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A New Polymorph of $Li_4P_2O_7$

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Abstract

The purpose of the present paper is to report the crystal structure of a new phase of tetralithium diphosphate identified by single-crystal X-ray diffraction. The structure consists of layers built from Li–O tetrahedra and pyrophosphate groups connected to each other through edges and vertices.

Comment

A tetralithium diphosphate obtained by hydrothermal treatment at 1000 atm (1 atm = 101 325 Pa) for 100 h with four formula units of $Li_4P_2O_7$ in a $P2_1/n$ cell of dimensions $a = 5.190(2)$, $b = 13.902(3)$, $c = 7.901(3)$ Å, $\beta = 89.97(3)$° was described recently (Yakubovich & Mel'nikov, 1994). The structure was described as the first lithium phosphate structure containing diphosphate groups formed by vertex-sharing PO_4 tetrahedra (see also Wenger & Armbruster, 1991; Tien & Hummel, 1961; Keffer, Mighell, Mauer, Swanson & Block, 1967; Averbuch-Pouchot & Durif, 1986). Comparison of the present structure with that described by Yakubovich & Mel'nikov (1994) is not possible as the published coordinates of the latter appear to contain errors.

The new phase reported here (Fig. 1) can be described in terms of P_2O_7 and LiO_4 units. The pyrophosphate groups (lower right-hand side of Fig. 1), built up from two PO_4 tetrahedra sharing a vertex, show typical geometry with two long P—O bonds [P1—O1 1.622 (1) and P2—O1 1.626 (1) Å] corresponding to the P—O—P bridge and three shorter P—O bonds in the range 1.504 (1) to 1.527 (1) Å (Leclaire, Benmoussa, Borel, Grandin & Raveau, 1988; Constentin, Borel, Grandin, Leclaire & Raveau, 1990). The LiO_4 tetrahedra are highly distorted with Li—O distances ranging from

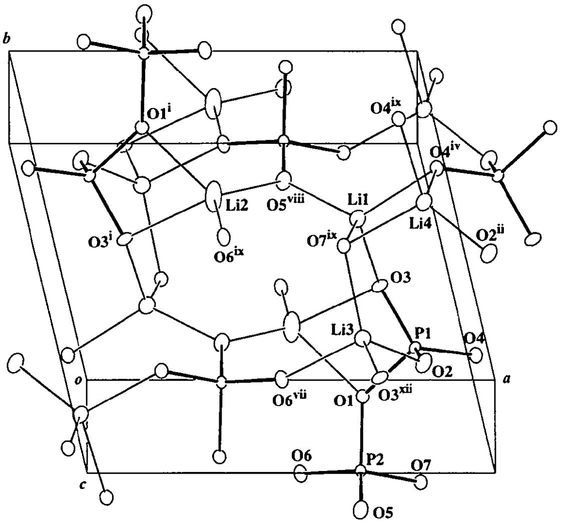

Fig. 1. Projection of the structure on the *ab* plane showing the atom labels. Displacement ellipsoids are represented at the 50% probability level. Symmetry codes: (i) $1-x$, $1-y$, $1-z$; (ii) $2-x$, $1-y$, $2-z$; (iv) $2-x$, $1-y$, $1-z$; (vii) $1-x$, $-y$, $1-z$; (viii) x, $1+y$, z; (ix) x, $1+y$, $1+z$; (xii) x, y, $1+z$.

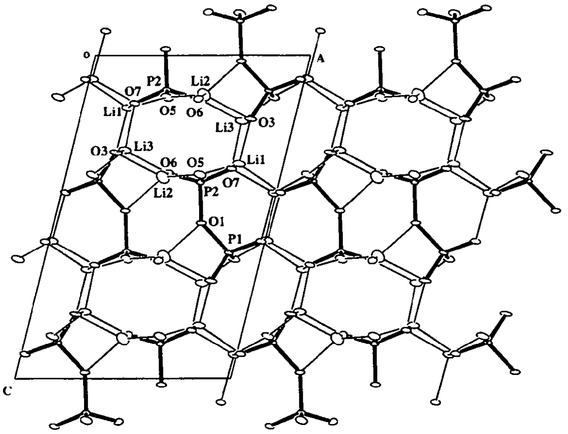

Fig. 2. The structure as drawn along the *b* axis of the pseudo monoclinic *A*-centred cell. All possible twofold axes appearing along **b** are destroyed by the relative situation of the P2—O5 and Li2—O6 bonds around them. See, for instance, the pseudo-twofold axis perpendicular to the eight-membered rings formed by the labelled atoms.

