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Synthesis, crystal structure, NMR characterization, Thermal analysis and Spectroscopic Characteristics of $[2,3\text{-}(CH_3)_2C_6H_3NH_3]_6P_6O_{18}.2H_2O$

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ABSTRACT

Single crystals of $[2,3\text{-}(CH_3)_2C_6H_3NH_3]_6P_6O_{18}.2H_2O$ were synthesized in aqueous solution. This compound crystalizes in the $P\bar{1}$ Triclinic unit cell with the parameters a = 9.97 Å, b = 16.06 Å, c =18.62 Å, $\alpha = 93.03°$, $\beta = 89.75°$, $\gamma = 93.85°$, and Z = 2. Its crystal structure, determined by X-ray diffraction, consists of inorganic layers parallel to the ***ac*** plane. The organic molecules are disposed parallel to the plane **bc** on either side of each inorganic layer on which are anchored by hydrogen bonds via their ammonium groups (N-H…O). Configuration of the asymmetric unit is characterized by FT-IR spectroscopy and solid state NMR study of ^{31}P.

Keywords:

Cyclohexaphosphate; X-ray diffraction; Crystal structure; NMR study; Thermal analysis and IR spectroscopy.

Academic Discipline And Sub-Disciplines

Materials Science

SUBJECT CLASSIFICATION

Chemistry Subject Classification

TYPE (METHOD/APPROACH)

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INTRODUCTION

The area of framework materials still develops and interest many laboratories not only because of the wide variety of structures but also due to their potential applications in different areas such as catalysis, sorption and separation processes (Mahesh *et al.*, 2002) [1]. Hybrid compounds resulting from the association of organic and inorganic species constitute an important family of these materials.

In the present work, we report synthesis, crystal structure, and characterization by IR spectroscopy, NMR and thermal analysis of the new cyclohexaphosphate of organic cation [2,3-$(CH_3)_2C_6H_3NH_3]_6P_6O_{18}.2H_2O$.

EXPERIMENTAL

Chemical preparation

Crystals of the title compound were obtained from acide-base reaction by adding dropwise an ethanolic solution (10 ml) of 2,3-dimethylaniline (18 mmol) to an aqueous solution (20 ml) of cyclohexaphosphoric acid (3 mmol). The reaction mixture was stirred at room temperature for few minutes. Crystals of the title compound appeared by slow evaporation at room temperature. The cyclohexaphosphoric acid $H_6P_6O_{18}$, was freshly produced by passing through an ion-exchange resin (Amberlite IR 120) the lithium salt $Li_6P_6O_{18}.6H_2O$, prepared from LiH_2PO_4 [2].

X-Ray diffraction

Single-crystal X-ray diffraction data were collected at 294 K by using Mach3 Enraf-Nonius diffractometer. Measurement conditions, structure solving and results are summarized in Table 1.

Table 1: Data Collection and Final Results of the Structure Determination

I. Crystal data	
Formula:	[*2,3*-$(CH_3)_2C_6H_3NH_3]_6P_6O_{18}.2H_2O$
Formula weight:	1223.94
System:	Triclinic
Space group:	$P\bar{1}$
Unit-cell parameters:	a = 9.97 Å, b = 16.06 Å, c =18.62 Å
	$\alpha = 93.03°$, $\beta = 89.75°$, $\gamma = 93.85°$
Z:	2
V ($Å^3$)	2971.6
F(000)	1290
Linear absorption factor μ(mm^{-1})	0.138
Crystal size mm^3	(0.70 x 0.40 x 0.15)
Morphology	Colorless prisms
II. Intensity measurements	
Diffractometer:	Enraf-Nonius MACH 3
Monochromator:	Graphite
Radiation:	Ag $K\bar{\alpha}$ (0.5608)
Temperature:	293 K
Density (calculated), $g.cm^{-3}$	1.368
Θ range for data collection, °C	2 - 28
Absorption Correction: refined from	
ΔF (DIFABS; Walker & Stuart, 1983) [3]	T_{min} = 0.90, T_{max} = 0. 0.97

Reflections measured	28961 (R_{int} = 0.012)
III. Structure determination	
Unique reflections included	8622 [(I) > 2 σ(I)]
Number of parameters refined	722
Residual Fourier density e Å^{-3}	-0.478 < ρ < 0.578
R indices (all data)	0.08
WR	0.23
Goodness of fit on F	0.87
Computer programs	Diamond [4], Ortep [5]

$$R = \left| \frac{\sum_{\overline{H}} \left| Fo(\overline{H}) \right| - \left| kFc(\overline{H}) \right|}{\sum_{\overline{H}} \left| Fo(\overline{H}) \right|} \right| \qquad Rw = \left| \frac{\sum_{\overline{H}} w(\overline{H}) \left(\left| F_O(\overline{H}) \right| - \left| kF_C(\overline{H}) \right| \right)^2}{\sum_{\overline{H}} w(\overline{H}) \left(\left| Fo(\overline{H}) \right| \right)^2} \right|$$

Atomic coordinates and the most significant geometrical characteristics of this structure are reported in Tables 2 and 3.

Table 2: Atomic Coordinates and U_{eq} for $[2,3\text{-}(CH_3)_2C_6H_3NH_3]_6P_6O_{18}.2H_2O$

Atoms	x(σ)	y(σ)	z(σ)	U_{eq} / U_{iso}*
P1	2.27339(8)	0.50956(5)	1.58323(4)	0.02889(18)
P2	2.29341(9)	0.57721(5)	1.43992(5)	0.03009(19)
P3	2.45439(9)	0.46418(5)	1.35602(5)	0.03080(19)
P4	2.23124(8)	0.50351(5)	0.92295(4)	0.02898(18)
P5	2.20959(8)	0.41199(5)	1.05534(4)	0.02962(18)
P6	2.03615(8)	0.51384(5)	1.14485(4)	0.03033(19)
O1	2.2717(2)	0.42051(14)	1.60101(12)	0.0381(5)
O2	2.1645(2)	0.55901(15)	1.61005(14)	0.0487(7)
O3	2.2832(3)	0.50836(15)	1.49855(12)	0.0534(7)
O4	2.1763(3)	0.56203(17)	1.39316(15)	0.0572(7)
O5	2.3293(2)	0.66126(14)	1.47323(13)	0.0393(6)
O6	2.4244(2)	0.55040(14)	1.39682(13)	0.0424(6)
O7	2.3496(2)	0.39868(14)	1.37316(13)	0.0399(6)
O8	2.5870(2)	0.44182(15)	1.39564(14)	0.0471(6)
O9	2.4865(3)	0.48029(16)	1.28030(13)	0.0530(7)
O10	2.3371(2)	0.45842(15)	0.88728(14)	0.0488(7)
O11	2.2323(2)	0.59535(14)	0.91682(12)	0.0388(6)
O12	2.2264(3)	0.48995(15)	1.00674(12)	0.0522(7)
O13	2.3225(3)	0.41795(18)	1.10526(15)	0.0590(8)
O14	2.1741(2)	0.33412(14)	1.01235(13)	0.0406(6)
O15	2.0765(2)	0.43300(14)	1.09868(14)	0.0453(6)
O16	2.1410(2)	0.58271(14)	1.13973(12)	0.0374(5)

