Crystal structure of hemicalcium diaquanickel(II) *catena*-(monoborodiphosphate) monohydrate, $Ca_{0.5}Ni(H_2O)_2[BP_2O_8] \cdot H_2O$

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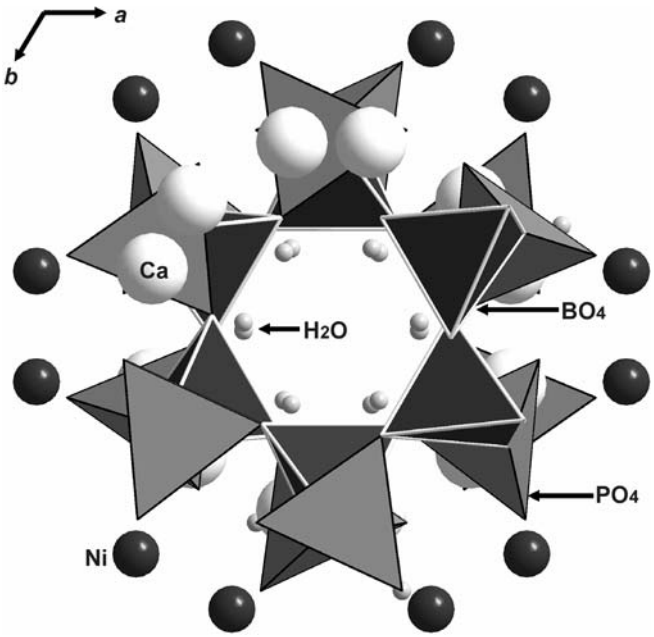
Received September 28, 2006, accepted and available on-line March 20, 2007; CSD no. 409899



Abstract

$BCa_{0.5}H_6NiO_{11}P_2$, hexagonal, $P6_122$ (no. 178), a = 9.3715(3) Å, c = 15.7261(6) Å, V = 1196.1 Å^3, Z = 6, $R_{gt}(F)$ = 0.052, $wR_{ref}(F^2)$ = 0.131, T = 295 K.

Source of material

$Ca_{0.5}Ni(H_2O)_2[BP_2O_8] \cdot H_2O$ was prepared by mild hydrothermal treatment of nickel oxide, calcium hydroxide, boric acid and phosphoric acid. A mixture of 0.2480 g $Ca(OH)_2$ (Aldrich, 95 %), 0.2500 g NiO (Alfa Aesar, 99 %), 0.4606 g B_2O_3 (Alfa Aesar, 99.98 %) and 2.3153 g H_3PO_4 (Merck, 85 %) was treated hydrothermally (molar ratio Ca:Ni:B:P = 1:1:4:6). The mixture was placed in a 10 ml Teflon-lined autoclave (filling degree 30 %), treated under autogenous pressure at 443 K for 8 days. The resulting product was filtered off, washed with water and dried at air. The chemical composition was confirmed by EDXS analysis.

Experimental details

The occupancy of the Ca1 site was refined freely and resulted in a value of 0.263(5). In the final refinement cycles it was fixed to 0.25. The positions of the hydrogen atoms close to O5 (coordinating water) were located in a Fourier difference map and refined as free variables, whereas the isotropic displacement parameters were restrained to $1.2U_{iso}$(O5). For the oxygen atom of the hydrate water (O6), a split model was assumed with an occupancy factor of 0.5. The corresponding hydrogen atoms could not be localized.

Discussion

Helical borophosphates emerge to be the largest group of compounds among the borophosphates [1]. The group of compounds with $^1_\infty[BP_2O_8^{3-}]$ helical chain anions have been synthesized in combination with different cations M^IM^{II} and M^{III} (M^I = Li, Na, K; M^{II} = Mg, Mn, Fe, Co, Ni Zn; M^{III} = Sc, In, Fe) [2-6]. The possibility of realizing de-/rehydration processes in helical borophosphates has been reported as well [4-7]. Our systematic investigation on borophosphate systems with nickel and alkali earth metals (Ca, Sr, and Ba) led to two new borophosphates of different composition: $CaNi[BP_2O_7(OH)_3]$ [8] and $Ca_{0.5}Ni(H_2O)_2[BP_2O_8] \cdot H_2O$. The title compound is the first example of helical borophosphates containing the cation combination $M^{II}_{0.5}M'^{II}$.

The crystal structure of the title compound reveals an infinite one-dimensional anionic partial structure. Condensation of PO_4 and BO_4 tetrahedra via common vertices leads to tetrahedral ribbons $^1_\infty[BP_2O_8^{3-}]$ which are arranged around a 6_1 screw axis to form chiral helices. 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. Interatomic distances and angles within the tetrahedral helices are similar to related borophosphates [1-8]. The central channel is filled by a helix made up of water molecules. The ribbons are connected via $NiO_4(H_2O)_2$ octahedra (four oxygen atoms of PO_4 groups and two water molecules) and the free threads of the helices are half-occupied by calcium ions fixed by an irregular surrounding of six oxygen atoms from adjacent phosphate groups. The Ni—O bond distances range from 2.05 Å – 2.15 Å. The overall resulting framework is related to the topology of chiral zincophosphates (CZP).

Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.12 × 0.11 × 0.05 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	32.11 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-7, φ/ω
$2\theta_{max}$:	63.28°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9797, 1248
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1173
$N(param)_{refined}$:	87
Programs:	SHELXS-97 [9], SHELXL-97 [10], DIAMOND [11]

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(51)	12*c*		0.546(8)	0.675(7)	0.258(3)	0.033
H(52)	12*c*		0.435(6)	0.620(6)	0.203(4)	0.033
Ca(1)	12*c*	0.25	0.6396(5)	0.7526(5)	0.0768(2)	0.0295(7)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	6*b*		0.44582(5)	2*x*	¼	0.0216(3)	0.0202(4)	0.0233(4)	½U_{22}	–0.0033(2)	0
P(1)	12*c*		0.6112(1)	0.8286(1)	0.41389(7)	0.0184(5)	0.0174(4)	0.0179(5)	0.0082(4)	–0.0016(4)	–0.0005(3)
O(1)	12*c*		0.5818(4)	0.8164(4)	0.5120(2)	0.019(1)	0.025(1)	0.016(1)	0.010(1)	–0.002(1)	–0.000(1)
O(2)	12*c*		0.7866(4)	0.9780(4)	0.3994(2)	0.024(1)	0.015(1)	0.025(2)	0.008(1)	0.002(1)	–0.001(1)
O(3)	12*c*		0.4820(4)	0.8606(4)	0.3763(2)	0.025(2)	0.028(2)	0.024(1)	0.014(1)	–0.005(1)	0.002(1)
O(4)	12*c*		0.6152(4)	0.6801(4)	0.3800(2)	0.031(2)	0.018(1)	0.023(1)	0.011(1)	–0.001(1)	–0.000(1)
O(5)	12*c*		0.5107(5)	0.7083(4)	0.2176(2)	0.030(2)	0.022(1)	0.029(2)	0.011(1)	–0.006(1)	–0.000(1)
O(6)	12*c*	0.5	0.847(2)	0.855(2)	0.152(1)	0.033(4)	0.048(5)	0.04(1)	0.024(3)	0.002(4)	0.014(5)
B(1)	6*b*		0.1514(4)	2*x*	¼	0.014(2)	0.019(2)	0.020(3)	½U_{22}	–0.001(2)	0

Acknowledgment. The authors would like to thank Mrs. P. Scheppan for EDXS analysis.

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