

## The Crystal Structure of Lithium Hydrogen Phosphite, $\text{LiH}_2\text{PO}_3$

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$\text{LiH}_2\text{PO}_3$  crystallizes in space group  $P2_1nb$  with  $a=5.169$ ,  $b=11.024$ ,  $c=5.060$  Å and  $Z=4$ . The structure has been determined by means of three-dimensional Patterson and electron density summations, a final  $R$  value of 0.063 having been obtained after least squares refinement based on 285 independent reflections.

One of the hydrogen atoms is directly bonded to the phosphorus atom, while the other forms part of a hydroxide group. The P—O bond distances within the  $\text{HPO}_3\text{OH}^-$  ion are 1.496, 1.511, and 1.559 Å. The lithium atom is tetrahedrally surrounded by oxygen atoms at distances of 1.91, 1.97, 1.97, and 2.00 Å.

The crystal structure of phosphorous acid,  $\text{H}_3\text{PO}_3$ , is well established from X-ray diffraction studies in 1957 by Furberg and Landmark<sup>1</sup> and X-ray and neutron diffraction studies in 1958 by Loopstra.<sup>2</sup> Few salts of this acid have, however, been investigated, and apart from recent work on  $\text{CuHPO}_3 \cdot 2\text{H}_2\text{O}$ <sup>3</sup> and  $\text{Cu}(\text{H}_2\text{PO}_3)_2$ ,<sup>4</sup> only the crystal structure of  $\text{MgHPO}_3 \cdot 6\text{H}_2\text{O}$ <sup>5</sup> has been reported earlier.

Chemical and structural investigations of different inorganic phosphorous and phosphoric compounds are being carried out by Prof. Maurin *et al.* in Montpellier, and, in connection with this work, crystals of  $\text{LiH}_2\text{PO}_3$  were prepared, and the cell dimensions and possible space groups were determined.<sup>6</sup> To establish the structure of this compound, a single crystal X-ray analysis was commenced at the Department of Inorganic Chemistry, University of Göteborg, suitable crystals very kindly being provided by Dr. G. Brun, Montpellier.

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## EXPERIMENTAL

The method of preparation of  $\text{LiH}_2\text{PO}_3$  has been described previously,<sup>6</sup> and the unit cell dimensions and the observed and calculated densities are also given in the same paper.

The crystal selected for investigation had the dimensions 0.34 (*a* axis)  $\times$  0.05 (*b* axis)  $\times$  0.08 (*c* axis) mm<sup>3</sup>. The  $0kl-4kl$  reflections were registered by Weissenberg multiple-film equi-inclination techniques using  $\text{CuK}\alpha$  radiation. A summary of the crystallographic data is given in Table 1.

Table 1. Crystallographic data for  $\text{LiH}_2\text{PO}_3$ .

Unit cell dimensions: <sup>6</sup>	$a = 5.169(2) \text{ \AA}$ $b = 11.024(2)$ $c = 5.060(2)$ $V = 288.29 \text{ \AA}^3$ $Z = 4.$
Formula weight:	$M = 87.93.$
Density (20°C): <sup>6</sup>	$D_m = 2.020 \text{ g}\cdot\text{cm}^{-3}$ $D_x = 2.025 \text{ g}\cdot\text{cm}^{-3}.$
Systematic absences:	$h0l: h+l=2n+1$ $hk0: k=2n+1.$
Space group:	$P2_1nb.$
General point position:	$(x,y,z); (1/2+x, 1/2-y, 1/2+z);$ $(1/2+x, -y, -z); (x, 1/2+y, 1/2-z).$
Crystal habit:	White needles.
Linear absorption coefficient:	$\mu = 63.0 \text{ cm}^{-1}$ ( $\text{CuK}\alpha, \lambda = 1.5418 \text{ \AA}$ ).

The intensities were estimated visually by comparison with an intensity scale prepared from timed exposures of a suitable crystal reflection. The values from the six films recorded for each layer line were scaled together using the program *SCALE*, with weights according to the formula  $w = \{1.0 + [(I - 12.0)/6.0]\}^{-1}$ . The inter-layer scale factors were initially chosen in agreement with the corresponding exposure times.