O17	1.9124(2)	0.54014(14)	1.10005(13)	0.0421(6)
O18	1.9917(3)	0.48881(16)	1.21660(12)	0.0461(6)
O19	2.1915(6)	0.1637(4)	1.0194(5)	0.217(3)
O20	2.3121(5)	0.8332(3)	1.4892(3)	0.159(2)
N1	2.4234(3)	0.58179(16)	1.17251(15)	0.0363(6)
N2	2.0929(3)	0.68263(16)	1.02656(15)	0.0380(7)
N3	1.9645(3)	0.61810(15)	1.32591(14)	0.0333(6)
N4	2.3984(3)	0.31696(17)	1.49877(15)	0.0389(7)
N5	2.0716(3)	0.39819(16)	1.33097(15)	0.0361(6)
N6	2.5409(3)	0.36406(16)	1.16619(14)	0.0330(6)
C1	2.4341(3)	0.6720(2)	1.18714(18)	0.0342(7)
C2	2.4631(3)	0.7226(2)	1.13042(19)	0.0364(7)
C3	2.4769(4)	0.8092(2)	1.1459(2)	0.0537(10)
C4	2.4595(5)	0.8392(3)	1.2155(3)	0.0677(13)
C5	2.4275(5)	0.7876(3)	1.2704(2)	0.0692(13)
C6	2.4154(4)	0.7031(2)	1.2563(2)	0.0492(10)
C7	2.4765(4)	0.6870(2)	1.05465(19)	0.0501(10)
C8	2.5114(6)	0.8689(3)	1.0879(3)	0.0835(16)
C9	2.1235(3)	0.7720(2)	1.0405(2)	0.0389(8)
C10	2.1304(4)	0.8232(2)	0.9830(2)	0.0489(9)
C11	2.1571(4)	0.9100(3)	0.9976(3)	0.0599(12)
C12	2.1724(5)	0.9384(3)	1.0674(3)	0.0749(15)
C13	2.1646(5)	0.8872(3)	1.1237(3)	0.0770(15)
C14	2.1397(4)	0.8020(3)	1.1113(2)	0.0567(11)
C15	2.1073(6)	0.7868(3)	0.9083(2)	0.0782(16)
C16	2.1686(6)	0.9681(3)	0.9366(3)	0.112(2)
C17	1.9790(3)	0.7073(2)	1.31540(18)	0.0354(7)
C18	1.8969(4)	0.7428(2)	1.2673(2)	0.0414(8)
C19	1.9142(4)	0.8289(2)	1.2610(2)	0.0547(11)
C20	2.0095(5)	0.8753(3)	1.3035(3)	0.0703(14)
C21	2.0856(5)	0.8386(3)	1.3512(3)	0.0721(14)
C22	2.0721(4)	0.7539(2)	1.3579(2)	0.0512(10)
C23	1.7931(4)	0.6907(3)	1.2246(2)	0.0626(12)
C24	1.8337(5)	0.8734(3)	1.2086(3)	0.0872(17)
C25	2.3613(4)	0.0871(2)	1.4533(3)	0.0566(11)
C26	2.3863(4)	0.1728(2)	1.4450(2)	0.0473(9)
C27	2.3639(3)	0.2272(2)	1.5042(2)	0.0402(8)
C28	2.3173(5)	0.2004(3)	1.5693(2)	0.0620(12)
C29	2.2937(5)	0.1155(3)	1.5763(3)	0.0812(16)
C30	2.3156(5)	0.0610(3)	1.5197(3)	0.0736(14)
C31	2.4385(5)	0.2066(3)	1.3774(2)	0.0691(13)
C32	2.3797(6)	0.0240(3)	1.3931(3)	0.0929(18)

C33	2.0520(4)	0.1708(3)	1.3661(3)	0.0606(12)
C34	2.0491(4)	0.2592(2)	1.3793(2)	0.0453(9)
C35	2.0780(3)	0.3072(2)	1.3220(2)	0.0392(8)
C36	2.1205(4)	0.2757(3)	1.2545(2)	0.0569(11)
C37	2.1256(5)	0.1912(3)	1.2443(3)	0.0770(15)
C38	2.0917(5)	0.1407(3)	1.2995(3)	0.0751(15)
C39	2.0142(5)	0.2972(3)	1.4511(2)	0.0670(13)
C40	2.0120(6)	0.1130(3)	1.4246(3)	0.105(2)
C41	2.6270(5)	0.1572(3)	1.2255(2)	0.0554(11)
C42	2.6320(4)	0.2432(2)	1.21996(18)	0.0378(8)
C43	2.5380(3)	0.2745(2)	1.17504(18)	0.0351(7)
C44	2.4467(4)	0.2244(3)	1.1351(2)	0.0539(10)
C45	2.4438(5)	0.1398(3)	1.1415(3)	0.0741(15)
C46	2.5324(5)	0.1068(3)	1.1856(3)	0.0704(14)
C47	2.7326(4)	0.3003(3)	1.2600(2)	0.0555(11)
C48	2.7238(6)	0.1161(3)	1.2729(3)	0.0943(19)
H1A	2.4379	0.5703	1.1260	0.054*
H1B	2.3414	0.5614	1.1842	0.054*
H1C	2.4842	0.5585	1.1984	0.054*
H2A	2.0921	0.6572	1.0679	0.057*
H2B	2.1553	0.6620	0.9976	0.057*
H2C	2.0127	0.6741	1.0057	0.057*
H3A	2.0240	0.6052	1.3583	0.050*
H3B	1.9789	0.5900	1.2844	0.050*
H3C	1.8818	0.6045	1.3414	0.050*
H4A	2.3567	-0.0310	1.4091	0.139*
H4B	2.4718	0.0277	1.3776	0.139*
H4C	2.3225	0.0347	1.3537	0.139*
H5A	1.9874	0.1452	1.4670	0.157*
H5B	2.0862	0.0806	1.4354	0.157*
H5C	1.9368	0.0762	1.4089	0.157*
H6A	2.7825	0.1583	1.2970	0.141*
H6B	2.7761	0.0793	1.2437	0.141*
H6C	2.6741	0.0848	1.3078	0.141*
H7A	2.4966	0.7316	1.0231	0.075*
H7B	2.3936	0.6571	1.0401	0.075*
H7C	2.5477	0.6496	1.0524	0.07 *
H8A	2.5214	0.8379	1.0429	0.125*
H8B	2.5941	0.9006	1.0998	0.125*
H8C	2.4407	0.9061	1.0840	0.125*
H15A	2.1155	0.8306	0.8750	0.117*
H15B	2.0188	0.7595	0.9049	0.117*

