

anisotropic thermal-motion behaviour of the equatorial and apical F atoms was interpreted as the consequence of a probable tilting of the chains along the *c* axis (Babel & Knoke, 1978); such behaviour is also observed for $\text{Pb}_2\text{MnFe}_2\text{F}_{12}\cdot 3\text{H}_2\text{O}$ with the apical F(2) and equatorial F(3) strongly distributed in the *ab* plane and in the *c* direction (see U_{ij} , Table 1) respectively. Nevertheless, as usual, the terminal F atom F(1) corresponds to a shorter *M*—F distance than the bridging ones [F(2), F(3)]. Although H atoms have not been located, the O(*w*)—F(3) distance, distinctly shorter than the other O(*w*)—F distances (Table 2), suggests that hydrogen bonding may occur through F(3); thus the H atom could occupy an (*x*0*z*) 6(*i*) position with $x \approx 0.35$, $z \approx 0.30$. Another related material showing triangular isolated octahedral chains is KCrF_4 (Dewan & Edwards, 1986; Kissel & Hoppe, 1987). Thermal behaviour and magnetic properties are now being investigated. Possible isotopic materials are being researched.

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Crystal Chemistry of *cyclo*-Hexaphosphates. XIX. Structure of Barium *cyclo*-Hexaphosphate Octahydrate

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Abstract. $\text{Ba}_3\text{P}_6\text{O}_{18}\cdot 8\text{H}_2\text{O}$, $M_r = 1029.966$, monoclinic, $C2/c$, $a = 20.98$ (2), $b = 7.227$ (3), $c = 17.44$ (1) Å, $\beta = 119.56$ (3)°, $V = 2300$ (5) Å³, $Z = 4$, $D_x = 2.974$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7017$ Å, $\mu = 5.764$ mm⁻¹, $F(000) = 1928$, $T = 294$ K, final $R = 0.041$ for 2699 reflections. The atomic arrangement can be described as being built of two layers of BaO_8 and BaO_{10} polyhedra approximately centred by planes $z = \frac{1}{4}$ and $\frac{3}{4}$ interconnected through the external oxygen atoms of the large P_6O_{18} groups. Inside a layer the Ba polyhedra assemble to form rings of eight polyhedra tiling the plane. The phosphoric ring anion has a twofold internal symmetry rarely observed in the crystal chemistry of *cyclo*-hexaphosphates. Hydrogen atoms could not be located.

Introduction. From a structural point of view very little is known about divalent cation *cyclo*-hexaphosphates. The chemical preparation and crystal structure of the cadmium salt, $\text{Cd}_3\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$, were first reported by Averbuch-Pouchot (1989*a*), later on the chemical preparation and characterization of the isotopic manganese salt were described by Averbuch-Pouchot & Durif (1989). The chemical preparation and crystal structure of the copper salt, $\text{Cu}_3\text{P}_6\text{O}_{18}\cdot 14\text{H}_2\text{O}$, have also been reported by Averbuch-Pouchot (1989*b*). Some chemical investigations by Lazarevski, Kubasova, Chudinova & Tananaev (1980, 1982*a,b*) showing the existence of several hydrated compounds, $\text{Cd}_3\text{P}_6\text{O}_{18}\cdot 16\text{H}_2\text{O}$, $\text{Mn}_3\text{P}_6\text{O}_{18}\cdot 9\text{H}_2\text{O}$, $\text{Co}_3\text{P}_6\text{O}_{18}\cdot 14\text{H}_2\text{O}$, $\text{Ni}_3\text{P}_6\text{O}_{18}\cdot 17\text{H}_2\text{O}$ and $\text{Cu}_3\text{P}_6\text{O}_{18}\cdot 14\text{H}_2\text{O}$, should also be mentioned. The

crystallographic investigation of the copper salt by Averbuch-Pouchot (1989b) confirms the hydration state reported by these authors. In addition, from the powder data given by these same authors it can be concluded that, in spite of a similar degree of hydration, the cobalt and copper salts are not isotypic.

