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Crystal Chemistry of *cyclo*-Hexaphosphates. X. Structure of Dicalcium Dilithium *cyclo*-Hexaphosphate Octahydrate

BY M. T. AVERBUCH-POUCHOT AND A. DURIF

Laboratoire de Cristallographie, associé à l'Université J. Fourier, CNRS, 166X, 38042 Grenoble CEDEX, France

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Abstract. Ca₂Li₂P₆O₁₈.8H₂O, *M*_r = 711.984, triclinic, *P* $\bar{1}$, *a* = 7.767 (2), *b* = 10.144 (3), *c* = 7.225 (2) Å, α = 105.17 (4), β = 102.76 (4), γ = 84.95 (4)°, *V* = 535.6 Å³, *D*_x = 2.207 Mg m⁻³, λ (Mo *K*α) = 0.7107 Å, μ = 1.082 mm⁻¹, *F*(000) = 360, room temperature, final *R* = 0.023 for 2764 reflections. The atomic arrangement can be described as successive layers of planes made by LiO₆ octahedra sharing corners with the P₆O₁₈ ring anions. These planes are interconnected in a three-dimensional manner by the CaO₇ polyhedra and the hydrogen bonds. The calcium–sodium salt is isotypic.

Introduction. *cyclo*-Hexaphosphates of monovalent–divalent cations belong to various structural types and have very different degrees of hydration. During a systematic investigation of this type of compound, we previously reported the existence and described the crystal structures of Mn₂Li₂P₆O₁₈.10H₂O (Averbuch-Pouchot, 1989) and Cd₂Na₂P₆O₁₈.14H₂O (Averbuch-Pouchot, 1990). In the present work we describe the chemical preparation and crystal structure of a new compound of this family, Ca₂Li₂P₆O₁₈.8H₂O. The calcium–sodium salt Ca₂Na₂P₆O₁₈.8H₂O is isotypic with the following unit-cell dimensions: *a* = 8.031 (4), *b* = 10.296 (5), *c* = 7.279 (3) Å, α = 105.69 (5), β = 103.27 (5), γ = 85.30 (5)°. Its preparation is similar to that described for the title compound.

Experimental. Crystals of the title compound were prepared by adding solid gypsum to an aqueous solution of lithium *cyclo*-hexaphosphate. After some days of evaporation at room temperature, crystals of Ca₂Li₂P₆O₁₈.8H₂O appeared as elongated triclinic prisms, sparingly soluble in water. The compound is stable for months at room temperature.

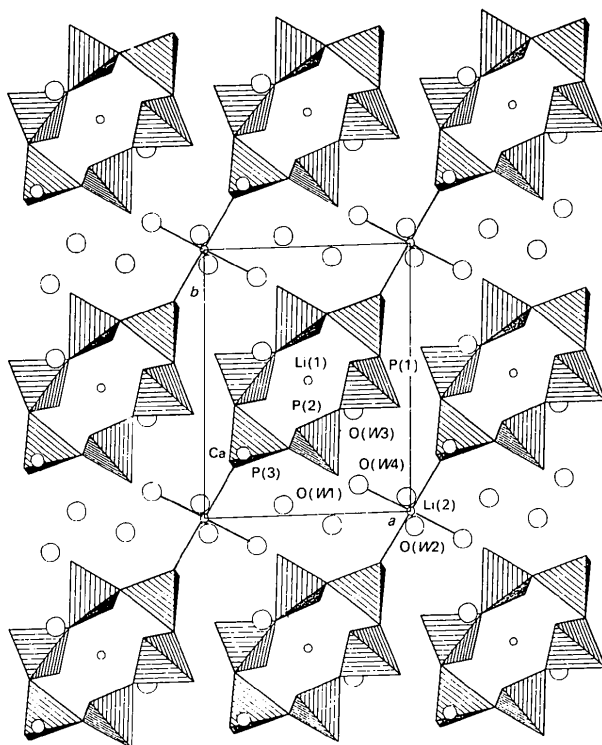
Crystal size: 0.18 × 0.22 × 0.12 mm. Density not measured. Phillips PW1100 diffractometer, graphite monochromator. 15 reflections (13.0 < θ < 17.0°) for refining unit-cell dimensions. $\omega/2\theta$ scan, scan width: 1.20°, scan speed: 0.02° s⁻¹. Total background measuring time: 10 s. 3827 reflections collected (3 < θ < 35°); $\pm h$, $\pm k$, *l*; *h*_{max} = 12, *k*_{max} = 16, *l*_{max} = 10. Two orientation and intensity control reflections ($\bar{1}2\bar{1}$ and $1\bar{2}1$) measured every three hours without any significant variation. 3556 reflections obtained after averaging Friedel pairs (*R*_{int} = 0.01). Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods (*MULTAN77*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1977). H atoms located by difference Fourier syntheses. Anisotropic full-matrix least-squares refinement (on *F*), isotropic for H atoms. Unit weights. Final refinements with 2764 reflections corresponding to *F* > 3 σ_F . Final *R* = 0.023 (*wR* = 0.028), *S* = 0.609, max. Δ/σ = 0.03, max. peak height in the final difference Fourier synthesis = 0.552 e Å⁻³. No secondary-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. Computer used: MicroVAX II.

