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Crystal Chemistry of *cyclo*-Hexaphosphates. VIII. Structure of Hydroxylammonium *cyclo*-Hexaphosphate Tetrahydrate

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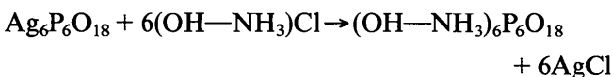
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Abstract. $(\text{NH}_3\text{OH})_6\text{P}_6\text{O}_{18}\cdot 4\text{H}_2\text{O}$, $M_r = 750.11$, triclinic, $P\bar{1}$, $a = 10.365$ (5), $b = 9.278$ (4), $c = 7.280$ (3) Å, $\alpha = 108.39$ (5), $\beta = 100.30$ (5), $\gamma = 96.02$ (5)°, $V = 643.8$ Å³, $Z = 1$, $D_x = 1.934$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.553$ mm⁻¹, $F(000) = 388$, $T = 298$ K, final $R = 0.028$ for 4750 reflections. The centrosymmetric P_6O_{18} ring anion is located at the centre of the unit cell. Three crystallographically independent hydroxylammonium groups co-exist in the atomic arrangement. The three-dimensional hydrogen-bond network is described.

Introduction. Investigation of organic cation-*cyclo*-hexaphosphates has been recently initiated by the characterization of the tris(ethylenediammonium) *cyclo*-hexaphosphate, $(\text{NH}_3\text{—CH}_2\text{—CH}_2\text{—NH}_3)_3\text{—P}_6\text{O}_{18}\cdot 2\text{H}_2\text{O}$ (Durif & Averbuch-Pouchot, 1989). In the present work we describe the preparation and crystal structure of a second example for such compounds, the hydroxylammonium *cyclo*-hexaphosphate tetrahydrate, $(\text{NH}_3\text{OH})_6\text{P}_6\text{O}_{18}\cdot 4\text{H}_2\text{O}$.

Experimental. Crystals of the title compound have been prepared by using a metathesis reaction similar to that described by Boule (1938) for the preparation of water soluble *cyclo*-triphosphates. Here the starting material is $\text{Ag}_6\text{P}_6\text{O}_{18}\cdot \text{H}_2\text{O}$ recently characterized by Averbuch-Pouchot (1989). Schematically the reaction is:



Crystals obtained by slow evaporation of an aqueous solution at room temperature have various morphologies: stout triclinic prisms or thick diamond-like plates. The title compound is stable at

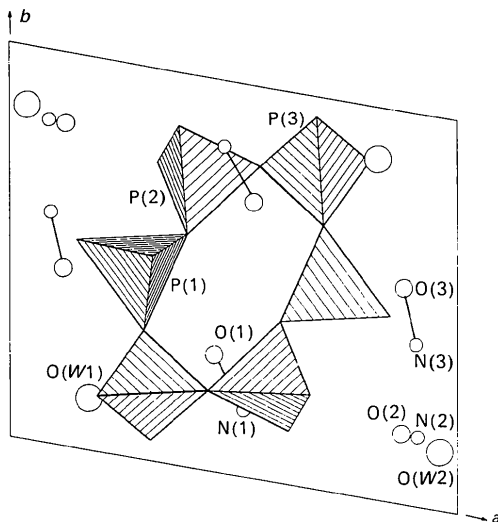
room temperature. Crystal size: $0.40 \times 0.40 \times 0.35$ mm. Density not measured. Philips PW1100 diffractometer, graphite monochromator. 19 reflections ($12.0 < \theta < 18.0^\circ$) for refining unit-cell dimensions. ω scan, scan width 1.20° , scan speed $0.02^\circ \text{ s}^{-1}$. Total background measuring time 6 s. 5532 reflections collected ($3 < \theta < 35^\circ$), $\pm h$, $\pm k$, l , $h_{\text{max}} = 16$, $k_{\text{max}} = 14$, $l_{\text{max}} = 11$. $\text{Sin}\theta/\lambda = 0.81$ Å⁻¹. Two orientation and intensity control reflections ($\bar{7}01$ and $70\bar{1}$) measured every four hours without any significant variation. 5169 reflections obtained after averaging Friedel pairs ($R_{\text{int}} = 0.008$). Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods (*MULTAN78*, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H atoms located by difference Fourier syntheses. Anisotropic full-matrix least-squares refinement (on F), isotropic for H atoms. Unit weights. Final refinements with 4750 reflections corresponding to $I > 4\sigma_I$. Final $R = 0.028$ ($wR = 0.033$), $S = 0.438$, max. $\Delta/\sigma = 0.07$, max. peak height in the final difference Fourier synthesis = $0.425 \text{ e } \text{Å}^{-3}$. Secondary extinction not refined. 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, on a MicroVAX II computer.

