SYNTHESIS, CRYSTAL STRUCTURE, THERMAL BEHAVIOR AND SPECTROSCOPIC STUDIES OF $[NC_5H_{12}^+]\bullet[H_2PO_4^-]$

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ABSTRACT: The title compound, $[NC_5H_{12}^+]\bullet[H_2PO_4^-]$, was synthesized hydrothermally at 453 K. Its structure, determined by single crystal X-ray diffraction, is trigonal with the space group $R\bar{3}$ (N°148) and the following unit cell parameters : a = 23.218(4) Å, c = 58.40(3) Å, V = 27266.9(1) Å^3 and Z = 18. The refinement of the data leads to a factor R of 0.056 and an R_w of 0.25 for 5159 reflections with I>4σ(I). The atomic arrangement presents extended corrugated chains strongly linked together by (O-H...O) hydrogen bonds, to delimit tunnels developing along the [001] direction. Organic cations, located inside the tunnels, are maintained to phosphate groups via weak (N-H...O) hydrogen bonds. X-ray powder diffraction, IR and NMR spectroscopic studies support basically the structure refinement.

Key Words: Hydrothermal Synthesis, X-ray diffraction, Infrared and NMR Spectroscopies, Thermogravimetric Analysis (TGA), Crystal Structure.

RESUME: Des cristaux de dihydrogénomonophosphate de cyclopentylammonium $[NC_5H_{12}^+]\bullet[H_2PO_4^-]$ ont été synthétisé par voie hydrothermale à 453 K. La structure de ce composé a été affinée dans le système trigonal (groupe d'espace $R\bar{3}$ (N°148), a = 23.218(4) Å, c = 58.40(3) Å, V = 27266.9(1) Å^3 and Z = 18) à partir de données de diffraction des rayons X sur monocristal jusqu'à des facteurs de confiance R = 0.056 et R_w = 0.25 pour 5159 réflexions avec I>4σ(I). L'arrangement atomique est caractérisé par des chaînes ondulées liées par des liaisons hydrogène (O-H...O) fortes faisant apparaître des tunnels qui se développent le long de la direction [001]. Les cations organiques, logés à l'intérieur de ces tunnels, sont maintenus aux groupements phosphates via de faibles liaisons hydrogène de type (N-H...O). La diffraction des rayons X sur poudre et les spectroscopies d'absorption IR et de résonance magnétique nucléaire RMN sont en bon accord avec l'étude structurale.

Mots clés: Synthèse Hydrothermale, Diffraction des Rayons X, Spectroscopies Infrarouge et RMN, Analyse Thermogravimétrique (ATG), Structure Cristalline.

INTRODUCTION

The possible interaction of the small dipole moments of $(HPO_4)^{2-}$ and $(H_2PO_4)^-$ units with dipole moments of the organic moieties may induce acentricity in new materials [1]. This has simulated great interest in the synthesis of novel amine phosphates and a large number of these compounds have been identified. Despite this, only limited amounts of characterization have been performed to date for cyclic alkylammonium hydrogen- and dihydrogen-monophosphate salts [2]. In the present paper, we report on the synthesis, crystal structure and characterization of a new cyclopentylammonium dihydrogenmonophosphate $[NC_5H_{12}^+]\bullet[H_2PO_4^-]$.

EXPERIMENTAL

Synthesis

The title compound was prepared hydrothermally from a mixture of CaO, H_3PO_4, HF, cyclopentylamine and water (molar ratio 1 : 3 : 3 : 4 : ~ 111). The reaction, run in a Parr 10 mL

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autoclave under autogenous pressure at 453 K for 5 days, leads to colorless sticks of $[NC_5H_{12}^+]\bullet[H_2PO_4^-]$ together with an unidentified powder. $[NC_5H_{12}^+]\bullet[H_2PO_4^-]$ can not be obtained from a mixture of equimolar proportions of cyclopentylamine and phosphoric acid in water and in the same preparative conditions.

Initial characterization was carried out using powder X-ray diffraction (XRD), thermogravimetric analysis, IR and NMR spectroscopic studies. The XRD pattern of this compound is entirely consistent with the pattern simulated from the coordinates of the single-crystal study (Fig. 1).

