A New Organic-Cation Cyclotetraphosphate $C_{10}H_{28}N_4P_4O_{12} \cdot 4H_2O$: Crystal Structure, Thermal Analysis, and Vibrational Spectra

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A new organic-cation phosphate of $C_{10}H_{28}N_4P_4O_{12} \cdot 4H_2O$ has been obtained. The crystal structure determination shows that this compound crystallizes in the triclinic system, space group $P-1$, with the following unit cell parameters: $a = 9.147(3)$ Å; $b = 9.258(3)$ Å; $c = 8.974(3)$ Å; $\alpha = 79.92(3)°$; $\beta = 117.41(3)°$; $\gamma = 116.58(3)°$. P_4O_{12} cycles, which present the strongest distortion in this kind of materials, are connected through O_W–H—O–P hydrogen bonds, so that bidimensional layers parallel to the ab plane are formed. These layers are themselves interconnected by means N–H—O–P hydrogen bonds originating from the $(C_{10}H_{28}N_4)^{4+}$ cations forming a three-dimensional network. The hydrated character of this phosphate is confirmed by the coupled TG-DTA thermal study which shows the successive loss of water molecules. The molecular arrangement within the structure has been confirmed by the IR spectroscopy. © 2001 Academic Press

Key Words: cation organic; phosphate cyclotetraphosphate; crystal structure; hydrogen-bond; IR spectroscopy; TG-DTA.

INTRODUCTION

Organic-cation phosphates have been intensively studied due to their many uses in various fields such as biomolecular sciences, catalysts, fuel cells, liquid crystal materials, nonlinear optics, and protonic conductors (1–6). Nevertheless, a bibliographical study on the organic condensed phosphates, and especially on the cyclotetraphosphates based on secondary amines, reveals that this field remains practically unexplored. To our knowledge, only a few compounds are characterized with the cyclic $(P_4O_{12})^{4-}$ anion (7). Most organic-cation phosphates are formed essentially in the way of H-bonds between phosphoric anions and organic groups which contain generally donor centers. As shown by several works on this type of material, water molecules

also play an important role for their structure cohesion and stability.

In the present paper, we report a detailed structural investigation of a new organic-cation cyclotetraphosphate with a cyclic amine, 1, 4, 8, 11-tetraazacyclotetradecane, $C_{10}H_{24}N_4$, which contains four donor centers. In addition, the compound has been characterized by thermal analysis and IR spectroscopy.

EXPERIMENTAL

Single crystals of $C_{10}H_{28}N_4P_4O_{12} \cdot 4H_2O$ have been prepared in two steps. An aqueous solution of cyclotetraphosphoric acid was first prepared by passing a solution of $Na_4P_4O_{12}$ through an ion-exchange resin in its protonated state (Amberlite IR 120). The sodium salt $Na_4P_4O_{12}$ was obtained by adding an aqueous solution of sodium sulfide $Na_2S_{(aq)}$ to $Cu_2P_4O_{12}$. The obtained $H_4P_4O_{12}$ acid solution was then added drop by drop to the 1, 4, 8, 11-tetraazacyclotetradecane amine at room temperature up to pH 7.

The so-obtained solution was then slowly evaporated until the formation of large colorless plates of $C_{10}H_{28}N_4P_4O_{12} \cdot 4H_2O$ which were stable under normal conditions of temperature and relative humidity.

Single-crystal data were collected on an Enraf-Nonius diffractometer using graphic-monochromated $MoK\alpha$ radiation (8, 9). A preliminary single-crystal investigation was performed using the Weissenberg technique in order to determine the symmetry and the space group. Main crystal features and all the experimental parameters used for the X-ray data collection and the structural determination and its final results are summarized in Table 1.

Thermal analysis measurements were performed, in air atmosphere, at a heating rate of 2°C/min using a Setaram TG-DTA 92 thermoanalyzer. The infrared spectra were recorded with a Perkin-Elmer IR-983 spectrometer using the KBr absorption technique.

