

water molecules and of K(1) atoms in such a plane. Figs. 1 and 2 report these two projections. The cohesion between these planes is established through the potassium polyhedra and the hydrogen bonds. The main interatomic distances and bond angles in this arrangement are given in Table 2.

The phosphoric ring anion observed in this arrangement is very regular with a P—P—P angle of 107.85° . H atoms of the $\text{Te}(\text{OH})_6$ group are only involved in hydrogen bonds interconnecting these groups to external O atoms of the phosphoric rings (Table 2).

$\text{Rb}_6\text{P}_6\text{O}_{18}\cdot 3\text{Te}(\text{OH})_6\cdot 4\text{H}_2\text{O}$. Here the P_6O_{18} ring anion located around the inversion centre at $\frac{1}{2}, 0, 0$ is significantly more distorted, with P—P—P angles ranging from 96.65 to 144.87° . A recent review of the geometry of this kind of ring anion (Averbuch-Pouchot & Durif, 1991) shows that this range of distortion is the common rule for P_6O_{18} rings having $\bar{1}$ internal symmetry. TeO_6 octahedra also located around inversion centres are almost regular as usually observed. The $\text{Te}(1)(\text{OH})_6$ and $\text{Te}(2)(\text{OH})_6$ groups aligned along the c axis are interconnected by one hydrogen bond: $\text{O}(6)\text{—H}(6)\cdots\text{O}(2)$ while the

third one, $\text{Te}(3)(\text{OH})_6$, does not establish such bonds with the other telluric groups. The H atoms of the $\text{Te}(\text{OH})_6$ groups are involved in hydrogen bonds connecting them either to the external O atoms of the P_6O_{18} ring, or to water molecules.

The very simple stacking of $\text{Te}(\text{OH})_6$ and P_6O_{18} groups is shown in Fig. 3, a projection of this atomic arrangement along the b axis. Table 4 gives the main interatomic distances and bond angles in this salt where within a range of 3.5 \AA the three independent Rb atoms have from seven to nine neighbours.

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Crystal Chemistry of *cyclo*-Hexaphosphates. XVIII. Structures of Ethylammonium *cyclo*-Hexaphosphate Tetrahydrate and Hydrazinium(1+) Hydrazinium(2+) *cyclo*-Hexaphosphate

BY M. T. AVERBUCH-POUCHOT AND A. DURIF

Laboratoire de Cristallographie, associé à l'Université J. Fourier, CNRS, 166 X, 38042 Grenoble CEDEX, France

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Abstract. $(\text{C}_2\text{H}_5\text{N})_6\text{P}_6\text{O}_{18}\cdot 4\text{H}_2\text{O}$, $M_r = 822.444$, monoclinic, $P2_1/a$, $a = 16.804(10)$, $b = 23.883(10)$, $c = 10.623(8) \text{ \AA}$, $\beta = 109.66(2)^\circ$, $V = 4015(8) \text{ \AA}^3$, $Z = 4$, $D_x = 1.360 \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$, $\mu = 0.351 \text{ mm}^{-1}$, $F(000) = 1744$, $T = 294 \text{ K}$, final $R = 0.035$ for 6795 independent reflections. $(\text{N}_2\text{H}_5)_2(\text{N}_2\text{H}_6)_2\text{P}_6\text{O}_{18}$, $M_r = 608.058$, triclinic, $P\bar{1}$, $a = 8.175(8)$, $b = 7.926(8)$, $c = 8.457(7) \text{ \AA}$, $\alpha = 105.05(2)$, $\beta = 102.08(2)$, $\gamma = 86.42(2)^\circ$, $V = 517.5(1.5) \text{ \AA}^3$, $Z = 1$, $D_x = 1.951 \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$, $\mu = 0.627 \text{ mm}^{-1}$, $F(000) = 312$, $T = 297 \text{ K}$, final $R = 0.032$ for 4869 independent reflections. The atomic arrangement of the ethylammonium salt is built up of arrays of P_6O_{18} ring anions and ethylammonium groups parallel to the c axis and arranged in an almost hexagonal way. This

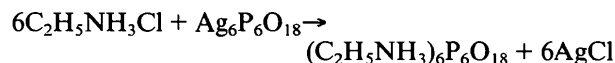
hexagonal packing is centred by a centrosymmetric cluster of eight water molecules forming a branched hexagon. The phosphoric ring anion has no internal symmetry. Six crystallographically independent ethylammonium groups coexist in the arrangement. The hydrogen-bond geometry is described. The second structure is a very simple one. The centrosymmetrical P_6O_{18} groups are located around the inversion centres at $0, 0, \frac{1}{2}$. The wide channels parallel to the c axis created by the anion stacking are lined by both hydrazinium(1+) and hydrazinium(2+) groups. The hydrogen-bond network is reported.

