systematic lengthening of H···O distances) due to the character of X-ray scattering. The coordination of the H_2O molecules is of type *O* class 3 according to the classification of Ferraris & Franchini-Angela (1972) and Chiari & Ferraris (1982) with significant fivefold coordination of all O atoms O5 to O9. The hydrogen-bonding scheme challenges the verification by neutron diffraction. Corresponding experiments are planned.

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Crystal Chemistry of *cyclo*-Hexaphosphates. XI. Structure of Ammonium Copper *cyclo*-Hexaphosphate Octahydrate

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Abstract. $Cu_2(NH_4)_2(P_6O_{18}).8H_2O$, $M_r = 781{\cdot}033$, triclinic, $P\bar{1}$, $a = 7{\cdot}413\,(3)$, $b = 9{\cdot}334\,(4)$, $c = 9{\cdot}634\,(4)$ Å, $\alpha = 116{\cdot}23\,(5)$, $\beta = 107{\cdot}98\,(5)$, $\gamma = 83{\cdot}10°$, $V = 569\,(1)$ Å^3, $Z = 1$, $D_x = 2{\cdot}280$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}7107$ Å, $\mu = 2{\cdot}280$ mm^{-1}, $F(000) = 394$, $T = 294$ K, final $R = 0{\cdot}030$ for 2293 reflections. The P_6O_{18} ring anions and the distorted CuO_6 octahedra form a two-dimensional network parallel to the *bc* plane. These layers are interconnected in a three-dimensional manner by the $(NH_4)O_8$ polyhedra and the hydrogen-bond network.

Introduction. Several divalent–monovalent cation *cyclo*-hexaphosphates have already been described by the authors: $Mn_2Li_2(P_6O_{18}).10H_2O$ (Averbuch-Pouchot, 1989), $Cd_2Na_2(P_6O_{18}).14H_2O$ (Averbuch-Pouchot, 1990), $Ca_2Li_2(P_6O_{18}).8H_2O$ and its isotype, the corresponding calcium–sodium salt (Averbuch-Pouchot & Durif, 1990). In the present work we describe the chemical preparation and crystal structure of ammonium copper *cyclo*-hexaphosphate octahydrate, $Cu_2(NH_4)_2(P_6O_{18}).8H_2O$.

Experimental. Crystals of the title compound have been prepared by using an almost saturated aqueous solution of ammonium *cyclo*-hexaphosphate, added with the stoichiometric amount of a copper hydroxycarbonate $[CuCO_3.Cu(OH)_2]$. In this slurry, drops of concentrated hydrochloric acid were added until the copper hydroxycarbonate disappeared. Crystals of $Cu_2(NH_4)_2(P_6O_{18}).8H_2O$ appear immediately as diamond-like plates. Polycrystalline samples can be prepared by slow evaporation at room temperature of an aqueous solution of copper chloride and ammonium *cyclo*-hexaphosphate corresponding to the stoichiometry $CuCl_2/(NH_4)_6(P_6O_{18}) = 3$. This salt is very sparingly water soluble.

Crystal size: $0{\cdot}19 \times 0{\cdot}19 \times 0{\cdot}10$ mm (a diamond-like plate). Density not measured. Philips PW1100 diffractometer, graphite monochromator. 15 reflections ($10 < \theta < 17°$) for refining unit-cell dimensions. ω scan, scan width: 1·20°, scan speed: 0·02° s^{-1}, total background measuring time: 6 s. 2651 reflections collected ($3 < \theta < 30°$), $\pm h$, $\pm k$, l, $h_{\max} = 10$, $k_{\max} = 12$, $l_{\max} = 13$. Two orientation and intensity control

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Table 1. *Final atomic coordinates and* B_{eq} *for non-*H *atoms* (B_{iso} *for* H *atoms*), *e.s.d.'s are given in parentheses*