H15C	2.1729	0.7470	0.8969	0.117*
H16A	2.1545	0.9364	0.8918	0.168*
H16B	2.2566	0.9963	0.9369	0.168*
H16C	2.1021	1.0084	0.9423	0.168*
H23A	1.7463	0.7256	1.1943	0.094*
H23B	1.7303	0.6638	1.2566	0.094*
H23C	1.8358	0.6490	1.1954	0.094*
H24A	1.7724	0.8337	1.1832	0.131*
H24B	1.8933	0.9001	1.1750	0.131*
H24C	1.7840	0.9146	1.2343	0.131*
H31A	2.4493	0.2665	1.3829	0.104*
H31B	2.3762	0.1907	1.3391	0.104*
H31C	2.5238	0.1847	1.3662	0.104*
H32A	2.4272	0.3266	1.4545	0.058*
H32B	2.4629	0.3336	1.5302	0.058*
H32C	2.3259	0.3452	1.5083	0.058*
H39A	1.9979	0.2538	1.4843	0.100*
H39B	1.9349	0.3273	1.4470	0.100*
H39C	2.0874	0.3348	1.4683	0.100*
H40A	2.0921	0.4212	1.2895	0.054*
H40B	2.1299	0.4184	1.3646	0.054*
H40C	1.9889	0.4102	1.3442	0.054*
H47A	2.7195	0.3570	1.2493	0.083*
H47B	2.8215	0.2868	1.2458	0.083*
H47C	2.7216	0.2940	1.3107	0.083*
H48A	2.6040	0.3900	1.1946	0.050*
H48B	2.4612	0.3826	1.1780	0.050*
H48C	2.5593	0.3744	1.1206	0.050*
H4	2.4697	0.8966	1.2258	0.081*
H5	2.4142	0.8100	1.3168	0.083*
H6	2.3948	0.6673	1.2929	0.059*
H12	2.1891	0.9956	1.0772	0.090*
H13	2.1761	0.9097	1.1704	0.092*
H14	2.1340	0.7661	1.1490	0.068*
H20	2.0212	0.9327	1.2991	0.084*
H21	2.1475	0.8711	1.3796	0.086*
H22	2.1246	0.7285	1.3904	0.061*
H44	2.3879	0.2473	1.1043	0.065*
H45	2.3811	0.1047	1.1156	0.089*
H46	2.5297	0.0492	1.1892	0.085*
H28	2.3021	0.2383	1.6074	0.074*
H29	2.2628	0.0956	1.6198	0.097*

H30	2.2994	0.0040	1.5256	0.088*
H36	2.1444	0.3112	1.2180	0.068*
H37	2.1519	0.1680	1.2001	0.092*
H38	2.0958	0.0833	1.2915	0.090*

U_{eq}= 4/3 $\sum_i \sum_j \beta_{ij} a_i a_j$

Table 3: Principal Intermolecular Distances (Å) and bond angles (°)

in $[2,3\text{-}(CH_3)_2C_6H_3NH_3]_6P_6O_{18}.2H_2O$

PO_4 Tetrahedron

P(1)	O(1)	O(2)	O(3)	O(8)
O(1)	**1.483(2)**	2.530(4)	2.429(3)	2.535(4)
O(2)	118.73(14)	**1.460(2)**	2.511(8)	2.478(4)
O(3)	105.06(13)	111.39(16)	**1.557(2)**	2.428(2)
O(8)	111.21(13)	108.63(15)	100.22(15)	**1.587(2)**
P(2)	O(3)	O(4)	O(5)	O(6)
O(3)	**1.594(2)**	2.462(3)	2.536(4)	2.449(3)
O(4)	107.32(16)	**1.460(2)**	2.558(3)	2.496(3)
O(5)	111.37(13)	120.98(15)	**1.477(2)**	2.458(2)
O(6)	100.22(15)	109.25(15)	105.71(13)	**1.601(2)**
P(3)	O(6)	O(7)	O(8)	O(9)
O(6)	**1.590(2)**	2.514(2)	2,460(3)	2.488(3)
O(7)	110.35(13)	**1. 477(2)**	2.554(4)	2.560(3)
O(8)	101.45(14)	106.15(14)	**1.591(2)**	2.499(2)
O(9)	108.37(14)	119.92(15)	109.01(16)	**1.477(2)**
P(4)	O(10)	O(11)	O(12)	O(17)
O(10)	**1.461(6)**	2.534(2)	2.525(2)	2.499(2)
O(11)	118.68(14)	**1.485(2)**	2.444(2)	2.533(3)
O(12)	111.93(16)	105.25(13)	**1.485(2)**	2.432(3)
O(17)	109.32(14)	110.47(13)	99.45(14)	**1.596(2)**
P(5)	O(12)	O(13)	O(14)	O(15)
O(12)	**1.582(2)**	2.456(2)	2.530(3)	2.441(3)
O(13)	107.57(16)	**1.461(3)**	2.552(2)	2.487(2)
O(14)	111.54(13)	120.95(15)	**1.471(2)**	2.443(2)
O(15)	100.34(15)	109.00(16)	105.45(14)	**1.592(2)**

P(6)	O(15)	O(16)	O(17)	O(18)
O(15)	**1.596(2)**	2.527(2)	2.456(2)	2.495(2)
O(16)	110.71(13)	**1.478(2)**	2.442(4)	2.540(3)
O(17)	101.12(14)	105.67(13)	**1.591(2)**	2.515(3)
O(18)	108.62(14)	118.86(15)	110.39(14)	**1.471(2)**

P1-P2	2.885(3)	P1-O8-P3	135.42(16)
P2-P3	2.924(3)	P2-O3-P1	135.49(16)
P1-P3	2.926(3)	P2-O6-P3	130.28(15)
P4-P5	2.9379(19)	P6-O17-P4	135.05(15)
P5-P6	2.9157(18)	P5-O12-P4	135.75(16)
P4-P6	2.900(3)	P6-O15-P5	132.37(15)
P1-P2-P3	120.4(8)	P6-P5-P4	109.1(8)
P2-P3-P1	99.04(8)	P4-P6-P5	123.1(8)
P3-P1-P2	110.3(8)	P5-P4-P6	98.9(8)

