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A lithium ethylenediphosphonate containing lithium chains and symmetric hydrogen bonds

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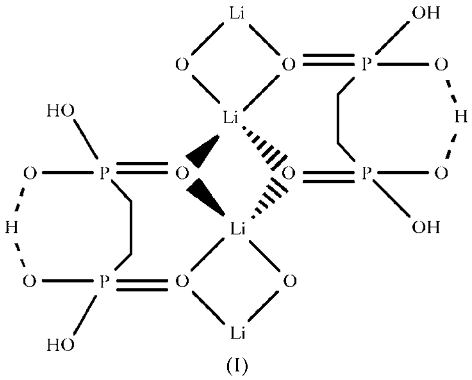
In the title compound, *catena*-poly[lithium-μ_3-ethylenediphosphonato], $[Li(C_2H_7O_6P_2)]_n$, the supramolecular monoclinic ($C2/c$) structure consists of one-dimensional lithium chains [Li$\cdots$Li = 2.7036 (8) Å] that are embedded within ethylenediphosphonate anions linked by strong symmetric hydrogen bonds [O$\cdots$O = 2.473 (3) Å]. The Li atoms and the H atom in the symmetric hydrogen bond reside on twofold rotation axes and there is an inversion center at the mid-point of the C—C bond of the ethylenediphosphonate ligand.

Comment

Lithium ions trapped within cavities of metal oxides, phosphates and organophosphonates have been sought owing to their potential to serve as electrolyte or electrode materials in lithium batteries. For example, Padhi and co-workers (Padhi *et al.*, 1997) discovered the electrochemical properties of $LiFePO_4$ in 1997, and it is the first cathode material with potentially low cost that could have an impact in electrochemical energy storage (Whittingham, 2004). In general, such Li-containing structures might provide a fundamental base for lithium insertion chemistry. Besides metal phosphates, metal organophosphonates are a class of materials with diverse structures and properties in the field of catalysis, ion exchange and non-linear optics. The observed structural variations may arise from the possibility of incorporation of different organic groups into inorganic matrices composed of multidentate metal phosphonates (Clearfield, 1996; Murugavel *et al.*, 2004). Despite the successful syntheses of large numbers of metal organophosphonates, lithium organophosphonates remain poorly understood and rare.



(I)

In this paper, we report the synthesis and structural characterization of *catena*-poly[lithium-μ_3-ethylenediphosphonato], (I), whose structure consists of one-dimensional lithium chains that are embedded within bidentate ethylenediphosphonate anions linked by strong symmetric hydrogen bonds.

Fig. 1 displays the X-ray crystal structure of the title compound. The coordination geometry around the lithium ions is quasi-tetrahedral, involving four μ-O atoms from four phosphonate ligands. Atoms Li1 and Li1*A* are bridged by two μ_2-O atoms (O3 and O3*A*), resulting in a centrosymmetric four-membered planar Li_2O_2 ring [the dihedral angle between alternating four-membered rings *A* and *B* is 84.6 (2)°]; the Li$\cdots$Li distance of 2.7036 (8) Å is similar to that of $Li_4[(MeGa)_6(\mu_3\text{-}O)_2(t\text{-}BuPO_3)_6](THF)_4$ (THF is tetrahydrofuran; Roesky *et al.*, 1997). In contrast to (I), $Li_4[(MeGa)_6(\mu_3\text{-}O)_2(t\text{-}BuPO_3)_6](THF)_4$ contains a finite four-atom lithium chain within two 12-membered macrocyclic rings and does not have short-range interactions between Li atoms of neighboring molecules. In (I), the lithium chains are not only trapped in ethylenediphosphonate anions but also extended through symmetric hydrogen bonds. These symmetric double-

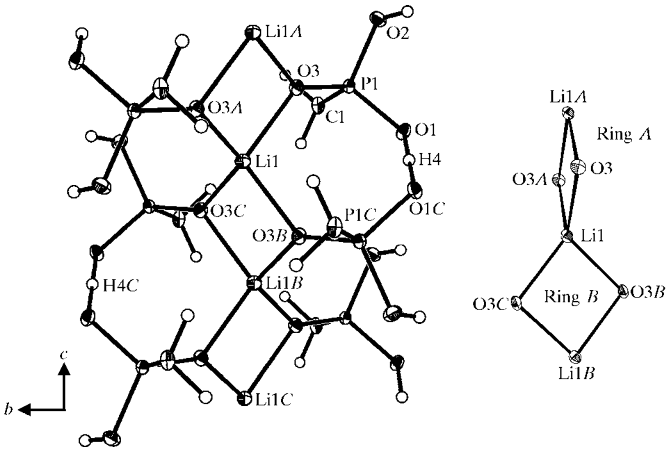


Figure 1
A view of (I) along the *b* axis, showing the atom labeling and displacement ellipsoids at the 20% probability level. Atoms Li1, O3*A*, Li1*A* and O3 form Li_2O_2 ring *A*, and atoms Li1, O3*B*, Li1*B* and O3*C* form ring *B*. Two adjacent phosphonate groups are connected by a symmetric hydrogen bond (P1—O1—H4$\cdots$O1*C*—P1*C*). Selected distances (Å): O1$\cdots$O1*C* = 2.472 (3); Li1—O3 = 1.962 (4); Li1—O3*A* = 1.905 (3). Selected angles (°): O3*A*—Li1—O3 = 91.29 (7); O3*B*—Li1—O3 = 109.6 (3); O3*C*—Li1—O3 = 121.81 (9); O3*B*—Li1—O3*A* = 121.81 (9); O3*C*—Li1—O3*A* = 123.0 (3); O3*B*—Li1—O3*C* = 91.29 (7). [Symmetry codes: (*A*) $1-x, 1-y, 1-z$; (*B*) $1-x, y, \frac{1}{2}-z$; (*C*) $x, 1-y, -\frac{1}{2}+z$; Li1*B* is at $(1-x, 1-y, -z)$; Li1*C* is at $(x, y, -1+z)$.]