A total of 303 independent reflections was estimated, of which 17 were too weak to be measured.

## STRUCTURE ANALYSIS AND REFINEMENT

All independent reflections, previously corrected for Lorentz' and polarization effects (program *DATAP2*), were summed in a three-dimensional Patterson synthesis (program *DRF*). The systematic absences (*cf.* Table 1) indicated the space group to be either  $P2_1nb$  or  $Pmnb$ . It was not possible, however, to successfully interpret the Patterson function on the basis of the centric space group, whereas a number of interatomic vectors could be explained on the basis of  $P2_1nb$ , yielding the positions of the phosphorus atom and one of the oxygen atoms ( $O_1$ ). The remaining oxygen and lithium atoms were easily located from two subsequent Fourier summations (program *DRF*).

In a preliminary isotropic refinement of the parameters of the phosphorus, oxygen, and lithium atoms, the scale factors between the layer lines were also varied. The *R* value, defined as  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  dropped to 0.087. At this stage the structure factors had been corrected for absorption errors (program *DATAP2*). Together with the absorption factors,  $\beta$  values to be used in the correction for secondary extinction, according to Zachariasen,<sup>7</sup>

were evaluated. The scale factor  $c$  in Zachariasen's formula was calculated to be 0.029 by means of the program *EXTCORR*, which also applied the correction factors to the structure factors.<sup>8</sup> The isotropic refinement was repeated, and a much improved agreement between the calculated and observed structure factors was obtained for the strong reflections ( $R=0.079$ ). The  $|F_c|$  value of one of the strongest reflections, namely 101, was still too high, and since this was likely to be due to primary extinction not being corrected for, the reflection was not included in the subsequent refinement.

After further refinement of the structure, allowing for anisotropic temperature vibrations ( $R=0.068$ ), a difference Fourier summation was calculated, from which it was possible to locate the positions of the hydrogen atoms, the peaks corresponding to the hydrogen atom attached to the phosphorus atom ( $H_1$ ) and the hydrogen atom of the hydroxide group ( $H_2$ ) having electron densities of 0.90 and 0.57  $e/\text{\AA}^3$ , respectively. Other peaks with electron densities of 0.5–0.6  $e/\text{\AA}^3$  were also present, but these could be disregarded owing to geometrical reasons.

In the final stages of the refinement the positional and isotropic temperature parameters of the hydrogen atoms were included and the  $R$  value converged to 0.063 (0.074 including the 101 reflection and unobserved reflections). The resulting positional and thermal parameters are given in Table 2 and the observed and calculated structure factors in Table 3. The atomic scattering factors calculated by Doyle and Turner<sup>9</sup> were used for P, O, and Li, and those devised by Stewart *et al.*<sup>10</sup> for H. The real part of the anomalous scattering for the phosphorus atom as given by Cromer<sup>11</sup> was taken into

Table 2. Final parameters for  $\text{LiH}_2\text{PO}_3$ . The anisotropic temperature factor is  $\exp[-2\pi(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+hka^*b^*U_{12}+hla^*c^*U_{13}+klb^*c^*U_{23})]$ . For all atoms except hydrogen, the  $B$  value has been obtained from the last isotropic refinement referred to in the text. Standard deviations are given in parentheses.

