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An open-framework borophosphate, LiCu₂BP₂O₈(OH)₂

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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{O}-\text{B}) = 0.002$ Å;
R factor = 0.019; wR factor = 0.054; data-to-parameter ratio = 11.7.

The open-framework alkaline-earth metal borophosphate, lithium dicopper(II) borophosphate dihydroxide, LiCu₂B-P₂O₈(OH)₂, was synthesized hydrothermally. Its structure may be regarded as a layer formed *via* BO₄ and PO₄ tetrahedra bonding together with distorted CuO₆ and LiO₆ octahedral units. Each P atom is connected to B, Li and Cu atoms through a bridging O atom. The B atom lies on a crystallographic twofold axis and the Li atom lies on a center of symmetry. The two metal centers are connected to each other by Cu—O—Li bonds.

Related literature

For chiral structures and potential applications in catalysis of borophosphates with the general formula $AM(\text{H}_2\text{O})_2\text{[BP}_2\text{O}_8]_y\text{H}_2\text{O}$ ($A = \text{Li, Na, K, NH}_4^+$; $M = \text{Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd}$) ($y = 0.5-1$), see: Ewald *et al.* (2007); Kniep *et al.* (1997). For related structures, see: Boy & Kniep (2001); Yang *et al.* (2008).

Experimental

Crystal data

LiCu ₂ BP ₂ O ₈ (OH) ₂	$c = 9.6585$ (12) Å
$M_r = 368.79$	$\beta = 91.0190$ (10)°
Monoclinic, $C2/c$	$V = 694.23$ (15) Å ³
$a = 15.0974$ (19) Å	$Z = 4$
$b = 4.7617$ (6) Å	Mo $K\alpha$ radiation

$\mu = 6.64$ mm⁻¹
 $T = 296$ K

0.20 × 0.18 × 0.17 mm

Data collection

Bruker APEXII CCD
diffractometer
Absorption correction: multi-scan
(SADABS; Bruker, 2007)
 $T_{\text{min}} = 0.350$, $T_{\text{max}} = 0.398$
(expected range = 0.285–0.324)

4076 measured reflections
925 independent reflections
897 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$
 $wR(F^2) = 0.054$
 $S = 1.18$
925 reflections
79 parameters
1 restraint

H atoms treated by a mixture of
independent and constrained
refinement
 $\Delta\rho_{\text{max}} = 0.63$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.53$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O4}-\text{H4}\cdots\text{O2}^{\text{i}}$	0.848 (10)	2.37 (3)	2.9535 (19)	126 (3)
$\text{O4}-\text{H4}\cdots\text{O5}^{\text{ii}}$	0.848 (10)	2.32 (2)	3.036 (2)	143 (3)

Symmetry codes: (i) $x, -y + 2, z + \frac{1}{2}$; (ii) $x, -y + 1, z + \frac{1}{2}$.

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2104).

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supplementary materials

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An open-framework borophosphate, $\text{LiCu}_2\text{BP}_2\text{O}_8(\text{OH})_2$

J. Zheng and A. Zhang

Comment

In the last decade, much attention has been paid to the large family of borophosphates with the general formula $AM(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8] \cdot y\text{H}_2\text{O}$ ($A=\text{Li}, \text{Na}, \text{K}, \text{NH}_4^+$; $M=\text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Cd}$) ($y=0.5-1$) due to their chiral structure property and potential applications for catalysts (Kniep *et al.*, 1997; Ewald *et al.*, 2007).

The crystal structure of $\text{LiCu}_2\text{BP}_2\text{O}_8(\text{OH})_2$ contains one unique Li atom, two Cu atoms, one boron atom, two phosphorus atoms, and eight oxygen atoms and two $-\text{OH}$ groups in the asymmetric unit of the framework. The borophosphate units are isolated anions linked by the bonds they form to Cu, Li and H. (Fig. 1) Each BO_4 tetrahedron belongs to the adjacent CuO_6 octahedra. The phosphorus atoms are allocated in regular tetrahedral environments with four types of oxygen atoms. Bond lengths and angles within the anionic partial structure are consistent with related borophosphates (Boy *et al.*, 2001; Yang *et al.* 2008). Li^+ is coordinated by the oxygen functions groups of PO_4 groups. Cu^{2+} is adjacent to six oxygen atoms, five from PO_4 groups and one BO_4 groups, but one of the five PO_4 links (O3) is also bonded to BO_4 (Fig.2)