Discussion. Table 1 reports the final atomic coordinates.* The P₆O₁₈ ring anion has $\bar{1}$ internal symmetry and so is built by three independent P atoms. As is commonly observed for six-membered

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52642 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates and B_{eq} with e.s.d.'s in parentheses

	x	y	z	B_{eq} (\AA^2)
Ca	0-19038 (5)	0-24157 (3)	0-82356 (5)	0-917 (5)
Li(1)	$\frac{1}{2}$	$\frac{1}{2}$	0	2-3 (1)
Li(2)	0	0	0	2-2 (1)
P(1)	0-79668 (6)	0-47973 (4)	0-75598 (7)	0-925 (7)
P(2)	0-53968 (6)	0-27179 (5)	0-59329 (7)	0-935 (7)
P(3)	0-19655 (6)	0-25937 (4)	0-32919 (7)	0-919 (7)
O(E11)	0-7039 (2)	0-5607 (1)	0-9110 (2)	1-21 (2)
O(E12)	0-9500 (2)	0-3905 (2)	0-8071 (2)	2-00 (3)
O(L12)	0-6550 (2)	0-3918 (1)	0-5794 (2)	1-24 (2)
O(L13)	0-1489 (2)	0-4205 (1)	0-3593 (2)	1-43 (2)
O(E21)	0-4453 (2)	0-3260 (1)	0-7572 (2)	1-36 (2)
O(E22)	0-6468 (2)	0-1434 (1)	0-5855 (2)	1-74 (3)
O(L23)	0-4082 (2)	0-2561 (2)	0-3850 (2)	1-42 (2)
O(E31)	0-1456 (2)	0-1883 (1)	0-1183 (2)	1-27 (2)
O(E32)	0-1234 (2)	0-2134 (1)	0-4743 (2)	1-37 (2)
O(W1)	0-6183 (2)	-0-0415 (2)	0-2172 (2)	1-90 (3)
O(W2)	0-0203 (2)	0-9436 (1)	0-2759 (2)	1-50 (3)
O(W3)	0-2784 (3)	0-6130 (2)	0-8194 (3)	2-78 (4)
O(W4)	0-2539 (2)	0-8918 (2)	0-9822 (2)	2-16 (3)
H(1W1)	0-376 (5)	-0-006 (4)	0-666 (6)	2-9 (9)*
H(2W1)	0-354 (5)	-0-007 (4)	0-839 (5)	2-5 (9)*
H(1W2)	0-032 (5)	0-027 (4)	0-353 (6)	2-9 (9)*
H(2W2)	0-115 (5)	0-909 (4)	0-303 (6)	2-9 (9)*
H(1W3)	0-290 (5)	0-596 (4)	0-711 (5)	2-3 (8)*
H(2W3)	0-203 (6)	0-578 (5)	0-805 (7)	5 (1)*
H(1W4)	0-259 (5)	0-807 (4)	0-929 (6)	2-9 (9)*
H(2W4)	0-322 (6)	0-914 (4)	0-085 (6)	4 (1)*

Fig. 1. Projection of the atomic arrangement of $\text{Ca}_2\text{Li}_2\text{P}_6\text{O}_{18}\cdot 8\text{H}_2\text{O}$ along the c axis.

rings with such symmetry, the P—P—P angles are very different; here they spread from 97-15 to 133-35°. The two Li atoms are located on inversion

Table 2. Main interatomic distances (\AA) and bond angles ($^\circ$) in the atomic arrangement of $\text{Ca}_2\text{-Li}_2\text{P}_6\text{O}_{18}\cdot 8\text{H}_2\text{O}$ with e.s.d.'s in parenthesesThe P_6O_{18} ring anion