Atom	$x/a$	$y/b$	$z/c$	$B \text{ \AA}^2$		
P	0.2460(0) <sup>a</sup>	0.1534(1)	0.1800(3)	1.17(7)		
O <sub>1</sub>	0.2007(15)	0.2868(4)	0.2316(10)	1.76(13)		
O <sub>2</sub>	0.5398(14)	0.1219(5)	0.1684(10)	1.87(15)		
O <sub>3</sub>	0.1242(16)	0.0702(4)	0.3777(10)	1.98(13)		
Li	0.2559(38)	0.4214(9)	-0.0186(25)	1.69(24)		
H <sub>1</sub>	0.665(14)	0.368(4)	0.470(11)	-1.0(0.9)		
H <sub>2</sub>	0.119(38)	0.351(9)	0.459(31)	5.0(3.4)		
	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
P	0.022(2)	0.016(1)	0.018(1)	0.005(2)	0.001(2)	0.002(1)
O <sub>1</sub>	0.022(4)	0.020(2)	0.022(2)	0.006(4)	0.014(5)	0.000(4)
O <sub>2</sub>	0.009(5)	0.026(3)	0.023(3)	-0.003(5)	0.001(4)	0.010(4)
O <sub>3</sub>	0.018(4)	0.017(2)	0.027(2)	0.006(4)	0.006(5)	0.012(4)
Li	0.011(8)	0.021(4)	0.036(6)	0.009(12)	0.006(11)	-0.011(9)

<sup>a</sup> Fixed to specify the origin.

Table 3. Observed and calculated structure factors for  $\text{LiH}_2\text{PO}_3$ . The columns are  $k$ ,  $10|F_o|$  and  $10|F_c|$ , respectively. (\* indicates reflections not included in the refinement.)

0 K 0	2 108 98	4 34 16	2 K 0	2 76 19	6 173 136	7 66 59
2 211 216	3 110 107	5 139 70	2 294 252	3 23 9	7 156 113	8 201 179
4 470 518	4 125 108	6 161 159	4 115 63	4 57 21	8 147 130	9 69 56
6 63 65	5 250 238	7 250 248	6 216 201	5 146 143	9 120 127	10 55 12
8 38 13*	6 42 1*	8 209 206	8 96 84	6 81 62	10 49 47	11 26 32
10 197 178	7 47 40	9 127 118	10 177 162	7 111 107	11 49 48	
12 51 52	8 38 53*	10 125 104	12 109 107	8 33 9		
14 136 172	9 118 112	11 49 46		9 49 65		
	10 69 62	12 78 75	2 K 1	10 54 54	0 158 169	4 K 2
0 K 1		13 85 92	1 85 24		1 262 239	0 169 164
1 17 4*	0 K 5	1 K 3	2 193 97	2 K 5	2 90 32	1 210 199
2 666 653	1 133 131	0 133 144	3 138 93	1 70 46	3 93 95	2 111 90
3 303 326	2 210 200	1 196 207	4 213 96	2 90 65	4 49 28	3 138 135
4 109 93	3 172 145	2 152 157	5 85 87	3 108 103	5 221 211	4 111 99
5 42 43	4 96 78	3 155 77	6 147 125	4 95 105	6 29 3	5 127 123
6 326 350	5 43 41	4 35 16	7 160 126	5 56 22	7 78 60	6 139 126
7 266 312	6 40 35	5 275 277	8 299 284	6 22 12	8 41 35	7 76 41