Organic groups

N(1) - C(1)	1.457(4)	C(2) - C(1) - N(1)	118.3(3)
C(1) - C(2)	1.385(5)	C(6) - C(1) - N(1)	118.8(3)
C(1) - C(6)	1.373(5)	C(6) - C(1) - C(2)	122.9(3)
C(2) - C(3)	1.402(5)	C(1) - C(2) - C(3)	117.5(3)
C(2) - C(7)	1.503(5)	C(1) - C(2) - C(7)	121.7(3)
C(3) - C(4)	1.373(6)	C(3) - C(2) - C(7)	120.8(3)
C(3) - C(8)	1.506(6)	C(2) - C(3) - C(4)	118.9(4)
C(4) - C(5)	1.374(6)	C(2) - C(3) - C(8)	121.1(4)
C(5) - C(6)	1.374(6)	C(4) - C(3) - C(8)	120.0(4)
		C(3) - C(4) - C(5)	122.4(4)
		C(4) - C(5) - C(6)	119.4(4)
		C(5) - C(6) - C(1)	119.0(4)
N(2) - C(9)	1.457(4)	C(10) - C(9) - N(2)	118.7(3)
C(9) - C(10)	1.384(5)	C(14) - C(9) - N(2)	118.1(3)
C(9) - C(14)	1.385(5)	C(14) - C(9) - C(10)	123.1(4)
C(10) - C(11)	1.413(5)	C(9) - C(10) - C(11)	118.0(4)
C(10) - C(15)	1.493(6)	C(9) - C(10) - C(15)	120.1(4)
C(11) - C(12)	1.361(7)	C(11) - C(10) - C(15)	121.8(4)
C(11) - C(16)	1.506(6)	C(10) - C(11) - C(12)	118.2(4)
C(12) - C(13)	1.365(7)	C(10) - C(11) - C(16)	120.0(5)
C(13) - C(14)	1.383(6)	C(12) - C(11) - C(16)	121.9(5)
		C(11) - C(12) - C(13)	123.2(4)
		C(12) - C(13) - C(14)	120.1(5)
		C(13) - C(14) - C(9)	117.4(4)

N(3) - C(17)	1.454(4)	C(18) - C(17) - N(3)	120.4(3)
C(17) - C(18)	1.386(5)	C(22) - C(17) - N(3)	116.8(3)
C(17) - C(22)	1.378(5)	C(18) - C(17) - C(22)	122.7(3)
C(18) - C(19)	1.394(5)	C(17) - C(18) - C(19)	117.5(4)
C(18) - C(23)	1.492(5)	C(17) - C(18) - C(23)	121.1(3)
C(19) - C(20)	1.391(6)	C(19) - C(18) - C(23)	121.4(4)
C(19) - C(24)	1.504(6)	C(18) - C(19) - C(20)	119.4(4)
C(20) - C(21)	1.354(6)	C(18) - C(19) - C(24)	121.9(4)
C(21) - C(22)	1.369(6)	C(20) - C(19) - C(24)	118.8(4)
		C(19) - C(20) - C(21)	121.4(4)
		C(20) - C(21) - C(22)	120.5(4)
		C(21) - C(22) - C(17)	118.5(4)
N(4) - C(25)	1.468(4)	C(26) - C(25) - N(4)	119.9(3)
C(25) - C(26)	1.396(5)	C(30) - C(25) - N(4)	121.0(4)
C(25) - C(30)	1.376(5)	C(30) - C(25) - C(26)	119.1(4)
C(26) - C(27)	1.399(5)	C(25) - C(26) - C(27)	120.2(5)
C(26) - C(31)	1.477(5)	C(25) - C(26) - C(31)	118.4(5)
C(27) - C(28)	1.391(6)	C(27) - C(26) - C(31)	122.4(5)
C(27) - C(32)	1.491(6)	C(26) - C(27) - C(28)	119.6(6)
C(28) - C(29)	1.361(7)	C(26) - C(27) - C(32)	118.0(6)
C(29) - C(30)	1.380(6)	C(28) - C(27) - C(32)	119.7(5)
		C(27) - C(28) - C(29)	118.4(5)
		C(28) - C(29) - C(30)	118.4(5)
		C(29) - C(30) - C(25)	118.4(5)
N(5) - C(33)	1.468(4)	C(34) - C(33) - N(5)	119.3(3)
C(33) - C(34)	1.367(5)	C(38) - C(33) - N(5)	116.4(3)
C(33) - C(38)	1.405(5)	C(38) - C(33) - C(34)	124.2(4)
C(34) - C(35)	1.430(5)	C(33) - C(34) - C(35)	116.4(4)
C(34) - C(39)	1.490(5)	C(33) - C(34) - C(39)	121.6(4)
C(35) - C(36)	1.374(6)	C(35) - C(34) - C(39)	122.0(4)
C(35) - C(40)	1.505(6)	C(34) - C(35) - C(36)	118.6(4)
C(36) - C(37)	1.370(7)	C(34) - C(35) - C(40)	119.9(5)
C(37) - C(38)	1.364(6)	C(36) - C(35) - C(40)	121.5(5)
		C(35) - C(36) - C(37)	123.2(4)
		C(36) - C(37) - C(38)	119.7(5)
		C(37) - C(38) - C(33)	117.7(4)
N(6) - C(41)	1.455(4)	C(42) - C(41) - N(6)	119.2(3)
C(41) - C(42)	1.395(5)	C(46) - C(41) - N(6)	117.6(3)

C(41) - C(46)	1.368(5)	C(46) - C(41) - C(42)	123.0(3)
C(42) - C(43)	1.387(5)	C(41) - C(42) - C(43)	117.1(3)
C(42) - C(47)	1.488(5)	C(41) - C(42) - C(47)	120.9(3)
C(43) - C(44)	1.392(6)	C(43) - C(42) - C(47)	122.0(4)
C(43) - C(48)	1.517(6)	C(42) - C(43) - C(44)	119.4(4)
C(44) - C(45)	1.360(7)	C(42) - C(43) - C(48)	121.8(4)
C(45) - C(46)	1.368(6)	C(44) - C(43) - C(48)	118.8(4)
		C(43) - C(44) - C(45)	121.7(4)
		C(44) - C(45) - C(46)	120.0(4)
		C(45) - C(46) - C(41)	118.7(4)

RESULTS AND DISCUSSION

Structure description

Asymmetric unity which constitutes the basic entity of this structure has the geometrical configuration depicted in the Ortep representation (Fig. 1).

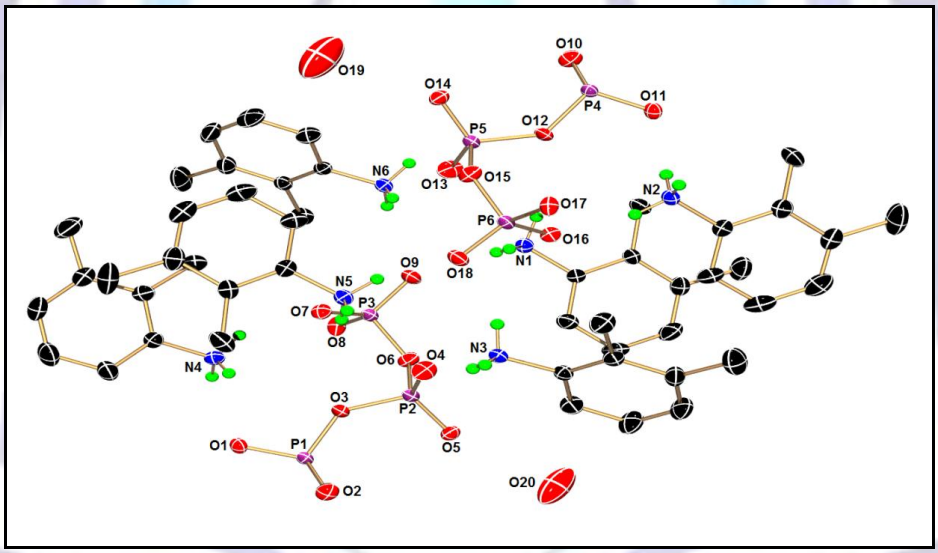

Figure 1: *ORTEP* Plot of the asymmetric unit of the title structure.