Discussion. Table 1 reports the final atomic coordinates.*

* 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 53118 (42 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} for non-H atoms: *e.s.d.*'s are given in parentheses
$$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{\AA}^2)$
P(1)	0.28199 (3)	0.49585 (3)	0.39028 (4)	1.103 (4)
P(2)	0.40646 (3)	0.76239 (3)	0.73136 (4)	0.995 (4)
P(3)	0.30424 (3)	0.17000 (3)	0.22317 (4)	1.004 (4)
O(L12)	0.39626 (9)	0.58996 (9)	0.5839 (1)	1.63 (1)
O(L13)	0.29873 (9)	0.32754 (9)	0.3920 (1)	1.40 (1)
O(E11)	0.15037 (8)	0.5286 (1)	0.4293 (1)	1.72 (1)
O(E12)	0.31926 (9)	0.5197 (1)	0.2119 (1)	1.78 (1)
O(E21)	0.37873 (9)	0.86386 (9)	0.6122 (1)	1.60 (1)
O(E22)	0.66977 (8)	0.2377 (1)	0.1145 (1)	1.78 (2)
O(L23)	0.55982 (8)	0.79580 (9)	0.8421 (1)	1.28 (1)
O(E31)	0.31287 (9)	0.05327 (9)	0.3234 (1)	1.62 (1)
O(E32)	0.19463 (9)	0.1420 (1)	0.0484 (1)	1.78 (2)
N(1)	0.5208 (1)	0.1704 (1)	0.7353 (1)	1.65 (2)
O(1)	0.5450 (1)	0.7016 (1)	0.2345 (2)	2.25 (2)
N(2)	0.0896 (1)	0.8220 (1)	0.4192 (2)	1.77 (2)
O(2)	0.1267 (1)	0.8206 (1)	0.2420 (1)	2.45 (2)
N(3)	0.9068 (1)	0.4123 (1)	0.1395 (2)	1.73 (2)
O(3)	0.8804 (1)	0.5498 (1)	0.1089 (2)	2.63 (2)
O(W1)	0.1757 (1)	0.1324 (1)	0.6666 (1)	2.06 (2)
O(W2)	0.9599 (1)	0.1501 (1)	0.2108 (2)	2.45 (2)

Fig. 1. Projection along the *c* axis of the atomic arrangement of $(\text{OH}-\text{NH}_3)_6\text{P}_6\text{O}_{18}\cdot 4\text{H}_2\text{O}$. The H atoms have been omitted for clarity.

The P_6O_{18} ring anion develops around the inversion centre located in $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and so is built by only three independent PO_4 tetrahedra. As is commonly observed for P_6O_{18} anions with $\bar{1}$ internal symmetry the ring is significantly distorted. The P—P—P angles vary between 93.48 (2) and 138.95 (2)°. In spite of this distortion, the local arrangement observed for the PO_4 tetrahedra (P—O distances and P—O—P or O—P—O angles as well as P—P distances) are in accordance with values generally observed in condensed phosphoric anions. The main geometrical features of this ring are reported in Table 2.

