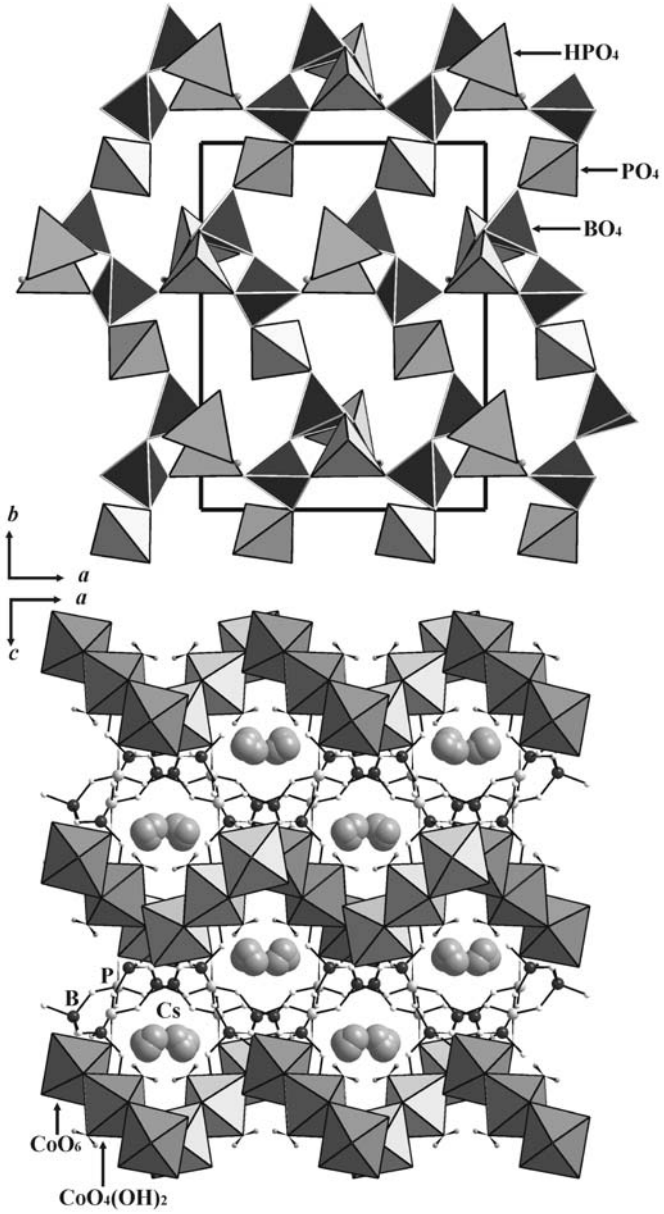
© by Oldenbourg Wissenschaftsverlag, München

Crystal structure of dicaesium diaquatricobalt(II) (phosphate-borate-hydrogenphosphate), $Cs_2Co_3(H_2O)_2[B_4P_6O_{24}(OH)_2]$

Prashanth W. Menezes, Stefan Hoffmann, Yurii Prots and Rüdiger Kniep*

Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden, Germany

Received September 12, 2008, accepted and available on-line November 25, 2008; CSD no. 409968



Abstract

$B_4Co_3Cs_2H_6O_{28}P_6$, orthorhombic, *Pbca* (no. 61), $a = 9.5526(4)$ Å, $b = 12.3190(4)$ Å, $c = 20.1123(8)$ Å, $V = 2366.8$ Å^3, $Z = 4$, $R_{gt}(F) = 0.038$, $wR_{ref}(F^2) = 0.094$, $T = 293$ K.

