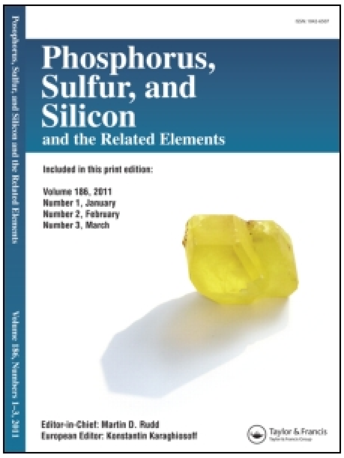

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Synthesis and Characterization of a New Mixed Organic Cyclohexaphosphate

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Synthesis and Characterization of a New Mixed Organic Cyclohexaphosphate

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Among the varieties of explored hybrid compounds, organic phosphates are particularly interesting in various fields. For this reason, research of such materials continue to develop. Single Crystals of a new cyclohexaphosphate $[2,6\text{-}(CH_3)_2C_6H_3NH_3]_4[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2P_6O_{18}.4H_2O$ *were synthesized for the first time in aqueous solution and characterized by single crystal X-ray diffraction. The title compound crystallizes in the* $P2_1/c$ *monoclinic unit-cell, with the parameters:* $a = 16.214(3)$ Å, $b = 14.340(4)$ Å, $c = 16.247(4)$ Å, $\beta = 115.25(2)^\circ$, $V = 3416(1)$ Å^3, $Z = 4$, $\rho_{cal} = 1.298 g.cm^{-3}$. *The crystal structure has been solved and refined to a final* $R = 0.064$ *and* $Rw = 0.156$ *for 5988 independent reflections. In this atomic arrangement, the inorganic entities,* $P_6O_{18}^{6-}$ *and* H_2O*, form layers located around the bc-planes. Between these layers, both organic molecules are located with a different orientation of their molecular planes. A characterization of this material, IR absorption and thermal analysis are reported, as well.*

Keywords Cyclohexaphosphate; crystal structure; X-ray diffraction; infrared spectroscopy

INTRODUCTION

Enormous growth in the field of hybrid framework materials has occurred over the past few years, due to their huge variety of intriguing structural topologies and their fascinating properties, as well as their great potential applications in many fields, such as catalysis, medicine, and magnetism.[1–2] Among them, organic phosphates still attract a lot of interest because of their applications in the fields of non-linear optics, material sciences, and so on[3].... Although the previous materials have been widely studied, the mixed organic cyclohexaphosphates

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have not been thoroughly investigated. In this article, we present the synthesis and the characterization of the $[2,6\text{-}(CH_3)_2C_6H_4NH_3]_4[2,6\text{-}(C_2H_5)_2C_6H_4NH_3]_2P_6O_{18}.4H_2O$. This inorganic-organic hybrid compound results from an interaction between the cyclohexaphosphoric acid, 2,6-diethylaniline and 2,6-dimethylaniline molecules.

$$\begin{aligned} &H_6P_6O_{18} \; + \; 4[2,6\text{-}(CH_3)_2C_6H_3NH_2] + \; 2[2,6\text{-}(C_2H_5)_2C_6H_3NH_2] \\ &\quad + 4H_2O \longrightarrow [2,6\text{-}(CH_3)_2C_6H_3NH_3]_4[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2 \\ &\quad P_6O_{18}.4H_2O \end{aligned}$$

RESULTS AND DISCUSSION

Crystal Structure

The determined monoclinic unit-cell has $a = c$. This induces the feeling of a more symmetrical unit-cell, but the intensity symmetry relations to be observed in an orthorhombic system are not verified. Consequently, the monoclinic unit-cell is retained for the intensity measurements and the structure resolution.

The final atomic coordinates of the title compound and equivalent isotropic displacement parameters (B_{eq}) are given in Table I. The asymmetric unit of the crystal structure, depicted in the ORTEP drawing (Figure 1), is built up from the half of the cyclohexaphosphate ring P_6O_{18}, two crystallographically distinct 2,6-xylidinium cations, one 2,6-diethylphenylammonium cation, and two water molecules.