Experimental

Blue block crystals were synthesized hydrothermally from a mixture of $\text{Cu}(\text{NO}_3)_2$, $\text{Li}_2\text{B}_4\text{O}_7$, water and H_3PO_4 . In a typical synthesis, 0.725 g $\text{Cu}(\text{NO}_3)_2$ were dissolved in a mixture of 5 mL water, 1.691 g $\text{Li}_2\text{B}_4\text{O}_7$ and 2 ml (85%) H_3PO_4 with constant stirring. Finally, the mixture was kept in a 30 ml Teflon-lined steel autoclave at 443 K for 6 days. The autoclave was slowly cooled to room temperature. Blue block crystals of the title compound were obtained.

Refinement

The H atoms of the coordinated water molecule were refined with $U_{\text{iso}}(\text{H})=2.4 U_{\text{eq}}(\text{O})$ and distance restraints $d(\text{O}-\text{H})$ of 0.86 (1) Å. The highest peak in the difference map is 0.63 e/Å, and 0.77 Å from O2, and the minimum peak is -0.53 e/Å, and 0.70 Å from Cu1.

Figures

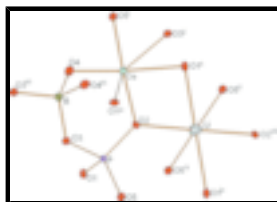


Fig. 1. The structure of $\text{LiCu}_2\text{BP}_2\text{O}_8(\text{OH})_2$. Displacement ellipsoids are drawn at 50% the probability level.

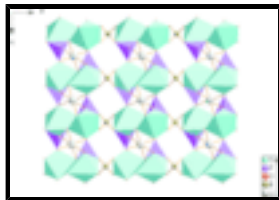


Fig. 2. Packing diagram of $\text{LiCu}_2\text{BP}_2\text{O}_8(\text{OH})_2$, viewed along b axis.

lithium dicopper borophosphate dihydroxide

Crystal data

$\text{LiCu}_2\text{BP}_2\text{O}_8(\text{OH})_2$

$M_r = 368.79$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 15.0974\ (19)\ \text{\AA}$

$b = 4.7617\ (6)\ \text{\AA}$

$c = 9.6585\ (12)\ \text{\AA}$

$\beta = 91.0190\ (10)^\circ$

$V = 694.23\ (15)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 712$

$D_x = 3.528\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3236 reflections

$\theta = 2.7\text{--}29.3^\circ$

$\mu = 6.64\ \text{mm}^{-1}$

$T = 296\ \text{K}$

Block, blue

$0.20 \times 0.18 \times 0.17\ \text{mm}$

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 296\ \text{K}$

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2007)

$T_{\min} = 0.350$, $T_{\max} = 0.398$

4076 measured reflections

925 independent reflections

897 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 29.3^\circ$

$\theta_{\min} = 2.7^\circ$

$h = -20 \rightarrow 20$

$k = -6 \rightarrow 6$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.019$

$wR(F^2) = 0.054$

$S = 1.18$

925 reflections

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0258P)^2 + 1.3109P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.63\ \text{e \AA}^{-3}$

