

Structure of Tetralithium Tetrametaphosphate Pentahydrate

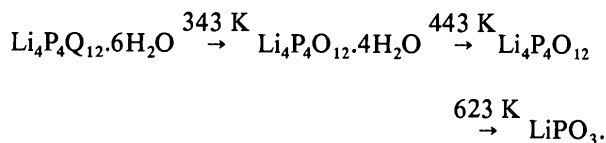
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Abstract. $\text{Li}_4\text{P}_4\text{O}_{12}\cdot 5\text{H}_2\text{O}$, $M_r = 433.71$, monoclinic, $C2/c$, $a = 17.073$ (8), $b = 17.029$ (8), $c = 13.554$ (6) Å, $\beta = 127.32$ (1)°, $V = 3133.8$ Å³, $Z = 8$, $D_x = 1.838$ Mg m⁻³, $\lambda(\text{Ag K}\alpha) = 0.5608$ Å, $\mu = 0.3$ mm⁻¹, $F(000) = 1744$, $T = 293$ K, final $R = 0.034$ for 3022 independent observed reflexions. The atomic arrangement may be schematically described as a stacking of alternating P_4O_{12} ring anions and cyclic $\text{Li}_8\text{O}_{16}(\text{H}_2\text{O})_6$ groups. Two of the five water molecules are of a zeolitic nature. The group of the five water molecules builds pentagonal rings with an average $\text{O}(W)\text{—O}(W)\text{—O}(W)$ angle of 107.6°, showing these rings to be flat.

Introduction. Hydrated lithium tetrametaphosphate was described for the first time by Grunze & Thilo (1955). These authors reported for this salt a chemical formula corresponding to a tetrahydrate: $\text{Li}_4\text{P}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$. Later on, a crystal-chemistry study by Grenier & Durif (1973) concluded that freshly prepared lithium tetrametaphosphate is a hexahydrate. From thermogravimetric experiments run with various aged specimens, these authors suspected that some of the water molecules must be of a zeolitic nature, with a departure of two of them at 343 K according to the following scheme:



In the present structural work, the first one on lithium tetrametaphosphate, we observe the existence of three constitutional water molecules and of two zeolitic ones leading thus to the formula of a pentahydrate for this salt.

Experimental. Crystals were prepared by using the process reported by Grenier & Durif (1973). Density not measured. $0.44 \times 0.42 \times 0.42$ mm fragment of crystal. Philips PW 1100 diffractometer, graphite monochromator. Systematic absences: hkl : $h + k = 2n$; $h0l$: $h = 2n$, $l = 2n$. 14 reflexions ($10 < \theta < 15^\circ$) for refining unit-cell dimensions. ω scan. 5603 reflexions measured

($3 < \theta < 30^\circ$), $\pm h, k, l$, $h_{\text{max}} = 30$, $k_{\text{max}} = 25$, $l_{\text{max}} = 19$. Scan width 1.20° , scan speed $0.02^\circ \text{ s}^{-1}$, total background measuring time 20 s. Two intensity and orientation reference reflexions (590 and 590) every 2 h, no variation. Lorentz–polarization correction, no absorption correction. Direct methods (*MULTAN77*, Main, Lessinger, Woolfson, Germain & Declercq, 1977) used for structure determination. Anisotropic full-matrix least-squares refinement (on F). Unit weights. Final refinement with 3022 reflexions corresponding to: (a) $I > 12\sigma_I$, (b) $\sin\theta/\lambda > 0.30$ Å⁻¹. Final $R = 0.034$ ($wR = 0.038$). For the complete set of 5603 reflexions $R = 0.051$. $S = 1.141$. Max. $\Delta/\sigma = 2.30$ (β_{13} of a zeolitic water molecule). Max. peak height in final difference Fourier synthesis 0.76 e \AA^{-3} . No extinction correction. Scattering factors for neutral atoms and f' , f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. H atoms could not be located.