The centrosymmetric phosphoric ring anions, centred around (0, ½, 0) and (0, 0, ½), are connected via their external oxygen atoms (O3, O6 and O8) to the water molecules (OW1 and OW2) by medium long [(O(W)-H. . . O] hydrogen bond to build a layer parallel to the bc plane. Organic groups 2,6-xylidinium and 2,6-diethylphenylammonium are located in accessible voids (Figure 2).

Inside this arrangement, the phosphoric ring is centrosymmetrical and thus built up by only three independent PO_4 tetrahedra $P(1)O_4$, $P(2)O_4$ and $P(3)O_4$. In the PO_4 tetrahedra, the P—O distances range in [1.459(3)–1.600(3)Å] and the O—P—O bond angles in [99.87(18) − 121.2(2)°] (Table II). All these distances and angles are in accordance with previous observations of PO_4 tetrahedra involved in other condensed phosphate anions.[4,5] The P—O—P and P—P—P angles have also common values. They range respectively from 132.0(2) to 134.0(2)° and from 101.56(7) to 109.06(6)°. It is the same for the P—P distances ranging from 2.903(2) and 2.934(2) Å, which are comparable

TABLE I Final Atomic Coordinates and $U_{eq.}$ ($Å^2$) for the Non-hydrogen Atoms. Estimated Standard Deviations are Given in Parentheses

Atoms	x(σ)	y(σ)	z(σ)	Ueq.
P1	−0.01984(8)	0.69496(8)	1.01946(8)	0.0382(3)
P2	0.02044(8)	0.60764(8)	0.87740(8)	0.0353(3)
P3	−0.07392(8)	0.42926(8)	0.82776(8)	0.0366(3)
O1	−0.1013(2)	0.6807(2)	1.0371(2)	0.0455(8)
O2	0.0116(3)	0.7900(2)	1.0136(2)	0.059(1)
O3	−0.0408(2)	0.6415(3)	0.9268(2)	0.056(1)
O4	−0.0222(2)	0.6421(2)	0.7834(2)	0.0533(9)
O5	0.1177(2)	0.6282(2)	0.9342(2)	0.0479(8)
O6	0.0099(2)	0.4981(2)	0.8805(2)	0.0509(9)
O7	−0.1613(2)	0.4782(2)	0.8012(2)	0.0456(8)
O8	−0.0643(2)	0.3616(2)	0.9090(2)	0.0529(9)
O9	−0.0531(2)	0.3788(3)	0.7609(2)	0.064(1)
OW1	0.0749(3)	0.1082(3)	0.1455(3)	0.078(1)
OW2	1.0067(4)	−0.0662(3)	0.1341(4)	0.123(2)
N1	0.2155(2)	0.0271(3)	0.5709(3)	0.044(1)
N2	0.1313(2)	0.2076(3)	0.3079(3)	0.043(1)
N3	0.8628(2)	0.1807(3)	0.0881(3)	0.048(1)
C1	0.3154(3)	0.0425(4)	0.6143(3)	0.048(1)
C2	0.3713(4)	−0.0315(4)	0.6166(4)	0.066(2)
C3	0.4656(4)	−0.0145(6)	0.6574(5)	0.093(2)
C4	0.4992(4)	0.0714(7)	0.6941(5)	0.099(2)
C5	0.4412(4)	0.1402(5)	0.6919(5)	0.093(2)
C6	0.3477(4)	0.1284(4)	0.6532(4)	0.064(2)
C7	0.3370(4)	−0.1280(5)	0.5819(5)	0.090(2)
C8	0.3308(9)	−0.1885(7)	0.6502(7)	0.174(5)
C9	0.2844(5)	0.2060(5)	0.6532(6)	0.100(3)
C10	0.3186(7)	0.2981(6)	0.6761(8)	0.157(4)
C11	0.2307(3)	0.2040(4)	0.3609(3)	0.044(1)
C12	0.2730(3)	0.1177(4)	0.3775(3)	0.052(1)
C13	0.3663(4)	0.1160(5)	0.4282(4)	0.071(2)
C14	0.4153(4)	0.1955(6)	0.4610(5)	0.090(2)
C15	0.3716(4)	0.2799(5)	0.4440(5)	0.086(2)
C16	0.2774(4)	0.2863(4)	0.3937(4)	0.061(1)
C17	0.2209(4)	0.0294(4)	0.3430(5)	0.077(2)
C18	0.2308(5)	0.3794(4)	0.3791(5)	0.097(2)
C19	0.7688(3)	0.1442(3)	0.0464(3)	0.047(1)
C20	0.7442(4)	0.0823(4)	−0.0249(4)	0.059(1)
C21	0.6543(5)	0.0506(5)	−0.0631(5)	0.087(2)
C22	0.5953(5)	0.0786(6)	−0.0276(6)	0.101(3)
C23	0.6219(4)	0.1399(6)	0.0431(6)	0.091(2)
C24	0.7105(4)	0.1747(4)	0.0826(4)	0.062(1)
C25	0.8090(5)	0.0517(5)	−0.0648(5)	0.092(2)
C26	0.7409(5)	0.2450(5)	0.1601(5)	0.089(2)

