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An open-framework borophosphate, $LiCu_2BP_2O_8(OH)_2$

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Key indicators: single-crystal X-ray study; T = 296 K; mean σ(O–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, $LiCu_2BP_2O_8(OH)_2$, was synthesized hydrothermally. Its structure may be regarded as a layer formed *via* BO_4 and PO_4 tetrahedra bonding together with distorted CuO_6 and LiO_6 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 $AM(H_2O)_2[BP_2O_8].yH_2O$ (A = Li, Na, K, NH_4^+; M = 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

$LiCu_2BP_2O_8(OH)_2$
M_r = 368.79
Monoclinic, $C2/c$
a = 15.0974 (19) Å
b = 4.7617 (6) Å
c = 9.6585 (12) Å
β = 91.0190 (10)°
V = 694.23 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 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_{min} = 0.350, T_{max} = 0.398
(expected range = 0.285–0.324)
4076 measured reflections
925 independent reflections
897 reflections with $I > 2\sigma(I)$
R_{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
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O2^{i}	0.848 (10)	2.37 (3)	2.9535 (19)	126 (3)
O4—H4···O5^{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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An open-framework borophosphate, $LiCu_2BP_2O_8(OH)_2$

Juan Zheng and Aiyun Zhang

S1. Comment

In the last decade, much attention has been paid to the large family of borophosphates with the general formula $AM(H_2O)_2[BP_2O_8].yH_2O$ (A=Li, Na, K, $NH4^+$; *M*=Mg, Mn, Fe, Co, Ni, Cu, Zn, 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 $LiCu_2BP_2O_8(OH)_2$ contains one unique Li atom, two Cu atoms, one boron atom, two phosphor atoms, and eight oxygen atoms and two –OH groups in the asymmetric unit of the framework. The borophosphate units are isolated anions linked by the bonds them form to Cu, Li and H. (Fig.1) Each BO_4 tetrahedron belongs to the adjacent CuO_6 octahedra. The phosphorous 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)

S2. Experimental

Blue block crystals were synthesized hydrothermally from a mixture of $Cu(NO_3)_2$, $Li_2B_4O_7$,water and H_3PO_4. In a typical synthesis, 0.725 g $Cu(NO_3)_2$ were dissolved in a mixture of 5 mL water, 1.691 g $Li_2B_4O_7$ 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 6days.The autoclave was slowly cooled to room temperature. Blue block crystals of thetitle compound were obtained.