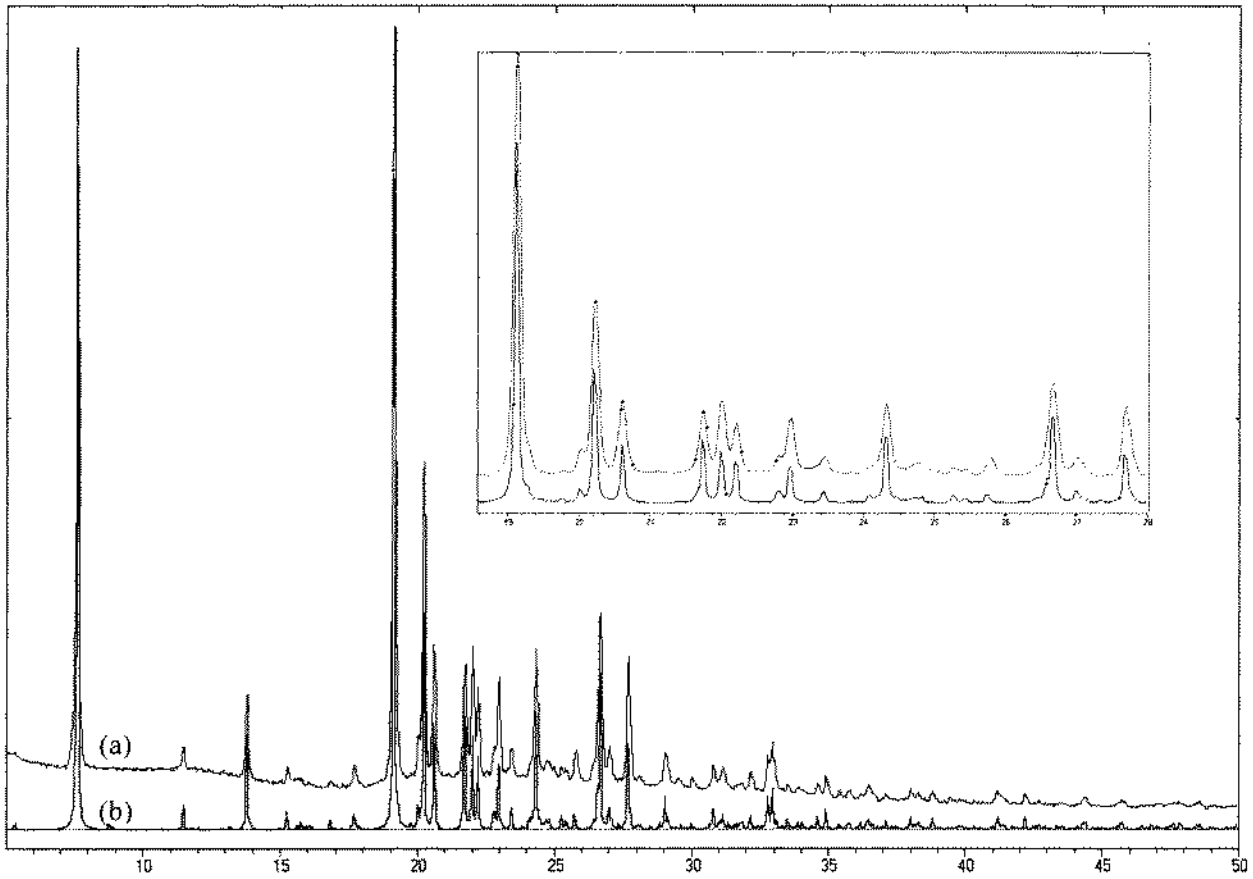

Figure 1 : X-ray powder diffraction pattern of $[NC_5H_{12}^+]\bullet[H_2PO_4^-]$: (a) experimental ; (b) simulated.

Physical measurements

- **Thermal Analysis :** TGA measurements were performed on a TA DTA-TGA SDT-2960 instrument in flowing N_2 with a heating rate of 5 $K.min^{-1}$ between room temperature and 400°C.
- **Infrared Spectroscopy :** IR data were collected in the 4000 - 400 cm^{-1} range with a Perkin-Elmer FT-IR 1000 spectrophotometer using KBr pellet technique. Spectra resolution was 4 cm^{-1}.
- **NMR spectroscopy** : ^{31}P MAS-NMR spectrum was recorded on a BRUKER Advance 300 spectrometer. The resonance frequency is 121.49 MHz. The chemical shifts were reported relative to 85 % H_3PO_4 as an external standard reference.

Structure determination

The reflections data were collected at room temperature on a Siemens AED-2 four circle diffractometer using the $\omega/2\theta$ scan technique. Intensities were corrected for Lorentz and polarization effects. A summary of crystal data and details of intensity measurement are presented in table I. Owing to the very small size of the crystal, numerous reflections were very weak and the reflections with $I > 4\sigma(I)$ were only used. The structure was solved in the centrosymmetric space

group $R\bar{3}$(N°148) by direct methods (SHELXS-97 [3]). The phosphorus atoms sites were first located. The O, C and N atoms were then deduced from Fourier difference maps (SHELXL-97 program[4]) and distances considerations. The examination of anisotropic thermal parameters, let conclude that some carbon atoms are disordered. Their distribution over two positions improves considerably the refinement. This disorder is observed in four of the seven crystallographically distinct cyclopentylammonium cations ; some of their carbon atoms are distributed between two sites (Fig. 2). A similar disorder has also been found in the structure of $[NC_5H_{12}^+]_2$•$[HPO_4^{2-}]$ earlier reported by Oliver et *al.* [2]. Hydrogen atoms of the hydroxyl groups, ammonium groups and the non disordered carbon atoms were placed geometrically ; their positions were calculated using the HFIX option of the SHELXL-97 program [4] and an overall $U_{(iso)}$ was fixed to 0.05 $Å^2$.

The final refinement with anisotropic thermal parameters for P, O, N and not disordered C atoms gives R = 0.056 and Rw = 0.25. The relatively high R factors can be due to the disorder observed in the organic cations. The atomic coordinates with equivalent isotropic ADPs and the main interatomic distances and angles are reported in table II and III, respectively. These final atomic coordinates and thermal parameters are deposited at the Cambridge Crystallographic Centre (CCDC 268718).

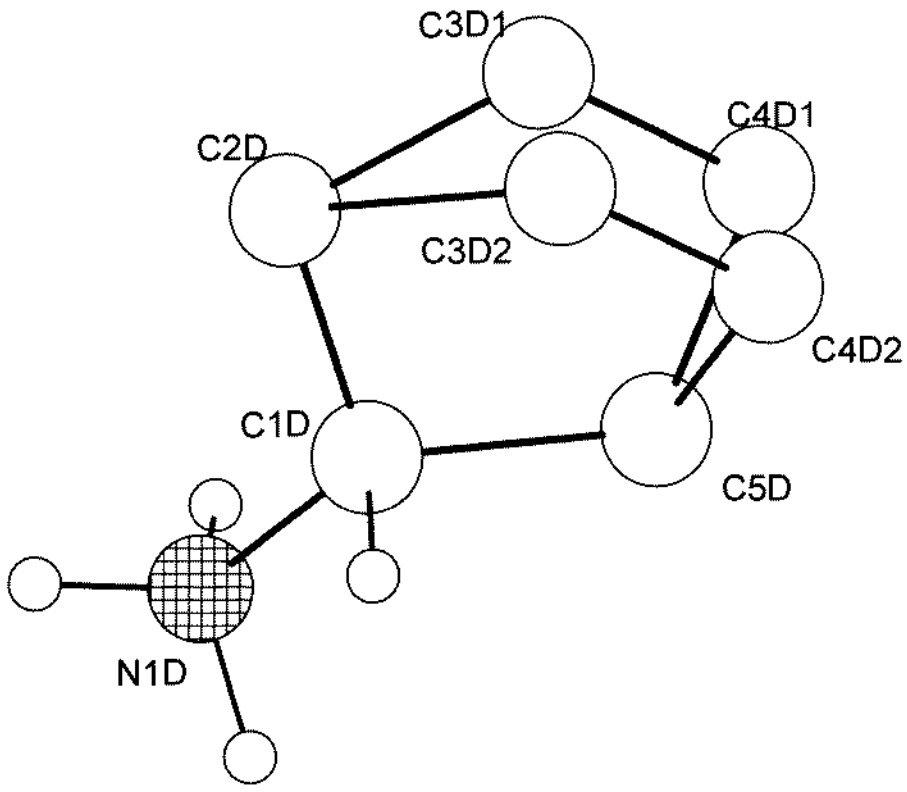

Figure 2 : View of a disordered cyclopentylammonium cation.

