

Synthesis and Characterization of a New Organic Cyclohexaphosphate: $[\text{NH}_3\text{-(CH}_2)_2\text{-NH}_2\text{-(CH}_2)_2\text{-NH}_3]_2\text{P}_6\text{O}_{18}\cdot 3\text{H}_2\text{O}$

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Abstract

Single crystals of the new cyclohexaphosphate $[\text{C}_4\text{H}_{16}\text{N}_3]_2\text{P}_6\text{O}_{18}\cdot 3\text{H}_2\text{O}$ were synthesized in aqueous solution. This compound crystallizes in a $P\bar{1}$ triclinic unit cell with the following parameters: $a = 8.416(5)$, $b = 10.1117(12)$, $c = 17.531(2)$ Å, $\alpha = 75.04(3)$, $\beta = 77.905(14)$, $\gamma = 89.53(5)^\circ$, $V = 1407.7(9)$ Å³ and $Z = 2$. Crystal structure has been determined by X-ray diffraction and refined to $R = 0.065$ using 8477 independent reflections. Atomic arrangement can be described by thick layers built by $\text{P}_6\text{O}_{18}^{6-}$ anions and water molecules. The organic entities are anchored between these layers through multiple H-bonds which connect the different species giving rise to a three-dimensional network.

Keywords: chemical preparation; crystal structure; infrared spectroscopy; thermal analysis

1. Introduction

The development of condensed phosphate materials, which have practical applications as catalysis, fertilizers, biotechnological materials and sorbents [1, 2], continues to be of primary interest in industrial and university laboratories [3]. So to benefit from these materials, it is very useful to have a good knowledge of their structural characteristics in order to understand and establish a correlation with their properties. In this work, we report synthesis, crystal structure, and characterization by IR spectroscopy and thermal analysis of the new cyclohexaphosphate of organic cation $[\text{C}_4\text{H}_{16}\text{N}_3]_2\text{P}_6\text{O}_{18}\cdot 3\text{H}_2\text{O}$.

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2. Experimental

2.1. Synthesis

Colorless plates of (I) were isolated by reacting drop wise dilute cyclohexaphosphoric acid (20 ml, 2.6 mmol) with an ethanolic solution of diethylenetriamine and *o*-anisidine in a molar ratio of 1:1 respectively and under continuous stirring, in an attempt at synthesizing a mixed organic cyclohexaphosphate. The cyclohexaphosphoric acid $\text{H}_6\text{P}_6\text{O}_{18}$, was produced from $\text{Li}_6\text{P}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$, prepared according the Schülke process [4], with an ion-exchange resin in H-state (Amberlite 120). When the diethylenetriamine used alone we obtain another cyclohexaphosphate $[\text{NH}_3\text{-(CH}_2)_2\text{-NH}_2\text{-(CH}_2)_2\text{-NH}_3]_2\text{P}_6\text{O}_{18} \cdot 2\text{H}_2\text{O}$ [5, 6].

2.2. Characterization

2.2.1 X-ray Diffraction

A single crystal was used for X-ray measurements. The intensity data collection was performed with a MACH3 Enraf-Nonius diffractometer operating at 292 K with the wavelength $\text{K}\alpha$ (Ag)=0.5608 Å. Structure was solved by direct methods using the SIR92 [7] program and refined by full matrix least-squares techniques based on F^2 with SHELXL software [8]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were constrained to calculated positions and refined using riding models. Relevant crystallographic structure data and refinement details are presented in Table 1, selected bond distances and angles in Table 2.

Table 1

Crystal data, intensity collection parameters and refinement results for $C_8H_{32}N_6, P_6O_{18}, 3H_2O$

Empirical formula	$C_8H_{32}N_6, P_6O_{18}, 3H_2O$
Formula weight ($g\ mol^{-1}$)	740.26 $g\ mol^{-1}$
Crystal system/space group	Triclinic/ $P\bar{1}$
a (Å)	8.416(5)
b (Å)	10.1117(12)
c (Å)	17.531(2)
α (deg.)	75.04(3)
β (deg.)	77.905(14)
γ (deg.)	89.53(5)
Volume (Å ³)	1407.7(9)
Z	2
Density (calc.) ($g\ cm^{-3}$)	1.746
F(000)	772
θ -Range for data collection (deg.)	2 - 28
Index ranges:	
	$-13 \leq h \leq 14, -16 \leq k \leq 16, -3 \leq l \leq 29$
Reflections collected	16194
Independent reflections	13750
Observed reflections [$I > 2\ \sigma(I)$]	8477
Data/restraints/parameters	13750/18/419
Goodness-of-fit on F^2	1.033
Final R indices [$I > 2\ \sigma(I)$]	R1=0.0653; WR2=0.1942
R indices (all data)	R1=0.1240; WR2=0.1673
Largest diff. peak and hole ($e\ \text{Å}^{-3}$)	0.54 and -0.44

