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The mixed-valent titanium phosphate, $\text{Li}_2\text{Ti}_2(\text{PO}_4)_3$, dilithium dititanium(III/IV) tris(orthophosphate)

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 Key indicators: single-crystal X-ray study; $T = 290$ K; mean $\sigma(\text{P}-\text{O}) = 0.004$ Å; R factor = 0.046; wR factor = 0.112; data-to-parameter ratio = 11.5.

The mixed-valent titanium phosphate, $\text{Li}_2\text{Ti}_2(\text{PO}_4)_3$, has been prepared by the reactive halide flux method. The title compound is isostructural with $\text{Li}_2\text{TiM}(\text{PO}_4)_3$ ($M = \text{Fe}, \text{Cr}$) and $\text{Li}_2\text{FeZr}(\text{PO}_4)_3$ and has the same ${}^3[\text{Ti}_2(\text{PO}_4)_3]^{2-}$ framework as the previously reported $\text{Li}_{3-x}\text{M}_2(\text{PO}_4)_3$ phases. The framework is built up from corner-sharing TiO_6 octahedra and PO_4 tetrahedra, one of which has 2 symmetry. The Li^+ ions are located on one crystallographic position and reside in the vacancies of the framework. They are surrounded by four O atoms in a distorted tetrahedral coordination. The classical charge-balance of the title compound can be represented as $\text{Li}^+{}_2(\text{Ti}^{3+}/\text{Ti}^{4+})(\text{PO}_4^{3-})_3$.

Related literature

The synthesis and structural characterization of stoichiometric $\text{Li}_2\text{TiM}(\text{PO}_4)_3$ ($M = \text{Fe}$ and Cr) and $\text{Li}_2\text{FeZr}(\text{PO}_4)_3$ have been reported by Patoux *et al.* (2004) and Catti (2001), respectively. For related phosphates with general formula $\text{Li}_{3-x}\text{M}_2(\text{PO}_4)_3$ ($0 \leq x \leq 1$), see: Wang & Hwu (1991) for $\text{Li}_{2.72}\text{Ti}_2(\text{PO}_4)_3$. For Li batteries based on $\text{Li}_{3-x}\text{M}_2(\text{PO}_4)_3$ phases, see: Yin *et al.* (2003). For ionic conductivities of these phases, see: Sato *et al.* (2000). For ionic radii, see: Shannon (1976). For structure validation, see: Spek (2009).

Experimental

Crystal data

 $\text{Li}_2\text{Ti}_2(\text{PO}_4)_3$
 $M_r = 394.59$

 Orthorhombic, *Pbcn*
 $a = 12.0344$ (5) Å

 $b = 8.5795$ (5) Å

 $c = 8.6794$ (4) Å

 $V = 896.14$ (7) Å³
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 2.39$ mm⁻¹
 $T = 290$ K

 $0.22 \times 0.16 \times 0.14$ mm

Data collection

Rigaku R-Axis RAPID diffractometer

 Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)

 $T_{\min} = 0.802$, $T_{\max} = 1.000$

6671 measured reflections

1004 independent reflections

 974 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.112$
 $S = 1.37$

1004 reflections

87 parameters

 $\Delta\rho_{\max} = 0.49$ e Å⁻³
 $\Delta\rho_{\min} = -0.74$ e Å⁻³

Data collection: *RAPID-AUTO* (Rigaku, 2006); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: locally modified version of *ORTEP* (Johnson, 1965); 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: WM2513).

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supporting information

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The mixed-valent titanium phosphate, $\text{Li}_2\text{Ti}_2(\text{PO}_4)_3$, dilithium dititanium(III/IV) tris(orthophosphate)

Yongho Kee, Seung-Soo Lee and Hoseop Yun

S1. Comment

Lithium metal phosphates, $\text{Li}_{3-x}\text{M}_2(\text{PO}_4)_3$, have been widely investigated as materials for secondary batteries (Yin *et al.*, 2003). It has been reported that the amount of Li can be determined in accordance with the oxidation states of metals (*M*), and Li occupancies are profoundly related to the ionic conductivity (Sato *et al.*, 2000). In attempts to control the amount of Li ions by using various metals with different oxidation states, a new member of this family with stoichiometric Li ($x=1$) has been found and we report here the synthesis and structural characterization of the mixed-valent title compound $\text{Li}_2\text{Ti}_2(\text{PO}_4)_3$, (I).