Thermal ellipsoids at 30% of probability.

This unit generates by symmetry the structure of the title compound (Fig. 2). This projection shows that the atomic arrangement of this compound can be considered as a typical layers organization, were the hexaphosphoric rings, interconnected by H-bonds, adopt a chair conformation and form an inorganic layer parallel to the ac plane. Dimethylanilinium Cations $[2,3\text{-}(CH_3)_2C_6H_3NH_3]^+$, obtained by protonation of the amine and presented in the mesh in six crystallographically independent groups, are located between the inorganic layers which are spaced 16.06 Å (= b). These organic entities establish H-bonds of type N-H...O with $[P6O18]^{6-}$ rings (listed in table 4) and develop electrostatic and Van Der Walls interactions for ensuring the cohesion and the stability of the crystal framework (Fig. 3).

It must be noted that both water molecules O(W1) and O(W2) are not involved in the inorganic layers which may explain their high thermal factors. Such thermal factor values were observed too in others structures (M. Bagieu-Beucher *et al.*, 1991) [6].

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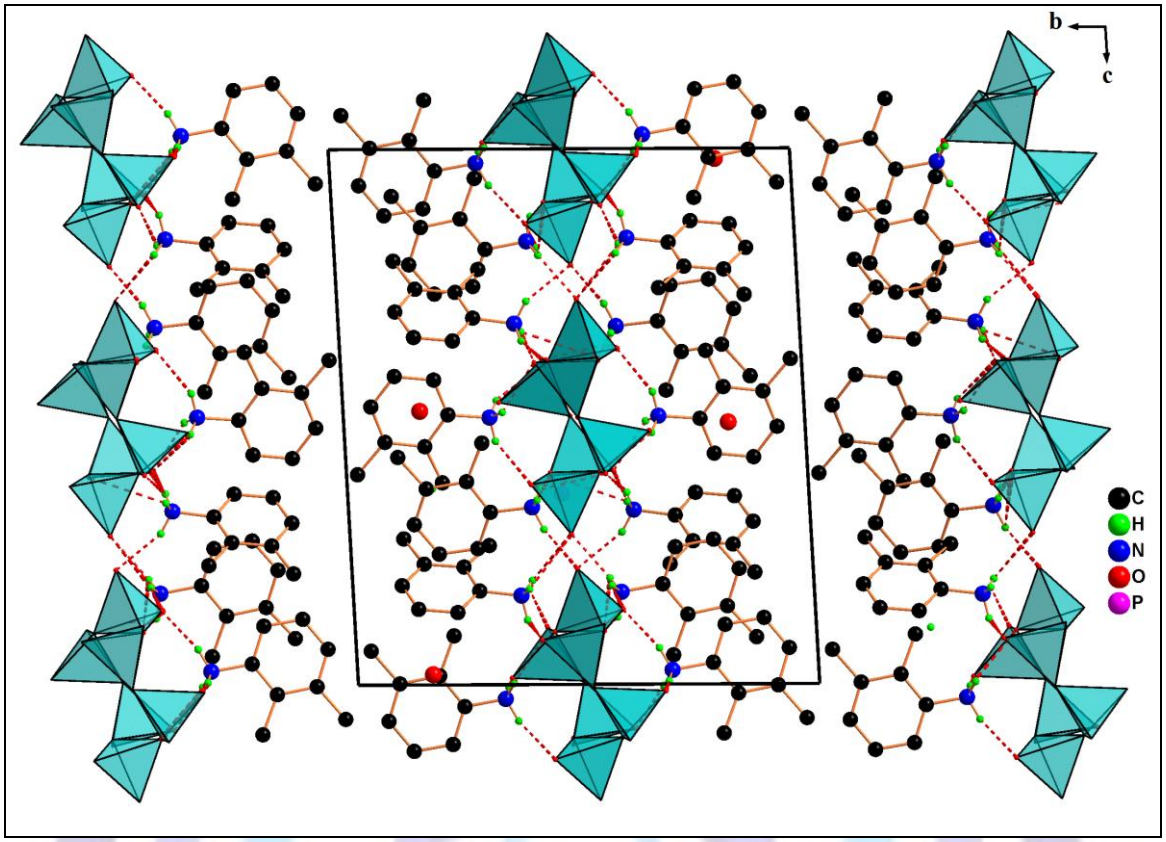

Figure 2: Projection of the crystal structure of $[2,3\text{-}(CH_3)_2C_6H_3NH_3]_6P_6O_{18}.2H_2O$, along the a axis, The phosphoric anions are given in tetrahedral representation .

Hydrogen bonds are shown as dashed lines.

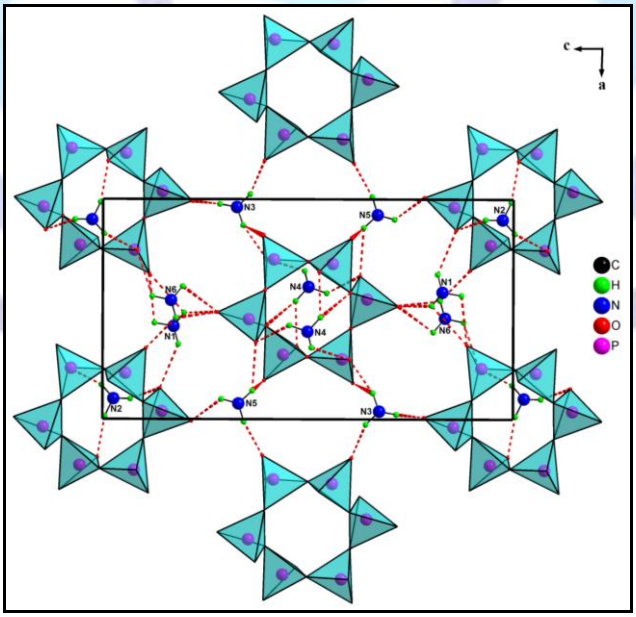

Figure 3: Projection along the b axis of the atomic arrangement of $2,3\text{-}(CH_3)_2C_6H_3NH_3]_6P_6O_{18}.2H_2O$. Phosphoric anions are given in a tetrahedral representation. The organic cations have been rendered ammonium group for clarity. Hydrogen bonds are plotted by dashed lines.

