Structural Characterization of a New Organic Cyclotetraphosphate, $[C_4H_8N_2H_4]_2P_4O_{12} \cdot 4H_2O$

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The title compound, $[C_4H_8N_2H_4]_2P_4O_{12} \cdot 4H_2O$, crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.733(3)$, $b = 10.511(2)$, $c = 7.715(2)\text{Å}$, $\alpha = 98.17(2)^\circ$, $\beta = 109.89(2)^\circ$, $\gamma = 82.79(2)^\circ$, $V = 581.7(3)\text{Å}^3$, $Z = 1$ and $D_x = 1.611\text{ g cm}^{-3}$. The atomic arrangement can be described as thick layers containing P_4O_{12} rings and water molecules spreading around the $z = (2n + 1)/2$ planes; between them are anchored piperazinium dications, giving rise to a three-dimensional network.

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The chemistry of condensed phosphates associated with organic cations that contain donor center has been the object of numerous investigations, whereas a few studies concerning cyclotetraphosphates on secondary amines have been characterized.¹⁻³ As a contribution to the elaboration of this compound family, we report in the present work on the synthesis and structural characterization of a new organic cation cyclotetraphosphate, $[C_4H_8N_2H_4]_2P_4O_{12} \cdot 4H_2O$, which results from an interaction between phosphoric acids and the piperazine molecule.^{4,5} This organic molecule is a biogenic diamine, which plays an important role as a deprotonated cation in biologic systems. Nevertheless, research on these phases was stimulated by their possible utilization in the biological domain.^{6,7}

Crystals of piperazine-1,4-dium cyclotetraphosphate tetrahydrate (Fig. 1) were prepared by slowly adding a stoichiometric amount of diphosphorus pentoxide to an aqueous solution of piperazine kept at low temperature ($T < 278\text{ K}$). The obtained solution was slowly evaporated at room temperature until crystallization occurred. A colorless crystal obtained in this way, was chosen to determine its structure by single-crystal X-ray diffraction. The crystal and experimental data are given in Table 1. All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were located by difference Fourier syntheses, and were not refined. The final atomic coordinates of the non-hydrogen atoms of $[C_4H_8N_2H_4]_2P_4O_{12} \cdot 4H_2O$ and their B_{eq} are reported in Table 2. An ORTEP drawing of the molecular structure containing one $P_4O_{12}^{4-}$ ring and two piperazinium cations with the atom labeling is shown in Fig. 2.

Fig. 1 Chemical diagram of the title compound.

The structure can be described as inorganic layers built up with $P_4O_{12}^{4-}$ ring anions and water molecules $O(W)$, spreading around the $z = (2n + 1)/2$ planes. Piperazinium dications ($C_4H_{12}N_2$)²⁺ are anchored onto anionic layers through hydrogen bonds, as shown in Fig. 3. Each dication is connected with two layers, thus ensuring the formation of a three-dimensional network.

Because the phosphoric ring anion is localized around the $(0, 0, 1/2)$ inversion center, it is symmetrical and built by only two independent PO_4 tetrahedra, $P(1)O_4$ and $P(2)O_4$. The P-P-P angle values, $81.95(5)$ and $98.05(5)^\circ$, show that this P_4O_{12} ring is strongly distorted from the ideal one, where the P-P-P angle is 90° . The largest deviation from the 90° value was observed in the structure of $C_{10}H_{28}N_4P_4O_{12} \cdot 4H_2O^3$, which shows, to date, the

Table 1 Crystal and experimental data

Chemical formula : $C_8H_{32}N_4O_{16}P_4$	
Formula weight = 564.25	
Crystal system : triclinic	
Space group : $P\bar{1}$	
$a = 7.733(3)\text{Å}$	$Z = 1$
$b = 10.511(2)\text{Å}$	$\alpha = 98.17(2)^\circ$
$c = 7.715(2)\text{Å}$	$\beta = 109.89(2)^\circ$
$V = 581.7(3)\text{Å}^3$	$\gamma = 82.79(2)^\circ$
Linear absorption factor =	$D_x = 1.611\text{ g cm}^{-3}$
$F(0\ 0\ 0) = 296$	2.136 cm^{-1}
Crystal dimensions [mm] :	$0.35 \times 0.1 \times 0.09$
θ range for data collection:	2 to 25°
No. of reflections measured	4351 ($R_{int} = 0.01$)
No. of reflections used	3006 with $I > 3\sigma(I)$
No. of parameters	145
$R = 0.035$	
$R_w = 0.036$	
Goodness-of-fit = 1.850	
$(\Delta/\sigma)_{max} = 0.01$	
$(\Delta\rho)_{max} = 0.43\text{ eÅ}^{-3}$	
$(\Delta\rho)_{min} = -0.59\text{ eÅ}^{-3}$	
Measurement: Enraf-Nonius MACH3	
Ag K α ($\lambda = 0.5608\text{ Å}$)	
Program system: TeXsan	
Structure determination: direct method (SIR 92)	
Refinement: full-matrix on F	

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Fig. 2 ORTEP drawing of the molecular structure containing one $P_4O_{12}^{4+}$ ring and two piperazinium cations with the atomic labeling.