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TABLE 1
Main Crystallographic Features, Parameters Used for the X-ray Collection, Strategy Used for the Crystal Structure Determination, and Its Final Results

Crystal data

$C_{10}H_{36}N_4O_{16}P_4$	$MoK\alpha$ radiation
$M = 592.31$ g mol^{-1}	$\lambda = 0.71069$ Å
Triclinic	Cell parameters from 25 reflections
Space group: $P-1$	$\theta = 10.5–14°$
$a = 9.147(3)$ Å $\quad \alpha = 79.92(3)°$	$\mu = 0.394$ mm^{-1}
$b = 9.258(3)$ Å $\quad \beta = 117.41(3)°$	$T = 293$ K
$c = 8.974(3)$ Å $\quad \gamma = 116.58(3)°$	Plate
$V = 602.9(3)$ Å^3	Dim:: $0.30 \times 0.14 \times 0.10$ mm
$Z = 1$	
$D_x = 1.631$ mgm^{-3}	Colorless

Data collection

CAD-4 Diffractometer	$R_{int} = 0.0152$
$\omega/2\theta$ Scans	$\theta_{max} = 25.97°$
Absorption correction: none	$h: 0 \rightarrow 11,\ k: -11 \rightarrow 10,\ l: -11 \rightarrow 9$
2516 Measured reflections	2 standard reflections
2360 Independent reflections	Frequency: 60 min
1823 Observed reflections:	Intensity decay: 0.6%
$\quad I > 2\sigma(I)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 10^{-3}$
$R(F^2 > 2\sigma(F^2)) = 0.0482$	$(\Delta\rho)_{max} = 0.620$ e Å^{-3}
$WR(F^2) = 0.1319$	$(\Delta\rho)_{min} = -0.527$ e Å^{-3}
$S = 1.15$	Extinction correction:
	$\quad$ SHELX (10–11)
2360 Reflections	Extinction coefficient: 0.005(4)
227 Parameters	Scattering Factors from
with restrictions: $d_{N2-H} =$	$\quad$ International Tables
$d_{C3-H} = 1.$ Å (12)	
$w = 1/[\sigma^2(F_o^2)$	For crystallography:
$\quad + (0.0555P)^2 + 0.6762P]$	(1992, Vol. C, tables 4.2.6.8
with $P = (F_o^2 + 2F_c^2)/3$	$\quad$ and 6.1.1.4)

TABLE 2
Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters, $U_{eq} = (\frac{1}{3})\Sigma_i \Sigma_j U_{ij}a_i^* a_j^* a_i a_j$

Atoms	x/a	y/b	z/c	U_{eq}
P1	0.2114(1)	0.1318(1)	0.2465(1)	0.0223(2)
P2	−0.1025(1)	−0.1789(1)	0.1136(1)	0.0224(2)
O_{E11}	0.4052(3)	0.1790(3)	0.2980(3)	0.0343(6)
O_{E21}	0.1545(3)	0.1675(3)	0.3608(3)	0.0314(6)
O_{E12}	−0.1284(4)	-0.3344(3)	0.1973(3)	0.0411(7)
O_{E22}	−0.2138(3)	−0.0951(3)	0.1008(3)	0.0276(5)
O_{L12}	0.1093(3)	−0.0609(3)	0.2026(3)	0.0265(5)
O_{L21}	0.1229(3)	0.2050(3)	0.0681(3)	0.0273(5)
O_{W1}	0.0688(4)	−0.5124(4)	0.2996(4)	0.0458(7)
O_{W2}	−0.3176(5)	−0.5178(4)	0.3801(4)	0.0533(8)
N1	−0.1909(4)	0.1902(4)	0.2064(4)	0.0274(6)
N2	−0.5704(5)	−0.3150(5)	0.2400(5)	0.055(1)
C1	−0.2239(5)	0.1303(5)	0.3590(4)	0.0321(8)
C2	−0.3978(5)	−0.0180(5)	0.3280(5)	0.0327(8)
C3	−0.3895(4)	−0.1686(4)	0.3038(3)	0.0161(6)
C4	−0.7163(5)	−0.2851(5)	0.0820(5)	0.0360(9)
C5	−0.3320(5)	0.2331(5)	0.0650(4)	0.0300(8)
H1W1	0.129(7)	−0.505(6)	0.406(7)	0.05(2)
H2W1	0.016(7)	−0.438(7)	0.284(7)	0.07(2)
H1W2	−0.267(6)	−0.470(6)	0.313(6)	0.04(2)
H2W2	−0.443(9)	−0.631(9)	0.340(8)	0.11(3)
H1N1	−0.093(6)	0.277(5)	0.230(5)	0.03(1)
H2N1	−0.174(5)	0.132(5)	0.171(5)	0.03(1)
H1N2	−0.619(7)	−0.349(6)	0.350(7)	0.07(2)
H2N2	−0.50(1)	−0.421(9)	0.246(9)	0.15(3)
H1C1	−0.124(6)	0.108(5)	0.439(5)	0.04(1)
H2C1	−0.237(5)	0.210(5)	0.388(5)	0.03(1)
H1C2	−0.498(5)	-0.017(5)	0.239(5)	0.03(1)
H2C2	−0.427(5)	-0.037(5)	0.417(5)	0.029(9)
H1C3	−0.316(5)	−0.188(5)	0.407(2)	0.04(1)
H2C3	−0.331(5)	−0.144(5)	0.239(4)	0.04(1)
H1C4	−0.744(5)	−0.201(5)	0.102(4)	0.021(9)
H2C4	−0.822(8)	−0.383(7)	0.046(7)	0.08(2)
H1C5	−0.450(6)	0.141(5)	0.029(5)	0.028(9)
H2C5	−0.344(6)	0.318(5)	0.105(5)	0.04(1)