Table 2Selected bond lengths (Å) and angles (°) for $P_6O_{18}^{6-}$ anion in $[C_4H_{16}N_3]_2P_6O_{18} \cdot 3H_2O$

P1-O1	1.598(12)	O3-P1-O2	119.5(8)	O14-P5-O15	118.6(9)
P1-O2	1.491(12)	O3-P1-O1	111.1(7)	O14-P5-O13	110.7(8)
P1-O3	1.466(13)	O2-P1-O1	105.4(7)	O15-P5-O13	106.4(8)
P1-O4	1.607(13)	O3-P1-O4	109.9(8)	O14-P5-O16	108.7(9)
P2-O4	1.595(12)	O2-P1-O4	108.8(7)	O15-P5-O16	109.9(8)
P2-O5	1.474(12)	O1-P1-O4	100.4(7)	O13-P5-O16	101.1(7)
P2-O6	1.488(12)	O5-P2-O6	118.6(7)	O17-P6-O18	118.9(8)
P2-O7	1.598(12)	O5-P2-O4	111.1(7)	O17-P6-O16	107.5(7)
P3-O1	1.604(12)	O6-P2-O4	106.1(7)	O18-P6-O16	109.2(7)
P3-O7	1.606(12)	O5-P2-O7	108.2(7)	O17-P6-O12	111.2(8)
P3-O8	1.472(13)	O6-P2-O7	110.9(7)	O18-P6-O12	107.9(8)
P3-O9	1.467(13)	O4-P2-O7	100.5(7)	O16-P6-O12	100.5(8)
P4-O10	1.471(14)	O9-P3-O8	120.2(8)	P1-O1-P3	132.0(8)
P4-O11	1.468(15)	O9-P3-O1	107.4(8)	P2-O4-P1	128.7(7)
P4-O12	1.609(13)	O8-P3-O1	110.7(7)	P2-O7-P3	131.8(8)
P4-O13	1.609(12)	O9-P3-O7	109.3(8)	P6-O12-P4	129.5(9)
P5-O13	1.587(13)	O8-P3-O7	106.5(7)	P5-O13-P4	135.2(8)
P5-O14	1.475(14)	O1-P3-O7	101.1(7)	P6-O16-P5	128.9(8)
P5-O15	1.487(13)	O11-P4-O10	121.2(10)	P1-P2-P3	120.4(8)
P5-O16	1.602(13)	O11-P4-O12	110.1(9)	P2-P3-P1	99.04(7)
P6-O12	1.597(13)	O10-P4-O12	105.6(8)	P3-P1-P2	110.3(8)
P6-O16	1.596(13)	O11-P4-O13	106.0(8)	P5-P4-P6	98.9(9)
P6-O17	1.480(13)	O10-P4-O13	110.8(8)	P6-P5-P4	109.1(8)
P6-O18	1.487(12)	O12-P4-O13	101.5(7)	P4-P6-P5	123.1(8)
	P1-P2	2.885(13)	P2-P3	2.924(13)	
	P1-P3	2.926(13)	P4-P5	2.955(12)	
	P5-P6	2.885(12)	P4-P6	2.900(13)	