Table I: Crystal data, intensity measurements and refinement parameters for $[NC_5H_{12}^+]$•$[H_2PO_4^-]$

Crystallographic Formula	$[NC_5H_{12}^+]_7$•$[H_2PO_4^-]_7$	
Molecular weight (g. mol^{-1})	1282	
Space group	$R\bar{3}$ (N°148)	
Cell parameters	Hexagonal setting	Rhomboedral setting
	a = 23.218(4) Å	a = 23.636(8) Å
	c = 58.40 (3) Å	α = 58.83 (2)°
Volume; Z	27266.9(1) $Å^3$; 18	
ρ_{calc}, $\rho_{exp.}$ (g. cm^{-3})	1.405, 1.562(6)	
Absorption coefficient (mm^{-1})	0.29	
Absorption correction	None	
T(K) of data collection	293(2)	
Diffractometer	Siemens AED-2	
Radiation (graphite monochromated)	MoKα 0.71073 Å	
Scan mode	ω-2θ	
Limiting indices	$-23 \leq h \leq 23$, $-25 \leq k \leq 27$, $-38 \leq l \leq 69$	
2θ limit	50°	
Number of independent reflections ($I > 4\sigma(I)$)	5159	
Number of refinement parameters	706	
Final R indices	R= 0.056; Rw = 0.25	
Goodness-of-fit on F^2	1.201	
Weighting scheme	$1/[\sigma^2(F_0^2)+(0.1331P)^2+0.05P]$, $P=[\max(0 \text{ à } F_0^2)+2F_c^2]/3$	

Table II : Atomic coordinates and equivalent thermal parameters in $[NC_5H_{12}^+]$•$[H_2PO_4^-]$

Atoms	x(σ)	y(σ)	z(σ)	B_{eq}(Å^2)	Occupancy
P(1)	0.40235(8)	0.42703(8)	-0.00853(3)	3.61(3)	
P(2)	0.65735(7)	0.73175(7)	0.06999(2)	2.79(3)	
P(3)	0.32135(7)	0.10007(7)	0.11802(2)	2.90(3)	
P(4)	0.56417(7)	0.55266(7)	0.15015(2)	3.11(3)	
P(5)	0.38688(7)	0.41088(7)	0.12051(2)	2.95(3)	
P(6)	0.34389(7)	0.23802(7)	0.07060(2)	2.76(3)	
P(7)	0.20165(6)	0.29947(7)	0.03053(2)	2.54(2)	
O(1)	0.4336(2)	0.4354(2)	0.01448(6)	4.45(9)	
O(2)	0.3391(2)	0.4336(2)	-0.00695(9)	5.1(1)	
O(3)	0.4469(2)	0.4842(3)	-0.02522(7)	5.2(1)	
O(4)	0.3855(3)	0.3613(2)	-0.01935(7)	5.1(1)	
O(5)	0.7174(2)	0.7721(2)	0.05507(6)	3.35(7)	
O(6)	0.6721(2)	0.7298(2)	0.09487(6)	3.78(8)	
O(7)	0.6074(2)	0.7578(2)	0.06718(9)	4.54(9)	
O(8)	0.6184(2)	0.6578(2)	0.06156(6)	4.31(9)	
O(9)	0.3447(2)	0.0805(2)	0.13895(6)	4.07(9)	
O(10)	0.2556(2)	0.0410(2)	0.10849(8)	4.43(9)	
O(11)	0.3046(2)	0.1550(2)	0.12316(6)	3.33(7)	
O(12)	0.3751(2)	0.1231(2)	0.09921(6)	3.82(8)	
O(13)	0.5373(2)	0.5542(2)	0.12679(6)	3.30(7)	
O(14)	0.5120(2)	0.4880(2)	0.16295(6)	3.78(8)	
O(15)	0.6262(2)	0.5436(2)	0.14787(8)	4.50(9)	
O(16)	0.5809(2)	0.6122(2)	0.16447(7)	4.38(9)	
O(17)	0.3894(2)	0.3905(2)	0.09640(6)	4.09(9)	
O(18)	0.4095(2)	0.4864(2)	0.12184(7)	3.83(8)	
O(19)	0.4250(2)	0.3951(2)	0.13780(6)	3.57(8)	
O(20)	0.3115(2)	0.3751(3)	0.12704(6)	4.39(9)	
O(21)	0.2899(2)	0.2148(2)	0.08949(6)	3.37(7)	

Table II (cont.) : Atomic coordinates and equivalent thermal parameters in $[NC_5H_{12}^+]$•$[H_2PO_4^-]$