Table 2. Main interatomic distances (\AA) and bond angles ($^\circ$) in the atomic arrangement of $(\text{HO}-\text{NH}_3)_6\text{P}_6\text{O}_{18}\cdot 4\text{H}_2\text{O}$: *e.s.d.*'s are given in parentheses

P(1) O_4 tetrahedron									
P(1)	O(L12)	O(L13)	O(E11)	O(E12)					
O(L12)	1.600 (1)	2.395 (2)	2.520 (2)	2.530 (2)					
O(L13)	97.16 (7)	1.593 (1)	2.520 (2)	2.537 (2)					
O(E11)	109.48 (8)	109.88 (8)	1.485 (1)	2.552 (2)					
O(E12)	109.71 (8)	110.61 (8)	118.01 (9)	1.492 (1)					
P(2) O_4 tetrahedron									
P(1)	O(L12)	O(L13)	O(E11)	O(E12)					
O(L12)	1.601 (1)	2.513 (2)	2.530 (2)	2.443 (2)					
O(E21)	108.97 (8)	1.485 (1)	2.558 (2)	2.552 (2)					
O(E22)	110.11 (8)	118.99 (9)	1.484 (1)	2.457 (2)					
O(L23)	99.61 (7)	111.73 (7)	105.67 (7)	1.598 (1)					
P(3) O_4 tetrahedron									
P(1)	O(L13)	O(L23)	O(E31)	O(E32)					
O(L13)	1.600 (1)	2.443 (2)	2.459 (2)	2.512 (2)					
O(L23)	104.34 (7)	1.597 (1)	2.529 (2)	2.474 (2)					
O(E31)	105.63 (7)	110.17 (8)	1.486 (1)	2.561 (2)					
O(E32)	109.27 (8)	106.98 (7)	119.46 (8)	1.480 (1)					
P(1)—P(2)		2.8734 (6)	P(2)—P(3)		2.9349 (6)				
P(1)—P(3)		2.9324 (6)							
P(1)—O(L12)—P(2)		127.67 (9)	P(2)—P(1)—P(3)		138.95 (2)				
P(1)—O(L13)—P(3)		123.41 (9)	P(1)—P(2)—P(3)		112.46 (2)				
P(2)—O(L23)—P(3)		133.41 (8)	P(1)—P(3)—P(2)		93.48 (2)				
N(1)—O(1)		1.408 (2)	N(3)—O(3)		1.408 (2)				
N(2)—O(2)		1.407 (2)							
N(O)—H...O		N(O)—H		H...O		N(O)—O		H...O	
O(1)—H(O1)...	O(E12)	0.85 (4)	1.84 (4)	2.685 (2)	171 (4)				
O(2)—H(O2)...	O(E31)	0.73 (4)	1.85 (4)	2.578 (2)	170 (4)				
O(3)—H(O3)...	O(E12)	0.86 (4)	1.85 (4)	2.682 (2)	164 (4)				
N(1)—H(1N1)...	O(E21)	0.89 (4)	1.95 (4)	2.844 (2)	175 (4)				
N(1)—H(2N1)...	O(E22)	0.89 (3)	1.88 (3)	2.753 (2)	166 (3)				
N(1)—H(3N1)...	O(E21)	0.91 (3)	1.98 (3)	2.846 (2)	159 (3)				
N(2)—H(1N2)...	O(E11)	0.84 (3)	2.05 (3)	2.878 (2)	168 (3)				
N(2)—H(2N2)...	O(W1)	0.87 (4)	1.99 (4)	2.815 (2)	157 (3)				
N(2)—H(3N2)...	O(W1)	0.87 (4)	1.97 (4)	2.819 (2)	165 (3)				
N(3)—H(1N3)...	O(E22)	0.89 (4)	1.88 (4)	2.741 (2)	162 (4)				
N(3)—H(2N3)...	O(2)	0.90 (4)	2.12 (4)	2.866 (2)	139 (3)				
N(3)—H(3N3)...	O(E11)	0.88 (4)	1.98 (4)	2.842 (2)	165 (4)				
O(W1)—H(1W1)...	O(E32)	0.77 (4)	1.99 (4)	2.724 (2)	162 (4)				
O(W1)—H(2W1)...	O(1)	0.72 (5)	2.40 (5)	2.982 (2)	138 (5)				
O(W2)—H(1W2)...	O(E32)	0.87 (5)	2.04 (5)	2.873 (2)	160 (5)				
O(W2)—H(2W2)...	O(E32)	0.85 (5)	2.04 (5)	2.887 (2)	178 (4)				
H(1W1)—O(W1)—H(2W1)		111 (5)	H(1W2)—O(W2)—H(2W2)		109 (4)				

Three crystallographically independent hydroxyl-ammonium groups are present in this atomic arrangement with various orientations. One of this group made by O(2) and N(2) is almost parallel to the *c* direction while the two remaining ones are located in (00*z*) planes. The O—N distances observed in these three independent groups are identical within the experimental errors, 1.407 (2) and 1.408 (2) Å.

