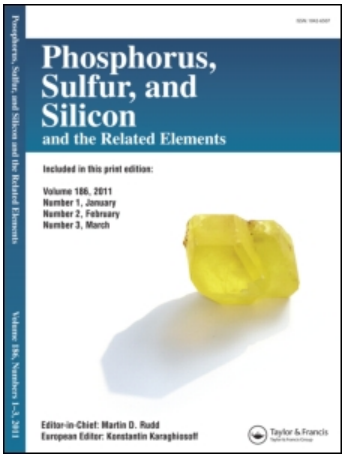

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Synthesis and Characterization of a New Cyclohexaphosphate, $(C_{10}H_{13}NH_3)_4(H_3O)_2(P_6O_{18}).3(H_2O)$

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Crystals of a new hybrid compound $(C_{10}H_{13}NH_3)_4(H_3O)_2(P_6O_{18}).3(H_2O)$ were synthesized in aqueous solution and characterized by X-ray diffraction, thermal analysis, and IR absorption. This compound crystallizes in a P-1 triclinic system unit cell with $a = 10.43(2)$ Å, $b = 16.09(3)$ Å, $c = 17.67(2)$ Å, $\alpha = 72.44(3)$, $\beta = 88.64(2)^\circ$, $\gamma = 85.11(3)^\circ$, $V = 2818.0(8)$ Å^3, and $Z = 2$. Crystal structure has been solved using direct methods and refined by least squares analyses ($R = 0.049$ and $Rw = 0.126$). The atomic arrangement can be described by thick layers built by $P_6O_{18}^{6-}$ anions, H_3O^+ cations and water molecules. The protonated amines are located between these inorganic layers, in order to balance the negative charge of the inorganic framework. The three-dimensional cohesion is assured by different interactions (electrostatic, H-bonds, Van Der Waals) established between the various molecular components.

Keywords Crystal structure; cyclohexaphosphate; infrared spectroscopy; ion oxonium; X-ray diffraction

INTRODUCTION

The design and synthesis of inorganic-organic hybrid materials have been of great interest due to their structural diversity and potential applications in various fields. Their benefits are due to a combination of desirable properties of the inorganic materials such as a wide range of electronic characteristics, mechanical hardness, and thermal stability and, on the other hand, structural variety, large polarizability, and easy processing of the organic molecules.[1–3] Among them, the phosphates are particularly interesting because of their applications in catalysis, bimolecular sciences and nonlinear optics, etc.[4] As a contribution to the study of this kind of material, we report the first structurally

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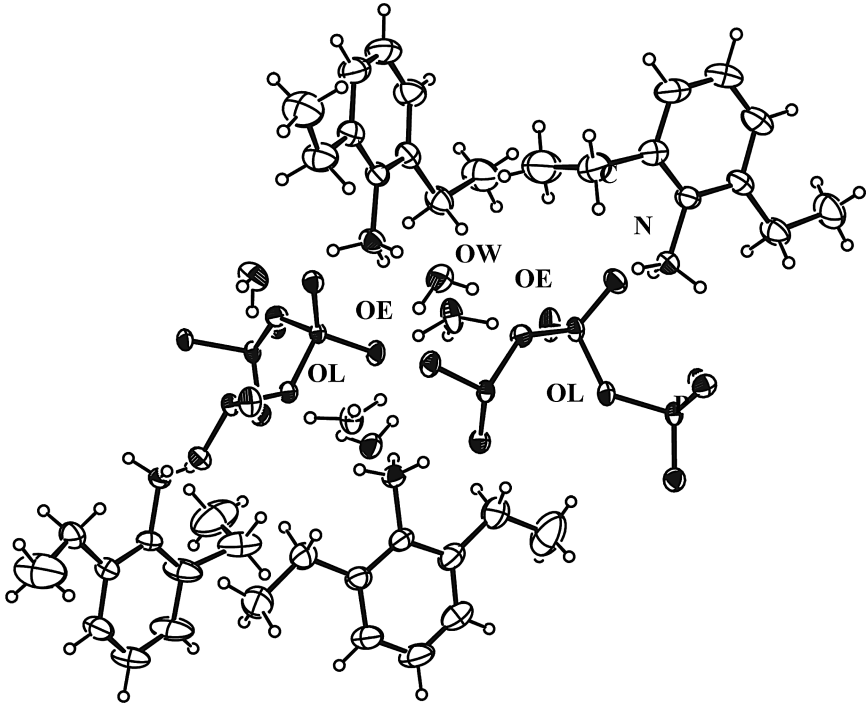

FIGURE 1 Asymmetric unit of $(C_{10}H_{13}NH_3)_4(H_3O)_2(P_6O_{18}).3(H_2O)$. Thermal ellipsoids are shown at 30% probability.

characterized compound that associates the oxonium and ammonium cations to the cyclohexaphosphate anion.