Introduction. The present investigation is part of a systematic study of the organic cation derivatives of *cyclo*-hexaphosphates. Some results in this field have

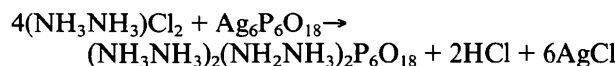
already been reported by the authors: tris(ethylenediammonium) *cyclo*-hexaphosphate dihydrate and copper bis(ethylenediammonium) *cyclo*-hexaphosphate hexahydrate (Durif & Averbuch-Pouchot, 1989), hydroxylammonium *cyclo*-hexaphosphate tetrahydrate (Durif & Averbuch-Pouchot, 1990) and tris(ethylenediammonium) *cyclo*-hexaphosphate tellurate dihydrate (Averbuch-Pouchot & Durif, 1990) have been prepared as stable compounds and their atomic arrangements determined.

Experimental. Crystals of the title compounds have both been prepared by Boullé's (1938) process using as starting materials ethylammonium chloride in one case and hydrazinium dichloride in the other case. The silver *cyclo*-hexaphosphate used in the two reactions has been prepared according to the method described by Averbuch-Pouchot (1989a).

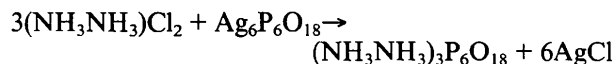
For the preparation of the ethylammonium salt the reaction was as expected:



while in the case of the hydrazinium salt the reaction was:



instead of the expected one:



so this compound is in fact a salt of hydrazinium(1+) and hydrazinium(2+).

Crystals of the ethylammonium salt are thick diamond-like plates, those of the hydrazinium salt are elongated triclinic prisms. Both species are very stable in normal conditions.

(C₂H₅NH₃)₆P₆O₁₈·4H₂O. Crystal size: 0.55 × 0.55 × 0.32 mm. Density not measured. Philips PW 1100 diffractometer, graphite monochromator. 23 reflections (10.0 < θ < 16.0°) for refining unit-cell dimensions. ω/2θ scan, scan width 1.20°, scan speed 0.03° s⁻¹, total background measuring time 6 s. 9174 reflections collected (3 < θ < 35°), ±h, k, l, h_{max} = 23, k_{max} = 33, l_{max} = 14. Two orientation and intensity control reflections (191 and 191) measured every 6 h without any significant variation. 8303 independent reflections (R_{int} = 0.02).

(NH₃NH₃)₂(NH₂NH₃)₂P₆O₁₈. Crystal size: 0.45 × 0.30 × 0.30 mm. Density not measured. Philips PW 1100 diffractometer, graphite monochromator. 18 reflections (10.0 < θ < 16.50°) for refining unit-cell dimensions. ω/2θ scan, scan width 1.40°; scan speed 0.03° s⁻¹, total background measuring time 6 s. 10 565 reflections collected (3 < θ < 30°), ±h, ±k, ±l, h_{max} = 14, k_{max} = 14, l_{max} = 15. Two orientation

