Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

$(NH_4)[B_3PO_6(OH)_3]\cdot 0.5H_2O$

Wei Liu[a]* and Jingtai Zhao[b]

[a]Institute of Material Science and Engineering, The Ocean University of China, Qingdao 266100, People's Republic of China, and [b]State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Science, Shanghai 200050, People's Republic of China Correspondence e-mail: weiliu@ouc.edu.cn

Received 2 September 2007; accepted 20 September 2007

Key indicators: single-crystal X-ray study; T = 296 K; mean σ(O–B) = 0.002 Å; H-atom completeness 88%; disorder in solvent or counterion; R factor = 0.038; wR factor = 0.099; data-to-parameter ratio = 12.7.

The title compound, ammonium *catena*-[monoboro-monodihydrogendiborate-monohydrogenphosphate] hemihydrate, was obtained under solvothermal conditions using glycol as the solvent. The crystal structure is constructed of one-dimensional infinite borophosphate chains, which are interconnected by ammonium ions and water molecules *via* a complex hydrogen-bond network to form a three-dimensional structure. The water molecules of crystallization are disordered over inversion centres, and their H atoms were not located.

Related literature

The related compounds $Li[B_3PO_6(OH)_3]$ (Hauf & Kniep, 1997) and $(NH_4)_2[B_3PO_7(OH)_2]$ (Hauf & Kniep, 1996) comprise similar borophosphate chains, but show a different periodicity of the rings and a replacement of PO_3OH by PO_4 for the latter. A review on the crystal chemical classification of borophosphates was published recently (Ewald *et al.*, 2007).

Experimental

Crystal data

$(NH_4)[B_3PO_6(OH)_3]\cdot 0.5H_2O$
M_r = 237.48
Triclinic, $P\overline{1}$
a = 4.3665 (2) Å
b = 9.3680 (4) Å
c = 10.8267 (8) Å
α = 81.532 (9)°
β = 85.369 (9)°
γ = 83.641 (8)°
V = 434.41 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.35 mm^{-1}
T = 296 (2) K
0.35 × 0.20 × 0.20 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.887, T_{max} = 0.993
(expected range = 0.833–0.932)
6501 measured reflections
1996 independent reflections
1788 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.099
S = 1.06
1996 reflections
157 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Table 1
Selected bond lengths (Å).

P1—O4	1.4984 (14)	B1—O3	1.470 (2)
P1—O2	1.5354 (13)	B2—O6	1.353 (2)
P1—O3	1.5487 (13)	B2—O7^{ii}	1.354 (3)
P1—O1	1.5503 (13)	B2—O9^{iii}	1.391 (2)
B1—O5	1.462 (2)	B3—O5	1.347 (2)
B1—O6^{i}	1.465 (2)	B3—O8^{iv}	1.363 (2)
B1—O1^{i}	1.466 (2)	B3—O9	1.386 (3)

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+2, -y+1, -z+1$; (iii) $x+1, y, z$; (iv) $-x+1, -y, -z+2$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O4^{v}	0.90 (3)	1.93 (3)	2.821 (3)	172 (3)
N1—H3···O2	0.94 (3)	1.92 (4)	2.849 (3)	169 (3)
N1—H5···O8^{vi}	0.92 (4)	2.04 (4)	2.942 (3)	168 (3)
N1—H6···O7^{i}	0.92 (4)	2.05 (4)	2.946 (3)	164 (3)
O7—H2···O6	0.81 (4)	1.92 (4)	2.7170 (19)	166 (3)
O8—H4···O9^{vii}	0.79 (4)	2.00 (4)	2.789 (2)	171 (3)
O2—H7···O2^{vi}	0.8201 (13)	1.6804 (13)	2.476 (2)	163.02 (5)
Ow···O5	–	–	2.869 (3)	–
Ow···O4	–	–	2.944 (2)	–

Symmetry codes: (i) $x-1, y, z$; (v) $-x, -y+1, -z+2$; (vi) $-x+1, -y+1, -z+2$; (vii) $x, y, z+1$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This work was supported by the opening project of the State Key Laboratory of High Performance Ceramics and Superfine Microstructure (SKL200706SIC).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2143).