RESULTS AND DISCUSSION

Crystal Structure

The asymmetric unit of the crystal structure, depicted in an ORTEP drawing (Figure 1), consists of two half phosphoric ring anions, two oxonium molecules, three water molecules and four crystallographically distinct 2,6-diethylphenylammonium cations. Two crystallographically independent P_6O_{18} phosphoric rings coexist inside the Unit-cell. They are built from $P(1)O_4$, $P(2)O_4$, and $P(3)O_4$ for the first one (I) and $P(4)O_4$, $P(5)O_4$ and $P(6)O_4$ for the second (II). The observed geometrical characteristics of these P_6O_{18} rings (P-O distances and P-O-P or O-P-O angles, as well as P-P distances) are similar to that observed in other cyclohexaphosphate[5] having the same internal symmetry

TABLE I Main Interatomic Distances (Å) and Bond Angles (°) in $P_6O_{18}^{6-}$ Anion of $(C_{10}H_{13}NH_3)_4(H_3O)_2(P_6O_{18}).3(H_2O)$[a]

		$P(1)O_4$ Tetrahedron		
P(1)	OE11	OE12	OL12	OL13
OE11	1.486(2)	2.570(3)	2.443(3)	2.528(3)
OE12	120.4(1)	1.476(2)	2.534(3)	2.439(3)
OL12	105.1(1)	111.5(1)	1.590(2)	2.508(3)
OL13	109.9(1)	104.9(1)	103.7(1)	1.599(2)
		$P(2)O_4$ Tetrahedron		
P(2)	OE21	OE22	OL12	OL23
OE21	1.468(2)	2.525(3)	2.492(3)	2.532(3)
OE22	118.1(1)	1.477(2)	2.489(3)	2.508(3)
OL12	108.8(1)	108.2(1)	1.596(2)	2.456(3)
OL23	111.0(1)	108.9(1)	100.3(1)	1.603(2)
		$P(3)O_4$ Tetrahedron		
P(3)	OE31	OE32	OL23	OL13
OE31	1.471(2)	2.544(3)	2.459(3)	2.543(3)
OE32	118.9(1)	1.483(2)	2.523(3)	2.492(3)
OL23	106.7(1)	110.2(1)	1.592(2)	2.443(3)
OL13	111.7(1)	107.8(1)	99.8(1)	1.600(2)
		$P(4)O_4$ Tetrahedron		
P(4)	OE41	OE42	OL45	OL46
OE41	1.481(2)	2.541 (3)	2.481(3)	2.520(3)
OE42	118.9(1)	1.470(2)	2.537(3)	2.463(3)
OL45	107.5(1)	111.7(1)	1.594(2)	2.447(3)
OL46	109.9(1)	106.9(1)	100.3(1)	1.594(2)
		$P(5)O_4$ Tetrahedron		
P(5)	OE51	OE52	OL45	OL56
OE51	1.477(2)	2.570(3)	2.514(3)	2.423(3)
OE52	121.1(1)	1.474(2)	2.447(3)	2.544(3)
OL45	109.5(1)	105.5(1)	1.599(2)	2.512(3)
OL56	103.9(1)	111.6(1)	103.7(1)	1.593(2)
		$P(6)O_4$ Tetrahedron		
P(6)	OE61	OE62	OL46	OL56
OE61	1.464(2)	2.550(3)	2.534(3)	2.493(3)
OE62	120.1(1)	1.480(2)	2.497(3)	2.501(3)
OL46	110.9(1)	107.7(1)	1.610(2)	2.459(3)
OL56	108.4(1)	108.0(1)	99.6(1)	1.609(2)
P(1)-P(2)		2.945(1)	P(1)-P(2)-P(3)	94.56(7)
P(2)-P(3)		2.909(1)	P(2)-P(1)-P(3)	102.30(7)
P(3)-P(1)		2.944(1)	P(1)-P(3)-P(2)	113.06(6)
P(4)-P(5)		2.937(1)	P(4)-P(5)-P(6)	91.56(7)
P(5)-P(6)		2.940(1)	P(5)-P(4)-P(6)	102.30(7)
P(6)-P(4)		2.905(1)	P(4)-P(6)-P(5)	113.06(6)
P(1)-OL13-P(3)		133.9(1)	P(4)-OL46-P(6)	130.1(1)
P(1)-OL12-P(2)		135.2(1)	P(4)-OL45-P(5)	133.8(1)
P(2)-OL23-P(3)		131.1(1)	P(5)-OL56-P(6)	133.0(1)

[a]Estimated standard deviations are given in parentheses.