2.2.2 Infrared Spectroscopy

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

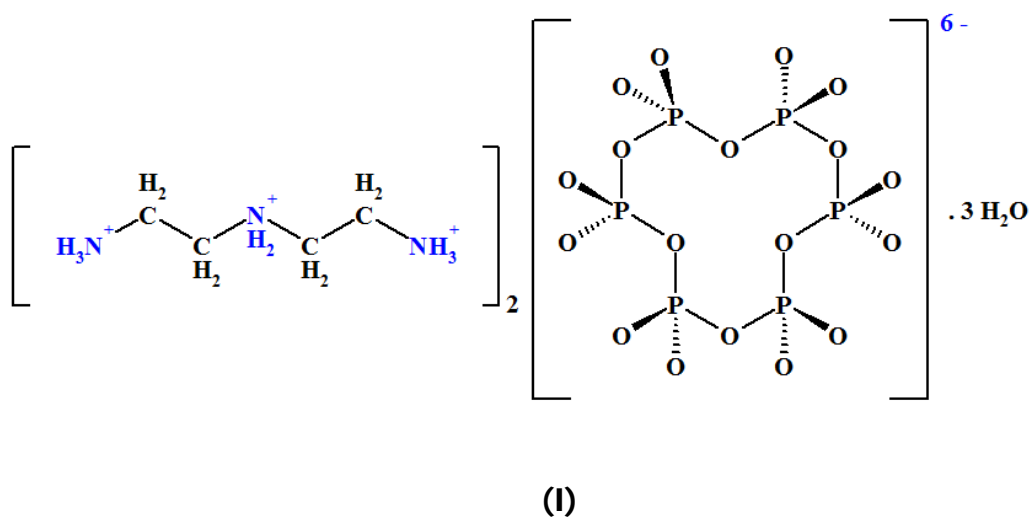
2.2.3 Thermal Analysis

Thermal Analysis was performed using the multimodule 92 Setaram analyzer operating from room temperature up to 400°C at an average heating rate of 5°C/min. The weight of the sample was 7.65 mg.

3. Results and Discussion

3.1. Structure Description

Structure of the organic cyclohexaphosphate $[\text{NH}_3\text{-(CH}_2)_2\text{-NH}_2\text{-(CH}_2)_2\text{-NH}_3]_2\text{P}_6\text{O}_{18}\cdot 3\text{H}_2\text{O}$ (**I**) consists of cyclic $\text{P}_6\text{O}_{18}^{6-}$ units, water molecules and diethylenetriammonium molecules (Fig. 1). The asymmetric unit consists of two half anions, two cations and three water molecules.



