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Crystal Chemistry of *cyclo*-Hexaphosphates.
I. Structure of Anhydrous Potassium *cyclo*-Hexaphosphate

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Abstract. $K_6P_6O_{18}$, $M_r = 708{\cdot}43$, cubic, $Pa\bar{3}$, $a = 15{\cdot}753\,(6)$ Å, $V = 3909\,(4)$ Å^3, $Z = 8$, $D_x = 2{\cdot}407$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 1{\cdot}879$ mm^{-1}, $F(000) = 2784$, $T = 293$ K, final $R = 0{\cdot}023$ for 1628 independent observed reflections. The P_6O_{18} ring anion has threefold symmetry. The ring anions are interconnected in a three-dimensional way by five different potassium polyhedra with various internal symmetries.

Introduction. The chemistry of *cyclo*-hexaphosphates was slow to develop and even today is poor if compared with that of *cyclo*-tri- or *cyclo*-tetraphosphates. Recently Schülke & Kayser (1985) reported an important improvement of the Griffith & Buxton (1965) process for the preparation of lithium *cyclo*-hexaphosphate, a good starting material for the preparation of *cyclo*-hexaphosphates. Using this salt, we previously reported chemical preparations and crystal structures for $Ag_6P_6O_{18}.H_2O$ (Averbuch-Pouchot, 1989*a*), $(NH_4)_6P_6O_{18}.H_2O$ (Averbuch-Pouchot, 1989*b*), $Cu_3P_6O_{18}.14H_2O$ (Averbuch-Pouchot, 1989*c*) and $Cd_3P_6O_{18}.6H_2O$ (Averbuch-Pouchot, 1989*d*). The present study is devoted to the chemical preparation and crystal structure of a new alkali *cyclo*-hexaphosphate: $K_6P_6O_{18}$.

Experimental. Crystals of the title compound are obtained by mixing solutions of $Li_6P_6O_{18}$ and KF in stoichiometric ratio according to the reaction:

$$Li_6P_6O_{18} + 6KF \rightarrow 6LiF + K_6P_6O_{18}.$$

After filtration of the insoluble lithium fluoride and total evaporation of the resulting solution at 333 K, crystals of $K_6P_6O_{18}$ appear as large cube-octahedra.

Density not measured. $0{\cdot}175 \times 0{\cdot}175 \times 0{\cdot}175$ mm cubic multifaceted crystal, Philips PW 1100 diffractometer, graphite monochromator. Systematic absences: $0kl$, $k = 2n$; $h0l$, $l = 2n$; $hk0$, $h = 2n$. 17 reflections ($13 < \theta < 16°$) for refining unit-cell dimensions. ω scan. Scan width = 1·20°, scan speed = 0·02° s^{-1}, total background measuring time: 10 s. 5039 reflections measured ($3 < \theta < 30°$), $h_{\max} = k_{\max} = l_{\max} = 25$, 2174 independent reflections. Two intensity and orientation reference reflections every 2 h (620 and 062): no significant variation. Lorentz and polarization corrections, no absorption correction. Direct methods (*MULTAN*77: Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1977) used for structure determination. Anisotropic full-matrix least-squares refinement (on F). Unit weights. Final refinement for 1628 reflections ($I > 4\sigma_I$). Final $R = 0{\cdot}023$ ($wR = 0{\cdot}024$), $S = 1{\cdot}652$, $\Delta/\sigma = 0{\cdot}01$, max. peak height in final difference Fourier synthesis 0·53 e Å^{-3}. Extinction factor (Stout & Jensen, 1968) refined, $g = 1{\cdot}20 \times 10^{-7}$. 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: MicroVAXII.

Discussion. Table 1 reports the final atomic parameters.* The atomic arrangement can be described as a stacking of P_6O_{18} ring anions interconnected in a three-dimensional way by five independent potassium polyhedra.

The ring anions are located around the threefold axis, so have the internal symmetry 3 and consequently are built up by only two independent PO_4 tetrahedra. Details dealing with bond distances and angles in this anionic group are reported in Table 2. Fig. 1 gives a projection along one of the ternary axis of a succession of two such rings. The P—P—P angles 105·8 and 103·4° are quite comparable to those commonly observed for P_6O_{18} rings with 3 or $\bar{3}$ internal symmetry: 112·2° for $Ag_6P_6O_{18}.H_2O$; 116·4 and 115·8° for $Cd_3P_6O_{18}.6H_2O$; 108·5° for $(NH_4)_6$-

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51855 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final atomic coordinates and B_{eq} values for* $K_6P_6O_{18}$

E.s.d.'s are given in parentheses.

