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Structure of a Calcium Ethylenediammonium Cyclotetraphosphate Hydrate

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Abstract. $\text{Ca}[\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\text{P}_4\text{O}_{12}\cdot 15/2\text{H}_2\text{O}$, $M_r = 553.19$, orthorhombic, $Pnma$, $a = 14.611(3)$, $b = 18.709(3)$, $c = 7.861(2)$ Å, $V = 2149(1)$ Å³, $Z = 4$, $D_x = 1.710$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.672$ mm⁻¹, $F(000) = 1148$, $T = 295$ K, final $R = 0.031$ for 2677 independent reflexions. The P_4O_{12} ring anion has a rather rare configuration, with two of the bonding O atoms located on a mirror plane. Organic groups are centrosymmetrical and all located in $y = 0.0$ and 0.5 planes. Ten of the 30 water molecules are statistically distributed on three general positions. The hydrogen-bond scheme is described.

Introduction. A monophosphate of ethylenediammonium, $\text{C}_2\text{H}_{10}\text{N}_2^{2+}\cdot\text{HPO}_4^{2-}$, has recently been described (Averbuch-Pouchot & Durif, 1987). Up to now no condensed phosphate containing the $\text{C}_2\text{H}_{10}\text{N}_2^{2+}$ group has been reported. The title compound is the first description of a series of *cyclo*-tetraphosphates characterized in the systems $(\text{C}_2\text{H}_{10}\text{N}_2)_2\text{P}_4\text{O}_{12}-M^{II}_2\text{P}_4\text{O}_{12}-\text{H}_2\text{O}$ ($M^{II} = \text{Ba}, \text{Sr}, \text{Pb}, \text{Ca}, \text{Mn}, \text{Cd}, \text{Co}, \text{Cu}, \text{Mg}, \text{Ni}$) (Averbuch-Pouchot, Durif & Guitel, 1988).

Experimental. Crystals were obtained by adding calcium carbonate and ethylenediamine in stoichiometric ratio to an aqueous solution of *cyclo*-tetraphosphoric acid kept at low temperature ($T < 278$ K); they appear as large orthorhombic prisms with various morphologies. Density not measured. Crystal size: $0.37 \times 0.30 \times 0.32$ mm. Nicolet XRD diffractometer, graphite monochromator. Systematic absences: $0kl$ ($k + l = 2n$), $hk0$ ($h = 2n$). 18 reflexions ($14 < \theta < 16^\circ$) for refining the

unit cell. ω scan; variable scan speed between 1 and 4° min⁻¹; scan width: 1.20° ; background measured for a time corresponding to 10% of the scan time; intensity and orientation reflexions: 0,14,0, 0,14,0, 10,0,0 with no significant variation; θ range $3\text{--}35^\circ$; 4767 reflexions measured (h,k,l); $h_{\text{max}} = 22$, $k_{\text{max}} = 28$, $l_{\text{max}} = 12$.

Lorentz and polarization corrections; no absorption correction. Direct methods: *MULTAN77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977) used for structure determination; H atoms located by difference-Fourier synthesis; anisotropic full-matrix least-squares refinements on F for non-H atoms, isotropic for H atoms; unitary weighting scheme; final refinements with a set of 2677 ($I > 4\sigma_I$); extinction not taken into account; final R value 0.031 ($wR = 0.031$); R factor for the 4767 independent reflexions: 0.068. Scattering factors for neutral atoms, f' and f'' from *International Tables for X-ray Crystallography* (1974). *SDP* (Enraf-Nonius, 1977) used for all calculations. $S = 0.977$; max. $\Delta/\sigma = 0.03$; max $\Delta\rho = 0.29$ e Å⁻³. Computer used: microVAX II.

