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Synthesis and Crystal Structure of the Lithium Cyclohexaphosphate Hydrate: $Li_6P_6O_{18} \cdot 9H_2O$

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Preparation and complete structural characterization by X-ray diffraction, IR absorption, DTA, and GTA are given for a new lithium cyclohexaphosphate hydrate: $Li_6P_6O_{18} \cdot 9H_2O$. This compound is monoclinic, $C2/c$, with a = 15.429(8), b = 11.794(5), c = 14.369(8) Å, β = 115.95(5), V = 2351(5) Å^3, Z = 4, R = 0.049, R_w = 0.052 for 1959 independent reflections with $I > 3\sigma(I)$. Layers of P_6O_{18} rings, with the $\bar{1}$ internal symmetry, are stacked along the c axis. Three Li coordination polyhedra (tetrahedra, pseudosquare or pseudosquare pyramid) share common edges as to form Li_3O_8 or Li_3O_9 groups. These cationic groups interconnect the rings in a three-dimensional way. Among the nine water molecules, five participate in the different lithium environments. The other ones are nonbonded water molecules and are disordered over several sites lying between the superimposed rings of two successive layers. © 1994 Academic Press, Inc.

INTRODUCTION

During a systematic investigation of monovalent cation cyclohexaphosphates a form of the lithium salt has been synthesized. Several lithium cyclohexaphosphates with different degrees of hydration have already been reported by Schülke and Kayser (1), namely: two forms of the anhydrous salt $Li_6P_6O_{18}$, one form of the monohydrate $Li_6O_6O_{18} \cdot H_2O$, two forms of the tetrahydrate $Li_6P_6O_{18} \cdot 4H_2O$, and one form of the hexahydrate $Li_6P_6O_{18} \cdot 6H_2O$. But only chemical preparation and nonindexed powder diagrams are given by the authors for identifying these compounds.

More recently, Trunov *et al.* (2) performed the crystal structure of the pentahydrate $Li_6P_6O_{18} \cdot 5H_2O$ which has the same diffraction pattern as $Li_6P_6O_{18} \cdot 6H_2O$. According to these authors, owing to the existence of a nonbonded water molecule with an occupancy rate of 0.5 in the studied structure, it is possible that the atomic arrangement contains a greater proportion of such water and thus becomes the structure of an hexahydrate. Nevertheless, the lithium cyclohexaphosphate, newly prepared from an aqueous solution at room temperature and named hexahydrate by all the previous authors, has never been actually observed until now.

The present work reports the chemical preparation and the crystal structure of another hydrate of lithium cyclohexaphosphate whose formula unit contains five bonded water molecules and about three nonbonded statistical ones.

EXPERIMENTAL

A. Chemical Preparation

In an aqueous solution of $Li_6P_6O_{18} \cdot H_2O$ heated at about 70°C was added dropwise the dimethylformamide (DMF) or the dimethylsulfoxide (DMSO) until the appearance of a very light turbidity. The resulting solution was kept at room temperature. A few hours later appeared crystals of a new lithium cyclohexaphosphate hydrate as multifaceted prisms. The crystals can be dissolved in water. The $Li_6P_6O_{18} \cdot 6H_2O$ used in this preparation has been obtained from Schülke and Kayser process (1). Moreover, it can be regenerated by slow addition of acetone to the aqueous solution of the new cyclohexaphosphate.

B. Characterization

The title compound and eventually other related phosphates have been studied through different techniques with experimental conditions described below.

1. X-ray diffraction. Powder diffraction patterns were registered using a Philips-Norelco diffractometer with the Cu$K\bar{\alpha}$ radiation (λ = 1.5418 Å) and a scan rate of $\frac{1}{2}$° or $\frac{1}{8}$° (θ)/min.

A preliminary single crystal study of the new compound has been realized with a Weissenberg camera (STOE) operating with the Cu$K\bar{\alpha}$ radiation.

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TABLE 1

Crystal Data and Experimental Parameters for Intensity Data Collection

Cell parameters refined from 16 reflections with $10 < \theta < 15°$	$a = 15.429(8)$, $b = 11.794(5)$, $c = 14.369(8)$ Å $\beta = 115.95(5)°$
Z, V, M_W	4, 2351 (5) Å^3, 663.90
Space group	$C2/c$
Density (calc.)	1.875 g cm^{-3}
$\mu(\text{Mo}K\bar{\alpha})$	0.575 mm^{-1}
Crystal dimensions	0.48 × 0.32 × 0.26 mm
Apparatus	Philips PW 1100
Wavelength	Mo$K\bar{\alpha}$ (0.7107 Å)
Monochromator	Graphite plate
Scan mode	$\omega/2\theta$
Theta range	2–35°
Scan width	1.20°
Scan speed	0.02° s^{-1}
Number of independent collected reflections	3693
Total background measuring time	6 sec
Intensity and orientation reference reflections	800, $\bar{8}00$

