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Crystal Chemistry of *cyclo*-Hexaphosphates. XIV. Structure of Silver Ammonium *cyclo*-Hexaphosphate Monohydrate

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Abstract. $Ag_3(NH_4)_3P_6O_{18}.H_2O$, $M_r = 869{\cdot}562$, trigonal, $R\bar{3}$, $a = 15{\cdot}172\ (5)$, $c = 13{\cdot}994\ (5)$ Å, $Z = 6$, $V = 2790\ (3)$ Å^3, $D_x = 3{\cdot}105$ Mg m^{-3}, $\lambda(\mathrm{Ag}\ K\bar{\alpha}) = 0{\cdot}5608$ Å, $\mu = 1{\cdot}873$ mm^{-1}, $F(000) = 2508$, room temperature, final $R = 0{\cdot}036$ for 2442 reflections. Pseudo-hexagonal rings built up by three silver atoms and three ammonium groups alternate with the P_6O_{18} groups along the ternary axes. The $Ag_3(NH_4)_3$ rings are centred by the water molecule.

Introduction. The crystal structures of ammonium *cyclo*-hexaphosphate monohydrate, $(NH_4)_3P_6O_{18}.H_2O$, and of the corresponding silver salt, $Ag_6P_6O_{18}.H_2O$, have already been described (Averbuch-Pouchot, 1989*a*,*b*). These two compounds have very similar unit cells: $a = 15{\cdot}445\ (10)$, $c = 7{\cdot}553\ (7)$ Å for the ammonium salt, $a = 14{\cdot}807\ (10)$, $c = 6{\cdot}597\ (7)$ Å for the silver salt.

Both crystallize with the space group $R\bar{3}$ and $Z = 3$. The title compound, $Ag_3(NH_4)_3P_6O_{18}.H_2O$, is also trigonal, $R\bar{3}$, and its unit cell is closely related to the previous ones. The observed a value is approximately halfway between the values measured for $a(\mathrm{Ag})$ and $a(\mathrm{NH_4})$ and the value of c is close to the sum $c(\mathrm{Ag}) + c(\mathrm{NH_4})$. These observations suggest that the atomic arrangement of the title compound must be very similar to those determined for the silver and ammonium salts with, in addition, an order between the associated cations to explain the doubling of the c axis.

Experimental. Crystals of the title compound have been prepared by adding a dilute aqueous solution of silver nitrate to a dilute aqueous solution of ammonium *cyclo*-hexaphosphate to obtain a ratio $Ag/NH_4 = 1/2$ in the resulting solution. After several weeks of evaporation at room temperature large crystals of $Ag_3(NH_4)_3P_6O_{18}.H_2O$ appeared as stout trigonal prisms. The compound is very sparingly soluble in water.

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Crystal size: 0·22 × 0·22 × 0·28 mm. Density not measured. Philips PW1100 diffractometer, graphite monochromator. 16 reflections (10·0 < θ < 16·0°) for refining unit-cell dimensions. $\omega/2\theta$ scan, scan width 1·20°, scan speed 0·03° s^{-1}, total background measuring time 6 s. 3036 reflections collected (3 < θ < 30°), h, k, $\pm l$, $h_{max} = 22$, $k_{max} = 22$, $l_{max} = 24$. Two orientation and intensity control reflections ($\bar{3}\bar{3}\bar{3}$ and 333) measured every 6 h without any significant variation. 2784 reflections obtained after averaging Friedel pairs ($R_{int} = 0{\cdot}024$). Lorentz and polarization corrections, no absorption correction. Structure solved by classical methods, interpretation of the Patterson map and successive Fourier syntheses, H atoms of the ammonium group located by difference Fourier syntheses. Owing to the high thermal factor of the water molecule the corresponding H atoms could not be located. In addition as this water molecule is located on a threefold axis its H atoms are evidently disordered. Anisotropic full-matrix least-squares refinement (on F), isotropic for H atoms. Unit weights. Final refinement cycles with 2442 reflections [$I > 3\sigma(I)$]. Final $R = 0{\cdot}036$, $wR = 0{\cdot}038$, $S = 1{\cdot}452$, max. $\Delta/\sigma = 0{\cdot}12$, max. peak height in the final difference Fourier synthesis = 0·440 e $Å^{-3}$. Secondary-extinction correction according to Stout & Jensen (1968) with $g = 8{\cdot}9 \times 10^{-7}$. 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.