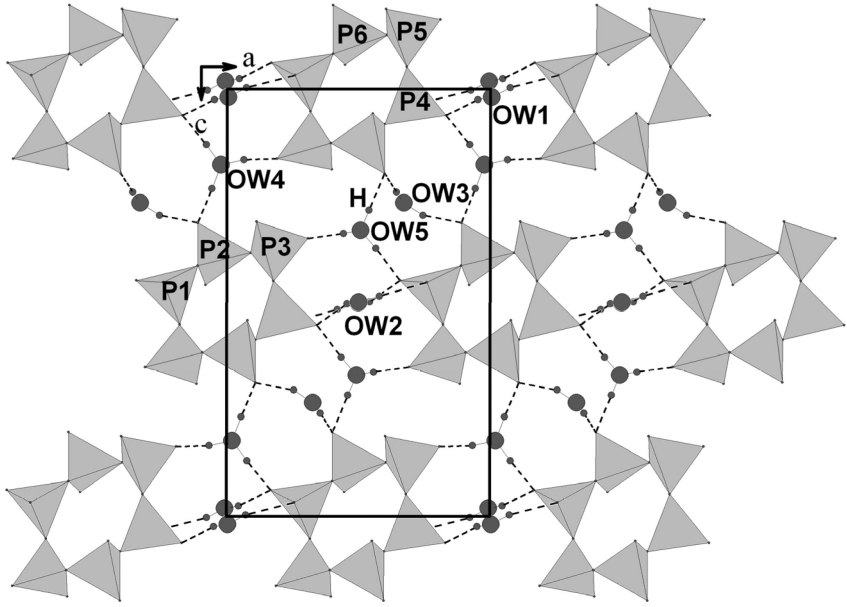

FIGURE 2 Projection of the inorganic framework in the structure of $(C_{10}H_{13}NH_3)_4(H_3O)_2(P_6O_{18}).3(H_2O)$ along the b-axis, showing the hydrogen bonding interactions.

(Table I). As illustrated in Figure 2, both independent rings P_6O_{18} are interconnected through O(W)-H...O(E) H-bonds originating from the oxonium groups and the water molecules, giving rise to anionic layers of formula $[(P_6O_{18})(H_3O)_2(H_2O)_3]^{3-}$ staked along the [010] direction. Inside each layer, the two crystallographically independent H_3O^+ ions exhibit a pyramidal configuration. The medium sum (332°) of the H-O-H angles of the H_3O^+ pyramid of the compound is comparable to the value (330°) reported for H_3O^+ in other crystals.[6] The H_3O^+ oxonium ion has strong hydrogen bonds with the external oxygen atoms of three P_6O_{18} rings. The O...H distances and O-H...O angles spread in the range from 1.39 to 1.64 Å and from 168.00 to179.00°, respectively (Table II). These distances are shorter than the normal O-H...O hydrogen bonds indicating that the $O\text{-}H^{\delta}\ldots O^{\delta}$ hydrogen bonds are stronger than those between neutral oxygen atoms.

Four independent 2,6-diethylphenylammonium cations are identified in this atomic arrangement. They are located between the successive inorganic layers to compensate their negative charges (Figure 3). The four phenyl rings of these cations are nearly planar, with an average rms deviation of 0.007 Å. These organic entities participate with water

TABLE II Hydrogen–Bond Scheme in $(C_{10}H_{13}NH_3)_4(H_3O)_2(P_6O_{18}).3(H_2O)$[a]