Discussion. Table 1 reports the final atomic coordinates.* The P_4O_{12} ring anion is built up of two crystallographically independent PO_4 tetrahedra and

* Lists of structure factors, anisotropic thermal parameters and additional bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44897 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates and B_{eq} for non-hydrogen atoms, B_{iso} for hydrogen atoms
$$B_{eq} = \frac{4}{3} \sum_i \sum_j a_i \cdot a_j \beta_{ij}$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Ca	0.40251 (3)	0.250	0.58839 (7)	1.786 (7)
P(1)	0.29006 (3)	0.17157 (2)	0.95940 (5)	1.578 (6)
P(2)	0.11731 (3)	0.17113 (2)	0.77327 (6)	1.831 (6)
O(1)	0.02254 (8)	0.16956 (7)	0.8397 (2)	2.73 (3)
O(2)	0.68272 (8)	0.34342 (7)	0.5671 (2)	2.18 (2)
O(3)	0.2889 (1)	0.250	0.0413 (2)	2.08 (3)
O(4)	0.1416 (1)	0.37700 (8)	0.6301 (2)	2.99 (3)
O(5)	0.32183 (9)	0.37715 (7)	0.0964 (2)	2.34 (2)
O(6)	0.6458 (1)	0.250	0.7854 (3)	2.09 (3)
O(7)	0.33751 (8)	0.32830 (7)	0.7934 (2)	2.14 (2)
O(W1)	0.2531 (1)	-0.00536 (9)	0.2203 (3)	3.96 (4)
O(W2)	0.8173 (1)	0.3407 (1)	0.0582 (2)	4.69 (4)
O(W3)	0.4790 (3)	0.250	0.3155 (4)	5.95 (8)
O(W4)	0.5141 (2)	0.3942 (2)	0.1470 (4)	4.26 (7)
O(W5)	0.4969 (3)	0.0580 (2)	0.0574 (6)	5.18 (9)
O(W6)	0.1300 (8)	0.287 (1)	0.315 (1)	11.3 (7)
N	0.4304 (1)	0.03042 (9)	0.6883 (3)	2.88 (3)
C	0.4498 (2)	-0.0008 (2)	0.5185 (3)	3.41 (4)
H(11)	0.776 (2)	0.467 (2)	0.333 (4)	5.3 (7)*
H(12)	0.714 (2)	0.463 (2)	0.817 (4)	5.8 (8)*
H(21)	0.311 (2)	0.152 (2)	0.349 (4)	4.5 (7)*
H(22)	0.763 (3)	0.364 (2)	0.003 (4)	7 (1)*
H(3)	0.000 (2)	0.209 (2)	0.215 (5)	8 (1)*
H(4)	0.051 (3)	0.396 (2)	0.445 (5)	3.0 (9)*
H(5)	0.954 (3)	0.403 (2)	0.410 (6)	2.4 (9)*
H(1M)	0.041 (2)	0.502 (2)	0.267 (4)	5.1 (7)*
H(2M)	0.945 (2)	0.422 (2)	0.801 (3)	4.5 (7)*
H(3M)	0.132 (2)	0.526 (2)	0.199 (4)	6.3 (8)*
H(1C)	0.573 (2)	0.055 (2)	0.472 (4)	6.2 (8)*
H(2C)	0.414 (2)	0.025 (2)	0.432 (4)	5.3 (7)*

* B_{iso} .

has mirror symmetry. The mirror plane contains two of the bonding O atoms of the ring. This type of conformation is not common in the crystal chemistry of *cyclo*-tetrphosphates. The only previously reported configuration of this type was observed in CaNa₂P₄O₁₂·5/2H₂O (Averbuch-Pouchot & Durif, 1988). Main interatomic distances and bond angles in the ring anion are reported in Table 2.

All the (CH₂)(NH₃)₂²⁺ groups are located in planes $y = 0$ and $y = \frac{1}{2}$ and are centrosymmetrical. Their main geometrical features are given in Table 2.