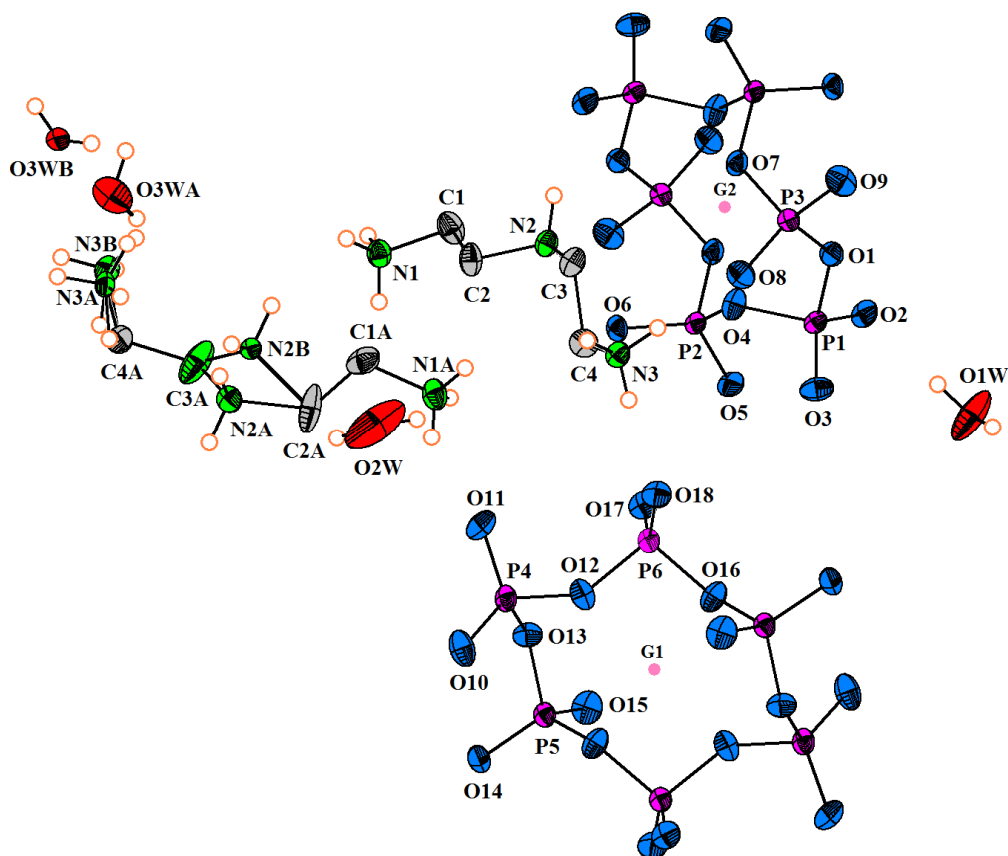


Fig. 1: Ortep view of the cyclohexaphosphoric anions and the independent organic cations of (I) with the atom-labeling scheme. P₆O₁₈ phosphoric rings are generated by inversion centers G1 and G2. Displacement ellipsoids are drawn at 40 % probability level. [Symmetry code: x, y, z].

The 3D framework is built up from parallel layers of anionic P₆O₁₈⁶⁻ rings connected via hydrogen bonds from water molecules (Fig. 2). The protonated organic cations are displayed in the interlayer spaces compensating their negative charges and participate in the Hydrogen bonding scheme with N-H...O interactions, assuring the cohesion of the network as shown in Fig. 3 and Table 3.

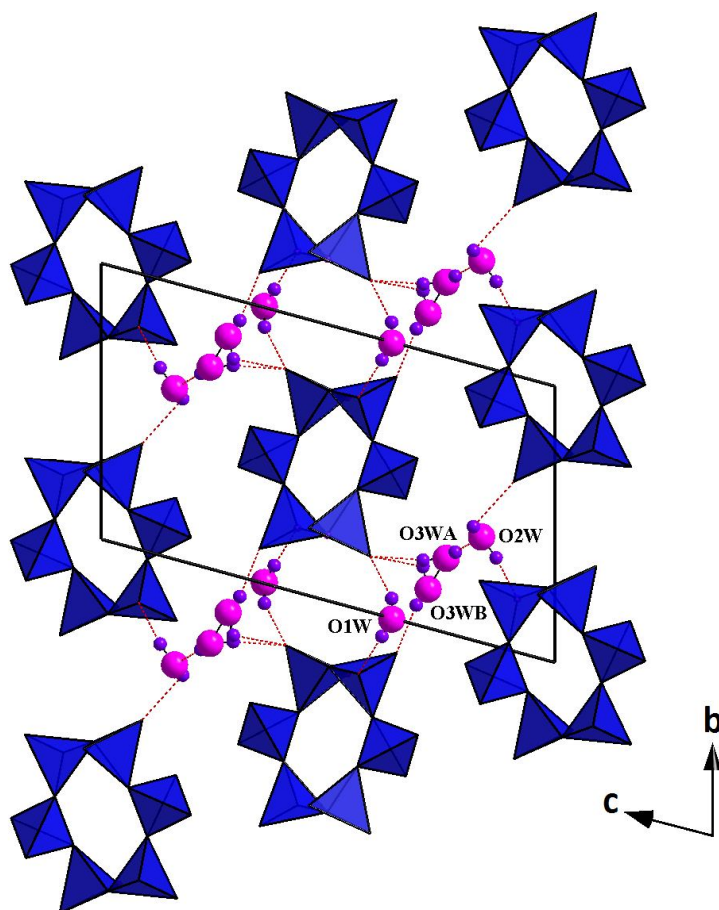


Fig. 2: Projection Along the a-axis of the atomic arrangement in $[\text{C}_4\text{H}_{16}\text{N}_{3.12}\text{P}_6\text{O}_{18} \cdot 3\text{H}_2\text{O}]$ showing Hydrogen-bond scheme connecting phosphoric rings

In this atomic arrangement, coexist two independent $\text{P}_6\text{O}_{18}^{6-}$ phosphoric rings which are located around the $(1/2, 1/2, 1/2)$ and $(1/2, 0, 0)$ inversion centers. Each one is centrosymmetric, thus it is built by only three independent PO_4^{3-} tetrahedra. Interatomic distances and bond angles in these anions are in accordance with the literature data [9, 10]. Averages of the P-O-P and P-P-P angles are 132.3° and 109.2° , respectively. These values are similar to their equivalents in some others cyclohexaphosphates [11, 12].