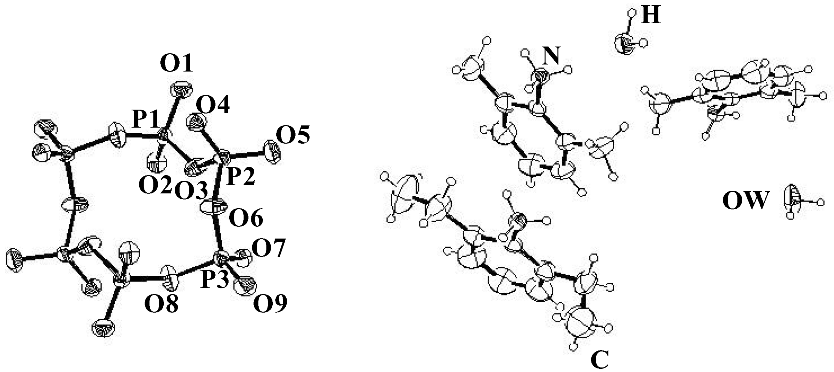

FIGURE 1 Asymmetric unit of $[2,6\text{-}(CH_3)_2C_6H_3NH_3]_4[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2P_6O_{18}.4H_2O$. Thermal ellipsoids are shown at 30% probability.

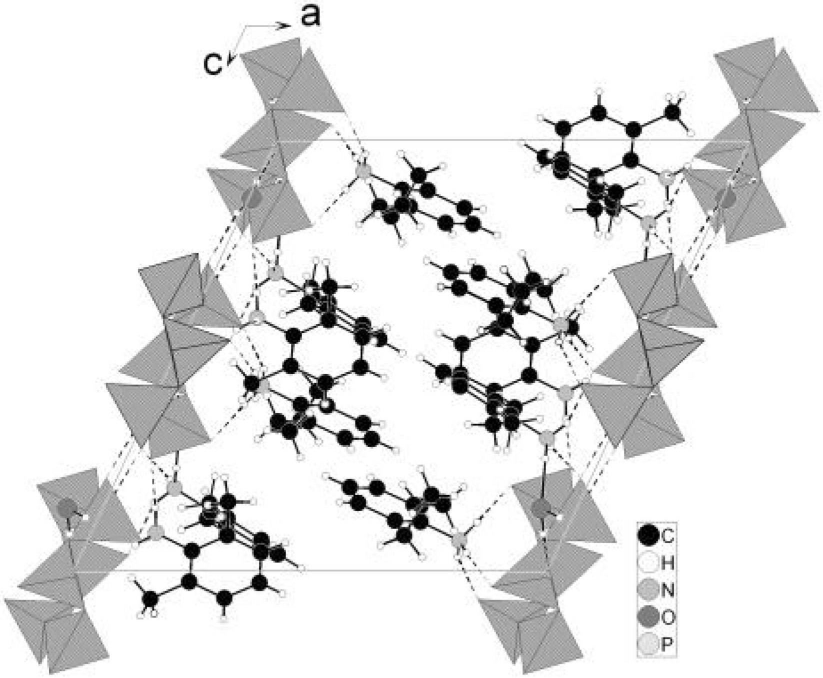

FIGURE 2 Projection of the structure of $[2,6\text{-}(CH_3)_2C_6H_3NH_3]_4[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2P_6O_{18}.4H_2O$, along the b axis. The phosphoric anion is given in a tetrahedral representation. Other atoms are indicated by their symbols. Hydrogen bonds are indicated by dotted lines.