The three-dimensional network of hydrogen bonds interconnecting the components of this atomic arrangement is described in Table 2. As is usual in compounds involving a condensed phosphoric anion

the bonding O atoms [O(L)] do not take part in such a network.

Fig. 1 depicts a projection of this structure along the c axis. The drawing has been produced using the program *STRUPLO* (Fischer, 1985).

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$\text{Ba}_3\text{CaCuSi}_6\text{O}_{17}$: A New $\{\text{B}, 1^1_\infty\}[\text{Si}_6\text{O}_{17}]$ Chain Silicate

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Abstract. Tribarium calcium copper hexasilicate, $\text{Ba}_3\text{CaCuSi}_6\text{O}_{17}$ (ideal stoichiometry), $M_r = 956.12$, orthorhombic, $B2mb$ [symmetry operators $(0,0,0), (\frac{1}{2}, 0, \frac{1}{2}) + x, y, z; x, -y, -z; x, \frac{1}{2} - y, z; x, \frac{1}{2} + y, -z]$, $a = 14.405$ (2), $b = 16.077$ (2), $c = 7.088$ (2) Å, $V = 1641.5$ (5) Å³, $Z = 4$, $D_x = 3.87$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7093$ Å, $\mu = 92.2$ cm⁻¹, room temperature, $F(000) = 1748$, $R = 0.052$, $wR = 0.050$ for 684 observed reflections. Crystals were formed as a by-product of the synthesis of Tl–Cu–Ca–Ba superconductors. The structure consists of SiO_4 tetrahedra which share corners to form distorted six-membered rings which in turn are linked by two corners to other rings to form chains of six-membered rings. The overall silicate anion topology is $\{\text{B}, 1^1_\infty\}[\text{Si}_6\text{O}_{17}]$ [in the notation of Liebau (1985). *Structural Chemistry of Silicates*. Berlin: Springer–Verlag]. Calcium and barium sites are eight coordinated, and the copper is in square-planar coordination.

Introduction. Hazen, Finger, Angel, Prewitt, Ross, Hadidiacos, Heaney, Veblen, Sheng, Ali & Hermann (1988) described the crystallography of a number of superconducting phases in the Tl–Ba–Ca–Cu–O system originally synthesized by Sheng & Hermann (1988*a,b*). These syntheses were carried out by annealing the experimental charge in a silica container, and in addition to the various superconducting phases found in the bulk of the sample,

reaction between the charge and the container produced a number of brilliantly coloured transparent phases. At least two of these were novel silicates of barium and copper. The structure of $\text{BaCuSi}_2\text{O}_6$, recently reported by Finger, Hazen & Hemley (1989), contains four-membered rings of silicate tetrahedra not connected into a framework by other tetrahedral sites. The structure of the second silicate, present as only a few minute multiple crystals, is described here.

Experimental. The largest clear, turquoise-coloured crystal from the experimental charge supplied by Sheng & Hermann (1988*a,b*) was selected for diffraction experiments. Approximately 20% of the volume of this crystal (approximate dimensions $0.04 \times 0.04 \times 0.015$ mm) was a second individual, misoriented by about 4° from the parent crystal. Preliminary experiments indicated that reflections with $h + l$ odd in hkl and k odd in $hk0$ were systematically absent. Data were collected with a Rigaku AFC-5 goniometer equipped with a rotating anode generator providing Mo $K\alpha$ radiation via a graphite monochromator out to $(\sin\theta)/\lambda = 0.7$ Å⁻¹, with $-20 < h < 20$, $0 < k < 22$, $0 < l < 9$, together with their Friedel pairs (four asymmetric units). The 240, $20\bar{2}$ and 042 reflections were monitored as intensity and orientation standards every 150 reflections; their intensities varied randomly by up to 5% from their means. No correction was made to the measured intensities for this variation, but the weights assigned in the least-squares procedures were modified appropriately (see below). A total of 4955 symmetry-allowed reflections were measured, of which 2724 were observed at $I >$

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