The structural analysis has been performed from data collection obtained with a Philips PW 1100 automatic diffractometer. The experimental conditions used during the measurements are detailed in Table 1. Corrections were applied for Lorentz and polatization effects but not for absorption. The structure was solved by a direct method using MULTAN 77 (3) in the case of a centrosymmetric symmetry. The light atoms (Li, H) were localized by difference-Fourier syntheses. All calculations were carried out using the Enraf-Nonius Structure Determination Package (4) with a MicroVax II computer. Atomic scattering factors were taken from the International Tables for X-ray Crystallography, Table 2-2B (5). Refinements were run using full-matrix least-squares and a unitary weighting scheme.

The figures were drawn using the program STRUPLO (6).

2. *Thermogravimetric and differential thermal analysis (TG and DTA).* Both analyses were performed using a Setaram analyzer. The powder samples (23 mg) were heated from room temperature to 700°C at heating rate of 13°C/min.

3. *Infrared (IR) absorption.* Spectra were recorded on a Perkin-Elmer spectrophotometer (IR 983G) using samples in spectroscopically pure KBr pellets.

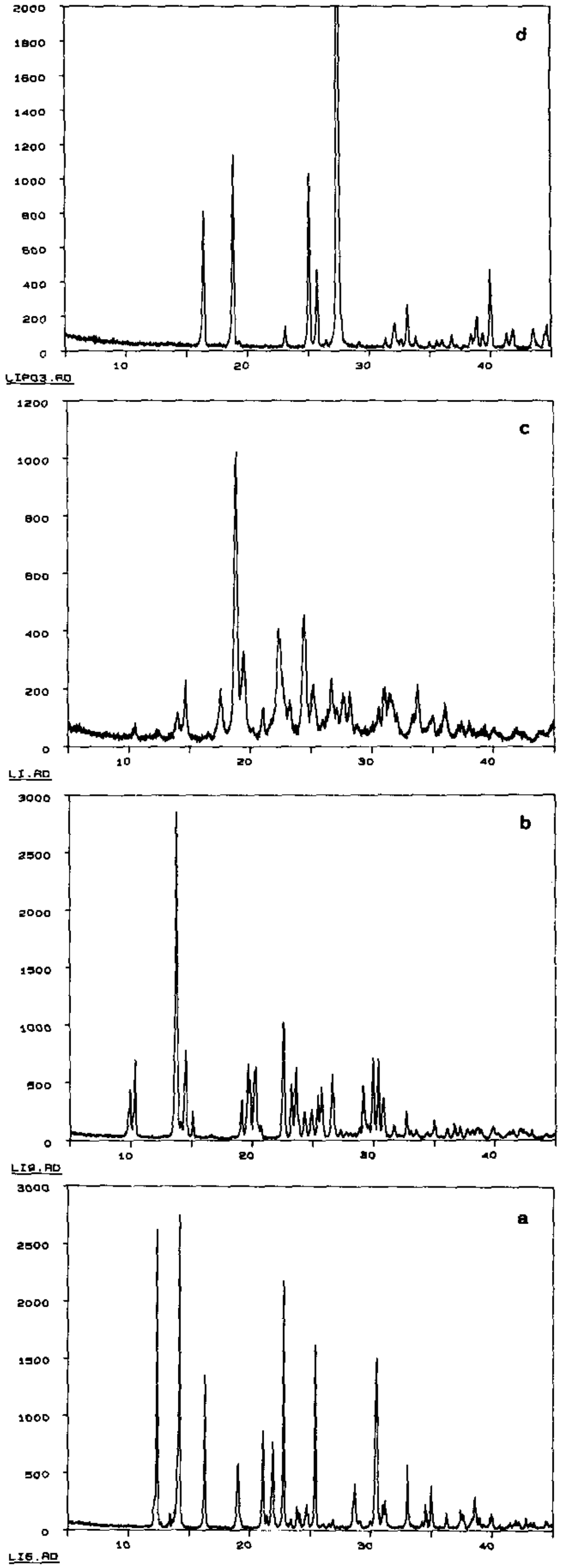

FIG. 1. X-ray diffraction diagrams of the phosphates: (a) $Li_6P_6O_{18} \cdot 6H_2O$, (b) $Li_6P_6O_{18} \cdot 9H_2O$, (c) $Li_6P_6O_{18}$(I), and (d) $LiPO_3$.