1.864 (3) to 2.104 (3) Å and O—Li—O angles in the range 69.7 (1)–130.8 (2)°. All of the outliers are around Li2, as this Li–O tetrahedron shares an edge with the PO_4 unit around P1. The O atoms O1, O2, O5 and O6 are three-coordinate and, as expected, show shorter bonds (Leclaire, Chardon, Grandin, Borel & Raveau, 1994) than those which are four-coordinate (O3, O4 and O7; the fourth bond is not shown in Fig. 1 for clarity).

The LiO_4 units share common edges (tetrahedra around Li1, Li4 and Li2, Li3) or vertices (tetrahedra around Li1, Li2 and Li3, Li4) and form eight-sided rings around the several pseudo-twofold axes of the pseudo-monoclinic *A*-centred cell in which this structure can also be described (see also below and Fig. 2). These rings build parallel infinite chains along the *a* axis held together by the pyrophosphate units.

Experimental

Crystals of $Li_4P_2O_7$ were isolated as a minor product from a mixture of nominal composition $Li_2VP_2O_x$. A mixture of Li_2CO_3, $(NH_4)_2HPO_4$ and NH_4VO_3 in the molar ratio 1:2:1 was heated to 673 K in order to eliminate CO_2, NH_3 and H_2O. The product was then finely ground and heated in a platinum crucible to 923 K for 24 h, cooled to 673 K at a rate of 3 K h^{-1} and finally quenched to room temperature.

Crystal data

$Li_4P_2O_7$
$M_r = 201.70$
Triclinic
$P\bar{1}$
$a = 8.5613\ (4)$ Å
$b = 7.1100\ (3)$ Å
$c = 5.18510\ (10)$ Å
$\alpha = 111.441\ (2)°$
$\beta = 89.986\ (3)°$
$\gamma = 103.065\ (4)°$
$V = 284.99\ (2)$ Å^3
$Z = 2$
$D_x = 2.350$ Mg m^{-3}
D_m not measured

Mo *Kα* radiation
$\lambda = 0.7107$ Å
Cell parameters from 42 reflections
$\theta = 10$–$20°$
$\mu = 1.48$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.3 × 0.2 × 0.2 mm
Colourless

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.726$, $T_{\max} = 0.744$
3603 measured reflections
3457 independent reflections
3262 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0102$
$\theta_{\max} = 39.76°$
$h = 0 \rightarrow 15$
$k = -12 \rightarrow 12$
$l = -9 \rightarrow 9$
2 standard reflections
frequency: 90 min
intensity decay: 0.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.095$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.590$ e Å^{-3}
$\Delta\rho_{\min} = -0.832$ e Å^{-3}

$S = 1.340$
3457 reflections
118 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 0.2635P]$ where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
P1	0.84610 (3)	0.22169 (4)	0.43831 (5)	0.00620 (6)
P2	0.63094 (3)	−0.21404 (4)	0.21355 (5)	0.00621 (6)
O1	0.68370 (10)	0.03788 (12)	0.3082 (2)	0.0113 (1)
O2	0.87523 (11)	0.25929 (15)	0.7411 (2)	0.0119 (1)
O3	0.79383 (10)	0.39768 (12)	0.3897 (2)	0.0098 (1)
O4	0.98189 (10)	0.15070 (13)	0.2699 (2)	0.0094 (1)
O5	0.62180 (11)	−0.2606 (2)	0.4757 (2)	0.0125 (1)
O6	0.47213 (10)	−0.26965 (14)	0.0469 (2)	0.0112 (1)
O7	0.76253 (10)	−0.29714 (13)	0.0411 (2)	0.0093 (1)
Li1	0.7914 (3)	0.6731 (4)	0.6444 (5)	0.0127 (4)
Li2	0.4520 (4)	0.7551 (6)	0.7016 (7)	0.0249 (6)
Li3	0.7543 (3)	0.4118 (4)	1.0161 (5)	0.0129 (4)
Li4	0.9882 (3)	0.8541 (4)	1.1100 (5)	0.0125 (4)