Table 4: Hydrogen-bonds geometry (Å, °) in $[2,3\text{-}(CH_3)_2C_6H_3NH_3]_6P_6O_{18}.2H_2O$

Atoms	D - H	H…A	D…A	D - H…A
N(1) - H(1A) ...O(10)^{iii}	0.89	2.33	2.733(4)	108
N(1) - H(1B) ...O(16)	0.89	2.22	2.885(4)	131
N(1) - H(1C) ...O(9)	0.89	2.03	2.753(4)	138
N(1) - H(1C) ...O(10)^{iii}	0.89	2.41	2.733(4)	102
N(2) - H(2A) ...O(16)	0.89	1.93	2.778(4)	160
N(2) - H(2A) ...O(17)^{i}	0.89	2.60	3.179(4)	124
N(2) - H(2B) ...O(11)	0.89	1.98	2.830(4)	158
N(2) - H(2C) ...O(14)^{i}	0.89	1.89	2.754(4)	164
N(3) - H(3A) ...O(4)^{ii}	0.89	1.85	2.690(4)	158
N(3) - H(3B) ...O(18)^{ii}	0.89	2.02	2.855(3)	157
N(3) - H(3C) ...O(2)	0.89	2.83	3.321(3)	115
N(3) - H(3C) ...O(1)	0.89	1.90	2.766(4)	165
N(4) - H(32A) ...O(7)	0.89	2.13	2.802(4)	131
N(4) - H(32B) ...O(5)^{iv}	0.89	2.07	2.763(4)	134
N(4) - H(32B) ...O(6)^{iv}	0.89	2.46	3.245(4)	148
N(4) - H(32C) ...O(1)	0.89	2.14	2.813(4)	131
N(5) - H(40A) ...O(18)	0.89	2.08	2.791(4)	136
N(5) - H(40B) ...O(4)	0.89	2.35	2.945(4)	124
N(5) - H(40B) ...O(7)	0.89	2.24	2.884(4)	129
N(5) - H(40C) ...O(2)^{ii}	0.89	1.83	2.709(4)	168
N(6) - H(48A) ...O(9)	0.89	2.45	2.829(4)	106
N(6) - H(48B) ...O(9)	0.89	2.41	2.829(4)	109
N(6) - H(48B) ...O(13)	0.89	2.07	2.675(4)	125
N(6) - H(48C) ...O(11)^{iii}	0.89	2.22	2.794(4)	122

Symmetry codes : i : -x,1-y,-z; ii : -x,1-y,1-z; iii : 1-x,1-y,-z ; iv : 1-x,1-y,1-z

NMR Results

Crystallographic study of the two phosphoric rings showed a slight difference in their geometry (Fig.4). The gap is close to 0.88°. To evaluate these results we have studied the solid state NMR of ^{31}P of the title compound. The CP/MAS-NMR experiments were performed at room temperature on a Bruker MSL 300 solid state high-resolution spectrometer operating at 121.495 MHz for ^{31}P. Chemical shift values are given with respect to 85% H_3PO_4 (negative shifts are to high field). The ^{31}P MAS-NMR spectrum of crystalline cyclohexaphosphate $[2,3\text{-}(CH_3)_2C_6H_3NH_3]_6P_6O_{18}.2H_2O$ is reported in Fig.5. It exhibits four resonance peaks at: -10.67, -19.8, -23.43 and -26.57 ppm. The existence of only 4 peaks shows that some crystallographically independent phosphorous of the two rings have very similar chemical environments. Analysis of geometrical characteristics of the six tetrahedra PO_4 shows effectively a chemical environment similarity of P2 with P5 and P3 with P6. This similarity gives two NMR peaks for these phosphorous with two others peaks for P1 and P4. The presence of this number of peaks, indicate that the title compound contains more than three crystallography independent phosphoric sites, and therefore two independent P_6O_{18} rings, which is in agreement with x-ray results. These chemical shift values agree with those of others cyclohexaphosphates [7].

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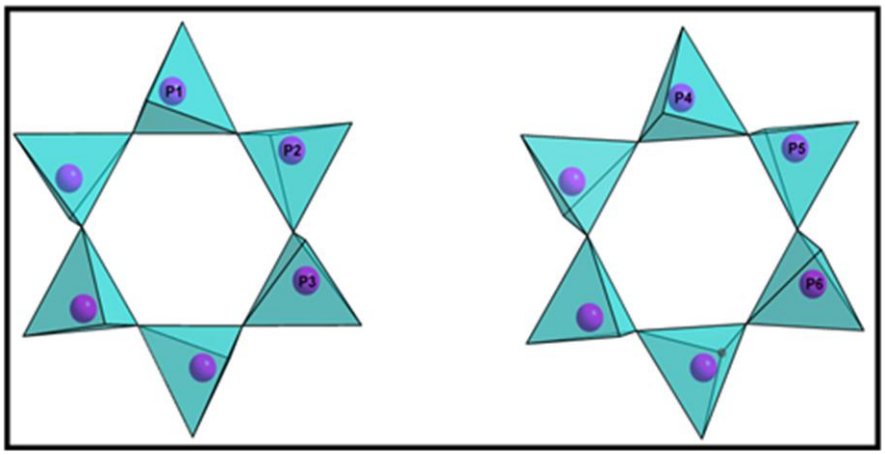

Figure 4: Ggeometry representation of the two P_6O_{18} rings in the structure of 2,3-$(CH_3)_2C_6H_3NH_3]_6P_6O_{18}.2H_2O$.

