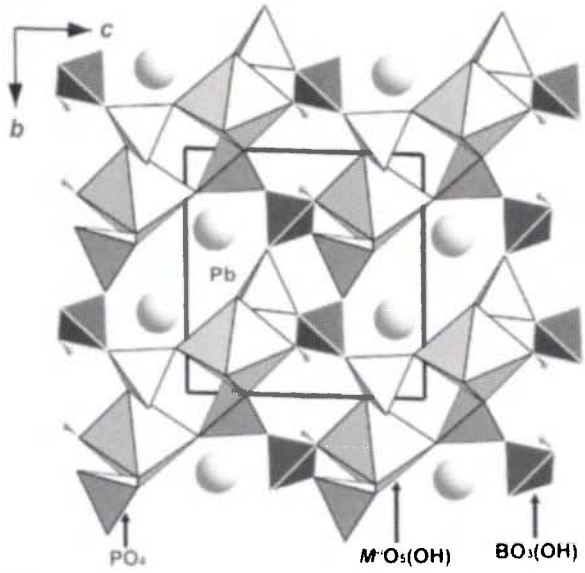
Z. Kristallogr. NCS 221 (2006) 431-433 / DOI 10.1524/ncrs.2006.0141

Crystal structures of lead(II) cobalt(II) (monophosphate-hydrogenmonoborate-monophosphate), $PbCo[BP_2O_8(OH)]$, and lead(II) zinc(II) (monophosphate-hydrogenmonoborate-monophosphate), $PbZn[BP_2O_8(OH)]$

H. B. Tanh Jeazet, P. W. Menezes, S. Hoffmann, Yu. Prots and R. Kniep*

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

Received October 12, 2006, accepted and available on-line December 15, 2006; CSD nos. 409900, 409901



Abstract

$BCoHO_9P_2Pb$, triclinic, $P\bar{1}$ (no. 2), a = 5.2208(2) Å, b = 7.8467(7) Å, c = 8.3422(3) Å, α = 89.473(8)°, β = 79.219(4)°, γ = 87.521(7)°, V = 335.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.034, $wR_{ref}(F^2)$ = 0.083, T = 293 K.

BHO_9P_2PbZn, triclinic, $P\bar{1}$ (no. 2), a = 5.2172(2) Å, b = 7.8432(7) Å, c = 8.3205(4) Å, α = 89.429(8)°, β = 79.239(5)°, γ = 87.536(8)°, V = 334.2 Å^3, Z = 2, $R_{gt}(F)$ = 0.046, $wR_{ref}(F^2)$ = 0.120, T = 293 K.

Source of material

$PbCo[BP_2O_8(OH)]$ and $PbZn[BP_2O_8(OH)]$ were synthesized under mild hydrothermal conditions. $PbCo[BP_2O_8(OH)]$ was prepared from the mixtures of 0.4007 g $Co(OOCCH_3)_2 \cdot 4H_2O$ (Alfa Aesar), 0.5 g $PbB_2O_4 \cdot H_2O$ (Alfa Aesar), 0.1987 g H_3BO_3 (Alfa Aesar) and 0.7880 g H_3PO_4 (Merck) in the molar ratio 1:1:2:5. 1 ml of HCl (37 %) was added to adjust the pH value to 1. The mixture was filled into a 10 ml autoclave (filling degree 30 %) and heated at 443 K for three weeks under autogenous pressure. $PbZn[BP_2O_8(OH)]$ was prepared from mixtures of 0.2618 g ZnO (Merck), 0.5 g $PbB_2O_4 \cdot H_2O$ (Alfa Aesar), 0.1987 g H_3BO_3 (Alfa Aesar) and 0.6304 g H_3PO_4 (Merck) in the molar ratio 2:1:2:4. The pH of the solution was adjusted to 1.5. The mixture was filled into a 10 ml autoclave (filling degree 30 %) and heated at 443 K for three weeks. The chemical composition of the title compounds were confirmed by chemical analyses.

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

Experimental details

The hydrogen atom for $PbCo[BP_2O_8(OH)]$ was located in a Fourier difference map and the O—H distance was fixed to 0.80 Å during the final refinement. In the case of $PbZn[BP_2O_8(OH)]$ the H atom could not be determined from the Fourier difference map.

Discussion

During past few years compounds with open framework structures like borophosphates have drawn much attention [1]. Our systematic studies on the systems MO-PbO_2-B_2O_3-P_2O_5-H_2O (M = Co, Zn) led to two novel borophosphates: $PbCo[BP_2O_8(OH)]$ and $PbZn[BP_2O_8(OH)]$. The charge of the borophosphate anion ($[BP_2O_8(OH)]^{4-}$) is compensated by two different divalent cations. The crystal structures of the title compounds are isotypic to the K-Sc [2], Rb-Sc [3], NH_4-In [4], K-In [5], K-Fe [6] and Rb-In [7] analogues.