8 310 298	7 144 133	6 78 69	9 104 89	7 98 111	9 116 118	8 53 36
9 41 2*	8 45 43	7 132 121	10 130 122		10 29 24	9 62 59
10 112 95		8 40 12*	11 37 36	2 K 6		10 65 73
11 89 73	0 K 6	9 166 148	12 114 114	0 70 65	3 K 4	
12 150 141	1 103 97	10 36 58	13 57 55	1 69 64	1 144 124	1 225 198
	2 29 10*	11 113 104		2 19 15	2 86 56	2 73 60
0 K 2	3 27 21*	12 34 24	2 K 2	3 18 7	3 205 195	3 222 186
0 425 464	4 131 148	1 K 4	0 241 196		4 66 64	4 44 19
1 291 312		1 127 107	1 135 140	3 K 0	5 57 6	5 48 46
2 279 283	1 K 0	2 136 128	2 216 205	2 291 228	6 38 18	6 51 21
3 45 40	2 359 362	3 208 194	3 110 49	4 317 251	7 162 167	7 107 99
4 97 99	4 198 19	4 39 6*	4 26 6	6 336 283	8 34 3	8 53 38
5 415 413	6 256 228	5 40 8*	5 167 154	8 289 286	9 65 80	9 86 96
6 164 182	8 347 367	6 97 67	6 163 172	10 50 39		4 K 4
7 39 21*	10 188 129	7 186 190	7 129 137	12 71 70		0 75 39
8 58 56	12 176 159	8 41 36	8 23 12*		0 85 80	1 158 148
9 199 202		9 149 133	9 109 81	3 K 1	1 143 122	2 45 33
10 100 90	1 K 1	10 43 23	10 96 89	0 418 362	2 40 14	3 72 59
11 37 22*	0 551 733*		11 148 134	1 209 203	3 33 26	4 36 29
12 36 27	1 207 152	1 K 5	12 40 21	2 243 204	4 103 103	5 143 147
	2 261 274	0 95 91	2 K 3	3 170 171	5 120 126	6 58 69
0 K 3	3 203 26	1 185 173	1 102 107	4 219 205	6 59 72	7 43 47
1 188 206	4 211 120	2 38 25*	2 72 11	5 102 61		4 K 5
2 60 57	5 162 161	3 57 54	3 154 160	6 243 221		1 28 31
3 282 338	6 180 174	4 110 102	4 33 6	7 34 12	2 166 145	2 62 70
4 56 63	7 53 44	5 105 95	5 39 38	8 89 91	4 214 199	
5 77 70	8 148 55	6 72 66	6 112 86	9 48 13	6 224 201	
6 147 154	9 68 64	7 63 54	7 178 132	10 115 111	8 90 81	
7 318 293	10 171 158	8 40 5	8 98 95	11 90 86	10 105 106	
8 165 153	11 67 62		9 183 179			
9 91 87	12 72 61	1 K 6	10 45 31	3 K 2	4 K 1	
10 37 3*		1 67 61	11 22 19	1 246 248	1 92 96	
11 61 58	1 K 2	2 104 110		2 194 204	2 215 187	
	1 241 17	3 43 40	2 K 4	3 209 204	3 101 93	
0 K 4	2 179 151	4 104 169	0 97 78	4 163 158	4 163 158	
0 56 55	3 221 236		1 17C 165	4 49 19	5 23 11*	
1 316 314				5 76 72	6 171 164	