P(1) O_4 tetrahedron				
P(1)	O(E11)	O(E12)	O(L12)	O(L13)
O(E11)	1-489 (1)	119-94 (9)	109-17 (7)	109-45 (8)
O(E12)	2-563 (2)	1-471 (2)	109-00 (8)	108-74 (10)
O(L12)	2-526 (2)	2-509 (2)	1-605 (1)	98-37 (8)
O(L13)	2-525 (2)	2-499 (2)	2-431 (2)	1-602 (2)

P(2) O_4 tetrahedron

P(2) O_4 tetrahedron				
P(2)	O(L12)	O(E21)	O(E22)	O(L23)
O(L12)	1-610 (2)	108-36 (8)	110-55 (9)	95-36 (8)
O(E21)	2-513 (2)	1-488 (2)	119-54 (10)	111-46 (8)
O(E22)	2-539 (2)	2-562 (2)	1-477 (2)	107-31 (8)
O(L23)	2-410 (2)	2-552 (2)	2-479 (2)	1-599 (1)

P(3) O_4 tetrahedron

P(3) O_4 tetrahedron				
P(3)	O(L13)	O(L23)	O(E31)	O(E32)
O(L13)	1-612 (1)	102-38 (8)	109-76 (8)	106-99 (8)
O(L23)	2-506 (2)	1-603 (1)	106-91 (8)	110-47 (8)
O(E31)	2-535 (2)	2-482 (2)	1-485 (1)	119-08 (8)
O(E32)	2-491 (2)	2-538 (2)	2-560 (2)	1-485 (2)

P(1)—P(2)	2-8674 (6)	P(1)—P(2)—P(3)	133-35 (2)
P(2)—P(3)	2-9063 (6)	P(1)—P(3)—P(2)	97-15 (2)
P(1)—P(3)	2-8770 (7)	P(2)—P(1)—P(3)	129-27 (2)

CaO $_7$ polyhedron

Ca—O(E11)	2-441 (1)	Ca—O(E32)	2-406 (1)
Ca—O(E12)	2-298 (2)	Ca—O(W1)	2-401 (2)
Ca—O(E21)	2-412 (2)	Ca—O(W2)	2-458 (2)
Ca—O(E31)	2-431 (2)		

Li $_6$ octahedra

Li(1)—O(E11)	2-032 (2)($\times 2$)	Li(2)—O(E31)	2-181 (1)($\times 2$)
Li(1)—O(E21)	2-134 (1)($\times 2$)	Li(2)—O(W2)	2-184 (2)($\times 2$)
Li(1)—O(W3)	2-329 (2)($\times 2$)	Li(2)—O(W4)	2-184 (2)($\times 2$)
Li(1)—P(1)	3-1594 (5)($\times 2$)	Li(2)—P(3)	3-2768 (4)
Li(1)—P(2)	3-2868 (4)($\times 2$)		

The hydrogen bonds

O(W)—H...O	O(W)—H	H...O	O(W)—H...O	O(W)—O
O(W1)—H(1W1)...O(E22)	0-85 (4)	1-96 (3)	169 (5)	2-801 (2)
O(W1)—H(2W1)...O(W4)	0-78 (5)	1-95 (5)	171 (4)	2-721 (3)
O(W2)—H(1W2)...O(E32)	0-88 (4)	1-98 (4)	160 (4)	2-830 (2)
O(W2)—H(2W2)...O(E22)	0-79 (4)	1-93 (4)	168 (3)	2-717 (2)
O(W3)—H(1W3)...O(L12)	0-78 (4)	2-27 (4)	164 (4)	3-025 (3)
...O(E12)	0-68 (5)	2-86 (5)	165 (5)	3-523 (3)
O(W3)—H(2W3)...O(L13)	0-68 (5)	2-73 (5)	142 (5)	3-297 (2)
O(W4)—H(1W4)...O(W3)	0-85 (4)	1-92 (4)	177 (2)	2-772 (2)
O(W4)—H(2W4)...O(W1)	0-80 (4)	2-32 (4)	142 (5)	2-993 (3)
H(1W1)—O(W1)—H(2W1)	106 (4)	H(1W3)—O(W3)—H(2W3)	99 (5)	
H(1W2)—O(W2)—H(2W2)	103 (4)	H(1W4)—O(W4)—H(2W4)	114 (4)	

centres and have sixfold coordination comprising four O atoms and two water molecules for the first one [Li(1)] and four water molecules and two O atoms for the second [Li(2)]. Within a range of 2-50 \AA the Ca atom, located in a general position, has sevenfold coordination comprising five O atoms and two water molecules.

Main interatomic distances and bond angles in the phosphoric anion as well as metal—oxygen distances in the associated cation coordinations are given in Table 2.