(I) is isostructural with mixed-metallic compounds such as $\text{Li}_2\text{TiM}(\text{PO}_4)_3$ ($M = \text{Fe}, \text{Cr}$; Patoux *et al.*, 2004) and $\text{Li}_2\text{FeZr}(\text{PO}_4)_3$ (Catti, 2001) for which detailed investigations based on powder diffraction data have been reported. The framework of the title compound is the same as that of the previously reported $\text{Li}_{3-x}\text{M}_2(\text{PO}_4)_3$ ($0 \leq x \leq 1$) phases such as $\text{Li}_{2.72}\text{Ti}_2(\text{PO}_4)_3$ (Wang & Hwu, 1991).

Figure 1 shows the local coordination environment of the Ti and P atoms. Two TiO_6 octahedra are joined to three PO_4 tetrahedra to form the $[\text{Ti}_2(\text{PO}_4)_3]$ unit. These units share a terminal oxygen atom, O4, to construct the two-dimensional slabs as shown in Figure 2. The three-dimensional framework, ${}_\infty^3[\text{Ti}_2(\text{PO}_4)_3]^{2-}$ (Fig. 3) is built up from these slabs which are interconnected along the *b* axis by sharing terminal oxygen atoms O1 and O6. The Li^+ ions reside in the vacancies and are surrounded by four O atoms in a distorted tetrahedral coordination. The Ti—O distances, ranging from 1.913 (4) to 2.045 (4) Å, are in good agreement with that calculated from their ionic radii (1.97 Å, Shannon, 1976), assuming a mixed III/IV valence.

Two crystallographically independent Li^+ sites have been reported for $\text{Li}_{3-x}\text{M}_2(\text{PO}_4)_3$ phases. The Li1 site is fully occupied, whereas the Li2 site is only partially occupied. The oxidation states of each metal have to be adjusted to meet the charge neutrality of these compounds. For example, the average oxidation state of Ti is +3.14 for $\text{Li}_{2.72}\text{Ti}_2(\text{PO}_4)_3$ assuming Ti to be mixed-valent (86% of Ti^{III} and 14% of Ti^{IV} ; Wang & Hwu, 1991). In the title compound, the Li1 site is fully occupied, whereas the Li2 site is vacant. For charge neutrality the Ti site is occupied by 50% of Ti^{III} and 50% of Ti^{IV} . Therefore, the classical charge balance of the compound can be represented by $\text{Li}_2^+(\text{Ti}^{3+}/\text{Ti}^{4+})(\text{PO}_4^{3-})_3$.

S2. Experimental

The title compound, $\text{Li}_2\text{Ti}_2(\text{PO}_4)_3$, was prepared by the reaction of elemental Ti (CERAC 99.5%) and P (CERAC 99.5%) powders. The pure elements were mixed and loaded in a silica tube with an elemental ratio of 1:3 in the presence of LiCl (Sigma-Aldrich 99%) as a reactive flux. The mass ratio of the reactants and the flux was 1:5. The tube was kept in air for 3 days for water adsorption. It was then evacuated to 0.133 Pa, sealed, and heated gradually (60 K/h) to 1123 K in a tube furnace, where it was kept for 72 h. The tube was cooled at a rate of 5 K/h to room temperature. Air- and water-stable black block-shaped crystals were isolated after the excess flux was removed with water. Qualitative analysis of the

crystals with an XRF indicated the presence of Ti and P.

S3. Refinement

The highest residual electron density ($0.49 \text{ e } \text{\AA}^{-3}$) is 1.24 \AA from the O3 site and the deepest hole ($-0.74 \text{ e } \text{\AA}^{-3}$) is 2.29 \AA from the O1 site. No additional symmetry, as tested by *PLATON* (Spek, 2009), was detected in this structure.