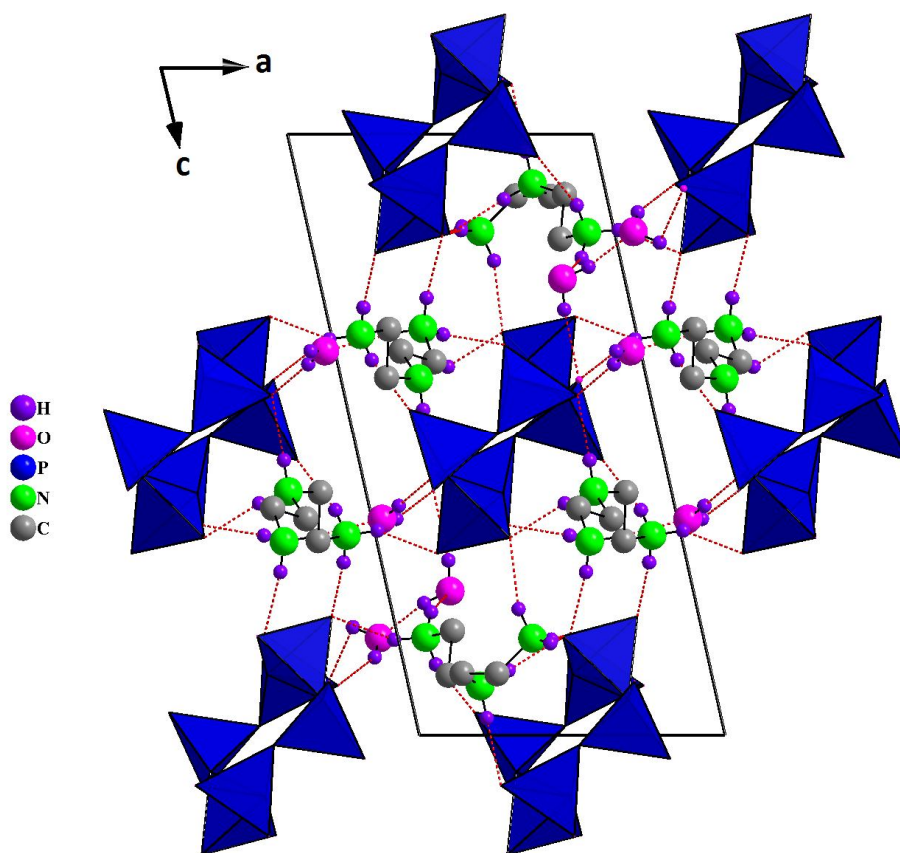


Fig. 3: Structure of $[C_4H_{16}N_3]_2P_6O_{18} \cdot 3H_2O$ Along the B-Axis Showing the Position of the Amine. Dotted Lines Represent the Various Hydrogen Bond Interactions

Nevertheless, this distortion is comparatively far from what is reported either in $Cs_6P_6O_{18} \cdot 6H_2O$ [13] or in higher phosphoric rings as in $(gua)_{10}P_{10}O_{30} \cdot 4H_2O$ [14], which shows the greatest distortion for the P-P-P angles ranging from 99.5 to 145.9°. This wide range of values can probably explain the pronounced distortion observed for the big rings compared with their smaller ring analogues.

Two independent organic groups exist in the asymmetric unit. A statistical disorder affects one molecule. In this latter, some atoms (N1, C1, C2, C3, C4) have relatively high thermal factors, while the Nitrogen atoms N2 and N3 have a static disorder, being split into two fragments, N2A, N2B and N3A, N3B respectively with various occupancy rates (0.65, 0.35, .045, 0.55) respectively.

Unlike what can be expected this disorder does not induce, as it can be supposed from interatomic bonding calculations, unusual C-C distances and C-C-C angles since they are in accordance with values observed for the same cation in others compounds [15, 16]. This kind of disorder is also observed in the related structure of $[\text{C}_6\text{H}_5\text{NH}_3]_6\text{P}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$ [17].

Examination of water molecules, involved in the structure, shows that O3W is disordered over two positions, O3WA and O3WB with occupancy rates of 0.55 and 0.45 respectively.