Two of the water molecules, O(W1) and O(W2), occupy the general position 8(*d*) while O(W3) is located in a mirror plane in $y = 0.25$ [4(*c*)]. The ten remaining water molecules are statistically distributed on three general positions, with various occupancy rates. So 4.41 water molecules [O(W4)] occupy the first general position, 3.9 [O(W5)] the second one and 1.69 [O(W6)] the last one. It is to be noticed that the coordinates of the last two correspond to a situation close to symmetry elements:

$$0.497, 0.004, 0.024 \text{ for O(W5)}$$

$$0.130, 0.287, 0.315 \text{ for O(W6)}$$

The atomic arrangement can easily be understood by considering Fig. 1, a projection along the *c* axis, showing the distribution of Ca atoms, ring anions and water molecules. The organic groups all located in planes $y = 0$ and 0.5 have been omitted in this projection and the two water molecules O(W5) and O(W6) statistically located close to symmetry elements

Table 2. Main interatomic distances (Å) and bond angles (°)

The P₄O₁₂ ring anion

P(1)O₄ tetrahedron

P(1)	O(2)	O(3)	O(5)	O(7)
O(2)	1.607 (1)	2.488 (2)	2.486 (2)	2.529 (2)
O(3)	1.607 (1)	1.602 (1)	2.465 (1)	2.539 (2)
O(5)	1.06.97 (8)	1.05.89 (8)	1.485 (1)	2.562 (2)
O(7)	1.10.11 (7)	1.10.98 (8)	1.19.64 (8)	1.478 (1)

P(2)O₄ tetrahedron

P(2)	O(1)	O(2)	O(4)	O(6)
O(1)	1.480 (1)	2.464 (2)	2.550 (2)	2.545 (2)
O(2)	1.06.17 (8)	1.601 (1)	2.534 (2)	2.508 (2)
O(4)	1.18.65 (9)	1.110.39 (8)	1.484 (2)	2.468 (2)
O(6)	1.11.29 (9)	1.03.13 (9)	1.06.17 (9)	1.601 (1)

P(1)—O(2)—P(2) 130.90 (9) P(1)—P(1) 2.9346 (6)

P(1)—O(3)—P(1) 132.61 (12) P(1)—P(2) 2.9174 (6)

P(2)—O(6)—P(2) 134.34 (13) P(2)—P(2) 2.9513 (6)

P(1)—P(1)—P(2) 90.16 (2)

P(1)—P(2)—P(2) 89.84 (2)

The CaO₇ polyhedron

Ca—O(1)	2.379 (1)	(× 2)
Ca—O(7)	2.376 (1)	(× 2)
Ca—O(W2)	2.398 (2)	(× 2)
Ca—O(W3)	2.419 (3)	

The (NH₃)(CH₂)₂(NH₃) group

C—N	1.484 (3)	N—C—C	110.8 (2)
C—C	1.496		

	O(N)—H	H...O	O(N)—O	O(N)—H...O
O(W1)—H(11)...O(5)	0.89 (3)	1.90 (3)	2.777 (2)	169 (3)
O(W1)—H(12)...O(4)	0.81 (3)	1.98 (3)	2.777 (2)	170 (3)
O(W2)—H(21)...O(5)	0.75 (3)	2.06 (3)	2.800 (2)	167 (3)
O(W2)—H(22)...O(4)	1.00 (4)	2.07 (4)	3.040 (2)	161 (3)
O(W3)—H(3)...O(W4)	0.86 (4)	2.22 (4)	3.048 (4)	160 (3)
O(W4)—H(4)...O(4)	0.90 (4)	2.00 (4)	2.884 (4)	166 (4)
O(W4)—H(5)...O(5)	1.00 (5)	1.99 (5)	2.855 (3)	143 (4)
O(W5)—H(4)...O(4)	1.16 (4)	2.00 (4)	2.849 (4)	127 (3)
O(W5)—H(5)...O(5)	0.99 (5)	1.99 (5)	2.848 (4)	142 (4)
N—H(1M)...O(W5)	0.92 (3)	1.89 (3)	2.804 (5)	173 (3)
N—H(2M)...O(1)	0.91 (3)	2.08 (3)	2.939 (2)	156 (2)
N—H(3M)...O(W1)	0.92 (3)	1.82 (3)	2.733 (2)	174 (3)
H(11)—W(1)—H(12)			101 (3)	
H(21)—W(2)—H(22)			105 (3)	
H(3)—W(3)—H(3)			126 (3)	