S3. Refinement

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

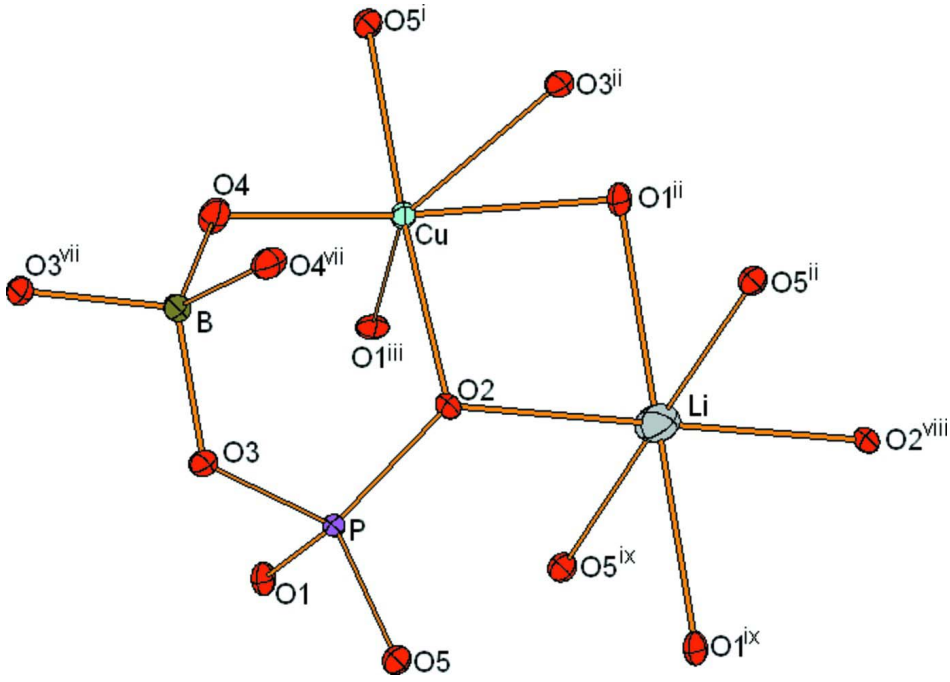

Figure 1

The structure of $LiCu_2BP_2O_8(OH)_2$. Displacement ellipsoids are drawn at 50% the probability level.

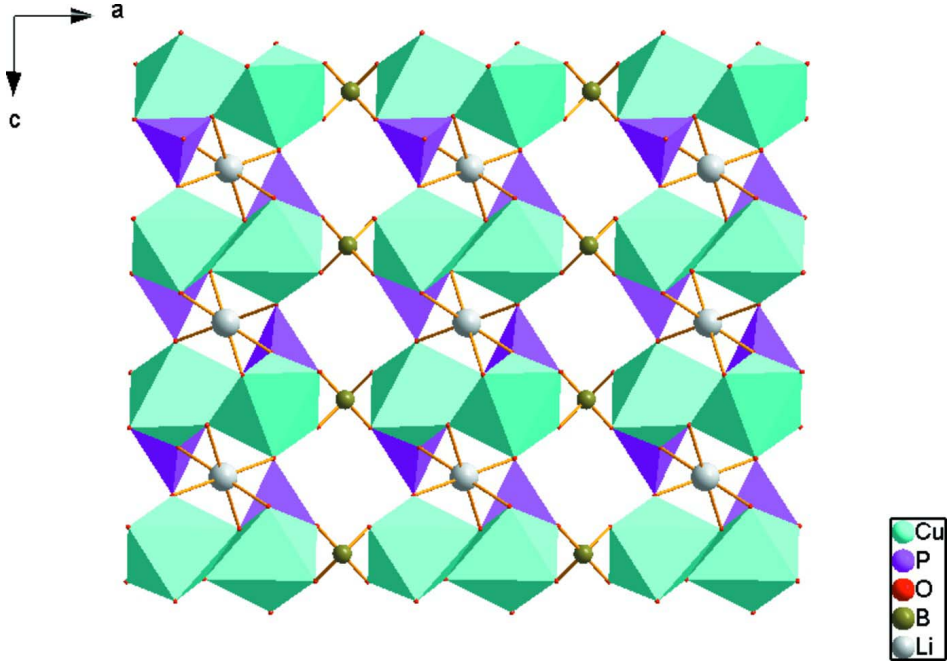

Figure 2

Packing diagram of $LiCu_2BP_2O_8(OH)_2$,viewed along *b* axis.

lithium dicopper borophosphate dihydroxide

Crystal data

$LiCu_2BP_2O_8(OH)_2$
$M_r = 368.79$
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 15.0974\ (19)$ Å
$b = 4.7617\ (6)$ Å
$c = 9.6585\ (12)$ Å
$\beta = 91.019\ (1)°$
$V = 694.23\ (15)$ Å^3
$Z = 4$
$F(000) = 712$
$D_x = 3.528$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3236 reflections
$\theta = 2.7–29.3°$
$\mu = 6.64$ mm^{-1}
$T = 296$ K
Block, blue
0.20 × 0.18 × 0.17 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
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 $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 29.3°$, $\theta_{min} = 2.7°$
$h = -20\rightarrow20$
$k = -6\rightarrow6$
$l = -12\rightarrow12$

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
79 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
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 $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.63$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{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 (Å²)

	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 (Å, º)

Cu1—O5^{i}	1.9415 (13)	P2—O1	1.5420 (14)
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 (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···O2^{i}	0.85 (1)	2.37 (3)	2.9535 (19)	126 (3)
O4—H4···O5^{x}	0.85 (1)	2.32 (2)	3.036 (2)	143 (3)

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