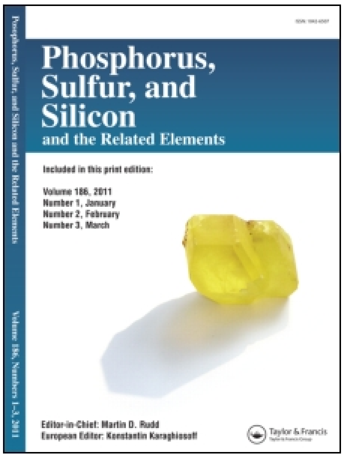

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Synthesis and Structural Characterization of a Novel Cyclotetraphosphate

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Synthesis and Structural Characterization of a Novel Cyclotetraphosphate

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The crystal structure of $(2\text{-}NH_2\text{-}5\text{-}ClC_5H_4N)_4P_4O_{12}.6H_2O$ *was determined by X-ray diffraction on a single crystal. This compound crystallizes in an orthorhombic unit cell Pccn with the parameters* $a = 25{,}387(7)$ Å, $b = 15{,}756(6)$ Å, $c = 9{,}750(5)$ Å, $V = 3900(2)$ Å^3, $Z = 4$, *and* $D_x = 1{,}605\ g.cm^{-3}$. *Crystal structure has been determined and refined to* $R = 0{,}036$, *using 7678 independent reflexions. This structure can be described as inorganic layers stacked along a-direction and held together through N-H... O hydrogen bonds, originating from the organic cations, giving rise to three-dimensional H-bonded assemblies. In addition, in this structure there is electrostatic, van der Waal forces and Cl... Cl interaction so as to increase the cohesion of 3D-network. Chemical preparation and characterization by RX diffraction, IR absorption, and thermal analysis are described.*

Keywords Crystal structure; cyclotetraphosphate; hydrogen bonds; infrared spectroscopy; thermal analysis

INTRODUCTION

Compounds combining organic and inorganic molecules are interesting materials because of their important supramolecular networks and their particular structural features. The supramolecular network becomes especially interesting when the cation and anion can participate in hydrogen bonding. In this regard, several studies have been done concerning organic salts of carboxylic acids and amines.[1] As a contribution to the elaboration of this kind of material, we report in this article a part of a new inorganic–organic compound, which associates the cyclotetraphosphate anion to the 2-amino-5-chloropyridinium cation. Its chemical preparation, crystal structure, and characterization by IR spectroscopy and thermal analysis are reported.

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RESULTS AND DISCUSSION

Crystal Structure

The molecular structure contains one $(P_4O_{12})^{4-}$ ring anion and two crystallographically independent organic entities. The P_4O_{12} involved in this structure is centrosymmetrical; it is built up by only to independent tetrahedra $P(1)O_4$ and $P(2)O_4$. The geometrical feature of the phosphoric anion (P-O and O-O distances and O-P-O, P-O-P and P-P-P angles), gathered in Table I, are in agreement with those observed in condensed phosphoric anions. Nevertheless, 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} in this structure presents the strongest distortion. Indeed, the angle values of the square formed by the four phosphorus atoms are 80.17(2)° and 99.83(2)°. Until now, the greatest distortion of P_4O_{12} has been observed in the structure of $C_{10}H_{28}N_4P_4O_{12}.4H_2O$.[2]

As shown in Figure 1, the complete atomic arrangement and the inorganic entities have a layered organization. Figure 2 represents a projection of a layer located in the (b, c) plane. It shows ribbons of alternating P_4O_{12} and water molecules OW3 running along the c-direction. These ribbons are linked together via chains of water molecules (OW1 and OW2) through OW-H…O, $d_{OW\ldots O}$ spreading from 2.740(3) to 2.807(4) Å, forming thereby a corrugated layer of

TABLE I Main Interatomic Distances (Å) and Bond Angles (°) in $P_4O_{12}^{4-}$ Anion of $(2\text{-}NH_2\text{-}5\text{-}ClC_5H_4N)_4P_4O_{12}.6H_2O$

