Crystal structure of lithium copper(II) monoaqua *catena*-[monoborodiphosphate] dihydrate, $LiCu(H_2O)[BP_2O_8] \cdot 2H_2O$

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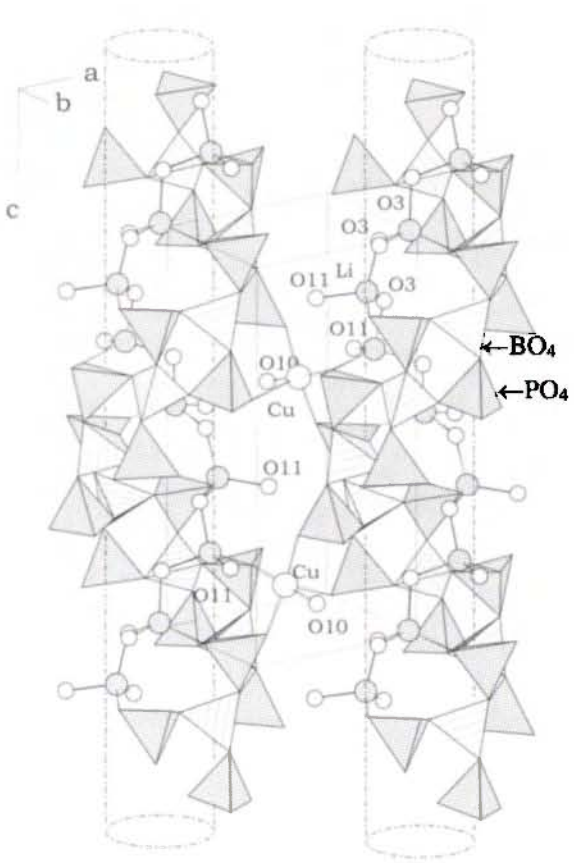

Abstract

$BCuLiO_{11}P_2$, hexagonal, $P6_1$ (No. 169), $a = 9.520(4)$ Å, $c = 15.438(6)$ Å, $V = 1211.7$ Å^3, $Z = 6$, $R_{gt}(F) = 0.029$, $wR_{ref}(F^2) = 0.102$, $T = 293$ K.

Source of material

$LiCu(H_2O)[BP_2O_8] \cdot 2H_2O$ was prepared by hydrothermal treatment of mixtures of 1.3 g $Li_2B_4O_7$, 6.4 g LiH_2PO_4, and 1.31 g $CuCl_2 \cdot 2H_2O$ (molar ratio 1:8:1). A concentrated aqueous solution of pH = 1 – 1.5 (HCl) was held at 433 K for two weeks in a teflon autoclave (20 ml, degree of filling: 50%).

Discussion

The crystal structure of $LiCu(H_2O)[BP_2O_8] \cdot 2H_2O$ contains infinite one-dimensional anionic partial structures. The condensation of BO_4 and PO_4 tetrahedra through common vertices leads to tetrahedral ribbons $^1_\infty[BP_2O_8^{3-}]$, which are arranged around 6_1 screw axes to from helical arrangements. The spiral ribbons are built up from four-membered rings in which BO_4 and PO_4 groups alternate. Each BO_4 tetrahedron belongs to the adjacent four-ring of tetrahedra along the ribbon in such a way that all vertices of the BO_4 groups participate in bridging functions with PO_4 tetrahedra. The phosphate groups occupy the borders of the ribbons with two terminal oxygen atoms. Bond lengths and angles within the anionic partial structure are consistent with related borophosphates (see [1,2] and refs. herein). The free loop of the borophosphate helix is occupied by Li^+ in a tetrahedral coordination by oxygen atoms from adjacent phosphate groups and water molecules ($O(3)_{H2O}$, $O(11)_{H2O}$). The double helix $\{Li[BP_2O_8]^{2-}\}$ is completed forming a central channel running along the 6_1 screw axis, and which is filled with water of crystallization ($O(3)_{H2O}$) resulting in the formula $LiCu(H_2O)[BP_2O_8] \cdot 2H_2O$. The water molecules form hydrogen bonds ($O(3)_{H2O} \cdots O(3)_{H2O} = 3.01$ Å) with each other along the spiral. Cu^{2+} is in a tetragonal pyramidal coordination (Cu—O = 1.978(5) – 2.346(5) Å; see also [3]) by oxygen functions of PO_4 groups and water molecules ($O(10)_{H2O}$).