D-H...A	D-H(Å)	H...A(Å)	D...A(Å)	D-H...A(°)
N1-H1A...OE12	0.8900	2.0700	2.943(3)	168.00
N1-H1B...OE31	0.8900	2.1000	2.910(3)	151.00
N1-H1C...OE21	0.8900	1.7700	2.656(3)	170.00
N2-H2A...OL56	0.8900	2.5200	3.301(4)	146.00
N2-H2B...OW1	0.8900	1.8800	2.724(4)	157.00
N2-H2C...OE12	0.8900	1.9100	2.788(3)	167.00
N3-H3A...OW3	0.8900	1.8800	2.768(4)	172.00
N3-H3B...OE11	0.8900	2.4600	3.034(4)	123.00
N3-H3B...OE52	0.8900	2.4100	2.970(3)	121.00
N3-H3C...OW2	0.8900	1.8200	2.702(4)	173.00
N4-H4A...OE61	0.8900	1.8600	2.740(3)	167.00
N4-H4B...OE42	0.8900	2.0500	2.850(3)	149.00
N4-H4C...OE52	0.8900	1.9600	2.839(3)	167.00
OW1-H120...OE42	0.8900	2.0100	2.840(3)	156.00
OW1-H220...OE41	0.8900	1.9200	2.765(3)	156.00
OW2-H121...OE22	1.0000	1.7300	2.713(3)	167.00
OW2-H221...OL46	0.8900	2.5900	3.304(3)	139.00
OW2-H221...OE62	0.8900	2.0100	2.848(3)	157.00
OW3-H123...OE32	0.9300	1.9600	2.871(3)	164.00
OW3-H223...OE31	0.8800	2.0400	2.903(3)	167.00
OW4-H119...OE41	1.0200	1.5500	2.564(3)	177.00
OW4-H219...OE51	1.0800	1.3900	2.452(3)	168.00
OW4-H319...OE22	1.0500	1.4700	2.513(3)	172.00
OW5-H122...OE22	0.9500	1.6000	2.547(3)	174.00
OW5-H222...OE62	0.9000	1.6300	2.526(3)	179.00
OW5-H322...OE11	0.8500	1.6400	2.489(3)	171.00
C7-H7B...OE12	0.9700	2.5400	3.408(5)	148.00
C9-H9B...OE31	0.9700	2.5500	3.297(6)	134.00
C27-H27A...OW2	0.9700	2.5300	3.317(6)	138.00
C29-H29B...OE52	0.9700	2.5200	3.351(4)	143.00
C37-H37B...OE61	0.9700	2.5300	3.445(5)	157.00
C39-H39B...OE42	0.9700	2.4600	3.271(6)	141.00

[a]Estimated standard deviations are given in parentheses.

molecules to the formation of H-bonds N-H...O and O-H...O, which connect the different entities of the $(C_{10}H_{13}NH_3)_4(H_3O)_2(P_6O_{18}).3(H_2O)$ structure. In addition, some H-phenyl atoms form weak C-H...O interactions with a H...O separation of 2.44 to 2.54 Å.

Thermal Analysis

Combined TGA-DTA curves of the title compound are shown in Figure 4. The strong endothermic peak around 84°C is due to the loss of hydration