TABLE II Main Interatomic Distances (Å) and Bond Angles (°) in $P_6O_{18}^{6-}$ Anion of $[2,6\text{-}(CH_3)_2C_6H_3NH_3]_4$ $[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2P_6O_{18}.4H_2O$. Estimated Standard Deviations are Given in Parentheses

		$P(1)O_4$ tetrahedron				
P(1)	O1	O2	O3	O8		
O1	1.480(3)	2.558(5)	2.447(4)	2.517(4)		
O2	120.1(2)	1.472(3)	2.495(5)	2.473(5)		
O3	105.6(2)	109.0(2)	1.600(3)	2.479(5)		
O8	110.3(2)	107.9(2)	102.5(2)	1.586(3)		
		$P(2)O_4$ tetrahedron				
P(2)	O4	O5	O3	O6		
O4	1.468(3)	2.539(5)	2.474(5)	2.515(5)		
O5	119.1(2)	1.478(3)	2.529(4)	2.449(4)		
O3	107.6(2)	110.7(2)	1.596(3)	2.449(5)		
O6	111.0(2)	106.2(2)	100.8(2)	1.584(3)		
		$P(3)O_4$ tetrahedron				
P(3)	O7	O9	O6	O8		
O7	1.471(3)	2.553(5)	2.449(5)	2.446(5)		
O9	121.2(2)	1.459(3)	2.460(5)	2.501(5)		
O6	110.8(2)	106.9(2)	1.600(3)	2.443(5)		
O8	106.0(2)	110.1(2)	99.9(2)	1.591(3)		
P(1)-P(2)	2.934(2)			P(1)-P(2)-P(3)	101.56(7)	
P(2)-P(3)	2.912(2)			P(2)-P(1)-P(3)	106.30(7)	
P(3)-P(1)	2.903(2)			P(1)-P(3)-P(2)	109.06(6)	
		P(1)-O8-P(3)	132.0(2)			
		P(1)-O3-P(2)	134.0(2)			
		P(2)-O6-P(3)	132.3(2)			

to values generally measured. For the organic cations, the main features measured are similar to intramolecular bond distances and angles usually reported for such molecules.[6] The interatomic bond lengths and angles spread with the respective ranges 1.35(1)–1.51(1) Å and 113.5(7)–124.1(5)° for $[2,6\text{-}(CH_3)_2C_6H_3NH_3]^+$ and 1.362(9)–1.522(9) Å and 116.8(6)–123.9(5) ° for $[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]^+$ (Table III). The phenyl rings of these groups are almost planar, with mean deviations of ± 0.007 and ± 0.011 Å for 2,6-xylidinium and ± 0.018 Å for 2,6-diethylphenylammonium.

The atomic arrangement of the title compound contains two crystallographically independent water molecules O(W1) and O(W2). Each one of these molecule pairs is linked by hydrogen bonds to three different P_6O_{18} rings, and thus contributes to the intralayer cohesion of this compound (Figure 3).