TABLE 2

X-Ray Powder Diffraction Data for $Li_6P_6O_{18}\cdot 6H_2O$ and $Li_6P_6O_{18}\cdot 9H_2O$

h	k	l	d_{cal} (Å)	d_{obs} (Å)	I/I_0
			$Li_6P_6O_{18}\cdot 6H_2O$		
0	1	0	7.233	7.232	100
1	1	0	6.670	6.668	4
−1	−1	1	6.281	6.282	84
0	−1	1	5.477	5.475	43
1	−1	0	4.676	4.676	25
−2	−1	0	4.233	4.232	50
−2	0	1	4.175	4.172	6
−1	1	1	4.070	4.073	38
−1	−2	1	3.917	3.917	42
−1	−1	2	3.823	3.823	5
−1	0	2	3.708	3.708	7
0	2	0	3.617	3.616	11
0	0	2	3.526	3.526	18
0	−2	1	3.434	3.435	2
0	−1	2	3.375	3.376	3
2	2	0	3.335	3.334	3
−1	−2	2	3.126	3.124	20
−1	1	2	2.946	2.945	85
−3	−2	1	2.938	2.939	60
−3	−1	2	2.890	2.891	6
−1	2	1	2.719	2.719	24
2	2	1	2.631	2.631	6
−3	0	2	2.606	2.605	19
			$Li_6P_6O_{18}\cdot 9H_2O$		
1	1	0	8.996	8.992	15
−1	1	1	8.599	8.600	23
0	0	2	6.450	6.451	100
−1	1	2	6.119	6.119	14
0	2	0	5.893	5.896	8
1	1	2	4.659	4.660	11
−3	1	2	4.536	4.535	23
2	2	0	4.498	4.498	17
−1	1	3	4.389	4.388	21
2	0	2	3.952	3.950	35
−4	0	2	3.840	3.839	16
1	3	0	3.781	3.780	21
−2	2	3	3.665	3.666	8
−2	0	4	3.580	3.579	8
1	3	1	3.518	3.518	12
0	2	3	3.474	3.475	15
−1	1	4	3.350	3.350	18
2	2	2	3.282	3.282	3
1	3	2	3.106	3.106	3
−3	3	2	3.069	3.069	16
−1	3	3	3.022	3.022	4
−5	1	2	2.992	2.992	25
0	4	0	2.947	2.947	13
−5	1	1	2.912	2.912	10
2	2	3	2.747	2.747	12
−6	0	2	2.568		
2	4	1	2.569	2.568	9

RESULTS AND DISCUSSION

A. Crystal Data

The study by film technique shows the symmetry to be monoclinic with two possible space groups: *Cc* or *C*2/*c* ($h\ k\ l$ with $h + k = 2n$ and $h\ 0\ l$ with $l = 2n$).

A least-squares refinement of the powder diffraction angular data obtained with a low scan speed leads to the following unit cell parameters:

$$a = 15.464(4),\ b = 11.786(3),\ c = 14.327(4)\ \text{Å},\quad \beta = 115.78(1)^\circ,\ V = 2351(2)\ \text{Å}^3$$

These values are comparable to those obtained with the four circle diffractometer data (cf. Table 1).

The starting material $Li_6P_6O_{18}\cdot 6H_2O$ [$a = 9.524(5)$, $b = 8.063(3)$, $c = 7.811(3)$ Å, $\alpha = 107.19(5)$, $\beta = 114.04(5)$, $\gamma = 65.19(4)^\circ$] and the new lithium salt can be rapidly distinguished by the indexed powder diagrams given in Table 2 and represented in Figs. 1a and 1b respectively.

B. Refinement and Unit Formula

The crystal structure determination confirms the choice of the centrosymmetric space group *C*2/*c* and the ring configuration of the phosphoric anion. At the last stage of the refinement ($R = 0.079$) after the localization of all the atoms relevant to the P_6O_{18} ring and to the Li coordination polyhedra, the difference-Fourier map revealed several significant peaks we attributed to fragments of water molecules, denoted O(W4), O(W5), O(W6), O(W7), and O(W8). Refinements of the occupancy-rates lead respectively to 0.346(7), 0.61(1), 0.28(1), 0.122(7), and 0.261(9) whose the sum x is the noninteger number 1.62(5). Thus the formula unit of the studied compound should be $Li_6P_6O_{18}\cdot(5 + 3.24)H_2O$. Owing to the high thermal motion of these fragments we did not determine their H atoms. Anisotropic full-matrix least-squares refinements (on F) for the non-H-atoms, isotropic ones for the H-atoms, were applied with 1959 reflections such that $I > 3\sigma(I)$ and $|F_o - F_c| \leq F_o/5$. In this case, the final R value is 0.049, the R_w value is 0.052. The maximum peak-height in the final difference-Fourier synthesis is $0.311\ e\ A^{-3}$.

