Crystal structure of lithium cadmium diaqua *catena*-[monoborodiphosphate]-monohydrate, $LiCd(H_2O)_2[BP_2O_8] \cdot H_2O$

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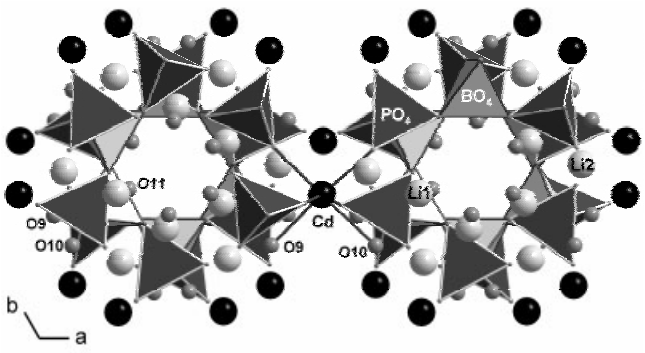

Abstract

$BCdH_6LiO_{11}P_2$, hexagonal, $P6_5$ (No. 170), a = 9.7111(6) , c = 16.012(1) Å, V = 1307.7 Å^3, Z = 6, $R_{gt}(F)$ = 0.055, $wR_{ref}(F^2)$ = 0.126, T = 293 K.

Source of material

$LiCd(H_2O)_2[BP_2O_8] \cdot H_2O$ was prepared under mild hydrothermal conditions. A mixture of 0.603 g $CdCl_2 \cdot 2.5H_2O$, 5.042 g LiOH, 1.568 g H_3BO_3 and 10 ml (85%) H_3PO_4 was heated at 363 K in deionized water (10 ml) under stirring until the components were completely dissolved . The solution (pH = 2.0 – 2.5) was transferred to a teflon autoclave (internal volume 27 ml, degree of filling 70%) and heated at 443 K for four days. The starting materials were of analytical grade and used without further purification.

Discussion

In the course of our systematic studies on Cd-based borophosphates, a series of compounds with the general formula $M^I_xCd_y(H_2O)_2[BP_2O_8] \cdot H_2O$ (M^I = Li, Na, K, NH_4^+; x = 0.5 – 1, y = 1 – 1.25, z = 0.5 – 1) [1,2] was found which forms a large family of borophosphate-hydrates [3,4]. Here we report the synthesis and structure of $LiCd(H_2O)_2[BP_2O_8] \cdot H_2O$.

The crystal structure of the title compound contains infinite one-dimensional borophosphate helical ribbons $^1_\infty\{[BP_2O_8]^{3-}\}$ around the 6_5 axes. The ribbons are built up of four-membered rings in which BO_4 and PO_4 groups alternate. Each BO_4 belongs to the adjacent four-ring of tetrahedra along the ribbon in such a way that all vertices of the BO_4 tetrahedron act as bridging corners with PO_4 tetrahedra. The terminal oxygen atoms in the phosphate groups which are located at the borders of the ribbons also act as ligands to complete the coordination sphere around Cd^{2+}. The Cd^{2+} ion is coordinated to the oxygen atoms of PO_4 groups (O3, O6, O7, O8) and water molecules ($O9_{H2O}$ and $O10_{H2O}$) (d(Cd—O) = 2.22 – 2.48 Å). These coordinating O atoms form an octahedron around cadmium: $Cd(O_P)_4(O_{H2O})_2$. Bond lengths and angles within the anionic partial structure are consistent with related borophosphates [5–8]. In contrast to other members of the family, the title structure contains two partially occupied Li positions (Li1 and Li2). Li^+ cations do not exhibit an ordered distribution in the free loops of the borophosphate helices ($^1_\infty\{[BP_2O_8]^{3-}\}$) like Na^+ or Li^+ in respective compounds [3,9]. The Li2 position is comparable with the partially occupied transition metal position in $(NH_4)_{0.4}Fe^{II}_{0.55}Fe^{III}_{0.5}(H_2O)_2[BP_2O_8] \cdot 0.6H_2O$ (**B**) and $(NH_4)_xCo_{((3-x)/2)}(H_2O)_2[BP_2O_8] \cdot (1-x)\,H_2O$ (x = 0.5) (**C**) [6,10]. In title compound (**A**), the $Li1^+$ cations (which are stuffed close to the helical channels; d(Li1—$O11_{H2O}$) = 1.95 Å) correspond to the NH_4^+ ions in **B** and **C**. The borophosphate helices in **A** are stabilized by additional Li2 within their free threads a situation which correspond to the partially occupied Fe and Co sites in **B** and **C**, respectively. The reason why it is Li2 but not Cd occupying this position might be because of the inadequate space for Cd (d(Li2—$O10_{H2O}$) = 1.74 Å). The summation of the two refined Li occupancies is almost unity and the result is reasonable in consideration of maintaining the charge neutrality. Li1 is in an irregular coordination by oxygen atoms (O1, O3) from adjacent phosphate groups and water molecules ($O10_{H2O}$, $O11_{H2O}$). Li2 is coordianted by oxygen atoms (O3, O6) from adjacent phosphate groups and water molecules ($O9_{H2O}$, $O10_{H2O}$, $O11_{H2O}$). The water position $O11_{H2O}$ shows disordering (large displacement parameters), which is characteristic for this structure family [10].