TABLE III Selected Bond Lengths (Å) and Bond Angles (°) in the Organic Groups of the $[2,6\text{-}(CH_3)_2C_6H_3NH_3]_4[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2P_6O_{18}.4H_2O$

		$[2,6\text{-}(C_2H_5)_2C_6H_3]N(1)H_3^+$			
C1 – N1	1.483(6)	C3—C4	1.37(1)	C6—C1	1.382(7)
C1—C2	1.385(7)	C4—C5	1.35(1)	C2—C7	1.508(8)
C2—C3	1.404(8)	C5—C6	1.382(8)	C7—C8	1.44(1)
C6—C9	1.514(9)	C9—C10	1.42(1)		
N1—C1—C2	117.9(5)	C1—C2—C7	124.1(5)	C5—C6—C9	121.5(6)
N1—C1—C6	118.3(4)	C3—C2—C7	119.3(6)	C1—C6—C9	122.0(5)
C2—C1—C6	123.7(5)	C2—C3—C4	120.7(7)	C6—C5—C4	122.5(7)
C1—C2—C3	116.6(6)	C3—C4—C5	120.0(6)	C1—C6—C5	116.4(6)
C6—C9—C10	119.6(7)	C2—C7—C8	113.5(7)		
		$[2,6\text{-}(CH_3)_2C_6H_3]N(2)H_3^+$			
N2—C11	1.469(6)	C13—C14	1.362(9)	C11—C16	1.381(7)
C11—C12	1.385(7)	C14—C15	1.369(9)	C12—C17	1.492(8)
C12—C13	1.381(7)	C15—C16	1.394(8)	C16—C18	1.503(8)
N2—C11—C12	118.3(4)	C13—C14—C15	119.7(6)	C11—C12—C17	122.1(5)
N2– C11—C16	118.7(4)	C14—C15—C16	121.3(6)	C13—C12—C17	120.6(5)
C11—C12—C13	117.3(5)	C15—C16—C11	117.0(5)	C11—C16—C18	122.8(5)
C12—C13—C14	121.8(6)	C16—C11—C12	122.9(5)	C15—C16—C18	120.2(6)
		$[2,6\text{-}(CH_3)_2C_6H_3]N(3)H_3^+$			
N3—C19	1.474(6)	C22—C23	1.36(1)	C24—C26	1.522(9)
C19—C20	1.377(7)	C23—C24	1.392(9)	C21—C22	1.37(1)
C20—C21	1.395(8)	C24—C19	1.380(7)	C20—C25	1.515(8)
N3—C19—C20	119.1(5)	C21—C22—C23	121.2(7)	C19—C20—C25	122.8(5)
N3—C19—C24	117.0(5)	C22—C23—C24	120.8(7)	C21—C20—C25	120.0(6)
C19—C20—C21	117.2(6)	C23—C24—C19	116.8(6)	C19—C24—C26	121.5(5)
C20—C21—C22	120.2(7)	C24—C19—C20	123.9(5)	C23—C24—C26	121.7(6)

The $[2,6\text{-}(CH_3)_2C_6H_3NH_3]_4[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2P_6O_{18}.4H_2O$ atomic arrangement exhibits two types of hydrogen bonds: (i) the O(W)—H. . .O interactions including four contacts, with H. . .O distances ranging from 1.80 to 2.06 Å, ensure the cohesion between anions in the layer; (ii) the N—H. . .O interactions, involving nine relatively long contacts with H. . .O in the range 1.78–2.43 Å, link organic groups to the anionic layers. All the D(Donor)–H. . . A(Acceptor) hydrogen bonds are listed in Table IV. These hydrogen bonds participate with other interactions (ionics, van der Waals . . .) to form a stable three-dimensional network.

Thermal Analysis

The TG curve of $[2,6\text{-}(CH_3)_2C_6H_3NH_3]_4[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2P_6O_{18}$ $4H_2O$ (Figure 4) exhibits two weight losses. The first experimental

