

cycle benzène au cycle thiazolium ont les valeurs suivantes: $S(1)-C(5)-N(2)-C(6) = 6,1$ (3), $C(5)-N(2)-C(6)-C(7) = -174,6$ (3), $N(2)-C(6)-C(7)-C(8) = -159,7$ (3) et $C(6)-C(7)-C(8)-C(13) = 109,8$ (3)°. Un réseau de liaisons hydrogène pratiquement linéaires assure la cohésion du cristal, en plus des contacts de van der Waals. Les caractéristiques géométriques des liaisons H sont les suivantes: $O(4)\cdots O(1^i)$ [(i) $-1+x, y, z$] = 2,807 (3), $O(4)-H(41) = 1,01$ (3), $H(41)\cdots O(1^i) = 1,80$ (3) Å, $O(4)-H(41)\cdots O(1^i) = 176$ (2)°; $O(4)\cdots O(3) = 2,827$, $O(4)-H(42) = 0,96$ (3), $H(42)\cdots O(3) = 1,88$ (3) Å, $O(4)-H(42)\cdots O(3) = 173$ (2)°; $O(5)\cdots O(2) = 2,778$, $O(5)-H(51) = 0,90$ (3), $H(51)\cdots O(2) = 1,88$ (3) Å, $O(5)-H(51)\cdots O(2) = 171$ (2)°; $O(5)\cdots O(4^{ii})$ [(ii) $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$] = 2,853, $O(5)-H(52) = 0,89$ (3), $H(52)\cdots O(4^{ii}) = 1,98$ (3) Å, $O(5)-H(52)\cdots O(4^{ii}) = 168$ (2)°. Enfin il existe une liaison hydrogène entre O(5) et la molécule

d'eau désordonnée $O(6^{iii})$ [(iii) $1-x, 1-y, -z$] = 2,851 Å ainsi qu'avec $O(6^{iv})$ [(iv) $1+x, y, z$] = 2,683 Å.

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Structure of Ethylenediammonium Dihydrogentetraoxophosphate(V) Pentahydrogenbis[tetraoxophosphate(V)]

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Abstract. $C_2H_{10}N_2^{2+} \cdot H_5P_2O_8^- \cdot H_2PO_4^-$, $M_r = 354.09$, monoclinic, $C2/c$, $a = 13.034$ (10), $b = 7.923$ (7), $c = 13.225$ (10) Å, $\beta = 107.43$ (5)°, $V = 1303$ (4) Å³, $Z = 4$, $D_x = 1.805$ Mg m⁻³, $\lambda(\text{Ag K}\alpha) = 0.5608$ Å, $\mu = 0.278$ mm⁻¹, $F(000) = 736$, $T = 293$ K, final $R = 0.024$ for 1883 unique reflexions. The main feature of this structure is the existence of $(H_5P_2O_8)^-$ clusters resulting from the association of two PO_4 tetrahedra related by centrosymmetry and linked by two statistical hydrogen bonds. These new groups are themselves interconnected with $(H_2PO_4)^-$ units through a three-dimensional network of hydrogen bonds. The C_2 - $H_{10}N_2^{2+}$ groups are isolated inside this anionic arrangement.

Introduction. The present work is part of a systematic investigation of the system $H_3PO_4-(CH_2)_2(NH_3)_2-H_2O$. Up to now only one compound has been synthesized and characterized: the ethylenediammonium monohydrogentetraoxophosphate $[(CH_2)_2(NH_3)_2]HPO_4$ studied by Averbuch-Pouchot & Durif (1987); it corresponds to the 1/1 stoichiometry $H_3PO_4/(CH_2)_2-$

$(NH_3)_2$. The title compound is the second obtained in this domain; its formula corresponds to stoichiometry 3/1.