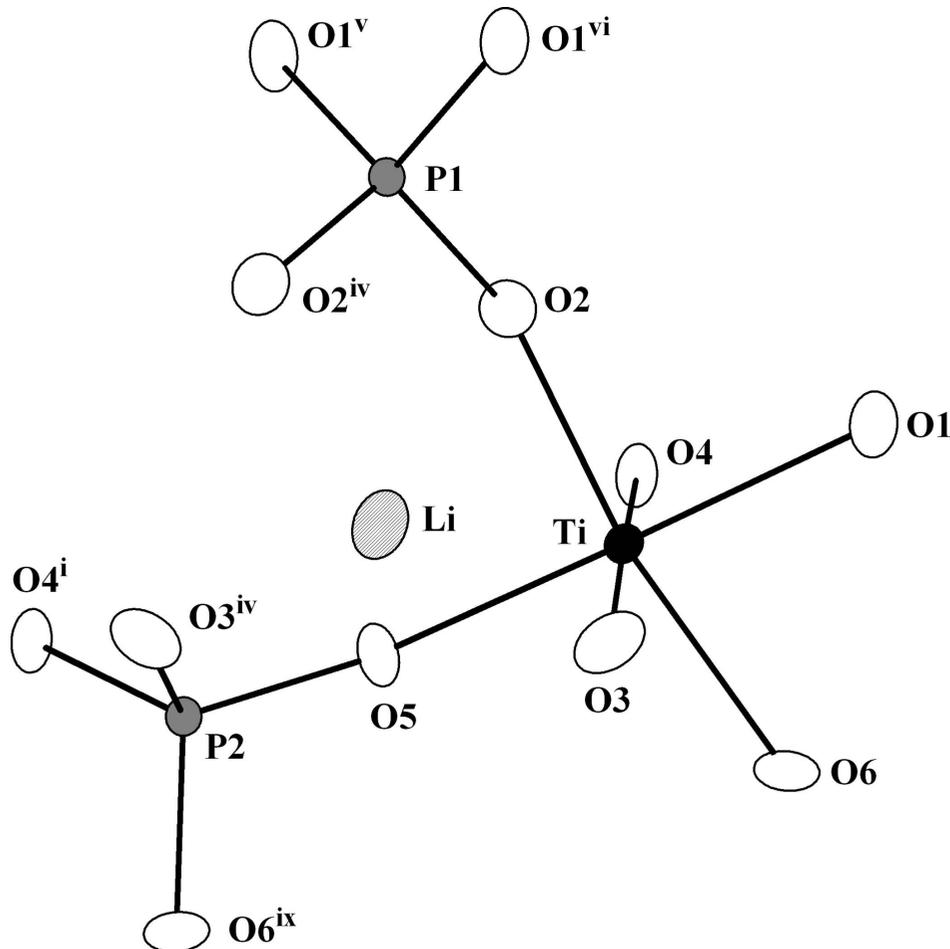
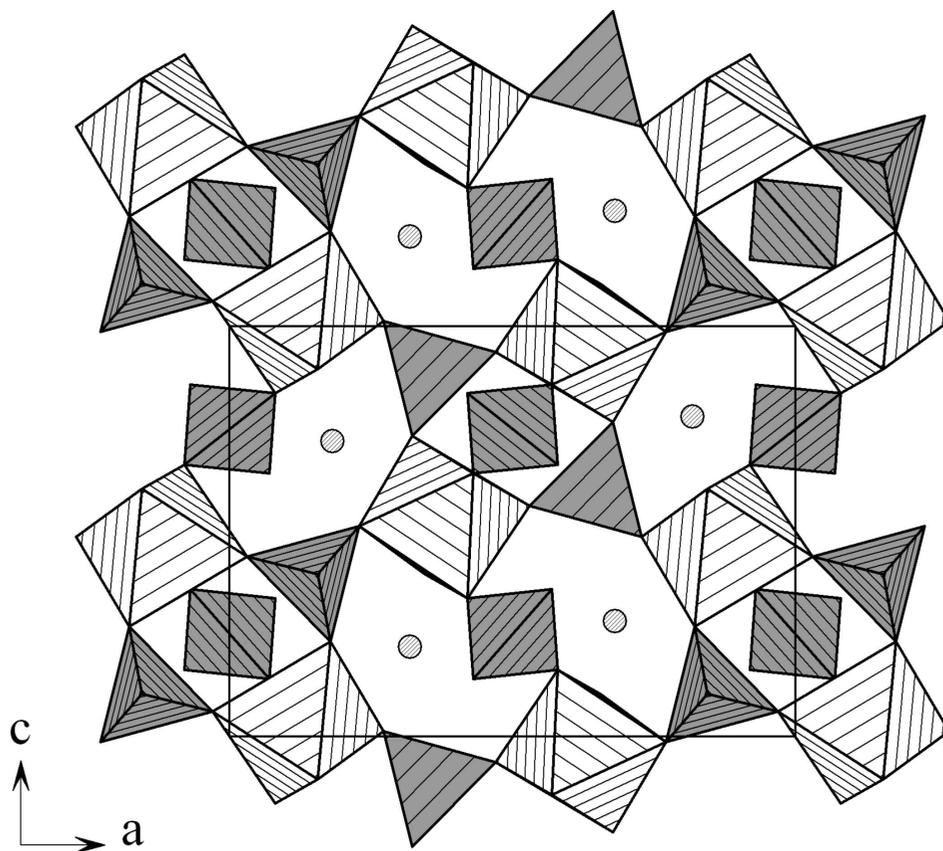