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O(22)	0.3604(2)	0.1832(2)	0.06532(6)	3.06(7)	
O(23)	0.3199(2)	0.2578(2)	0.04998(6)	3.97(8)	
O(24)	0.4093(2)	0.2975(2)	0.08005(8)	4.27(9)	
O(25)	0.2245(2)	0.3454(2)	0.05107(6)	2.83(6)	
O(26)	0.1275(2)	0.2756(2)	0.02511(6)	3.89(9)	
O(27)	0.2016(2)	0.2343(2)	0.03738(8)	4.48(9)	
O(28)	0.2399(2)	0.3286(2)	0.00910(7)	5.1(1)	
N(1A)	0.2788(2)	0.0731(2)	0.03585(7)	3.30(9)	
C(1A)	0.2204(3)	0.0820(3)	0.03350(9)	3.2(1)	
C(2A)	0.1844(3)	0.0720(4)	0.0565(1)	4.5(1)	
C(3A)	0.1134(4)	0.0461(4)	0.0498(1)	5.8(1)	
C(4A)	0.1016(3)	0.0058(5)	0.0289(1)	6.8(2)	
C(5A)	0.1681(3)	0.0325(3)	0.01686(9)	3.7(1)	
N(1B)	0.6098(2)	0.5525(2)	0.08921(7)	3.33(9)	
C(1B)	0.5885(3)	0.4869(3)	0.0790(1)	4.9(1)	
C(2B)	0.6421(5)	0.4915(5)	0.0620(1)	6.1(1)	
C(3B1)	0.677(1)	0.463(1)	0.0738(3)	5.2(5)*	0.42(3)
C(3B2)	0.652(2)	0.429(2)	0.0708(4)	9.0(5)	0.58(3)
C(4B1)	0.632(19)	0.423(2)	0.0943(5)	9.4(8)*	0.42(3)
C(4B2)	0.602(1)	0.390(1)	0.0867(3)	6.6(5)*	0.58(3)
C(5B)	0.5788(5)	0.4367(4)	0.0974(2)	7.8(2)	
N(1C)	0.2205(2)	0.2822(2)	0.09452(7)	3.01(9)	
C(1C)	0.1544(3)	0.2411(3)	0.1058(1)	4.1(1)	
C(2C)	0.1619(4)	0.2067(5)	0.1270(1)	6.6(2)	
C(3C)	0.1295(5)	0.1342(4)	0.1201(2)	7.6(2)	
C(4C)	0.0769(5)	0.1249(4)	0.1037(2)	8.1(2)	
C(5C)	0.1064(4)	0.1854(4)	0.0900(1)	5.8(1)	
N(1D)	0.3639(2)	0.4317(2)	0.05435(8)	3.44(9)	
C(1D)	0.3745(4)	0.4999(4)	0.0542(2)	7.7(2)	
C(2D)	0.3308(5)	0.5118(5)	0.0674(2)	8.1(2)	
C(3D1)	0.3697(7)	0.5893(7)	0.0714(3)	6.1(5)*	0.62(3)
C(3D2)	0.372(1)	0.596(2)	0.0567(4)	10.0(1)*	0.38(3)
C(4D1)	0.4421(9)	0.6092(8)	0.0711(4)	7.3(5)*	0.62(3)
C(4D2)	0.441(1)	0.613(1)	0.0582(6)	8.3(7)*	0.38(3)
C(5D)	0.4479(3)	0.5521(4)	0.0611(2)	7.3(2)	
N(1E)	0.7348(2)	0.1186(2)	0.15283(7)	3.33(9)	
C(1E)	0.7400(3)	0.1837(3)	0.1571(1)	3.7(1)	
C(2E)	0.7341(4)	0.2161(4)	0.1356(1)	5.7(1)	
C(3E)	0.7090(6)	0.2592(5)	0.1439(2)	7.8(2)	
C(4E)	0.6650(5)	0.2245(5)	0.1630(2)	7.8(2)	
C(5E)	0.6864(4)	0.1793(4)	0.1727(1)	5.1(1)	
N(1F)	0.3748(3)	0.2597(3)	0.00755(8)	3.9(1)	
C(1F)	0.4372(4)	0.2581(4)	0.0114(1)	5.3(1)	
C(2F)	0.4867(4)	0.3173(5)	0.0253(2)	7.4(2)	
C(3F1)	0.557(2)	0.354(3)	0.0122(5)	8.5(9)*	0.37(4)
C(3F2)	0.5540(9)	0.322(1)	0.0171(3)	7.2(9)*	0.63(4)
C(4F1)	0.552(2)	0.311(2)	-0.0069(5)	7.2(9)*	0.37(4)
C(4F2)	0.539(1)	0.276(1)	-0.0033(3)	6.7(5)*	0.63(4)
C(5F)	0.4705(4)	0.2588(5)	-0.0115(1)	7.1(2)	
N(1G)	0.6165(3)	0.7258(3)	0.13742(8)	4.3(1)	
C(1G)	0.5566(7)	0.7245(7)	0.1311(2)	9.8(3)	
C(2G1)	0.5230(8)	0.741(1)	0.1524(3)	9.4(5)*	0.58(1)
C(2G2)	0.499(1)	0.685(1)	0.1495(4)	7.5(5)*	0.42(1)
C(3G)	0.4534(7)	0.715(2)	0.1409(3)	15.2(6)	
C(4G1)	0.479(1)	0.755(1)	0.1214(4)	8.5(5)*	0.58(1)
C(4G2)	0.446(1)	0.681(1)	0.1231(5)	8.1(6)*	0.42(1)
C(5G1)	0.5528(7)	0.7712(8)	0.1202(3)	6.5(4)*	0.58(1)
C(5G2)	0.512(1)	0.687(1)	0.1168(4)	7.4(5)*	0.42(1)

* B_{iso}

Table III : Selected inter-atomic distances (Å) and angle in $[NC_5H_{12}^+]\cdot[H_2PO_4^-]$

$[P(1)O_4]$ Tetrahedron	**$[P(2)O_4]$ Tetrahedron**	**$[P(3)O_4]$ Tetrahedron**	**$[P(4)O_4]$ Tetrahedron**
P(1)-O(1) = 1.494(4)	P(2)-O(5) = 1.509(4)	P(3)-O(9) = 1.496(4)	P(4)-O(13) = 1.508(4)
P(1)-O(2) = 1.553(5)	P(2)-O(6) = 1.498(4)	P(3)-O(10) = 1.559(4)	P(4)-O(14) = 1.568(4)
P(1)-O(3) = 1.552(4)	P(2)-O(7) = 1.562(4)	P(3)-O(11) = 1.536(4)	P(4)-O(15) = 1.562(5)
P(1)-O(4) = 1.511(5)	P(2)-O(8) = 1.567(4)	P(3)-O(12) = 1.544(4)	P(4)-O(16) = 1.492(4)
<P(1)-O> = 1.527	<P(2)-O> = 1.534	<P(3)-O> = 1.534	<P(4)-O> = 1.532
O(1)-P(1)-O(4) =111.7(3)	O(6)-P(2)-O(5) = 115.1(2)	O(9)-P(3)-O(11) = 111.9(2)	O(14)-P(4)-O(13) = 108.9(2)
O(1)-P(1)-O(3) =112.4(3)	O(6)-P(2)-O(7) = 109.7(3)	O(9)-P(3)-O(12) = 109.5(2)	O(14)-P(4)-O(15) = 103.5(3)
O(1)-P(1)-O(2) = 110.9(3)	O(5)-P(2)-O(8) = 110.3(3)	O(11)-P(3)-O(12) = 110.4(2)	O(13)-P(4)-O(15) = 110.2(2)
O(4)-P(1)-O(3) = 109.0(3)	O(6)-P(2)-O(8) = 106.7(3)	O(9)-P(3)-O(10) = 111.6(3)	O(16)-P(4)-O(14) = 109.7(2)
O(4)-P(1)-O(2) = 110.1(3)	O(5)-P(2)-O(7) = 109.5(2)	O(11)-P(3)-O(10) = 104.9(2)	O(13)-P(4)-O(16) = 113.9(2)
O(3)-P(1)-O(2) = 102.3(3)	O(8)-P(2)-O(7) = 104.9(3)	O(12)-P(3)-O(10) = 108.5(3)	O(15)-P(4)-O(16) = 110.1(3)
<O-P(1)-O> = 109.4	<O-P(2)-O> = 109.37	<O-P(3)-O> =109.47	<O-P(4)-O> = 109.38

