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Structure of Ammonium *cyclo*-Hexaphosphate Monohydrate

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Abstract. $(NH_4)_6P_6O_{18}.H_2O$, $M_r = 600·07$, trigonal, $R\bar{3}$, $a = 15·445\ (10)$, $c = 7·553\ (7)$ Å, $V = 1560\ (3)$ Å^3, $Z = 3$, $D_x = 1·915$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0·624$ mm^{-1}, $F(000) = 930$, $T = 295$ K, final $R = 0·018$ for 915 independent reflexions ($I > 9\sigma_I$). $(NH_4)_6$ rings of $\bar{3}$ symmetry alternate with P_6O_{18} rings of same symmetry along the $\bar{3}$ axis. A water molecule not belonging to the cation coordination is located at the center of the ammonium ring. The hydrogen-bond scheme is described.

Introduction. Recently Schülke & Kayser (1985) described a process permitting the production of large amounts of a lithium *cyclo*-hexaphosphate with an almost theoretical yield and a very good purity. Thus the crystal chemistry of *cyclo*-hexaphosphates, which was very slow to develop due to the lack of a convenient starting material, can now be explored systematically. We recently described chemical preparations and crystal structures for: $Ag_6P_6O_{18}.H_2O$ (Averbuch-Pouchot, 1988*a*), $Cd_3P_6O_{18}.6H_2O$ (Averbuch-Pouchot, 1988*b*) and $Cu_3P_6O_{18}.14H_2O$ (Averbuch-Pouchot, 1989).

In the present paper we report the chemical preparation and crystal structure of a new type of *cyclo*-hexaphosphate: $(NH_4)_6P_6O_{18}.H_2O$.

Experimental. Crystals were obtained by a metathesis reaction using $Ag_6P_6O_{18}.H_2O$ (Averbuch-Pouchot, 1988*a*) as starting material. The reaction is:

$$Ag_6P_6O_{18}.H_2O + 6NH_4Cl \rightarrow (NH_4)_6P_6O_{18}.H_2O + 6AgCl.$$

The insoluble silver chloride is removed by filtration and the resulting solution is slowly evaporated at room temperature. After some days, crystals of $(NH_4)_6P_6O_{18}.H_2O$ appear as calcite-like rhombohedra. Rhombohedron: 0·24 × 0·16 × 0·19 mm. Philips PW 1100 diffractometer, graphite monochromator. Systematic absences: h,k,l $-h+k+l = 3n$. 22 reflexions ($14·5 < \theta < 17·8°$) for refining unit-cell dimensions, ω scan, 3793 reflexions measured ($3 < \theta < 35°$), $\pm h,\pm k,l$, $h_{max} = 20$, $k_{max} = 20$, $l_{max} = 12$. Scan width: 1·20°, scan speed: 0·02° s^{-1}, total background measuring time: 10 s. Two intensity and orientation reflexions (006 and 00$\bar{6}$) measured every two hours without significant variation. 1315 independent reflexions ($R_{int} = 0·015$). Lorentz and polarization corrections, no absorption correction. Crystal structure solved by direct methods (*MULTAN*77: Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1977).

Table 1. *Final atomic coordinates and* B_{eq} *values for* $(NH_4)_6P_6O_{18}.H_2O$

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

B_{iso} for H atoms.

	x	y	z	B_{eq}/B_{iso}(Å^2)
P	0·19978 (2)	0·05297 (2)	0·93177 (4)	1·275 (4)
O(1)	0·20799 (7)	0·09611 (7)	0·7529 (1)	2·19 (2)
O(2)	0·28823 (7)	0·05384 (7)	1·0105 (2)	2·21 (2)
O(*L*)	0·16345 (7)	0·10577 (6)	1·0738 (1)	2·12 (2)
N	0·13201 (9)	0·41185 (8)	0·0784 (2)	2·02 (2)
H(1)	0·290 (1)	0·929 (1)	0·071 (3)	1·3 (4)
H(2)	0·398 (1)	0·225 (1)	0·979 (3)	1·1 (4)
H(3)	0·148 (1)	0·424 (1)	0·186 (3)	1·0 (4)
H(4)	0·672 (1)	0·133 (1)	0·973 (3)	1·2 (4)
O(*W*)	0	0	0·5	11·8 (2)

Anisotropic full-matrix least-squares refinement (on F) for non-H atoms, isotropic for H atoms. H atoms located by difference-Fourier synthesis. Final refinement with 915 reflexions ($I > 9\sigma_I$). Final $R = 0·018$ ($wR = 0·023$). Unit weights. For the complete set of 1315 independent reflexions $R = 0·025$. Extinction refined to $g = 1·84 \times 10^{-7}$ (Stout & Jensen, 1968). Max. $\Delta/\sigma = 0·02$. Max. peak height in final difference-Fourier map = 0·23 e Å^{-3}. $S = 0·374$. 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. Atomic parameters are given in Table 1.*