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 doi:10.1107/S1600536807046193

supplementary materials

Acta Cryst. (2007). E**63**, i185 [**doi:10.1107/S1600536807046193**]

$(NH_4)[B_3PO_6(OH)_3]\cdot 0.5H_2O$

W. Liu and J. Zhao

Comment

In the asymmetic unit of the title compound three crystallographically distinct boron atoms are present. Two of them are coordinated by three O-atoms to form nearly triagonal planar BO_3 units, which are interconnected with one BO_4 tetrahedron to form a 6-membered borate ring. The slightly distorted PO_4 tetrahedron bridges the borate rings by sharing common vertices with the BO_4 groups, leading to an infinite borophosphate chain (Fig.1) extending parallel to the *a* axis (Fig. 2). According to the latest review on the crystal chemistry of borophosphates (Ewald *et al.*, 2007), the functional building units (FBU) are of the type 2Δ2□:<2Δ□>□, forming cB zweier-single chains.

A complex hydrogen-bond network (Fig. 2) consolidates the borophosphate chains into a three-dimensional structure. The OH groups of parallel chains interact with the intermediate NH_4 cations *via* N—H···O hydrogen bonds and with terminal framework O atoms *via* O—H···O hydrogen bonds. The latter type of hydrogen bonds is also observed for the water molecules which are located on inversion centres.

In comparison to $(NH_4)[B_3PO_6(OH)_3]\cdot 0.5H_2O$, the structures of the related compounds $Li[B_3PO_6(OH)_3]$ (Hauf & Kniep, 1997) and $(NH_4)_2[B_3PO_7(OH)_2]$ (Hauf & Kniep, 1996) comprise similar borophosphate chains. However, $Li[B_3PO_6(OH)_3]$ comprises cB single-chains with a different periodicity in which the rings alternate with $P^{2/4}$ units, and $(NH_4)_2[B_3PO_7(OH)_2]$ is made up of borophosphae chains where the PO_3OH group is replaced by PO_4, resulting in a different stacking of the chains and thus a different hydrogen bonding scheme.

Experimental

The title compound was prepared under solvothermal conditons. 1.04 g of $(NH_4)_2B_4O_7$ (SCR, >99.5%), 0.9 g $NH_4H_2PO_4$ (SCR, >99.5%) and 5 ml of glycol (SCR, >99%) were placed in a Teflon-lined stainless steel autoclave and heated to 403 K for 5 d, followed by cooling to room temperature. Colourless rod-shaped crystals were obtained.

Refinement

H atoms bonded to N and to framework-O atoms were located in a difference map and were refined with N—H = 0.90–0.94 and O—H = 0.79–0.82 Å. The O atom (Ow) of the water molecule is situated on an inversion centre. It was not possible to locate the corresponding H atoms, which points to a disorder due to the formation of various hydrogen bonds.

Figures

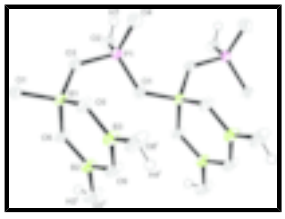

Fig. 1. View of a part of the infinite borophospate chains, with atom labels and 50% probability displacement ellipsoids. H atoms are displayed as spheres of arbitrary radius. [Symmetry code: (i) −*x*, −*y*, −*z*.]

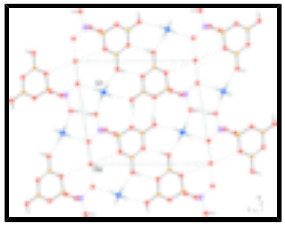

Fig. 2. The packing of the title compound, as viewed down the *a* axis, showing the hydrogen bonding scheme (dashed lines). Colour code: B yellow; P pink; O red; N blue; H white.

ammonium *catena*-[monoboro-mono-dihydrogendiborate-monohydrogenphosphate] hemihydrate

