A Neutron Diffraction Refinement of the Crystal Structure of Lithium Hydrogen Phosphite, LiH$_2$PO$_3$

By Göran B. Johansson and Oliver Lindqvist

Department of Inorganic Chemistry, Chalmers University of Technology and the University of Göteborg,
P.O. Box S-402 20 Göteborg 5, Sweden

LiH$_2$PO$_3$ crystallizes in the orthorhombic space group $P2_1nb$ with $a = 5·169$ (2), $b = 11·024$ (2), $c = 5·060$ (2) Å, $Z = 4$. The structure was solved previously from X-ray film data [Philippot & Lindqvist, *Acta Chem. Scand.* (1970). **24**, 2803–2810]. In the present investigation, the structure was refined to $R = 0·024$ based on 387 independent neutron intensities. Improved dimensions of the tetrahedral HPO$_2$OH$^-$ ion have been obtained: P–H = 1·396, P–O = 1·497 and 1·506, P–OH = 1·586 Å. The structure contains a strong O–H···O hydrogen bond with O–H = 1·018, O···H = 1·547, O–O = 2·558 Å. Li is tetrahedrally coordinated by O atoms, the Li–O distances being 1·922–2·032 Å.

Introduction

The structure of phosphorous acid, H$_3$PO$_3$, has been determined both from X-ray (Furberg & Landmark, 1957) and neutron diffraction (Loopstra, 1958). These two studies have confirmed that one H is linked directly to the P atom, as had been indicated from Raman (Simon & Fehér, 1937) and infrared (Corbridge & Lowe, 1954) spectra. The P–H distance has been determined accurately in PH$_3$ (microwaves; Burrus, Jache & Gordy, 1954) and Ca(H$_2$PO$_2$)$_2$ (neutron diffraction; Loopstra, 1958) to be 1·42 and 1·39 Å respectively. However, the P–H length in phosphites(III) is not well established. In the neutron diffraction study of H$_3$PO$_3$, the H atoms directly linked to the P atoms were not clearly resolved, but Loopstra (1958) suggested the value 1·39 Å for P–H based on results from Ca(H$_2$PO$_2$)$_2$. In the previous X-ray investigation of LiH$_2$PO$_3$ (Philippot & Lindqvist, 1970) approximate positions for the H atoms indicated a very short P–H distance, 1·17 (6) Å.

Experimental

Large crystals of LiH$_2$PO$_3$, suitable for neutron diffraction, were prepared and kindly provided by Dr G. Brun, Montpellier. The crystal, a plate with a volume of 20mm^3 (Fig. 1), was mounted on a com-

puter-controlled Hilger & Watts four-circle diffractometer at the Swedish Atomic Energy reactor R2 at Studsvik. A doubly monochromated neutron beam (Stedman, Almqvist, Raunio & Nilsson, 1969) of wavelength 1·210 Å was used, and measurements were performed in an ω–2θ step-scan mode. All 485 reflexions with h, k and $l \geq 0$ were measured out to $\sin \theta/\lambda = 0·7$, including $h0l$ with $h + l = 2n + 1$ and $hk0$ with $k = 2n + 1$, which were thus checked to be systematically absent. The primary data were reduced to integrated intensities with *STUKC* written by R. Liminga (Lundgren, 1974). Those 380 reflexions with $I > 3\sigma_{count}$ were regarded as significant and used in the subsequent refinement.

Lorentz and absorption corrections were made with *DATAPH* (Coppens, Leiserowitz & Rabinovich, 1965, modified by W. C. Hamilton). The absorption coefficient was determined experimentally to be 1·78 cm^{-1} for $\lambda = 1·210$ Å. This value corresponds to an incoherent scattering cross-section of 47 b for H, assuming 35 b for Li (*International Tables for X-ray Crystallography*, 1962).

Refinement

Refinement was started from the coordinates obtained by Philippot & Lindqvist (1970). Neutron scattering lengths given by Bacon (1972) were used for all atoms. The final cycles were carried out with *UPALS* (Lund-