RESULTS AND DISCUSSION

Structure Description

The nominal compound crystallizes in the triclinic system, space group $P-1$, with the following unit cell parameters: $a = 9.147(3)$ Å; $b = 9.258(3)$ Å; $c = 8.974(3)$ Å; $\alpha = 79.92(3)°$; $\beta = 117.41(3)°$; $\gamma = 116.58(3)°$. From a general point of view, the atomic arrangement of this phosphate can be described as a succession of two types of layers parallel to the [100] axis. As shown in Fig. 1, the first layer ($y = 0$) contains simultaneously the phosphoric anions and the organic cations. These layers alternate with those located at $y = \frac{1}{2}$ containing only the water molecules. Table 2 summarizes the fractional atomic coordinates.

The phosphoric $(P_4O_{12})^{4-}$ anion is localized around the (000) inversion center. It is built up of only two independent PO_4 tetrahedra. Interatomic distances and bond angles in this ring, given in Table 3, are in good agreement with those

observed for others cyclotetraphosphates known to date (13–15). The $P-O_E$ (O_E, external oxygen of P_4O_{12}) average distances [1.479(3); 1.481(3) Å] are shorter than the $P-O_L$ (O_L, oxygen of the P–O–P bridge) distances [1.616(2); 1.603(3) Å].

Distortion indices of various distances and angles in the two $P(1)O_4$ and $P(2)O_4$ tetrahedra, calculated according to Baur's method (16), are ID(P–O) = 0.0444 and 0.0394; ID(O–O) = 0.0096 and 0.0142; ID(O–P–O) = 0.0371 and 0.0378, respectively. This shows a strong distortion of the P–O distances compared to O–O ones. However, averages of the P–O (1.547; 1.542 Å) and O–O (2.519; 2.510 Å) distances of the two independent PO_4 tetrahedra remain practically the same compared to those observed for condensed phosphates (17, 18). This is probably due to the significant difference between the $P-O_L$ and $P-O_E$ distances, and to the participation of external oxygen atoms in the hydrogen
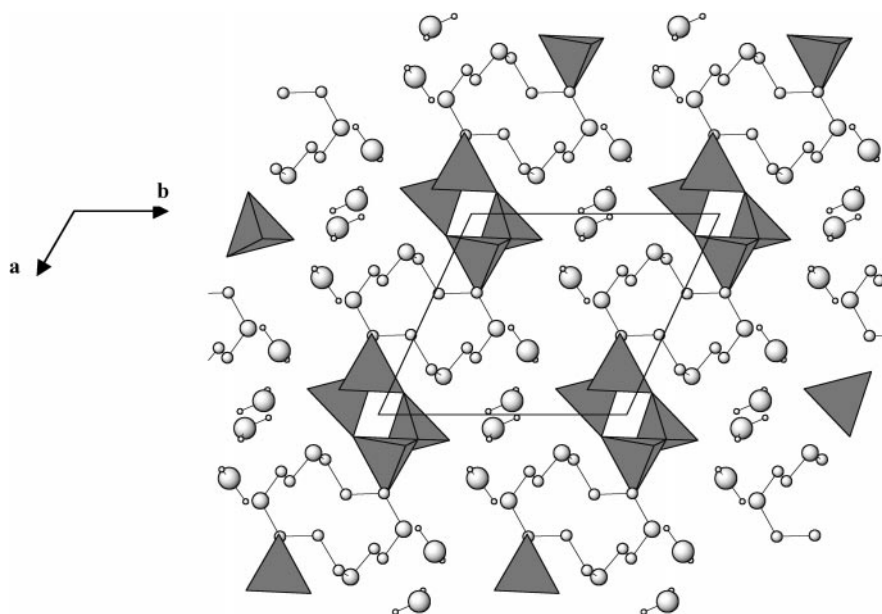
FIG. 1. Projection along the c axis of the $C_{10}H_{28}N_4P_4O_{12}\cdot4H_2O$ structure. By order of decreasing sizes, the circles represent oxygen, nitrogen, carbon and hydrogen atoms. Hydrogen atoms of the organic molecule are omitted.

