

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

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

The title borophosphate $\text{LiNi}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot\text{H}_2\text{O}$ was synthesized under hydrothermal conditions. The crystal structure is isotypic with the Mg analogue and features helical $[\text{BP}_2\text{O}_8]^{3-}$ 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 $\text{O}-\text{H}\cdots\text{O}$ 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

$\text{LiNi}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot\text{H}_2\text{O}$
 $M_r = 320.44$
Hexagonal, $P6_322$
 $a = 9.3359$ (3) Å
 $c = 15.7497$ (11) Å
 $V = 1188.82$ (10) Å³

$Z = 6$
Mo $K\alpha$ radiation
 $\mu = 2.91$ mm⁻¹
 $T = 296$ K
 $0.22 \times 0.20 \times 0.17$ 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 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$

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

$\Delta\rho_{\text{max}} = 0.68$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.39$ 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 ⁱⁱⁱ	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, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O3—H3A \cdots O5 ^{iv}	0.81	2.01	2.746 (4)	151
O3—H3A \cdots O2 ^{iv}	0.81	2.60	3.165 (4)	128
O6—H6 \cdots O4 ^{vi}	0.83	2.52	3.331 (4)	167
O6—H6 \cdots O1 ^{vi}	0.83	2.66	3.092 (4)	114
O3—H3B \cdots O1	0.83	2.00	2.810 (4)	167
O3—H3B \cdots 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.

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

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supplementary materials

Acta Cryst. (2009). E65, i42 [doi:10.1107/S1600536809014652]

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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 $\text{LiNi}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot\text{H}_2\text{O}$ 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 $[\text{BP}_2\text{O}_8]^{3-}$ (Fig. 1), whereby each BO_4 tetrahedron shares its vertices with four PO_4 tetrahedra. Bond lengths 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 $\{\text{Li}[\text{BP}_2\text{O}_8]^{2-}\}$ 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 $\text{LiNi}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot\text{H}_2\text{O}$ (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 $\text{Ni}(\text{NO}_3)_2$, $\text{Li}_2\text{B}_4\text{O}_7$, water and H_3PO_4 . In a typical synthesis, 0.87 g $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ was dissolved in a mixture of 5 mL water, 1.691 g $\text{Li}_2\text{B}_4\text{O}_7$ 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 1.29 Å from atom H6, and the minimum peak is 0.48 Å from atom P2.

Figures

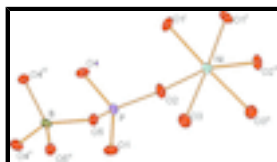


Fig. 1. A part of the structure of $\text{LiNi}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot\text{H}_2\text{O}$ with displacement ellipsoids drawn at the 50% the probability level. Symmetry codes: (i) $1 - y, 1 - x, 0.16667 - z$; (ii) $1 - x, 1 - x + y, 0.33333 - z$; (iii) $x - y, x, -0.16667 + z$; (iv) $y, x, 0.66667 - z$; (v) $y, -x + y, 0.16667 + z$; (vi) $x, x - y, 0.83333 - z$.

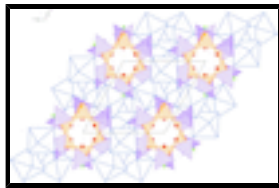


Fig. 2. Polyhedral diagram for $\text{LiNi}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot\text{H}_2\text{O}$ in projection along $[001]$. Colour code: purple P, orange B, blue Ni, red OW6 and green Li.

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Crystal data

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

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	$R_{\text{int}} = 0.049$
$T = 296 \text{ K}$	$\theta_{\text{max}} = 29.5^\circ$
φ and ω scans	$\theta_{\text{min}} = 2.5^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 2007)	$h = -10 \rightarrow 11$
$T_{\text{min}} = 0.567$, $T_{\text{max}} = 0.638$	$k = -8 \rightarrow 11$
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
$R[F^2 > 2\sigma(F^2)] = 0.026$	$w = 1/[\sigma^2(F_o^2) + (0.0284P)^2 + 2.1868P]$
$wR(F^2) = 0.065$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.14$	$(\Delta/\sigma)_{\text{max}} = 0.001$
708 reflections	$\Delta\rho_{\text{max}} = 0.68 \text{ e \AA}^{-3}$
75 parameters	$\Delta\rho_{\text{min}} = -0.39 \text{ e \AA}^{-3}$
	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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (\AA^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)

supplementary materials

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 ($\text{\AA}, ^\circ$)

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

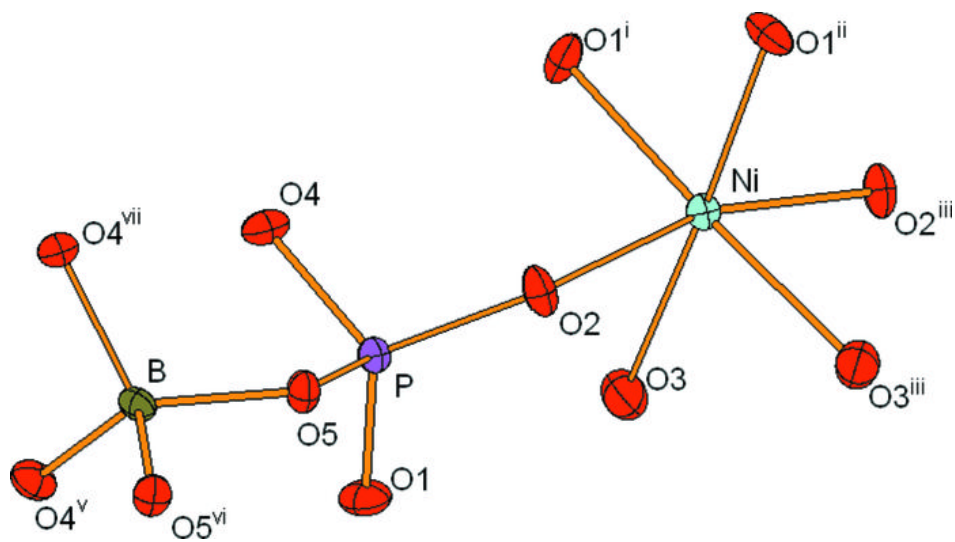


Fig. 2