C. Thermal Results

The DTA curve (Fig. 2) exhibits six endothermic peaks.

—The peaks lying at 128, 172, 236 and 298°C define four stages of dehydration. To each of these peaks corresponds a weight loss confirmed by a peak on the DTG curve representing the derivative of the TGA curve (Fig. 2). The whole weight loss accompanying the dehydration is evidenced in the TG curve and is equivalent to the departure of nine water molecules per formula unit of

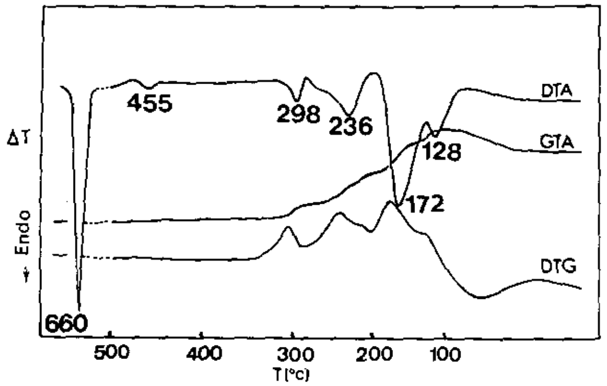

FIG. 2. Thermogravimetric and differential thermal analysis curves for $Li_6P_6O_{18} \cdot 9H_2O$.

cyclohexaphosphate (experimental and calculated weight percentage of the water content are 23.8 and 23.93% respectively), therefore an excess of 0.76 H_2O relatively to the refinement result. In this case the calculated weight loss being 22.5% the difference between the results cannot be explained by the measurement accuracy (cf. discussion in the last part of the structure description). The complete dehydration occurring at about 298°C leads to a crystalline form which was identified to $Li_6P_6O_{18}$(I) (1) by X-ray diffraction (cf. Fig. 1c).

—The peak observed at 455°C reveals a decomposition of the cyclohexaphosphate resulting in the lithium polyphosphate $LiPO_3$ (7), the powder pattern of which is illustrated by the Fig. 1d.

—The peak at 660°C indicates the melt of $LiPO_3$.

So, the thermal behavior of the title compound can be summarized by the following schema:

$$Li_6P_6O_{18} \cdot 9H_2O \rightarrow Li_6P_6O_{18} \cdot nH_2O \rightarrow Li_6P_6O_{18}(I) \rightarrow 6LiPO_3$$

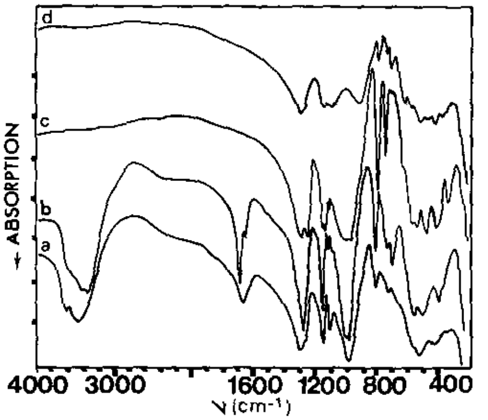

FIG. 3. IR spectra of the phosphates: (a) $Li_6P_6O_{18} \cdot 6H_2O$, (b) $Li_6P_6O_{18} \cdot 9H_2O$, (c) $Li_6P_6O_{18}$(I), and (d) LiPO3.

D. *IR Absorption Analysis*

The IR spectra of $Li_6P_6O_{18} \cdot 6H_2O$ (a), $Li_6P_6O_{18} \cdot 9H_2O$ (b), $Li_6P_6O_{18}$(I) (c), and $LiPO_3$ (d) can be compared in Fig. 3. The results of the previous thermal analysis are confirmed by the IR spectra study. The water characteristic vibrations have disappeared after the complete dehydration.

—Between 1300 and 600 cm^{-1} the spectra (a), (b), and (c) show valency vibration bands characteristic of phosphates with ring anions. Among these bands can be distinguished:

* the vibration bands of the [O–P–O] end groups at high frequencies:

$$1200 < \nu_{as} < 1300\ cm^{-1} \text{ and } 1100 < \nu_s < 1200\ cm^{-1}$$

* the valency vibrations of the [P–O–P] ring groups represented by a wide band centered at about 980 cm^{-1} which can be attributed to the ν_{as} (P–O–P) antisymmetric vibrations and by a double band between 700 and 800 cm^{-1} which can be related to the ν_s (P–O–P) symmetric vibrations.