Table 1. Final atomic coordinates and B_{eq} values for (C₂H₅NH₃)₆P₆O₁₈·4H₂O

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

$$B_{\text{eq}} = (4/3)\sum_i\sum_j\beta_{ij}a_i\cdot a_j$$

	x	y	z	B _{eq} (Å ²)
P(1)	0.60039 (3)	0.17091 (2)	0.53502 (5)	1.900 (9)
P(2)	0.59322 (3)	0.08582 (2)	0.33349 (5)	1.773 (9)
P(3)	0.54836 (3)	0.14564 (2)	0.08140 (5)	1.714 (9)
P(4)	0.40908 (3)	0.22723 (2)	0.03184 (5)	1.870 (9)
P(5)	0.32237 (3)	0.18009 (2)	0.20356 (5)	1.859 (9)
P(6)	0.42116 (3)	0.19872 (3)	0.49059 (5)	2.19 (1)
O(L12)	0.57681 (9)	0.11139 (6)	0.4630 (1)	2.15 (3)
O(L23)	0.53973 (9)	0.12992 (7)	0.2229 (1)	2.29 (3)
O(L34)	0.45618 (9)	0.17192 (6)	0.0087 (1)	2.10 (3)
O(L45)	0.39469 (9)	0.21450 (7)	0.1703 (1)	2.33 (3)
O(L56)	0.3724 (1)	0.16458 (7)	0.3565 (1)	2.44 (3)
O(L16)	0.51367 (9)	0.20469 (7)	0.4797 (2)	2.46 (3)
O(E11)	0.66080 (9)	0.20140 (7)	0.4841 (2)	2.65 (3)
O(E12)	0.6256 (1)	0.16192 (7)	0.6811 (1)	2.91 (3)
O(E21)	0.68327 (9)	0.08734 (7)	0.3474 (2)	2.78 (3)
O(E22)	0.5483 (1)	0.03125 (6)	0.3095 (2)	2.59 (3)
O(E31)	0.61469 (9)	0.18869 (7)	0.1018 (2)	2.59 (3)
O(E32)	0.5525 (1)	0.09432 (7)	0.0049 (2)	2.61 (3)
O(E41)	0.4668 (1)	0.27599 (7)	0.0569 (2)	2.84 (3)
O(E42)	0.32690 (9)	0.22936 (7)	-0.0800 (2)	2.68 (3)
O(E51)	0.25136 (9)	0.21858 (8)	0.1921 (2)	2.97 (3)
O(E52)	0.3039 (1)	0.12633 (7)	0.1296 (2)	2.84 (3)
O(E61)	0.3879 (1)	0.25667 (8)	0.4831 (2)	3.45 (4)
O(E62)	0.4220 (1)	0.16283 (9)	0.6040 (2)	3.82 (4)
N(1)	0.1235 (1)	0.52777 (9)	0.7481 (2)	3.09 (4)
N(2)	0.1808 (1)	0.78537 (9)	0.3183 (2)	2.86 (4)
N(3)	0.3416 (1)	0.76162 (9)	0.1012 (2)	2.75 (4)
N(4)	0.2168 (1)	0.83184 (9)	0.7070 (2)	3.03 (4)
N(5)	0.0844 (1)	0.57524 (9)	0.2310 (2)	2.88 (4)
N(6)	0.1146 (1)	0.21697 (9)	0.2821 (2)	2.72 (4)
C(11)	0.1309 (2)	0.5221 (1)	0.6143 (3)	4.35 (7)
C(12)	0.2813 (2)	0.0125 (2)	0.3786 (4)	6.25 (9)
C(21)	0.3516 (2)	0.3395 (1)	0.7469 (3)	4.02 (6)
C(22)	0.1377 (2)	0.8814 (2)	0.3504 (4)	5.30 (9)
C(31)	0.3973 (2)	0.7115 (2)	0.1320 (3)	4.95 (7)
C(32)	0.3875 (3)	0.6787 (2)	0.2454 (4)	6.7 (1)
C(41)	0.1730 (2)	0.8653 (2)	0.7808 (3)	4.53 (7)
C(42)	0.1193 (2)	0.9102 (2)	0.6942 (4)	6.56 (9)
C(51)	0.1674 (2)	0.5773 (1)	0.2113 (3)	4.46 (7)
C(52)	0.3273 (2)	0.0337 (2)	0.8862 (4)	6.60 (9)
C(61)	0.1018 (3)	0.1662 (1)	0.3537 (3)	5.57 (8)
C(62)	0.1794 (3)	0.1500 (2)	0.4618 (4)	6.8 (1)
O(H1)	0.1691 (1)	0.42036 (8)	0.8748 (2)	3.50 (4)
O(H2)	0.4906 (2)	0.3920 (1)	0.0408 (3)	6.88 (8)
O(H3)	0.3450 (2)	0.4567 (1)	0.9619 (4)	7.58 (8)
O(H4)	0.3553 (2)	0.5717 (1)	0.9705 (5)	11.5 (1)

and intensity control reflections (060 and 060) measured every 6 h without any significant variation. 5500 independent reflections after averaging Friedel pairs (R_{int} = 0.017).

For both data collections, Lorentz and polarization corrections no absorption correction. The two structures were solved by direct methods using MULTAN77, (Main, Lessinger, Woolfson, Germain & Declercq, 1977). H atoms were located by difference Fourier syntheses. For the two crystal structures, anisotropic full-matrix least-squares refinements (on F), isotropic for H atoms. Unit weights. 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 operating on a MicroVAX II used for all calculations.

For (C₂H₅NH₃)₆P₆O₁₈·4H₂O, final R = 0.035 (wR = 0.036) for 6795 reflections corresponding to I >

$3\sigma(I)$. $S = 1.287$. Maximum peak height in the final difference Fourier map = $0.358 \text{ e } \text{\AA}^{-3}$. Maximum $\Delta/\sigma = 0.05$.

For $(\text{NH}_3\text{NH}_3)_2(\text{NH}_2\text{NH}_3)_2\text{P}_6\text{O}_{18}$, final $R = 0.032$ ($wR = 0.036$) for 4869 reflections corresponding to $I > 3\sigma(I)$. $S = 0.445$, Maximum peak height in the final difference Fourier map = $0.696 \text{ e } \text{\AA}^{-3}$. Maximum $\Delta/\sigma = 0.05$.