Fig. 3 Atomic arrangement of $[C_4H_8N_2H_4]_2P_4O_{12} \cdot 4H_2O$ in projection along the a direction. The phosphoric anions are given in the tetrahedra representation. The other atoms are labeled on the figure. The hydrogen bonds are denoted by dotted lines.

greatest distortion for the same angles (angle values of $80.24(5)$ and $99.76(5)^\circ$). The P-O-P angles have an average of $132.40(8)^\circ$ with extrema of $131.90(8)$ and $132.91(8)^\circ$, while the average of the P-P distance is $2.9291 \text{ \AA}$ with extrema of $2.9226(9)$ and $2.9356(8) \text{ \AA}$. Two centrosymmetrical and crystallographically independent piperazinium dications ($C_4H_{12}N_2^{2+}$, in a chair conformation, coexist in this arrangement, and are located around the $(1/2, 0, 0)$ and $(0, 1/2, 0)$ inversion centers. The anchorage of both $(C_4H_{12}N_2)^{2+}$ dications is made by six short ($< 2.73 \text{ \AA}$) and two long hydrogen bonds,⁸ ensuring the interconnection between layers, and thus giving rise to a three-dimensional network. The first $C_4H_{12}N_2(1)$ group is strongly linked to adjacent layers through two types of hydrogen bonds, $N(1)-H \cdots O(E)$ and $N(1)-H \cdots O(W)$, with $N \cdots O$ distances of $2.697(2)$ and $2.712(2) \text{ \AA}$, respectively, whereas the second one, $C_4H_{12}N_2(2)$, is connected to four anion layers via one type of hydrogen bond $N(2)-H \cdots O(E)$, with $N \cdots O$ distances

Table 2 Final atomic coordinates and B_{eq} ($\text{\AA}^2$) for the non-hydrogen atoms in $[C_4H_8N_2H_4]_2P_4O_{12} \cdot 4H_2O$

Atoms	x	y	z	B_{eq}
P(1)	0.93565(4)	0.89152(3)	0.6453(4)	1.526(6)
P(2)	0.90377(4)	1.17329(3)	0.6519(4)	1.585(6)
O(W1)	0.4189(1)	0.3385(1)	0.6247(2)	3.78(3)
O(W2)	0.7023(2)	0.4116(1)	1.2787(2)	5.28(4)
O(E11)	0.8031(1)	0.81769(8)	0.6815(1)	2.26(2)
O(E12)	1.1241(1)	0.90031(8)	0.7761(1)	2.33(2)
O(L12)	0.9391(1)	0.83641(8)	0.4418(1)	2.03(2)
O(L21)	0.8331(1)	1.03229(8)	0.6046(1)	2.08(2)
O(E21)	0.9987(1)	1.20006(9)	0.8537(1)	2.44(2)
O(E22)	0.7464(1)	1.26155(8)	0.5587(1)	2.61(2)
N(1)	0.9250(2)	0.4089(1)	1.0720(2)	2.93(3)
N(2)	0.6554(1)	0.9467(1)	0.9462(1)	2.22(2)
C(1)	0.8036(2)	0.5007(1)	0.9447(2)	3.51(3)
C(2)	0.8955(3)	0.5375(1)	0.8201(2)	3.63(3)
C(3)	0.5631(2)	0.8670(1)	1.0270(2)	2.50(3)
C(4)	0.4766(2)	0.9517(1)	1.1558(2)	2.59(3)

Estimated standard deviations are given in parentheses.

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

of $2.704(2)$ and $2.779(2) \text{ \AA}$. The distances (C-C, N-C) and angles (N-C-C, C-N-C) have their usual values, which are quite similar to that observed for the same organic group associated with other phosphoric anions, such as $H_2PO_4^{4-}$ and $H_2P_2O_7^{2-}$.⁵

The atomic arrangement of the title compound contains two crystallographically independent water molecules O(W1) and O(W2). These letters are connected as pairs; each one is linked by hydrogen bonds to three different P_4O_{12} rings, and thus contribute to the intralayer cohesion of this compound. The O $\cdots$ H distances and O-H $\cdots$ O angles range from 1.77 to $1.93 \text{ \AA}$ and 161.4 to 172.4° , respectively. The crystallographic information file (CIF) is available as supplementary material in CCDC (no. 212938).

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