—In the same frequency domain, the spectrum (d) displays bands of which position and number characterize a condensed phosphate with a linear chain anion (8). The intense absorption band centered at about 900 cm^{-1} is the most typical. The nature of the vibration corresponding to the different observed bands is given in Table 3.

The IR absorption results agree also with those obtained by X-ray diffraction.

E. *Structure Description*

The final atomic coordinates of the whole structure are reported in Table 4.[2] The main geometrical features of the P_6O_{18} ring and the Li polyhedra as well as a part of the hydrogen-bond scheme are described in Table 5.

Figure 4 shows the atomic arrangement, projected along the **b** axis, consisting of P_6O_{18} ring layers stacked along the **c** axis. Figure 5 represents only one anionic layer projected along the **c** axis, with the P_6O_{18} rings centered on the inversion centers (4a) and (4b). The Li coordination polyhedra gather themselves in Li_3O_8 and Li_3O_9 groups interconnecting the rings in a three-dimensional way. Nonbonded water molecules are distributed between the quasi-superimposed rings of two successive layers.

1. The P_6O_{18} ring-anion. As for the great majority of the presently known cyclohexaphosphates, the P_6O_{18} ring has $\bar{1}$ internal symmetry. It is rather regular since the P–P–P angles spread from 111.22° to 126.94° (from 106° to 122° in $Li_6P_6O_{18} \cdot 5H_2O$ (2)).

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[2] Lists of structure factors and anisotropic thermal parameters are available on request.

TABLE 3

Frequencies (cm^{-1}) of IR Absorption Bands for (a) $Li_6P_6O_{18} \cdot 6H_2O$, (b) $Li_6P_6O_{18} \cdot 9H_2O$, (c) $Li_6P_6O_{18}$(I), and (d) $LiPO_3$

(a)	(b)	(c)	(d)	Vibration
3630	3640	—	—	
3460	3420	—	—	ν(OH)
—	3340	—	—	
1665	1680	—	—	δ(HOH)
1655	1650	—	—	
1300	1315	1290	1300	
1280	1270	1270	—	$\nu_{as}(PO_2)$
1260	—	—	1260	
—	1150	1160	—	
1145	—	1140	1145	
1095	1110	1110	1110	$\nu_s(PO_2)$
—	1080	—	1080	
—	1000	1010	—	
980	980	980	—	ν_{as}(POP)
—	—		910	
800	800	800	785	ν_s(POP)
—	—	740	725	
—	695	—	700	
—	—	630	610	
585	580	570	570	
—	540	540	520	$\delta(PO_2)$
—	500	480	480	
—	—	—	460	
—	—	—	420	
420	390	410	370	δ(POP)
340	390	330	350	

2. *The Li coordination.* Three types of coordination of the Li atom coexist in this structure. Li(1)O_4 and Li(2)O_4 are distorted tetrahedra, the last one being built by both two oxygen of the rings and two water molecules O(W1) and O(W2). Li(4)O_4 is a pseudosquare centered on the $\bar{1}$ center (4c) and Li(3)O_5 a pseudosquare pyramid whose aperture is O(W3) situated on the twofold axis. It is worth noticing that all the external oxygen atoms of the phosphoric rings participate to the environment of the Li atoms.

Li(2)O_4, Li(4)O_4, and Li(2)O_4'' (sharing the edges O(E11)–O(E31) form Li_3O_8 groups which interconnect the rings inside an anionic layer, along the [$\bar{1}$ 1 0] direction at $z \approx 0$, along the [1 1 0] direction at $z \approx 0.5$ (Fig. 5). Li(1)O_4, Li(3)O_4, and Li(1)O_4' sharing the edges O(E12)–O(E21) form Li_3O_9 groups which intereonnect the rings both inside a layer and between the layers along the **c** direction (Fig. 4).

This type of linkage between the Li polyhedra differs essentially from that observed in $Li_6P_6O_{18} \cdot 5H_2O$ where the LiO_4 tetrahedra form six-membered groups Li_6O_{16} joined together by a common edge.

3. *The water molecules.* O(W1), O(W2) and O(W3) take part in the coordination of the Li atoms. The first water molecule is connected by H-bonds to the O(E22) and O(E32) oxygen atoms of different rings maintaining in that manner a certain cohesion between the successive layers. Other H-bonds starting from O(W2) are directed towards O(W1) belonging to different Li_3O_8 groups in a same layer and complete thus the intralayer cohesion.

