Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

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

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Received 22 March 2009; accepted 20 April 2009

Key indicators: single-crystal X-ray study; T = 296 K; mean σ(O–B) = 0.007 Å; R factor = 0.026; wR factor = 0.065; data-to-parameter ratio = 9.4.

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

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

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
708 independent reflections
684 reflections with $I > 2\sigma(I)$
R_{int} = 0.049

Refinement

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

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*.

This work was supported by the Main Teacher Project of Hena Province (grant No. 649082) and the Foundation of Graduate Produce (reference 2008-M-17).

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

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supporting information

Acta Cryst. (2009). E**65**, i42 [doi:10.1107/S1600536809014652]

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Juan Zheng and Aiyun Zhang

S1. 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 $LiNi(H_2O)_2[BP_2O_8]·H_2O$ 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 $LiNi(H_2O)_2[BP_2O_8]·H_2O$ (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.

S2. 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 $Ni(NO_3)_2·6H_2O$ 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.

S3. Refinement

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

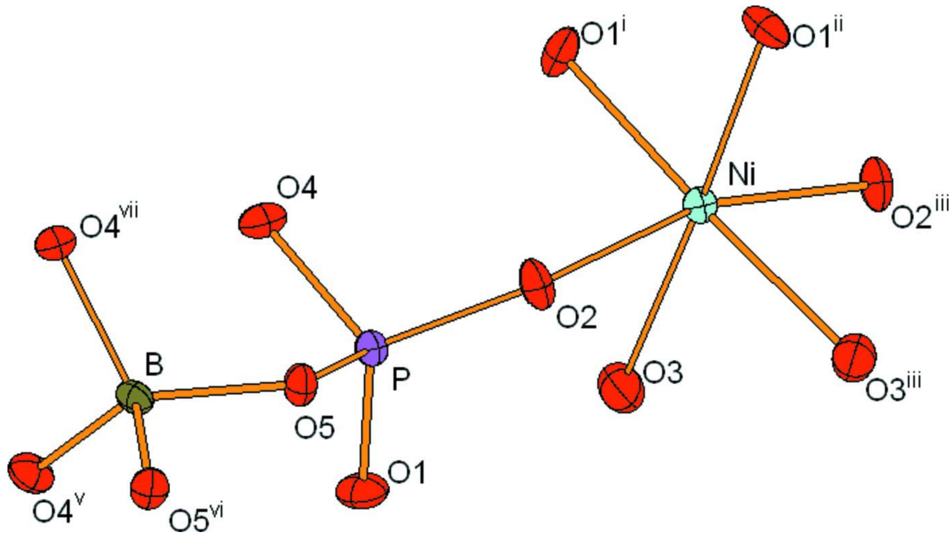

Figure 1

A part of the structure of $LiNi(H_2O)_2[BP_2O_8]·H_2O$ 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*.

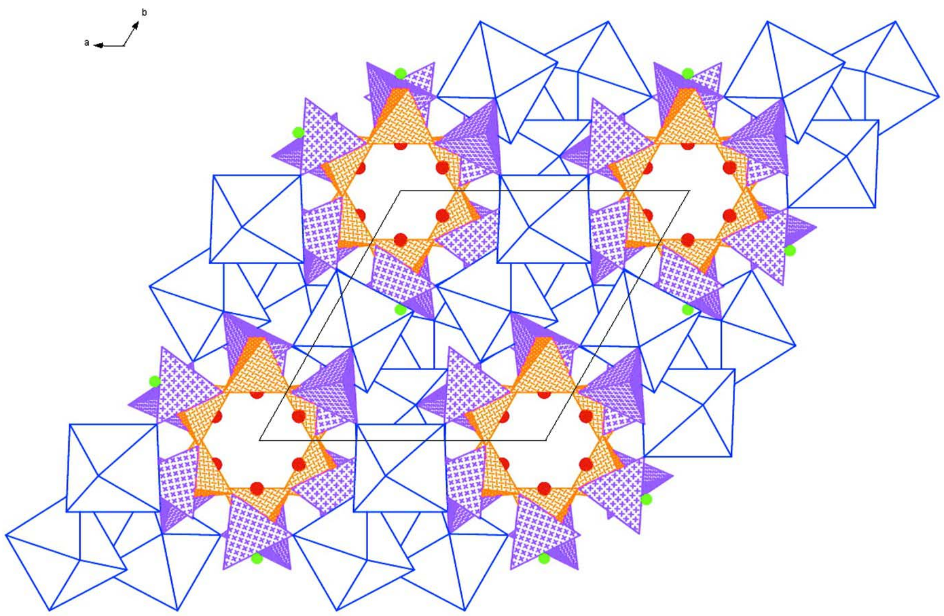

Figure 2

Polyhedral diagram for $LiNi(H_2O)_2[BP_2O_8]·H_2O$ 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

$LiNi(H_2O)_2[BP_2O_8]·H_2O$
M_r = 320.44
Hexagonal, $P6_522$
Hall symbol: P 65 2 (0
a = 9.3359 (3) Å
c = 15.7497 (11) Å

V = 1188.82 (10) Å^3
Z = 6
F(000) = 960
D_x = 2.686 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1684 reflections
θ = 2.5–29.5°
μ = 2.91 mm^{-1}
T = 296 K
Block, green
0.22 × 0.20 × 0.17 mm

Data collection

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

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.065
S = 1.14
708 reflections
75 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0284P)^2 + 2.1868P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}
Absolute structure: Flack (1983), 235 Friedel pairs
Absolute structure 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, º)

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, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*A*···O5^{viii}	0.81	2.01	2.746 (4)	151
O3—H3*A*···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—H3*B*···O1	0.83	2.00	2.810 (4)	167
O3—H3*B*···O2	0.83	2.54	2.955 (4)	112

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