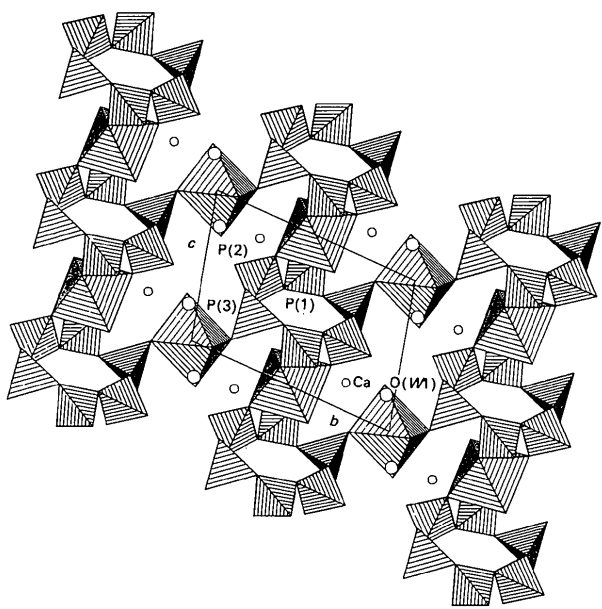


Fig. 2. Projection of the atomic arrangement of Ca₂Li₂P₆O₁₈·8H₂O along the *a* axis.

As shown by Fig. 1, a projection along the *c* axis, the centrosymmetric P₆O₁₈ ring anion located around the inversion centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and the centrosymmetric Li(2)O₆ octahedron share two O atoms so as to

build an infinite chain parallel to [110]. These chains are themselves interconnected along the *c* direction by the second lithium octahedron, Li(1)O₆, also centrosymmetric, so as to form planes parallel to [110] (Fig. 2). The connections between the phosphoric groups and the lithium octahedra are different. The Li(1)O₆ octahedron shares four O atoms with its two adjacent phosphoric groups while Li(2)O₆ shares two. These planes are themselves interconnected in a three-dimensional manner by the CaO₇ polyhedra and the hydrogen bonds whose main geometrical features are given in Table 2. The drawings were made with *STRUPLO* (Fischer, 1985).

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Structure of Ho₂Ba₂Cu_{1+x}Pt_{1-x}O₈ (*x* = 0·1)

BY YOKO SAITO, KAZUTOSHI UKEI, TOETSU SHISHIDO AND TSUGUO FUKUDA

Institute for Materials Research, Tohoku University, Katahira, Aoba-ku, Sendai 980, Japan

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Abstract. Ho₂Ba₂Cu_{1+x}Pt_{1-x}O₈ (*x* = 0·1), *M_r* = 978·0, orthorhombic, *Pcmm*, *a* = 10·303 (2), *b* = 5·668 (1), *c* = 13·178 (3) Å, *Z* = 4, *D_x* = 8·44 Mg m⁻³, Mo *Kα*, λ = 0·71073 Å, μ = 50·1 mm⁻¹, *F*(000) = 1648, room temperature, final *R* = 0·064 for 1473 [*I*_o > 3σ(*F*_o)] unique reflections. The crystal is isomorphous with Er₂Ba₂Cu_{1·1}Pt_{0·9}O₈ and is composed of a one-dimensional structure of Cu, O and Pt ions running parallel to the *b* axis.

Introduction. Recently, during the synthesis of single crystals of ErBa₂Cu₃O₇ which shows high-*T_c* superconductivity, a new compound Er₂Ba₂Cu_{1·1}Pt_{0·9}O₈ which incorporates the element Pt from a Pt crucible, was obtained (Shishido, Fukuda, Toyota, Ukei & Sasaki, 1987) and its structural studies were reported

(Ukei, Shishido & Fukuda, 1988). The same type of compound with Y as the rare-earth element has been studied (Swinnea & Steinfink, 1987; Lalignat, Ferey, Hervieu & Raveau, 1987).

As an extension of the investigations of this series of R₂Ba₂(Cu,Pt)₂O₈ (*R* = a rare-earth element) compounds, the Ho compound has been prepared to determine the crystal structure.

Experimental. The crystal was prepared with reference to the preparation of Er₂Ba₂Cu_{1·1}Pt_{0·9}O₈ as described elsewhere (Shishido *et al.*, 1987). Crystal size 0·63 × 0·1 × 0·1 mm; Rigaku AFC-6A four-circle diffractometer, graphite-monochromated Mo *Kα* radiation; lattice parameters from 16 reflections (60 < 2θ < 63°); ω-2θ scan mode, scan speed 4°