$[H_2P(5)O_4]$ Tetrahedron	**$[H_2P(6)O_4]$ Tetrahedron**	**$[H_2P(7)O_4]$ Tetrahedron**
P(5)-O(17) = 1.496(4)	P(6)-O(21) = 1.550(4)	P(7)-O(25) = 1.515(4)
P(5)-O(18) = 1.561(4)	P(6)-O(22) = 1.533(4)	P(7)-O(26) = 1.554(4)
P(5)-O(19) = 1.508(4)	P(6)-O(23) = 1.493(4)	P(7)-O(27) = 1.555(4)
P(5)-O(20) = 1.564(4)	P(6)-O(24) = 1.556(4)	P(7)-O(28) = 1.487(4)
<P(5)-O> = 1.532	<P(6)-O> = 1.533	<P(7)-O> = 1.528
O(17)-P(5)-O(18) = 111.0(2)	O(23)-P(6)-O(22) = 112.4(2)	O(28)-P(7)-O(25) = 115.3(2)
O(17)-P(5)-O(19) =115.7(2)	O(23)-P(6)-O(21) = 108.6(2)	O(28)-P(7)-O(26) = 107.1(3)
O(17)-P(5)-O(20) = 105.8(2)	O(22)-P(6)-O(21) = 110.4(2)	O(25)-P(7)-O(26) = 110.3(2)
O(18)-P(5)-O(19) = 109.4(2)	O(23)-P(6)-O(24) = 111.2(3)	O(28)-P(7)-O(27) = 111.5(3)
O(19)-P(5)-O(20) = 110.2(2)	O(22)-P(6)-O(24) = 105.6(2)	O(27)-P(7)-O(25) = 108.1(2)
O(18)-P(5)-O(20) = 104.0(3)	O(21)-P(6)-O(24) = 108.5(2)	O(26)-P(7)-O(27) = 104.0(3)
<O-P(5)-O> = 109.35	<O-P(6)-O> = 109.45	<O-P(7)-O> = 109.38

$[NC_5H_{12}(A)]^+$ Cation	**$[C_5NH_{12}(C)]^+$ Cation**	**$[C_5NH_{12}(E)]^+$ Cation**	**$[NC_5H_{12}(G)]^+$ Cation**
N(1A)–C(1A) = 1.477(7)	N(1C)–C(1C) = 1.494(7)	N(1E)–C(1E) = 1.477(7)	N(1G)–C(1G) = 1.42(1)
C(1A)–C(2A) = 1.535(8)	C(1C)–C(2C) = 1.53(1)	C(1E)–C(2E) = 1.505(9)	C(1G)–C(5G1) = 1.30(2)
C(1A)–C(5A) = 1.532(8)	C(1C)–C(5C) = 1.523(9)	C(1E)–C(5E) = 1.503(9)	C(1G)–C(5G2) = 1.28(2)
C(2A)–C(3A) = 1.495(9)	C(2C)–C(3C) = 1.51(1)	C(2E)–C(3E) = 1.47(1)	C(1G)–C(2G1) = 1.62(2)
C(3A)–C(4A) = 1.480(1)	C(3C)–C(4C) = 1.48(4)	C(3E)–C(4E) = 1.45(1)	C(1G)–C(2G2) = 1.59(2)
C(4A)–C(5A) = 1.516(9)	C(4C)–C(5C) = 1.474(9)	C(4E)–C(5E) = 1.48(1)	C(2G1)–C(3G) = 1.566(9)
			C(2G2)–C(3G) = 1.62(2)
$[NC_5H_{12}(B)]^+$ Cation	**$[NC_5H_{12}(D)]^+$ Cation**	**$[NC_5H_{12}(F)]^+$ Cation**	C(3G)-C(4G2) = 1.26(3)
N(1B)–C(1B) = 1.470(8)	N(1D)–C(1D) = 1.474(9)	N(1F)–C(1F) = 1.484(8)	C(3G)-C(4G1) = 1.40(2)
C(1B)–C(2B) = 1.555(10)	C(1D)–C(2D) = 1.41(1)	C(1F)–C(2F) = 1.51(1)	C(4G1)-C(5G1) = 1.57(2)
C(1B)–C(5B) = 1.515(11)	C(1D)–C(5D) = 1.57(1)	C(1F)–C(5F) = 1.54(1)	C(4G2)-C(5G2) = 1.36(5)
C(2B)–C(3B1) = 1.459(18)	C(2D)–C(3D1) = 1.57(2)	C(2F)–C(3F1) = 1.58(3)	
C(2B)–C(3B2) = 1.65(3)	C(2D)–C(3D2) = 1.80(4)	C(2F)–C(3F2) = 1.59(2)	
C(3B1)–C(4B1) = 1.56(3)	C(3D1)–C(4D1) = 1.51(2)	C(3F1)–C(4F1) = 1.46(4)	
C(3B2)–C(4B2) = 1.41(3)	C(3D2)–C(4D2) = 1.43(4)	C(3F2)-C(4F2) = 1.42(3)	
C(4B1)-C(5B) = 1.43(2)	C(4D1)-C(5D) = 1.52(2)	C(4F1)-C(5F) = 1.67(3)	
C(4B2)-C(5B) = 1.56(2)	C(4D2)-C(5D) = 1.52(3)	C(4F2)-C(5F) = 1.50(2)	

RESULTS AND DISCUSSION

Description of the structure and discussion

The asymmetric unit of $[NC_5H_{12}^+]\bullet[H_2PO_4^-]$ contains seven crystallographically independent phosphate groups and seven crystallographically distinct organic cations. In the atomic arrangement, the $(H_2PO_4)^-$ entities are linked together through strong (O-H...O) hydrogen bonds (Table IV) to form extended corrugated chains, $\infty(H_2PO_4)^-$, with a medium axis parallel to the *c* direction. These chains, organized around 3_1 axis, are held together through strong hydrogen bonding to delimit tunnels within which the cyclopentylammonium cations lie (Fig. 3-4). An extensive hydrogen bonding network exists between the phosphates groups and the cyclopentylammonium cations (Table IV). Each organic entity is anchored on to the anionic network via the ammonium groups allowing a certain flexibility of the cycles what could explain the disorder observed in this structure.