Table 2. Main interatomic distances (\AA) and bond angles ($^\circ$) in the atomic arrangement of $(\text{C}_2\text{H}_5\text{NH}_3)_6\text{P}_6\text{O}_{18}\cdot 4\text{H}_2\text{O}$

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

The P_6O_{18} ring anion

P(1) O_4 tetrahedron

P(1)	O(L12)	O(L16)	O(E11)	O(E12)
O(L12)	1.599 (2)	2.500 (2)	2.540 (2)	2.493 (2)
O(L16)	102.98 (8)	1.595 (2)	2.458 (2)	2.540 (2)
O(E11)	110.47 (10)	105.55 (9)	1.491 (2)	2.541 (2)
O(E12)	108.04 (9)	111.31 (10)	117.52 (9)	1.480 (2)

P(2) O_4 tetrahedron

P(2)	O(L12)	O(L23)	O(E21)	O(E22)
O(L12)	1.612 (2)	2.454 (2)	2.553 (2)	2.455 (2)
O(L23)	99.28 (8)	1.609 (2)	2.541 (2)	2.516 (2)
O(E21)	111.74 (9)	111.15 (9)	1.470 (2)	2.547 (2)
O(E22)	104.82 (10)	108.82 (8)	119.06 (10)	1.485 (2)

P(3) O_4 tetrahedron

P(3)	O(L23)	O(L34)	O(E31)	O(E32)
O(L23)	1.602 (2)	2.451 (2)	2.510 (2)	2.542 (2)
O(L34)	99.53 (8)	1.608 (1)	2.542 (2)	2.469 (2)
O(E31)	109.09 (9)	110.86 (9)	1.478 (2)	2.551 (2)
O(E32)	110.81 (9)	105.90 (8)	118.89 (10)	1.485 (2)

P(4) O_4 tetrahedron

P(4)	O(L34)	O(L45)	O(E41)	O(E42)
O(L34)	1.601 (2)	2.499 (2)	2.532 (2)	2.472 (2)
O(L45)	102.72 (9)	1.598 (2)	2.462 (2)	2.540 (2)
O(E41)	110.38 (9)	106.09 (9)	1.482 (2)	2.566 (2)
O(E42)	106.22 (9)	110.72 (9)	119.48 (10)	1.489 (1)

P(5) O_4 tetrahedron

P(5)	O(L45)	O(L56)	O(E51)	O(E52)
O(L45)	1.602 (2)	2.445 (2)	2.498 (2)	2.550 (2)
O(L56)	99.47 (8)	1.602 (1)	2.542 (2)	2.471 (2)
O(E51)	108.30 (10)	111.16 (10)	1.478 (2)	2.543 (2)
O(E52)	111.48 (10)	106.39 (9)	118.40 (9)	1.483 (2)

P(6) O_4 tetrahedron

P(6)	O(L56)	O(L16)	O(E61)	O(E62)
O(L56)	1.606 (1)	2.485 (2)	2.545 (2)	2.477 (2)
O(L16)	101.47 (9)	1.604 (2)	2.461 (2)	2.547 (2)
O(E61)	110.81 (8)	105.63 (10)	1.484 (2)	2.550 (3)
O(E62)	106.93 (10)	111.56 (10)	119.06 (12)	1.475 (2)

P(1)—O(L12)—P(2)	131.2 (1)	P(1)—P(2)—P(3)	105.50 (2)
P(2)—O(L23)—P(3)	129.3 (1)	P(2)—P(3)—P(4)	115.69 (2)
P(3)—O(L34)—P(4)	134.0 (1)	P(3)—P(4)—P(5)	99.58 (2)
P(4)—O(L45)—P(5)	131.4 (1)	P(4)—P(5)—P(6)	111.07 (2)
P(5)—O(L56)—P(6)	136.0 (1)	P(5)—P(6)—P(1)	108.46 (2)
P(6)—O(L16)—P(1)	135.7 (1)	P(6)—P(1)—P(2)	104.47 (2)

P(1)—P(2)	2.9248 (8)	P(4)—P(5)	2.9167 (9)
P(2)—P(3)	2.9021 (7)	P(5)—P(6)	2.9741 (7)
P(3)—P(4)	2.9535 (7)	P(6)—P(1)	2.9628 (8)