	$P(1)O_4$ tetrahedron			
P(1)	O(E11)	O(E12)	O(L12)	O(L21)
O(E11)	1.479(2)	2.551(2)	2.465(3)	2.527(2)
O(E12)	119.57(10)	1.473(2)	2.536(2)	2.461(2)
O(L12)	106.07(9)	110.86(10)	1.605(2)	2.463(2)
O(L21)	110.10(9)	106.19(9)	105.29(6)	1.603(2)
	$P(2)O_4$ tetrahedron			
P(2)	O(E21)	O(E22)	O(L12)	O(L21)
O(E21)	1.474(2)	2.559(2)	2.538(2)	2.541(2)
O(E22)	120.08(9)	1.479(2)	2.475(2)	2.472(2)
O(L12)	110.70(9)	106.47(10)	1.609(2)	2.508(2)
O(L21)	111.13(8)	106.46(9)	100.03(9)	1.605(2)
P(1)–P(2)	2.9136(10)	P(2)–P(1)	2.919(2)	
P(2)–P(1)–P(2)	80.17(2)	P(1)–P(2)–P(1)	99.83(2)	
P(1)–O(L12)–P(2)	130.54(10)	P(2)–O(L21)–P(1)	130.50(10)	

Estimated standard deviations are given in parentheses. The underlined digits in the table are the bond lengths P-O.

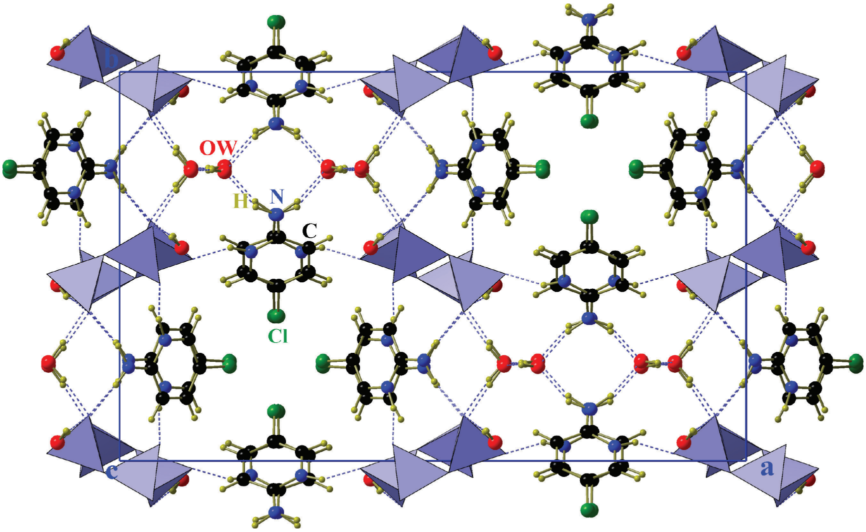


FIGURE 1 Projection along the a-axis of $(2\text{-}NH_2\text{-}5\text{-}ClC_5H_4N)_4P_4O_{12}.6H_2O$ structure. The phosphoric anions are given in tetrahedral representation. The other atoms are labeled in the figure. Hydrogen bonds are denoted by dotted lines.

composition $[P_4O_{12}(H_2O)_6]_n{}^{4n-}$. The different layers, stacked along the *a*-direction are held together through N-H. . . O hydrogen bonds, with distances $d_{N...O}$ ranging from 2.654(2) to 2.896(3) Å, originating from the organic cations, giving rise to three-dimensional H-bonded assembly.

Main bond lengths and angles of the organic cation are presented in Table II. The average of C-N distances in pyridine ring is 1.340 Å and C-C is 1.380 Å. These values are comparable to those observed in substituted-pyridine.[3] The C-N-C angle of pyridine is very sensitive to protonation. In comparison with other methyl-aminopyridine salts,[4,5] the complete protonation of the heterocycle in both organic cations is indicated by the enlarged angles of C1-N1-C5 (123.2(2)°) and C10-N4-C6 (123.4(2)°) and the reduced angles of N1-C1-C2 (117.7(2)°) and N4-C7-C6 (116.9(2)°). The two bond lengths Cl(1)-C4 (1,732(3) Å) and Cl(2)-C(9) (1,725(3) Å) are within the range of values reported in the bibliography.[6] The two independent organic entities display an almost coplanar configuration with mean deviations of ±0.0032 and ±0.0046 Å.

It seems that a structural comparison of the title compound $[2\text{-}NH_2\text{-}5\text{-}ClC_5H_4N]_4P_4O_{12}.6H_2O$ (I) to $[2\text{-}NH_2\text{-}5\text{-}CH_3C_5H_4N]_4P_4O_{12}.6H_2O$ (II)[7] appears appropriate, because these two compounds differ only from the nature of the substituent on the pyridine ring.

