Cu2—O12^{ii}	1.990 (3)	Cu9—O36^{iii}	1.934 (3)
Cu2—O21	1.925 (3)	Cu9—O41	1.926 (3)
Cu2—O26^{iii}	2.010 (3)	Cu9—O42^{viii}	1.961 (3)
Cu2—O34^{iv}	1.967 (3)	Cu9—O43^{viii}	1.969 (3)
Cu3—O11A	1.908 (5)	B1—O12	1.354 (7)
Cu3—O11B	1.91 (2)	B1—O13	1.370 (7)
Cu3—O13^{ii}	1.850 (4)	B1—O11B	1.40 (3)
Cu3—O21	1.921 (3)	B1—O11A	1.405 (8)
Cu3—O22	1.970 (3)	B21—O21	1.451 (6)
Cu4—O25	1.903 (3)	B21—O22	1.555 (6)
Cu4—O33	1.921 (3)	B21—O23	1.422 (6)
Cu4—O34^v	1.994 (3)	B21—O24	1.506 (6)
Cu4—O35	1.916 (3)	B22—O22	1.394 (6)
Cu5—O21^{vi}	2.324 (3)	B22—O25	1.348 (7)
Cu5—O23	1.868 (3)	B22—O26	1.355 (6)
Cu5—O24^{vi}	2.037 (3)	B31—O31	1.465 (6)
Cu5—O25	1.954 (3)	B31—O32	1.552 (6)
Cu5—O33	1.874 (3)	B31—O33	1.415 (6)
Cu6—O23	1.897 (3)	B31—O34	1.505 (6)
Cu6—O24^{vi}	2.013 (3)	B32—O32	1.415 (6)
Cu6—O31^{iv}	2.333 (3)	B32—O35	1.355 (6)
Cu6—O34^{iv}	2.090 (3)	B32—O36	1.359 (6)
Cu6—O35^{iii}	1.913 (3)	B4—O41	1.349 (6)
Cu7—O24^{vi}	1.958 (3)	B4—O42	1.389 (6)
Cu7—O31	1.931 (3)	B4—O43	1.381 (6)
Cu7—O36^{iii}	1.994 (3)		

Symmetry codes: (i) $-x, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x, y + 1, z$; (iv) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (v) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (vi) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (vii) $-x + 1, y - \frac{1}{2}, -z - \frac{1}{2}$; (viii) $-x + 1, y + \frac{1}{2}, -z - \frac{1}{2}$.

Atom O11 is disordered over two sites separated by 0.66 (3) Å. The site-occupation factors of O11A and O11B were fixed at 0.80 and 0.20, respectively, and no restraints were employed.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *BS* (Ozawa & Kang, 2004); software used to prepare material for publication: *SHELXTL*.

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