inorganic compounds

Lithium manganese(II) diaquaborophosphate monohydrate

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The title compound, $LiMn(H_2O)_2[BP_2O_8] \cdot H_2O$, is built up of an open framework of helical borophosphate ribbons interconnected by $MnO_4(H_2O)_2$ octahedra, forming one-dimensional channels along [001] occupied by Li^+ cations and disordered H_2O molecules (site occupancy 0.5). The Li cations reside in two partially occupied sites [occupancies = 0.42 (3) and 0.289 (13)] near the helices.

Related literature

For related structures, see: Boy & Kniep (2001a,b) for $LiCu(H_2O)_2[BP_2O_8] \cdot (H_2O)$ and $LiZn(H_2O)_2[BP_2O_8] \cdot H_2O$; Ge *et al.* (2003) for $LiCd(H_2O)_2[BP_2O_8] \cdot H_2O$; Lin *et al.* (2008) for $LiMg(H_2O)_2[BP_2O_8] \cdot H_2O$. For related literature, see: Ewald *et al.* (2006); Kniep *et al.* (1997).

Experimental

Crystal data

$LiMn(H_2O)_2[BP_2O_8] \cdot H_2O$	$Z = 6$
$M_r = 316.68$	Mo $K\alpha$ radiation
Hexagonal, $P6_522$	$\mu = 2.01$ mm^{-1}
$a = 9.5765$ (4) Å	$T = 295$ (2) K
$c = 15.857$ (1) Å	$0.16 \times 0.12 \times 0.12$ mm
$V = 1259.4$ (1) Å^3	

Data collection

Rigaku AFC-7 CCD diffractometer	9731 measured reflections
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)	1230 independent reflections
	1223 reflections with $I > 2\sigma(I)$
$T_{min} = 0.740$, $T_{max} = 0.795$	$R_{int} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$	Only H-atom coordinates refined
$wR(F^2) = 0.097$	$\Delta\rho_{max} = 0.61$ e Å^{-3}
$S = 1.19$	$\Delta\rho_{min} = -0.44$ e Å^{-3}
1230 reflections	Absolute structure: Flack (1983), 443 Friedel pairs
85 parameters	Flack parameter: -0.01 (4)
1 restraint	

Table 1
Selected geometric parameters (Å, °).

Mn1—O4[i]	2.133 (3)	B1—O1[iv]	1.463 (4)
Mn1—O3	2.139 (3)	B1—O2[ii]	1.470 (4)
Mn1—O5	2.311 (4)	Li1—O5[ii]	2.111 (4)
P1—O3	1.504 (3)	Li1—O3[ii]	2.112 (17)
P1—O4	1.510 (3)	Li2—O6[v]	1.95 (3)
P1—O1[ii]	1.553 (3)	Li2—O6[vi]	1.98 (3)
P1—O2[iii]	1.560 (2)	Li2—O4[v]	2.11 (3)
O5—H1	0.82 (7)	Li2—O5[vii]	2.18 (3)
O5—H2	0.81 (2)		
B1[viii]—O1—P1[ii]	129.4 (2)	P1—O3—Mn1	128.38 (17)
B1—O2—P1[ix]	131.1 (2)		

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H1$\cdots$O4[x]	0.83 (7)	2.09 (7)	2.878 (5)	159.80
O5—H2$\cdots$O2[i]	0.81 (4)	2.09 (5)	2.845 (5)	155.74

Symmetry codes: (i) $y, -x+y+1, z+\frac{1}{6}$; (x) $-x+y, y, -z+\frac{1}{2}$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005) and *ATOMS* (Dowty, 2004); software used to prepare material for publication: *SHELXL97*.

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supplementary materials

Lithium manganese(II) diaquaborophosphate monohydrate

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Comment

A large family of compounds contains helical borophosphate anions $_\infty^1[BP_2O_8]^{3-}$ with various combinations of metal cations (M^IM^{II}, $M_{0.5}^IM^{II}$, M^{III}) (Kniep *et al.*, 1997; Ewald *et al.*, 2006). To date, the only Li-containing members are $LiM^{II}(H_2O)_2[BP_2O_8]\cdot H_2O$ (M^{II} = Cu, Zn, Cd, Mg) (Boy & Kniep, 2001a, 2001b; Ge *et al.*, 2003; Lin *et al.*, 2008). The structure of $LiMn(H_2O)_2[BP_2O_8]\cdot H_2O$ is reported here.