Experimental. Two processes can be used to prepare the title compound. The first one consists of adding an aqueous solution of barium chloride in small fractions to an aqueous solution of lithium *cyclo*-hexaphosphate. A white precipitate appears at each addition but dissolves on stirring. The two aqueous solutions are used in stoichiometric proportions. The resulting solution is slowly evaporated at room temperature until the title compound crystallizes. In the second process an excess of solid barium hydroxide is added and *cyclo*-hexaphosphoric acid itself is produced through the use of ion-exchange resins (Amberlite IR120). The so-obtained mixture is then filtered and the resulting solution evaporated at room temperature.

Crystal size $0.12 \times 0.12 \times 0.18$ mm. Density not measured. Philips PW 1100 diffractometer, graphite monochromator. 18 reflections ($9.70 < \theta < 11.20^\circ$) for refining unit-cell dimensions. ω scan, scan width 1.20° , scan speed $0.02^\circ \text{ s}^{-1}$, total background measuring time 6 s. 3119 reflections collected ($3 < \theta < 32.50^\circ$), $\pm h, k, l$: $h_{\text{max}} = 31, k_{\text{max}} = 11, l_{\text{max}} = 22$. Two orientation and intensity control reflections ($\bar{5}11$ and $\bar{5}11$) measured every 6 h without any significant variation. Lorentz and polarization corrections, no absorption correction.

The crystal structure was solved using direct methods (*MULTAN77*; Main, Lessinger, Woolfson, Germain & Declercq, 1977) for the location of the heavy atoms and successive Fourier syntheses. Hydrogen atoms were not located. Anisotropic full-matrix least-squares refinement (on F); unit weights. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B). Enraf-Nonius (1977) *SDP* used for all calculations. Computer used MicroVAX II. No secondary-extinction correction. The results are for final refinements with 2699 reflections [$I > 3\sigma(I)$]. Final $R = 0.041$ ($wR = 0.047$), $S = 3.330$, maximum $\Delta/\sigma = 0.0$, maximum peak height in the final difference Fourier synthesis = $0.76 \text{ e } \text{\AA}^{-3}$. Table 1 reports the final atomic coordinates for this atomic arrangement.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54605 (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} values for $\text{Ba}_3\text{P}_6\text{O}_{18} \cdot 8\text{H}_2\text{O}$

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

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j a_i \cdot b_j \beta_{ij}$$

	x	y	z	B_{eq} (\AA^2)
Ba(1)	0.29249 (2)	0.89119 (5)	0.71863 (2)	1.059 (6)
Ba(2)	0	0.26714 (8)	$\frac{1}{2}$	1.121 (9)
P(1)	0.12812 (8)	0.8848 (2)	0.7833 (1)	0.94 (3)
P(2)	0.46599 (8)	0.8279 (3)	0.3701 (1)	1.08 (3)
P(3)	0.37650 (8)	0.1503 (2)	0.5828 (1)	0.99 (3)
O(L13)	0.3733 (3)	0.3394 (7)	0.6286 (3)	1.41 (9)
O(E11)	0.3130 (2)	0.2796 (7)	0.7222 (3)	1.34 (9)
O(E12)	0.3743 (3)	0.5911 (7)	0.7222 (3)	1.7 (1)
O(E21)	0.4431 (3)	-0.0167 (7)	0.8343 (3)	1.5 (1)
O(E22)	0.4351 (3)	0.2565 (9)	0.9222 (3)	1.9 (1)
O(L23)	0.4472 (2)	0.8127 (8)	0.0725 (3)	1.4 (1)
O(E31)	0.3873 (3)	0.0068 (7)	0.1425 (3)	1.6 (1)
O(E32)	0.3138 (3)	0.1509 (8)	0.4908 (3)	1.5 (1)
O(L12)	0.4513 (2)	0.3101 (7)	0.7903 (3)	1.34 (9)
O(W1)	0.1979 (2)	0.5914 (8)	0.6366 (3)	1.51 (9)
O(W2)	0.2206 (3)	0.1019 (9)	0.0265 (4)	2.5 (1)
O(W3)	0.1658 (3)	0.8670 (9)	0.1343 (4)	2.1 (1)
O(W4)	0.4432 (4)	0.361 (1)	0.0767 (4)	3.1 (2)