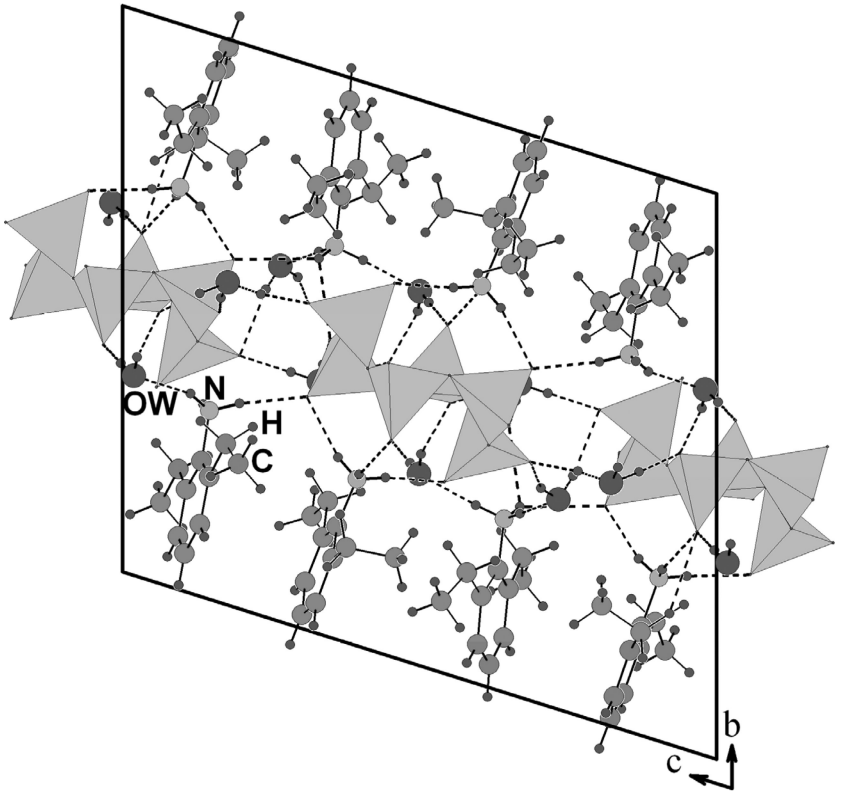

FIGURE 3 Projection of the structure of $(C_{10}H_{13}NH_3)_4(H_3O)_2(P_6O_{18}).3(H_2O)$, along the a axis. The P_6O_{18} ring is given in a tetrahedral representation. Other atoms are indicated by their symbols. Hydrogen bonds are indicated by dotted lines.

water molecules. The calculated weight loss for this process is 7.38°/°, and the observed weight loss is 7.72°/°. After 150°C, a significant weight loss is observed for a series of weak ATD peaks. This can be interpreted by a decomposition of P_6O_{18} ring and combustion of the organic groups, which give a viscous matter of polyphosphoric acids with a black residue of carbon.

IR Spectroscopy

The IR spectrum of the crystallized $(C_{10}H_{13}NH_3)_4(H_3O)_2(P_6O_{18}).3H_2O$ is shown in Figure 5. In this spectrum, we identify the main characteristic bands of the cyclohexaphosphate anion. Some characteristic bands

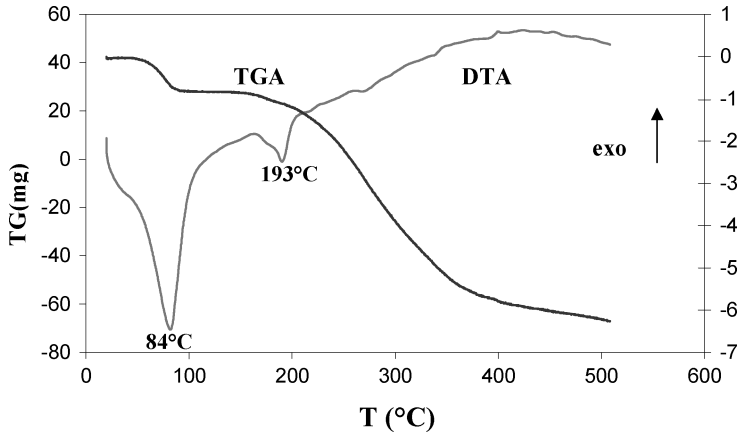

FIGURE 4 DTA and TGA thermograms of the title compound at rising temperature.

of the organic molecule could be assigned, too. Their performed assignments are as follows.

- The strong bands observed in the ranges 1350–1180, 1180–1060, 1060–960, and 850–660 cm^{-1} can be assigned to stretching vibrations ν_{as}(OPO), ν_{s}(OPO), ν_{as}(POP), and ν_{s}(POP), respectively. [7] Nevertheless, special caution must be paid in attribution of these bands

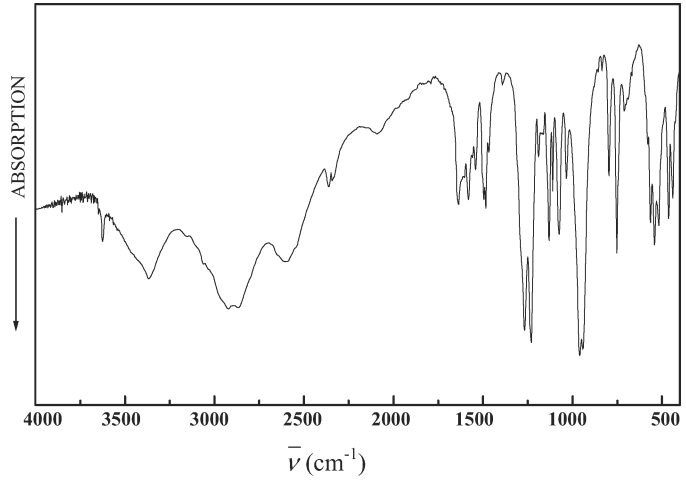

FIGURE 5 IR spectrum of $(C_{10}H_{13}NH_3)_4(H_3O)_2(P_6O_{18}).3(H_2O)$ in KBr pellet.