$$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}(Å^2)
Cu(1)	0	0	0	1·12 (1)
Cu(2)	$\frac{1}{2}$	$\frac{1}{2}$	0	1·45 (1)
P(1)	0·0588 (1)	0·77460 (9)	0·35030 (8)	1·03 (1)
P(2)	0·8224 (1)	0·21588 (9)	0·32442 (8)	1·06 (1)
P(3)	0·7343 (1)	0·87383 (9)	0·14231 (8)	1·01 (1)
O(*E*11)	0·2049 (3)	0·8862 (3)	0·3759 (3)	1·69 (5)
O(*E*12)	0·0759 (4)	0·6025 (3)	0·2460 (3)	1·81 (5)
O(*L*12)	0·0376 (3)	0·7988 (3)	0·5193 (2)	1·38 (4)
O(*L*13)	0·8497 (3)	0·8310 (3)	0·2887 (2)	1·57 (4)
O(*E*21)	0·6970 (3)	0·3542 (3)	0·3761 (3)	1·69 (5)
O(*E*22)	0·9401 (3)	0·2067 (3)	0·2222 (3)	1·78 (5)
O(*L*23)	0·6903 (3)	0·0580 (3)	0·2378 (3)	1·33 (4)
O(*E*31)	0·5514 (3)	0·7850 (3)	0·0642 (3)	1·67 (5)
O(*E*32)	0·8603 (3)	0·8550 (3)	0·0410 (2)	1·59 (5)
O(*W*1)	0·2383 (3)	0·9628 (3)	0·1396 (2)	1·57 (5)
O(*W*2)	0·2379 (3)	0·5575 (3)	0·0067 (3)	2·16 (6)
O(*W*3)	0·5729 (4)	0·5419 (3)	0·2250 (3)	2·38 (6)
O(*W*4)	0·4102 (4)	0·1856 (3)	0·5242 (3)	2·13 (6)
N	0·2936 (4)	0·3481 (4)	0·3092 (4)	2·15 (7)
H(1*W*1)	0·314 (8)	0·888 (6)	0·089 (6)	2 (1)*
H(2*W*1)	0·226 (8)	0·923 (6)	0·195 (6)	2 (1)*
H(1*W*2)	0·847 (8)	0·486 (6)	0·063 (6)	2 (1)*
H(2*W*2)	0·206 (8)	0·567 (7)	0·088 (6)	3 (1)*
H(1*W*3)	0·587 (8)	0·637 (6)	0·293 (6)	3 (1)*
H(2*W*3)	0·605 (8)	0·477 (7)	0·249 (6)	3 (1)*
H(1*W*4)	0·338 (8)	0·105 (7)	0·493 (6)	3 (1)*
H(2*W*4)	0·507 (9)	0·847 (7)	0·458 (7)	4 (2)*
H(1N)	0·254 (9)	0·448 (7)	0·345 (7)	3 (2)*
H(2N)	0·293 (9)	0·290 (8)	0·373 (7)	5 (2)*
H(3N)	0·379 (9)	0·348 (7)	0·284 (7)	4 (2)*
H(4N)	0·21 (1)	0·314 (8)	0·221 (8)	5 (2)*

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in the atomic arrangement of* $Cu_2(NH_4)_2(P_6O_{18}).8H_2O$, *e.s.d.'s are given in parentheses*

The P_6O_{18} ring anion

The P(1)O_4 tetrahedron

P(1)	O(*E*11)	O(*E*12)	O(*L*12)	O(*L*13)
O(*E*11)	1·483 (3)	2·536 (3)	2·532 (4)	2·546 (3)
O(*E*12)	117·3 (1)	1·486 (2)	2·538 (3)	2·514 (3)
O(*L*12)	110·5 (1)	110·7 (2)	1·597 (3)	2·355 (3)
O(*L*13)	111·6 (1)	109·3 (1)	95·1 (1)	1·595 (2)

The P(2)O_4 tetrahedron

P(2)	O(*L*12)	O(*E*21)	O(*E*22)	O(*L*23)
O(*L*12)	1·595 (2)	2·509 (3)	2·468 (4)	2·510 (2)
O(*E*21)	109·0 (1)	1·486 (2)	2·567 (4)	2·481 (3)
O(*E*22)	106·9 (1)	120·2 (2)	1·475 (3)	2·521 (4)
O(*L*23)	103·2 (1)	106·6 (1)	109·7 (1)	1·607 (2)

The P(3)O_4 tetrahedron

P(3)	O(*L*13)	O(*L*23)	O(*E*31)	O(*E*32)
O(*L*13)	1·598 (3)	2·467 (3)	2·491 (3)	2·519 (4)
O(*L*23)	101·0 (1)	1·600 (2)	2·481 (3)	2·549 (3)
O(*E*31)	108·2 (2)	107·4 (1)	1·477 (2)	2·555 (4)
O(*E*32)	109·1 (1)	111·0 (1)	118·7 (1)	1·493 (3)

P(1)—P(2)	2·945 (1)	P(2)—P(3)	2·922 (1)
P(1)—P(3)	2·965 (1)		

P(1)—O(*L*12)—P(2)	134·6 (2)	P(2)—P(1)—P(3)	138·87 (4)
P(1)—O(*L*13)—P(3)	136·4 (2)	P(1)—P(2)—P(3)	97·36 (4)
P(2)—O(*L*23)—P(3)	131·4 (2)	P(1)—P(3)—P(2)	95·54 (3)