Table 1. Data collection and handling.

Crystal:	turquoise, hexagonal bipyramids, size 0.10 × 0.10 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	31.52 cm^{-1}
Diffractometer, scan mode:	Philips PW 1100 updated by STOE, ω/2θ
$2\theta_{max}$:	59.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7096, 1226
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1134
$N(param)_{refined}$:	145
Programs:	SHELXS-97 [4], SHELXL-97 [5], DIAMOND [6]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Li	6*a*	–0.120(2)	0.128(2)	–0.033(1)	0.026(7)	0.019(6)	0.028(7)	0.007(6)	0.001(5)	–0.009(5)
Cu	6*a*	0.11234(8)	0.56682(9)	0.54254(5)	0.0125(3)	0.0126(3)	0.0078(3)	0.0092(3)	–0.0016(3)	–0.0028(3)
B	6*a*	0.3039(7)	0.1587(7)	0.0439(5)	0.009(2)	0.009(3)	0.007(2)	0.005(2)	0.003(2)	0.000(2)
P(1)	6*a*	0.1966(2)	0.3751(2)	0.0389(1)	0.0065(6)	0.0064(6)	0.0065(6)	0.0040(5)	0.0011(5)	0.0008(5)
P(2)	6*a*	0.3910(2)	0.2359(2)	0.2152(1)	0.0067(6)	0.0064(5)	0.0058(5)	0.0036(5)	–0.0011(5)	–0.0007(5)
O(1)	6*a*	0.0333(5)	0.3501(6)	0.0090(3)	0.012(2)	0.016(2)	0.013(2)	0.011(2)	–0.002(2)	–0.002(2)
O(2)	6*a*	0.0991(9)	0.190(1)	0.6753(4)	0.043(4)	0.085(6)	0.017(3)	0.047(4)	–0.007(3)	–0.007(3)
O(3)	6*a*	0.1829(5)	0.2065(5)	0.0250(3)	0.010(2)	0.008(2)	0.011(2)	0.004(2)	–0.003(1)	–0.002(1)
O(4)	6*a*	0.2168(5)	0.2030(5)	0.2330(3)	0.005(2)	0.011(2)	0.015(2)	0.005(2)	0.002(1)	0.001(2)
O(5)	6*a*	0.2233(5)	0.4142(5)	0.1377(3)	0.008(2)	0.006(2)	0.008(2)	0.001(2)	0.004(2)	0.003(2)
O(6)	6*a*	0.3993(6)	0.0922(5)	0.2508(3)	0.018(2)	0.010(2)	0.015(2)	0.010(2)	–0.004(2)	0.001(2)
O(7)	6*a*	0.3440(5)	0.5073(5)	–0.0056(3)	0.010(2)	0.012(2)	0.011(2)	0.003(2)	0.006(2)	0.001(2)
O(8)	6*a*	0.4155(5)	0.2529(6)	0.1148(3)	0.010(2)	0.012(2)	0.006(2)	0.006(2)	–0.001(2)	–0.003(1)
O(9)	6*a*	0.4969(6)	0.2237(6)	0.4046(3)	0.019(2)	0.010(2)	0.017(2)	0.008(2)	–0.008(2)	–0.002(2)
O(10)	6*a*	0.5156(6)	0.3988(5)	0.2525(3)	0.013(2)	0.010(2)	0.009(2)	0.004(2)	–0.002(2)	–0.001(2)
O(11)	6*a*	0.6851(6)	0.1404(7)	–0.0136(4)	0.013(2)	0.025(3)	0.039(3)	0.010(2)	0.000(2)	0.009(2)

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