Crystal data

$(NH_4)[B_3PO_6(OH)_3]\cdot 0.5H_2O$	$Z = 2$
$M_r = 237.48$	$F_{000} = 240$
Triclinic, $P\overline{1}$	$D_x = 1.808$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 4.3665$ (2) Å	Cell parameters from 2516 reflections
$b = 9.3680$ (4) Å	$\theta = 5$–55º
$c = 10.8267$ (8) Å	$\mu = 0.35$ mm^{-1}
$\alpha = 81.532$ (9)º	$T = 296$ (2) K
$\beta = 85.369$ (9)º	Rod, colourless
$\gamma = 83.641$ (8)º	0.35 × 0.20 × 0.20 mm
$V = 434.41$ (4) Å^3	

Data collection

Bruker SMART CCD diffractometer	1996 independent reflections
Radiation source: fine-focus sealed tube	1788 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.024$
$T = 296(2)$ K	$\theta_{max} = 27.5$º
ω scans	$\theta_{min} = 2.7$º
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$h = -5\rightarrow5$
$T_{min} = 0.887$, $T_{max} = 0.993$	$k = -12\rightarrow12$
6501 measured reflections	$l = -14\rightarrow13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	All H-atom parameters refined
$wR(F^2) = 0.099$	$w = 1/[\sigma^2(F_o^2) + (0.0522P)^2 + 0.3672P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
1996 reflections	$\Delta\rho_{max} = 0.41$ e Å^{-3}
157 parameters	$\Delta\rho_{min} = -0.48$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
P1	0.38071 (10)	0.32784 (5)	0.87493 (4)	0.01661 (15)
B1	−0.0816 (4)	0.2710 (2)	0.73583 (18)	0.0161 (4)
B2	1.2037 (5)	0.2978 (2)	0.52774 (19)	0.0215 (4)
B3	0.2114 (5)	0.0630 (2)	0.6493 (2)	0.0223 (4)
O1	0.5814 (3)	0.29141 (15)	0.75672 (12)	0.0209 (3)
O2	0.4119 (3)	0.48339 (14)	0.89765 (12)	0.0231 (3)
O3	0.0456 (3)	0.33077 (15)	0.83671 (12)	0.0229 (3)
O4	0.4403 (3)	0.21875 (15)	0.98843 (13)	0.0263 (3)
O5	0.0212 (3)	0.11655 (13)	0.73935 (12)	0.0213 (3)
O6	1.0000 (3)	0.35280 (13)	0.61382 (12)	0.0202 (3)
O7	0.6934 (4)	0.62278 (16)	0.57923 (14)	0.0333 (4)
O8	0.6974 (4)	0.08201 (16)	1.33756 (16)	0.0391 (4)
O9	0.3100 (3)	0.15115 (14)	0.54252 (12)	0.0255 (3)
N1	−0.0636 (5)	0.6964 (2)	0.8055 (2)	0.0339 (4)
Ow	0.0000	0.0000	1.0000	0.0738 (10)
H1	−0.195 (7)	0.730 (3)	0.866 (3)	0.044 (8)*
H2	0.768 (8)	0.539 (4)	0.580 (3)	0.060 (10)*
H3	0.073 (8)	0.620 (4)	0.842 (3)	0.055 (9)*
H4	0.603 (8)	0.104 (4)	1.399 (3)	0.055 (9)*
H5	0.026 (8)	0.774 (4)	0.762 (3)	0.058 (9)*
H6	−0.167 (9)	0.665 (4)	0.745 (4)	0.070 (11)*
H7	0.4445 (1)	0.4834 (1)	0.9712 (1)	0.048 (1)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0144 (2)	0.0187 (2)	0.0176 (2)	−0.00196 (16)	0.00014 (17)	−0.00570 (17)
B1	0.0148 (8)	0.0170 (9)	0.0166 (9)	−0.0014 (7)	0.0017 (7)	−0.0044 (7)
B2	0.0244 (10)	0.0182 (9)	0.0200 (10)	0.0017 (8)	0.0036 (8)	−0.0024 (7)