The borophosphate helices, built up of four-membered rings of alternating BO_4 and PO_4 tetrahedra, extend along the 6_5 screw axis (Fig. 1 and 2). These helices are interconnected by Jahn-Teller-distorted Mn^{2+}-centred octahedra, with four oxygen atoms (O3, O4) from PO_4 groups and two (O5) from water molecules at the vertices (Fig. 3). Unlike the compounds containing Cu and Zn (Boy & Kniep, 2001a, 2001b) but similar to those containing Cd and Mg (Ge *et al.*, 2003; Lin *et al.*, 2008), there are two distinct Li sites: Li1 is close to the outer wall of the borophosphate helices and Li2 is situated at the free loops (inner wall) of the helices. The sum of occupancies of these Li sites refines to almost unity, as required to maintain charge neutrality in the compound.

Experimental

$LiMn(H_2O)_2[BP_2O_8]\cdot H_2O$ was obtained in the presence of boric acid as a flux. A mixture of 0.1149 g $MnCO_3$, 1.484 g H_3BO_3, and 0.6235 g LiH_2PO_4 was ground to a homogeneous powder, which was transferred to a teflon autoclave with 10 ml inline (degree of filling 10%) where it was heated at 443 K for four days.

Refinement

The hydrogen atoms connected to O5 were located from difference Fourier maps with displacement parameters fixed as 1.2*U(O5), whereas those connected to O6 belonging to the disordered water molecules were not located. The sum of the occupancies of Li sites was restrained to maintain charge neutrality within the entire compound. The occupancy of the O6 site associated with the disordered water molecules was fixed at 0.5.

supplementary materials

Figures
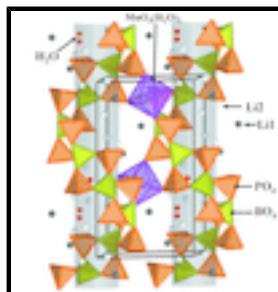
Fig. 1. Linkage of borophosphate helices in $LiMn(H_2O)_2[BP_2O_8]\cdot H_2O$ through $MnO_4(H_2O)_2$ octahedra (BO_4, green tetrahedra; PO_4, orange tetrahedra; MnO_6, violet octahedra; Li, black spheres; H_2O, red spheres).
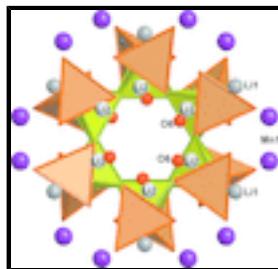
Fig. 2. Section of $LiMn(H_2O)_2[BP_2O_8]\cdot H_2O$ viewed along the c axis (colour scheme as in Fig. 1).
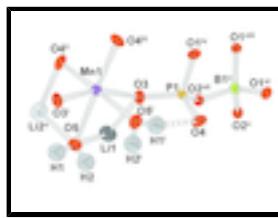
Fig. 3. Coordination environment of Mn, B, and P atoms, with displacement ellipsoids drawn at the 50% probability level (symmetry codes: (i) -x+y, y, 1/2-z; (ii) 1-x, 1-x+y, 1/3-z; (iii) y,1-x+y, 1/6+z; (iv) 1-y,1-x, 1/6-z; (v) x-y, x,-1/6+z; (vi) 1+x-y, 1-y,-z, (vii) x-y, 1-y,-z; (viii) 1+x-y,1+x,-1/6+z).

