

A mixed indium–iron lithium diphosphate, $\text{In}_{0.51}\text{Fe}_{0.49}\text{LiP}_2\text{O}_7$

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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{P–O}) = 0.001$ Å; disorder in main residue; R factor = 0.013; wR factor = 0.032; data-to-parameter ratio = 41.4.

The structure of $\text{In}_{0.51}\text{Fe}_{0.49}\text{LiP}_2\text{O}_7$ consists of a three-dimensional network constructed from $(\text{In}^{\text{III}}/\text{Fe}^{\text{III}})\text{O}_6$ octahedra and P_2O_7 groups. Each $M^{\text{III}}\text{O}_6$ octahedron is linked to six PO_4 tetrahedra belonging to five different P_2O_7 groups and shares two corners with the same P_2O_7 group so as to build infinite chains or rather parallel columns of $[\text{M}^{\text{III}}\text{P}_2\text{O}_{11}]$ running along the a axis. The linkage between these chains or columns defines heptagonal tunnels parallel to $[100]$ in which the Li^+ ions are located in off-centred positions. The $\text{In}_{0.51}\text{Fe}_{0.49}\text{LiP}_2\text{O}_7$ compound can be regarded as one composition of the continuous solid solution between LiFeP_2O_7 and LiInP_2O_7 whose structure is isotypic with the $A^{\text{I}}\text{FeP}_2\text{O}_7$ ($A^{\text{I}} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ and Ag) diphosphate family.

Related literature

For physical properties and potential applications of $A^{\text{I}}M^{\text{III}}\text{P}_2\text{O}_7$ ($A^{\text{I}} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ and Ag ; $M^{\text{III}} = \text{Al}, \text{Ga}, \text{Cr}, \text{Fe}, \text{In}, \text{Y}$) diphosphates, see: Terebilenko *et al.* (2010); Hizhnyi *et al.* (2008); Whangbo *et al.* (2004); Vitins *et al.* (2000). For isotypic structures, see: Tran Qui *et al.* (1987); Rouse *et al.* (2002). For a closely related structure, see: Zouihri *et al.* (2011). For background to bond-valence analysis, see: Brown & Altermatt (1985).

Experimental

Crystal data

$\text{In}_{0.51}\text{Fe}_{0.49}\text{LiP}_2\text{O}_7$
 $M_r = 267.10$
 Monoclinic, $P2_1$
 $a = 4.8698$ (2) Å
 $b = 8.2761$ (4) Å
 $c = 6.9980$ (3) Å
 $\beta = 109.650$ (2)°

$V = 265.62$ (2) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 4.25$ mm⁻¹
 $T = 296$ K
 $0.11 \times 0.08 \times 0.04$ mm

Data collection

Bruker X8 APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1999)
 $T_{\text{min}} = 0.673$, $T_{\text{max}} = 0.845$

13153 measured reflections
 4262 independent reflections
 4200 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.013$
 $wR(F^2) = 0.032$
 $S = 1.04$
 4262 reflections
 103 parameters
 2 restraints

$\Delta\rho_{\text{max}} = 0.74$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.55$ e Å⁻³
 Absolute structure: Flack (1983),
 1965 Friedel pairs
 Flack parameter: 0.021 (6)

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2162).

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supporting information

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A mixed indium–iron lithium diphosphate, $\text{In}_{0.51}\text{Fe}_{0.49}\text{LiP}_2\text{O}_7$

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S1. Comment

As reported in a previous study, physical properties and potential applications of $A^1M^{\text{III}}\text{P}_2\text{O}_7$ ($A^1 = \text{Li, Na, K, Rb, Cs}$ and Ag ; $M^{\text{III}} = \text{Al, Ga, Cr, Fe, In, Y}$) diphosphates have attracted the interest of several researchers (Zouihri *et al.* (2011); Terebilenko *et al.* (2010); Hizhnyi *et al.* (2008); Whangbo *et al.* (2004); Vitins *et al.* (2000)). In this context, the present work reports on the determination of $\text{In}_{0.51}\text{Fe}_{0.49}\text{LiP}_2\text{O}_7$ crystal structure from X-ray diffraction single-crystal data.