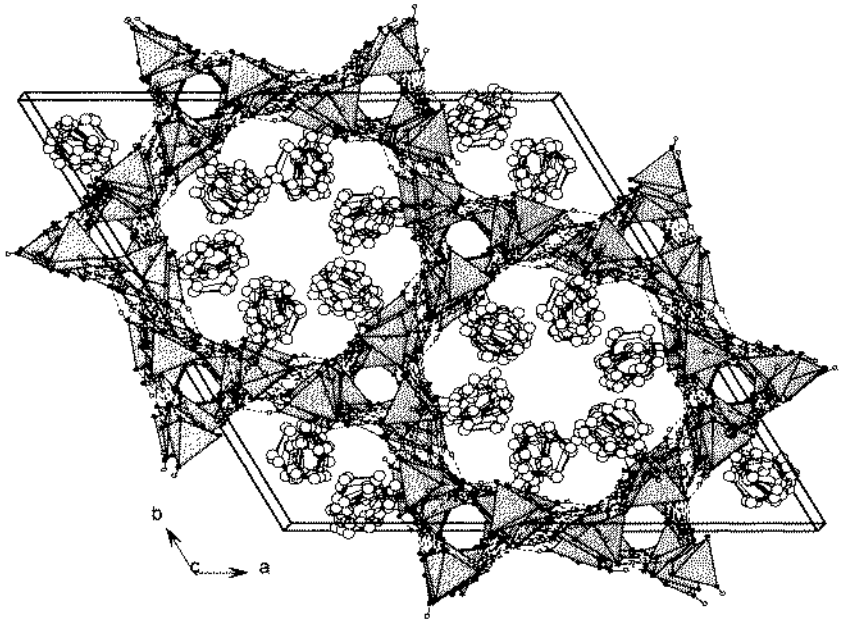

Figure 3 : Perspective view of the structure of $[NC_5H_{12}^+]\bullet[H_2PO_4^-]$.

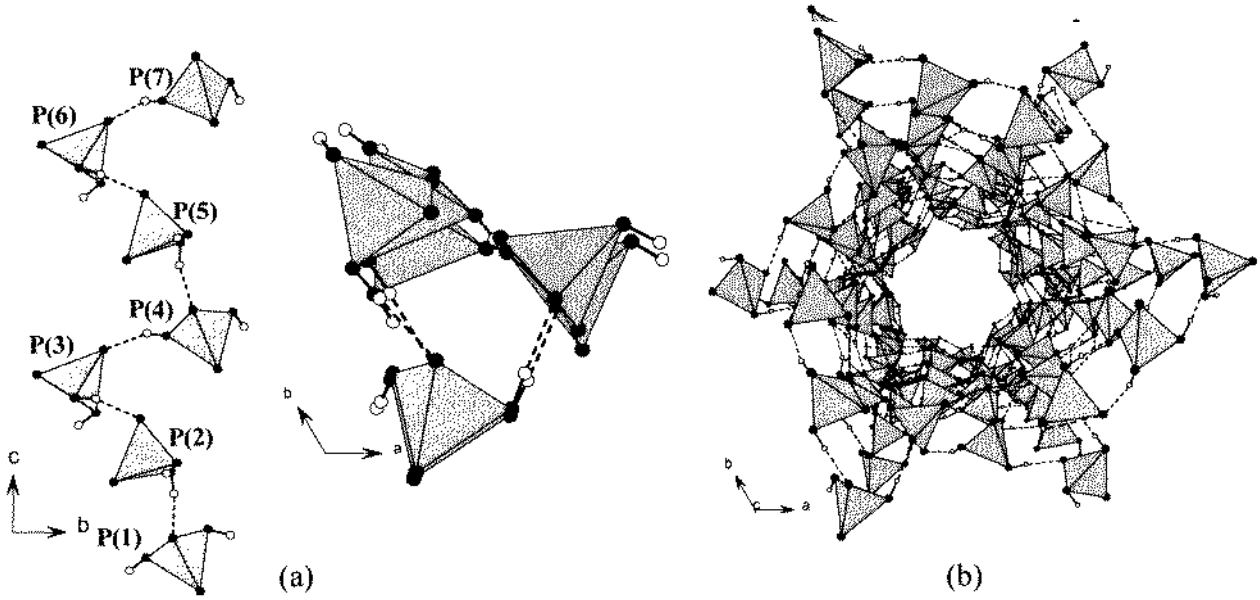

Figure 4 : Infinite chains $\infty(H_2PO_4)^-$ (a) and tunnels (b) in $[NC_5H_{12}^+]\bullet[H_2PO_4^-]$.

The geometrical features of the seven distinct phosphorus groups are quite regular (Table III) : the P-O distances vary from 1.487(4) to 1.568(4) Å and the O-P-O angles vary from 102.3(3) to 115.7(2)°. The lowest distances (1.487(4)-1.536(4) Å) correspond to P=O bond length while the longest (1.544(4)-1.568(4) Å) correspond to the P-O(H) bonds. These distances are in good agreement with given in the literature [1, 2, 15]. For the cyclopentylammonium cations the N-C and C-C distances lying respectively within the range (1.41(1)-1.484(8) Å) and (1.26(3)-1.80(4) Å) (Table III) are very close to those observed in the structure of $[NC_5H_{12}^+]_2$•$[HPO_4^{2-}]$ obtained with the same organic amine [2].

Table IV : Hydrogen-bond scheme in $[NC_5H_{12}^+]$•$[H_2PO_4^-]$

D–H...A	H...A (Å)	D...A (Å)	D-H...A (°)
O(2)–H(2)...O(28)	1.77	2.552(6)	158.1
O(3)–H(3)...O(1)^{i}	1.73	2.528(6)	165.1
O(7)–H(7)...O(25)^{ii}	1.83	2.631(5)	166.3
O(8)–H(8)...O(4)^{i}	1.72	2.499(6)	158.6
O(10)–H(10)...O(6)^{iii}	1.80	2.604(6)	168.0
O(12)–H(12)...O(22)	1.73	2.541(5)	168.1
O(14)–H(14)...O(19)	1.757	2.557(6)	164.49
O(15)–H(15)...O(9)^{iv}	1.814	2.627(6)	170.86
O(18)–H(18)...O(13)	1.77	2.589(6)	173.8
O(20)–H(20)...O(16)^{v}	1.75	2.532(6)	158.4
O(21)–H(21)...O(11)	1.74	2.527(5)	160.3
O(24)–H(24)...O(17)	1.79	2.605(6)	170.6
O(26)–H(26)...O(5)^{vi}	1.87	2.494(5)	132.0
O(27)–H(27)...O(23)	1.98	2.623(6)	134.2
N(1A)–H(1A1)...O(22)	2.0	2.871(6)	166.5
N(1A)–H(1A2)...O(28)^{vii}	1.94	2.821(6)	172.3
N(1A)–H(1A3)...O(5)^{iii}	1.94	2.821(6)	172.3
N(1B)–H(1B1)...O(13)	1.90	2.777(6)	169.3
N(1B)–H(1B2)...O(8)	2.00	2.854(6)	161.5
N(1B)–H(1B3)...O(12)^{iv}	1.96	2.840(6)	171.1
N(1C)–H(1C1)...O(21)	1.90	2.768(6)	165.6
N(1C)–H(1C2)...O(20)	1.98	2.857(6)	170.8
N(1C)–H(1C3)...O(25)	2.04	2.910(6)	167.1
N(1D)–H(1D1)...O(17)	1.92	2.804(6)	170.6
N(1D)–H(1D2)...O(1)	1.95	2.813(6)	164.2
N(1D)–H(1D3)...O(25)	1.95	2.837(6)	171.0
N(1E)–H(1E1)...O(19)^{iii}	1.92	2.810(6)	172.8
N(1E)–H(1E2)...O(9)^{viii}	1.87	2.760(6)	176.5
N(1E)–H(1E3)...O(11)^{iii}	1.99	2.869(6)	171.2
N(1F)–H(1F1)...O(23)	1.89	2.778(7)	175.1
N(1F)–H(1F2)...O(26)^{vi}	2.24	3.112(7)	166.3
N(1F)–H(1F3)...O(4)	1.86	2.741(7)	170.0
N(1G)–H(1G1)...O(6)	1.90	2.780(6)	169.5
N(1G)–H(1G2)...O(16)	1.93	2.820(7)	173.9
N(1G)–H(1G3)...O(14)^{ix}	2.21	3.098(7)	171.8