79 parameters

$$\Delta\rho_{\min} = -0.52 \text{ e } \text{\AA}^{-3}$$

1 restraint

Extinction correction: SHELXL97 (Sheldrick, 2008),

$$F_c^* = kF_c [1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$$

Primary atom site location: structure-invariant direct methods

Extinction coefficient: 0.0350 (13)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.350210 (15)	1.20604 (5)	0.77155 (2)	0.00731 (13)
P2	0.35630 (3)	0.67849 (9)	0.58833 (5)	0.00503 (14)
O3	0.44649 (9)	0.5916 (3)	0.65917 (14)	0.0085 (3)
O2	0.34451 (9)	0.9972 (3)	0.59584 (13)	0.0080 (3)
O1	0.28531 (9)	0.5146 (3)	0.66790 (13)	0.0074 (3)
O5	0.35401 (9)	0.5717 (3)	0.44007 (13)	0.0085 (3)
O4	0.44543 (9)	0.9550 (3)	0.83773 (13)	0.0101 (3)
B	0.5000	0.7756 (6)	0.7500	0.0069 (5)
Li	0.2500	1.2500	0.5000	0.0201 (11)
H4	0.425 (2)	0.852 (6)	0.901 (2)	0.024*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01075 (17)	0.00604 (17)	0.00510 (16)	0.00214 (8)	-0.00107 (9)	-0.00075 (7)
P2	0.0066 (2)	0.0042 (2)	0.0042 (2)	-0.00019 (15)	-0.00068 (16)	0.00003 (15)
O3	0.0084 (6)	0.0069 (6)	0.0100 (6)	0.0005 (5)	-0.0034 (5)	-0.0008 (5)
O2	0.0118 (6)	0.0048 (6)	0.0072 (6)	0.0011 (5)	-0.0018 (5)	-0.0006 (5)
O1	0.0082 (6)	0.0068 (6)	0.0073 (6)	0.0005 (5)	0.0014 (4)	0.0022 (5)
O5	0.0130 (7)	0.0076 (6)	0.0049 (6)	0.0003 (5)	-0.0001 (5)	-0.0001 (5)
O4	0.0119 (6)	0.0116 (7)	0.0067 (6)	0.0041 (5)	0.0004 (5)	0.0000 (5)
B	0.0079 (13)	0.0056 (12)	0.0073 (13)	0.000	-0.0006 (10)	0.000
Li	0.021 (3)	0.017 (2)	0.022 (3)	0.006 (2)	-0.012 (2)	-0.006 (2)

Geometric parameters (\AA , $^\circ$)

Cu1—O5 ⁱ	1.9415 (13)	P2—O1	1.5420 (14)
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supplementary materials

Cu1—O2	1.9674 (14)	P2—O3	1.5686 (14)
Cu1—O4	1.9676 (14)	B—O4 ^{iv}	1.467 (2)
Cu1—O1 ⁱⁱ	2.0213 (13)	B—O3 ^{iv}	1.471 (2)
Cu1—O1 ⁱⁱⁱ	2.3242 (13)	Li—O2 ^v	2.0723 (14)
P2—O5	1.5195 (13)	Li—O1 ⁱⁱ	2.1143 (13)
P2—O2	1.5300 (15)	Li—O5 ⁱⁱ	2.2758 (14)
O5 ⁱ —Cu1—O2	177.21 (6)	P2—O5—Cu1 ^{viii}	127.40 (8)
O5 ⁱ —Cu1—O4	92.77 (6)	P2—O5—Li ^{vi}	89.42 (6)
O2—Cu1—O4	89.64 (6)	Cu1 ^{viii} —O5—Li ^{vi}	124.75 (6)
O5 ⁱ —Cu1—O1 ⁱⁱ	91.48 (6)	B—O4—Cu1	125.51 (9)
O2—Cu1—O1 ⁱⁱ	85.80 (6)	O4 ^{iv} —B—O4	108.8 (2)
O4—Cu1—O1 ⁱⁱ	161.34 (6)	O4 ^{iv} —B—O3	108.09 (7)
O5 ⁱ —Cu1—O1 ⁱⁱⁱ	90.91 (5)	O4—B—O3	112.53 (8)
O2—Cu1—O1 ⁱⁱⁱ	89.63 (5)	O4 ^{iv} —B—O3 ^{iv}	112.53 (8)
O4—Cu1—O1 ⁱⁱⁱ	108.74 (6)	O4—B—O3 ^{iv}	108.09 (7)
O1 ⁱⁱ —Cu1—O1 ⁱⁱⁱ	89.35 (3)	O3—B—O3 ^{iv}	106.9 (2)
O5—P2—O2	112.09 (8)	O2—Li—O2 ^v	180.0
O5—P2—O1	107.21 (8)	O2—Li—O1 ⁱⁱ	80.86 (5)
O2—P2—O1	113.33 (8)	O2 ^v —Li—O1 ⁱⁱ	99.14 (5)
O5—P2—O3	109.13 (8)	O2—Li—O1 ^{ix}	99.14 (5)
O2—P2—O3	109.99 (8)	O2 ^v —Li—O1 ^{ix}	80.86 (5)
O1—P2—O3	104.75 (7)	O1 ⁱⁱ —Li—O1 ^{ix}	180.0
B—O3—P2	124.48 (13)	O2—Li—O5 ⁱⁱ	91.82 (5)
P2—O2—Cu1	122.61 (8)	O2 ^v —Li—O5 ⁱⁱ	88.18 (5)
P2—O2—Li	129.39 (8)	O1 ⁱⁱ —Li—O5 ⁱⁱ	68.18 (5)
Cu1—O2—Li	96.37 (6)	O1 ^{ix} —Li—O5 ⁱⁱ	111.82 (5)
P2—O1—Cu1 ^{vi}	106.24 (7)	O2—Li—O5 ^{ix}	88.18 (5)
P2—O1—Li ^{vi}	95.01 (6)	O2 ^v —Li—O5 ^{ix}	91.82 (5)
Cu1 ^{vi} —O1—Li ^{vi}	93.45 (6)	O1 ⁱⁱ —Li—O5 ^{ix}	111.82 (5)
P2—O1—Cu1 ^{vii}	123.34 (8)	O1 ^{ix} —Li—O5 ^{ix}	68.18 (5)
Cu1 ^{vi} —O1—Cu1 ^{vii}	125.56 (6)	O5 ⁱⁱ —Li—O5 ^{ix}	180.0
Li ^{vi} —O1—Cu1 ^{vii}	102.45 (5)		