The H-atoms of the O(W3) water molecule on the twofold axis have not been determined because of the presence of the O(W8) fragment in general position quite near of O(W3). A refinement of this position with the scattering factor of an H-atom increases the *R* value (0.052 instead of 0.049) and gives again a distinct peak at the same position in the difference-Fourier synthesis.

TABLE 4

Final Atomic Coordinates and B_{eq} (B_{iso} for H atoms) for $Li_6P_6O_{18} \cdot 9H_2O$

Atom	*x*	*y*	*z*	$B_{eq}{}^a/B_{iso}$	N^b
P(1)	0.09453(7)	0.20127(9)	0.58642(8)	1.53(2)	
P(2)	0.11657(7)	−0.21049(9)	0.48456(8)	1.43(2)	
P(3)	0.20707(7)	0.00746(9)	0.57128(9)	1.67(2)	
O(E11)	0.1428(2)	0.2719(3)	0.5377(3)	2.62(6)	
O(E12)	0.1069(2)	0.2293(3)	0.6917(2)	2.54(7)	
O(L12)	0.0169(2)	0.1977(3)	−0.0087(2)	2.35(7)	
O(L13)	0.1229(2)	0.0721(3)	0.5846(3)	2.48(6)	
O(E21)	0.0987(2)	−0.2604(3)	0.3827(2)	1.88(6)	
O(E22)	0.1845(2)	−0.2683(3)	0.5800(2)	2.09(7)	
O(L23)	0.1477(2)	−0.0822(3)	0.4836(2)	2.41(7)	
O(E31)	0.2546(2)	0.0853(3)	0.5270(3)	2.66(7)	
O(E32)	0.2329(3)	0.4467(3)	0.8312(3)	2.70(8)	
O(W1)	0.1552(3)	0.4828(3)	0.1305(3)	2.81(8)	
O(W2)	0.4636(3)	−0.0033(4)	0.6031(3)	4.0(1)	
O(W3)	0.000	0.9642(5)	0.250	4.8(2)	0.5
O(W4)	0.000	0.1513(9)	0.250	6.1(3)	0.346(7)
O(W5)	0.9198(8)	0.214(2)	0.239(1)	12.8(5)	0.61(1)
O(W6)	0.147(1)	0.184(2)	0.301(2)	7.6(6)	0.28(1)
O(W7)	0.000	0.339(3)	0.250	5.8(9)	0.122(7)
O(W8)	0.044(1)	0.042(1)	0.256(1)	4.8(5)	0.261(9)
Li(1)	0.6912(5)	0.2114(7)	0.3238(5)	1.8(1)	
Li(2)	0.1433(6)	0.4296(7)	0.5111(6)	2.5(2)	
Li(3)	0.000	0.806(1)	0.250	2.5(2)	0.5
Li(4)	0.250	0.250	0.500	8.5(4)	0.5
H(1W1)	0.316(4)	0.986(7)	0.313(5)	3(2)	
H(2W1)	0.832(5)	0.416(7)	0.382(5)	4(2)	
H(1W2)	0.021(5)	0.488(7)	0.128(5)	4(2)	
H(2W2)	0.059(5)	0.512(8)	0.462(6)	6(2)	

[a] $B_{eq} = \frac{4}{3} \Sigma_i \Sigma_j \mathbf{a}_i \cdot \mathbf{b}_j \cdot \beta_{ij}$.

[b] *N* is the fractional site occupancy. Estimated standard deviations are given in parentheses.

O(W8), as the other fragments, O(W5) and O(W6) in general positions, O(W4), and O(W7) in special positions, are not involved in the associated-cation polyhedra. Otherwise, all these disordered molecules and O(W3) are situated rather close to each other on or around the twofold axis at $z \approx \pm 0.25$, O(W4) being the central part of this assembly. Thus are formed "aqueous layers" inserted between the anionic layers at $z \approx 0$ and 0.5. As it is often observed in highly hydrated compounds, the thermal factors of the nonbonded water molecules are significantly larger than those belonging to the cation coordination. Nevertheless, all the corresponding thermal ellipsoids are well definite, the directions of the maximum vibration amplitudes lying in the layer plane. Lastly, it must be noticed that the simple addition of the 3.24 disordered water molecules in the structure involves a decrease of 3% for the *R* value, that would confirm the real contribution of this type of water to the cyclohexaphosphate structure.

