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Lithium manganese(II) diaquaborophosphate monohydrate

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Key indicators: single-crystal X-ray study; T = 295 K; mean σ(Mn–O) = 0.004 Å; H-atom completeness 67%; disorder in main residue; R factor = 0.040; wR factor = 0.097; data-to-parameter ratio = 14.5.

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 (2001*a*,*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

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

Data collection

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

Refinement

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

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···A	D—H	H···A	D···A	D—H···A
O5—H1···O4^{x}	0.83 (7)	2.09 (7)	2.878 (5)	159.80
O5—H2···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 data and figures for this paper are available from the IUCr electronic archives (Reference: MG2052).

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supporting information

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Lithium manganese(II) diaquaborophosphate monohydrate

Rong-Chuan Zhuang, Xue-Yun Chen and Jin-Xiao Mi

S1. Comment

A large family of compounds contains helical borophosphate anions $_{\infty}^{1}[BP_2O_8]^{3-}$ with various combinations of metal cations ($M^{I}M^{II}$, $M_{0.5}^{I}M^{II}$, 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.

S2. Experimental

$LiMn(H_2O)_2[BP_2O_8].H_2O$ 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.

S3. 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.

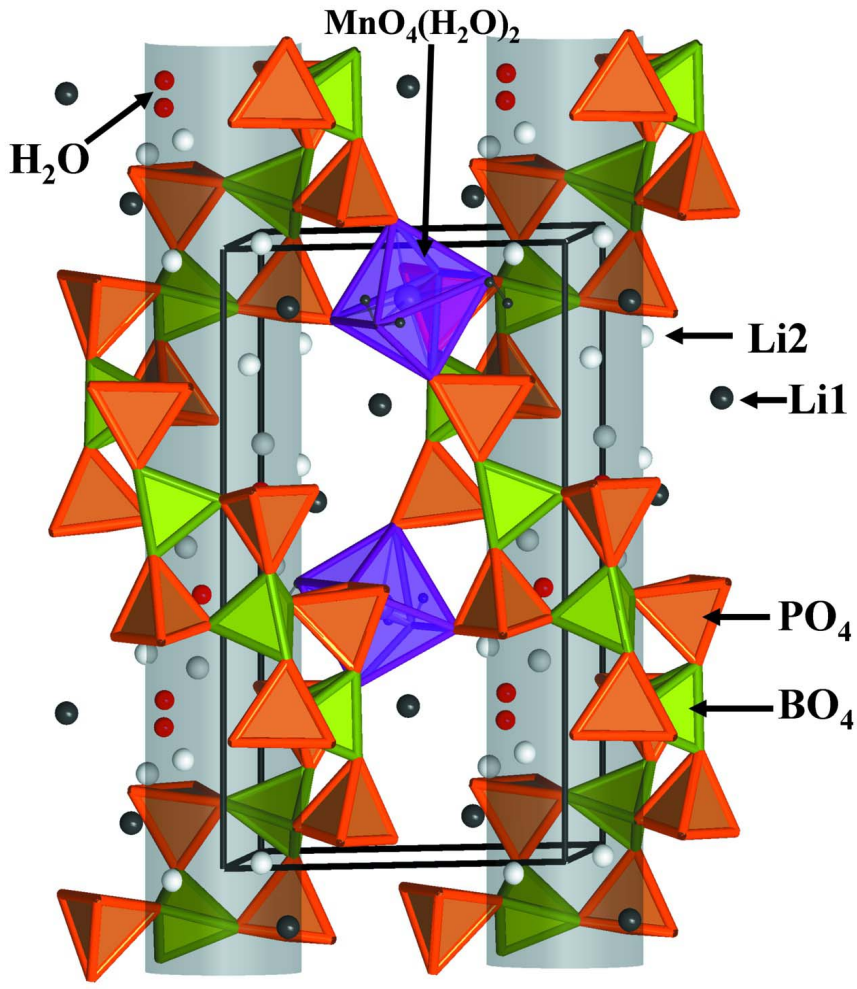

Figure 1

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).

