Crystal structure of diaqua(magnesium, cobalt) bis(hydroxyboro)bis-phosphate monohydrate, $Mg_{1-x}Co_x(H_2O)_2[B_2P_2O_8(OH)_2] \cdot H_2O$ ($x \approx 0.25$)

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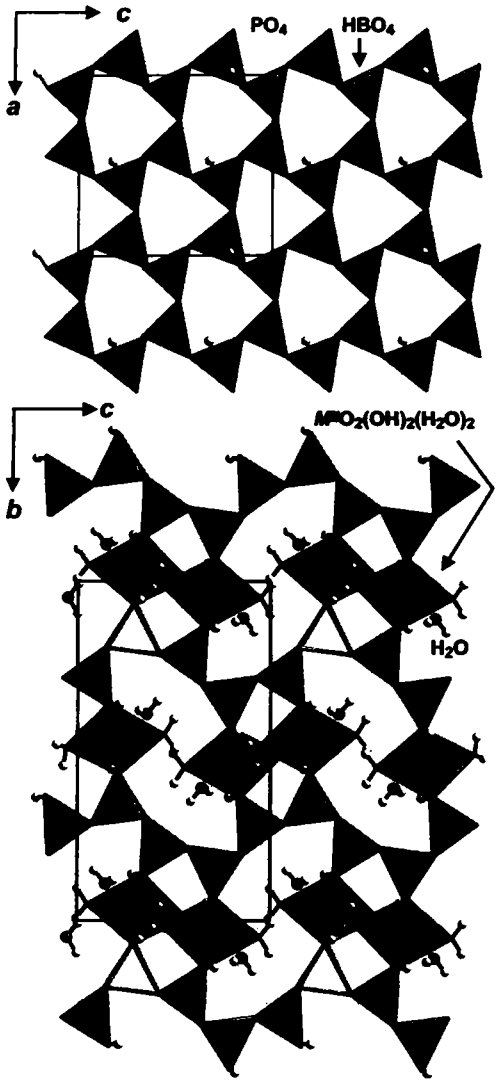

Abstract

$B_2Co_{0.23}H_8Mg_{0.77}O_{13}P_2$, monoclinic, $P12_1/c1$ (no. 14), $a = 7.7591(5)$ Å, $b = 14.654(1)$ Å, $c = 8.2382(5)$ Å, $\beta = 90.26(1)°$, $V = 936.7$ Å^3, $Z = 4$, $R_{gt}(F) = 0.040$, $wR_{ref}(F^2) = 0.098$, $T = 293$ K.

Source of material

A single phase product of the title compound was obtained hydrothermally from an aqueous solution of magnesium hydroxide (Merck, extra pure), cobalt chloride (Alfa Aesar, 99.9%), boric acid (Roth, 99.9%) and phosphoric acid (Merck, 85%). A mixture of 0.500 g (8.573 mmol) $Mg(OH)_2$, 0.557 g (4.287 mmol) $CoCl_2$, 3.181 g (45.687 mmol) H_3BO_3, and 7.907 g (68.589 mmol) 85 % H_3PO_4 was placed in a 20 ml Teflon autoclave which was then filled with water up to a filling degree of 50 %. The reaction was performed at 443 K in a chamber furnace. After a reaction duration of 13 days the autoclave was removed from the furnace and allowed to cool down to room temperature. The raw product was separated from the mother liquor by vacuum filtration, washed with water and acetone before dried in air at 333 K. X-ray powder diffraction gave no evidence for any crystalline impurities. Chemical analyses of powdered samples dissolved in acids comprise a ratio of Co:Mg = 0.27(1):0.73(1) that confirms the composition determined in the structure refinement (investigations of different single crystals gave no significant deviation from this composition). The presence of Co^{2+} in the investigated compound is also evidenced by EDX analyses and the rose color of the crystals.

Discussion

The crystal structure of $Mg_{1-x}Co_x(H_2O)_2[B_2P_2O_8(OH)_2] \cdot H_2O$ ($x \approx 0.25$) represents one of the few examples of borophosphates with a layered anionic partial structure [1-3]. Isotypic with the pure magnesium compound [1] it comprises a 2D arrangement of distorted phosphate and hydrogenborate groups that are connected in alternating fashion via common corners to form a corrugated 6^3 net (figure, top). In the hydrogenborate groups B—O distances range from 1.441(2) Å to 1.485(2) Å of which the B—OH bonds are the shortest (1.441(2) Å and 1.449(2) Å). The O–B–O angles have values between 106.2(2)° and 113.9(2)°. In the phosphate groups P—O distances range from 1.500(2) Å to 1.546(2) Å and O–P–O angles vary between 105.5(1)° and 113.8(1)°. Sixfold coordination by two oxygen atoms, two OH-groups and two water molecules is found for the metal cations. The oxo- and hydroxo ligands originate from two phosphate respectively two hydrogenborate units and are located on the equatorial positions of the octahedron with almost equal distances (M^{II}—O = 2.078(2) Å – 2.095(2) Å). The apical positions are occupied by water molecules with M^{II}—OH_2 distances of 2.044(2) Å and 2.185(2) Å. The O–M^{II}–O angles between ligands on adjacent corners range from 84.39(5)° to 95.16(6)°. As shown in a view along the a axis (figure, bottom), the magnesium octahedra interconnect the corrugated layers, and ten-membered polyhedral ring channels are formed along [100] in which the hydrate water is located. Hydrogen bonds of structural relevance are found between the anionic framework and the hydrate water, as well as inbetween the water molecules. Due to long distances between the participating oxygen atoms (> 2.70 Å) the interactions are weak. Most of the hydrogen bonds are not directional with O–H···O angles significantly deviating from 180°.

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Table 1. Data collection and handling.