Final atomic coordinates and B_{eq} are reported in Table 1.*

Discussion. The two crystallographically independent P_4O_{12} ring anions observed in this atomic arrangement have a twofold symmetry. Examination of the interatomic distances and bond angles in these rings (Table 2) shows that they also have a strong pseudofourfold symmetry. Fig. 1 gives a projection along the b axis of part of this arrangement showing the respective locations of the P_4O_{12} rings and Li atoms.

Three of the four Li atoms have a tetrahedral coordination comprising three O atoms and one water molecule [Li(2) and Li(4)] or four O atoms [Li(1)]. The last Li atom [Li(3)] has a fivefold coordination: a square pyramid built up of four O atoms and one water molecule. These LiO_4 or LiO_5 polyhedra link themselves so as to form a large ring located around the twofold axis. The global formula of such a ring corresponds to $\text{Li}_8\text{O}_{16}(\text{H}_2\text{O})_6$. Li atoms in the fivefold

* Lists of observed and calculated structure factors and of anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42568 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

coordination have a common edge with each of the two adjacent LiO_4 tetrahedra while two adjacent LiO_4 tetrahedra share a corner. The mean plane of such a ring is perpendicular to the b axis. Fig. 2 gives the projection of an $\text{Li}_8\text{O}_{16}(\text{H}_2\text{O})_6$ ring along the b axis.

Table 1. Final atomic coordinates and B_{eq} for $\text{Li}_4\text{P}_4\text{O}_{12}\cdot 5\text{H}_2\text{O}$

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
P(1)	0.10931 (4)	0.21852 (4)	0.72686 (5)	1.29 (1)
P(2)	0.10514 (4)	0.22532 (4)	0.94042 (5)	1.25 (1)
P(3)	0.10694 (4)	0.47358 (4)	0.22564 (5)	1.103 (9)
P(4)	0.10625 (4)	0.47192 (4)	0.44027 (5)	1.070 (9)
O(W1)	0.3302 (7)	0.3359 (6)	0.506 (2)	24.3 (6)
O(W2)	0.1202 (2)	0.0111 (2)	0.4616 (4)	4.88 (9)
O(W3)	0.0058 (2)	0.2491 (2)	0.1389 (3)	4.59 (7)
O(W4)	0.1691 (2)	0.1354 (2)	0.2255 (3)	4.55 (8)
O(W5)	0.0823 (3)	-0.0047 (3)	0.190 (1)	15.4 (4)
O(E11)	0.8239 (1)	0.1498 (1)	0.7280 (2)	2.02 (4)
O(E12)	0.1187 (1)	0.2823 (1)	0.6603 (2)	2.27 (4)
O(L12)	0.1129 (1)	0.2586 (1)	0.8361 (2)	1.55 (3)
O(L21)	0.0003 (1)	0.1824 (1)	0.6394 (2)	1.36 (3)
O(E21)	0.1020 (1)	0.2945 (1)	0.0042 (2)	1.89 (4)
O(E22)	0.1790 (1)	0.1637 (1)	0.0161 (2)	2.30 (4)
O(E31)	0.1129 (1)	0.4083 (1)	0.1581 (1)	1.68 (3)
O(E32)	0.1801 (1)	0.5383 (1)	0.2786 (2)	1.63 (3)
O(L34)	0.9999 (1)	0.5135 (1)	0.1396 (2)	1.28 (3)
O(E41)	0.1819 (1)	0.5347 (1)	0.5036 (1)	1.57 (3)
O(E42)	0.3915 (1)	0.0938 (1)	0.4858 (2)	1.67 (3)
O(L43)	0.8913 (1)	0.4330 (1)	0.1662 (1)	1.26 (3)
Li(1)	0.1898 (3)	0.3784 (3)	0.1031 (3)	1.56 (8)
Li(2)	0.3113 (3)	0.1227 (3)	0.3127 (4)	1.98 (9)
Li(3)	-0.0010 (3)	0.3306 (4)	0.4736 (5)	2.4 (1)
Li(4)	0.2316 (3)	0.0638 (3)	0.0405 (4)	2.06 (9)

