inorganic compounds

Lithium diaquanickel(II) *catena*-borodiphosphate(V) monohydrate

Juan Zheng and Aiyun Zhang*

Department of Physics and Chemistry, Henan Polytechnic University, Jiaozuo 454000, People's Republic of China
Correspondence e-mail: zay@hpu.edu.cn

The title borophosphate $LiNi(H_2O)_2[BP_2O_8]\cdot H_2O$ was synthesized under hydrothermal conditions. The crystal structure is isotypic with the Mg analogue and features helical $[BP_2O_8]^{3-}$ borophosphate ribbons, constructed by BO_4 (2 symmetry) and PO_4 tetrahedra. The borate groups share all their oxygen apices with adjacent phosphate tetrahedra. The ribbons are connected *via* Ni^{2+} cations that are located on twofold rotation axes. The cations have a slightly distorted octahedral oxygen coordination by four O atoms from the anion and by two water molecules. The voids within the helices are occupied by Li^+ cations, likewise located on twofold rotation axes, in an irregular environment of five O atoms. The structure is stabilized by O—H···O hydrogen bonds between coordinated or uncoordinated water molecules and O atoms that are part of the helices.

Related literature

For the isotypic Mg analogue, see: Lin *et al.* (2008). For other borophosphates, see: Boy & Kniep (2001); Kniep *et al.* (1998). A review on the structural chemistry of borophosphates is given by Ewald *et al.* (2007).

Experimental

Crystal data

$LiNi(H_2O)_2[BP_2O_8]\cdot H_2O$	$Z = 6$
$M_r = 320.44$	Mo $K\alpha$ radiation
Hexagonal, $P6_522$	$\mu = 2.91$ mm^{-1}
$a = 9.3359$ (3) Å	$T = 296$ K
$c = 15.7497$ (11) Å	$0.22 \times 0.20 \times 0.17$ mm
$V = 1188.82$ (10) Å^3	

Data collection

Bruker APEXII CCD area-detector diffractometer	Absorption correction: multi-scan (*SADABS*; Bruker, 2007) $T_{min} = 0.567$, $T_{max} = 0.638$
6139 measured reflections	684 reflections with $I > 2\sigma(I)$
708 independent reflections	$R_{int} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	$\Delta\rho_{max} = 0.68$ e Å^{-3}
$wR(F^2) = 0.065$	$\Delta\rho_{min} = -0.39$ e Å^{-3}
$S = 1.14$	Absolute structure: Flack (1983), 235 Friedel pairs
708 reflections	Flack parameter: 0.01 (3)
75 parameters	
H-atom parameters constrained	

Table 1
Selected bond lengths (Å).

Ni1—O1^i	2.048 (3)	P2—O5	1.556 (3)
Ni1—O2	2.070 (3)	O6—Li	2.12 (2)
Ni1—O3	2.130 (3)	B—O5^{ii}	1.461 (5)
P2—O1	1.503 (3)	B—O4^{iii}	1.471 (5)
P2—O2	1.510 (3)	Li—O2^{iv}	2.113 (13)
P2—O4	1.546 (3)	Li—O3^v	2.164 (4)

Symmetry codes: (i) $-x + 1, -x + y + 1, -z + \frac{1}{3}$; (ii) $x, x - y, -z + \frac{5}{6}$; (iii) $y, x, -z + \frac{2}{3}$; (iv) $-y + 1, x - y, z - \frac{1}{3}$; (v) $x, x - y, -z - \frac{1}{6}$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···O5^{iv}	0.81	2.01	2.746 (4)	151
O3—H3A···O2^{iv}	0.81	2.60	3.165 (4)	128
O6—H6···O4^{vi}	0.83	2.52	3.331 (4)	167
O6—H6···O1^{vi}	0.83	2.66	3.092 (4)	114
O3—H3B···O1	0.83	2.00	2.810 (4)	167
O3—H3B···O2	0.83	2.54	2.955 (4)	112

Symmetry codes: (iv) $-y + 1, x - y, z - \frac{1}{3}$; (vi) $x - y, -y, -z$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2227).

References

Boy, I. & Kniep, R. J. (2001). *Z. Kristallogr. New Cryst. Struct.* **216**, 9–10.
Bruker (2007). *APEX2, SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Ewald, B., Huang, Y.-X. & Kniep, R. (2007). *Z. Anorg. Allg. Chem.* **633**, 1517–1540.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Kniep, R., Engelhardt, H. & Hauf, C. (1998). *Chem. Mater.* **10**, 2930–2934.
Lin, J.-R., Huang, Y.-X., Wu, Y.-H. & Zhou, Y. (2008). *Acta Cryst.* E**64**, i39–i40.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Lithium diaquanickel(II) *catena*-borodiphosphate(V) monohydrate

J. Zheng and A. Zhang

Comment

With increasing interest in microporous materials, the synthesis of compounds like borophosphates with open framework structures have drawn much attention during the past few years. These compounds show a rich crystal chemistry (Kniep *et al.*, 1998; Ewald *et al.*, 2007).