Table 1. Data collection and handling.

Crystal:	colorless hexagonal bipyramid, size 0.09 × 0.09 × 0.12 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	29.23 cm^{-1}
Diffractometer, scan mode:	Rigaku CCD, ϕ
$2\theta_{max}$:	56.54°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8466, 1719
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1718
$N(param)_{refined}$:	134
Programs:	SHELXLS-97 [11], SHELXL-97 [12], DIAMOND [13]

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
B	6*a*		1.152(1)	–0.148(1)	0.326(1)	0.012(2)
Li(1)	6*a*	0.66(5)	0.867(4)	–0.230(4)	–0.105(3)	0.03
Li(2)	6*a*	0.34	0.640(7)	–0.013(8)	0.168(5)	0.03
H(1)	6*a*		0.8303	0.3811	0.4600	0.05
H(2)	6*a*		0.7647	0.1608	0.4911	0.05
H(3)	6*a*		0.6897	0.2172	0.1344	0.05
H(4)	6*a*		0.7876	0.2343	0.2211	0.05
H(5)	6*a*		0.8607	0.7325	0.0183	0.05
H(6)	6*a*		0.9696	0.9013	0.0076	0.05

Table 3. 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}
Cd	6*a*	0.89804(8)	0.4507(1)	0.1594(1)	0.0162(4)	0.0155(4)	0.0111(4)	0.0077(3)	–0.0002(4)	–0.0035(3)
P(1)	6*a*	1.2166(3)	0.3817(3)	0.1599(2)	0.013(1)	0.015(1)	0.011(2)	0.009(1)	–0.002(1)	0.002(1)
P(2)	6*a*	1.2195(3)	–0.1636(3)	0.1602(2)	0.012(1)	0.016(1)	0.003(1)	0.0067(9)	0.001(1)	0.001(1)
O(1)	6*a*	1.1954(9)	0.2136(9)	0.1748(6)	0.012(3)	0.020(4)	0.012(5)	0.005(3)	0.003(3)	0.001(3)
O(2)	6*a*	1.2292(9)	–0.1821(9)	0.2557(6)	0.015(4)	0.011(3)	0.009(5)	0.007(3)	0.000(3)	–0.001(3)
O(3)	6*a*	1.066(1)	0.369(1)	0.1978(7)	0.037(6)	0.040(6)	0.042(7)	0.035(5)	0.013(5)	0.001(5)
O(4)	6*a*	1.1947(9)	–0.0178(9)	0.1450(5)	0.016(3)	0.011(2)	0.005(3)	0.005(2)	–0.003(2)	0.001(2)
O(5)	6*a*	1.2277(9)	0.412(1)	0.0642(6)	0.016(3)	0.011(2)	0.005(3)	0.005(2)	–0.003(2)	0.001(2)
O(6)	6*a*	0.866(1)	0.489(1)	0.2930(6)	0.033(5)	0.015(4)	0.018(5)	0.016(4)	0.001(4)	0.000(3)
O(7)	6*a*	1.370(1)	0.510(1)	0.1930(6)	0.031(5)	0.016(4)	0.013(5)	0.007(4)	–0.009(4)	–0.002(3)
O(8)	6*a*	1.076(1)	–0.300(1)	0.1212(6)	0.027(5)	0.015(4)	0.018(5)	0.003(4)	–0.001(4)	0.002(4)
O(9)	6*a*	0.817(1)	0.295(1)	0.4553(7)	0.029(5)	0.014(4)	0.036(7)	–0.003(4)	–0.010(4)	0.003(4)
O(10)	6*a*	0.703(1)	0.178(1)	0.2055(9)	0.028(5)	0.032(6)	0.061(9)	0.013(5)	0.001(5)	–0.012(5)
O(11)	6*a*	0.902(2)	–0.178(3)	0.014(1)	0.09(1)	0.17(2)	0.08(2)	0.09(1)	–0.03(1)	–0.01(1)

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