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Structural Characterization of $[Li(DME)PH_2]_\infty$ (DME = 1,2-Dimethoxyethane): Parent of the Lithium Diorganophosphides

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The structure of $[Li(DME)PH_2]_\infty$ in the solid state consists of an infinite polymer of alternating Li and P atoms. The vertices of the chain are four-coordinate, distorted-tetrahedral lithium atoms that are bonded to two P atoms and a 1,2-dimethoxyethane unit. The P atoms are located between each Li vertex such that the Li–P–Li angle is almost linear (176.9 (1)°): Li–P = 2.550 (8), 2.597 (8) Å; Li–O = 2.063 (7), 2.036 (7) Å. Crystal data: $C_4H_{12}PO_2Li$, M_r = 130.05, orthorhombic, $P2_12_12_1$, a = 6.956 (2) Å, b = 8.773 (1) Å, c = 13.455 (2) Å, V = 821.1 (5) Å^3, D_c = 1.052 g cm^{-3}, Z = 4, μ(Mo Kα) = 2.524 cm^{-1}. Refinement of 451 reflections ($I > 3\sigma(I)$) out of 880 unique observed reflections ($3° < 2\theta < 50°$) gave R and R_w values of 0.0591 and 0.0645, respectively.

Structural details on a number of lithium diorganophosphides ($LiPR_2$) have recently been reported. Interest in these compounds stems from their importance as PR_2^- transfer agents[1,2] and also from the properties and structures of lithium reagents in general.[3,4]

Structures of the ionic $[Li(12\text{-crown-}4)_2][PPh_2]$,[5] dimeric $[LiP(CH(SiMe_3)_2)]_2$,[6] and tetranuclear $[Li_2(\mu_3\text{-}t\text{-}Bu_2P)(\mu\text{-}t\text{-}Bu_2P)(THF)]_2$[7] have been described as well as those of the polymeric species $[Li(Et_2O)PPh_2]_\infty$, $[Li(THF)_2PPh_2]_\infty$, and $[Li(THF)P(C_6H_{11})_2]_\infty$.[8] We describe here the X-ray crystal structure of the parent lithium phosphide $LiPH_2$ as its 1,2-dimethoxyethane (DME) adduct $[Li(DME)PH_2]_\infty$ (**1**). **1** is also an infinite polymer in the solid state although there are some significant differences from the structures of the other polymeric phosphides described by Power and co-workers.[8]

Results and Discussion

$LiPH_2$ crystallizes from 1,2-dimethoxyethane (DME) as the solvate $[Li(DME)PH_2]_\infty$[9] in the orthorhombic space group $P2_12_12_1$ with four formula units per unit cell. The compound is an infinite chain of alternating Li and P atoms. The chain structure is propogated by a 2-fold screw along the b axis. a view of the repeat unit of the polymer is shown in Figure 1. In Figure 2, the atom-labeling scheme employed for the DME ligand is shown. Crystallographic data are presented in Table I, and bond lengths and angles are given in Tables II and III, respectively. Positional parameters are given in Table IV.

There is a significant difference between the structure of **1** and the infinite chains of Li–P–Li–P atoms found in $[Li(Et_2O)PPh_2]_\infty$, $[Li(THF)PPh_2]_\infty$, and $[Li(THF)P(C_6H_{11})_2]_\infty$.[8] In **1**, the vertices of the chain consist of four-coordinate, distorted-tetrahedral lithium atoms bonded to two P atoms and a DME. The P atoms are located between each Li vertex such that the Li–P–Li angle is almost linear (176.9 (1)°) (Figure 3). The LiDME groups alternate their positions above and below the chain. In the $LiPPh_2$ and $LiPCy_2$ chains described by Power and co-workers, the framework consists of alternating Li and P atoms at the vertices