Source of material

The preparation was carried out hydrothermally by treating a mixture of 1.2037 g CsOH (Alfa Aesar, 99.9 %), 2.0003 g $Co(C_2H_3O_2)_2 \cdot 4H_2O$ (Alfa Aesar, 99.9 %), 1.1180 g B_2O_3 (Chempur, 99.99 %) and 5.5542 g H_3PO_4 (Merck, 85 %) in the molar ratio Cs : Co : B : P = 1 : 1 : 2 : 6. 10 ml of deionized water were added, and the system was stirred at 373 K. The mixture was then filled into a 20 ml Teflon-lined autoclave (filling degree 60 %) and heated at 443 K under autogenous pressure for twelve days. The reaction product was filtered, washed with deionized water/acetone and finally dried in air at 333 K. The product contained pink platelet crystals with dimensions ranging from 0.1 to 0.2 mm. The chemical composition of the title compound is consistent with EDXS analytical data.

Discussion

The hydrothermal method is extensively adopted to synthesize a number of cobalt borophosphates exhibiting a large variety of structure types [1-5]. Our extensive studies on borophosphates containing cobalt as well as alkali metals (Li, Na, K, Rb, Cs) led to the preparation of $Cs_2Co_3(H_2O)_2[B_4P_6O_{24}(OH)_2]$. The crystal structure of the title compound is isotypic to the $Rb_2Co_3(H_2O)_2[B_4P_6O_{24}(OH)_2]$ [6], $(C_2H_{10}N_2)\ M^{II}[B_2P_3O_{12}(OH)]$ (M^{II} = Mg, Mn, Fe, Co, Zn, Cd) [7-9] and $(C_4H_{16}N_3)Cd[B_2P_3O_{12}(OH)]Cl$ [8]. The anionic partial structure of $Cs_2Co_3(H_2O)_2[B_4P_6O_{24}(OH)_2]$ comprises of layers of distorted borate, phosphate and hydrogenphosphate tetrahedra which are connected *via* common vertices. The $^2_\infty[B_4P_6O_{24}(OH)_2]^{8-}$ layers contain three- and nine-membered rings of borate and phosphate tetrahedra. The trimetric units $Co_3O_{12}(H_2O)_2$ are formed by CoO_6 and $CoO_4(OH)_2$ coordination octahedra (each $CoO_4(OH)_2$ octahedron is connected by two opposite edges to the two neighbouring CoO_6 octahedra). The interconnection of the borophosphate layers with the trimeric octahedral units results in an three-dimensional framework which contains channels running along [010]. The cross section of the channels is defined by eight-membered rings consisting of two CoO_6 coordination octahedra, two borate tetrahedra, two phosphate tetrahedra and two hydrogenphosphate groups. Caesium ions reside within the channels and are disordered over three crystallographic independent sites [6]. The coordination sphere of Cs^+ is formed by nine oxygen species of the tetrahedral layers, one -OH group and one H_2O molecule. The distances *d*(Cs—O) range between 3.018(5) Å and 3.772(4) Å. The distances *d*(Co—O) range from 2.001(2) Å to 2.245(2) Å. The bond distances B—O, P—O and angles (∠O–B–O, ∠O–P–O) in the borophosphate anions correspond to respective values in related borophosphates [3-9].

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

Table 1. Data collection and handling.

Crystal:	pink platelet, size 0.140 × 0.140 × 0.065 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	56.43 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7, φ/ω
$2\theta_{max}$:	59.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	19726, 3446
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3289
$N(param)_{refined}$:	217
Programs:	SHELXS-97 [10], SHELXL-97 [11], DIAMOND [12]

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

Atom	Site	x	y	z	U_{iso}
H(1)	8c	0.128(6)	0.128(5)	0.505(3)	0.04(1)
H(2)	8c	0.296(6)	0.078(4)	0.440(3)	0.03(1)
H(3)	8c	0.405(5)	0.095(4)	0.406(2)	0.02(1)