The ethylammonium groups

N(1)—C(11)	1.474 (4)	N(1)—C(11)—C(12)	112.0 (2)
C(11)—C(12)	1.469 (5)	P(2)—C(21)—C(22)	111.8 (2)
N(2)—C(21)	1.481 (4)	N(3)—C(31)—C(32)	111.6 (3)
C(21)—C(22)	1.493 (5)	N(4)—C(41)—C(42)	111.4 (3)
N(3)—C(31)	1.485 (4)	N(5)—C(51)—C(52)	110.7 (3)
C(31)—C(32)	1.492 (6)	N(6)—C(61)—C(62)	111.9 (3)
N(4)—C(41)	1.477 (4)		
C(41)—C(42)	1.501 (5)		
N(5)—C(51)	1.478 (4)		
C(51)—C(52)	1.493 (6)		
N(6)—C(61)	1.485 (4)		
C(61)—C(62)	1.471 (5)		

Table 2 (cont.)

The hydrogen bonds

O(N)—H—O	O(N)—H	H—O	O(N)—O	O(N)—H—O
N(1)—H(1N1)···O(W1)	0.86 (2)	2.04 (3)	2.878 (3)	165 (2)
N(1)—H(2N1)···O(E22)	0.82 (3)	1.93 (3)	2.743 (3)	177 (3)
N(1)—H(3N1)···O(E52)	0.94 (3)	1.82 (3)	2.766 (3)	175 (3)
N(2)—H(1N2)···O(E61)	0.89 (3)	1.97 (3)	2.809 (3)	156 (2)
N(2)—H(2N2)···O(E42)	0.75 (3)	2.13 (3)	2.828 (3)	155 (3)
N(2)—H(3N2)···O(E11)	0.91 (3)	1.90 (2)	2.799 (2)	168 (3)
N(3)—H(1N3)···O(E12)	0.94 (3)	1.92 (3)	2.851 (2)	173 (2)
N(3)—H(2N3)···O(E42)	0.87 (3)	2.01 (3)	2.870 (3)	167 (3)
N(3)—H(3N3)···O(E31)	0.82 (3)	1.96 (3)	2.768 (3)	169 (3)
N(4)—H(1N4)···O(E61)	0.86 (3)	1.97 (3)	2.829 (2)	172 (3)
N(4)—H(2N4)···O(E21)	0.91 (3)	1.86 (3)	2.745 (3)	164 (3)
N(4)—H(3N4)···O(E51)	0.82 (3)	2.19 (3)	2.893 (3)	143 (3)
N(5)—H(1N5)···O(E32)	0.93 (2)	1.89 (2)	2.811 (2)	170 (3)
N(5)—H(2N5)···O(E22)	0.94 (3)	1.87 (3)	2.806 (3)	172 (3)
N(5)—H(3N5)···O(E62)	0.95 (3)	1.81 (3)	2.754 (3)	169 (3)
N(6)—H(1N6)···O(E51)	0.89 (3)	1.88 (3)	2.771 (3)	175 (2)
N(6)—H(2N6)···O(E11)	0.93 (3)	1.88 (3)	2.808 (2)	172 (2)
N(6)—H(3N6)···O(E41)	0.91 (3)	1.93 (3)	2.814 (2)	163 (3)
O(W1)—H(1W1)···O(E32)	0.78 (4)	2.01 (4)	2.774 (3)	166 (3)
O(W1)—H(2W1)···O(E12)	0.88 (3)	1.89 (3)	2.760 (2)	170 (3)
O(W2)—H(1W2)···O(E41)	0.76 (4)	2.06 (4)	2.813 (3)	174 (4)
O(W2)—H(2W2)···O(W3)	0.46 (3)	2.37 (3)	2.775 (4)	152 (4)
O(W3)—H(1W3)···O(W1)	0.74 (3)	2.21 (3)	2.917 (3)	163 (3)
O(W3)—H(2W3)···O(W4)	0.74 (4)	2.20 (4)	2.751 (5)	132 (4)
O(W4)—H(1W4)···O(E52)	0.95 (4)	1.93 (4)	2.842 (3)	161 (4)
O(W4)—H(2W4)···O(W2)	0.54 (3)	2.33 (3)	2.770 (5)	141 (4)

H(1W1)—O(W1)—H(2W1)	110 (3)	H(1W2)—O(W2)—H(2W2)	98 (4)
H(1W3)—O(W3)—H(2W3)	89 (4)	H(1W4)—O(W2)—H(2W4)	121 (4)

Table 3. Final atomic coordinates and B_{eq} values for $(\text{NH}_3\text{NH}_2)_2(\text{NH}_3\text{NH}_3)_2\text{P}_6\text{O}_{18}$