The CuO_6 octahedra

Cu(1)—O(*E*22)	2·287 (2) (× 2)	Cu(2)—O(*E*31)	2·499 (3) (× 2)
Cu(1)—O(*E*32)	2·030 (3) (× 2)	Cu(2)—O(*W*2)	1·965 (3) (× 2)
Cu(1)—O(*W*1)	1·962 (2) (× 2)	Cu(2)—O(*W*3)	1·929 (3) (× 2)

The $(NH_4)O_8$ polyhedron

N—O(*E*12)	2·893 (4)	N—O(*E*32)	2·961 (3)
N—O(*E*21)	2·860 (4)	N—O(*W*1)	3·243 (4)
N—O(*E*21)	3·064 (3)	N—O(*W*3)	3·384 (5)
N—O(*E*22)	2·794 (4)	N—O(*W*4)	2·948 (5)

The hydrogen bonds

O(N)—H···O	O(N)—H	H···O	O(N)—O	O(N)—H—O
O(*W*1)—H(1*W*1)···O(*E*31)	0·90 (5)	1·93 (6)	2·778 (3)	156 (4)
O(*W*1)—H(2*W*1)···O(*E*11)	0·81 (7)	1·97 (7)	2·754 (4)	164 (4)
O(*W*2)—H(1*W*2)···O(*E*12)	0·75 (5)	2·02 (5)	2·774 (3)	179 (7)
O(*W*2)—H(2*W*2)···O(*E*12)	0·85 (7)	1·94 (7)	2·769 (4)	166 (5)
O(*W*3)—H(1*W*3)···O(*W*4)	0·83 (5)	1·80 (5)	2·604 (3)	161 (8)
O(*W*3)—H(2*W*3)···O(*E*21)	0·73 (7)	1·95 (7)	2·660 (4)	163 (5)
O(*W*4)—H(1*W*4)···O(*E*11)	0·86 (6)	2·04 (6)	2·884 (3)	165 (6)
O(*W*4)—H(2*W*4)···O(*E*11)	0·66 (6)	2·18 (6)	2·816 (3)	164 (7)
N—H(1N)···O(*E*12)	0·89 (6)	2·17 (7)	2·893 (4)	138 (5)
N—H(2N)···O(*W*4)	0·98 (9)	2·03 (8)	2·948 (5)	156 (6)
N—H(3N)···O(*E*21)	0·74 (8)	2·25 (6)	2·860 (4)	141 (7)
N—H(4N)···O(*E*32)	0·82 (6)	2·24 (6)	2·961 (3)	148 (7)

H(1*W*1)—O(*W*1)—H(2*W*1)	97 (6)	H(1*W*2)—O(*W*2)—H(2*W*2)	121 (6)
H(1*W*3)—O(*W*3)—H(2*W*3)	102 (6)	H(1*W*4)—O(*W*4)—H(2*W*4)	99 (7)

reflections ($0\bar{2}5$ and $02\bar{5}$) measured every 2 h without any significant variation. 2631 reflections kept after averaging Friedel pairs (R_{int} = 0·032). Lorentz and polarization corrections, no absorption correction. Structure solved by classical methods: study of the three-dimensional Patterson function and successive Fourier syntheses. H atoms located by difference Fourier syntheses. Anisotropic full-matrix least-squares refinements (on *F*), isotropic for H atoms. Unit weights. Final refinements with 2293 reflections ($F > 2\sigma_F$). Final R = 0·030 (wR = 0·034), S = 0·951, max. Δ/σ = 0·04, max. peak height in the final difference Fourier synthesis = 0·716 e Å^{-3}. No secondary-extinction correction. 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.

Discussion. Table 1 reports the final atomic coordinates.* The P_6O_{18} ring anion is centrosymmetric, located around the inversion centre at 0, 0, 1/2. As usually observed for P_6O_{18} groups with such a $\bar{1}$ internal symmetry the P—P—P angles depart significantly from the theoretical value corresponding to a planar ring: here they spread from 95·54 to 138·87°. The P(2)O_4 and the P(3)O_4 tetrahedra have no special features and their main geometrical characteristics, reported in Table 2, are quite similar to what is commonly observed in condensed phosphoric anions, whereas in the P(1)O_4 tetrahedron an unusual feature occurs. The O(*L*)—P—O(*L*) angle observed in this tetrahedron is 95·1°, departing significantly from the value generally observed in such anions (100·0°). The small value of this angle induces a short O(*L*)—O(*L*) distance (2·355 Å) rather unusual in this type of anion. In spite of this anomaly, the average values observed in this tetrahedron

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53813 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

for the P—O distances and the O—P—O angles (1·540 Å and 109·1°) are the normal ones.