Table 1. *Final neutron diffraction parameters in* LiH$_2$PO$_3$

The anisotropic temperature factor is exp $[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}) \times 10^{-4}]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	0·245	0·1535 (1)	0·1802 (3)	109 (4)	21 (1)	103 (5)	0 (2)	−4 (4)	8 (2)
O(1)	0·2044 (5)	0·2868 (1)	0·2303 (38)	195 (5)	22 (1)	130 (5)	7 (2)	36 (4)	8 (2)
O(2)	0·5443 (4)	0·1226 (1)	0·1661 (38)	118 (5)	38 (1)	145 (5)	15 (2)	21 (4)	13 (2)
O(3)	0·1234 (4)	0·0696 (1)	0·3772 (3)	132 (5)	27 (1)	187 (5)	5 (1)	35 (4)	23 (2)
Li	0·2617 (9)	0·4203 (4)	−0·0126 (9)	174 (16)	38 (3)	192 (14)	1 (5)	0 (12)	−7 (5)
H(1)	0·6577 (8)	0·3712 (3)	0·4246 (7)	335 (13)	68 (2)	203 (11)	−2 (5)	−84 (11)	9 (4)
H(2)	0·1236 (6)	0·3405 (3)	0·5003 (6)	195 (9)	56 (2)	203 (11)	−7 (4)	42 (8)	0 (4)

gren, 1974). The parameters varied were: an overall scale factor, atomic coordinates, anisotropic temperature factors and an isotropic extinction parameter. The quantity minimized was $\sum w |F_o - F_c|^2$, where the weights were calculated from $w = [\sigma^2_{count} + (0.025F_o)^2]^{-1}$.

Table 2. Weight analysis after the last cycle of refinement

The quantities $w\Delta^2$ are normalized sums, for equal numbers of reflexions within each F_o interval.

F_o interval	$w\Delta^2$
0·0– 6·4	1·23
6·4– 8·4	1·65
8·4–10·4	0·76
10·4–12·5	0·97
12·5–14·9	1·07
14·9–17·9	1·58
17·9–20·0	0·64
20·0–24·1	0·71
24·1–28·4	0·35
28·4–59·3	1·04

$R = \sum |F_o - |F_c||/\sum F_o = 0.024$
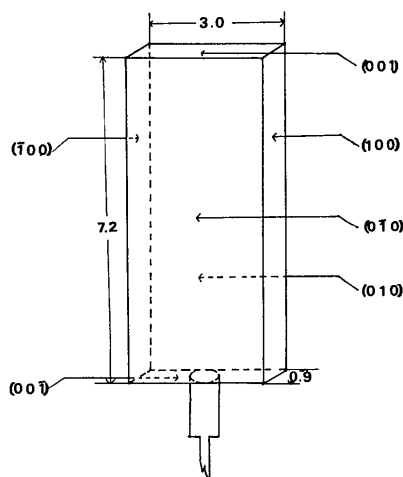$R_w = (\sum w |F_o - |F_c||^2/\sum wF_o^2)^{1/2} = 0.030$

Fig. 1. The dimensions (mm) of the LiH₂PO₃ crystal used for the neutron data collection.

A final $R(=\sum|F_o - |F_c||/\sum F_o)$ of 0·024 was obtained and the corresponding set of parameters is given in Table 1.* A weight analysis is shown in Table 2.

Discussion

Interatomic distances and angles found in the X-ray (Philippot & Lindqvist, 1970) and neutron diffraction studies are compared in Table 3. There are no significant differences ($> 3\sigma$) except for the P–H(1) distance,

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31206 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Interatomic distances (Å) and angles (°) in LiH₂PO₃ as obtained in the neutron and X-ray investigations

	Neutron	X-ray
P–H(1)	1·396 (4)	1·17 (6)
P–O(3)	1·497 (2)	1·496 (6)
P–O(1)	1·506 (2)	1·511 (5)
P–O(2)	1·586 (2)	1·559 (7)
O(1)–P–O(2)	110·7 (1)	112·0 (4)
O(1)–P–O(3)	115·6 (1)	114·6 (3)
O(1)–P–H(1)	107·5 (2)	108 (3)
O(2)–P–O(3)	107·9 (1)	107·4 (4)
O(2)–P–H(1)	103·4 (2)	106 (4)
O(3)–P–H(1)	111·2 (2)	109 (3)
O(2)——H(2)	1·018 (4)	1·17 (16)
O(1)···H(2)	1·547 (4)	1·42 (15)
O(1)···H(2)–O(2)	171·6 (3)	165 (10)
P——O(2)–H(2)	110·1 (2)	108 (9)
Li–O(3)	1·922 (5)	1·913 (13)
Li–O(1)	1·940 (5)	1·972 (13)
Li–O′(3)	1·954 (5)	1·977 (21)
Li–O(2)	2·032 (5)	1·996 (16)
O(1)–Li–O(2)	104·3 (2)	104·4 (7)
O(1)–Li–O′(3)	111·7 (2)	110·2 (8)
O(1)–Li–O(3)	111·6 (3)	110·8 (7)
O(2)–Li–O′(3)	108·3 (2)	109·9 (7)
O(2)–Li–O(3)	106·2 (2)	107·6 (8)
O′(3)–Li–O(3)	114·1 (2)	113·7 (7)

