Crystal structure of cobalt manganese mono aqua *catena*-[mono-hydrogenborate-tris(hydrogenphosphate)], (Co_{0.6}Mn_{0.4})₂(H₂O)[BP₃O₉(OH)₄]

Ya-Xi Huang^{I,II}, Yurii Prots^I and Rüdiger Kniep^{*I}

^I Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40, 01187 Dresden, Germany

^{II} Xiamen University, Department of Materials Science and Engineering, College of Materials, 361005 Xiamen, P. R. China

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Abstract

BCo_{1.20}H₆Mn_{0.80}O₁₄P₃, orthorhombic, *P*2₁2₁2₁ (no. 19), *a* = 7.1355(6) Å, *b* = 8.7321(8) Å, *c* = 16.405(2) Å, *V* = 1022.2 Å³, *Z* = 4, *R*_g(*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), P₂O₅ (4.260 g), and B₂O₃ (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 auto-

clave (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.

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-B₂O₃-P₂O₅-H₂O [1], we successfully synthesized a series of compounds with the common chemical formula *M*^{II}[BPO₄(OH)] (*M*^{II} = Mn, Fe, Co) [2] containing edge-sharing *M*^{II}O₆ octahedral helical chains wound around 3₁ or 3₂ screw axes and showing low dimensional magnetic properties. Here, we report on a new compound containing both manganese and cobalt, and also forming edge-sharing octahedral chains.

The crystal structure of (Co_{0.6}Mn_{0.4})₂(H₂O)[BP₃O₉(OH)₄] is isostructural to Mg₂(H₂O)[BP₃O₉(OH)₄] [3], which is constructed from infinite zigzag-shaped chains of distorted *M*^{II}O₄(OH)(H₂O) and *M*^{II}O₅(OH) octahedra by sharing common edges interconnected by borophosphate tetramers, resulting in a 3D framework structure. The borophosphate tetramer is built from a central hydrogenborate tetrahedron open-branched by three adjacent hydrogenphosphate tetrahedra (HPO₄) 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}O₄(OH)(H₂O) and *M*^{II}O₅(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.

* Correspondence author (e-mail: kniep@cpfs.mpg.de)

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°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	8978, 3150
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2995
$N(\text{param})_{\text{refined}}$:	203
Programs:	SHELXS-97 [4], SHELXL-97 [5], DIAMOND [6]

Table 2. Atomic coordinates and displacement parameters (in Å²).

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

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Co(1)	4a	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)	4a	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)	4a	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)	4a	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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)

References

1. Ewald, B.; Huang, Y.-X.; Kniep, R.: Structural Chemistry of Borophosphates, Metalborophosphates, and Related Compounds. *Z. Anorg. Allg. Chem.* **633** (2007) 1517–1540.
2. Huang, Y.-X.; Ewald, B.; Prots, Yu.; Schnelle, W.; Kniep, R.: Chirality and Magnetism in a Novel Series of Isotypic Borophosphates: $M^{\text{II}}[\text{BPO}_4(\text{OH})_2]$ ($M^{\text{II}} = \text{Mn, Fe, Co}$). *Inorg. Chem.* **45** (2006) 7578–7580.
3. Ewald, B.; Öztan, Y.; Prots, Yu.; Kniep, R.: Structural Patterns and Dimensionality in Magnesium Borophosphates: The Crystal Structures of $\text{Mg}_2(\text{H}_2\text{O})[\text{BP}_3\text{O}_9(\text{OH})_4]$ and $\text{Mg}(\text{H}_2\text{O})_2[\text{B}_2\text{P}_2\text{O}_8(\text{OH})_2] \cdot \text{H}_2\text{O}$. *Z. Anorg. Allg. Chem.* **631** (2005) 1615–1621.
4. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
5. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
6. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 3.1a. Crystal Impact, Bonn, Germany 1998.