In an attempt to synthesize an Indium-Iron Lithium Diphosphate, we obtained the following compound of formula: $\text{In}_{0.51}\text{Fe}_{0.49}\text{LiP}_2\text{O}_7$. The calculated valences for the mixed site $(\text{In/Fe})^{\text{III}+}$, Li^+ and $\text{P}^{\text{V}+}$ ions are as expected, viz. 3.23, 0.91 and 5.0, respectively. A three-dimensional view of the $\text{In}_{0.51}\text{Fe}_{0.49}\text{LiP}_2\text{O}_7$ crystal structure along the a axis, is shown in Fig. 1. The structural network of this phosphate is built up from $(\text{In/Fe})\text{O}_6$ (to be noted MO_6) octahedra linked to P_2O_7 diphosphate groups by a corner-sharing. The $M^{\text{III}}\text{O}_6$ octahedra are almost regular with homogeneous $M^{\text{III}}\text{—O}$ bond lengths ranging from 2.0225 (9) Å to 2.1230 (6) Å. Each MO_6 octahedron is surrounded by six PO_4 tetrahedra belonging to five different P_2O_7 groups and shares two corners with the same P_2O_7 group as shown in Fig.1 and Fig.2. This induces a 3-D framework in which heptagonal channels parallel to $[100]$ direction are formed. The Li^+ cations are located in the tunnels but in off-centred positions as shown in Fig.2. Although, the coordination sphere of each Li^+ cation is composed of four O^{2-} anions located at Li—O distances ranging from 1.956 (3) to 2.107 (3) Å and the fifth at 2.676 (4) Å, in a distorted bipyramidal geometry. Furthermore, the diphosphate group exhibits an almost eclipsed conformation with a P—O—P angle of 131.07 (5) °. This value is intermediate between 128.8 (2) ° and 132.7 (4) ° observed for LiFeP_2O_7 and LiInP_2O_7 respectively) (Rousse *et al.* (2002); Tran Qui *et al.* (1987)). This is not surprising because $\text{In}_{0.51}\text{Fe}_{0.49}\text{LiP}_2\text{O}_7$ can be regarded as one composition of the continuous solid solution between LiFeP_2O_7 and LiInP_2O_7 whose structure is isotypic with the $A^1M^{\text{III}}\text{P}_2\text{O}_7$ ($A^1 = \text{Li, Na, K, Rb, Cs}$ and Ag ; $M^{\text{III}} = \text{Al, Sc, Cr, Fe, Ga, Y}$ and In) diphosphates family.

S2. Experimental

Single crystals of the title compound, $\text{In}_{0.51}\text{Fe}_{0.49}\text{LiP}_2\text{O}_7$ phase, were synthesized by flux methods. Indeed, mixture of 0.0004 mole In_2O_3 , 0.0004 mole Fe_2O_3 , and 0.004 mole $(\text{NH}_4)_2\text{HPO}_4$ were added to 0.0008 mole $\text{B}(\text{OH})_3$ and 0.0008 mole LiBO_2 as flux and heated to 1323 K in a platinum crucible. The mixture is lowered to 1223 K with a speed of 0.5°min^{-1} and maintained at this temperature for 20 h and then followed by slow cooling to room temperature at a rate of 0.5°min^{-1} resulted in colourless crystals of the title compound.

S3. Refinement

The space group is not centro symmetric and the polar axis restraint is generated automatically by Shelxl program. Friedel opposites reflections are not merged. The refinement of the occupancies of the two metal In and Fe and the bond valence sum calculations led to a site occupancy factor of 0.514 (2) for In and 0.486 (2) for Fe. The refinement with a fixed weights (WGHT 0.1) led to a goodness of fit <1 ($\text{GooF} = S = 0.407$). The reflection 002 is omitted because the

difference between its calculated and observed intensities is very large. The highest and deepest hole residual peak in the final difference Fourier map are located at 0.60 Å and 0.51 Å, from Fe1.