Table I. Crystal Structure Parameters for **1**

Description of Crystal	
color	clear
habit	prism
max cryst dimens, mm^3	0.50 × 0.20 × 0.20
cryst system	orthorhombic
space group	$P2_12_12_1$ (No. 19)
unit cell params	
a, Å	6.956 (2)
b, Å	8.773 (1)
c, Å	13.455 (2)
V, Å^3	821.1 (5)
no. of asymmetric units per unit cell	4
formula	$C_4H_{12}PO_2Li$
fw	130.05
calcd density, g cm^{-3}	1.052
μ_{calcd}, cm^{-1}	2.524
Data Collection	
radiation (λ, Å)	Mo Kα (0.710 73)
scan technique	$\theta/2\theta$
scan width, deg	0.8 + 0.35 tan θ
range of indices h,k,l	+8,+7,+14
2θ range, deg	3.0–50.0
no. of reflcns measd	880
std reflcns	
intensity	244, 008
orientation	327, 341
decay of stds, %	1.5
min % transmission	98.0322
max % transmission	99.8923
av % transmission	98.9293
Structure Determination	
no of reflcns used ($I > 3\sigma(I)$)	451
no. of refined params	73
data/parameter ratio	6.178
shift/error ratio	0.005
esd of an observn of unit wt	5.8593
R	0.0591
R_w	0.0645

Table II. Bond Lengths (Å) for **1**[a]

P–Li	2.550 (8)	O2–C3	1.462 (5)
P–Li′	2.597 (8)	O2–C4	1.456 (6)
O1–C1	1.454 (6)	O2–Li	2.036 (7)
O1–C2	1.448 (5)	C2–C3	1.498 (8)
O1–Li	2.063 (7)		

[a] In this and the following tables, numbers in parentheses are estimated standard deviations in the least significant digits.

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(9) Schäfer, V. H.; Fritz, G.; Hölderich, W. *Z. Anorg. Chem.* **1977**, *428*, 222.

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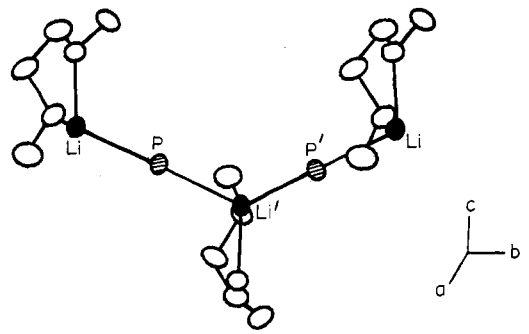

Figure 1. ORTEP view of a short section of the polymeric chain of **1**.

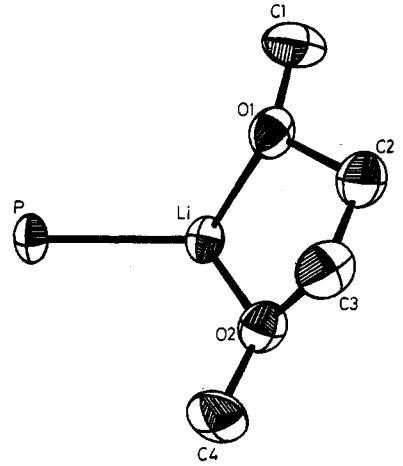

Figure 2. Detail of the asymmetric unit of **1** showing the atom-numbering scheme employed.

Table III. Bond Angles (deg) for **1**

Li–P–Li′	176.9 (1)	O2–C3–C2	107.8 (4)
C1–O1–C2	113.6 (4)	P–Li–P′	117.0 (2)
C1–O1–Li	121.0 (3)	P–Li–O1	118.5 (4)
C2–O1–Li	103.1 (4)	P–Li–O2	114.9 (4)
C3–O2–C4	112.9 (1)	P–Li–O1′	105.1 (3)
C3–O2–Li	109.9 (3)	P–Li–O2′	113.6 (4)
C4–O2–Li	127.9 (4)	O1–Li–O2	82.7 (3)
O1–C2–C3	107.1 (5)		

Table IV. Fractional Coordinates for **1**[a]

atom	x	y	z	B, Å^2
P	0.4923 (8)	0.7583 (3)	0.7537 (3)	5.33 (5)
O1	0.8545 (9)	0.4844 (9)	0.8958 (4)	5.9 (2)
O2	0.509 (1)	0.5014 (9)	0.9879 (4)	5.8 (1)
C1	1.009 (2)	0.427 (2)	0.8330 (8)	8.2 (4)
C2	0.826 (2)	0.396 (2)	0.9854 (8)	7.4 (3)
C3	0.682 (2)	0.480 (2)	1.0477 (7)	6.9 (3)
C4	0.361 (2)	0.588 (1)	1.0396 (8)	7.4 (3)
Li	0.579 (2)	0.510 (2)	0.841 (1)	4.7 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