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j\beta_{ij}.$$

	x	y	z	$B_{\rm eq}$(Å^2)
K(1)	0·0	0·0	0·5	2·026 (5)
K(2)	0·5	0·0	0·5	1·586 (4)
K(3)	0·732	0·732	0·73249 (3)	1·821 (3)
K(4)	0·75612 (3)	0·62017 (3)	0·94141 (3)	2·048 (7)
K(5)	0·128	0·128	0·12827 (3)	1·516 (3)
P(1)	0·57798 (3)	0·55892 (3)	0·77471 (3)	1·115 (7)
P(2)	0·65484 (3)	0·82806 (3)	0·95358 (3)	1·175 (7)
O(*L*12)	0·59398 (9)	0·5116 (1)	0·6851 (1)	1·89 (3)
O(*L*21)	0·5236 (1)	0·63882 (9)	0·7443 (1)	2·16 (3)
O(*E*11)	0·5241 (1)	0·5033 (1)	0·8271 (1)	2·23 (3)
O(*E*12)	0·6587 (1)	0.5923 (1)	0·8088 (1)	2·19 (3)
O(*E*21)	0·5748 (1)	0·8556 (1)	0·9129 (1)	1·85 (3)
O(*E*22)	0·7251 (1)	0·7959 (1)	0·9003 (1)	2·23 (3)

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *for* $K_6P_6O_{18}$

The P_6O_{18} ring

$P(1)O_4$ tetrahedron

P(1)	O(*L*12)	O(*L*21)	O(*E*11)	O(*E*12)
O(*L*12)	1·616 (2)	2·473 (2)	2·497 (2)	2·540 (2)
O(*L*21)	100·67 (8)	1·596 (2)	2·502 (2)	2·470 (2)
O(*E*11)	107·79 (9)	109·13 (9)	1·473 (2)	2·558 (2)
O(*E*12)	110·33 (9)	106·91 (9)	120·25 (9)	1·477 (2)

$P(2)O_4$ tetrahedron

P(2)	O(*L*12)	O(*L*21)	O(*E*21)	O(*E*22)
O(*L*12)	1·604 (2)	2·485 (2)	2·463 (2)	2·545 (2)
O(*L*21)	101·46 (9)	1·606 (2)	2·555 (2)	2·454 (2)
O(*E*21)	106·02 (8)	111·80 (8)	1·479 (2)	2·555 (2)
O(*E*22)	111·25 (9)	105·34 (9)	119·55 (9)	1·478 (2)

P(1)—P(2)	2·9572 (7)	P(2)—P(1)—P(2)	105·82 (2)
P(1)—P(2)	2·9172 (7)	P(1)—P(2)—P(1)	103·39 (2)

P(1)—O(*L*12)—P(2)	130·0 (1)
P(1)—O(*L*21)—P(2)	134·9 (1)

The KO_x polyhedra

$K(1)O_{12}$ polyhedron

K(1)—O(*L*12)	3·276 (2) (×6)	K(1)—O(*E*21)	2·906 (2) (×6)

$K(2)O_6$ polyhedron

K(2)—O(*E*11)	2·750 (2) (×6)

$K(3)O_6$ polyhedron

K(3)—O(*E*12)	2·770 (2) (×3)	K(3)—O(*E*22)	2·829 (2) (×3)

$K(4)O_6$ polyhedron

K(4)—O(*L*21)	3·107 (2)	K(4)—O(*E*21)	2·905 (2)
K(4)—O(*E*11)	2·799 (2)	K(4)—O(*E*21)	2·673 (2)
K(4)—O(*E*12)	2·629 (2)	K(4)—O(*E*22)	2·885 (2)

$K(5)O_6$ polyhedron

K(5)—O(*E*11)	2·736 (2) (×3)	K(5)—O(*E*22)	2·638 (2) (×3)

$P_6O_{18}.H_2O$. Up to now the only large departure from such values has been observed in $Cu_3P_6O_{18}.14H_2O$ where P—P—P angles, in the centrosymmetrical ring, vary in the range 96·3 to 139·9°. The local geometry of the oxygen tetrahedra around the P atoms is similar to that previously observed in all condensed phosphate anions.

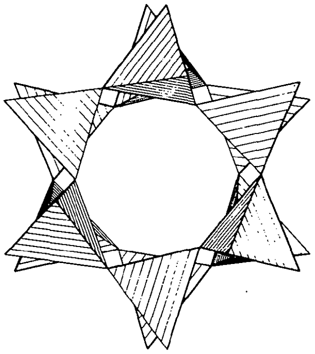

Fig. 1. Projection along [111] of two successive P_6O_{18} ring anions.

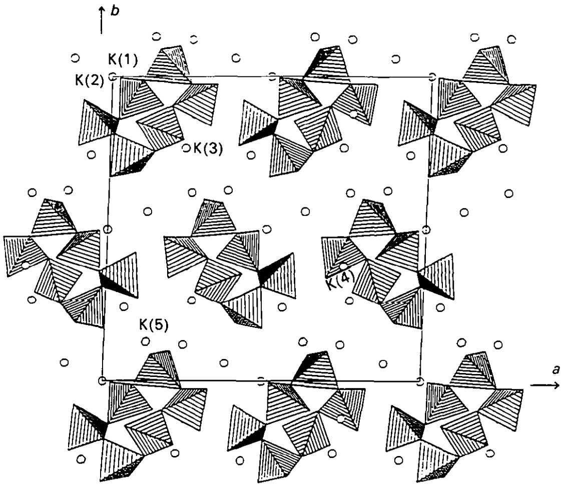

Fig. 2. Projection along [001] of the atomic arrangement of $K_6P_6O_{18}$ for $-0·22 < z < 0·60$.