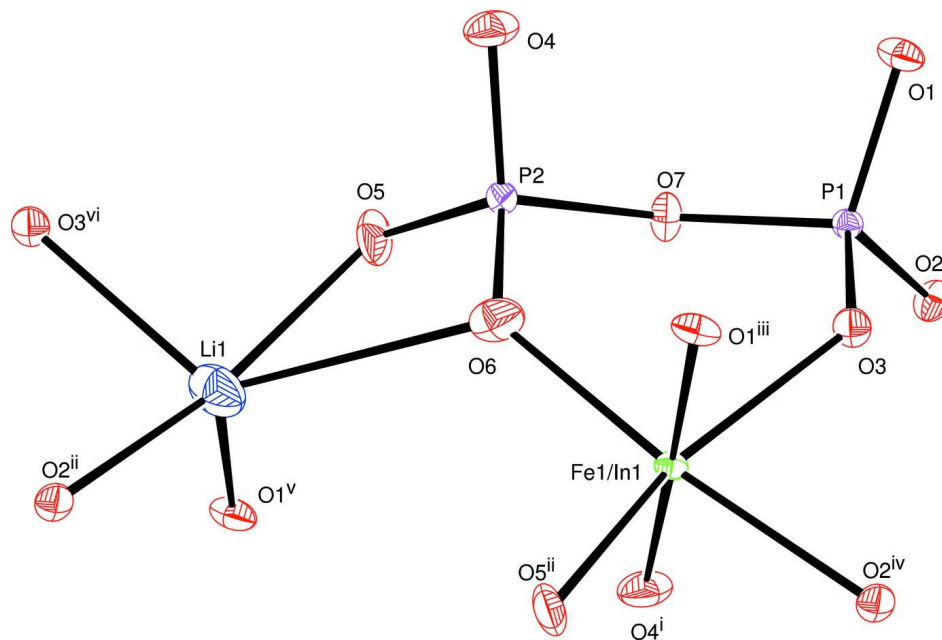
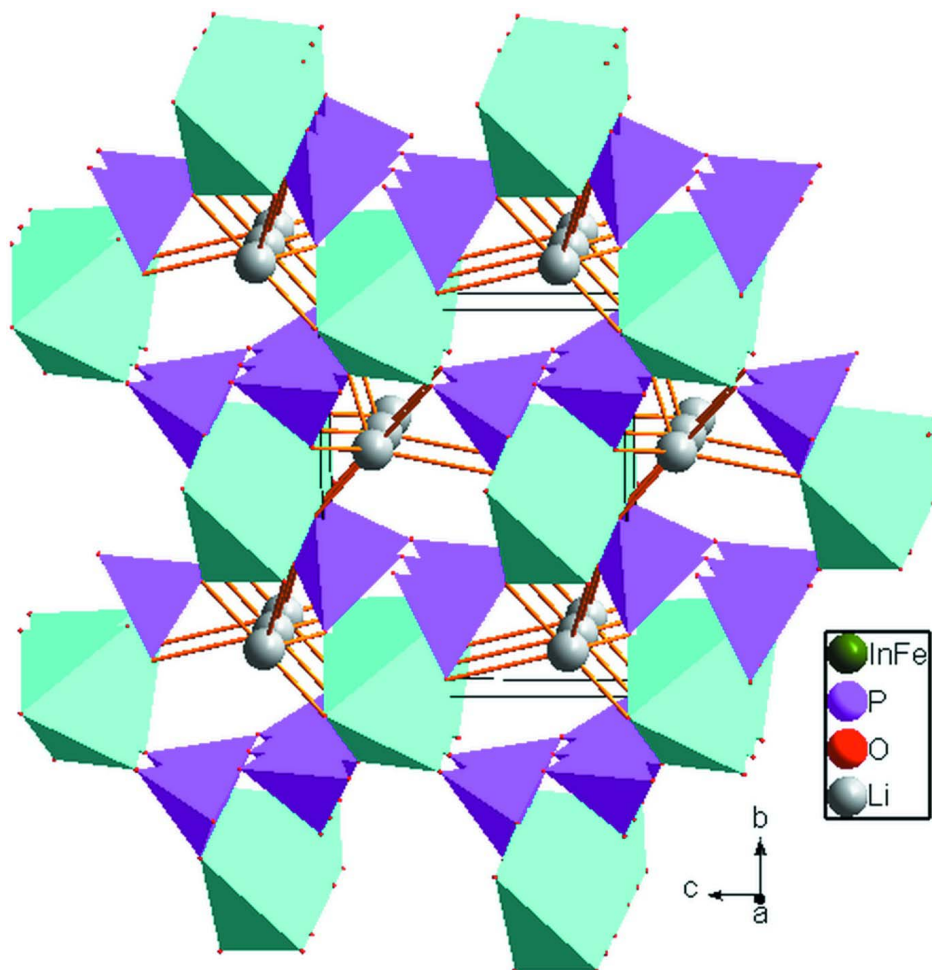


Figure 1

Partial plot of $\text{In}_{0.51}\text{Fe}_{0.49}\text{LiP}_2\text{O}_7$ crystal structure showing polyhedra linkage. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (i) $x + 1, y, z$; (ii) $-x, y - 1/2, -z + 1$; (iii) $-x, y - 1/2, -z + 2$; (iv) $-x + 1, y - 1/2, -z + 2$; (v) $-x, y + 1/2, -z + 1$; (vi) $x, y, z + 1$; (vii) $-x, y + 1/2, -z + 2$; (viii) $-x + 1, y + 1/2, -z + 2$; (ix) $x + 1, y, z + 1$; (x) $x - 1, y, z$; (xi) $x, y, z - 1$; (xii) $x - 1, y, z - 1$.