bonds network. Thus, one can admit that PO_4 tetrahedra of the P_4O_{12} cycle is described by a regular arrangement of oxygen atoms with a slight shift of phosphorus atoms from the center of gravity. Instead of a $-43m$ ideal symmetry, the local symmetry of the studied PO_4 tetrahedra would be $3m$.

It is important to note that a recent review of the various geometries observed in this kind of condensed phosphates shows that the P_4O_{12} ring in this structure presents the strongest distortion (15, 17–21). Indeed, the angle values of the square formed by the four phosphorus atoms are $80.24(5)°$ and $99.76(5)°$. To date, the most accentuated distortion of P_4O_{12} has been observed in the structure of $[H_3N(CH_2)_3NH_3]_2P_4O_{12}\cdot2H_2O$ (angle values: $81.11°$, $98.89°$) (19).

Furthermore, the atomic arrangement of $C_{10}H_{28}N_4$ $P_4O_{12}\cdot4H_2O$ contains only one independent $(C_{10}H_{28}N_4)^{4+}$ cation. It is localized around the (1/2 0 0) inversion center. Its geometrical characteristics are reported in Table 4. N–C, C–C distances, and N–C–C, C–N–C, C–C–C angles correspond also to values generally observed in this family of materials (7, 22, 23).

As shown in Fig. 2, the water molecules are connected as pairs. Each pair is connected by hydrogen bonds to three different P_4O_{12} groups to form a two-dimensional layer parallel to the (001) plane. Among the four hydrogen of the two independent $-NH_2$, only one establishes H-bond with an external oxygen of P_4O_{12} group (N_1–H_2—O_{E22} with $d_{N1-OE22} = 2.850(5)$ Å), forming infinite arrangements along the [100] direction. The remaining hydrogen atoms are connected to the oxygen atoms of the water molecules (O_W). Thus, a 3D network of hydrogen bonds is formed. Table 5 gives main geometrical features of the H-bond scheme.

In this structure, the water molecules play a very important role in the cohesion of the various groups, since they

TABLE 3
Main Interatomic Distances (Å) and Bond Angles (°) in the P_4O_{12} Ring

		$P(1)O_4$ tetrahedron		
P1	$\mathbf{O_{E11}}$	$\mathbf{O_{E21}}$	$\mathbf{O_{L12}}$	$\mathbf{O_{L21}}$
$\mathbf{O_{E11}}$	**1.474(3)**	119.8(2)	106.4(2)	110.9(2)
$\mathbf{O_{E21}}$	2.558(3)	**1.483(2)**	109.0(2)	106.9(2)
$\mathbf{O_{L12}}$	2.479(4)	2.486(3)	**1.621(2)**	102.6(2)
$\mathbf{O_{L21}}$	2.541(3)	2.527(3)	2.521(3)	**1.611(2)**
		$P(2)O_4$ tetrahedron		
P2	$\mathbf{O_{E12}}$	$\mathbf{O_{E22}}$	$\mathbf{O_{L12}}$	$\mathbf{O_{L21}}$
$\mathbf{O_{E12}}$	**1.472(3)**	119.0(2)	107.5(2)	107.6(2)
$\mathbf{O_{E22}}$	2.554(4)	**1.490(2)**	110.3(2)	110.7(2)
$\mathbf{O_{L12}}$	2.482(4)	2.539(3)	**1.603(3)**	100.1(2)
$\mathbf{O_{L21}}$	2.483(3)	2.545(3)	2.458(3)	**1.602(2)**