The crystal structure of $LiNi(H_2O)_2[BP_2O_8]\cdot H_2O$ is isotypic with that of the Mg analogue (Lin *et al.* 2008) and contains an infinite one-dimensional anionic structure. The condensation of BO_4 and PO_4 tetrahedra leads to helical ribbons with composition $[BP_2O_8]^{3-}$ (Fig. 1), whereby each BO_4 tetrahedron shares its vertices with four PO_4 tetrahedra. Bond lenghts and angles within the anionic structure are consistent with related borophosphates (Boy & Kniep, 2001; Lin *et al.*, 2008).

The free loop of the borophosphate helix is occupied by Li^+ cations, which are coordinated by with five O atoms, two from phosphate groups (O2) and three from water molecules (O3), thus completing an helical unit $\{Li[BP_2O_8]^{2-}\}$ with a central channel running along the 6_5 screw axis. The channels are filled up with water of crystallization (O6). The Ni^{2+} cations, located on a twofold rotation axis, are surrounded in a distorted octahedral coordination by four O atoms from adjacent phosphate groups and two water molecules, leading to the overall formula $LiNi(H_2O)_2[BP_2O_8]\cdot H_2O$ (Fig. 2). The Ni—O distances range from 2.048 (3)–2.130 (3) Å and are in the usual range. The crystal structure is stabilized by O—H···O hydrogen bonds between coordinated or uncoordinated water molecules and O atoms that are part of the helices.

Experimental

Green block-shaped crystals were synthesized hydrothermally from a mixture of $Ni(NO_3)_2$, $Li_2B_4O_7$, water and H_3PO_4. In a typical synthesis, 0.87 g $Ni(NO_3)_2\cdot6H_2O$ was dissolved in a mixture of 5 mL water, 1.691 g $Li_2B_4O_7$ and 2 ml H_3PO_4 ($85\%_{wt}$) under constant stirring. Finally, the mixture was kept in a 30 ml Teflon-lined steel autoclave at 443 K for 6d. The autoclave was slowly cooled to room temperature.

Refinement

The highest peak in the difference map is 1.29Å from atom H6, and the minimum peak is 0.48Å from atom P2.

Figures
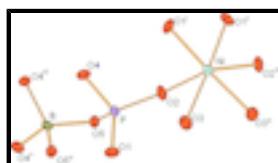
Fig. 1. A part of the structure of $LiNi(H_2O)_2[BP_2O_8]\cdot H_2O$ with displacement ellipsoids drawn at the 50% the probability level. Symmetry codes: (i) 1 - *y*, 1 - *x*, 0.16667 - *z*; (ii) 1 - *x*, 1 - *x* + *y*, 0.33333 - *z*; (iii) *x*-*y*, *x*, -0.16667 + *z*; (iv) *y*, *x*, 0.66667 - *z*; (v) *y*, -*x* + *y*, 0.16667 + *z*; (vi) *x*, *x*-*y*, 0.83333 - *z*.

supplementary materials
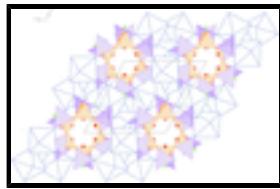
Fig. 2. Polyhedral diagram for LiNi(H$_2$O)$_2$[BP$_2$O$_8$]·H$_2$O in projection along [001]. Colour code: purple P, orange B, blue Ni, red OW6 and green Li.

Lithium diaquanickel(II) *catena*-borodiphosphate(V) monohydrate

Crystal data

LiNi(H$_2$O)$_2$[BP$_2$O$_8$]·H$_2$O	$Z = 6$
$M_r = 320.44$	$F_{000} = 960$
Hexagonal, $P6_522$	$D_x = 2.686$ Mg m^{-3}
Hall symbol: P 65 2 (0	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 9.3359$ (3) Å	Cell parameters from 1684 reflections
$b = 9.3359$ (3) Å	$\theta = 2.5$–29.5º
$c = 15.7497$ (11) Å	$\mu = 2.91$ mm^{-1}
$\alpha = 90º$	$T = 296$ K
$\beta = 90º$	Block, green
$\gamma = 120º$	$0.22 \times 0.20 \times 0.17$ mm
$V = 1188.82$ (10) Å^3	