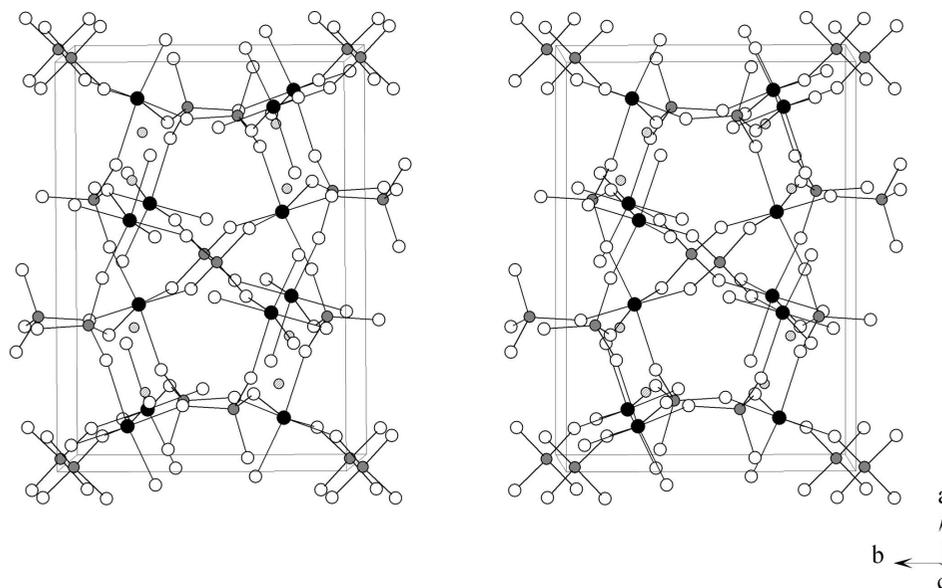