P1–P2	P1–P2	P2–P1–P2	P1–P2–P1	P1–O_{L12}–P2	P1–O_{L21}–P2
2.932(2) Å	2.925(2) Å	80.24(5)°	99.76(5)°	130.9(2)°	131.1(2)°

O_{w1}–H1W1 = 0.83(5) Å O_{w1}–H1W2 = 0.89(5) Å
O_{w1}–H2W1 = 1.00(6) Å O_{w2}–H2W2 = 1.12(7) Å
H1W1–O_{w1}–H2W1 = 100(4)°   H1W2–O_{w2}–H2W2 = 121(4)°

TABLE 4
Bond Lengths (Å) and Angles (°) in the Organic Cation

N1–H1N1	0.86(4)	C1–H1C1	0.96(4)
N1–H2N1	0.77(4)	C1–H2C1	0.89(4)
N2–H1N2	1.00(4)	C2–H1C2	0.90(4)
N2–H2N2	1.00(4)	C2–H2C2	0.92(4)
N1–C1	1.496(5)	C3–H1C3	1.00(4)
N1–C5	1.487(4)	C3–H2C3	1.00(4)
N2–C3	1.515(5)	C4–H1C4	0.98(4)
N2–C4	1.523(5)	C4–H2C4	0.94(6)
C1–C2	1.505(6)	C5–H1C5	0.97(4)
C2–C3	1.488(5)	C5–H2C5	0.98(4)
C4–C5	1.514(5)		
C5–N1–C1	116.1(3)	H1N1–N1–H2N1	103(4)
N1–C1–C2	114.7(3)	C5–N1–H1N1	104(3)
N1–C5–C4	110.0(3)	C1–N1–H1N1	111(3)
C3–C2–C1	113.1(3)	C5–N1–H2N1	108(3)
C3–N2–C4	113.4(3)	C1–N1–H2N1	113(3)
C2–C3–N2	114.9(3)	C3–N2–H1N2	107(3)
C5–C4–N2	114.1(3)	C4–N2–H1N2	109(3)
C3–N2–H2N2	96(4)	C4–N2–H2N2	124(4)
H1N2–N2–H2N2	107(4)	N1–C1–H1C1	107(3)
C2–C1–H1C1	109(3)	N1–C1–H2C1	104(3)
C2–C1–H2C1	106(3)	H1C1–C1–H2C1	116(4)
C3–C2–H1C2	105(3)	C1–C2–H1C2	116(3)
C3–C2–H2C2	105(3)	C1–C2–H2C2	112(3)
H1C2–C2–H2C2	104(4)	C2–C3–H1C3	105(3)
N2–C3–H1C3	109(3)	C2–C3–H2C3	107(3)
N2–C3–H2C3	114(3)	H1C3–C3–H2C3	107(4)
C5–C4–H1C4	106(2)	N2–C4–H1C4	112(2)
C5–C4–H2C4	106(4)	N2–C4–H2C4	109(4)
H1C4–C4–H2C4	110(4)	N1–C5–H1C5	111(3)
C4–C5–H1C5	109(2)	N1–C5–H2C5	109(3)
C4–C5–H2C5	112(3)	H1C5–C5–H2C5	106(3)
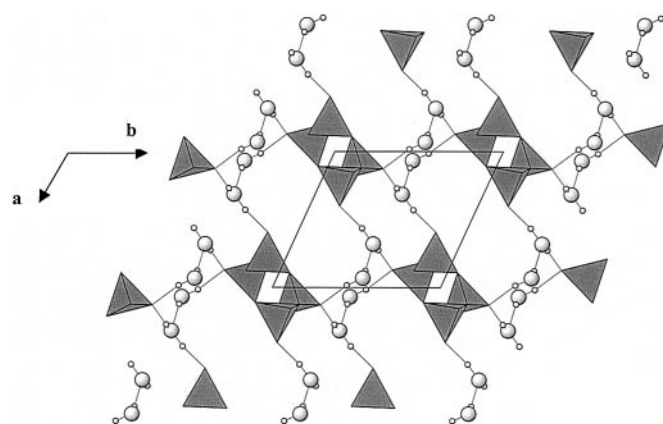
FIG. 2. Projection along the c axis of the P_4O_{12} groups with water molecules. Hydrogen bonds are dotted.