As previously reported concerning the total number of water molecules the thermogravimetric measurements give a number of 9 H_2O for one formula unit $Li_6P_6O_{18}$

TABLE 5

Main Interatomic Distances (Å) and Bond Angles (°) for $Li_6P_6O_{18} \cdot 9H_2O$

The P_6O_{18} ring anion

The P(1)O_4 tetrahedron

P(1)	O(E11)	O(L12)	O(L13)	O(E12)
O(E11)	**1.481(4)**	107.2(2)	109.4(2)	119.4(2)
O(L12)	2.473(5)	**1.589(4)**	100.6(2)	110.0(2)
O(L13)	2.506(5)	2.445(4)	**1.588(4)**	108.6(2)
O(E12)	2.554(6)	2.512(4)	2.490(5)	**1.477(4)**

The P(2)O_4 tetrahedron

P(2)	O(E21)	O(L12)	O(L23)	O(E22)
O(E21)	**1.487(3)**	109.3(2)	107.1(2)	118.8(2)
O(L12)	2.510(5)	**1.589(4)**	102.4(2)	107.4(2)
O(L23)	2.476(4)	2.477(5)	**1.589(3)**	110.7(2)
O(E22)	2.553(4)	2.473(4)	2.524(4)	**1.479(3)**

The P(3)O_4 tetrahedron

P(3)	O(E31)	O(L13)	O(L23)	O(E32)
O(E31)	**1.482(4)**	109.8(2)	107.1(2)	118.9(2)
O(L13)	2.512(6)	**1.588(4)**	101.4(2)	108.9(2)
O(L23)	2.473(5)	2.461(5)	**1.592(3)**	109.4(2)
O(E32)	2.553(5)	2.500(4)	2.511(4)	**1.483(3)**

P(1)–O(L12)–P(2)	137.1(2)	P(1)–P(2)–P(3)	111.23(5)
P(1)–O(L13)–P(3)	135.1(2)	P(1)–P(3)–P(2)	121.82(5)
P(2)–O(L23)–P(3)	134.1(2)	P(2)–P(1)–P(3)	126.92(5)

P(1)–P(2)	2.959(2)
P(2)–P(3)	2.936(2)
P(3)–P(4)	2.930(2)

The Li coordination polyhedra

The Li(1)O_4 tetrahedron

Li(1)	O(E12)	O(E21)	O(E22)	O(E32)
O(E12)	**1.903(7)**	93.4(3)	128.2(5)	117.9(4)
O(E21)	2.827(5)	**1.981(10)**	108.2(4)	114.7(4)
O(E22)	3.446(4)	3.166(5)	**1.929(7)**	95.3(3)
O(E32)	3.310(5)	3.317(5)	2.874(4)	1.960(9)

The Li(2)O_4 tetrahedron

Li(2)	O(E11)	O(E31)	O(W1)	O(W2)
O(E11)	**1.900(9)**	92.6(4)	110.5(5)	122.0(4)
O(E31)	2.737(5)	**1.889(11)**	122.5(4)	107.7(5)
O(W1)	3.156(5)	3.358(6)	**1.942(10)**	103.0(4)
O(W2)	3.366(5)	3.099(5)	3.045(5)	**1.949(8)**

The Li(3)O_5 polyhedron		The Li(4)O_4 "square"	
Li(3)–O(E12)	2.194(5) (×2)	Li(4)–O(E11)	1.970(4) (×2)
Li(3)–O(E21)	2.008(6) (×2)	Li(4)–O(E31)	1.976(3) (×2)
LI(3)–O(W3)	1.862(14)	O(E11)–Li(4)–O(E31)	92.1(2) (×2)
		O(E11)–Li(4)–O(E31)″	87.9(2) (×2)
Li(1)–Li(3)	2.889(8)	Li(2)–Li(4)	2.730(9)

The hydrogen bonds

O–H . . . O	O–H	H . . . O	O–O	O–H–O
O(W1)–H(1W1) . . . O(E32)	0.74(6)	2.03(7)	2.723(5)	158(8)
O(W1)–H(2W1) . . . O(E22)	0.85(8)	1.87(8)	2.723(5)	174.(4)
O(W2)–H(1W2) . . . O(W1)	0.81(7)	2.06(8)	2.817(6)	155(7)
O(W2)–H(2W2) . . . O(W1)	0.85(8)	2.22(7)	3.045(5)	164(9)

H(1W1)–O(W1)–H(2W1)	102(7)
H(1W2)–O(W2)–H(2W2)	110(8)

Note. Estimated standard deviations are given in parentheses.