Table 2. Main interatomic distances (\AA) and bond angles ($^\circ$) in the atomic arrangement of $\text{Ba}_3\text{P}_6\text{O}_{18} \cdot 8\text{H}_2\text{O}$

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

P_6O_{18} anion				
P(1) O_4 tetrahedron				
P(1)	O(L13)	O(E11)	O(E12)	O(L12)
O(L13)	1.586 (6)	2.547 (9)	2.437 (8)	2.475 (6)
O(E11)	111.6 (3)	1.493 (6)	2.593 (7)	2.544 (6)
O(E12)	104.6 (3)	120.5 (3)	1.494 (5)	2.500 (7)
O(L12)	101.3 (3)	109.9 (3)	107.1 (3)	1.614 (4)
P(2) O_4 tetrahedron				
P(2)	O(E21)	O(E22)	O(L23)	O(L12)
O(E21)	1.478 (5)	2.556 (9)	2.534 (6)	2.515 (8)
O(E22)	119.3 (4)	1.484 (7)	2.477 (8)	2.515 (9)
O(L23)	111.2 (3)	107.3 (3)	1.592 (4)	2.454 (6)
O(L12)	108.8 (3)	108.6 (3)	99.9 (3)	1.613 (6)
P(3) O_4 tetrahedron				
P(3)	O(L13)	O(L23)	O(E31)	O(E32)
O(L13)	1.602 (6)	2.463 (9)	2.517 (7)	2.496 (7)
O(L23)	100.5 (3)	1.601 (6)	2.559 (9)	2.448 (6)
O(E31)	109.4 (3)	112.2 (3)	1.481 (6)	2.580 (7)
O(E32)	107.6 (3)	104.7 (3)	120.5 (3)	1.490 (4)
P(1)—O(L12)—P(2)	125.2 (4)	P(1)—P(2)	2.865 (2)	
P(2)—O(L23)—P(3)	138.9 (4)	P(2)—P(3)	2.990 (2)	
P(3)—O(L13)—P(1)	133.3 (4)	P(3)—P(1)	1.926 (3)	
P(2)—P(1)—P(3)	98.95 (7)			
P(1)—P(2)—P(3)	116.38 (9)			
P(1)—P(3)—P(2)	102.55 (6)			
$\text{Ba}(1)\text{O}_{10}$ polyhedron				
Ba(1)—O(E11)	2.836 (5)	Ba(1)—O(E31)	2.978 (7)	
Ba(1)—O(E11)	2.978 (6)	Ba(1)—O(W1)	2.806 (5)	
Ba(1)—O(E12)	2.748 (5)	Ba(1)—O(W1)	2.830 (6)	
Ba(1)—O(E21)	2.865 (4)	Ba(1)—O(W2)	2.919 (6)	
Ba(1)—O(W3)	2.934 (6)	Ba(1)—O(W3)	2.902 (6)	
$\text{Ba}(2)\text{O}_8$ polyhedron				
Ba(2)—O(E12)	2.746 (6) ($\times 2$)	Ba(2)—O(E31)	2.720 (5) ($\times 2$)	
Ba(2)—O(E21)	2.785 (6) ($\times 2$)	Ba(2)—O(W4)	2.803 (7) ($\times 2$)	

Discussion. Fig. 1 reports a projection of the atomic arrangement along the b axis.