Experimental. Single crystals are easily prepared by mixing 40 cm³ H_3PO_4 (85%) with 10 cm³ ethylenediamine. Thick diamond-like plates appear some days later after slow evaporation of the solution at room temperature or some hours later after heating the solution at 353 K. Crystal size: 0.5 × 0.3 × 0.3 mm. Density not measured. Philips PW 1100 diffractometer, graphite monochromator. Systematic absences: hkl , $h + l = 2n$; $h0l$, $h = 2n$ and $l = 2n$. Unit cell refinement with 20 reflexions ($11 < \theta < 16^\circ$) and ω scan. 2925 reflexions collected ($3 < \theta < 30^\circ$), $\pm h, k, l$, $h_{\max} = 22$, $k_{\max} = 14$, $l_{\max} = 22$. Scan width: 1.20°; scan speed: 0.03° s⁻¹; total background measuring time: 10 s. Two intensity and orientation (732 and 732) reference reflexions every two hours, no significant variation. Lorentz and polarization corrections, no absorption correction. Unit weights. Structure solved by direct methods with *MULTAN78* (Main, Hull,

Table 1. Final atomic coordinates and $B_{eq}(\text{\AA}^2)$ for $(CH_2)_2(NH_3)_2 \cdot H_5P_2O_8 \cdot H_2PO_4^-$; e.s.d.'s are reported in parentheses

$$B_{eq} = \frac{1}{3} \sum_i \sum_j a_i \cdot a_j \cdot \beta_{ij}$$

	x	y	z	B_{eq}
P(1)	0	0.17652 (6)	$\frac{1}{2}$	1.467 (7)
P(2)	0.37860 (2)	0.21310 (4)	0.40870 (3)	1.451 (4)
O(1)	0.09418 (8)	0.3016 (1)	0.26071 (9)	2.51 (2)
O(2)	0.02194 (9)	0.0679 (1)	0.34826 (8)	2.52 (2)
O(3)	0.08852 (8)	0.5636 (1)	0.01769 (8)	2.32 (2)
O(4)	0.34992 (8)	0.3652 (1)	0.46961 (8)	2.23 (2)
O(5)	0.02059 (8)	0.2381 (1)	0.62591 (9)	2.40 (2)
O(6)	0.21595 (8)	0.3186 (2)	0.68611 (8)	2.53 (2)
C	0.2180 (1)	0.7461 (2)	0.5566 (1)	1.96 (2)
N	0.31329 (9)	0.1169 (2)	0.12041 (9)	1.99 (2)

Table 2. Main interatomic distances (\AA) and bond angles ($^\circ$) in the atomic arrangement of $(CH_2)_2(NH_3)_2 \cdot H_5P_2O_8 \cdot H_2PO_4^-$

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

P(1)O ₄ tetrahedron				
P(1)	O(1)	O(2)	O(1)	O(2)
O(1)	1.551 (1)	110.14 (6)	100.55 (6)	112.51 (7)
O(2)	2.512 (2)	1.513 (1)	112.51 (7)	110.66 (6)
O(1)	2.386 (2)	2.548 (1)	1.551 (1)	110.14 (6)
O(2)	2.548 (1)	2.386 (2)	2.512 (2)	1.513 (1)

P(2)O ₄ tetrahedron				
P(2)	O(3)	O(4)	O(5)	O(6)
O(3)	1.511 (1)	109.83 (6)	106.34 (6)	114.37 (6)
O(4)	2.510 (2)	1.556 (1)	108.26 (6)	107.41 (6)
O(5)	2.462 (2)	2.528 (2)	1.564 (1)	110.51 (6)
O(6)	2.525 (1)	2.458 (2)	2.512 (1)	1.493 (1)

P(1)–P(2)	4.4003 (3)	P(1)–O(1)–H(1)	115 (2)
P(1)–P(2)	4.7307 (5)	P(2)–O(3)–H(3)	113 (4)
P(1)–P(2)	4.7577 (3)	P(2)–O(4)–H(4)	112 (3)
P(2)–P(2)	4.7614 (4)	P(2)–O(5)–H(5)	114 (2)
P(2)–P(2)	4.7182 (5)		