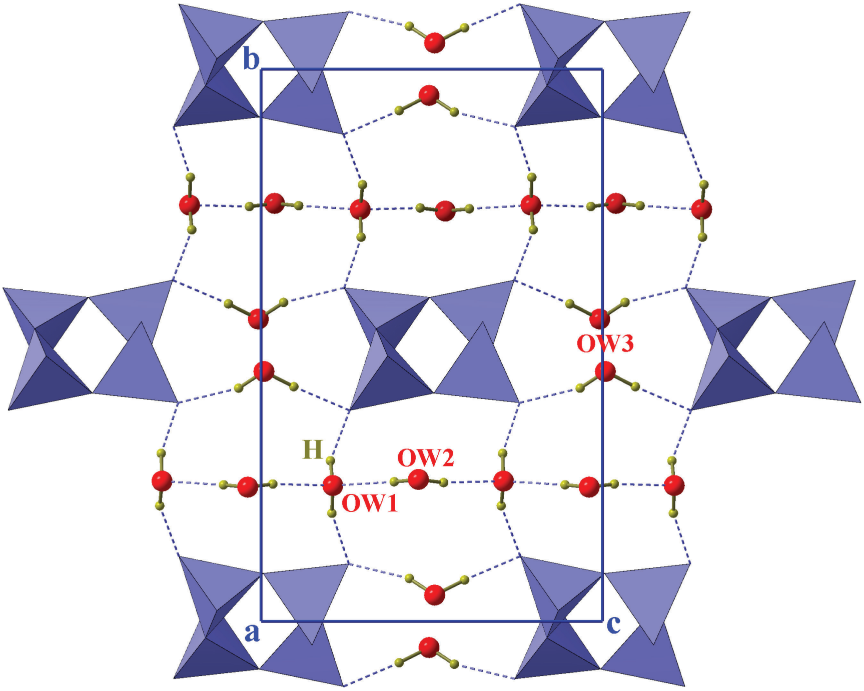
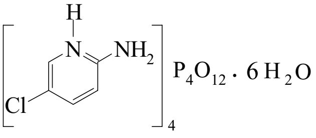


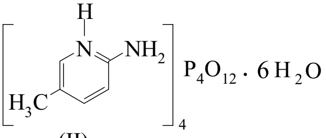
FIGURE 2 A projection of the $[P_4O_{12}(H_2O)_6]_n$ layer located in the (b, c) plane.

TABLE II Main Interatomic Distances (Å) and Bond Angles (°) in Organic Groups of $(2\text{-}NH_2\text{-}5\text{-}ClC_5H_4N)_4P_4O_{12}.6H_2O$

		$[2\text{-}NH_2\text{-}5\text{-}ClC_5H_4N(1)]^+$			
N1–C1	1.343(3)	C1–C2	1.408(3)	C4–C5	1.353(3)
N1–C5	1.356(3)	C2–C3	1.359(4)	C4–Cl1	1.732(3)
N2–C1	1.325(3)	C3–C4	1.400(3)		
C1–C2–C3	120.3(2)	C1–N1–C5	123.2(2)	C2– C1–N2	123.3(2)
C2–C3–C4	119.4(2)	N1–C1–C2	117.7(2)	Cl1–C4–C3	120.7(2)
C3–C4–C5	119.9(2)	N1–C1 –N2	119.0(2)	Cl1–C4–C5	119.4(2)
N1– C5–C4	119.5(2)				
		$[2\text{-}NH_2\text{-}5\text{-}ClC_5H_4N(2)]^+$			
N3–C6	1.323(3)	C6–C7	1.412(3)	C9–C10	1.350(3)
N4–C6	1.352(3)	C7–C8	1.359(4)	C9–Cl2	1.725(3)
N4–C10	1.342(3)	C8–C9	1.402(3)		
C6–C7–C8	120.4(2)	C10–N4– C6	123.4(2)	C7–C6–N3	123.3(3)
C7–C8–C9	119.8(2)	N4–C6–C7	116.9(2)	Cl2–C9–C8	120.2(2)
C8–C9–C10	119.0(2)	N4–C6–N3	119.8(2)	Cl2–C9–C10	120.8(2)
C9–C10–N4	120.5(2)				

Estimated standard deviations are given in parentheses.