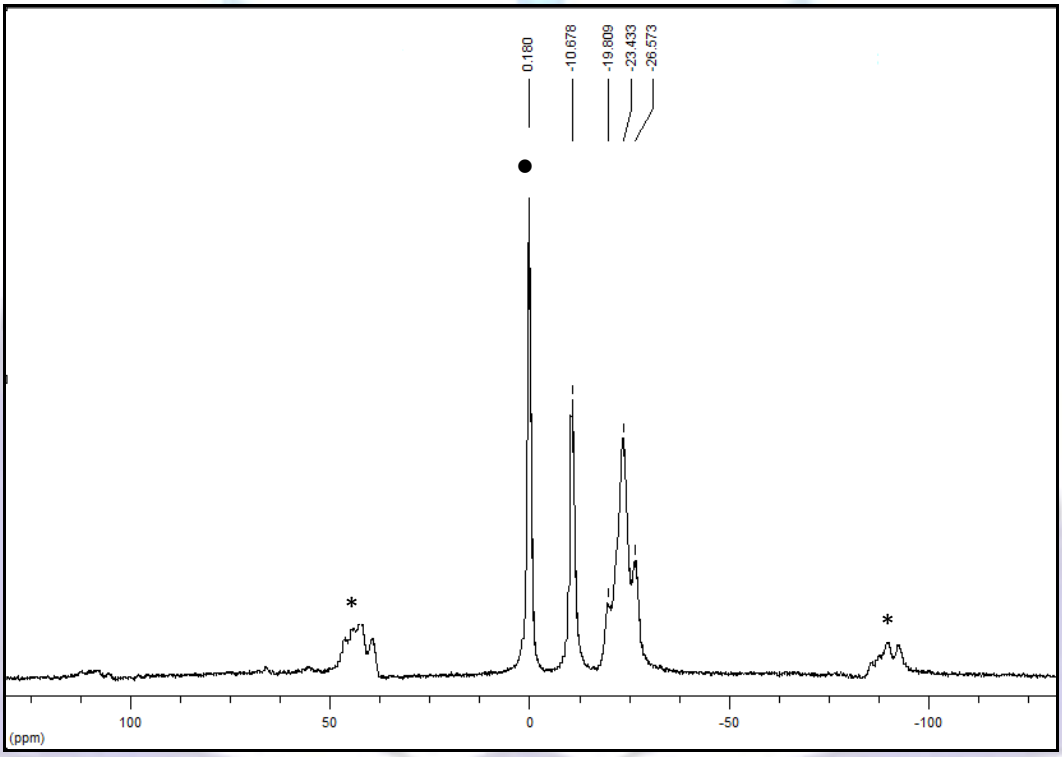

Figure 5: ^{31}P MAS-NMR spectrum of 2,3-$(CH_3)_2C_6H_3NH_3]_6P_6O_{18}.2H_2O$. H_3PO_4: Reference, * Spinning side bands.

Thermal analysis

Thermal analysis was performed, using the multimodule 92 Staram analyzer, from room temperature to 400°C at a speed of 5°C/min. The simultaneous TGA–DTA analysis curves (Fig.6) of $[2,3\text{-}(CH_3)_2C_6H_3NH_3]_6P_6O_{18}.2H_2O$ exhibits a very intense endothermic peak, at 65°C, on the DTA curve. Thermogravimetric analysis (TGA) shows that this peak is accompanied with a weight loss of 2.83% comparable to the theoretical loss (2.9%) relative to the dehydration of the title material. the departure of water molecules at this low temperature is due to the thermal agitation of water molecules and their isolation in the network. The Series of DTA endothermic peaks occurring at 205°C, 224°C and 237°C, accompanied by a significant weight loss, correspond to a pyrolysis of organic molecules. The resulting product is a consisting liquid of polyphosphoric acids contaminated of black carbon. This decomposition is occurred before the material melting. These phenomena are confirmed by DSC performed in the same temperature range (Fig 7).

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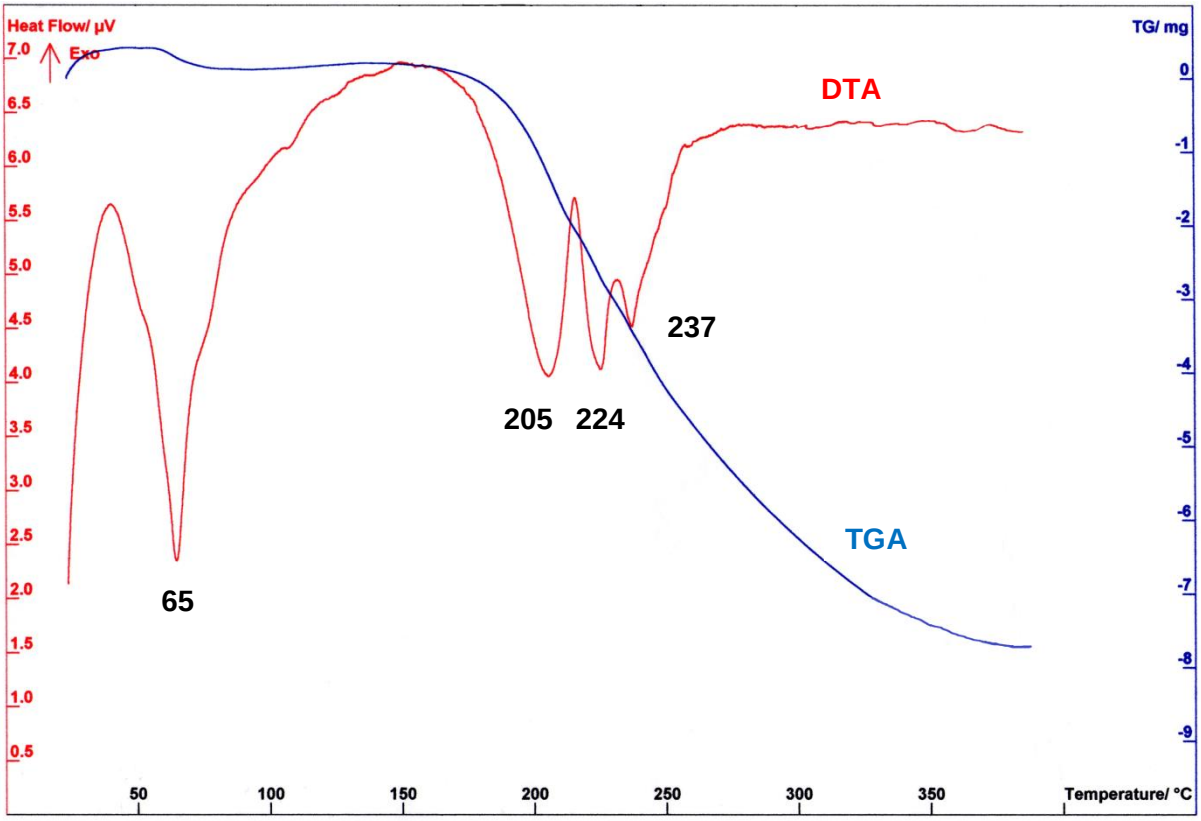

Figure 6: DTA and TGA curves of $2,3\text{-}(CH_3)_2C_6H_3NH_3]_6P_6O_{18}.2H_2O$.