Figure 1

A view showing the local coordination environments of Ti and P atoms with the atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. (Symmetry codes: (i) $0.5-x, 0.5-y, 1/2+z$; (iv) $1-x, y, 0.5-z$; (v) $x, 1-y, 1/2+z$; (vi) $1-x, 1-y, -z$; (ix) $x, -y, 1/2+z$).

**Figure 2**

The polyhedral representation of the slab structure built up from $[\text{Ti}_2(\text{PO}_4)_3]$ units. Li atoms are located in the vacancies.

**Figure 3**

A stereoscopic view of $\text{Li}_2\text{Ti}_2(\text{PO}_4)_3$, viewed down the c axis.

dilithium ditanium(III/IV) tris(orthophosphate)*Crystal data*Li₂Ti₂(PO₄)₃ $M_r = 394.59$ Orthorhombic, *Pbcn*

Hall symbol: -P 2n 2ab

 $a = 12.0344$ (5) Å $b = 8.5795$ (5) Å $c = 8.6794$ (4) Å $V = 896.14$ (7) Å³ $Z = 4$ $F(000) = 764$ $D_x = 2.925$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 6390 reflections

 $\theta = 3.3$ – 27.4° $\mu = 2.39$ mm⁻¹ $T = 290$ K

Block, black

 $0.22 \times 0.16 \times 0.14$ mm*Data collection*Rigaku R-AXIS RAPID
diffractometer

Radiation source: sealed tube

Graphite monochromator

 ω scansAbsorption correction: multi-scan
(*ABSCOR*; Higashi, 1995) $T_{\min} = 0.802$, $T_{\max} = 1.000$

6671 measured reflections

1004 independent reflections

974 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.035$ $\theta_{\max} = 27.4^\circ$, $\theta_{\min} = 3.4^\circ$ $h = -14 \rightarrow 14$ $k = -11 \rightarrow 11$ $l = -11 \rightarrow 11$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.046$ $wR(F^2) = 0.112$ $S = 1.37$

1004 reflections

87 parameters

0 restraints

 $w = 1/[\sigma^2(F_o^2) + (0.P)^2 + 10.7789P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.49$ e Å⁻³ $\Delta\rho_{\min} = -0.74$ e Å⁻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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Li	0.1812 (9)	0.2861 (13)	0.2191 (12)	0.020 (2)
Ti	0.38824 (7)	0.25295 (11)	0.03788 (11)	0.0077 (2)
P1	0.5	0.5399 (2)	0.25	0.0086 (4)
P2	0.35246 (11)	0.10469 (15)	0.39437 (15)	0.0069 (3)
O1	0.4200 (3)	0.3537 (5)	-0.1627 (5)	0.0186 (9)
O2	0.4304 (4)	0.4408 (5)	0.1413 (5)	0.0219 (10)
O3	0.5306 (4)	0.1556 (5)	0.0618 (5)	0.0217 (10)
O4	0.2282 (3)	0.3271 (5)	0.0130 (4)	0.0152 (8)
O5	0.3221 (3)	0.1629 (5)	0.2322 (4)	0.0137 (8)
O6	0.3443 (3)	0.0729 (4)	-0.1040 (5)	0.0146 (8)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Li	0.019 (5)	0.025 (5)	0.017 (5)	0.002 (4)	0.005 (4)	-0.004 (4)
Ti	0.0076 (4)	0.0079 (4)	0.0078 (4)	0.0006 (3)	0.0001 (3)	-0.0007 (4)
P1	0.0114 (9)	0.0075 (8)	0.0071 (8)	0	0.0023 (7)	0
P2	0.0060 (6)	0.0079 (6)	0.0067 (6)	0.0001 (5)	-0.0003 (5)	-0.0001 (5)
O1	0.018 (2)	0.025 (2)	0.0126 (18)	-0.0112 (17)	0.0036 (17)	-0.0017 (17)
O2	0.031 (3)	0.018 (2)	0.016 (2)	-0.0095 (18)	-0.0074 (19)	0.0006 (17)
O3	0.021 (2)	0.019 (2)	0.025 (2)	0.0074 (17)	-0.0096 (19)	-0.0075 (18)
O4	0.017 (2)	0.020 (2)	0.0087 (17)	0.0098 (16)	-0.0012 (16)	0.0001 (15)
O5	0.0107 (18)	0.021 (2)	0.0096 (17)	0.0007 (15)	0.0008 (16)	0.0035 (16)
O6	0.0131 (19)	0.0084 (18)	0.022 (2)	-0.0007 (14)	-0.0049 (17)	0.0013 (16)

Geometric parameters (\AA , $^\circ$)