The anionic partial structure contains open branched four-membered rings $[B_2P_4O_{16}(OH)_2]^{8-}$, which are formed by alternating borate and phosphate tetrahedra sharing common corners with two phosphate branches. The condensation of the borophosphate anions with $MO_5(OH)$ (M = Co; Zn) octahedra via common corners results in an overall three-dimensional framework which contains elliptical channels running along [100]. The cross section of the channels is defined by eight-membered rings consisting of two M-coordination octahedra, four phosphate tetrahedra and two borate groups. Lead ions reside within the open channels. In the case of $PbCo[BP_2O_8(OH)]$, the Co—O bond distances range from 2.04 Å to 2.18 Å. The bond distances for Zn—O in $PbZn[BP_2O_8(OH)]$ range from 2.03 Å to 2.21 Å. Bond lengths and angles of the borophosphate anions in both compounds are similar to their K-Sc, Rb-Sc, NH_4-In, K-In, K-Fe and Rb-In analogues by considering bond lengths d(P—O) and d(B—O) as well as bond angles [2-7].

1. Lead(II) cobalt(II) (monophosphate-hydrogenmonoborate-monophosphate), $PbCo[BP_2O_8(OH)]$

Table 1. Data collection and handling.

Crystal:	red platelet, size 0.090 × 0.080 × 0.025 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	280.44 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-7 & Mercury CCD, φ/ω
$2\theta_{max}$:	67.16°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6406, 2233
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2122
$N(param)_{refined}$:	131
Programs:	SHELXL-97 [8], DIAMOND [9]

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

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	0.31(2)	0.247(9)	0.62(1)	0.019

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}
Pb(1)	2*i*	0.72571(4)	0.30597(3)	0.08890(3)	0.0119(1)	0.0137(1)	0.0176(1)	−0.00023(8)	−0.00226(8)	−0.00088(8)
Co(1)	2*i*	0.2696(1)	0.2020(1)	0.80335(9)	0.0068(3)	0.0089(3)	0.0107(3)	−0.0004(2)	−0.0026(2)	0.0005(2)
P(1)	2*i*	0.1956(3)	0.5669(2)	0.2978(2)	0.0052(5)	0.0074(6)	0.0097(5)	−0.0009(4)	−0.0005(4)	−0.0003(4)
P(2)	2*i*	0.2272(3)	0.0640(2)	0.1804(2)	0.0049(5)	0.0079(6)	0.0090(5)	−0.0006(4)	−0.0013(4)	−0.0005(4)
B(1)	2*i*	0.120(1)	0.2511(7)	0.4552(7)	0.011(2)	0.005(2)	0.009(2)	0.001(2)	−0.001(2)	−0.002(2)
O(1)	2*i*	0.0281(8)	0.4349(5)	0.7959(5)	0.010(2)	0.009(2)	0.018(2)	0.002(1)	−0.007(2)	−0.004(1)
O(2)	2*i*	0.0484(8)	0.1273(5)	0.3422(5)	0.012(2)	0.009(2)	0.013(2)	−0.002(1)	0.002(1)	−0.005(1)
O(3)	2*i*	0.1001(8)	0.9077(5)	0.1308(5)	0.011(2)	0.010(2)	0.013(2)	−0.002(1)	−0.003(1)	−0.003(1)
O(4)	2*i*	0.1298(8)	0.6852(6)	0.4475(5)	0.010(2)	0.013(2)	0.013(2)	0.000(1)	0.002(1)	−0.004(1)
O(5)	2*i*	0.2278(8)	0.2118(5)	0.0562(5)	0.016(2)	0.010(2)	0.010(2)	−0.003(1)	−0.008(1)	0.005(1)
O(6)	2*i*	0.2664(8)	0.3885(5)	0.3608(5)	0.015(2)	0.007(2)	0.015(2)	−0.002(1)	−0.003(2)	0.003(1)
O(7)	2*i*	0.2898(9)	0.1728(6)	0.5577(5)	0.018(2)	0.020(2)	0.012(2)	0.008(2)	−0.004(2)	0.001(2)
O(8)	2*i*	0.4427(8)	0.6214(5)	0.1848(5)	0.007(2)	0.011(2)	0.015(2)	−0.001(1)	0.001(1)	0.001(1)
O(9)	2*i*	0.5078(8)	0.0276(5)	0.2034(5)	0.007(2)	0.013(2)	0.020(2)	0.001(1)	−0.004(1)	0.000(2)

2. Lead(II) zinc(II) (monophosphate-hydrogenmonoborate-monophosphate), PbZn[$BP_2O_8(OH)$]

Table 4. Data collection and handling.