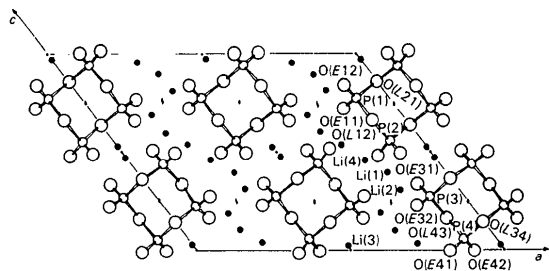


Fig. 1. Projection along the b axis of the atomic arrangement of $\text{Li}_4\text{P}_4\text{O}_{12}\cdot 5\text{H}_2\text{O}$. The two independent P_4O_{12} anions are superimposed in this projection. Water molecules are not represented.

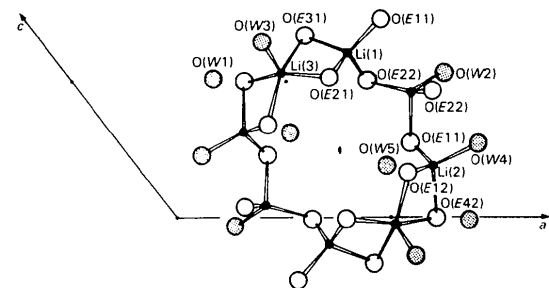


Fig. 2. Projection along the b axis of the $\text{Li}_8\text{O}_{16}(\text{H}_2\text{O})_6$ ring. In addition, unbounded water molecules are represented.

Table 2. Main interatomic distances (\AA) and bond angles ($^\circ$) in the atomic arrangement of $\text{Li}_4\text{P}_4\text{O}_{12}\cdot 5\text{H}_2\text{O}$

The first ring anion				
P(1)	O(E11)	O(E12)	O(L12)	O(L21)
O(E11)	1.482 (2)	2.558 (3)	2.547 (3)	2.450 (3)
O(E12)	119.3 (1)	1.482 (2)	2.478 (3)	2.523 (3)
O(L12)	111.5 (1)	107.1 (1)	1.597 (2)	2.505 (3)
O(L21)	105.0 (1)	109.7 (1)	103.0 (1)	1.604 (2)
P(2)	O(E21)	O(E22)	O(L12)	O(L21)
O(E21)	1.481 (2)	2.540 (3)	2.472 (3)	2.522 (3)
O(E22)	118.6 (1)	1.474 (2)	2.549 (3)	2.468 (3)
O(L12)	106.6 (1)	111.9 (1)	1.602 (2)	2.513 (3)
O(L21)	109.4 (1)	106.3 (1)	103.0 (1)	1.608 (2)
P(1)—O(L12)—P(2)	133.6 (1)	P(1)—P(2)	2.941 (1)	
P(1)—O(L21)—P(2)	130.3 (1)	P(1)—P(2)	2.914 (1)	
P(2)—P(1)—P(2)	89.75 (3)	P(1)—P(2)—P(1)	90.07 (3)	
The second ring anion				
P(3)	O(E31)	O(E32)	O(L34)	O(L43)
O(E31)	1.482 (2)	2.571 (3)	2.530 (3)	2.462 (3)
O(E32)	120.2 (1)	1.484 (2)	2.484 (3)	2.523 (3)
O(L34)	110.0 (1)	106.9 (1)	1.604 (2)	2.516 (3)
O(L43)	105.7 (1)	109.5 (1)	103.2 (1)	1.605 (2)
P(4)	O(E41)	O(E42)	O(L34)	O(L43)
O(E41)	1.485 (2)	2.569 (3)	2.495 (3)	2.525 (3)
O(E42)	119.6 (1)	1.488 (2)	2.536 (3)	2.489 (3)
O(L34)	107.6 (1)	110.1 (1)	1.606 (2)	2.501 (3)
O(L43)	109.2 (1)	106.8 (1)	102.1 (1)	1.611 (2)
P(3)—O(L34)—P(4)	128.7 (1)	P(3)—P(4)	2.895 (1)	
P(3)—O(L43)—P(4)	130.2 (1)	P(3)—P(4)	2.916 (1)	
P(3)—P(4)—P(3)	89.35 (3)	P(4)—P(3)—P(4)	90.64 (3)	