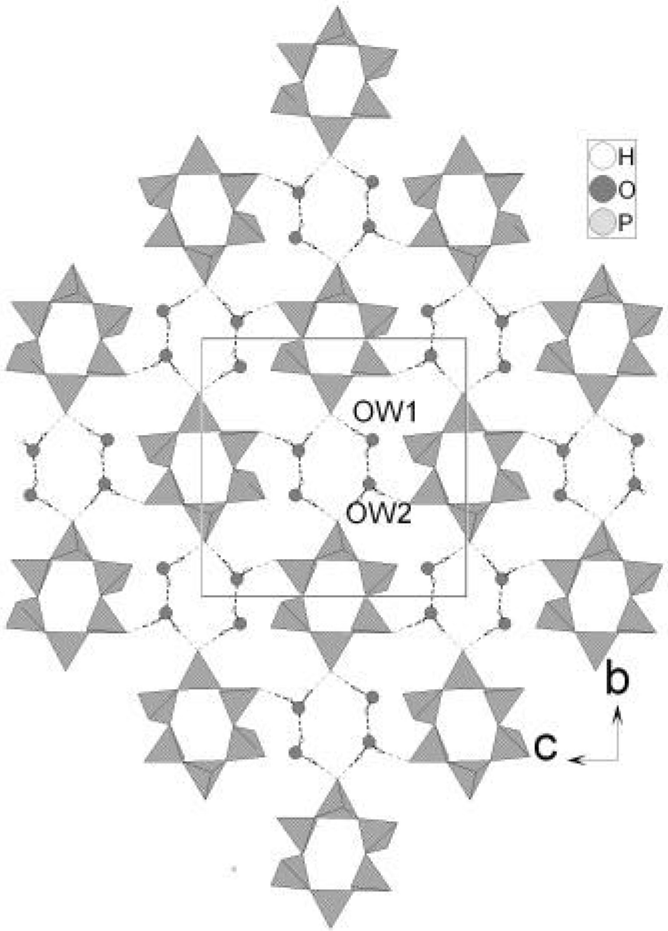

FIGURE 3 Projection of the anionic arrangement along the a axis. The phosphoric anion is given in a tetrahedral representation. (H bonds are represented by full and dashed lines).

weight loss (9.08%) was observed accurately between 60 and 165°C. It corresponds to the loss of four water molecules (calculated weight loss 10.78%). The second experimental weight loss (53.77%) observed in the temperature range of 169–410°C, can be assigned to a partial decomposition of the organic components (calculated 59.00%). This decomposition led to a black viscous material containing a carbon deposit. A similar thermal behavior is found for other organic cyclophosphates.[7]

TABLE IV Hydrogen–bond Scheme in $[2,6\text{-}(CH_3)_2C_6H_3NH_3]_4[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2P_6O_{18}.4H_2O$. Estimated Standard Deviations are Given in Parentheses

D—H···A	D—H(Å)	H···A(Å)	D···A(Å)	D—H···A(°)
N1-H1A···O5	0.8900	2.2200	3.067(5)	158.00
N1-H1B···O1	0.8900	2.0500	2.931(5)	169.00
N1-H1C···O7	0.8900	1.7800	2.671(5)	175.00
N2-H15A···O1	0.8900	1.9800	2.788(5)	151.00
N2-H15B···OW1	0.8900	1.9100	2.788(6)	170.00
N2-H15C···O4	0.8900	1.9700	2.781(5)	152.00
N3-H16A···O2	0.8900	2.4300	3.150(7)	138.00
N3-H16B···O9	0.8900	1.8000	2.684(5)	172.00
N3-H16C···O5	0.8900	1.9200	2.800(5)	168.00
OW1-H83···O2	0.9800	1.8000	2.772(5)	170.00
OW1-H84···OW2	1.0000	1.8400	2.709(7)	143.00
OW2-H90···O2	1.0100	1.8900	2.868(6)	163.00
OW2-H91···O4	0.8500	2.0600	2.874(7)	161.00

IR Spectroscopy

Figure 5 shows the infrared spectrum of $[2,6\text{-}(CH_3)_2C_6H_3NH_3]_4[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2P_6O_{18}.4H_2O$. The most important IR bands attributed to vibrations of this compound are reported in Table V. So, the absorption bands, between 4000 and 1350 cm^{-1} correspond to the O(N,C)—H stretching and bending vibrations of water molecules and organic groups. The strong bands observed in the ranges 1350–1180, 1180–1060, 1060–960, and 850–660 cm^{-1} can be assigned to stretching