Table 1 reports the final atomic coordinates.*

Table 1. *Final atomic coordinates and B_{eq}/B_{iso} values*

H atoms were refined isotropically. 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}/B_{iso} ($Å^2$)
Ag	0·75100 (2)	0·04512 (2)	0·23827 (2)	1·865 (4)
N	0·2841 (2)	0·4387 (2)	0·4076 (2)	2·11 (5)
P(1)	0·13372 (5)	0·50939 (5)	0·19984 (6)	1·18 (1)
P(2)	0·27890 (5)	0·46408 (5)	0·69981 (6)	1·21 (1)
O(*L*1)	0·2130 (2)	0·5082 (2)	0·1242 (2)	1·61 (4)
O(*E*11)	0·5417 (2)	0·5740 (2)	0·1538 (2)	1·98 (4)
O(*E*21)	0·6593 (2)	0·5180 (2)	0·9612 (2)	2·03 (5)
O(*L*2)	0·9430 (2)	0·1059 (2)	0·9578 (2)	1·64 (4)
O(*E*12)	0·9566 (2)	0·5725 (2)	0·3234 (2)	2·14 (5)
O(*E*22)	0·8875 (2)	0·1037 (2)	0·1280 (2)	1·90 (4)
O(*W*)	0·000	0·000	0·750 (1)	10·4 (3)
H(1N)	0·921 (5)	0·805 (5)	0·702 (5)	3 (2)
H(2N)	0·678 (5)	0·515 (5)	0·554 (5)	3 (2)
H(3N)	0·382 (5)	0·161 (5)	0·562 (5)	3 (2)
H(4N)	0·974 (5)	0·734 (5)	0·707 (5)	4 (2)

Discussion. As suggested by the unit-cell dimensions (see *Introduction*), the atomic arrangement of the title compound is closely related to the crystal structures of $Ag_6P_6O_{18}.H_2O$ and $(NH_4)_6P_6O_{18}.H_2O$. In these two compounds the P_6O_{18} ring anions, with $\bar{3}$ internal symmetry, alternate with hexagonal rings of associated cations along the $\bar{3}$ axis. In each case these hexagonal rings, Ag_6 or $(NH_4)_6$, are centred by the water molecule located on the threefold axis. These main features are maintained in the present arrangement.

The description of the crystal structure can be made simply by examining the configuration along the $\bar{3}$ axis located at the origin of the unit cell. A first type of P_6O_{18} ring anion, built up by the $P(2)O_4$ tetrahedron, is located around this threefold axis at $z = 0$ while the second P_6O_{18} group, built up by the $P(1)O_4$ tetrahedron, is found at $z = 0{\cdot}5$. Halfway between the phosphoric groups, at $z = 0{\cdot}25$ and 0·75, are located pseudo-hexagonal rings of associated cations made by three silver atoms and three ammonium groups centred by the water molecule located on the $\bar{3}$ axis. So the two main differences between the $Ag_6P_6O_{18}.H_2O$ and the $(NH_4)_6P_6O_{18}.H_2O$ structures and the present arrangement rest on two points: the existence of two crystallographically independent P_6O_{18} groups, and the composition of the associated cation rings.

The two P_6O_{18} ring anions whose main geometrical features are reported in Table 2 are quite similar to what was previously reported for such rings with internal symmetry $\bar{3}$ or 3. The pseudo-hexagonal ring $Ag_3(NH_4)_3$ is much more distorted than the homogeneous Ag_6 or $(NH_4)_6$ rings already observed. Here the N—Ag—N and Ag—N—Ag angles are 92·62 (8) and 145·9 (1)°, respectively. The distances to the central water molecules are O(*W*)—N = 3·154 (4) and O(*W*)—Ag = 4·166 (1) Å. Within 3 Å the Ag atom has fivefold coordination, while within 3·5 Å the NH_4^+ group has ninefold coordination including the water molecule. In the case of silver the distances Ag–O vary within the range 2·360 to 2·652 Å, for the ammonium group the nine N—O distances spread from 2·829 to 3·431 Å. It is to be noticed that two bonding O atoms [O(*L*1) and O(*L*2)] take part in the coordination of the ammonium group, a feature not very usual in the crystal chemistry of condensed phosphates. This ammonium group is an almost regular tetrahedron with N—H distances ranging from 0·85 to 1·02 Å and H—N—H angles varying from 100 to 121° with an average of 109°.

The main features of the hydrogen-bond scheme are described in Table 2. Fig. 1 gives a projection along the c axis of part of this arrangement. The

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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 53687 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in the atomic arrangement of* $Ag_3(NH_4)_3P_6O_{18}.H_2O$

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

The $P(1)_6O_{18}$ ring anion

P(1)	O(*L*1)	O(*L*1)	O(*E*11)	O(*E*21)
O(*L*1)	1·609 (3)	2·477 (4)	2·487 (4)	2·528 (3)
O(*L*1)	101·2 (1)	1·596 (3)	2·523 (4)	2·473 (3)
O(*E*11)	107·1 (1)	110·1 (1)	1·481 (3)	2·573 (4)
O(*E*21)	109·6 (1)	106·7 (2)	120·4 (2)	1·485 (3)

P(1)—P(1) 2·916 (1)

P(1)—O(*L*1)—P(1)	131·0 (2)	P(1)—P(1)—P(1)	110·36 (3)