(I)


(II)

The chloro-containing compound (I) exhibits different engagements in intermolecular connection (OW-H ... OW, OW-H... OE and N-H... O), which are more complex than in (II). Thus, leading two crystallographically independent organic cations are arranged in different directions as shown by the dihedral angle (112.7°) formed between them (Figure 3). These entities have a double role in the structure. One of them $[2\text{-}NH_2\text{-}5\text{-}ClC_5H_4N(1)]^+$ interconnects two adjacent ring anions belonging to the same layer to increase the stability of the intralayer and making them undulate. The second one $[2\text{-}NH_2\text{-}5\text{-}ClC_5H_4N(2)]^+$ joins the layers through N-H... O hydrogen bonds to give a three-dimensional network. In addition, in this structure there is Cl... Cl

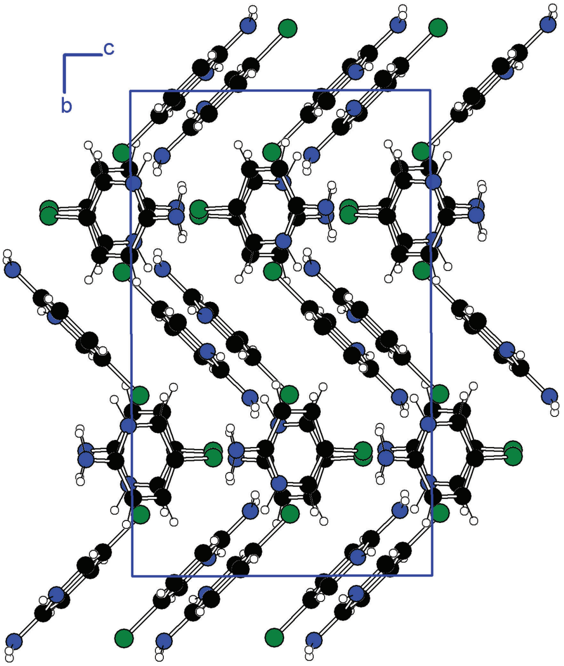


FIGURE 3 The organic cations arrangement of $(2\text{-}NH_2\text{-}5\text{-}ClC_5H_4N)_4P_4O_{12}\cdot 6H_2O$.

interaction,[8] with distances $d_{Cl...Cl}$ spreading from 3,588 to 3,870 Å, in order to increase the cohesion of the three-dimensional network. These repartitions as well as orientation of these organic groups are quite different from methyl-containing compound (II). Furthermore, the independent organic groups in (II) are arranged in almost parallel sets and form between them a dihedral angle in the vicinity of 12.71°. They link adjacent layers of $[P_4O_{12}(H_2O)_6]_n^{4n-}$ through $-NH_2$ groups performing a three-dimensional network.

We can also note that the packing (I) yielded the relatively highest symmetry if compared to (II). Thus, (I) is orthorhombic (Pccn), whereas the methyl-containing molecule (II) has a triclinic symmetry ($P\bar{1}$). These observations demonstrate that the hal…hal interactions in competition with hydrogen bonds play an important role in the crystal structure. These results allow us to conclude that the structure of organic cyclotetraphosphates is highly influenced by the nature of the substituents on the pyridine ring.

Thermal Analysis

The simultaneously recorded differential thermal analysis and thermogravimetric analysis curves of the title compound are given in Figure 4. The DTA curve shows that the cyclotetraphosphate hexahydrate undergoes a complete dehydration at 365 K, as is well confirmed by the weight loss observed on TGA curve (% water experimental 11.46, calculated 11.31). The second endothermic peak at 403 K, without weight loss on the TGA curve, corresponds to the melting of the anhydrous phosphate. The melted compound undergoes decomposition in a wide temperature range of 428–730 K. This phenomenon corresponds to the several DTA peaks and the significant weight loss clearly observed on TGA curve. After this decomposition, a viscous substance of polyphosphoric acids contaminated with a carbon black is obtained.

IR Spectroscopy

IR spectrum of this compound (Figure 5) has been recorded in the frequency range of 450–4000 cm^{-1}. All bands were assigned according to the literature.[9]

The strong bands appearing in the regions 1350–1220, 1150–1100, 1080–980, and 750–680 cm^{-1} originate from symmetric and asymmetric vibrations ν_{as}(OPO), ν_s(OPO), ν_{as}(POP), and ν_s(POP), respectively. Nevertheless, it is necessary to take precautions in the assignment of these bands because of their possible overlapping with ν(C-C) and