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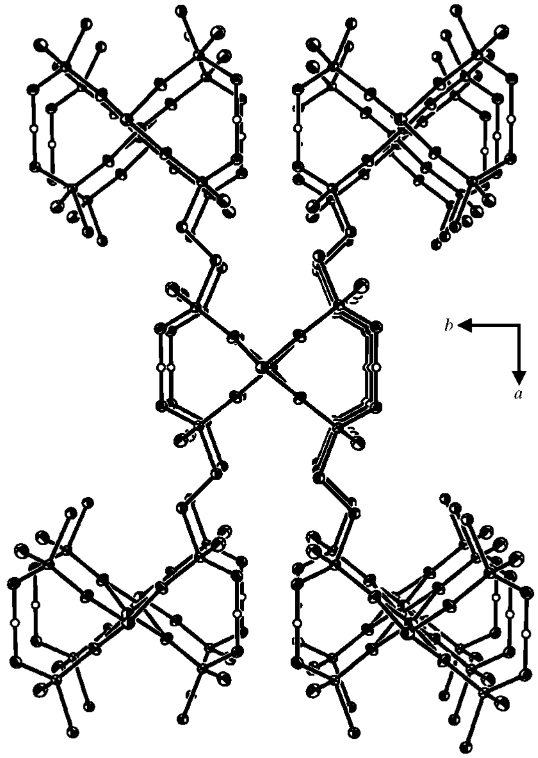

Figure 2
The packing of (I), viewed along the *c* direction, showing how each lithium chain is linked to other chains by ethylenediphosphonate ligands.

minimum hydrogen bonds are found between two *c*-glide symmetry-related O atoms from two phosphonate groups (Table 1). According to Alcock (1990), symmetric hydrogen bonds typically display a shorter (about 2.47 Å) O···O distance than do asymmetric hydrogen bonds (about 2.5–3.0 Å).

Two neighboring lithium ions are bridged by a pair of P═O units from two bidentate phosphonate ligands, with a slightly shorter P—O bond [1.4916 (16) Å] for the O atom coordinated to the lithium ion than for the non-coordinated O atoms [1.5384 (16) and 1.5685 (18) Å]. The P═O bond length is similar to those observed previously (Henderson *et al.*, 2003; Roesky *et al.*, 1997).

The alternation of adjacent linked rings *A* and *B* gives rise to infinite Li chains along the *c* axis. Viewed along the *c* axis, the crystal packing reveals that individual lithium chains are interconnected by ethylenediphosphonate ligands (Fig. 2). Each ethylenediphosphonate ligand in (I) coordinates to two Li atoms through its two phosphonate O atoms, thus acting as a bridging bidentate ligand, further linking the $(Li_2O_2)_n$ sheets into a novel covalent three-dimensional network.

Experimental

Lithium nitrate (0.0344 g, 0.5 mmol) and ethylenediphosphonic acid (0.3791 g, 2.0 mmol) were dissolved in ethanol (5 ml), and dimethyl carbonate (4 ml, 47.4 mmol) was added. The solution was stirred for several minutes and transferred to an autoclave for hydrothermal synthesis. The temperature was first increased to 393 K and then to 473 K at a rate of 120 K h^{-1}. The solution was kept at 473 K for 4 d, and then cooled to 343 K at a rate of 9 K h^{-1} and finally cooled naturally to room temperature. Transparent crystals suitable for single-crystal X-ray diffraction studies were filtered off and washed with ethanol. The crystals were stable for up to a few weeks; however, deliquescence was observed after several months.

Crystal data

$[Li(C_2H_7O_6P_2)]$
$M_r = 195.96$
Monoclinic, $C2/c$
$a = 16.1716\ (19)$ Å
$b = 8.4880\ (10)$ Å
$c = 5.3893\ (6)$ Å
$\beta = 107.836\ (2)^\circ$
$V = 704.20\ (14)$ Å^3
$Z = 4$
$D_x = 1.848$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.59$ mm^{-1}
$T = 293\ (2)$ K
Plate, colorless
0.42 × 0.24 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.824$, $T_{\max} = 0.892$
2124 measured reflections
799 independent reflections
749 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$
$\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.094$
$S = 0.98$
799 reflections
64 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0647P)^2 + 1.1079P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.47$ e Å^{-3}
$\Delta\rho_{\min} = -0.52$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H4···O1$^{\rm i}$	1.24	1.24	2.472 (3)	180 (1)

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

All H-atom parameters were initially refined freely. In the final cycles, the H atoms of CH_2 and OH groups were placed in calculated positions, with C—H = 0.97 Å (CH_2) and O—H = 0.82 Å, and refined as riding, with $U_{\rm iso}$(H) values set at 1.2 (CH_2) or 1.5 (OH) times $U_{\rm eq}$ of the parent atom. The H atom on phosphonate atom O1 was initially refined freely with occupancy factors of 0.6–0.7 and finally fixed with an occupancy factor of 0.5 to represent the state of double-minimum potential. The displacement parameter was set at $1.5U_{\rm eq}$(O1).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXTL* (Sheldrick, 1997*b*); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3018). Services for accessing these data are described at the back of the journal.

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