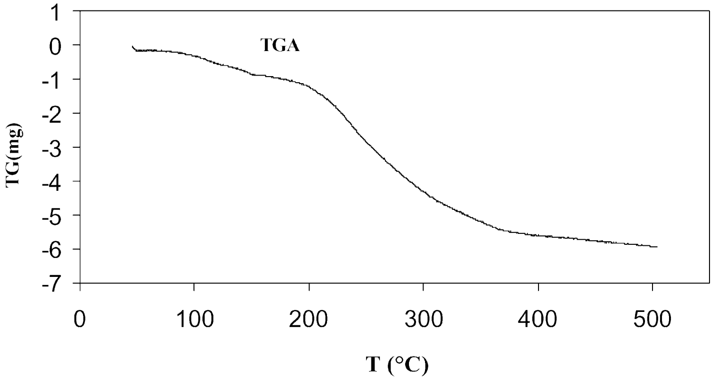

FIGURE 4 TGA curve of $[2,6\text{-}(CH_3)_2C_6H_3NH_3]_4[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2P_6O_{18}.4H_2O$ between room temperature and 500°C.

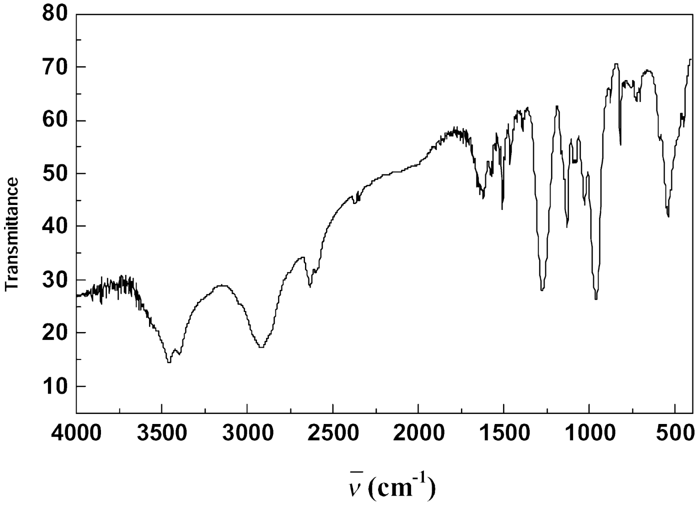

FIGURE 5 IR spectrum of $[2,6\text{-}(CH_3)_2C_6H_3NH_3]_4[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2 P_6O_{18}.4H_2O$ in KBr pellet.

vibrations $\nu_{as}(OPO^-)$, $\nu_s(OPO^-)$, $\nu_{as}(POP)$ and $\nu_s(POP)$, respectively.[8] Nevertheless, special caution must be paid in attribution of these bands because of their possible overlapping with ν(C—N) stretching vibration and δ(C–H) bending vibration bands. We note that the supplementary

TABLE V Assignments of the Most Characteristic IR Bands of $[2,6\text{-}(CH_3)_2C_6H_3NH_3]_4[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2 P_6O_{18}.4H_2O$

Frequencies	Assignments	Frequencies	Assignments
3457	$\nu(H_2O)$ libre		
3394	$\nu(C_{ar}$ - H)	1267	
2914	$\nu(NH_3^+)$	1157	$\nu_{as}(OPO^-)$
2903	$\nu(\text{-}CH_3)$	1126	$\nu(C_{ar}\text{-}N)$
	$\nu(\text{-}CH_2)$	1089	$\nu_s(OPO^-)$
2630		1073	$\delta_{d.p}(C_{ar}$ - H)
2601	Combination bands	1020	$\nu_{as}(POP)$
2037		954	ν(C-C)
1649	$\delta(\text{-}CH_3)$	870	
1618	$\nu(C{=}C)_{ar}$	813	$\nu_s(POP)$
1574	$\delta_{as}(NH_3^+)$	722	$\delta_{h.p}(C_{ar}$ - H)
1555	$\delta_s(NH_3^+)$	700	$\delta(C{=}C)_{ar}$
1520	$\delta(\text{-}CH_2)$	697	δ(POP)
1461		585	$\delta(OPO^-)$
1383		535	
		474	
		437	

frequency in the ν_s(OPO) domain can be assigned to the stretching ν(C—C) vibrations.[9]Frequencies below 660 cm^{-1}can be assigned to bending vibrations of P_6O_{18} ring.