Discussion. The phosphoric anion P_6O_{18} is built up by six corner-sharing PO_4 tetrahedra. It has $\bar{3}$ symmetry

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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 51541 (10 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 2. *Main interatomic distances* (Å) *and bond angles* (°) *for* $(NH_4)_6P_6O_{18}.H_2O$

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

The PO_4 tetrahedron

P	O(1)	O(2)	O(*L*)	O(*L*)
O(1)	1·483 (1)	2·561 (2)	2·544 (1)	2·469 (1)
O(2)	119·30 (6)	1·484 (1)	2·476 (2)	2·542 (1)
O(*L*)	110·65 (6)	106·32 (6)	1·609 (1)	2·482 (1)
O(*L*)	106·54 (5)	111·14 (5)	101·48 (4)	1·597 (1)
	P—P	2·9544 (5)	P—O(*L*)—P	134·35 (6)
			P—P—P	108·51 (1)

The ammonium coordination

N—O(1)	2·796 (2)	N—O(2)	3·101 (2)
N—O(1)	2·841 (2)	N—O(2)	3·074 (2)
N—O(2)	2·854 (2)	N—O(*L*)	3·209 (2)
N—O(1)	3·264 (2)	N—O(2)	3·256 (2)

The hydrogen bonds

	N—H	H···O	N···O	N—H···O
N—H(1)···O(2)	0·88 (2)	1·99 (2)	2·854 (2)	167 (2)
N—H(2)···O(2)	0·88 (2)	2·33 (2)	3·101 (2)	147 (2)
N—H(3)···O(1)	0·84 (2)	2·02 (2)	2·841 (2)	165 (2)
N—H(4)···O(1)	0·84 (2)	1·95 (2)	2·796 (2)	176 (2)

and so is constructed by only one crystallographically independent tetrahedron. Its geometrical features are quite similar to those observed in previously investigated P_6O_{18} rings with the same internal symmetry (Table 2). The NH_4 groups also form $(NH_4)_6$ rings around the $\bar{3}$ axis with an N—N distance of 3·975 (2) Å and an N—N—N angle of 108·56 (3)°. P_6O_{18} and $(NH_4)_6$ rings alternatate along the $\bar{3}$ axis separated by a distance of $c/2$.

Within a range of 3·5 Å the ammonium group is eight-coordinated with N—O distances ranging from 2·796 to 3·264 Å (Table 2). A three-dimensional network of hydrogen bonds connects the NH_4 groups to the external O atoms of the phosphoric ring. Numerical details of this network are reported in Table 2.

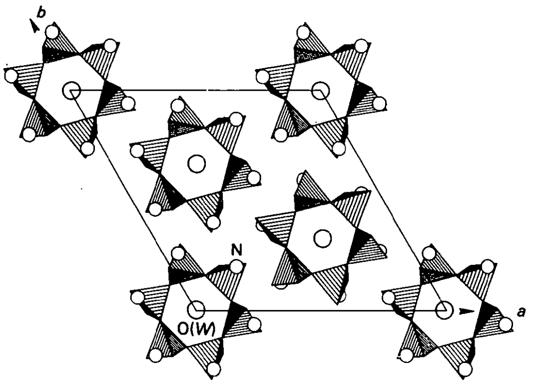

Fig. 1. Projection along the *c* axis of the atomic arrangement of $(NH_4)_6P_6O_{18}.H_2O$.

In addition it is worth noticing the existence on the $\bar{3}$ axis of a water molecule not belonging to the cation coordination. Located at 0, 0, $\frac{1}{2}$ this water molecule is exactly at the center of gravity of the $(NH_4)_6$ ring at a distance of 3·658 (9) Å from the N atoms.

Fig. 1 shows a projection of this atomic arrangement along the *c* axis.

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Redetermination of the Crystal Structure of Mo_4P_3

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Abstract. Mo_4P_3, $M_r = 476·68$, orthorhombic, *Pnma*, $a = 12·4316$ (11), $b = 3·1581$ (6), $c = 20·4468$ (30) Å, $V = 802·7$ (3) Å^3, $Z = 8$, D_m not measured, $D_x = 7·89$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu_{\text{Mo } K\alpha} = 12·9$ mm^{-1}, $F(000) = 1704$, $T = 293$ K, 1476 reflections, $R = 0·032$, $wR = 0·039$. Lattice built up from MoP_6 and MoP_5 polyhedra. Mo—P distances range from 2·375 to 3·002 Å.

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