The two Cu atoms are located on inversion centres, Cu(1) at (0,0,0) Cu(2) at (1/2, 1/2, 0). Both have an octahedral coordination made by four O atoms and two water molecules for Cu(1) and four water molecules and two O atoms for Cu(2). The distortion of the Cu(2)O_6 octahedron is significantly larger than that of Cu(1)O_6, Cu—O distances varying from 1·962 to 2·287 Å in Cu(1)O_6 and from 1·929 to 2·499 Å in Cu(2)O_6. Within a range of 3·50 Å the ammonium group has an eightfold coordination made by five O atoms and three water molecules with N—O distances varying from 2·794 to 3·384 Å.

The atomic arrangement can be easily described as a succession of ribbons built up by the P_6O_{18} phosphoric ring anions and by the Cu(1)O_6 octahedra spreading parallel to the **c** direction. These ribbons are themselves interconnected along the **b** direction by the Cu(2)O_6 octahedra so as to form a layer parallel to the *bc* plane. The connections so established by the CuO_6 octahedra between the phosphoric groups are not identical; the Cu(1)O_6 octahedra share four of their O atoms with the two adjacent P_6O_{18} groups while Cu(2)O_6 octahedra share only two. Fig. 1 is a projection of this atomic arrangement along the *a* axis. The three-dimensional cohesion is established between these layers by the ammonium polyhedra and the hydrogen-bond network. Table 2 gives the main interatomic distances and bond angles in this atomic arrangment. The drawing was made with *STRUPLO* (Fischer, 1985).

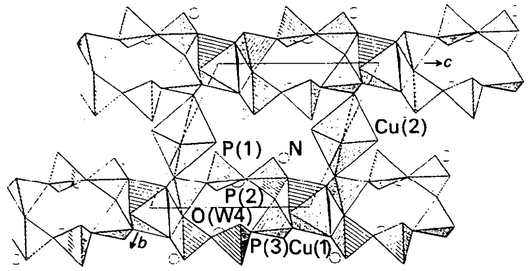

Fig. 1. Projection along the *a* axis of the atomic arrangement of $Cu_2(NH_4)_2P_6O_{18}.8H_2O$. The H atoms have been omitted.

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Crystal Chemistry of *cyclo*-Hexaphosphates. XIII. Structure of Silver Lithium *cyclo*-Hexaphosphate Dihydrate

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Abstract. $Ag_4Li_2P_6O_{18}.2H_2O$, $M_r = 955{\cdot}206$, triclinic, $P\bar{1}$, $a = 8{\cdot}408\ (2)$, $b = 7{\cdot}602\ (2)$, $c = 7{\cdot}566\ (2)$ Å, $\alpha = 107{\cdot}47\ (3)$, $\beta = 106{\cdot}09\ (3)$, $\gamma = 72{\cdot}64\ (3)°$, $V = 430{\cdot}8\ (4)$, $Z = 1$, $D_x = 3{\cdot}681$ Mg m^{-3}, $\lambda(\text{Ag }K\alpha) = 0{\cdot}5608$ Å, $\mu = 2{\cdot}562$ mm^{-1}, $F(000) = 448$, room temperature, final $R = 0{\cdot}033$ for 3318 reflections. The present atomic arrangement has a layer organization. Planes of corner-sharing LiO_4 tetrahedra and P_6O_{18} ring anions alternate with planes of Ag atoms. The hydrogen-bond scheme is described.

Introduction. Up to now only two mixed monovalent cation *cyclo*-hexaphosphates have been investigated: $Li_3Na_3P_6O_{18}.12H_2O$ and $Li_3K_3P_6O_{18}.H_2O$ (Averbuch-Pouchot, 1989). These two compounds correspond to a 1/1 order between the associated cations. In the present work we describe the chemical preparation and crystal structure of a 1/2 order in this class of compound: $Ag_4Li_2P_6O_{18}.2H_2O$.

Experimental. Crystals of the title compound have been prepared by adding an aqueous solution of silver nitrate to an aqueous solution of lithium *cyclo*-hexaphosphate so as to obtain a ratio Ag/Li = 2 in the resulting solution. After some days of evaporation at room temperature large elongated irregular prisms of $Ag_4Li_2P_6O_{18}.2H_2O$ appeared in the solution. The compound is very sparingly soluble in water.

Crystal size: 0·16 × 0·24 × 0·30 mm. Density not measured. Philips PW1100 diffractometer, graphite monochromator. 16 reflections ($10{\cdot}0 < \theta < 17{\cdot}0°$) for

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