Crystal structure of ammonium aluminum *catena*-[monohydrogen-monoborate-bis(monophosphate)], $(NH_4)Al[BP_2O_8(OH)]$

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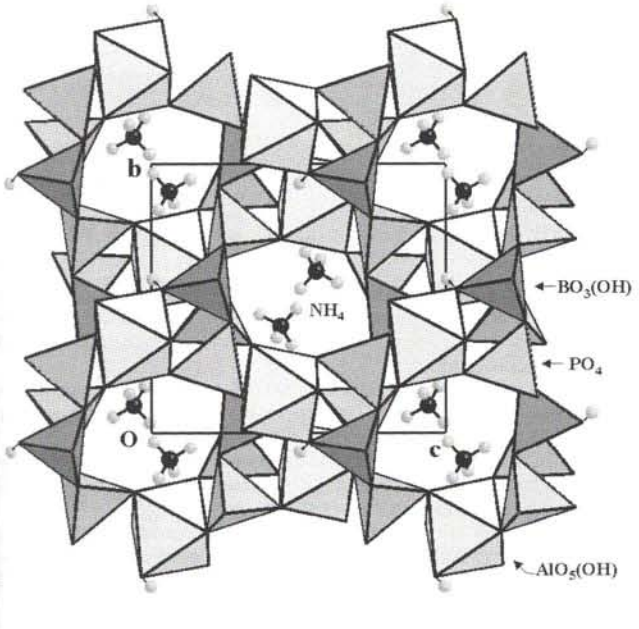

Abstract

$AlBH_5NO_9P_2$, monoclinic, $P12_1/c1$ (No. 14), $a = 9.234(2)$ Å, $b = 8.370(1)$ Å, $c = 9.413(2)$ Å, $\beta = 103.670(7)°$, $V = 706.9$ Å^3, $Z = 4$, $R_{gt}(F) = 0.038$, $wR_{ref}(F^2) = 0.089$, $T = 295$ K.

Source of material

$(NH_4)Al[BP_2O_8(OH)]$ was synthesized under mild hydrothermal conditions. The reactions were carried out with mixtures of $(NH_4)H_2PO_4$ (2.300 g), $Al(H_3PO_4)_3$ (3.179 g), H_3BO_3 (0.618 g) and 3 ml 85% H_3PO_4 in aqueous solution (molar ratio of (NH_4) : Al : B : P = 2 : 1 : 1 : 7.5). The mixture was filled in 20 ml teflon autoclave (filling degree is about 50%). The autoclave was placed in an oven with subsequent heating at 413 K for 7 days. The starting materials were all of analytical grade and were used without further purification.

Discussion

The richness of the borophosphate compounds in systems containing Ga and In [1-6], and the report of a similar Al-compound, $NaAl[BP_2O_7(OH)_3]$ [7], attracted our further systematic investigations on the Al systems. The structure of the title compound is isotypic to $CsFe[BP_2O_8(OH)]$, $RbAl[BP_2O_8(OH)]$ and $CsAl[BP_2O_8(OH)]$ [8-10].

The structure is characterized by isolated $AlO_5(OH)$ octahedra sharing common O-corners with five phosphate tetrahedra and one common (OH)-corner with the hydrogenborate group to form a three-dimensional network structure. The anionic partial structure shows open-branched vierer-single chains $[BP_2O_8(OH)]^{4-}$, which are formed by alternating hydrogenborate and phosphate tetrahedra sharing common O-corners. Ammonium groups are distributed within the open elliptical channels running along the *a* axis. In the $AlO_5(OH)$ octahedron, the Al—O bond distances range from 1.847 Å to 1.903 Å; the bond distance *d*(Al—OH) = 1.994 Å is slightly longer. Bond lengths and angles of hydrogenborate and phosphate tetrahedra within the anionic chains are similar to other related borophosphates [1-6].

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.07 × 0.07 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.76 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7-CCD, 300 images, $\Delta\varphi = 0.8$, $60-\omega$ scan, $\Delta\omega = 0.8°$, $\chi = 90°$
$2\theta_{max}$:	63.64°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5460, 2034
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1811
$N(param)_{refined}$:	143
Programs:	SHELXL-97 [11], DIAMOND [12]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*e*	0.875(5)	0.073(6)	0.504(5)	0.05
H(2)	4*e*	0.601(5)	0.172(6)	0.023(5)	0.05
H(3)	4*e*	0.692(5)	0.036(6)	0.007(5)	0.05
H(4)	4*e*	0.648(5)	0.058(6)	0.132(5)	0.05
H(5)	4*e*	0.760(6)	0.146(6)	0.075(5)	0.05

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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}
P(1)	4*e*	0.42925(6)	0.06653(7)	0.29677(6)	0.0056(3)	0.0075(3)	0.0060(3)	0.0009(2)	0.0009(2)	0.0002(2)
P(2)	4*e*	0.91509(6)	0.76246(7)	0.22092(6)	0.0055(3)	0.0075(3)	0.0075(3)	-0.0007(2)	0.0008(2)	-0.0005(2)
Al(1)	4*e*	0.70511(8)	0.84794(9)	0.43057(8)	0.0077(3)	0.0088(3)	0.0070(3)	0.0002(2)	0.0014(2)	-0.0003(2)
B(1)	4*e*	0.8350(3)	0.4469(3)	0.1974(3)	0.006(1)	0.008(1)	0.013(1)	0.0004(8)	0.0012(9)	0.0005(9)
O(1)	4*e*	0.5807(2)	0.9917(2)	0.3073(2)	0.0071(7)	0.0112(8)	0.0101(8)	0.0030(6)	0.0019(6)	0.0021(6)
O(2)	4*e*	0.4186(2)	0.1568(2)	0.4340(2)	0.0110(8)	0.0125(8)	0.0082(8)	0.0001(6)	0.0035(6)	-0.0021(6)
O(3)	4*e*	0.3943(2)	0.1704(2)	0.1603(2)	0.0112(8)	0.0104(8)	0.0090(8)	0.0038(6)	0.0026(6)	0.0029(6)
O(4)	4*e*	0.3116(2)	0.9275(2)	0.2712(2)	0.0066(7)	0.0099(8)	0.0134(8)	-0.0011(6)	0.0024(6)	-0.0021(6)
O(5)	4*e*	0.8469(2)	0.7790(2)	0.0596(2)	0.0139(8)	0.0123(8)	0.0096(8)	-0.0041(6)	-0.0014(6)	0.0001(6)
O(6)	4*e*	0.8410(2)	0.8696(2)	0.3117(2)	0.0119(8)	0.0113(8)	0.0139(9)	0.0004(6)	0.0071(7)	-0.0004(6)
O(7)	4*e*	0.0844(2)	0.8008(2)	0.2525(2)	0.0046(7)	0.0087(8)	0.0177(9)	-0.0009(6)	0.0016(6)	-0.0030(6)
O(8)	4*e*	0.9146(2)	0.5860(2)	0.2712(2)	0.0126(8)	0.0085(8)	0.0123(8)	-0.0017(6)	0.0002(6)	0.0000(6)
O(9)	4*e*	0.8106(2)	0.0367(2)	0.5361(2)	0.0123(8)	0.0140(8)	0.0099(8)	-0.0021(7)	0.0028(6)	0.0002(6)
N(1)	4*e*	0.6835(4)	0.1020(4)	0.0607(3)	0.030(2)	0.024(1)	0.023(1)	-0.005(1)	0.008(1)	-0.007(1)

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