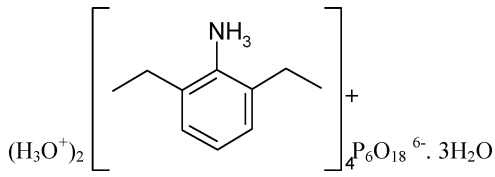

FIGURE 6 Schematic formulation of $(C_{10}H_{13}NH_3)_4(H_3O)_2(P_6O_{18}).3(H_2O)$.

because of their overlapping with ν(C-N) stretching vibration and δ(C-H) bending vibrations bands. We note that the supplementary frequency in the ν_s(OPO) domain can be assigned to the stretching ν(C-C) vibrations.[8]

- Frequencies below 660 cm^{-1} can be assigned to bending vibrations of P_6O_{18} ring, and those in the range of 4000–1350 cm^{-1} are attributed to O(N,C)-H stretching and bending modes.

EXPERIMENTAL

Synthesis of $(C_{10}H_{13}NH_3)_4(H_3O)_2(P_6O_{18}).3(H_2O)$

The title compound was prepared by an acid/base reaction in two steps. In the first one, an aqueous solution of cyclohexaphosphoric acid was obtained from $Li_6P_6O_{18}.6H_2O$ [9] (5 g, 8 mmol in 100 mL of water) protonated with an ion exchange resin in its H-state (Amberlite IR 120). In the second step, an ethanolic solution of the $C_{10}H_{13}NH_2$ (5.25 mL, 32 mmol) was added dropwise to a solution of $H_6P_6O_{18}$, with continuous stirring. When the resulting solution changes aspect, it is slowly evaporated at room temperature until the formation of colourless and transparent crystals (3 g, yield: 24.68%) of $(C_{10}H_{13}NH_3)_4(H_3O)_2(P_6O_{18}).3(H_2O)$ (Figure 6).

Investigation Techniques

X-Ray Diffraction

Crystal data and experimental parameters used during the measurement are reported in Table III. The crystal structure solution carried out with direct methods from SHELXS-97.[10] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the organic 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 648791.

TABLE III Crystal Data, Intensity Measurements, and Structure Determination of $(C_{10}H_{13}NH_3)_4(H_3O)_2(P_6O_{18}).3(H_2O)$

Empirical Formula	$(C_{10}H_{13}NH_3)_4(H_3O)_2(P_6O_{18}).3(H_2O)$
Formula weight	1166.87 (g mol^{-1})
Crystal system	triclinic
Space group	P-1
a	10.43(2) (Å)
b	16.09(3) (Å)
c	17.67(2) (Å)
α	72.44(3)°
β	88.64(2)°
β	85.11(3)°
Z	2
V	2818.0(8) ($Å^3$)
ρ calc(g/cm^3)	1.375
F(0 0 0)	1236
μ(MoKα)	0.269 (mm^{-1})
Size (mm)	0.15 * 0.20 * 0.35
Index ranges	$-12 \leq h \leq 12$; $-19 \leq k \leq 18$; $-20 \leq l \leq 0$
Independent reflections	9876
Refined parameters	667
Goodness-of-fit	1.019
R (anisotropic) ($I > 2\sigma(I)$)	0.049
Rw (anisotropic)	0.126

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.

IR spectrum was recorded in the range 4000–4400 $cm^{-1}$with a "Perkin-Elmer Spectrum 1000" spectrophotometer using a sample dispersed in spectroscopically pure KBr pellet.

CONCLUSION

In conclusion, we have prepared and characterized by X-ray diffraction, thermal behaviour and IR analysis a novel solid state material with formula $(C_{10}H_{13}NH_3)_4(H_3O)_2(P_6O_{18}).3(H_2O)$. The compound is the first example of a structure that combines oxonium groups and cyclohexaphosphate anions. The packing of this hybrid compound shows strong and moderate interlocking between the inorganic and the organic entities by a multidirectional hydrogen-bonding network. Such interactions are known to exist in many systems of biological importance.

We think it is possible to synthesize other oxonium cyclohexaphosphates, under appropriate conditions. Further experiments should determine the influence of the main reaction parameters (temperature, pH, and concentration) in the synthesis of new oxonium cyclohexaphosphates.

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