Li—O4	1.909 (11)	P1—O2 ^{iv}	1.521 (4)
Li—O6 ⁱ	1.979 (11)	P1—O1 ^v	1.528 (4)
Li—O1 ⁱ	1.994 (12)	P1—O1 ^{vi}	1.528 (4)
Li—O5	2.001 (11)	P1—Li ^{vii}	3.048 (11)
Li—Ti ⁱ	2.909 (10)	P1—Li ^{viii}	3.048 (11)
Li—Ti	2.960 (10)	P2—O3 ^{iv}	1.522 (4)
Li—P2	2.997 (11)	P2—O6 ^{ix}	1.527 (4)
Li—P2 ⁱⁱ	2.998 (11)	P2—O4 ⁱ	1.531 (4)
Li—P1 ⁱⁱⁱ	3.048 (11)	P2—O5	1.537 (4)
Ti—O2	1.913 (4)	P2—Li ⁱ	2.998 (11)
Ti—O3	1.917 (4)	O1—P1 ^{vi}	1.528 (4)
Ti—O1	1.981 (4)	O1—Li ⁱⁱ	1.994 (12)
Ti—O5	2.019 (4)	O3—P2 ^{iv}	1.522 (4)
Ti—O4	2.039 (4)	O4—P2 ⁱⁱ	1.531 (4)
Ti—O6	2.045 (4)	O6—P2 ^x	1.527 (4)
Ti—Li ⁱⁱ	2.909 (10)	O6—Li ⁱⁱ	1.979 (11)
P1—O2	1.521 (4)		
O4—Li—O6 ⁱ	131.3 (6)	O2—P1—O1 ^{vi}	111.9 (2)
O4—Li—O1 ⁱ	140.7 (6)	O2 ^{iv} —P1—O1 ^{vi}	107.1 (2)
O6 ⁱ —Li—O1 ⁱ	82.7 (4)	O1 ^v —P1—O1 ^{vi}	106.6 (4)
O4—Li—O5	84.2 (4)	O3 ^{iv} —P2—O6 ^{ix}	110.1 (2)
O6 ⁱ —Li—O5	114.2 (5)	O3 ^{iv} —P2—O4 ⁱ	108.0 (2)
O1 ⁱ —Li—O5	99.8 (5)	O6 ^{ix} —P2—O4 ⁱ	109.5 (2)
O2—Ti—O3	94.55 (19)	O3 ^{iv} —P2—O5	110.8 (2)
O2—Ti—O1	89.61 (18)	O6 ^{ix} —P2—O5	108.5 (2)
O3—Ti—O1	96.49 (19)	O4 ⁱ —P2—O5	109.9 (2)
O2—Ti—O5	92.03 (18)	P1 ^{vi} —O1—Ti	144.9 (3)
O3—Ti—O5	95.45 (18)	P1 ^{vi} —O1—Li ⁱⁱ	119.3 (4)
O1—Ti—O5	167.79 (17)	Ti—O1—Li ⁱⁱ	94.1 (3)
O2—Ti—O4	92.14 (19)	P1—O2—Ti	155.2 (3)
O3—Ti—O4	172.33 (19)	P2 ^{iv} —O3—Ti	168.1 (3)

O1—Ti—O4	87.31 (17)	P2 ⁱⁱ —O4—Li	120.8 (4)
O5—Ti—O4	80.54 (16)	P2 ⁱⁱ —O4—Ti	142.1 (2)
O2—Ti—O6	170.86 (18)	Li—O4—Ti	97.1 (4)
O3—Ti—O6	88.11 (17)	P2—O5—Li	115.2 (4)
O1—Ti—O6	81.39 (17)	P2—O5—Ti	142.7 (2)
O5—Ti—O6	96.43 (16)	Li—O5—Ti	94.8 (4)
O4—Ti—O6	85.86 (16)	P2 ^x —O6—Li ⁱⁱ	127.8 (4)
O2—P1—O2 ^{iv}	112.1 (3)	P2 ^x —O6—Ti	138.0 (3)
O2—P1—O1 ^v	107.1 (2)	Li ⁱⁱ —O6—Ti	92.6 (4)
O2 ^{iv} —P1—O1 ^v	111.9 (2)		

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