Five independent potassium polyhedra coexist inside the atomic arrangement. All are more or less distorted octahedra. K(1) and K(2) potassium atoms are located on a $\bar{3}$ axis. Within a range of 3 Å K(1) atoms have six neighbours, building a distorted octahedron with O—K—O angles of 76 and 104°. The $K(2)O_6$ polyhedra are less distorted with O—K—O angles of 83·4 and 96·6°. K(3) and K(5) potassium atoms, located on 3 axes, still have sixfold coordination but with a larger distortion from the octahedral symmetry. K(4) is the only potassium in a general position; its coordination polyhedron departs significantly from a regular octahedron (Table 2).

Fig. 2 shows a projection of this atomic arrangement along [001], for $-0·22 < z < 0·60$.

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Crystal Chemistry of *cyclo*-Hexaphosphates.
II. Structure of Copper *cyclo*-Hexaphosphate Tetradecahydrate

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Abstract. $Cu_3P_6O_{18}.14H_2O$, $M_r = 916{\cdot}67$, triclinic, $P\bar{1}$, $a = 10{\cdot}944$ (8), $b = 7{\cdot}539$ (4), $c = 8{\cdot}974$ (4) Å, $\alpha = 110{\cdot}49$ (5), $\beta = 110{\cdot}14$ (5), $\gamma = 77{\cdot}82$ (5)°, $V = 647$ (1) Å^3, $Z = 1$, $D_x = 2{\cdot}350$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 3{\cdot}039$ mm^{-1}, $F(000) = 461$, $T = 293$ K, final R value = 0·036 for 3439 reflections. Alternating corner-sharing P_6O_{18} ring anions and $CuO_4(H_2O)_2$ octahedra form chains spreading along the c axis. These chains are themselves interconnected by a centrosymmetrical cluster of two edge-sharing CuO-$(H_2O)_5$ octahedra.

Introduction. The present study is part of a systematic study of the crystal chemistry of *cyclo*-hexaphosphates.

In previous articles we reported chemical preparations and crystal structures of various monovalent *cyclo*-hexaphosphates (Averbuch-Pouchot, 1989*a*,*c*) and of the first example of a bivalent-cation *cyclo*-hexaphosphate: $Cd_3P_6O_{18}.6H_2O$ (Averbuch-Pouchot, 1989*b*). The present work is devoted to the crystal chemistry of another divalent-cation *cyclo*-hexaphosphate: $Cu_3P_6O_{18}.14H_2O$.

The present structural study confirms the hydration state previously observed for this compound during investigations of its thermal behaviour with polycrystalline samples (Lazarevski, Kubasova, Chudinova & Tananaev, 1980, 1982).

Experimental. Crystals of the title compound can be obtained by several processes: adding water solutions of $CuCl_2$ [or $Cu(NO_3)_2$] to an aqueous solution of $Li_6P_6O_{18}.6H_2O$ or adding a water solution of copper nitrate to a solution of guanidinium *cyclo*-hexaphosphate in stoichiometric ratio. After some days of evaporation of the resulting solutions at room temperature, crystals of $Cu_3P_6O_{18}.14H_2O$ appear as turquoise calcite-like pseudo-rhombohedra. Density not measured. 0·30 × 0·30 × 0·15 mm crystal. Philips PW 1100 diffractometer, graphite monochromator. 18 reflections ($14 < \theta < 16°$) 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. 4707 reflections measured ($3 < \theta < 35°$), $\pm h$, $\pm k$, l, $h_{\max} = 17$, $k_{\max} = 12$, $l_{\max} = 12$. Two intensity and orientation reflections (051 and $0\bar{5}\bar{1}$) measured every three hours without significant variation. 4273 independent reflections ($R_{\rm int} = 0{\cdot}009$). Lorentz and polarization corrections, no absorption correction. Crystal structure by investigation of the Patterson map and successive Fourier syntheses. Anisotropic full-matrix least-squares refinement (on F) for non-H atoms, isotropic for H atoms. H atoms located by difference-Fourier map. Unit weights. Final refinement with 3439 reflections ($I > 9\sigma_I$).

Final $R = 0{\cdot}036$ ($wR = 0{\cdot}041$), $S = 0{\cdot}984$, max. $\Delta/\sigma = 0{\cdot}03$. Max. peak height in final difference-Fourier syntheses 1·425 e Å^{-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. Computer used: MicroVAX II.

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