LiO_n polyhedra

$\text{Li}(1)\text{O}_4$ tetrahedron

Li(1)—O(E11)	1.908 (5)	Li(1)—O(E31)	1.931 (5)
Li(1)—O(E21)	1.911 (5)	Li(1)—O(E41)	1.949 (5)
Average O—Li—O 109.25			

$\text{Li}(2)\text{O}_4$ tetrahedron

Li(2)—O(E12)	1.911 (6)	Li(2)—O(E42)	1.930 (5)
Li(2)—O(E32)	1.959 (5)	Li(2)—O(W4)	1.964 (6)
Average O—Li—O 109.55			

$\text{Li}(3)\text{O}_4$ polyhedron

Li(3)—O(E12)	2.233 (6)	Li(3)—O(E21)	2.018 (6)
Li(3)—O(W3)	2.025 (7)	Li(3)—O(E31)	2.110 (6)
Li(3)—O(E42) 2.051 (6)			

$\text{Li}(4)\text{O}_4$ tetrahedron

Li(4)—O(E22)	1.857 (6)	Li(4)—O(E32)	1.998 (5)
Li(4)—O(W2)	1.980 (6)	Li(4)—O(E41)	1.964 (5)
Average O—Li—O 109.29			

P—Li distances

P(1)—Li(1)	3.196 (4)	P(2)—Li(1)	3.144 (5)
P(1)—Li(2)	3.212 (5)	P(2)—Li(3)	3.201 (5)
P(1)—Li(3)	3.337 (6)	P(2)—Li(4)	3.242 (5)
P(3)—Li(1)	3.200 (4)	P(4)—Li(1)	3.096 (5)
P(3)—Li(2)	3.089 (5)	P(4)—Li(2)	3.173 (5)
P(3)—Li(3)	3.251 (6)	P(4)—Li(3)	3.218 (5)
P(3)—Li(4)	3.068 (5)	P(4)—Li(4)	3.051 (5)

Li—Li distances

Li(1)—Li(3)	2.842 (7)	Li(2)—Li(3)	2.853 (7)
Li(1)—Li(4)	3.118 (7)	Li(2)—Li(4)	3.222 (7)

Distances and bond angles in the pentagonal $(\text{H}_2\text{O})_5$ ring

O(W1)—O(W2)	2.693 (13)	O(W2)—O(W1)—O(W3)	106.8 (6)
O(W1)—O(W3)	2.790 (14)	O(W1)—O(W2)—O(W5)	110.1 (4)
O(W2)—O(W5)	2.763 (6)	O(W1)—O(W3)—O(W4)	107.4 (3)
O(W3)—O(W4)	2.989 (5)	O(W3)—O(W4)—O(W5)	102.9 (2)
O(W4)—O(W5)	2.693 (6)	O(W2)—O(W5)—O(W4)	110.6 (18)

Thus the atomic arrangement of $\text{Li}_4\text{P}_4\text{O}_{12}\cdot 5\text{H}_2\text{O}$ may be schematically represented as a stacking of alternate P_4O_{12} and $\text{Li}_8\text{O}_{16}(\text{H}_2\text{O})_6$ rings along the twofold axes.

In addition, the existence of two water molecules should be noted: $\text{O}(W1)$ and $\text{O}(W5)$ not bonded to the associated cations. During the structure determination, they appeared to be affected by large thermal factors. In such cases, it is always difficult to decide if the magnitude of these factors corresponds to the mobility of this type of water or to a partially occupied crystallographic site.

The group of five water molecules builds pentagonal rings around the c axis. In these pentagonal rings the average $\text{O}(W)\text{—O}(W)\text{—O}(W)$ angle is 107.6° showing these rings to be flat within the experimental-error range since this value should be 108° for a flat regular pentagon.