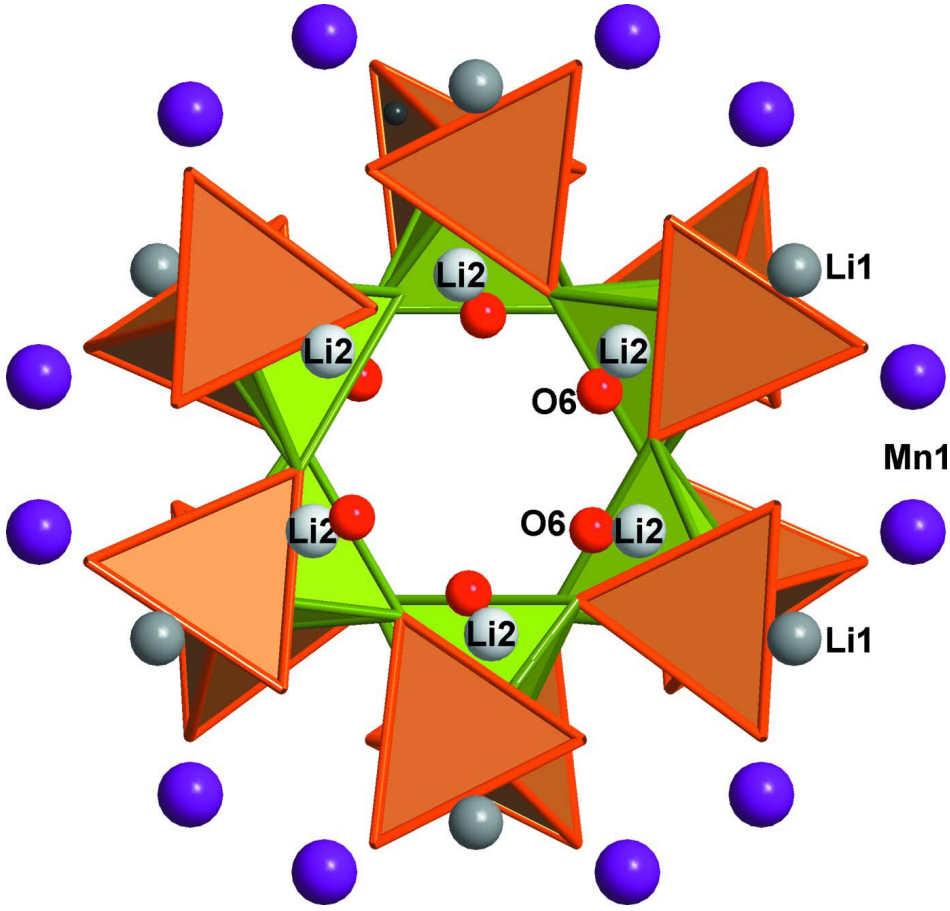

Figure 2

Section of $LiMn(H_2O)_2[BP_2O_8]\cdot H_2O$ viewed along the *c* axis (colour scheme as in Fig. 1).

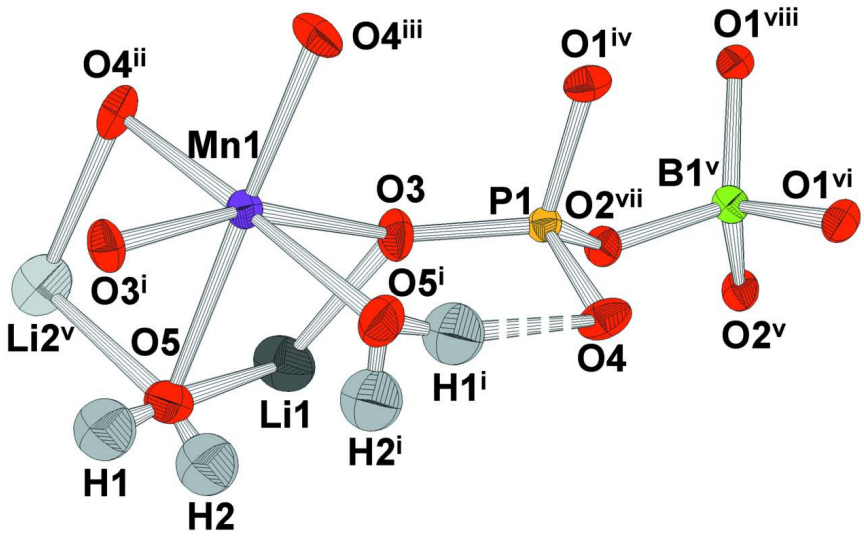

Figure 3

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

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

Data collection

Rigaku AFC-7 CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 14.6306 pixels mm^{-1}
thin–slice $\Delta\varphi$=0.6 & $\Delta\omega$=0.6 scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
$T_{min} = 0.740$, $T_{max} = 0.795$
9731 measured reflections
1230 independent reflections
1223 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 30.0°$, $\theta_{min} = 2.5°$
$h = -13\rightarrow13$
$k = -13\rightarrow12$
$l = -19\rightarrow22$

Refinement

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

	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, º)

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—O3^{iii}	162.68 (17)	O5—Li1—O3	85.4 (4)
O4^{i}—Mn1—O5	178.14 (13)	O3^{iv}—Li1—O3	112.6 (14)
O4^{ii}—Mn1—O5	83.95 (13)	O5^{iv}—Li1—O6^{ii}	80.8 (8)
O3—Mn1—O5	80.01 (12)	O5—Li1—O6^{ii}	96.8 (9)
O3^{iii}—Mn1—O5	88.19 (12)	O3^{iv}—Li1—O6^{ii}	122.4 (7)
O4^{i}—Mn1—O5^{iii}	83.95 (13)	O3—Li1—O6^{ii}	124.3 (8)
O4^{ii}—Mn1—O5^{iii}	178.14 (14)	O5^{iv}—Li1—O6^{xi}	96.8 (9)
O3—Mn1—O5^{iii}	88.19 (12)	O5—Li1—O6^{xi}	80.8 (8)
O3^{iii}—Mn1—O5^{iii}	80.01 (12)	O3^{iv}—Li1—O6^{xi}	124.3 (8)
O5—Mn1—O5^{iii}	94.2 (2)	O3—Li1—O6^{xi}	122.4 (7)
O3—P1—O4	115.17 (17)	O6^{ii}—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—O6^{i}	104.2 (18)
Li1—O5—H2	103 (4)	O6^{ix}—Li2—O6^{i}	115.0 (14)
Li2^{xi}—O5—H2	162 (4)	O6^{xii}—Li2—O6^{i}	13.8 (7)
Mn1—O5—H2	107 (4)	O4^{ix}—Li2—O6^{i}	125.5 (12)
H1—O5—H2	84 (5)	O5^{xiii}—Li2—O6^{i}	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)	O6^{i}—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, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H1···O4^{iii}	0.83 (7)	2.09 (7)	2.878 (5)	159.80
O5—H2···O2^{i}	0.81 (4)	2.09 (5)	2.845 (5)	156

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