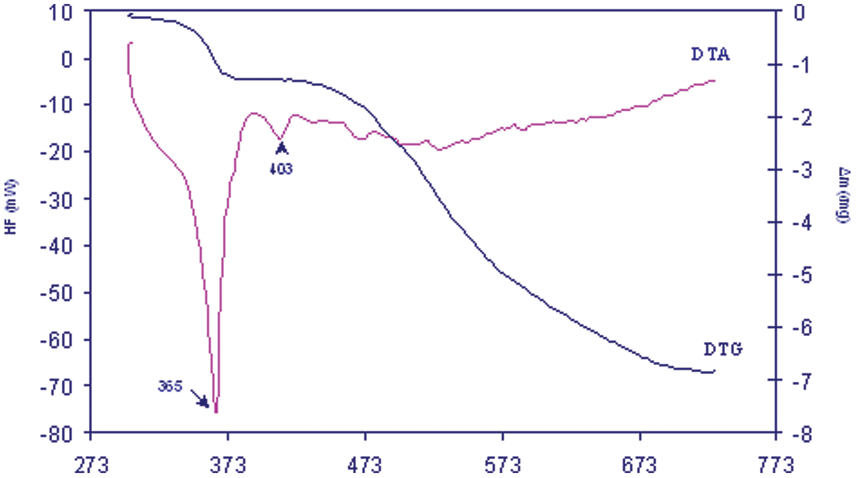


FIGURE 4 DTA and TGA thermograms of the title compound at rising temperature.

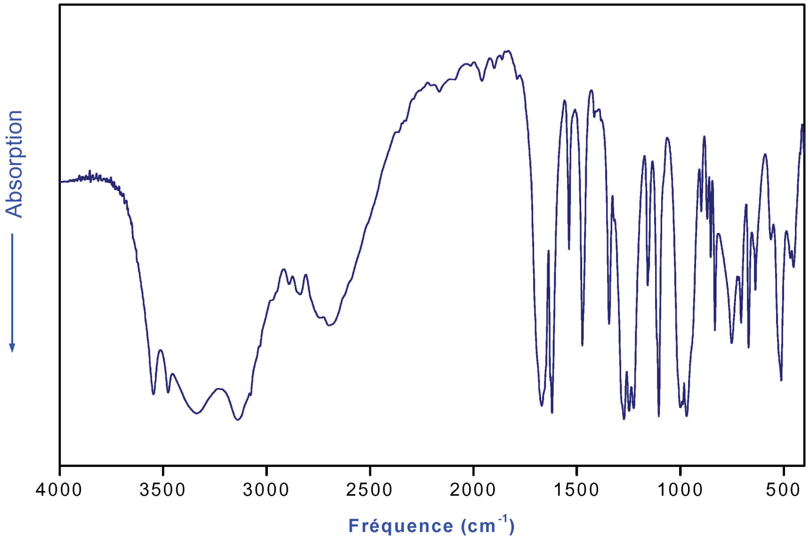


FIGURE 5 IR spectrum of (2-NH_2-5-$ClC_5H_4N)_4P_4O_{12}.6H_2O$ in KBr pellets.

ν_s(C-N). The two vibration bands observed at 705 and 751 cm^{-1} are the most characteristic feature of cyclotetraphosphate spectra and indicate the local symmetry C_i of P_4O_{12} as confirmed by X-rays results. Bands below 600 cm^{-1} correspond to the bending of the P_4O_{12} ring. For the

TABLE III Main Interatomic Distances (Å) and Bond Angles (°) in the Hydrogen of $(2\text{-}NH_2\text{-}5\text{-}ClC_5H_4N)_4P_4O_{12}.6H_2O$

D–H...A	D–H(Å)	H...A(Å)	D...A(Å)	D–H...A(°)
O(W1)–H(1W1)...O(E22)	0.99	1.80	2.757(3)	162.8
O(W1)–H(2W1)...O(E11)	0.93	1.85	2.740(3)	158.2
O(W2)–H(1W2)...O(W1)	0.96	1.89	2.807(4)	157.9
O(W2)–H(2W2)...O(W1)	0.88	1.91	2.785(3)	168.7
O(W3)–H(1W3)...O(E22)	0.94	1.96	2.864(3)	161.7
O(W3)–H(2W3)...O(E11)	1.04	1.93	2.971(3)	175.2
N(1)–H(N1)...O(E21)	0.99	1.72	2.688(3)	164.1
N(2)–H(1N2)...O(E22)	0.90	2.00	2.889(3)	170.5
N(2)–H(2N2)...O(E11)	0.98	1.93	2.876(3)	163.7
N(3)–H(1N3)...O(W2)	0.97	1.95	2.896(3)	163.8
N(3)–H(2N3)...O(W2)	0.96	1.96	2.833(3)	150.8
N(4)–H(N4)...O(E12)	0.95	1.76	2.654(2)	154.8
H(1W1)–O(W1)–H(2W1)			102.5	
H(1W2)–O(W2)–H(2W2)			100.3	
H(1W3)–O(W3)–H(2W3)			105.8	