**Figure 2**

Perspective view along [100] of the $\text{In}_{0.51}\text{Fe}_{0.49}\text{LiP}_2\text{O}_7$ framework structure showing tunnels where lithium cations are located.

indium iron lithium diphosphate

Crystal data

$\text{In}_{0.51}\text{Fe}_{0.49}\text{LiP}_2\text{O}_7$

$M_r = 267.10$

Monoclinic, $P2_1$

Hall symbol: P 2yb

$a = 4.8698 (2) \text{ \AA}$

$b = 8.2761 (4) \text{ \AA}$

$c = 6.9980 (3) \text{ \AA}$

$\beta = 109.650 (2)^\circ$

$V = 265.62 (2) \text{ \AA}^3$

$Z = 2$

$F(000) = 254$

$D_x = 3.340 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 276 reflections

$\theta = 2.4\text{--}34.1^\circ$

$\mu = 4.25 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Prism, colourless

$0.11 \times 0.08 \times 0.04 \text{ mm}$

Data collection

Bruker X8 APEXII CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator
 ω and φ scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1999)
 $T_{\min} = 0.673$, $T_{\max} = 0.845$
13153 measured reflections
4262 independent reflections
4200 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$
 $\theta_{\text{max}} = 45.0^\circ$, $\theta_{\text{min}} = 3.1^\circ$
 $h = -9 \rightarrow 9$
 $k = -16 \rightarrow 16$
 $l = -6 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.013$
 $wR(F^2) = 0.032$
 $S = 1.04$
4262 reflections
103 parameters
2 restraints
Primary atom site location: structure-invariant
direct methods
Secondary atom site location: difference Fourier
map

$w = 1/[\sigma^2(F_o^2) + (0.0043P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.74 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.55 \text{ e } \text{\AA}^{-3}$
Extinction correction: *SHELXL97* (Sheldrick,
2008), $F_c^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0116 (11)
Absolute structure: Flack (1983), 1965 Friedel
pairs
Absolute structure parameter: 0.021 (6)

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
In1	0.279204 (12)	0.015329 (8)	0.764879 (9)	0.00719 (2)	0.5138 (15)
Fe1	0.279204 (12)	0.015329 (8)	0.764879 (9)	0.00719 (2)	0.4862 (15)
P1	0.10011 (4)	0.33286 (3)	0.97617 (3)	0.00688 (3)	
P2	-0.29679 (4)	0.23110 (3)	0.58018 (3)	0.00860 (4)	
O1	-0.09909 (15)	0.33270 (9)	1.10229 (11)	0.01212 (10)	
O2	0.30388 (14)	0.47713 (8)	1.01372 (10)	0.01034 (9)	
O3	0.25898 (14)	0.17252 (8)	0.99381 (10)	0.01044 (9)	
O4	-0.56214 (17)	0.19541 (11)	0.63576 (14)	0.01698 (14)	
O5	-0.36828 (19)	0.31921 (11)	0.37968 (11)	0.01694 (14)	
O6	-0.11997 (18)	0.08092 (10)	0.57623 (14)	0.01796 (13)	
O7	-0.09802 (15)	0.35652 (9)	0.74311 (10)	0.01196 (10)	
Li1	-0.3013 (6)	0.1486 (3)	0.1793 (4)	0.0222 (4)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
In1	0.00727 (2)	0.00677 (2)	0.00816 (2)	0.00070 (2)	0.00341 (1)	0.00021 (2)
Fe1	0.00727 (2)	0.00677 (2)	0.00816 (2)	0.00070 (2)	0.00341 (1)	0.00021 (2)