The P_6O_{18} ring anion. In the present arrangement the phosphoric ring is located around the twofold axis and so is built up of three independent PO_4 tetrahedra. Up to now only two P_6O_{18} ring anions have been observed with such an internal symmetry, the first in $Ca_2(NH_4)_2P_6O_{18} \cdot 6H_2O$ (Averbuch-Pouchot, 1990) and the second, more recently, in $Ce_2P_6O_{18} \cdot 6H_2O$ (Bagieu-Beucher & Rzaigui, 1991). The main geometrical features of the present ring are reported in Table 2. The P—P distances and the P—O—P angles are those commonly measured in all condensed phosphoric anions. The P—P—P angles spread in a range of 98.95 to 116.38° while in the two previous reported examples of P_6O_{18} groups with a twofold internal symmetry these same ranges

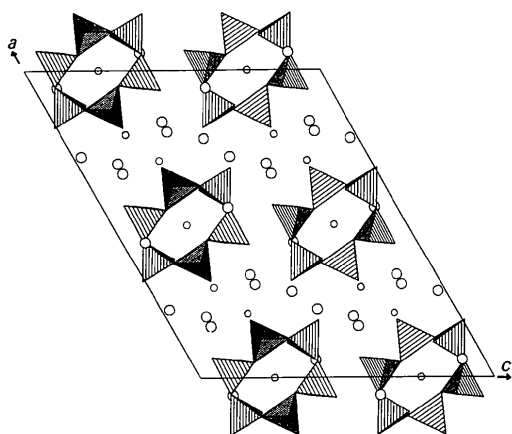


Fig. 1. Projection along the b axis of the atomic arrangement of $Ba_3P_6O_{18} \cdot 8H_2O$. The smaller empty circles are barium atoms, the larger ones represent water molecules.

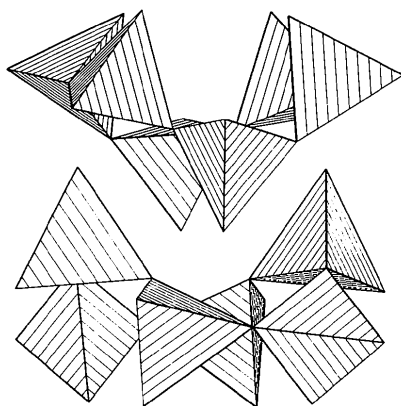


Fig. 2. Upper part: projection of a ring along the a axis. Lower part: projection of a ring along the c axis.

are 87.8 – 116.1° for $Ca_2(NH_4)_2P_6O_{18} \cdot 6H_2O$ and 87.5 – 115.6° for $Ce_2P_6O_{18} \cdot 6H_2O$. In spite of what might be suggested by Fig. 1, the present ring is far from being flat. Fig. 2 reports projections along b and c of an isolated anion showing clearly an organization made by two stages of tetrahedra.

The BaO_n polyhedra. Two crystallographically independent barium atoms are present in this arrangement, one in a general position and the other on the twofold axis. Within a range of 3 \AA , the first has ten oxygen neighbours including three water molecules while the second has a more regular eightfold coordination including two water molecules. All these barium polyhedra are located in two layers approximately centred by planes $z = \frac{1}{4}$ and $\frac{3}{4}$. Inside these layers, through corner and edge sharing they build a tiling whose repetition unit is a ring of eight BaO_n polyhedra assembled to form a non-convex polygon. The Ba—Ba distances in this two-dimensional framework are rather short (4.3998 and 4.2079 \AA). Table 2 gives the main interatomic distances in these two BaO_n polyhedra. Thus, in this atomic arrangement the cohesion between the two layers of barium polyhedra is performed through the external oxygen atoms of the large phosphoric ring anions.

Probably owing to the presence of the heavy cations, hydrogen atoms could not be located with a sufficient degree of accuracy. The drawings have been performed using the *STRUPLO* program (Fischer, 1985).

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