Crystal structure of cobalt manganese monoaqua *catena*-[monohydrogenborate-tris(hydrogenphosphate)], $(Co_{0.6}Mn_{0.4})_2(H_2O)[BP_3O_9(OH)_4]$

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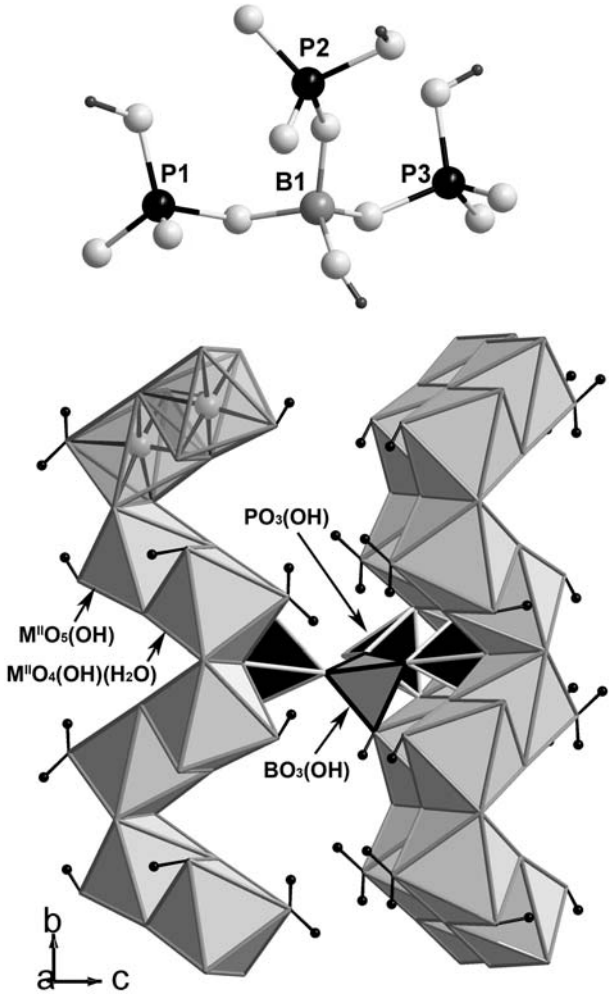

Abstract

$BCo_{1.20}H_6Mn_{0.80}O_{14}P_3$, orthorhombic, $P2_12_12_1$ (no. 19), a = 7.1355(6) Å, b = 8.7321(8) Å, c = 16.405(2) Å, V = 1022.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.049, $wR_{ref}(F^2)$ = 0.119, T = 295 K.

Source of material

Reactions were carried out by mixing MnO (0.710 g), CoO (0.750 g), P_2O_5 (4.260 g), and B_2O_3 (0.624 g) with 5 ml deionized water. The mixture was stirred at 373 K (for evaporation of water). The resulting violet gel was transferred into a Teflon autoclave (volume 20 ml; filling degree 30 %; pH < 0.5) and was held at 443 K for 3 days. After vacuum filtration and washing, the purple crystalline compound (prismatic habit), was first examined by X-ray powder diffraction which proved purity of the sample. Chemical analyses resulted in Mn : Co ratio of 3 : 2 which agrees with the results of the single crystal structure refinement.

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Experimental details

Hydrogen atoms were located from difference Fourier maps. The isotropic displacement parameters were fixed at U_{iso} = 1.2 U_{eq}(O).

Discussion

During our investigations on the systems M^{II}O-B_2O_3-P_2O_5-H_2O [1], we successfully synthesized a series of compounds with the common chemical formula $M^{II}[BPO_4(OH)]$ (M^{II} = Mn, Fe, Co) [2] containing edge-sharing $M^{II}O_6$ octahedral helical chains wound around 3_1 or 3_2 screw axes and showing low dimensional magnetic properties. Here, we report on a new compound containing both mangenese and cobalt, and also forming edge-sharing octahedral chains.

The crystal structure of $(Co_{0.6}Mn_{0.4})_2(H_2O)[BP_3O_9(OH)_4]$ is isostructural to $Mg_2(H_2O)[BP_3O_9(OH)_4]$ [3], which is constructed from infinite zigzag-shaped chains of distorted $M^{II}O_4(OH)(H_2O)$ and $M^{II}O_5(OH)$ octahedra by sharing common edges interconnected by borophosphate tetrahedra, resulting in a 3D framework structure. The borophosphate tetramer is built from a central hydrogenborate tetrahedron open-branched by three adjacent hydrogenphosphate tetrahedra (HPO_4) by sharing common vertices (figure, top). The distances (B—O) and angles O–B–O range from 145.0(7) pm to 148.4(6) pm and 102.1(4)° to 112.5(4)°, respectively. For the hydrogenphosphate groups, the distances (P—O) and angles O–P–O range from 150.5(3) pm to 157.3(3) pm and 101.6(2)° to 113.1(2)°, respectively. Both crystallographically independent M^{II} sites are in octahedral coordination. M1 is coordinated by five oxygen atoms and one OH group. M2 is surrounded by four oxygen atoms, one OH group, and one water molecule. The M^{II}—O distances range from 208.3(4) pm to 224.2(4) pm. The O–M^{II}–O bond angles (*cis*-positions) range from 80.74° to 99.16° and the O–M^{II}–O bond angles between ligands in axial position are close to 180°. The resulting distorted $M^{II}O_4(OH)(H_2O)$ and $M^{II}O_5(OH)$ octahedra are alternately interconnected *via* common edges to form zigzag chains running along [010] with angles M^{II}–M^{II}–M^{II} of 108.2° and 111.5°, respectively (figure, bottom). The replacement of magnesium by transition metals may result in systems with interesting low dimensional magnetic properties. Attempt to prepare the single phase manganese or cobalt compounds failed up to now.