It should be noted that diethylenetriamine (DETA) has been involved in several anionic matrices, in particular phosphate anions such as HPO_4^{2-} [15], $\text{P}_4\text{O}_{12}^{4-}$ [16] and $\text{P}_6\text{O}_{18}^{6-}$ [5, 6]. The comparison of this structure with those published elsewhere [5, 6] shows that these structures have a similarly typical layered organization and the same protonation of the organic cations. Furthermore, they are built up by a large number of similar hydrogen bonds formed between R-NH₃ groups, H₂O molecules and phosphoric anions. In spite of these similarities, they present several differences in their crystal data, internal symmetry of the cyclohexaphosphoric anions and particularly the geometry of the phosphoric rings which shows significant distortion for the P-P-P angles and the diethylenetriammonium which has different conformations.

Table 3Hydrogen-bond geometry (Å, °) in $[C_4H_{16}N_3]_2P_6O_{18} \cdot 3H_2O$

D-H...A	D-H	H...A	D...A	D-H...A
N1-H1A...O14	0.89	1.964	2.846	170.64
N1-H1B...O3	0.89	1.920	2.754	155.49
N1-H1C...O1W	0.89	1.927	2.796	164.86
N2-II2A...O2	0.90	1.851	2.742	170.02
N2-H2B...O6	0.90	1.823	2.714	170.10
N3-H3A...O8	0.89	1.865	2.733	164.58
N3-H3B...O18	0.89	1.833	2.722	175.62
N3-II3C...O5	0.89	1.975	2.779	149.54
N1A-H1A1...O10	0.80	1.886	2.747	162.37
N1A-H1A2...O3WA	0.89	2.160	2.932	144.86
N1A-H1A3...O18	0.89	2.138	2.945	150.46
N1B-H1B1...O3WB	0.89	2.229	2.726	114.93
N1B-H1B2...O18	0.89	2.450	2.945	115.55
N1B-H1B3...O10	0.89	1.962	2.747	146.37
N2A-H2A3...O15	0.90	1.920	2.813	171.46
N2A-H2A4...O17	0.90	1.807	2.704	174.14
N2B-II2N1...O17	0.90	1.713	2.603	169.63
N2B-H2N2...O5	0.90	1.959	2.848	168.80
N3A-H3A3...O14	0.89	2.012	2.849	156.38
N3A-H3A4...O6	0.89	2.016	2.854	156.40
N3A-H3A5...O17	0.89	2.279	3.091	151.73
N3B-H3N3...O14	0.89	2.052	2.923	165.81
N3B-H3N4...O2W	0.89	2.172	3.010	156.70
N3B-H3N5...O6	0.89	2.066	2.943	168.05
O1W-H1W1...O9	0.86(6)	2.082(3)	2.807(3)	142.51(2)
O1W-II2W1...O3WB	0.86(2)	2.344(3)	3.003(3)	134.38(2)
O2W-H1W2...O15	0.86(7)	2.035(1)	2.838(2)	157.32(1)
O2W-H2W2...O11	0.86(7)	2.311(1)	2.723(2)	109.20(1)
O3WB-H1W3...O9	0.86(7)	1.848(3)	2.657(3)	158.93(2)
O3WB-H2W3...O3	0.86(7)	1.955(3)	2.768(3)	161.81(2)

3.2 IR spectroscopy

The infrared spectrum (Fig. 4) shows:

* Broad bands in the range of $3400\text{-}2900\text{ cm}^{-1}$ which are assigned to O–H stretching of water molecules as well as to NH_2 and CH_2 stretching vibrations. The broadness of the corresponding bands is indicative of the formation of hydrogen bonds of varying strengths in the structure. The observed bands in the $1680\text{-}1350\text{ cm}^{-1}$ region, were due to the bending vibrations of O–H, CH_2 and NH_2 [18, 19].

* Various stretching and bending vibration bands, observed in the range 1350-600 cm^{-1} , are characteristics of cyclohexaphosphoric anion [20]. In this type of anion, the vibrations of the O-P-O groups appear at relatively high frequencies in the 1200-1300 cm^{-1} region. Those corresponding to the P-O-P groups give rise to a broad band ν_{as} at about 960 cm^{-1} and a doublet ν_{s} between 800 and 700 cm^{-1} . Frequencies below 670 cm^{-1} are attributed to the bending, the translation and the rotation of the $\text{P}_6\text{O}_{18}^{6-}$ ring. C-C bending and NH_3 torsion may occur in this region.