B3	0.0268 (10)	0.0168 (9)	0.0218 (10)	−0.0010 (8)	0.0045 (8)	−0.0021 (8)
O1	0.0134 (6)	0.0309 (7)	0.0207 (6)	−0.0026 (5)	0.0003 (5)	−0.0117 (5)
O2	0.0285 (7)	0.0187 (6)	0.0242 (7)	−0.0022 (5)	−0.0054 (5)	−0.0083 (5)
O3	0.0131 (6)	0.0341 (7)	0.0244 (7)	−0.0020 (5)	0.0004 (5)	−0.0151 (6)
O4	0.0267 (7)	0.0255 (7)	0.0247 (7)	−0.0015 (5)	−0.0008 (6)	0.0014 (5)
O5	0.0254 (7)	0.0164 (6)	0.0203 (6)	−0.0004 (5)	0.0068 (5)	−0.0021 (5)
O6	0.0238 (6)	0.0157 (6)	0.0190 (6)	0.0021 (5)	0.0039 (5)	−0.0012 (5)
O7	0.0507 (10)	0.0181 (7)	0.0247 (7)	0.0054 (6)	0.0147 (7)	0.0020 (6)
O8	0.0572 (11)	0.0165 (7)	0.0360 (9)	0.0054 (7)	0.0233 (8)	0.0003 (6)
O9	0.0356 (8)	0.0159 (6)	0.0216 (7)	0.0024 (5)	0.0110 (6)	−0.0019 (5)
N1	0.0409 (11)	0.0272 (9)	0.0313 (10)	−0.0006 (8)	0.0034 (9)	−0.0018 (8)
Ow	0.104 (3)	0.061 (2)	0.0554 (19)	−0.0294 (19)	−0.0163 (19)	0.0156 (15)

Geometric parameters (Å, °)

P1—O4	1.4984 (14)	B3—O9	1.386 (3)
P1—O2	1.5354 (13)	O1—B1^{iii}	1.466 (2)
P1—O3	1.5487 (13)	O2—H7	0.8202 (13)
P1—O1	1.5503 (13)	O6—B1^{iii}	1.465 (2)
B1—O5	1.462 (2)	O7—B2^{ii}	1.354 (3)
B1—O6^{i}	1.465 (2)	O7—H2	0.81 (4)
B1—O1^{i}	1.466 (2)	O8—B3^{iv}	1.363 (2)
B1—O3	1.470 (2)	O8—H4	0.79 (4)
B2—O6	1.353 (2)	O9—B2^{i}	1.391 (2)
B2—O7^{ii}	1.354 (3)	N1—H1	0.90 (3)
B2—O9^{iii}	1.391 (2)	N1—H3	0.94 (3)
B3—O5	1.347 (2)	N1—H5	0.92 (4)
B3—O8^{iv}	1.363 (2)	N1—H6	0.92 (4)
O4—P1—O2	112.48 (8)	O5—B3—O9	121.62 (17)
O4—P1—O3	111.15 (8)	O8^{iv}—B3—O9	119.41 (17)
O2—P1—O3	105.07 (8)	B1^{iii}—O1—P1	129.61 (11)
O4—P1—O1	113.18 (8)	P1—O2—H7	109.52 (12)
O2—P1—O1	110.67 (8)	B1—O3—P1	131.73 (11)
O3—P1—O1	103.64 (7)	B3—O5—B1	123.09 (15)
O5—B1—O6^{i}	111.34 (14)	B2—O6—B1^{iii}	123.07 (14)
O5—B1—O1^{i}	109.82 (14)	B2^{ii}—O7—H2	109 (2)
O6^{i}—B1—O1^{i}	107.39 (14)	B3^{iv}—O8—H4	111 (2)
O5—B1—O3	110.95 (14)	B3—O9—B2^{i}	118.75 (15)
O6^{i}—B1—O3	110.65 (14)	H1—N1—H3	109 (3)
O1^{i}—B1—O3	106.51 (13)	H1—N1—H5	108 (3)
O6—B2—O7^{ii}	123.54 (17)	H3—N1—H5	116 (3)
O6—B2—O9^{iii}	120.76 (17)	H1—N1—H6	112 (3)
O7^{ii}—B2—O9^{iii}	115.63 (16)	H3—N1—H6	110 (3)
O5—B3—O8^{iv}	118.96 (18)	H5—N1—H6	103 (3)