account. The structure factors were weighted according to the formula  $w = (a + F_o + cF_o^2 + dF_o^3)^{-1}$  in the refinement,<sup>12</sup> and an acceptable weighting scheme was obtained with  $a = 3.0$ ,  $c = 0.08$ , and  $d = 0.0012$ .

A final difference map was calculated using the parameters of Table 2. Except for a few fluctuations of the order of  $\pm 0.5 e/\text{\AA}^3$  in the close vicinity of the phosphorus and two of the oxygen positions, the electron density varied between  $-0.3$  and  $0.3 e/\text{\AA}^3$ . This result was considered to provide adequate confirmation of the results of the refinement.

The least squares refinement was carried out with the full matrix program *LALS*. All calculations were performed on an IBM 360/65 computer, and the programs used will shortly be described elsewhere.<sup>13</sup>

## DISCUSSION

Fig. 1 shows a projection of the structure of  $\text{LiH}_2\text{PO}_3$  along the  $a$  axis, and illustrates the linking of the  $\text{HPO}_2\text{OH}^-$  ions by hydrogen bonds to form chains through the structure. Each lithium atom is tetrahedrally co-ordinated by oxygen atoms from four different  $\text{HPO}_2\text{OH}^-$  groups, and can thus be

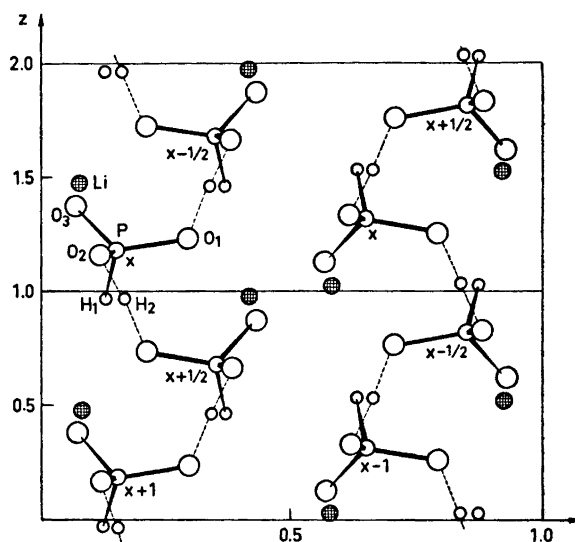


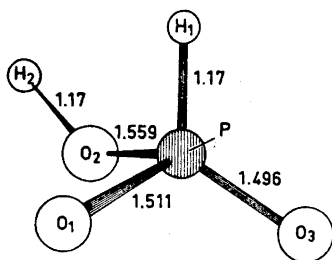
Fig. 1. The structure of  $\text{LiH}_2\text{PO}_3$  viewed along the  $a$  axis. The hydrogen bonds, which are marked as dotted lines, form crossing chains directed along  $(101)$  and  $(-101)$ , respectively.

regarded as connecting the anions to form a three-dimensional net. The oxygen atom which does not take part in the hydrogen bonding is linked to two lithium atoms.

Interatomic distances and angles within the  $\text{HPO}_2\text{OH}^-$  ion, calculated with the program *DISTAN*, are given in Table 4. As shown in Fig. 2, the phosphorus atom forms four nearly tetrahedral bonds to the hydrogen and the three oxygen atoms. As expected, one of the hydrogen atoms ( $\text{H}_1$ ) in the anion, is directly bonded to P. The P-H distance, 1.17 Å, is, however, very much shorter than the values found in  $\text{PH}_3$ <sup>14</sup> and  $\text{Ca}(\text{H}_2\text{PO}_2)_2$ ,<sup>2</sup> i.e. 1.42 Å and 1.39 Å, respectively, and the P-H bond in  $\text{H}_3\text{PO}_3$  has been shown to have the

Table 4. Distances (Å) and angles (°) in the phosphite ion,  $\text{HPO}_2\text{OH}^-$ . (Standard deviations are given in parentheses).

	P-O <sub>1</sub>	1.511(5)		
	P-O <sub>2</sub>	1.559(7)		
	P-O <sub>3</sub>	1.496(6)		
	P-H <sub>1</sub>	1.17(6)		
O <sub>1</sub> -P-O <sub>2</sub>	112.0(4)		O <sub>1</sub> -O <sub>2</sub>	2.545(8)
O <sub>1</sub> -P-O <sub>3</sub>	114.6(3)		O <sub>1</sub> -O <sub>3</sub>	2.531(7)
O <sub>2</sub> -P-O <sub>3</sub>	107.4(4)		O <sub>2</sub> -O <sub>3</sub>	2.462(10)
O <sub>1</sub> -P-H <sub>1</sub>	108(3)		O <sub>1</sub> -H <sub>1</sub>	2.17(5)
O <sub>2</sub> -P-H <sub>1</sub>	106(4)		O <sub>2</sub> -H <sub>1</sub>	2.19(7)
O <sub>3</sub> -P-H <sub>1</sub>	109(3)		O <sub>3</sub> -H <sub>1</sub>	2.18(6)
P-O <sub>2</sub> -H <sub>2</sub>	108(9)		O <sub>2</sub> -H <sub>2</sub>	1.17(16)

Fig. 2. The  $\text{HPO}_2\text{OH}^-$  anion.