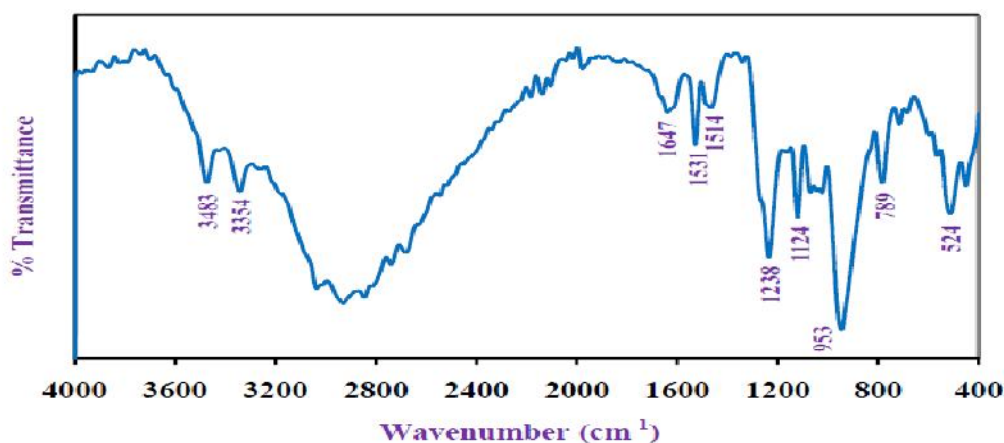


Fig. 4: IR Absorption Spectrum of $[\text{C}_4\text{H}_{16}\text{N}_3]_2\text{P}_6\text{O}_{18} \cdot 3\text{H}_2\text{O}$

3.3 Thermal Analysis

Fig.5 shows the thermal gravimetric (TG) and differential thermal analyses (DTA) of the $[\text{NH}_3\text{-(CH}_2)_2\text{-NH}_2\text{-(CH}_2)_2\text{-NH}_3]_2\text{P}_6\text{O}_{18} \cdot 3\text{H}_2\text{O}$. The DTA curve shows a broad endothermic peak at 103 °C followed by a series of endothermic peaks in a wide temperature range [125 - 400°C]. The first one corresponds to the departure of 3 water molecules, well confirmed by the weight loss observed on the TGA curve (% experimental: 7.32, % calculated: 7.29). The obtained anhydrous residual substance remains stable until 125 °C, where it begins to undergo a pyrolysis indicated by a succession of endothermic peaks accompanied by an important weight loss in a wide temperature range. The obtained viscous residue corresponds probably to a mixture of polyphosphoric acids.

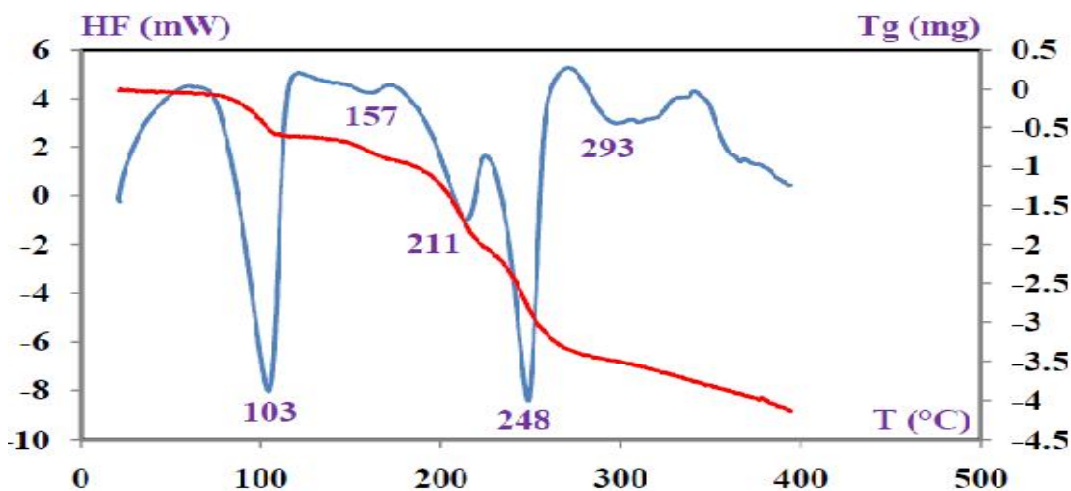


Fig. 5: DTA and TGA Curves of $[C_4H_{16}N_3]_2P_6O_{18} \cdot 3H_2O$ at the rising Temperature

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