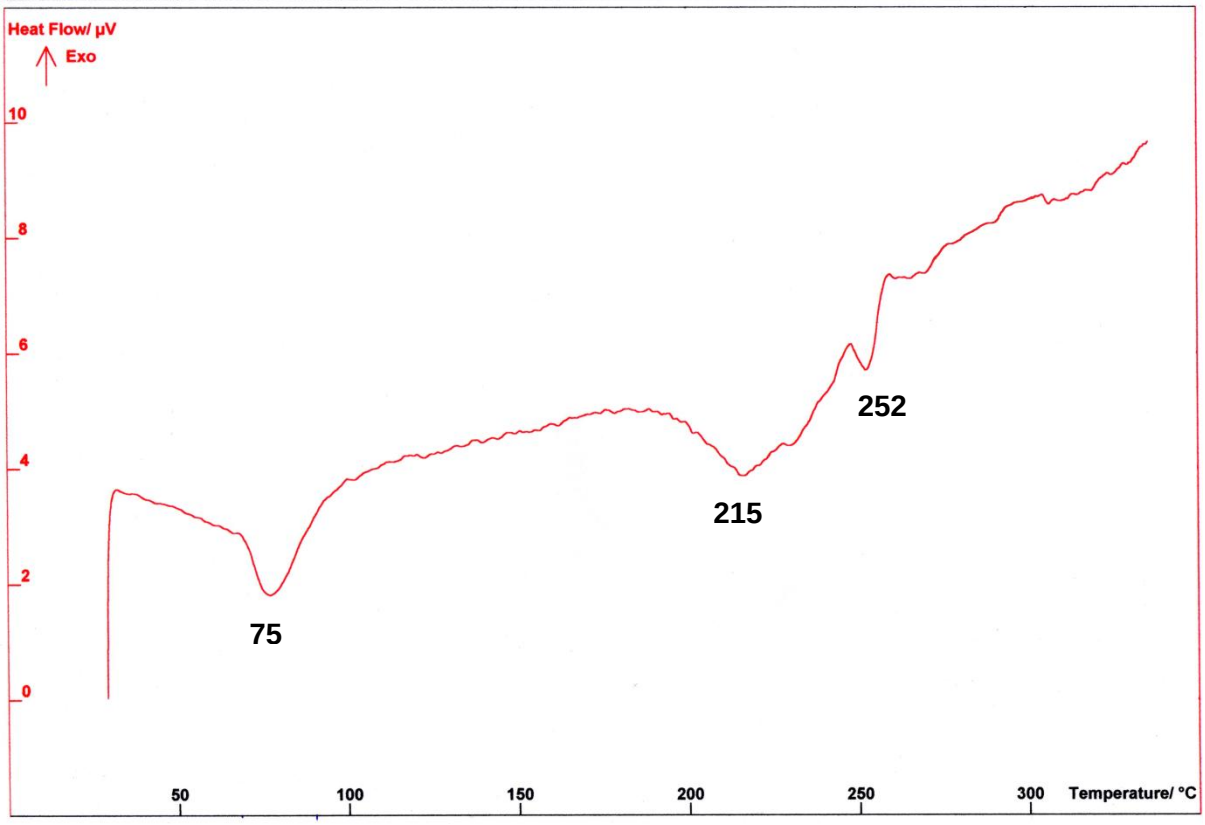

Figure 7: DSC curves of $[2,3\text{-}(CH_3)_2C_6H_3NH_3]_6P_6O_{18}.2H_2O$.

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IR Absorption Spectroscopy

The infrared spectrum (Fig. 8) was recorded in the range 400-4000 cm^{-1} using the NICOLET IR 200 FT-IR infrared spectrometer. This spectrum exhibits characteristics bands of the different components of the analyzed product. The bands at 1247, 1121 and 1069 cm^{-1} are characteristics of asymmetric and symmetric vibrations of OPO groups, those at 1032, 952,780 and 710 cm^{-1} are due to the asymmetric and symmetric vibrations of POP groups [8]. The intense bands at 1579 and 1600 cm^{-1} are characteristics of an aromatic ring, a band to 3449 cm^{-1} relating to the aromatic NH_2 group. The bands at 780 cm^{-1} and 710 cm^{-1}, corresponding to deformation vibrations of C-C and C-H groups, show that the aromatic ring is 1,2,3-trisubstituted. The large band at 2880 cm^{-1} and that at 1639 cm^{-1} correspond to the stretching vibration and deformation vibration respectively of water molecules. The assignment shows that the vibraionnal spectroscopic data are in agreement with the composition of single-crystal X-ray diffraction results.

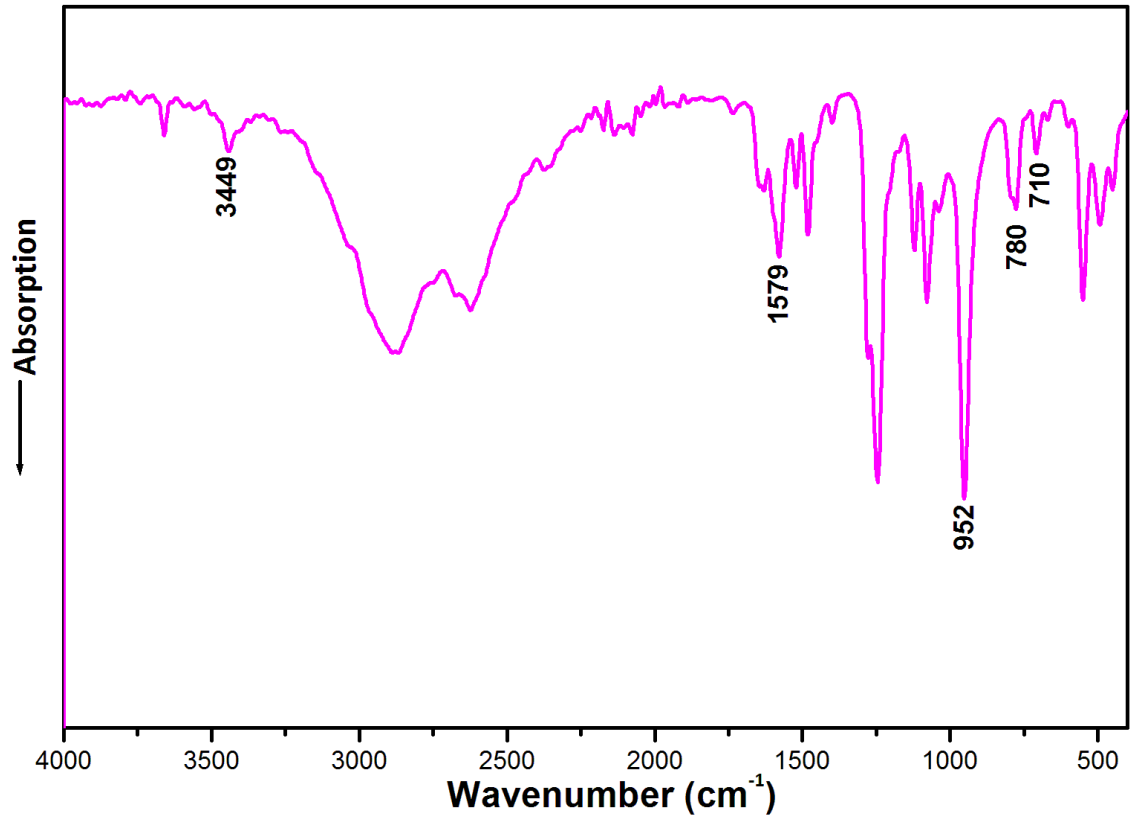

Figure 8: IR spectrum of $[2,3\text{-}(CH_3)_2C_6H_3NH_3]_6P_6O_{18}.2H_2O$.

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