Table 2. *Selected geometric parameters (Å, °)*

P1—O2	1.504 (1)	Li1—O7$^{\rm iii}$	2.011 (3)
P1—O4	1.520 (1)	Li2—O5$^{\rm i}$	1.864 (3)
P1—O3	1.521 (1)	Li2—O6$^{\rm iii}$	1.874 (3)
P1—O1	1.622 (1)	Li2—O1$^{\rm iv}$	2.085 (3)
P2—O6	1.503 (1)	Li2—O3$^{\rm iv}$	2.104 (3)
P2—O5	1.510 (1)	Li3—O6$^{\rm v}$	1.939 (3)
P2—O7	1.527 (1)	Li3—O3$^{\rm vi}$	2.009 (3)
P2—O1	1.626 (1)	Li3—O7$^{\rm iii}$	2.011 (3)
O2—Li3	1.912 (3)	Li4—O2$^{\rm vii}$	1.870 (2)
O3—Li1	1.925 (3)	Li4—O7$^{\rm iii}$	1.949 (3)
Li1—O5$^{\rm i}$	1.925 (3)	Li4—O4$^{\rm ii}$	1.975 (3)
Li1—O4$^{\rm ii}$	2.007 (3)	Li4—O4$^{\rm iii}$	1.977 (3)
O2—P1—O4	112.71 (5)	O5$^{\rm i}$—Li2—O6$^{\rm iii}$	120.4 (2)
O2—P1—O3	113.45 (5)	O5$^{\rm i}$—Li2—O1$^{\rm iv}$	115.6 (2)
O4—P1—O3	114.49 (5)	O6$^{\rm iii}$—Li2—O1$^{\rm iv}$	114.5 (2)
O2—P1—O1	108.70 (5)	O5$^{\rm i}$—Li2—O3$^{\rm iv}$	130.8 (2)
O4—P1—O1	107.08 (5)	O6$^{\rm iii}$—Li2—O3$^{\rm iv}$	95.5 (1)
O3—P1—O1	99.18 (5)	O1$^{\rm iv}$—Li2—O3$^{\rm iv}$	69.7 (1)
O6—P2—O5	114.86 (5)	O2—Li3—O6$^{\rm v}$	111.7 (1)
O6—P2—O7	113.69 (5)	O2—Li3—O3$^{\rm vi}$	112.7 (1)
O5—P2—O7	111.59 (5)	O6$^{\rm v}$—Li3—O3$^{\rm vi}$	96.7 (1)
O6—P2—O1	102.26 (5)	O2—Li3—O7$^{\rm iii}$	116.1 (1)
O5—P2—O1	107.19 (5)	O6$^{\rm v}$—Li3—O7$^{\rm iii}$	105.6 (1)
O7—P2—O1	106.20 (5)	O3$^{\rm vi}$—Li3—O7$^{\rm iii}$	112.6 (1)
O5$^{\rm i}$—Li1—O3	103.1 (1)	O2$^{\rm vii}$—Li4—O7$^{\rm iii}$	115.0 (1)
O5$^{\rm i}$—Li1—O4$^{\rm ii}$	122.7 (1)	O2$^{\rm vii}$—Li4—O4$^{\rm ii}$	117.6 (1)
O3—Li1—O4$^{\rm ii}$	108.5 (1)	O7$^{\rm iii}$—Li4—O4$^{\rm ii}$	97.3 (1)
O5$^{\rm i}$—Li1—O7$^{\rm iii}$	113.3 (1)	O2$^{\rm vii}$—Li4—O4$^{\rm iii}$	123.5 (1)
O3—Li1—O7$^{\rm iii}$	115.6 (1)	O7$^{\rm iii}$—Li4—O4$^{\rm iii}$	104.3 (1)
O4$^{\rm ii}$—Li1—O7$^{\rm iii}$	94.2 (1)	O4$^{\rm ii}$—Li4—O4$^{\rm iii}$	94.6 (1)

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

Metrically speaking, the only axis which seems to be maintained between our structure and the $P2_1/n$ structure of Yakubovich & Mel'nikov (1994) is the *a* axis, which also corresponds to a pseudo-twofold axis of an *A*-centred cell in which our $P\bar{1}$ cell can be metrically transformed using $A = a$, $B = -c$, $C = 2b + c$, with dimensions $a = 8.56$, $b = 5.18$, $c = 13.23$ Å and $\beta = 104°$. This pseudo-monoclinic cell gives a distribution of intensities very different from the expected $2/m$ symmetry and, if one plots the $P\bar{1}$ structure on that cell, only pseudo-twofold axes appear (see Fig. 2).

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *LSUCRE* (Appleman, 1996). Data reduction: *XRAY*80 (Stewart, 1980). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1158). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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