Data collection

Bruker APEXII CCD area-detector diffractometer	708 independent reflections
Radiation source: fine-focus sealed tube	684 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.049$
$T = 296$ K	$\theta_{max} = 29.5º$
φ and ω scans	$\theta_{min} = 2.5º$
Absorption correction: multi-scan (SADABS; Bruker, 2007)	$h = -10 \rightarrow 11$
$T_{min} = 0.567$, $T_{max} = 0.638$	$k = -8 \rightarrow 11$
6139 measured reflections	$l = -18 \rightarrow 14$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.026$	$w = 1/[\sigma^2(F_o^2) + (0.0284P)^2 + 2.1868P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.065$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.14$	$\Delta\rho_{max} = 0.68$ e Å^{-3}
708 reflections	$\Delta\rho_{min} = -0.39$ e Å^{-3}
75 parameters	Extinction correction: none

Primary atom site location: structure-invariant direct methods

Absolute structure: Flack (1983), 235 Friedel pairs

Secondary atom site location: difference Fourier map

Flack parameter: 0.01 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and $R-$ factors based on ALL data will be even larger.

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

	x	y	z	$U_{iso}*/U_{eq}$
Ni1	0.55533 (4)	0.44467 (4)	0.0833	0.0098 (2)
P2	0.38859 (12)	0.21675 (12)	0.24795 (7)	0.0093 (3)
O5	0.4156 (3)	0.2355 (3)	0.34570 (16)	0.0108 (6)
O4	0.2137 (3)	0.1899 (4)	0.23106 (18)	0.0129 (7)
O3	0.4865 (4)	0.1970 (4)	0.05090 (19)	0.0214 (7)
O2	0.5200 (4)	0.3782 (3)	0.21028 (17)	0.0142 (7)
O1	0.3853 (4)	0.0644 (4)	0.21452 (17)	0.0151 (7)
O6	0.2044 (10)	0.1022 (5)	−0.0833	0.079 (2)
B	0.3037 (8)	0.1518 (4)	0.4167	0.0090 (13)
Li	0.466 (3)	0.2331 (13)	−0.0833	0.080 (5)
H3A	0.5738	0.2196	0.0284	0.096*
H6	0.1509	0.0382	−0.1223	0.096*
H3B	0.4428	0.1571	0.0973	0.096*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0098 (3)	0.0098 (3)	0.0100 (3)	0.0050 (3)	0.0013 (3)	0.0013 (3)
P2	0.0097 (5)	0.0097 (5)	0.0086 (5)	0.0050 (4)	0.0015 (4)	0.0015 (4)
O5	0.0095 (14)	0.0126 (16)	0.0089 (13)	0.0044 (12)	0.0014 (11)	0.0016 (11)
O4	0.0131 (16)	0.0132 (15)	0.0157 (16)	0.0091 (13)	−0.0022 (12)	−0.0030 (12)
O3	0.0277 (18)	0.0162 (18)	0.0231 (17)	0.0130 (14)	0.0121 (14)	0.0049 (14)
O2	0.0143 (16)	0.0134 (14)	0.0101 (13)	0.0032 (13)	0.0021 (12)	0.0040 (11)
O1	0.0211 (17)	0.0159 (16)	0.0147 (14)	0.0140 (14)	0.0008 (14)	−0.0017 (12)
O6	0.083 (6)	0.061 (3)	0.100 (6)	0.042 (3)	0.000	−0.024 (4)
B	0.012 (3)	0.009 (2)	0.007 (3)	0.0059 (15)	0.000	0.001 (2)
Li	0.094 (15)	0.089 (10)	0.058 (10)	0.047 (8)	0.000	0.011 (10)

Geometric parameters (Å, °)