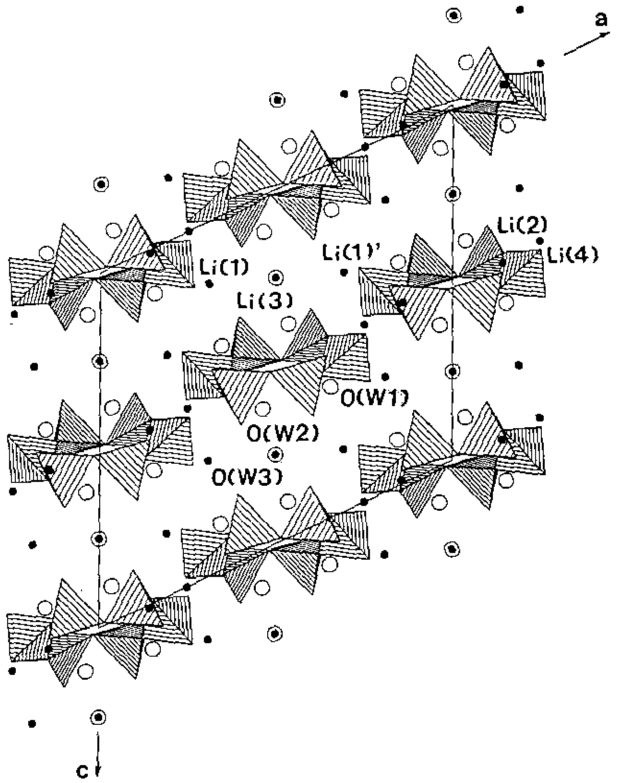

FIG. 4. Projection along the **b** axis of the atomic arrangement of $Li_6P_6O_{18} \cdot 9H_2O$. Li(1)′ is the equivalent position of Li(1) by the twofold axis symmetry ($z = \pm 0.25$). In this projection, the fragments O(W4) and O(W7) are superimposed to the O(W3) position on the twofold axis. The other fragments O(W5), O(W6), and O(W8) would be projected in general positions near this axis.

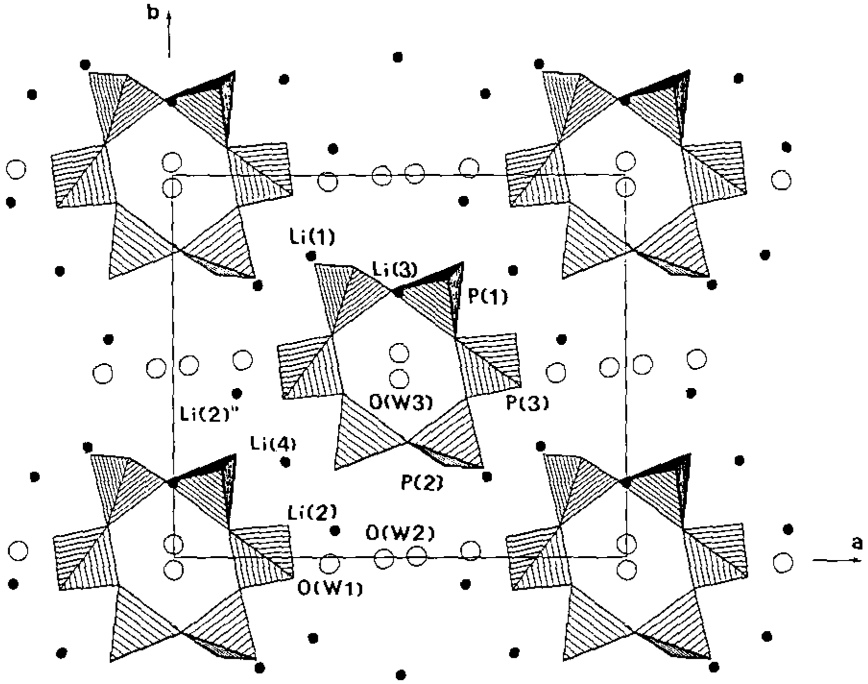

FIG. 5. Projection along the c axis of the atomic arrangement of $Li_6P_6O_{18} \cdot 9H_2O$ with $0.25 < y < 0.75$. The PO_4 tetrahedra of the P_6O_{18} groups are denoted by the names of their central P atoms. Li(2)'' is the equivalent position of Li(2) by inversion around Li(4) in (4*d*). The water molecule fragments are not represented.

while the crystallographic study leads scarcely to 8.24 H_2O. But it is possible that the structural arrangement contains more water fragments, owing to the disordered character of these nonbonded water molecules and to the vacant space between the superimposed rings.

Otherwise the discrepancy between these results can be explained by some remarks about this type of compound. Indeed it has been observed that the number of water molecules depend essentially of the conditions of preparation and also of the sample age. So, a slight modification in the chemical preparation or experiments dispersed in the time can give different degrees of hydration without modifying the general motif of this structure. Such a behavior has already been pointed out by Trunov *et al.* (2) for the pentahydrate $Li_6P_6O_{18} \cdot 5H_2O$ structure which can be also the structure of a hexahydrate or in certain conditions of a tetrahydrate.

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