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

$$B_{\text{eq}} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
P(1)	0.28808 (4)	0.84072 (4)	0.53859 (4)	1.269 (4)
P(2)	0.00459 (4)	0.30620 (4)	0.69467 (4)	1.260 (4)
P(3)	0.18826 (4)	0.03972 (4)	0.84784 (4)	1.258 (4)
O(L12)	0.0923 (1)	0.7878 (1)	0.4899 (1)	1.65 (1)
O(L13)	0.2874 (1)	0.0003 (1)	0.6982 (1)	1.81 (2)
O(L23)	0.0284 (1)	0.1482 (1)	0.7830 (1)	1.97 (2)
O(E11)	0.6112 (1)	0.3065 (1)	0.4134 (2)	2.26 (2)
O(E12)	0.3300 (1)	0.9111 (1)	0.4062 (1)	1.86 (2)
O(E21)	0.1679 (1)	0.3633 (1)	0.6783 (1)	1.86 (2)
O(E22)	0.8915 (1)	0.4374 (1)	0.7791 (1)	1.93 (2)
O(E31)	0.8790 (1)	0.1234 (1)	0.1367 (1)	1.97 (2)
O(E32)	0.2968 (1)	0.1531 (2)	-0.0058 (1)	2.35 (2)
N(1)	0.7852 (2)	0.8172 (2)	0.7122 (1)	1.70 (2)
N(2)	0.2823 (1)	0.3434 (1)	0.3994 (1)	1.64 (2)
N(3)	0.2942 (2)	0.6111 (2)	-0.0106 (2)	2.17 (2)
N(4)	0.5555 (2)	0.3284 (2)	0.8907 (2)	2.47 (2)

Tables 1 and 3 report the final atomic coordinates for these two atomic arrangements.* Drawings were made using *STRUPLO* (Fischer, 1985).

Discussion. $(\text{C}_2\text{H}_5\text{NH}_3)_6\text{P}_6\text{O}_{18}\cdot 4\text{H}_2\text{O}$. This atomic arrangement has a very strong pseudo-hexagonal symmetry and can be simply described as being built up of arrays of ethylammonium groups and P_6O_{18}

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and distances and bond angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53960 (106 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

ring anions which are both parallel to the c axis. These arrays are arranged in an almost regular hexagonal way as can be seen in Fig. 1. This pseudo-hexagonal stacking is centred by a centrosymmetrical cluster of eight water molecules forming a branched hexagon.

The P_6O_{18} ring anion. The main geometrical features of this ring are reported in Table 2. Having no internal symmetry, this phosphoric group is thus built up of six independent PO_4 tetrahedra. Up to now the only reported example of a P_6O_{18} with no internal symmetry was found by Lugt, Durif & Martin (1974), Lugt & Durif (1974) and Lugt (1969) in $Cu_2Li_2P_6O_{18}$. The phosphoric ring reported in the present work is fairly regular since the P—P—P angles vary from 99.58 to 115.69° (Table 2). A recent review of the various geometries observed in this kind of ring (Averbuch-Pouchot & Durif, 1991) shows that for the majority of previously reported P_6O_{18} groups the distortion is much larger, with P—P—P angles spreading from 95.5 to 145.9°.

The ethylammonium groups. Six independent $C_2H_5NH_3$ groups coexist in this atomic arrangement. N—C and C—C distances and C—C—N angles in these six groups are reported in Table 2, showing they are very similar; the N—C—C angles, for instance, spread within a range of 110.7 to 112.0°. Among the 18 H atoms of these groups one only establishes a hydrogen bond with a water molecule (Table 2); the remaining ones are connected to the external O atoms of the phosphoric rings. This

Table 4. *Main interatomic distances (Å) and bond angles (°) in the atomic arrangement of $(NH_3NH_2)_2(NH_3NH_3)_2P_6O_{18}$*

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

The P_6O_{18} ring anion

P(1) O_4 tetrahedron

P(1)	O(L12)	O(L13)	O(E11)	O(E12)
O(L12)	1.621 (1)	2.471 (1)	2.523 (1)	2.530 (2)
O(L13)	100.54 (5)	1.593 (1)	2.524 (1)	2.478 (1)
O(E11)	108.84 (6)	110.40 (6)	1.480 (1)	2.548 (2)
O(E12)	109.29 (6)	107.43 (6)	118.78 (7)	1.480 (1)

P(2) O_4 tetrahedron

P(2)	O(L12)	O(L23)	O(E21)	O(E22)
O(L12)	1.604 (1)	2.481 (1)	2.481 (1)	2.523 (1)
O(L23)	101.49 (5)	1.599 (1)	2.537 (2)	2.492 (1)
O(E21)	107.01 (6)	110.89 (6)	1.480 (1)	2.560 (1)
O(E22)	109.30 (5)	107.55 (6)	119.16 (6)	1.488 (1)