Lithium manganese diaquaborophosphate monohydrate

Crystal data

$LiMn(H_2O)_2[BP_2O_8]\cdot H_2O$	$D_x = 2.505$ Mg m^{-3}
$M_r = 316.68$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hexagonal, $P6_522$	Cell parameters from 6263 reflections
Hall symbol: P 65 2 (0 0 1)	$\theta = 2.5–33.2°$
$a = 9.5765$ (4) Å	$\mu = 2.01$ mm^{-1}
$c = 15.857$ (1) Å	$T = 295$ K
$V = 1259.4$ (1) Å^3	Hexagonal bipyramid, pale pink
$Z = 6$	$0.16 \times 0.12 \times 0.12$ mm
$F(000) = 942$	

Data collection

Rigaku AFC-7 CCD diffractometer	1230 independent reflections
Radiation source: fine-focus sealed tube	1223 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.032$
Detector resolution: 14.6306 pixels mm^{-1}	$\theta_{max} = 30.0°$, $\theta_{min} = 2.5°$

thin–slice Δφ=0.6 & Δω=0.6 scans	$h = -13 \rightarrow 13$
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)	$k = -13 \rightarrow 12$
$T_{min} = 0.740$, $T_{max} = 0.795$	$l = -19 \rightarrow 22$
9731 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: difference Fourier map
Least-squares matrix: full	Only H-atom coordinates refined
$R[F^2 > 2\sigma(F^2)] = 0.040$	$w = 1/[\sigma^2(F_o^2) + (0.008P)^2 + 5.1269P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.097$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.19$	$\Delta\rho_{max} = 0.62$ e Å^{-3}
1230 reflections	$\Delta\rho_{min} = -0.44$ e Å^{-3}
85 parameters	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
1 restraint	Extinction coefficient: 0.0054 (19)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 443 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: −0.01 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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, convention-al 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	$U_{iso}*/U_{eq}$	Occ. (<1)
Mn1	0.44888 (4)	0.89775 (9)	0.2500	0.0163 (2)	
P1	0.61636 (10)	0.83327 (10)	0.08453 (6)	0.0134 (2)	
O1	0.0204 (3)	0.2129 (3)	0.06593 (16)	0.0181 (5)	
O2	0.7681 (3)	0.1804 (3)	0.01267 (14)	0.0158 (5)	
O3	0.4860 (3)	0.8589 (4)	0.12112 (17)	0.0227 (6)	
O4	0.6237 (4)	0.6903 (3)	0.11938 (17)	0.0228 (6)	
O5	0.1884 (4)	0.7081 (4)	0.2127 (2)	0.0340 (8)	
O6	0.9000 (19)	0.8166 (12)	0.2717 (7)	0.079 (3)*	0.50
B1	0.8493 (3)	0.1507 (3)	0.0833	0.0140 (9)	
Li1	0.2428 (18)	0.7572 (18)	0.0833	0.034 (4)	0.42 (3)
Li2	0.899 (4)	0.763 (3)	0.3479 (16)	0.034 (4)	0.289 (13)

H1	0.133 (8)	0.683 (7)	0.256 (4)	0.041*
H2	0.179 (7)	0.620 (4)	0.218 (4)	0.041*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0170 (3)	0.0165 (4)	0.0153 (3)	0.00826 (18)	0.0028 (2)	0.000
P1	0.0153 (4)	0.0131 (4)	0.0113 (3)	0.0068 (3)	0.0011 (3)	−0.0005 (3)
O1	0.0139 (11)	0.0196 (12)	0.0200 (12)	0.0077 (10)	−0.0012 (9)	−0.0060 (9)
O2	0.0195 (12)	0.0185 (11)	0.0106 (9)	0.0104 (10)	−0.0029 (9)	−0.0024 (8)
O3	0.0222 (14)	0.0306 (15)	0.0177 (12)	0.0151 (12)	0.0028 (10)	−0.0046 (11)
O4	0.0348 (16)	0.0150 (12)	0.0177 (11)	0.0117 (11)	−0.0008 (12)	0.0022 (10)
O5	0.0280 (17)	0.0233 (15)	0.0393 (17)	0.0041 (13)	0.0118 (14)	−0.0065 (14)
B1	0.0157 (17)	0.0157 (17)	0.011 (2)	0.0083 (19)	0.0013 (16)	0.0013 (16)
Li1	0.036 (7)	0.036 (7)	0.023 (8)	0.012 (8)	0.003 (6)	0.003 (6)
Li2	0.036 (7)	0.036 (7)	0.023 (8)	0.012 (8)	0.003 (6)	0.003 (6)