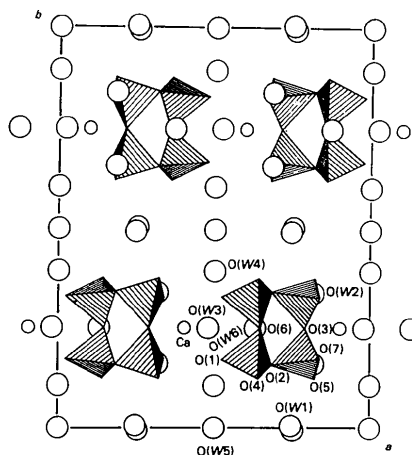


Fig. 1. Projection along the *c* axis of the atomic arrangement of Ca[(CH₂)₂(NH₃)₂]P₄O₁₂·15/2H₂O. H atoms are not shown and statistically distributed water molecules are placed in idealized positions (see Discussion).

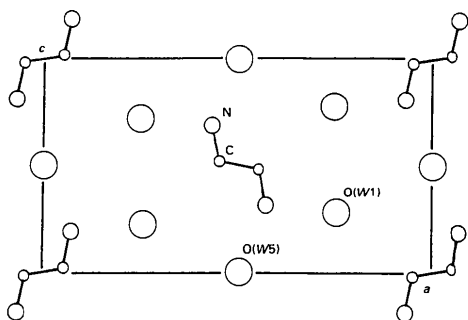


Fig. 2. Distribution of the organic groups and water molecules in a plane close to $y=0.5$; H atoms are not shown.

have been drawn in their idealized positions: 0.5, 0, 0 for O(W5) and 0.130, 0.25, 0.315 for O(W6). Fig. 2 shows the distribution of the organic groups and water molecules in the plane $y=0.5$. H atoms are not shown.

A very intricate three-dimensional network of hydrogen bonds is reported in Table 2. The Ca atoms, located on a mirror plane, have a sevenfold coordination made of four O atoms and three water molecules with Ca—O distances ranging from 2.376 to 2.419 Å. Some H atoms belonging to the disordered water molecules could not be located.

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Structure of Bis(2,2'-bipyridyl)thiocyanatocopper(II) Nitrate Monohydrate

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Abstract. $[\text{Cu}(\text{NCS})(\text{C}_{10}\text{H}_8\text{N}_2)_2]\text{NO}_3 \cdot \text{H}_2\text{O}$, $M_r = 514.02$, triclinic, $P\bar{1}$, $a = 12.098$ (4), $b = 12.810$ (5), $c = 7.777$ (2) Å, $\alpha = 102.80$ (3), $\beta = 107.56$ (2), $\gamma = 76.03$ (3)°, $V = 1100.6$ (6) Å³, $Z = 2$, $D_m = 1.556$, $D_x = 1.551$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $\mu = 0.2183$ mm⁻¹, $F(000) = 526$, $T = 293$ K, $R = 0.041$ for 4104 unique observed reflections. The Cu atom is pentacoordinated to the four N atoms of the bipyridyl ligands and the N atom of the thiocyanato group in a

The high thermal factor observed for the O(W6) water molecule can be explained by considering its surroundings. Within a range of 3.5 Å this molecule has only three neighbours [O(W2), O(W3) and O(W4)] while all the other water molecules either belong to the coordination polyhedron of the Ca atom or are closely connected to an NH₃ group with N—O distances ranging from 2.733 to 2.939 Å.

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near-regular trigonal bipyramidal arrangement, where only three distances differ significantly: 1.992 (2) (average) for the axial bonds, 2.079 (3) (average) and 2.010 (3) Å for the equatorial bonds.

Introduction. This structure determination is a contribution to the study of the chemistry of copper complexes with different donor ligands coordinated by atoms usually found in natural proteins such as N, S and O