organic cations, the stretching vibration of OH, NH_3, and CH_2 have the highest energy, between 3400–2800 cm^{-1}, wile the OH-bending vibrations and stretching vibrations C-C and C-N of the pyridine ring appear in the range of 1650–1400 cm^{-1}. Frequencies in the 900–675 cm^{-1} range are related to $\delta(C_{ar}\text{-}H)$ out plan and stretching $\nu(C\text{-}Cl)$ modes.

EXPERIMENTAL PART

Synthesis of $(2\text{-}NH_2\text{-}5\text{-}ClC_5H_4N)_4P_4O_{12}.6H_2O$

Single crystals of $(2\text{-}NH_2\text{-}5\text{-}ClC_5H_4N)_4P_4O_{12}.6H_2O$ have been prepared by slowly adding cyclotetraphosphoric acid (4.1 mmol) to an ethanolic solution of 2-amino-5-chloropyridine (2.1 g, 16.4 mmol in 5 mL of ethanol). This acid is freshly prepared by adding a stoichiometric amount of phosphorus pentoxyde (2 g, 16.4 mmol) to ice water.

Shematically, produced reactions are as follows:

$$P_4O_{10} + 2H_2O \rightarrow H_4P_4O_{12} \text{ and}$$

$$4(2\text{-}NH\text{-}5\text{-}ClC_5H_4N) + H_4P_4O_{12} + 6H_2O \rightarrow (2\text{-}NH_2\text{-}5\text{-}ClC_5H_4N)_4P_4O_{12}.6H_2O$$

After some days of evaporation at room temperature, prismatic crystal appears in the remaining solution with suitable dimension for a

TABLE IV Crystal Data, Intensity Measurements, and Structure Determination of $(2\text{-}NH_2\text{-}5\text{-}ClC_5H_4N)_4P_4O_{12}.6H_2O$

Empirical Formula	$(2\text{-}NH_2\text{-}5\text{-}ClC_5H_4N)_4P_4O_{12}.6H_2O$
Formula weight	942.25 (g. mol^{-1})
Crystal system	orthorhombic
Space group	Pccn
a	25.387(7) (Å)
b	15.756(6) (Å)
c	9.750(5) (Å)
Z	4
V	3900(2) (Å^3)
ρ_{calc} (g/cm^3)	1.605
F(0 0 0)	1936
μ(AgK$\bar{\alpha}$)	2.852 (mm^{-1})
Size (mm)	0.50 × 0.35 × 0.20
Index ranges	$-38 \leq h \leq 38$; $-23 \leq k \leq 23$; $-14 \leq l \leq 0$
independent reflections	7678
refined parameters	244
Goodness-of-fit	1.700
R (anisotropic) ($I > 2\sigma(I)$)	0.036
Rw (anisotropic)	0.038

crystallographic study. These crystals are stable in air under normal conditions of temperature and hygrometry.

Investigation Techniques

X-ray diffraction

Crystal data and experimental parameters used during the measurement are reported in Table IV. The structure was solved using the direct methods and refined by a full-matrix least squares technique.[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 671874.

Physical measurements

Thermal analysis was performed using the "multimodule 92 Setaram analyzer" operating from room temperature up to 773 K at an average heating rate of 5K/min.

IR spectrum was recorded in the range 4000-400 cm^{-1} with a "Perkin-Elmer Spectrum 1000" spectrophotometer using a sample dispersed in spectroscopically pure KBr pellets.

CONCLUSION

In conclusion, we have prepared and characterized by X-ray diffraction, thermal behaviour and IR analysis a novel solid state material with formula $(2\text{-NH}_2\text{-5-ClC}_5\text{H}_4\text{N})_4\text{P}_4\text{O}_{12}.6\text{H}_2\text{O}$. The present study shows that it is profitable to investigate the structures of organic condensed phosphate, not only because of novel structure feature, but also because of the novel robust hydrogen bonded network and hal. . . hal interactions exhibited by this title compound which may give rise to interesting properties.

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