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}
Cs(1)	8c	0.553(7)	0.3517(2)	0.4113(2)	0.3510(1)	0.0337(6)	0.0250(5)	0.0457(5)	0.0107(4)	0.0139(5)	0.0058(3)
Cs(2)	8c	0.249(3)	0.3076(3)	0.3946(2)	0.3415(1)	0.0337(6)	0.0250(5)	0.0457(5)	0.0107(4)	0.0139(5)	0.0058(3)
Cs(3)	8c	0.195(7)	0.3371(4)	0.3958(3)	0.3628(3)	0.0337(6)	0.0250(5)	0.0457(5)	0.0107(4)	0.0139(5)	0.0058(3)
Co(1)	8c		0.18984(4)	0.18616(3)	0.08108(2)	0.0087(2)	0.0093(2)	0.0110(2)	–0.0008(1)	0.0002(1)	0.0000(1)
Co(2)	4a		0	0	0	0.0115(3)	0.0146(3)	0.0138(3)	–0.0000(2)	–0.0014(2)	–0.0011(2)
B(1)	8c		0.2929(3)	0.0968(3)	0.2110(2)	0.009(1)	0.011(1)	0.011(1)	–0.001(1)	–0.001(1)	–0.001(1)
B(2)	8c		0.4306(3)	0.2656(2)	0.1732(2)	0.009(1)	0.010(1)	0.010(1)	–0.000(1)	0.001(1)	0.0022(9)
P(1)	8c		0.01700(7)	0.15924(6)	0.21740(4)	0.0069(3)	0.0102(3)	0.0094(3)	–0.0001(2)	0.0009(2)	–0.0003(2)
P(2)	8c		0.01243(8)	0.22641(6)	0.45448(4)	0.0093(3)	0.0149(3)	0.0106(3)	0.0002(2)	–0.0022(2)	–0.0001(2)
P(3)	8c		0.27324(8)	0.43582(6)	0.12359(4)	0.0103(3)	0.0072(3)	0.0110(3)	–0.0008(2)	–0.0010(2)	0.0003(2)
O(1)	8c		0.0173(2)	0.1895(2)	0.1450(1)	0.0104(9)	0.015(1)	0.0089(9)	–0.0007(7)	0.0018(7)	0.0007(7)
O(2)	8c		0.0353(2)	0.2400(2)	0.3784(1)	0.0118(9)	0.031(1)	0.0109(9)	–0.0007(9)	–0.0021(8)	0.0020(9)
O(3)	8c		0.0666(2)	0.3257(2)	0.4918(1)	0.018(1)	0.0142(9)	0.015(1)	0.0001(8)	–0.0062(8)	–0.0014(8)
O(4)	8c		0.1110(3)	0.1268(2)	0.4692(1)	0.023(1)	0.020(1)	0.017(1)	0.0075(9)	–0.0037(9)	–0.0015(9)
O(5)	8c		0.1463(2)	0.0924(2)	0.2374(1)	0.0087(9)	0.0128(9)	0.016(1)	0.0012(7)	0.0003(8)	0.0034(7)
O(6)	8c		0.1577(2)	0.0155(2)	0.0760(1)	0.015(1)	0.0098(9)	0.0151(9)	0.0015(7)	–0.0023(8)	0.0016(7)
O(7)	8c		0.1804(2)	0.3549(2)	0.0880(1)	0.018(1)	0.0099(9)	0.016(1)	–0.0019(8)	–0.0053(8)	0.0009(8)
O(8)	8c		0.3125(2)	0.1927(2)	0.1714(1)	0.0090(9)	0.0140(9)	0.0105(9)	–0.0039(7)	–0.0025(7)	0.0032(7)
O(9)	8c		0.3220(2)	–0.0022(2)	0.1725(1)	0.014(1)	0.015(1)	0.015(1)	0.0052(8)	–0.0044(8)	–0.0040(8)
O(10)	8c		0.3620(3)	0.0516(2)	0.4296(1)	0.013(1)	0.023(1)	0.021(1)	–0.0004(9)	0.0022(9)	0.0048(9)
O(11)	8c		0.3652(2)	0.1977(2)	0.0271(1)	0.011(1)	0.031(1)	0.017(1)	–0.0042(9)	0.0021(8)	–0.0019(9)
O(12)	8c		0.3862(2)	0.0897(2)	0.2688(1)	0.0094(9)	0.0146(9)	0.0110(9)	–0.0031(7)	–0.0025(7)	0.0024(7)
O(13)	8c		0.3868(3)	0.3788(2)	0.1653(1)	0.022(1)	0.0084(9)	0.027(1)	0.0004(8)	–0.012(1)	0.0012(8)
O(14)	8c		0.5055(2)	0.2614(2)	0.2381(1)	0.0117(9)	0.0124(9)	0.0114(9)	–0.0021(7)	–0.0033(8)	0.0028(7)