Crystal:	colorless platelet, size 0.060 × 0.060 × 0.015 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	292.54 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-7 & Mercury CCD, φ/ω
$2\theta_{max}$:	67.18°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5262, 2207
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1967
$N(param)_{refined}$:	128
Programs:	SHELXL-97 [8], DIAMOND [9]

Table 5. 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}
Pb(1)	2*i*	0.72921(6)	0.30740(4)	0.08904(4)	0.0143(2)	0.0177(2)	0.0200(2)	−0.0005(1)	−0.0018(1)	−0.0013(1)
Zn(1)	2*i*	0.2754(2)	0.1999(1)	0.8022(1)	0.0096(4)	0.0143(5)	0.0143(4)	−0.0005(3)	−0.0026(3)	−0.0009(3)
P(1)	2*i*	0.1981(4)	0.5663(2)	0.2983(2)	0.0075(7)	0.0105(9)	0.0112(8)	−0.0013(6)	−0.0005(6)	−0.0008(6)
P(2)	2*i*	0.2272(4)	0.0634(2)	0.1804(2)	0.0073(8)	0.0118(9)	0.0107(8)	0.0001(6)	−0.0001(6)	−0.0010(6)
B(1)	2*i*	0.122(2)	0.253(1)	0.456(1)	0.011(3)	0.010(4)	0.011(3)	0.003(3)	0.002(3)	−0.002(3)
O(1)	2*i*	0.024(1)	0.4344(7)	0.7982(8)	0.010(2)	0.015(3)	0.023(3)	0.002(2)	−0.006(2)	−0.004(2)
O(2)	2*i*	0.048(1)	0.1266(7)	0.3420(7)	0.008(2)	0.012(3)	0.018(3)	−0.002(2)	0.003(2)	0.000(2)
O(3)	2*i*	0.103(1)	0.9059(7)	0.1294(7)	0.014(2)	0.011(3)	0.014(2)	0.001(2)	0.001(2)	−0.002(2)
O(4)	2*i*	0.130(1)	0.6849(8)	0.4481(7)	0.010(2)	0.019(3)	0.013(2)	−0.002(2)	0.000(2)	−0.005(2)
O(5)	2*i*	0.230(1)	0.2117(8)	0.0546(7)	0.011(2)	0.017(3)	0.013(2)	−0.004(2)	−0.008(2)	0.005(2)
O(6)	2*i*	0.267(1)	0.3876(8)	0.3624(7)	0.021(3)	0.011(3)	0.014(2)	−0.009(2)	−0.003(2)	0.004(2)
O(7)	2*i*	0.286(1)	0.1710(8)	0.5588(7)	0.022(3)	0.019(3)	0.012(3)	0.006(2)	−0.002(2)	0.004(2)
O(8)	2*i*	0.446(1)	0.6197(8)	0.1866(7)	0.011(2)	0.018(3)	0.013(3)	0.002(2)	0.002(2)	−0.002(2)
O(9)	2*i*	0.506(1)	0.0283(8)	0.2054(8)	0.008(2)	0.017(3)	0.022(3)	0.002(2)	−0.006(2)	−0.003(2)

Acknowledgments. The authors would like to thank Dr. G. Auffermann for chemical analyses and 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.
2. Menezes, P. W.; Hoffmann, S.; Prots, Yu.; Kniep, R.: Crystal structure of potassium scandium (monophosphate-hydrogenmonoborate-monophosphate), KSc[$BP_2O_8(OH)$]. Z. Kristallogr. NCS **221** (2006) 251-252.
3. Menezes, P. W.; Hoffmann, S.; Prots, Yu.; Kniep, R.: Crystal structure of rubidium scandium (monophosphate-hydrogenmonoborate-monophosphate), RbSc[$BP_2O_8(OH)$]. Z. Kristallogr. NCS **221** (2006) 253-254.
4. Mi, J.-X.; Li, M.-R.; Mao, S.-Y.; Huang, Y.-X.; Wei, Z.-B.; Zhao, J.-T.; Kniep, R.: Crystal structure of ammonium indium (monophosphate-hydrogenmonoborate-monophosphate), NH_4In[$BP_2O_8(OH)$]. Z. Kristallogr. NCS **217** (2002) 5-6.
5. Mao, S.-Y.; Li, M.-R.; Huang, Y.-X.; Mi, J.-X.; Wei, Z.-B.; Zhao, J.-T.; Kniep, R.: Crystal structure of potassium indium (monophosphate-hydrogenmonoborate-monophosphate), KIn[$BP_2O_8(OH)$]. Z. Kristallogr. NCS **217** (2002) 3-4.
6. Boy, I.; Cordier, G.; Eisenmann, B.; Kniep, R.: Oligomeric Tetrahedral Anions in Borophosphates: Synthesis and Crystal Structures of NaFe[$BP_2O_7(OH)_3$] and $K_2Fe_2[B_2P_4O_{16}(OH)_2]$. Z. Naturforsch. **53b** (1998) 165-170.
7. Huang, Y.-X.; Zhao, J.-T.; Mi, J.-X.; Borrmann, H.; Kniep, R.: Crystal structure of rubidium indium (monophosphate-hydrogenmonoborate-monophosphate), RbIn[$BP_2O_8(OH)$]. Z. Kristallogr. NCS **217** (2002) 163-164.
8. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
9. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 2.0f. Crystal Impact, Bonn, Germany 1998.