This result confirms the hydrated character of the nominal compounds and the existence of four water molecules per unit formula. According to the H-bond scheme within the asymmetrical unit which shows the existence of several types of H-bonds having different forces, one can assume that the first and the second water departures correspond to the O_{W2} molecule, followed by the O_{W1} molecule which is much more connected to the network.

The last peak at 235°C, which is accompanied by the final important weight loss corresponds to the product degradation.

intervene in seven hydrogen bonds out of eight established in the asymmetrical unit. Among these eight H-bonds, only three could be considered as strong according the well known Blessing's and Brown's criterion: $d_{N1—ow1} = 2.655(5)$ Å, $d_{ow1—ow2} = 2.685(5)$ Å and $d_{ow1—OE12} = 2.724(4)$ (24, 25). The five remaining hydrogen bonds are weak and their distances vary from 2.736(5) to 3.297(6) Å.

Thermal Analysis

Figure 3 shows the simultaneously recorded differential thermal analysis and thermogravimetric analysis curves of the $C_{10}H_{28}N_4P_4O_{12}\cdot4H_2O$ compounds.

The TG curve reveals three weight losses corresponding to the three endothermic peaks at 77, 100, and 166°C detected in the DTA curve. The first peak at 77°C corresponds to the departure of the first water molecule (% water: experimental, 2.90; calculated, 3.04). The departure of the second water molecule is observed at 100°C (% water: experimental, 3.16; calculated, 3.04). The peak at 166°C corresponds to the departure of the two remaining water molecules (% water: experimental, 5.90; calculated, 6.07).

IR Spectroscopy

The IR spectrum of $C_{10}H_{28}N_4P_4O_{12}\cdot4H_2O$ phosphate is illustrated in Fig. 4. Theoretically, the ideal symmetry of the $(P_4O_{12})^{4-}$ cycle is D_{4h}. As mentioned above, the symmetry of the studied ring is C_i. According to the theoretical group analysis, the number of normal modes is 42, given by the

TABLE 5
Bond Lengths (Å) and Angles (°) in the Hydrogen Bonding Scheme

O(N)–H—O	O(N)–H (Å)	H—O (Å)	O(N)—O (Å)	O(N)–H—O(°)
N1–H1N1—$O_{W1}^{(i)}$	0.86(4)	1.84(5)	2.656(5)	158(4)
N1–H2N1—O_{E22}	0.76(4)	2.14(5)	2.850(5)	155(4)
N2–H1N2—$O_{W1}^{(ii)}$	1.00(4)	2.47(4)	3.225(5)	125(3)
N2–H2N2—O_{W2}	1.00(4)	2.33(4)	3.297(6)	146(4)
O_{w1}–H1W1—$O_{W2}^{(iii)}$	0.83(5)	1.89(5)	2.687(5)	160(5)
O_{w1}–H2W1—O_{E12}	1.00(6)	1.75(6)	2.724(4)	162(5)
O_{w2}–H1W2—O_{E12}	0.89(5)	1.87(5)	2.752(5)	169(4)
O_{w2}–H2W2—$O_{E11}^{(iv)}$	1.12(7)	1.63(8)	2.736(5)	165(6)