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

References

1. Kniep, R.; Engelhardt, H.; Hauf, C.: A First Approach to Borophosphate Structural Chemistry. Chem. Mater. **10** (1998) 2930-2934, and references therein.
2. Ewald, B.; Huang, Y.-X.; Kniep, R.: Strcutural Chemistry of Borophosphates, Metalloborophosphates, and Related Compounds. Z. Anorg. Allg. Chem. **633** (2007) 1517-1540.
3. Schäfer, G.; Carrillo-Cabrera, W.; Schnelle, W.; Borrmann, H.; Kniep, R.: Synthesis and Crystal Structure of $((NH_4)_xCo_{3/2-x/2})(H_2O)_2[BP_2O_8]\cdot(1-x)(H_2O)$ ($x = 0.5$). Z. Anorg. Allg. Chem. **628** (2002) 289-294.
4. Huang, Y.-X.; Ewald, B.; Schnelle, W.; Prots, Yu.; Kniep, R.: Chirality and Magnetism in a Novel Series of Isotypic Borophosphates: $M(II)[BPO_4(OH)_2]$ (M(II) = Mn, Fe, Co). Inorg. Chem. **45** (2006) 7578-7580.
5. Tanh Jeazet, H. B.; Menezes, P. W.; Hoffmann, S.; Prots, Yu.; Kniep, R.: Crystal structures of lead (II) cobalt (II) (monophosphate-hydrogen-monoborate-monophosphate), $PbCo[BP_2O_8(OH)]$, and lead (II) zinc (II) (monophosphate-hydrogenmonoborate-monophosphate), $PbZn[BP_2O_8(OH)]$. Z. Kristallogr. NCS **221** (2006) 431-433.
6. Engelhardt, H.; Schnelle, W.; Kniep, R.: $Rb_2Co_3(H_2O)_2[B_4P_6O_{24}(OH)_2]$: Ein Borophosphat mit Tetraeder-Schichtverband-Anionenteilstruktur und Oktaeder-Trimeren ($Co_3(II)O_{12}(H_2O)_2$). Z. Anorg. Allg. Chem. **626** (2000) 1380-1386.
7. Sevov, S. C.: Synthesis and Structure of $Co[B_2P_3O_{12}(OH)]\cdot C_2H_{10}N_2$: The First Metal Borophosphate with an Open Framework Structure. Angew. Chem. Int. Ed. **35** (1996) 2630-2632.
8. Liu, W.; Ge, M. H.; Yang, X.-X.; Chen, H.; Li, M.; Zhao, J.-T.: Hydrothermal Synthesis and Characterization of Two Organically Templated Cadmium Borophosphates with Novel Structures. Inorg. Chem. **43** (2004) 3910-3914.
9. Kniep, R.; Schäfer, G.: Isotype Borophosphate $M^{II}(C_2H_{10}N_2)[B_2P_3O_{12}(OH)]$ (M^{II} = Mg, Mn, Fe,Ni, Cu, Zn): Verbindungen mit Tetraeder-Schichtverbänden. Z. Anorg. Allg. Chem. **626** (2000) 141-147.
10. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
11. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
12. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 3.1f. Crystal Impact, Bonn, Germany 1998.