same magnitude as in  $\text{Ca}(\text{H}_2\text{PO}_2)_2$ .<sup>2</sup> This is also supported by the results of IR investigations which show the P–H stretching vibration to have similar values in phosphites ( $2430\text{--}2300\text{ cm}^{-1}$ ) and in hypophosphites ( $2400\text{--}2280\text{ cm}^{-1}$ ).<sup>15</sup> According to the precision in the present work, with  $3\sigma_{\text{P-H1}} = 0.018\text{ \AA}$ , the P–H bond ought, however, to be significantly shorter in  $\text{LiH}_2\text{PO}_3$  than in  $\text{Ca}(\text{H}_2\text{PO}_2)_2$  and in  $\text{H}_3\text{PO}_3$ . Though, bearing in mind that the accuracy of the X-ray data is just above the limit which permits the recognition of hydrogen atoms, this effect must be interpreted very carefully. Similarly, the negative temperature factor of  $\text{H}_1$ , which indicates an excess of negative charge on this atom, might be a result of insufficient accuracy in the data. A more reliable value of the P–H bond length in  $\text{LiH}_2\text{PO}_3$ , obtained, for instance, from a neutron diffraction study, is required before the influence of the polarizing lithium atom on the  $\text{HPO}_2\text{OH}^-$  group can be discussed profitably.

Table 5. P–OH and P–O bond lengths in phosphite compounds.

Compound	Reference	$d(\text{P-OH})\text{ \AA}$	$d(\text{P-O})\text{ \AA}$
$\text{H}_3\text{PO}_3$	1	1.53(2)	1.45(2)
		1.54(2)	1.49(2)
		1.54(2)	
		1.55(2)	
$\text{H}_3\text{PO}_3$	2	1.54(1)	1.48(1)
		1.55(2)	1.51(1)
		1.55(1)	
		1.56(1)	
$\text{CuHPO}_3 \cdot 2\text{H}_2\text{O}$	3		1.514(12)
			1.498(12)
			1.516(12)
$\text{Cu}(\text{H}_2\text{PO}_3)_2$	4	1.561(10)	1.497(9)
		1.579(11)	1.499(9)
			1.504(10)
			1.512(8)
$\text{MgHPO}_3 \cdot 6\text{H}_2\text{O}$	5		1.51(2) 3 distances
$\text{LiH}_2\text{PO}_3$	Present work	1.559(7)	1.496(6)
			1.511(5)

One of the three oxygen atoms of the phosphite ion is situated at a significantly longer distance from the phosphorus atom than the other two, *i.e.* the distance P–O<sub>2</sub> is longer by 0.05–0.06 Å than P–O<sub>1</sub> and P–O<sub>3</sub>. This is also to be expected, since O<sub>2</sub> forms part of the hydroxide group in the HPO<sub>2</sub>OH<sup>–</sup> ion. A comparison between the P–O and P–OH bond distances in some different phosphite compounds is given in Table 5. Averages calculated from all the values listed in this table give bond distances of 1.500 Å and 1.551 Å for P–O and P–OH, respectively, which are in good agreement with the results obtained in this investigation.

Table 6. Intermolecular distances less than 3.2 Å. The symmetry code applied to the co-ordinates in Table 2 gives the position of atom 2. Standard deviations are given in parentheses.

Atom 1	Atom 2	Distance Å	Symmetry code
O <sub>1</sub>	H <sub>2</sub>	1.42(15) <sup>a</sup>	<i>x,y,z</i>
H <sub>1</sub>	H <sub>2</sub>	2.36(21)	1+ <i>x,y,z</i>
O <sub>1</sub>	O <sub>2</sub>	2.567(8) <sup>a</sup>	<i>x</i> –1/2, 1/2– <i>y</i> , 1/2+ <i>z</i>
O <sub>1</sub>	H <sub>1</sub>	2.83(7)	<i>x,y,z</i>
H <sub>1</sub>	H <sub>2</sub>	2.83(21)	<i>x,y,z</i>
O <sub>2</sub>	H <sub>1</sub>	2.95(5)	<i>x,y</i> –1/2, 1/2– <i>z</i>
O <sub>3</sub>	O <sub>2</sub>	2.96(12)	<i>x,y</i> –1/2, 1/2– <i>z</i>
O <sub>1</sub>	H <sub>2</sub>	2.98(17)	1/2+ <i>x</i> , 1/2– <i>y</i> , <i>z</i> –1/2
O <sub>3</sub>	H <sub>1</sub>	3.08(6)	<i>x</i> –1/2, 1/2– <i>y</i> , 1/2+ <i>z</i>
O <sub>3</sub>	H <sub>2</sub>	3.12(10)	<i>x,y,z</i>
H <sub>1</sub>	H <sub>2</sub>	3.13(11)	1/2+ <i>x</i> , 1– <i>y</i> , 1– <i>z</i>
O <sub>1</sub>	O <sub>2</sub>	3.134(7)	<i>x</i> –1/2, 1/2– <i>y</i> , <i>z</i> –1/2
O <sub>1</sub>	H <sub>1</sub>	3.15(7)	<i>x</i> –1, <i>y</i> , <i>z</i>
O <sub>2</sub>	O <sub>3</sub>	3.154(7)	1/2+ <i>x</i> , – <i>y</i> , 1– <i>z</i>
O <sub>2</sub>	H <sub>1</sub>	3.18(5)	<i>x,y,z</i>
O <sub>1</sub>	O <sub>3</sub>	3.197(7)	<i>x</i> , 1/2+ <i>y</i> , 1/2– <i>z</i>