Symmetry codes: (i) *x*−1, *y*, *z*; (ii) −*x*+2, −*y*+1, −*z*+1; (iii) *x*+1, *y*, *z*; (iv) −*x*+1, −*y*, −*z*+2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O4^{v}	0.90 (3)	1.93 (3)	2.821 (3)	172 (3)
N1—H3···O2	0.94 (3)	1.92 (4)	2.849 (3)	169 (3)
N1—H5···O8^{vi}	0.92 (4)	2.04 (4)	2.942 (3)	168 (3)
N1—H6···O7^{i}	0.92 (4)	2.05 (4)	2.946 (3)	164 (3)
O7—H2···O6	0.81 (4)	1.92 (4)	2.7170 (19)	166 (3)
O8—H4···O9^{vii}	0.79 (4)	2.00 (4)	2.789 (2)	171 (3)
O2—H7···O2^{vi}	0.8201 (13)	1.6804 (13)	2.476 (2)	163.02 (5)
Ow—···.O5	.	.	2.869 (3)	.
Ow—···.O4	.	.	2.944 (2)	.

Symmetry codes: (v) −*x*, −*y*+1, −*z*+2; (vi) −*x*+1, −*y*+1, −*z*+2; (i) *x*−1, *y*, *z*; (vii) *x*, *y*, *z*+1.

Fig. 1

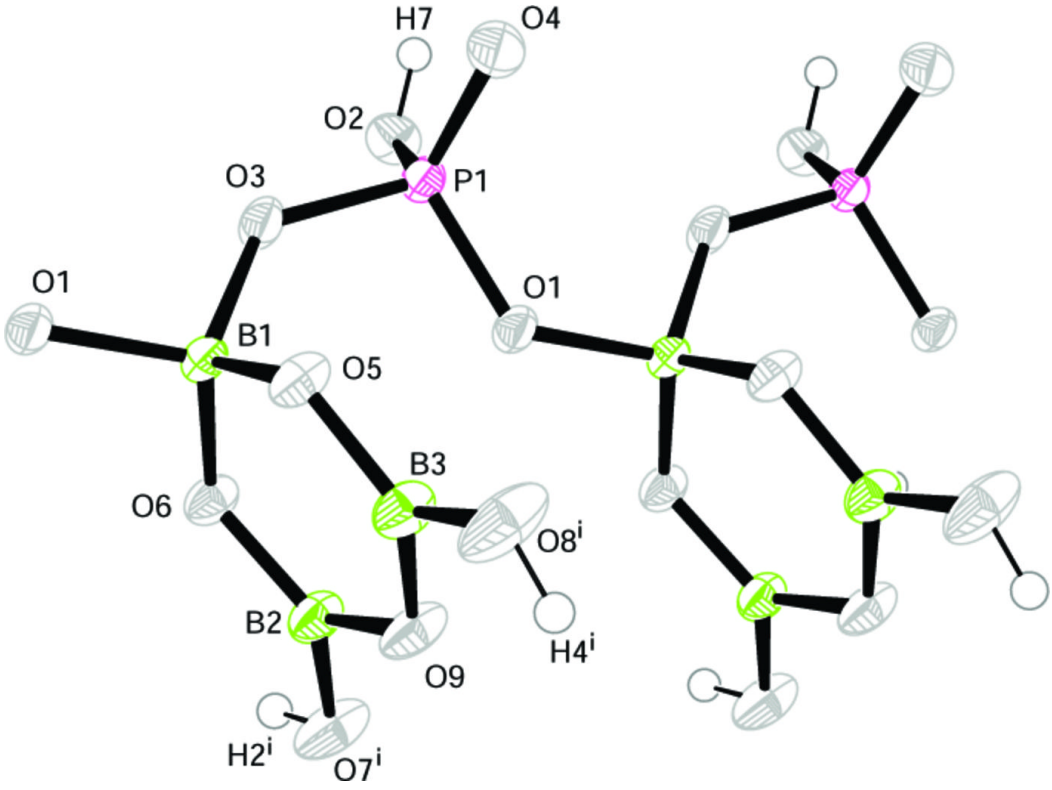

Fig. 2