P(3) O_4 tetrahedron

P(3)	O(L13)	O(L23)	O(E31)	O(E32)
O(L13)	1.596 (1)	2.502 (1)	2.536 (2)	2.469 (1)
O(L23)	103.13 (6)	1.598 (1)	2.452 (1)	2.520 (1)
O(E31)	110.90 (6)	105.40 (6)	1.482 (1)	2.562 (1)
O(E32)	106.71 (6)	109.80 (6)	119.69 (7)	1.480 (1)

P(1)—O(L12)—P(2)	124.69 (7)	P(1)—P(2)—P(3)	110.31 (1)
P(2)—O(L23)—P(3)	133.12 (7)	P(2)—P(3)—P(1)	94.06 (1)
P(3)—O(L13)—P(1)	133.43 (7)	P(2)—P(1)—P(3)	108.48 (1)

P(1)—P(2)	2.8565 (4)	P(1)—P(3)	2.9291 (4)
P(2)—P(3)	2.9339 (5)		

The NH_3-NH_3 and NH_2-NH_3 groups

N(1)—N(2)	1.436 (1)	N(3)—N(4)	1.439 (2)
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The hydrogen bonds

	N—H	H...O	N—O	O—H—O
N(1)—H(1N1)...O(E12)	0.89 (3)	1.76 (3)	2.646 (2)	175 (2)
N(1)—H(2N1)...O(E32)	0.93 (3)	1.72 (3)	2.653 (2)	174 (2)
N(1)—H(3N1)...O(E31)	0.94 (2)	1.91 (2)	2.789 (1)	155 (2)
N(2)—H(1N2)...O(E22)	0.89 (3)	1.88 (3)	2.734 (2)	159 (2)
N(2)—H(2N2)...O(E11)	0.88 (2)	1.80 (2)	2.668 (2)	171 (2)
N(2)—H(3N2)...O(E21)	0.82 (3)	1.87 (3)	2.678 (2)	167 (2)
N(3)—H(1N3)...O(E22)	0.92 (3)	1.93 (3)	2.826 (2)	163 (2)
N(3)—H(2N3)...O(E31)	0.99 (3)	1.80 (3)	2.781 (2)	174 (3)
N(3)—H(3N3)...O(E21)	0.91 (3)	2.25 (2)	2.878 (1)	126 (2)
N(4)—H(1N4)...O(E12)	0.81 (2)	2.20 (2)	3.011 (2)	176 (3)
N(4)—H(2N4)...O(E32)	0.88 (3)	2.15 (3)	2.990 (2)	158 (2)

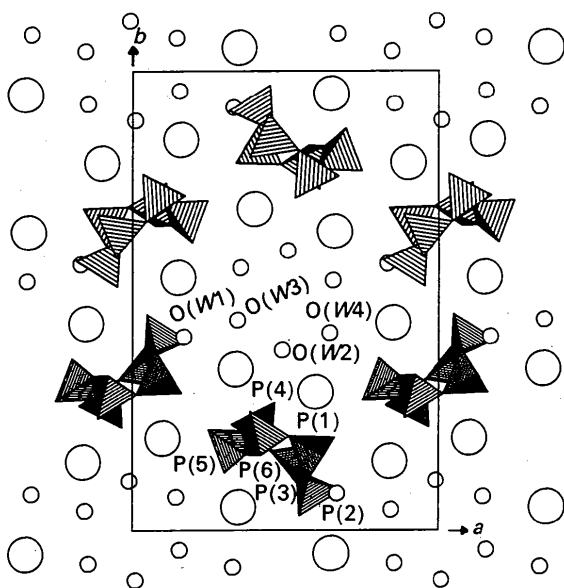


Fig. 1. Projection along the c axis of the atomic arrangement of $(C_2H_5NH_3)_6P_6O_{18} \cdot 4H_2O$. The small empty circles represent the water molecules, the large ones represent the channels containing the arrays of ethylammonium groups.