Symmetry codes: (i) $x, -y+2, z+1/2$; (ii) $x, y+1, z$; (iii) $-x+1/2, y+1/2, -z+3/2$; (iv) $-x+1, y, -z+3/2$; (v) $-x+1/2, -y+5/2, -z+1$; (vi) $x, y-1, z$; (vii) $-x+1/2, y-1/2, -z+3/2$; (viii) $x, -y+2, z-1/2$; (ix) $-x+1/2, -y+3/2, -z+1$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H4 \cdots O2 ⁱ	0.848 (10)	2.37 (3)	2.9535 (19)	126 (3)
O4—H4 \cdots O5 ^x	0.848 (10)	2.32 (2)	3.036 (2)	143 (3)

Symmetry codes: (i) $x, -y+2, z+1/2$; (x) $x, -y+1, z+1/2$.

Fig. 1

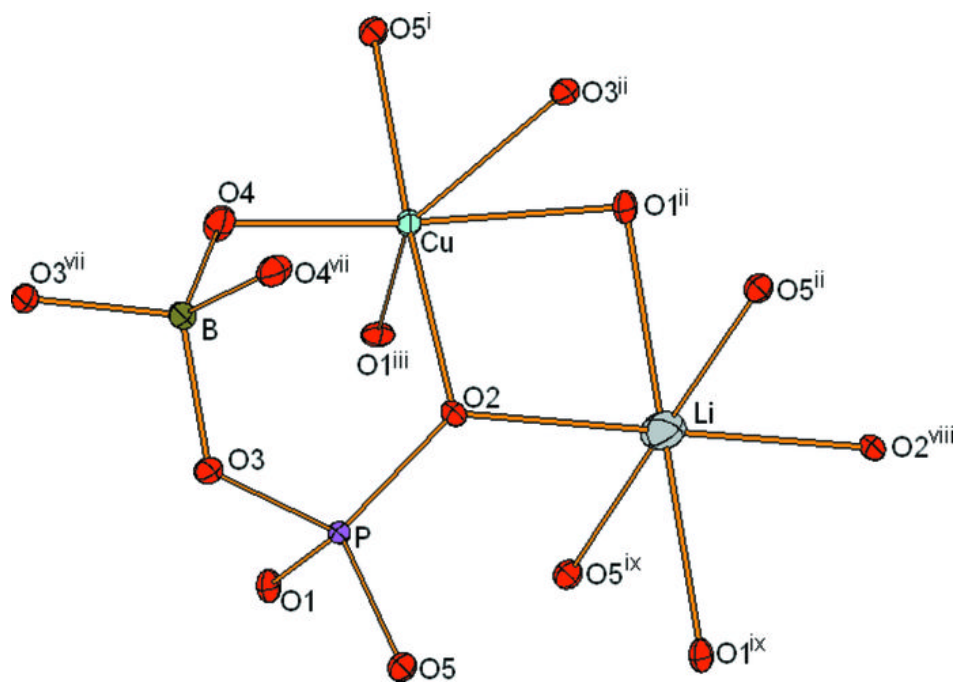


Fig. 2