Crystal:	rose, irregular, size 0.040 × 0.080 × 0.090 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	10.19 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-7 & Mercury CCD, ω/φ
$2\theta_{max}$:	60°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8290, 2645
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2304
$N(param)_{refined}$:	197
Programs:	SHELXL-97 [4], DIAMOND [5]

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

Atom	Site	x	y	z	U_{iso}
H(91)	4*e*	–0.018(6)	0.637(3)	0.785(5)	0.05(1)
H(101)	4*e*	0.526(5)	0.447(3)	0.824(5)	0.03(1)
H(111)	4*e*	0.229(7)	0.905(4)	0.001(7)	0.08(2)
H(112)	4*e*	0.246(6)	0.993(3)	–0.004(6)	0.05(1)
H(121)	4*e*	0.158(5)	0.981(3)	0.610(5)	0.04(1)
H(122)	4*e*	0.270(6)	1.044(3)	0.574(6)	0.06(1)
H(131)	4*e*	0.342(7)	0.119(3)	0.819(6)	0.06(1)
H(132)	4*e*	0.233(6)	0.148(3)	0.913(6)	0.05(1)

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}
M	4*e*	0.24867(7)	0.53571(4)	0.79951(7)	0.0121(3)	0.0095(3)	0.0145(3)	–0.0004(2)	0.0003(2)	–0.0014(2)
B(1)	4*e*	0.9204(3)	0.2833(2)	0.0576(3)	0.012(1)	0.010(1)	0.0106(9)	0.0003(8)	0.0005(8)	–0.0004(8)
B(2)	4*e*	0.4204(3)	0.3358(2)	0.7683(3)	0.009(1)	0.011(1)	0.013(1)	0.0003(8)	–0.0013(8)	–0.0010(8)
P(1)	4*e*	0.57174(7)	0.28701(4)	0.06110(6)	0.0088(3)	0.0108(3)	0.0105(2)	–0.0000(2)	–0.0002(2)	0.0007(2)
P(2)	4*e*	0.07005(7)	0.16152(4)	0.27051(6)	0.0090(3)	0.0106(3)	0.0102(2)	0.0005(2)	–0.0002(2)	0.0010(2)
O(1)	4*e*	0.0494(2)	0.0607(1)	0.2953(2)	0.0153(8)	0.0108(7)	0.0192(7)	0.0005(6)	0.0010(6)	0.0016(6)
O(2)	4*e*	0.5504(2)	0.1962(1)	0.1530(2)	0.0106(7)	0.0124(7)	0.0138(7)	0.0006(6)	0.0039(6)	0.0029(6)
O(3)	4*e*	0.5544(2)	0.3700(1)	0.1670(2)	0.0161(8)	0.0140(8)	0.0181(7)	–0.0015(6)	0.0031(6)	–0.0042(6)
O(4)	4*e*	0.0527(2)	0.2165(1)	0.4292(2)	0.0118(8)	0.0179(8)	0.0122(7)	–0.0006(6)	0.0019(6)	–0.0035(6)
O(5)	4*e*	0.9383(2)	0.1952(1)	0.1437(2)	0.0113(8)	0.0136(8)	0.0120(7)	–0.0005(6)	–0.0015(6)	0.0031(6)
O(6)	4*e*	0.4371(2)	0.2148(1)	0.4238(2)	0.0108(8)	0.0183(8)	0.0130(7)	0.0012(6)	–0.0021(6)	–0.0034(6)
O(7)	4*e*	0.2497(2)	0.7829(1)	0.5210(2)	0.0099(7)	0.0146(8)	0.0113(7)	0.0008(6)	0.0004(5)	–0.0013(5)
O(8)	4*e*	0.2487(2)	0.1869(1)	0.2015(2)	0.0093(7)	0.0148(7)	0.0098(6)	0.0003(6)	–0.0007(5)	0.0010(5)
O(9)	4*e*	0.0668(2)	0.6377(1)	0.8373(2)	0.0145(8)	0.0133(8)	0.0172(7)	0.0021(6)	–0.0031(6)	–0.0037(6)
O(10)	4*e*	0.4338(2)	0.4331(1)	0.7888(2)	0.0136(8)	0.0110(8)	0.0214(8)	0.0006(6)	–0.0027(6)	–0.0022(6)
O(11)	4*e*	0.2411(3)	0.9513(2)	0.0526(2)	0.051(1)	0.019(1)	0.0185(9)	–0.0012(9)	–0.0009(9)	–0.0009(8)
O(12)	4*e*	0.2546(2)	0.9904(1)	0.5606(2)	0.0177(9)	0.0192(9)	0.0160(8)	–0.0005(7)	0.0014(7)	0.0001(6)
O(13)	4*e*	0.2474(3)	0.1091(2)	0.8561(3)	0.029(1)	0.021(1)	0.0265(9)	–0.0053(8)	0.0036(8)	–0.0037(8)

$M = Co_{0.233(4)}Mg_{0.767}$

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References

1. Ewald, B.; Öztan, Y.; Prots, Yu.; Kniep, R.: Structural Patterns and Dimensionality in Magnesium Borophosphates: The Crystal Structures of $Mg_2(H_2O)[BP_3O_9(OH)_4]$ and $Mg(H_2O)_2[B_2P_2O_8(OH)_2] \cdot H_2O$. Z. Anorg. Allg. Chem. **631** (2005) 1615-1621.
2. Kniep, R.; Engelhardt, H.; Hauf, C.: A First Approach to Borophosphate Structural Chemistry. Chem. Mater. **10** (1998) 2930-2934.
3. Ewald, B.; Kniep, B.: Structural Chemistry of Borophosphates, in preparation.
4. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
5. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 2.0f. Crystal Impact, Bonn, Germany 1998.