Note. (i) $x, 1 + y, z$; (ii) $-1 + x, y, z$; (iii) $-x, -1 - y, 1 - z$; (iv) $-1 + x, -1 + y, z$.
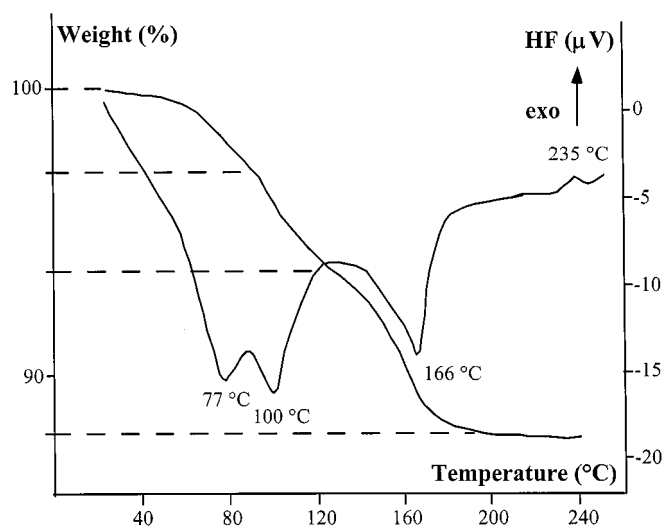
FIG. 3. TG-DTA Thermograms of the $C_{10}H_{28}N_4P_4O_{12}\cdot4H_2O$.

FIG. 4. IR Spectrum of $C_{10}H_{28}N_4P_4O_{12}\cdot4H_2O$ at 300 K.

reduced representation:

$$\Gamma_{int} = 21A_u + 21A_g.$$

The A_u modes are active in the IR spectroscopy, whereas the A_g modes are active in RAMAN. The 21 IR-active modes could be divided into 8 stretching modes and 13 deformation modes.
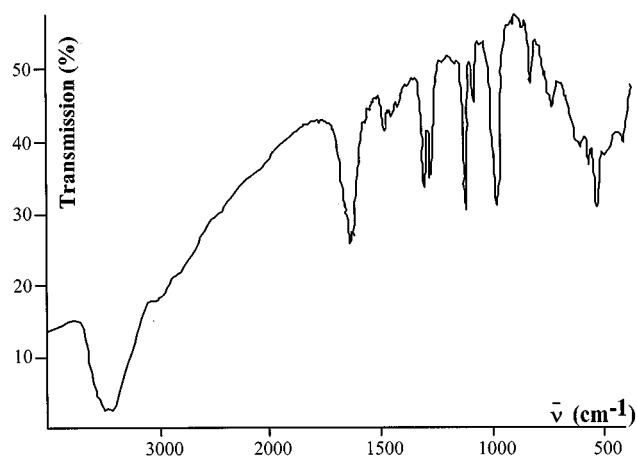
We have already resolved the crystal structure and attributed the main bands in the IR spectrum of the (1,4-$HOC_6H_4NH_3)_4P_4O_{12}\cdot6H_2O$ cyclotetraphosphate in which the P_4O_{12} ring has the same local symmetry (C_i) (18). In order to attribute each band in the IR spectrum of $C_{10}H_{28}N_4P_4O_{12}\cdot4H_2O$, we have compared in Table 6, the recorded frequencies with those observed in (1,4-$HOC_6H_4NH_3)_4P_4O_{12}\cdot6H_2O$ and $(NH_2NH_3)_4P_4O_{12}$ cylotetraphosphates (18, 26). As can be seen, all the vibrational

TABLE 6
Vibrational Frequencies and Assignments in the P_4O_{12} Stretching Regions: Comparison with Experimental Frequencies for $(NH_2NH_3)P_4O_{12}$ and $(1-4,HOC_6H_4NH_3)_4P_4O_{12}\cdot6H_2O$

Movement	Site group		$(NH_2NH_3)_4P_4O_{12}$ (26), $\bar{v}_{obs}$ (cm^{-1})	$(1,4-HOC_6H_4NH_3)_4P_4O_{12}\cdot6H_2O$ (18), $\bar{v}_{obs}$ (cm^{-1})	$C_{10}H_{28}N_4P_4O_{12}\cdot4H_2O$ (This work), $\bar{v}_{obs}$ (cm^{-1})
	C_i	IR			
$v_a(OPO^-)$	A_u	+	1280	1277 (vs)	1298 (vs)
	A_u	+	1235	1260 (vs)	1273 (vs)
	A_g	−			
	A_g	−			
$v_s(OPO^-)$	A_u	+	1135	1115 (vs)	1111 (vs)
	A_u	+	1100	1098 (vs)	1076 (s)
	A_g	−			
	A_g	−			
$v_a(POP)$	A_u	+	1000	993 (s)	972 (b)
	A_u	+	985	958 (vs)	
	A_g	−			
	A_g	−			
$v_s(POP)$	A_u	+	745	747 (s)	724 (m)
	A_u	+	700	700 (s)	690 (w)
	A_g	−			
	A_g	−			