Hydrogen bonds				
O(N)–H...O	O(N)–H	H...O	O(N)–H...O	O(N)–O
O(1)–H(1)...O(6)	0.82 (2)	1.72 (2)	177 (3)	2.546 (1)
O(3)–H(3)...O(3)	0.77 (4)	1.68 (4)	167 (6)	2.432 (2)
O(4)–H(4)...O(2)	0.59 (2)	1.96 (2)	173 (3)	2.542 (1)
O(5)–H(5)–O(2)	0.75 (3)	1.80 (3)	166 (3)	2.533 (2)
N–H(1N)...O(4)	0.75 (2)	2.24	147 (2)	2.899 (2)
N–H(2N)...O(6)	0.84 (2)	1.92	166 (2)	2.746 (2)
N–H(3N)...O(5)	0.87 (2)	2.11	154 (2)	2.917 (2)

Ethylenediammonium group			
C–N	1.478 (2)	C–C–N	110.5 (1)
C–C	1.514 (2)		

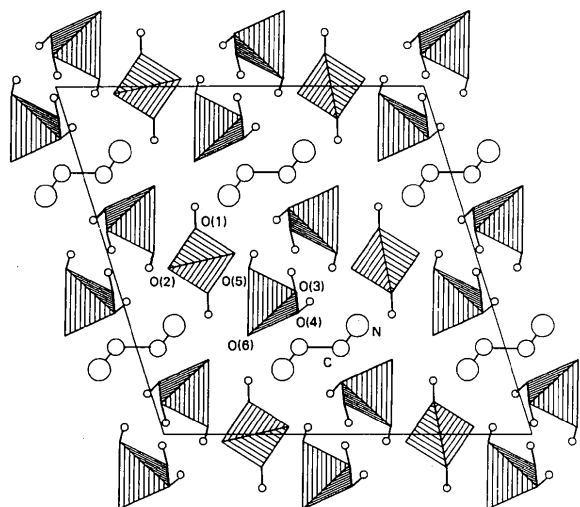


Fig. 1. Projection along the b axis of the atomic arrangement of $(CH_2)_2(NH_3)_2 \cdot H_5P_2O_8 \cdot H_2PO_4^-$.

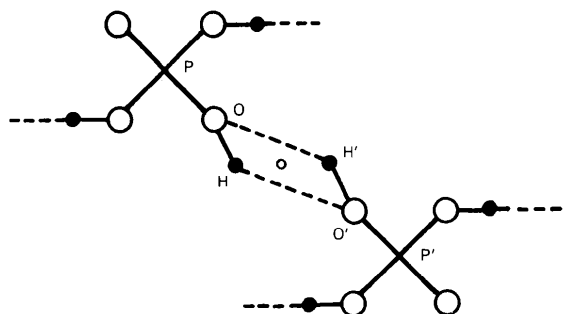


Fig. 2. Schematic representation of the centrosymmetric cluster $(H_5P_2O_8)^-$ in $(CH_2)_2(NH_3)_2 \cdot H_5P_2O_8 \cdot H_2PO_4^-$.

Lessinger, Germain, Declercq & Woolfson, 1978). H atoms located by difference Fourier map. Anisotropic full-matrix least-squares refinement (on F) for non-H atoms, isotropic for H atoms. Final refinement cycles with 1883 independent reflexions ($I > 9\sigma_I$). Final $R = 0.024$ ($wR = 0.027$). $S = 0.420$. Max. $\Delta/\sigma = 0.02$. Max. peak height in final difference Fourier

synthesis: 0.195 e \AA^{-3} . The final R value = 0.035 for the complete set of 2925 unique reflexions. No extinction correction. Scattering factors for neutral atoms and f' , f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. Computer used: MicroVAX-II.

Discussion. Table 1* reports the final atomic coordinates. Fig. 1 is a projection of the atomic arrangement along the b axis.