<sup>a</sup> Involved in hydrogen bonding.

Only the hydrogen atom, H<sub>2</sub> of the hydroxide group participates in hydrogen bonding. As is expected, H<sub>1</sub> is not involved in any hydrogen bonds, the closest intermolecular oxygen atom being as remote as 2.83 Å (*cf.* Table 6). The hydrogen bond O<sub>2</sub>–H···O<sub>1</sub> seems to be fairly strong, the O<sub>1</sub>–O<sub>2</sub> distance being 2.567(8) Å. This is in good agreement with the corresponding values

Table 7. Distances (Å) and angles (°) within the LiO<sub>4</sub> tetrahedra. Standard deviations are given in parentheses.

Li–O <sub>1</sub> <sup>a</sup>	1.972(13)	O <sub>1</sub> –Li–O <sub>2</sub>	104.4(7)
Li–O <sub>2</sub>	1.996(16)	O <sub>1</sub> –Li–O <sub>3</sub>	110.8(7)
Li–O <sub>3</sub>	1.913(13)	O <sub>1</sub> –Li–O <sub>3</sub> '	110.2(8)
Li–O <sub>3</sub> '	1.977(21)	O <sub>2</sub> –Li–O <sub>3</sub>	107.6(8)
		O <sub>2</sub> –Li–O <sub>3</sub> '	109.9(7)
		O <sub>3</sub> –Li–O <sub>3</sub> '	113.7(7)

<sup>a</sup> The notation refers to Table 2 applying the following symmetry operations: Li–(*x*, *y*, *z*); O<sub>1</sub>–(*x*, *y*, *z*); O<sub>2</sub>–(*x*–1/2, 1/2–*y*, *z*–1/2); O<sub>3</sub>–(*x*, 1/2–*y*, 1/2–*z*); O<sub>3</sub>'–(1/2+*x*, 1/2–*y*, *z*–1/2).

found in  $\text{H}_3\text{PO}_3$ ,<sup>2</sup> (2.525 Å–2.599 Å). The position of  $\text{H}_2$  is rather uncertain, the O–H bond distance being 1.17 Å with an estimated standard deviation of 0.16 Å. The mean O–H distance in  $\text{H}_3\text{PO}_3$  obtained by Loopstra<sup>2</sup> was 0.97 Å, but as he pointed out this value would appear to be slightly too short, in view of the strong hydrogen bonding. The values quoted in the *International Tables* are longer, and the average O–H distance tabulated for  $\text{KH}_2\text{PO}_4$  is 1.08 Å.<sup>14</sup>

The  $\text{LiO}_4$  tetrahedra show only minor distortions from regularity (cf. Table 7). The average Li–O distance is 1.965 Å which seems reasonable in comparison with the corresponding value of 1.98 Å given in the *International Tables*.<sup>14</sup> In a recent investigation of  $\text{NH}_4\text{LiSO}_4$ ,<sup>16</sup> this mean value was found to be as low as 1.915 Å, but since the standard deviations range from 0.018 Å to 0.105 Å for the Li–O bond lengths in  $\text{NH}_4\text{LiSO}_4$ , the difference is not significant.

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