TABLE 7
Tentative Assignments of the Observed IR Frequencies Outside the Stretching Domain of P_4O_{12} Rings

$C_{24}H_{32}N_4O_4P_4O_{12}\cdot6H_2O(18)$		$C_{10}H_{28}N_4P_4O_{12}\cdot4H_2O$	
3112 (w)	$\nu(H_2O)$	3443 (b)	$\nu(H_2O)$
3065 (w)	$+\nu(C-H)$	3024 (w)	$+\nu(CH_2)$
2914 (b)	$+\nu(NH_3^+)$	2976 (w)	$+\nu(NH_2^+)$
2666 (m)	$+\nu(OH)_{ph}$		
1878 (w)	Combination	1638 (s)	$\delta(H_2O)$
1834 (w)	bands^a	1588 (s)	$+$
1503 (s)	$+$	1536 (w)	Combination
1473 (m)	$\nu(C=C)$	1512 (w)	bands^a
1455 (m)	of the organic	1488 (w)	$+$
1386 (m)	cation	1482 (m)	$\delta(CH_2)$
1362 (m)		1452 (w)	
1223 (s)	$\nu(C-O)$	1428 (w)	
1172 (s)	$+\nu(C-N)$	1392 (w)	
860 (w)	$+\delta(C-H)$ in plan	1355 (w)	
826 (s)			
666 (w)	$\delta(C-H)$ out plan $+$	928 (m)	$\nu(C-C-N)+$
650 (w)	$\delta(O-H)_{ph}$ out	880 (m)	$\nu(C-N-C)$
	plan	816 (w)	
		759 (w)	
574 (s)	Deformation	560 (m)	Deformation
551 (m)	vibrations	526 (s)	vibrations
510 (s)	$+$	404 (m)	$+$
472 (m)	external modes		external modes
446 (m)			
386 (m)			
358 (s)			

^{a}Combination bands between C–H out of plane. w, weak; m, medium; b, broad; s, strong.

frequencies characteristic of the P_4O_{12} cycle has been observed in the case of the $C_{10}H_{28}N_4P_4O_{12}\cdot4H_2O$ compound. Nevertheless, special caution must be paid in attribution of $\nu_{as}(OPO^-)$ and $\nu_s(POP)$ vibration bands because of their possible overlapping with $\nu(C-N)$ vibration and $\delta(C-H)$ deformation vibration bands, respectively.

On the other hand, intensive bibliographic research (27, 28) allows us to attribute easily the remaining experimental vibration bands characteristic of the organic molecule. All these vibrational bands are assigned in Table 7.

CONCLUSIONS

The crystal structure of the $C_{10}H_{28}N_4P_4O_{12}\cdot4H_2O$ has been determined. Its symmetry is triclinic, space group $P-1$, $Z=1$. The structure of this organic-cation phosphate is organized as a succession of two types of layers. One contains only the water molecule, while the second contains simultaneously organic and inorganic groups. An intensive review of earlier works concerning organic-cation cyclophosphates shows that the P_4O_{12} cycle of this studied compound appears to present the strongest distortion known to date. Furthermore, the water molecules participate in seven of eight hydrogen bonds established in the asymmetrical unit. This shows the important role played by the water molecules in the cohesion and stability of this structure.

The hydrated character of $C_{10}H_{28}N_4P_4O_{12}\cdot4H_2O$ phosphate is confirmed by the coupled TG-DTA technique, which shows the successive departure of water molecules. IR spectrum has been indexed by comparison with other studied cyclotetraphosphates. It shows that this material reveals several bands characteristic of P_4O_{12} cycle and 1, 4, 8, 11-tetraazacyclotetradecane.

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