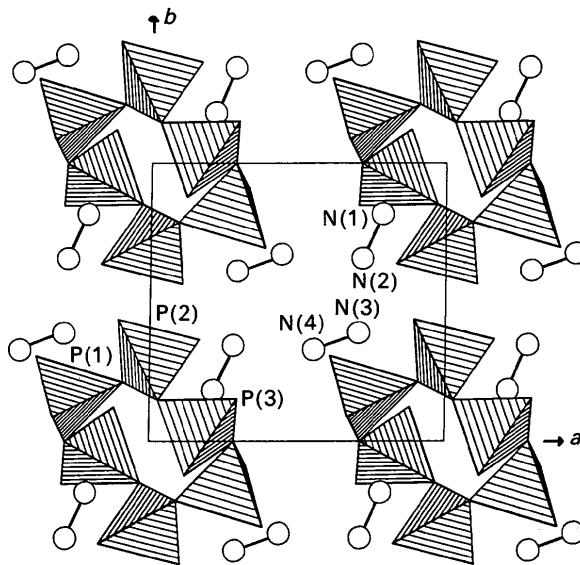


Fig. 2. Projection along the c axis of the atomic arrangement of $(NH_3NH_2)_2(NH_3NH_3)_2P_6O_{18}$.

observation can probably be explained by the existence of the cluster of water molecules discussed below.

The water molecule cluster. The water molecules of this compound are not dispersed inside the arrangement but they assemble themselves to form a centrosymmetric cluster of eight molecules. The central part of this group is an almost regular hexagon built by O(W2), O(W3) and O(W4). Angles O(W3)—O(W2)—O(W4), O(W2)—O(W3)—O(W4) and O(W2)—O(W4)—O(W3) are respectively 123.7 (1), 120.4 (1) and 111.1 (1)° while the distances O(W2)—O(W3), O(W3)—O(W4) and O(W2)—O(W4) are respectively 2.775 (4), 2.751 (5) and 2.770 (5) Å. Inside this ring the water molecules are tied by strong hydrogen bonds (Table 2). Two centrosymmetric branches complete this cluster; they start from the O(W3) water molecule of the hexagon and are built by O(W1) with a distance O(W3)—O(W1) = 2.917 (3) Å. O(W1) is not connected by hydrogen bonds to the central hexagon. Similar polygonal clusters of water molecules have already been observed by the authors in condensed phosphate chemistry: an almost regular pentagon of water molecules has been observed in $\text{Li}_4\text{P}_4\text{O}_{12}\cdot 5\text{H}_2\text{O}$ (Averbuch-Pouchot & Durif, 1986), and an almost regular hexagon with $\bar{3}$ internal symmetry in $\text{Cd}_3\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$ (Averbuch-Pouchot, 1989b) and $\text{Mn}_3\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$ (Averbuch-Pouchot & Durif, 1989). The present arrangement thus provides the first example of a branched polygon of water molecules.

$(\text{NH}_3\text{NH}_3)_2(\text{NH}_2\text{NH}_3)_2\text{P}_6\text{O}_{18}$. For the second title compound the atomic arrangement is rather simple. Here the ring anion is centrosymmetric and develops around the inversion centre located at $0,0,\frac{1}{2}$. If compared with the other P_6O_{18} ring anions of $\bar{1}$ internal symmetry the present one is not very distorted, the P—P—P angles ranging from 94.06 to 110.31°. The

main geometrical features of this ring are reported in Table 4. As mentioned in the *Experimental* section two types of cations coexist in the atomic arrangement: a hydrazinium(1+), $\text{NH}_2\text{—NH}_3$, and a hydrazinium(2+), $\text{NH}_3\text{—NH}_3$. The first one consists of N(3) and N(4) and the second one consists of N(1) and N(2) with almost identical N—N distances (1.436 and 1.439 Å). As can be seen in Fig. 2 these groups are lining the central channel parallel to the *c* axis and are connected to the external O atoms of the rings by hydrogen bonds whose details are reported in Table 4.

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Structure of a Cobalt Magnesium Diphosphate: $(\text{Mg}_x\text{Co}_{1-x})_2\text{P}_2\text{O}_7$

BY D. RIOU, A. LECLAIRE AND B. RAVEAU

Laboratoire de Cristallographie et Sciences des Matériaux, CRISMAT URA 1318, ISMRA, 14050 Caen CEDEX, France

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Abstract. $(\text{Mg}_{0.54}\text{Co}_{0.46})_2\text{P}_2\text{O}_7$, $M_r = 254.42$, monoclinic, $P2_1/c$, $a = 6.977$ (1), $b = 8.330$ (2), $c = 9.032$ (9) Å, $\beta = 113.74$ (1)°, $V = 480.45$ Å³, $Z = 4$, $D_x = 3.519$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu =$

47.916 cm⁻¹, $F(000) = 495.2$, $T = 293$ K, $R = 0.029$, $wR = 0.034$ for 1306 independent reflections with $I \geq 3\sigma(I)$. The structure of $(\text{Mg}_{0.54}\text{Co}_{0.46})_2\text{P}_2\text{O}_7$ is isotypic with $\alpha\text{-Mg}_2\text{P}_2\text{O}_7$ and $\alpha\text{-Co}_2\text{P}_2\text{O}_7$. The Co and Mg