Table 1. Data collection and handling.

Crystal:	purple prism, size 0.06 × 0.08 × 0.16 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	34.92 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7 CCD, φ/ω
$2\theta_{max}$:	62.00°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8978, 3150
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2995
$N(param)_{refined}$:	203
Programs:	SHELXS-97 [4], SHELXL-97 [5], DIAMOND [6]

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

Atom	Site	x	y	z	U_{iso}
H(5)	4*a*	0.80(1)	0.666(7)	0.690(4)	0.023
H(11)	4*a*	0.26(1)	0.49(1)	0.907(4)	0.026
H(12)	4*a*	0.78(1)	0.347(9)	0.620(5)	0.032
H(13)	4*a*	0.17(1)	0.682(9)	0.574(4)	0.029
H(14A)	4*a*	0.21(1)	0.39(1)	0.534(5)	0.046
H(14B)	4*a*	0.19(1)	0.21(1)	0.578(5)	0.046

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}
Co(1)	4*a*	0.70(4)	0.3175(1)	0.69202(8)	0.70555(4)	0.0129(3)	0.0145(3)	0.0184(3)	–0.0002(3)	–0.0002(2)	0.0015(2)
Mn(1)	4*a*	0.30	0.3175(1)	0.69202(8)	0.70555(4)	0.0129(3)	0.0145(3)	0.0184(3)	–0.0002(3)	–0.0002(2)	0.0015(2)
Co(2)	4*a*	0.50(4)	0.3186(1)	0.31958(8)	0.69436(4)	0.0140(3)	0.0154(4)	0.0201(3)	0.0015(3)	0.0005(2)	–0.0011(2)
Mn(2)	4*a*	0.50	0.3186(1)	0.31958(8)	0.69436(4)	0.0140(3)	0.0154(4)	0.0201(3)	0.0015(3)	0.0005(2)	–0.0011(2)
B(1)	4*a*		0.1534(8)	0.9172(7)	0.5837(3)	0.015(2)	0.024(3)	0.015(2)	0.001(2)	0.002(2)	–0.004(2)
P(1)	4*a*		0.9481(1)	0.4973(2)	0.76338(6)	0.0110(4)	0.0183(5)	0.0136(4)	0.0005(5)	0.0002(3)	–0.0015(5)
P(2)	4*a*		0.4857(1)	0.5001(2)	0.86281(6)	0.0114(4)	0.0142(5)	0.0134(4)	0.0003(5)	–0.0007(3)	0.0000(4)
P(3)	4*a*		0.6338(2)	0.5227(2)	0.58083(7)	0.0140(5)	0.0284(7)	0.0128(5)	0.0011(5)	0.0005(4)	0.0001(4)
O(1)	4*a*		0.4711(5)	0.3597(4)	0.8087(2)	0.014(2)	0.014(2)	0.021(2)	0.001(1)	–0.003(1)	0.000(1)
O(2)	4*a*		0.1421(4)	0.5044(4)	0.7244(2)	0.015(1)	0.014(1)	0.021(1)	0.001(2)	0.004(1)	0.000(1)
O(3)	4*a*		0.9833(5)	0.4784(5)	0.8568(2)	0.015(1)	0.037(2)	0.016(1)	–0.001(2)	0.004(1)	–0.002(1)
O(4)	4*a*		0.6701(4)	0.5028(5)	0.9126(2)	0.014(1)	0.018(2)	0.022(1)	0.003(2)	–0.002(1)	–0.005(1)
O(5)	4*a*		0.8436(6)	0.6466(4)	0.7487(2)	0.015(2)	0.017(2)	0.025(2)	0.000(1)	–0.002(1)	–0.002(1)
O(6)	4*a*		0.4666(5)	0.6486(4)	0.8164(2)	0.015(2)	0.016(2)	0.021(2)	0.001(1)	–0.001(1)	–0.001(1)
O(7)	4*a*		0.8379(6)	0.3599(4)	0.7334(2)	0.015(2)	0.020(2)	0.021(2)	–0.001(1)	0.002(1)	–0.001(1)
O(8)	4*a*		0.4779(5)	0.5179(5)	0.6426(2)	0.016(1)	0.025(2)	0.019(2)	–0.001(2)	0.002(1)	0.001(1)
O(9)	4*a*		0.5594(5)	0.5532(5)	0.4948(2)	0.014(2)	0.034(2)	0.018(2)	0.000(1)	0.001(1)	0.001(1)
O(10)	4*a*		0.7777(6)	0.6501(5)	0.5981(2)	0.028(2)	0.030(2)	0.026(2)	–0.003(2)	0.004(2)	0.000(2)
O(11)	4*a*		0.3344(5)	0.4943(5)	0.9326(2)	0.015(1)	0.030(2)	0.020(1)	–0.000(2)	0.005(1)	–0.003(2)
O(12)	4*a*		0.7370(6)	0.3674(5)	0.5761(3)	0.032(2)	0.023(2)	0.024(2)	0.006(2)	0.012(2)	0.002(2)
O(13)	4*a*		0.1912(6)	0.7554(5)	0.5959(2)	0.027(2)	0.020(2)	0.025(2)	–0.000(2)	–0.002(2)	0.002(1)
O(14)	4*a*		0.1971(8)	0.3063(6)	0.5759(3)	0.052(3)	0.031(2)	0.032(2)	0.000(2)	–0.015(2)	–0.003(2)

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