Table 2 reports the main interatomic distances and bond angles in this atomic arrangement.

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Structure of Tetraesium Tetrametaphosphate Tetrahydrate

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Abstract. $\text{Cs}_4\text{P}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$, $M_r = 916.56$, tetragonal, $P4_1$, $a = 9.466$ (5), $c = 21.933$ (9) Å, $V = 1965.3$ Å³, $Z = 4$, $D_x = 3.107$ Mg m⁻³, $\lambda(\text{Ag K}\alpha) = 0.5608$ Å, $\mu = 4.05$ mm⁻¹, $F(000) = 1664$, $T = 293$ K, final $R = 0.035$ for 1654 independent observed reflexions. The atomic arrangement may be described as alternating layers of P_4O_{12} ring anions and caesium polyhedra perpendicular to the c axis. The rubidium salt $\text{Rb}_4\text{P}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$ is isotypic, with $a = 9.163$ (3), $c = 21.356$ (8) Å, $D_x = 2.703$ Mg m⁻³ and $V = 1793.8$ Å³.

Introduction. Various alkali-metal tetrametaphosphates have previously been described: $\text{Li}_4\text{P}_4\text{O}_{12}\cdot 5\text{H}_2\text{O}$ (Averbuch-Pouchot & Durif, 1986), two crystalline forms of $\text{Na}_4\text{P}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$ (Ondik, 1964; Ondik, Block & MacGillavry, 1961), $\text{Na}_4\text{P}_4\text{O}_{12}\cdot \text{H}_2\text{O}$ and $\text{Na}_4\text{P}_4\text{O}_{12}$ (Wiench & Jansen, 1983), $\text{K}_4\text{P}_4\text{O}_{12}\cdot 2\text{H}_2\text{O}$ (Averbuch-Pouchot & Durif, 1985*b*), $\text{K}_4\text{P}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$ (Averbuch-Pouchot & Durif, 1985*a*) but, up to now, nothing was known concerning the rubidium and caesium tetrametaphosphates. In the present study, we describe the crystal structure of caesium tetrametaphosphate tetrahydrate: $\text{Cs}_4\text{P}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$.

Experimental. Rubidium and caesium tetrametaphosphate tetrahydrates have been synthesized by slowly adding the stoichiometric amount of P_4O_{10} to a water

solution of the appropriate carbonate kept at 273 K. The resulting solution is then slowly evaporated at room temperature. Crystals of these two salts are large distorted octahedra.

Density not measured. Cubic fragment $0.25 \times 0.25 \times 0.25$ mm. Philips PW 1100 diffractometer, graphite monochromator. Systematic absences: $00l$, $l = 4n$. 18 reflexions ($9 < \theta < 12^\circ$) for refining unit-cell dimensions. ω scan. 2087 reflexions measured ($3 < \theta < 25^\circ$), hkl , $h_{\text{max}} = 14$, $k_{\text{max}} = 14$, $l_{\text{max}} = 33$. Scan width 1.20° , scan speed $0.02^\circ \text{ s}^{-1}$, total background measuring time 20 s. Two orientation and intensity reflexions (008 and $00\bar{8}$) every 2 h, no variation. Lorentz and polarization correction, no absorption correction. Classical methods for structure determination: Patterson and successive Fourier syntheses. Anisotropic full-matrix least-squares refinement (on F). Unit weights. Final refinement with 1654 reflexions corresponding to $I > 6\sigma(I)$. Final $R = 0.035$ ($wR = 0.040$). For the complete set of unique reflexions (2087) $R = 0.043$. Extinction coefficient refined: 0.34×10^{-8} (Stout & Jensen, 1968). $S = 4.12$. Max. $\Delta/\sigma = 0.29$ [β_{11} of $\text{O}(W4)$]. Max. peak height in final difference Fourier synthesis $0.692 \text{ e } \text{Å}^{-3}$. Scattering factors for neutral atoms and f' , f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. H atoms could not be located.