Ni1—O1[i]	2.048 (3)	O4—B[i]	1.471 (5)
Ni1—O1[ii]	2.048 (3)	O3—Li	2.164 (4)
Ni1—O2[iii]	2.070 (3)	O2—Li[iv]	2.113 (13)
Ni1—O2	2.070 (3)	O1—Ni1[v]	2.048 (3)
Ni1—O3	2.130 (3)	O6—Li	2.12 (2)
Ni1—O3[iii]	2.130 (3)	B—O5[vi]	1.461 (5)
Ni1—Li	3.137 (5)	B—O4[vii]	1.471 (5)
Ni1—Li[iv]	3.137 (5)	B—O4[v]	1.471 (5)
P2—O1	1.503 (3)	Li—O2[iii]	2.113 (13)
P2—O2	1.510 (3)	Li—O2[viii]	2.113 (13)
P2—O4	1.546 (3)	Li—O3[ix]	2.164 (4)
P2—O5	1.556 (3)	Li—Ni1[viii]	3.137 (5)
O5—B	1.461 (5)		
O1[i]—Ni1—O1[ii]	92.58 (18)	B—O5—P2	131.6 (3)
O1[i]—Ni1—O2[iii]	88.53 (11)	B[i]—O4—P2	127.8 (3)
O1[ii]—Ni1—O2[iii]	101.19 (12)	Ni1—O3—Li	93.87 (18)
O1[i]—Ni1—O2	101.19 (12)	P2—O2—Ni1	127.36 (17)
O1[ii]—Ni1—O2	88.53 (11)	P2—O2—Li[iv]	129.2 (4)
O2[iii]—Ni1—O2	166.00 (17)	Ni1—O2—Li[iv]	97.1 (2)
O1[i]—Ni1—O3	86.52 (13)	P2—O1—Ni1[v]	140.72 (18)
O1[ii]—Ni1—O3	177.55 (12)	O5[vi]—B—O5	103.4 (4)
O2[iii]—Ni1—O3	81.08 (11)	O5[vi]—B—O4[vii]	111.43 (15)
O2—Ni1—O3	89.40 (11)	O5—B—O4[vii]	114.16 (15)
O1[i]—Ni1—O3[iii]	177.55 (12)	O5[vi]—B—O4[v]	114.16 (15)
O1[ii]—Ni1—O3[iii]	86.52 (13)	O5—B—O4[v]	111.43 (16)
O2[iii]—Ni1—O3[iii]	89.40 (11)	O4[vii]—B—O4[v]	102.6 (4)
O2—Ni1—O3[iii]	81.08 (11)	O2[iii]—Li—O2[viii]	106.9 (9)
O3—Ni1—O3[iii]	94.47 (19)	O2[iii]—Li—O6	126.5 (5)
O1[i]—Ni1—Li	72.0 (4)	O2[viii]—Li—O6	126.5 (5)
O1[ii]—Ni1—Li	138.23 (8)	O2[iii]—Li—O3	79.3 (3)
O2[iii]—Ni1—Li	41.9 (3)	O2[viii]—Li—O3	95.5 (4)
O2—Ni1—Li	131.83 (17)	O6—Li—O3	94.3 (6)
O3—Ni1—Li	43.50 (9)	O2[iii]—Li—O3[ix]	95.5 (4)
O3[iii]—Ni1—Li	107.3 (4)	O2[viii]—Li—O3[ix]	79.3 (3)
O1[i]—Ni1—Li[iv]	138.23 (8)	O6—Li—O3[ix]	94.3 (6)
O1[ii]—Ni1—Li[iv]	72.0 (4)	O3—Li—O3[ix]	171.3 (11)
O2[iii]—Ni1—Li[iv]	131.83 (17)	O2[iii]—Li—Ni1	40.91 (9)
O2—Ni1—Li[iv]	41.9 (3)	O2[viii]—Li—Ni1	118.8 (6)
O3—Ni1—Li[iv]	107.3 (4)	O6—Li—Ni1	103.3 (4)

O3^{iii}—Ni1—Li^{iv}	43.50 (9)	O3—Li—Ni1	42.64 (13)
Li—Ni1—Li^{iv}	143.2 (5)	O3^{ix}—Li—Ni1	134.5 (3)
O1—P2—O2	115.38 (17)	O2^{iii}—Li—Ni1^{viii}	118.8 (6)
O1—P2—O4	105.45 (17)	O2^{viii}—Li—Ni1^{viii}	40.91 (9)
O2—P2—O4	111.07 (18)	O6—Li—Ni1^{viii}	103.3 (4)
O1—P2—O5	112.24 (16)	O3—Li—Ni1^{viii}	134.5 (4)
O2—P2—O5	105.75 (16)	O3^{ix}—Li—Ni1^{viii}	42.64 (13)
O4—P2—O5	106.70 (15)	Ni1—Li—Ni1^{viii}	153.4 (7)

Symmetry codes: (i) $x-y$, x, $z-1/6$; (ii) $-x+1$, $-x+y+1$, $-z+1/3$; (iii) $-y+1$, $-x+1$, $-z+1/6$; (iv) $-x+y+1$, $-x+1$, $z+1/3$; (v) y, $-x+y$, $z+1/6$; (vi) x, $x-y$, $-z+5/6$; (vii) y, x, $-z+2/3$; (viii) $-y+1$, $x-y$, $z-1/3$; (ix) x, $x-y$, $-z-1/6$.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3A···O5^{viii}	0.81	2.01	2.746 (4)	151
O3—H3A···O2^{viii}	0.81	2.60	3.165 (4)	128
O6—H6···O4^{x}	0.83	2.52	3.331 (4)	167
O6—H6···O1^{x}	0.83	2.66	3.092 (4)	114
O3—H3B···O1	0.83	2.00	2.810 (4)	167
O3—H3B···O2	0.83	2.54	2.955 (4)	112

Symmetry codes: (viii) $-y+1$, $x-y$, $z-1/3$; (x) $x-y$, $-y$, $-z$.

Fig. 1

Fig. 2