Geometric parameters (Å, °)

Mn1—O4^i	2.133 (3)	O5—H1	0.82 (7)
Mn1—O4^{ii}	2.133 (3)	O5—H2	0.81 (2)
Mn1—O3	2.139 (3)	O6—O6^{ix}	0.71 (2)
Mn1—O3^{iii}	2.139 (3)	O6—Li2	1.31 (3)
Mn1—O5	2.311 (4)	O6—Li2^{ix}	1.95 (3)
Mn1—O5^{iii}	2.311 (3)	O6—Li2^{xii}	1.98 (3)
P1—O3	1.504 (3)	O6—Li2^x	2.45 (3)
P1—O4	1.510 (3)	O6—Li1^{xiii}	2.53 (3)
P1—O1^{iv}	1.553 (3)	B1—O1^{xiv}	1.463 (4)
P1—O2^v	1.560 (2)	B1—O1^{xv}	1.463 (4)
O1—B1^{vi}	1.463 (4)	B1—O2^{iv}	1.470 (4)
O1—P1^{iv}	1.553 (3)	Li1—O5^{iv}	2.111 (4)
O1—Li2^{vii}	2.65 (3)	Li1—O3^{iv}	2.112 (17)
O2—B1	1.470 (4)	Li2—O6^{ix}	1.95 (3)
O2—P1^{viii}	1.560 (2)	Li2—O6^{xii}	1.98 (3)
O3—Li1	2.112 (17)	Li2—O4^{ix}	2.11 (3)
O4—Li2^{ix}	2.11 (3)	Li2—O5^{xiii}	2.18 (3)
O4—Mn1^x	2.133 (3)	Li2—Li2^{xii}	2.30 (6)
O5—Li1	2.111 (4)	Li2—O6^i	2.45 (3)
O5—Li2^{xi}	2.18 (3)		
O4^i—Mn1—O4^{ii}	97.89 (17)	O2—B1—O2^{iv}	102.6 (4)
O4^i—Mn1—O3	100.17 (11)	O5^{iv}—Li1—O5	177.6 (17)
O4^{ii}—Mn1—O3	91.22 (11)	O5^{iv}—Li1—O3^{iv}	85.4 (4)
O4^i—Mn1—O3^{iii}	91.22 (11)	O5—Li1—O3^{iv}	96.0 (5)
O4^{ii}—Mn1—O3^{iii}	100.17 (11)	O5^{iv}—Li1—O3	96.0 (5)