such that the PPh_2 and Li (solvate) units occupy opposite sides of the chain throughout the structure (Figure 3). In these complexes, the Li–P–Li angles range from 126.0 (3) to 145.6 (3)°. It seems likely that the difference in structures is due to the minimal steric requirements imparted by the P–*H* units vs. alkyl or aryl substituents. This aspect has been discussed for aryl- and alkylphosphides by Power.[8] Unfortunately, the P–*H* atoms could not be located in the X-ray structure so that the full geometry about P could not be determined. The other metric parameters for the structure appear to be fairly normal. Thus, the P–Li distances of 2.550 (8) and 2.597 (8) Å are similar to those found in [Li(THF)$_2$PPh$_2$]$_\infty$ (2.63 (2), 2.63 (2) Å), in which the Li atoms

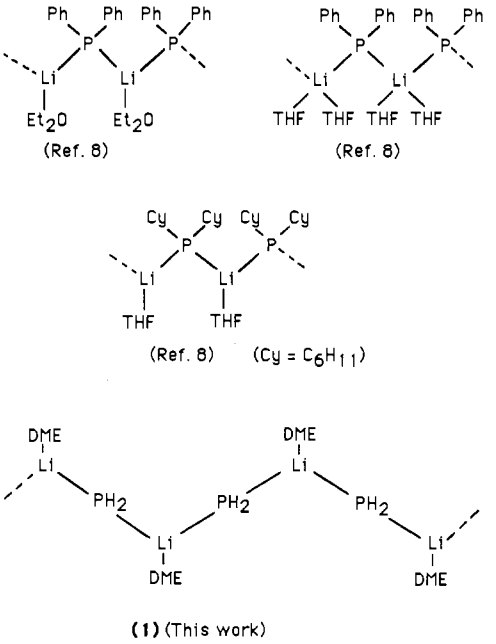

Figure 3. Overall structures of **1** and other polymeric lithium phosphides.

also have four-coordinate, distorted-tetrahedral geometries. The Li–O distances of 2.063 (7) and 2.036 (7) Å are slightly longer than those observed in [Li(THF)$_2$PPh$_2$]$_\infty$ (1.94 (2), 1.99 (2) Å).

Experimental Section

The compound was prepared by the literature method[9] and was recrystallized from hexane at −20 °C. Crystals of **1** were mounted under nitrogen in thin-walled glass capillaries. Data were collected on an Enraf-Nonius CAD-4 diffractometer at 23 ± 2 °C using graphite-monochromated Mo Kα radiation. All calculations were performed on a PDP 11/44 computer using the Enraf-Nonius software package SDP-PLUS.[10] Unit cell parameters were obtained by carefully centering 25 reflections having 2θ values between 24 and 30°. The space group $P2_12_12_1$ was uniquely determined by systematic absences [$h00$ (h odd), $0k0$ (k odd), $00l$ (l odd)]. Data were collected in the $+h,+k,+l$ octant between 2θ values of 3 and 50°. The check reflections indicated a 1.5% decay of standards, and so no decay correction was applied. An empirical absorption correction (ψ scan) was applied (program EAC). The data were corrected for Lorentz and polarization effects and the structure solved by Patterson synthesis followed by successive cycles of difference Fourier maps and least-squares refinements. A non-Poisson contribution weighting scheme with an experimental instability factor $P = 0.04$[11] was used in the final stages of refinement. Only one of the hydrogen atoms of the DME group was located, and those of the PH_2 groups were not. Therefore, H atoms were omitted from the final refinement. Final R and R_w values were 0.0591 and 0.0645, respectively. The maximum peak in the final difference Fourier map had a height of 0.32 Å and was located 1.17 Å from C(4). Supplementary material is available.[12]

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Supplementary Material Available: A table of thermal parameters (1 page); a listing of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

(10) "SDP-PLUS", 4th ed.; B. A. Frenz and Associates: College Station, TX, 1981.

(11) P is used in the calculation of $\sigma(I)$ to downweight intense reflections in the least-squares refinement. The function minimized was $\sum w(|F_o| - |F_s|)^2$ where $w = 4(F_o)^2/[\sum(F_o)^2]^2$, for which $[\sum(F_o)^2]^2 = [S^2(C + R^2B) + [P(F_o)^2]^2]/(L_p)^2$, where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count and L_p is the Lorentz–polarization factor.

(12) See paragraph at end of paper regarding supplementary material.