EXPERIMENTAL PART

Synthesis of $[2,6\text{-}(CH_3)_2C_6H_3NH_3]_4[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2P_6O_{18}.4H_2O$

Crystals of $[2,6\text{-}(CH_3)_2C_6H_3NH_3]_4[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2P_6O_{18}.4H_2O$ were prepared in two steps. In the first one, a concentrated solution of cyclohexaphosphoric acid was prepared by passing a solution of $Li_6P_6O_{18}$ (3 g, 4.8 mmol) through an ion exchange resin in its H-state (Amberlite IR 120). The lithium salt was prepared according to the procedure of Schulke and Kayser.[10] In the second step, the obtained solution was immediately neutralized by an alcoholic solution of the $[2,6\text{-}(CH_3)_2C_6H_3NH_2]$ (2.36 mL, 19.2 mmol) and $[2,6\text{-}(C_2H_5)_2C_6H_3NH_2]$ (1.58 mL, 9.6 mmol) amines in a molar ratio of 2:1 respectively.

After several days of slow evaporation at room temperature, prismatic crystals appear in the remaining solution with suitable dimensions for a crystallographic study.

Investigation Techniques

X- ray Diffraction

The intensity data collection was performed using a Mach III Enraf-Nonius diffractometer operating at 296 K with the wavelength $K\alpha(Mo) = 0.7107$ Å. The strategy used for the structure determination and its final results are gathered in Table VI. The structure was solved by SHELX-S 86 and refined by full matrix least-squares techniques based on F2 using SHELX-L.[11] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the amine molecules were placed geometrically and not refined. Crystallographic data (CIF) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No CCDC 630086.

Physical Measurements

Thermal analysis was performed using the "multimodule 92 Setaram analyzer" operating from room temperature up to 500°C at an average heating rate of 5°C/min.

TABLE VI Crystal Data, Intensity Measurements and Structure Determination of $[2,6\text{-}(CH_3)_2C_6H_3NH_3]_4[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2P_6O_{18}.4H_2O$

Empirical formula	$C_{52}H_{88}N_6O_{22}P_6$
Formula weight	667.55 (g mol^{-1})
Crystal system	monoclinic
Space group	$P2_1/c$
a	16.214(3) (Å)
b	14.340(4) (Å)
c	16.247(4) (Å)
β	115.25(2)°
Z	4
V	3416(1) (Å^3)
ρ calc(g/cm^3)	1.298
F(0 0 0)	1416
μ(MoKα)	0.231 (mm^{-1})
Size (mm)	0.3 - 0.3 - 0.15
Index ranges	$h_{max} = 17, k_{max} = 17, l_{max} = 19$
Independent reflections	5988
Refined parameters	356
Goodness-of-fit	1.028
R (anisotropic) ($I > 2\sigma(I)$)	0.064
Rw (anisotropic)	0.156

IR spectrum was recorded in the range 4000–400 cm^1 with a “Perkin-Elmer Spectrum 1000” spectrophotometer using sample dispersed in spectroscopically pure KBr pellet.

CONCLUSION

The literature reports two cyclohexaphosphates of mixed organic cations :

$$(1,6\text{-}NH_3C_6H_{12}NH_3)_2(1\text{-}C_{10}H_7NH_3)_2P_6O_{18}.2H_2O^{12}$$

$$\text{and } (1,6NH_3C_6H_{12}NH_3)(C_6H_5NH_3)_4P_6O_{18}.6H_2O.^{13}$$

The title compound $[2,6\text{-}(CH_3)_2C_6H_3NH_3]_4[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2P_6O_{18}.4H_2O$ is the third one. In spite of the analogy of some geometrical features of the cyclic P_6O_{18} in these compounds, their atomic arrangement are different (Unit-Cell, synthesis, hydrogen-bonds, degrees of hydration, the incorporated organic groups, etc.). Such differences confer surely to these compounds’ different properties. A comparative investigation of crystallographical, thermal, and spectroscopic characteristics of these three materials should be reported subsequently.

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