The PO_4 tetrahedra are distributed around two sites: P(1) in the special position $4(e)$ on the twofold axis, P(2) in the general position $8(f)$. The $P(1)O_4$ tetrahedron forms a quite symmetric unit $(H_2PO_4)^-$ with the hydrogen bonds $O(1)–H(1) \cdots O(6)$ related by twofold symmetry. $P(2)O_4$ is also a peculiar tetrahedron in this structure, as it is bonded to three hydrogen atoms:

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles in the $(NH_3)^+–(CH_2)_2–(NH_3)$ group have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51469 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

H(3), H(4) and H(5), the first one being statistically distributed on an eightfold position. So, two and 'a half' hydrogen bonds can start from this tetrahedron: the ordinary hydrogen bonds O(4)–H(4)···O(2) and O(5)–H(5)···O(2)' and the 'statistical' one O(3)–H(3)···O(3)'. The characteristic feature of the structural arrangement is the linkage of such a tetrahedron to an equivalent one by inversion symmetry [around the site 4(b)] through the 'statistical' hydrogen bonds: O(3)–H(3)···O(3)' and O(3)'–H(3)'···O(3). The result of this type of connection between the two P(2)O₄ tetrahedra can be considered as a cluster of formula (H₅P₂O₈)⁻. The detailed representation of such a group is schematically drawn in Fig. 2. The internal distance P(2)–P(2) is 4.7614 Å, shorter than in the (H₂P₂O₈)⁴⁻ cluster of (CH₂)₂(NH₃)₂·HPO₄ (4.847 Å) (Averbuch-Pouchot & Durif, 1987), but longer than in the (H₂P₂O₈)⁴⁻ group of the sodium salt (CH₂)₂(NH₃)₂·2Na₂HPO₄·6H₂O (4.320 Å) (Averbuch-Pouchot, Durif & Guitel, 1987).

The organic entity (CH₂)₂(NH₃)₂²⁺ is centrosymmetric with the inversion point located on the site 4(c).

So, the atomic arrangement of this compound is built up by (H₅P₂O₈)⁻ clusters interconnected by (H₂PO₄)⁻ units to form arrays in three dimensions. In this

manner, each (H₂PO₄)⁻ group which is centered on the 2 axis is surrounded by four clusters (H₅P₂O₈)⁻ at different levels: $z=0, 1$ along **c** and $z=\frac{1}{2}$ along **a** + **c**/2 (Fig. 1). The relative distances P(1)–P(2) between each type of anion are 4.4003, 4.7307 and 4.7577 Å. The (CH₂)₂(NH₃)₂ entities are isolated in this three-dimensional network of hydrogen bonds, alternating with the anionic arrays at $z=\frac{1}{4}$ and $\frac{3}{4}$.

Table 2 gives the main interatomic distances, bond angles and details of the hydrogen-bond scheme.

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A Neutron Diffraction Study at 30 K of a Cage Compound, 5-Hydroxy-7,10-dimethyltetracyclo[4.4.0.0^{3,9}.0^{4,8}]decan-2-one

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Abstract. C₁₂H₁₆O₂, *M_r* = 192.3, monoclinic, *P*2₁/*c*, *a* = 10.744 (3), *b* = 15.211 (4), *c* = 11.986 (3) Å, β = 93.94 (3)°, λ = 1.2602 (2) Å (from measurements on a ruby crystal), *V* = 1954 (1) Å³, *Z* = 8, *D_x* = 1.31 g cm⁻³, m.p. 357.2–357.7 K, *T* = 30 K, *R* = 4.79% for 3196 reflexions. The structural unit is a dimer held together by weak hydrogen bonds. Dimerization occurs in two ways. Structural details for a reaction pathway involving intramolecular hydrogen

transfer of a methine hydrogen to a trans-annular keto-carbon atom are considered.

Introduction. The use of crystallographic data in mapping reaction pathways has been one of the more attractive developments in organic chemistry (Bürgi & Dunitz, 1983), with a link between the statics of the crystal structures and the dynamics of the reacting systems particularly well established for interactions of