Symmetry codes : i = -x+1, -y+1, -z ; ii = -y+1, x-y+1, z ; iii = -y+1, x-y, z ; iv = -x+y+1, -x+1, z ; v = y-1/3, -x+y+1/3, -z+1/3 ; vi = -x+y, -x+1, z ; vii = y, -x+y, -z ; viii = y+2/3, -x+y+1/3, -z+1/3 ; ix= x-y+2/3, x+1/3, -z+1/3.

Thermal Analysis

The thermal analysis of $[NC_5H_{12}^+]$•$[H_2PO_4^-]$ gives a total weight loss of 47.7 % in two steps (Fig. 5). The weight loss of 13.9 % in the range 140 - 240°C can be attributed to the loss of water molecules coming from the dehydration of $(H_2PO_4)^-$ groups (calculated 9.8 %). The weight loss of 33.84 % should corresponds to the beginning of the degradation of the organic molecule (the calculated weight loss for an achieved degradation is 47 %). The slight difference between

experimental and calculated weight losses can he explained hy the fact that the degradation of the organic molecule, not completed at 400°C, starts while the loss of water molecules is not achieved.

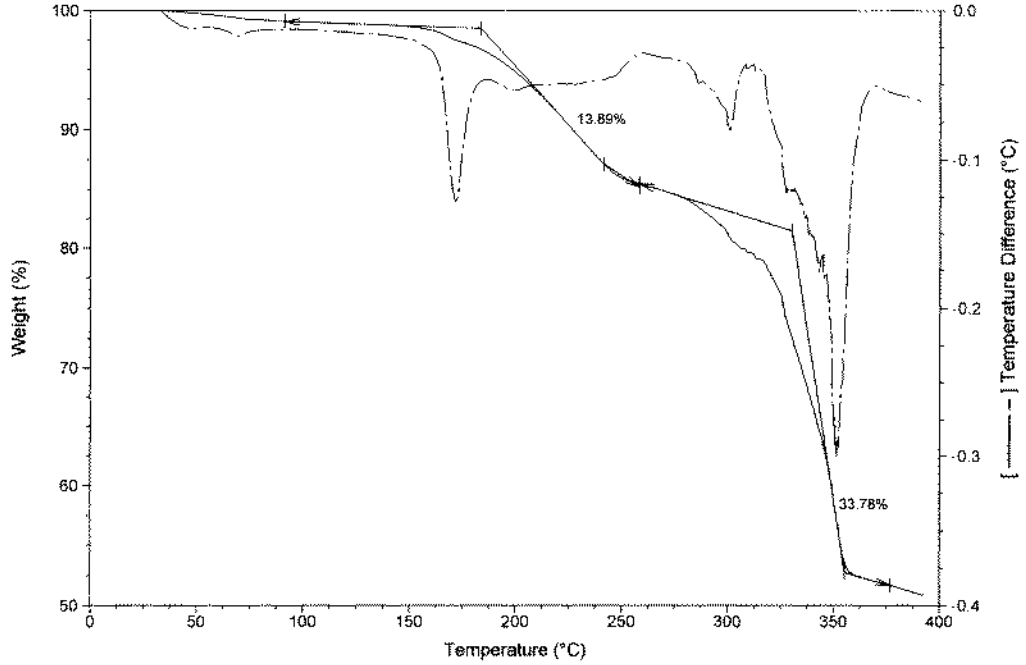

Figure 5 : TGA-DTA curves showing thermal behavior of $[NC_5H_{12}^+]\bullet[H_2PO_4^-]$.

Infrared Spectroscopy

Infrared spectrum of $[NC_5H_{12}^+]\bullet[H_2PO_4^-]$ is presented in figure 6. As a whole, the ohserved bands can be regrouped in three domains : (600-400 cm^{-1}) and (1200-900 cm^{-1}) corresponding to the bending and stretching modes of the (PO_4) groups, and (3500-1200 cm^{-1}) attributed to combination of (N(C,O)-H) bending and stretching modes. In tahle V we report the proposal vibrational assignments that have heen carried out on the basis of comparison with infrared spectra of the as-synthesized organic hydrogen phosphates and others reported from the literature [5-10].