P1	0.00698 (6)	0.00674 (7)	0.00732 (7)	-0.00058 (5)	0.00292 (5)	-0.00079 (5)
P2	0.00781 (7)	0.01113 (9)	0.00698 (7)	-0.00074 (6)	0.00265 (5)	-0.00012 (6)
O1	0.0138 (2)	0.0115 (2)	0.0150 (2)	-0.00187 (18)	0.0100 (2)	-0.0021 (2)
O2	0.00973 (19)	0.0089 (2)	0.0116 (2)	-0.00300 (15)	0.00246 (16)	0.00044 (16)
O3	0.0116 (2)	0.0086 (2)	0.0107 (2)	0.00203 (16)	0.00313 (17)	-0.00045 (16)
O4	0.0118 (2)	0.0212 (4)	0.0209 (3)	-0.0004 (2)	0.0093 (2)	0.0037 (3)
O5	0.0205 (3)	0.0217 (4)	0.0069 (2)	-0.0039 (3)	0.0023 (2)	0.0026 (2)
O6	0.0149 (3)	0.0128 (3)	0.0271 (4)	0.0001 (2)	0.0082 (2)	-0.0071 (3)
O7	0.0137 (2)	0.0108 (2)	0.0083 (2)	0.00030 (18)	-0.00045 (17)	-0.00100 (17)
Li1	0.0273 (11)	0.0189 (10)	0.0245 (10)	-0.0051 (8)	0.0140 (8)	-0.0082 (8)

Geometric parameters (Å, °)

In1—O6	2.0225 (9)	P2—O4	1.4988 (8)
In1—O4 ⁱ	2.0258 (8)	P2—O5	1.5142 (8)
In1—O5 ⁱⁱ	2.0350 (8)	P2—O6	1.5176 (8)
In1—O3	2.0916 (6)	P2—O7	1.6038 (7)
In1—O1 ⁱⁱⁱ	2.1133 (7)	Li1—O5	2.092 (2)
In1—O2 ^{iv}	2.1230 (6)	Li1—O6	2.676 (3)
P1—O1	1.5152 (7)	Li1—O2 ⁱⁱ	1.956 (2)
P1—O2	1.5179 (7)	Li1—O1 ^v	1.985 (3)
P1—O3	1.5200 (7)	Li1—O3 ^{vi}	2.107 (3)
P1—O7	1.6034 (7)		
O6—In1—O4 ⁱ	86.47 (4)	O2—P1—O7	102.40 (4)
O6—In1—O5 ⁱⁱ	102.03 (3)	O3—P1—O7	107.75 (4)
O4 ⁱ —In1—O5 ⁱⁱ	100.84 (3)	O4—P2—O5	112.69 (4)
O6—In1—O3	92.90 (3)	O4—P2—O6	112.79 (5)
O4 ⁱ —In1—O3	90.42 (3)	O5—P2—O6	109.43 (5)
O5 ⁱⁱ —In1—O3	161.74 (3)	O4—P2—O7	108.06 (5)
O6—In1—O1 ⁱⁱⁱ	91.67 (3)	O5—P2—O7	104.05 (4)
O4 ⁱ —In1—O1 ⁱⁱⁱ	177.82 (3)	O6—P2—O7	109.42 (4)
O5 ⁱⁱ —In1—O1 ⁱⁱⁱ	80.65 (3)	P1—O7—P2	131.07 (5)
O3—In1—O1 ⁱⁱⁱ	88.54 (3)	O2 ⁱⁱ —Li1—O1 ^v	104.95 (12)
O6—In1—O2 ^{iv}	171.79 (3)	O2 ⁱⁱ —Li1—O5	170.56 (15)
O4 ⁱ —In1—O2 ^{iv}	91.17 (3)	O1 ^v —Li1—O5	82.36 (10)
O5 ⁱⁱ —In1—O2 ^{iv}	86.14 (3)	O2 ⁱⁱ —Li1—O3 ^{vi}	82.74 (10)
O3—In1—O2 ^{iv}	79.25 (2)	O1 ^v —Li1—O3 ^{vi}	104.76 (14)
O1 ⁱⁱⁱ —In1—O2 ^{iv}	90.52 (3)	O5—Li1—O3 ^{vi}	89.67 (10)
O1—P1—O2	114.15 (4)	O2 ⁱⁱ —Li1—O6	119.23 (13)
O1—P1—O3	111.10 (4)	O1 ^v —Li1—O6	114.95 (11)
O2—P1—O3	112.79 (4)	O5—Li1—O6	61.10 (7)
O1—P1—O7	107.97 (4)	O3 ^{vi} —Li1—O6	124.85 (11)

Symmetry codes: (i) $x+1, y, z$; (ii) $-x, y-1/2, -z+1$; (iii) $-x, y-1/2, -z+2$; (iv) $-x+1, y-1/2, -z+2$; (v) $x, y, z-1$; (vi) $x-1, y, z-1$.