O3—Mn1—O3ⁱⁱⁱ	162.68 (17)	O5—Li1—O3	85.4 (4)
O4ⁱ—Mn1—O5	178.14 (13)	O3^{iv}—Li1—O3	112.6 (14)
O4ⁱⁱ—Mn1—O5	83.95 (13)	O5^{iv}—Li1—O6ⁱⁱ	80.8 (8)
O3—Mn1—O5	80.01 (12)	O5—Li1—O6ⁱⁱ	96.8 (9)
O3ⁱⁱⁱ—Mn1—O5	88.19 (12)	O3^{iv}—Li1—O6ⁱⁱ	122.4 (7)
O4ⁱ—Mn1—O5ⁱⁱⁱ	83.95 (13)	O3—Li1—O6ⁱⁱ	124.3 (8)
O4ⁱⁱ—Mn1—O5ⁱⁱⁱ	178.14 (14)	O5^{iv}—Li1—O6^{xi}	96.8 (9)
O3—Mn1—O5ⁱⁱⁱ	88.19 (12)	O5—Li1—O6^{xi}	80.8 (8)
O3ⁱⁱⁱ—Mn1—O5ⁱⁱⁱ	80.01 (12)	O3^{iv}—Li1—O6^{xi}	124.3 (8)
O5—Mn1—O5ⁱⁱⁱ	94.2 (2)	O3—Li1—O6^{xi}	122.4 (7)
O3—P1—O4	115.17 (17)	O6ⁱⁱ—Li1—O6^{xi}	16.0 (5)
O3—P1—O1^{iv}	111.97 (16)	O6—Li2—O6^{ix}	10.8 (10)
O4—P1—O1^{iv}	104.62 (16)	O6—Li2—O6^{xii}	90.8 (17)
O3—P1—O2^v	105.62 (15)	O6^{ix}—Li2—O6^{xii}	101.7 (15)
O4—P1—O2^v	111.81 (15)	O6—Li2—O4^{ix}	119.9 (19)
O1^{iv}—P1—O2^v	107.54 (14)	O6^{ix}—Li2—O4^{ix}	110.3 (14)
B1^{vi}—O1—P1^{iv}	129.4 (2)	O6^{xii}—Li2—O4^{ix}	138.2 (14)
B1—O2—P1^{viii}	131.1 (2)	O6—Li2—O5^{xiii}	117.8 (18)
P1—O3—Mn1	128.38 (17)	O6^{ix}—Li2—O5^{xiii}	114.8 (14)
Li1—O5—H1	157 (4)	O6^{xii}—Li2—O5^{xiii}	102.8 (13)
Li2^{xi}—O5—H1	93 (4)	O4^{ix}—Li2—O5^{xiii}	87.8 (11)
Mn1—O5—H1	107 (4)	O6—Li2—O6ⁱ	104.2 (18)
Li1—O5—H2	103 (4)	O6^{ix}—Li2—O6ⁱ	115.0 (14)
Li2^{xi}—O5—H2	162 (4)	O6^{xii}—Li2—O6ⁱ	13.8 (7)
Mn1—O5—H2	107 (4)	O4^{ix}—Li2—O6ⁱ	125.5 (12)
H1—O5—H2	84 (5)	O5^{xiii}—Li2—O6ⁱ	99.1 (11)
Li2—O6—Li2^{ix}	146 (2)	O6—Li2—O1^{xvi}	100.4 (16)
O1^{xiv}—B1—O1^{xv}	103.7 (4)	O6^{ix}—Li2—O1^{xvi}	100.1 (12)
O1^{xiv}—B1—O2	113.70 (14)	O6^{xii}—Li2—O1^{xvi}	89.1 (11)
O1^{xv}—B1—O2	111.75 (14)	O4^{ix}—Li2—O1^{xvi}	59.9 (8)
O1^{xiv}—B1—O2^{iv}	111.75 (14)	O5^{xiii}—Li2—O1^{xvi}	139.4 (13)
O1^{xv}—B1—O2^{iv}	113.70 (14)	O6ⁱ—Li2—O1^{xvi}	83.4 (9)

Symmetry codes: (i) *y*, −*x*+*y*+1, *z*+1/6; (ii) −*x*+1, −*x*+*y*+1, −*z*+1/3; (iii) −*x*+*y*, *y*, −*z*+1/2; (iv) −*y*+1, −*x*+1, −*z*+1/6; (v) *x*−*y*, −*y*+1, −*z*; (vi) *x*−1, *y*, *z*; (vii) −*y*+1, *x*−*y*, *z*−1/3; (viii) *x*−*y*+1, −*y*+1, −*z*; (ix) −*x*+*y*+1, *y*, −*z*+1/2; (x) *x*−*y*+1, *x*, *z*−1/6; (xi) *x*−*y*, *x*, *z*−1/6; (xii) *y*, *x*, −*z*+2/3; (xiii) *y*, −*x*+*y*, *z*+1/6; (xiv) −*y*+1, −*x*, −*z*+1/6; (xv) *x*+1, *y*, *z*; (xvi) −*x*+*y*+1, −*x*+1, *z*+1/3.

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O5—H1···O4ⁱⁱⁱ	0.83 (7)	2.09 (7)	2.878 (5)	159.80
O5—H2···O2ⁱ	0.81 (4)	2.09 (5)	2.845 (5)	156.

Symmetry codes: (iii) −*x*+*y*, *y*, −*z*+1/2; (i) *y*, −*x*+*y*+1, *z*+1/6.

Fig. 1

Fig. 2

Fig. 3