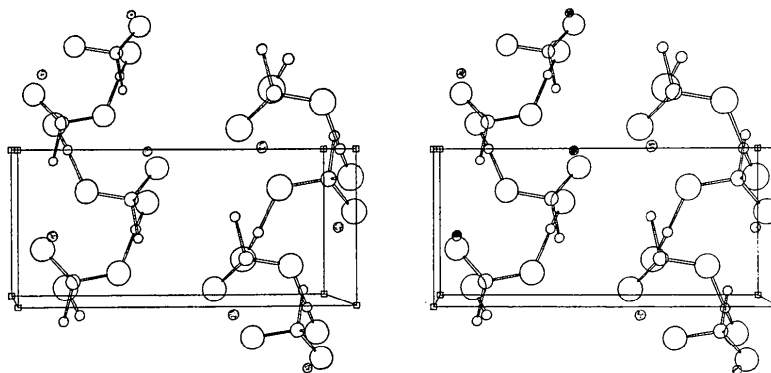Fig. 2. A stereoscopic view (ORTEP) of the LiH₂PO₃ structure along a. The HPO₂OH⁻ ions are connected via hydrogen bonds to form crossing chains.

which is shorter in the X-ray investigation. Part of this deviation is probably due to underestimated standard deviations of the H(1) coordinates in the X-ray work. The P–H length of 1·396 (6) Å is nearly the same as the 1·39 and 1·4206 (5) Å in calcium hypophosphite (Loopstra, 1958) and phosphine (Burrus *et al.*, 1954), respectively, indicating that the P–H bond has similar character for the different oxidation states.

The crystal structure was described in the X-ray paper, but is also indicated in Fig. 2. The Li^+ ion is tetrahedrally surrounded by O atoms from four different $HPO_2(OH)^-$ ions. The coordination is similar to that found in $LiHCOO.H_2O$ (Enders-Beumer & Harkema, 1973) and $LiNH_3SO_4$ (Vilminot, Anderson & Brown, 1973), in which the Li–O distances are 1·923 (4)–1·974 (4) and 1·939 (6)–1·981 (5) Å respectively. The most significant deviation from a regular Li–O tetrahedron is that the Li–O(2) distance is about 0·1 Å longer than the others, which seems to be reasonable, since O(2) belongs to the hydroxyl group. Octahedral Li–O coordination has also been found in $LiH_3(SeO_3)_2$ with Li–O distances of 2·13–2·22 Å (Tellgren & Liminga, 1972).

The hydrogen bond $O(2)$–$H(2)\cdots O(1)$ is fairly strong, since O(1)–O(2) is 2·558 (4) and O(2)–H(2) 1·018 (6) Å. The O–H bond is usually long in strong hydrogen bonds and the O(2)–H(2) distance fits well into plots of the O–H length against the O–O and O$\cdots$H distances for a number of known hydrogen bonds (Hamilton & Ibers, 1968).

The difference between the P–OH and P–O terminal bonds is nearly 0·1 Å (Table 3 and Fig. 3). Similar distances are found in phosphates, *e.g.* in $KH_5(PO_4)_2$, which has also been investigated by means of X-rays (Philippot & Lindqvist, 1971) and neutrons (Philippot, Richard, Roudault & Maurin, 1972), where the P–OH and P–O terminal bonds were found to be 1·548–1·560 (3) and 1·497–1·510 (3) Å, respectively.

The O atoms have, in addition to the P–O bond, two interactions with other atoms. Of the two terminal O atoms, O(1) acts as an acceptor in the hydrogen bond and as a member of the LiO_4 tetrahedron, while O(3) is coordinated to two Li^+ ions. The similarity between the P–O(1) and P–O(2) bonds indicates that the Li^+ ion has a rather limited polarizing effect on the phosphite anion.
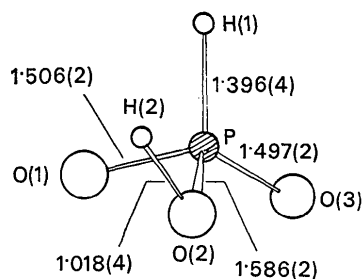
Fig. 3. The HPO_2OH^- anion.

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