The $P(2)_6O_{18}$ ring anion

P(2)	O(*L*2)	O(*L*2)	O(*E*12)	O(*E*22)
O(*L*2)	1·596 (2)	2·473 (3)	2·538 (3)	2·471 (3)
O(*L*2)	101·5 (2)	1·599 (2)	2·496 (3)	2·522 (3)
O(*E*12)	111·0 (2)	108·2 (2)	1·482 (2)	2·553 (4)
O(*E*22)	106·5 (2)	109·6 (1)	118·7 (2)	1·486 (2)

P(2)—P(2) 2·907 (1)

P(2)—O(*L*2)—P(2)	131·0 (2)	P(2)—P(2)—P(2)	110·32 (3)

AgO_5 polyhedron

Ag—O(*E*11)	2·428 (2)	Ag—O(*E*21)	2·362 (2)
Ag—O(*E*12)	2·360 (3)	Ag—O(*E*22)	2·370 (2)
Ag—O(*E*22)	2·652 (3)		

$(NH_4)O_9$ polyhedron

N—O(*L*1)	3·158 (4)	N—O(*E*11)	2·823 (4)
N—O(*E*11)	3·334 (4)	N—O(*E*21)	2·853 (4)
N—O(*E*21)	3·298 (5)	N—O(*L*2)	3·431 (4)
N—O(*E*12)	2·934 (4)	N—O(*E*22)	2·884 (3)
N—O(*W*)	3·154 (4)		

The hydrogen bonds

N—H···O	N—H	H···O	N—O	N—H—O
N—H(1N)···O(*E*21)	0·98 (8)	1·93 (8)	2·853 (4)	155 (5)
N—H(2N)···O(*E*22)	0·85 (6)	2·09 (6)	2·884 (3)	156 (9)
N—H(3N)···O(*E*11)	1·02 (8)	1·83 (9)	2·823 (4)	165 (5)
N—H(4N)···O(*E*12)	0·94 (9)	2·08 (9)	2·934 (4)	150 (5)

drawing was prepared using the *STRUPLO* program (Fischer, 1985).

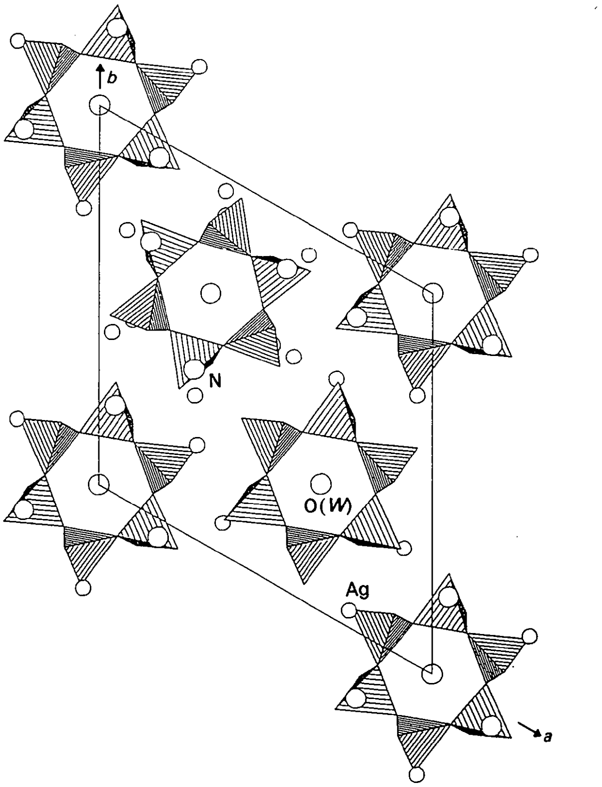

Fig. 1. Projection of the atomic arrangement of $Ag_3(NH_4)_3P_6O_{18}.H_2O$ along the *c* axis. The H atoms have been omitted and the projection is restricted to $-0{\cdot}10 < z < 0{\cdot}50$.

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Crystal Chemistry of *cyclo*-Hexaphosphates. XV. Structures of Sodium Ammonium *cyclo*-Hexaphosphate Dihydrate and Sodium Rubidium *cyclo*-Hexaphosphate Hexahydrate

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Abstract. $Na_2(NH_4)_4P_6O_{18}.2H_2O$, $M_r = 627{\cdot}992$, monoclinic, $P2_1/n$, $a = 13{\cdot}363\ (7)$, $b = 11{\cdot}580\ (12)$, $c = 6{\cdot}809\ (5)$ Å, $\beta = 101{\cdot}87\ (5)°$, $V = 1031\ (2)$ Å^3, $Z = 2$, $D_x = 2{\cdot}022$ Mg m^{-3}, $\lambda(\text{Ag } K\alpha) = 0{\cdot}5608$ Å, $\mu = 0{\cdot}353$ mm^{-1}, $F(000) = 640$, room temperature, final $R = 0{\cdot}023$ for 3892 independent reflections.

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