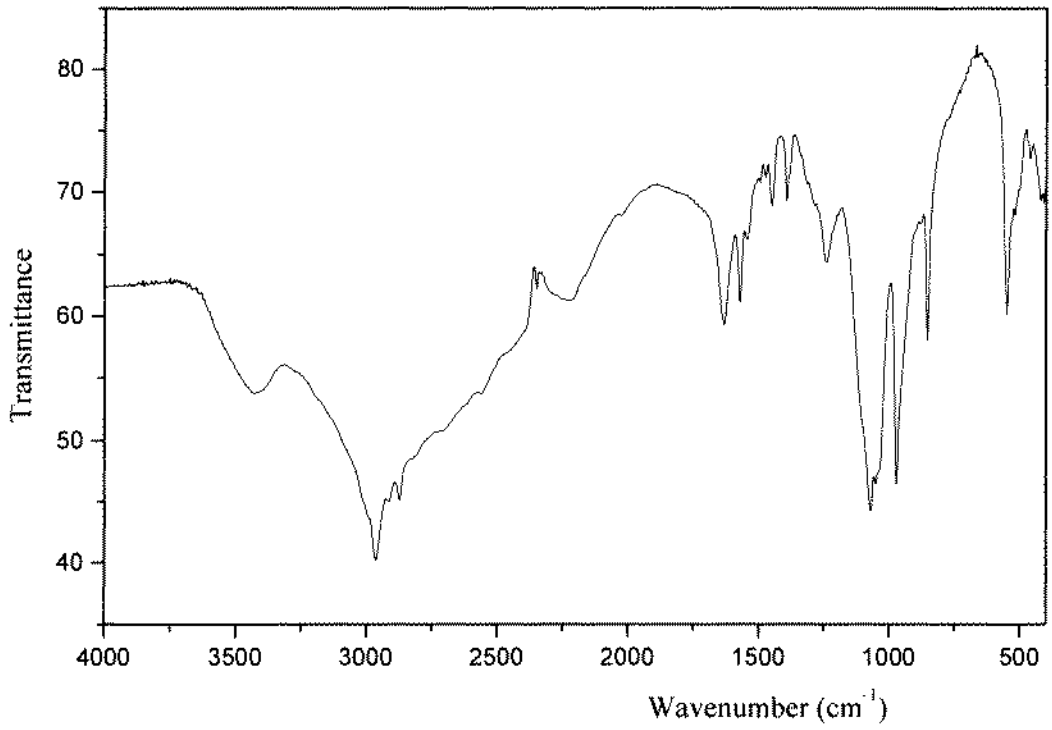

Figure 6 : IR spectrum of $[NC_5H_{12}^+]\bullet[H_2PO_4^-]$.

Table V: Band attribution of IR spectrum of $[NC_5H_{12}^+]\bullet[H_2PO_4^-]$

Bands (cm^{-1})	Attribution
3425 (m) ; 3000 (sh) 2972 (w) ; 2964(m) 2915 (w) ; 2872(w) 2714 (w) ; 2561 (w) 2453 (w) ; 2213 (m) 2023 (w)	$\nu_{(O\text{-}H)}$, $\nu_{(C\text{-}H)}$ + $\nu_{(N\text{-}H)}$
1571 (s) ; 1544 (w) ; 1495 (w) ; 1473 (w) ; 1446 (s)	$\delta_{s(NH3)}$ + $\delta_{s(CH2)}$
1385 (s) ; 1346 (w) 1305 (sh) ; 1275 (sh) 1240(s)	$\delta_{as(NH3)}$ + $\delta_{as(CH2)}$ + $\delta_{dp(P\text{-}O\text{-}H)}$
1070 (s) ; 1049 (s) 1034 (sh)	$\nu_{3(vas(P\text{-}O))}$ + $\nu_{(C\text{-}C)}$ + $\nu_{(C\text{-}N)}$
972 (s) ; 850 (s)	$\nu_{1(vs(P\text{-}O))}$ + $\delta_{hp(P\text{-}O\text{-}H)}$
548 (s) ; 515 (w)	$\nu_4(\delta_{O\text{-}P\text{-}O})$
461 (w) ; 417 (m)	$\nu_{2(\delta s(O\text{-}P\text{-}O))}$ + $\delta_{(C\text{-}C)}$ + $\delta_{(C\text{-}N)}$

s, strong ; m, medium ; w, weak ; sh, shoulder

NMR Spectroscopy

^{31}P MAS solid state NMR spectrum of $[NC_5H_{12}^+]\bullet[H_2PO_4^-]$ is reported in figure 7. Two resonance peaks at -2.22 and 0.9 ppm are observed. Their chemical shift values are in the range of those in phosphates reported in literature [11-13]. These two signals with an intensity ratio close to 2 : 5 are in agreement with the presence of seven phosphorus atoms in the framework, which is consistent with the crystal structure results. On the basis of the study of Un & Klein [14] and X-ray structural analysis, the lower field signal (δ = -2.22 ppm) might correspond to P(7) and P(1) phosphorus atoms. In fact these two phosphorus atoms present a lower P-O bond length average (<P(1)-O>=1.527 Å, <P(2)-O>=1.528 Å). The sharp peak at 0.9 ppm might be attributed to the five remaining phosphorus atoms presenting a similar <P-O> distances (<P(2)-O> = <P(3)-O>=1.534 Å, <P(4)-O> = <P(5)-O>=1.532 Å, <P(6)-O>=1.533 Å).

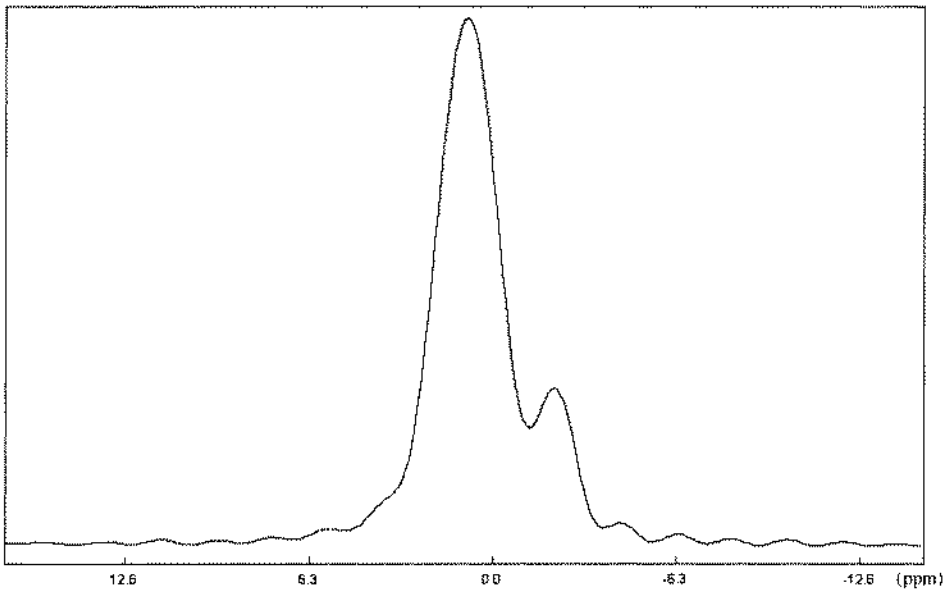

Figure 7 : ^{31}P MAS NMR spectrum of $[NC_5H_{12}^+]\bullet[H_2PO_4^-]$

CONCLUSION

In summary, synthesis, crystal structure, thermal behavior, IR and ^{31}P MAS NMR spectroscopic studies of a novel cyclopentylammonium dihydrogenmonophosphate $[NC_5H_{12}^+]\bullet[H_2PO_4^-]$ have been described. The structure consists of infinite corrugated chains linked together via strong H bonds to delimit channels within which the organic cations lie. The IR spectrum analyzed by comparison with those of others hydrogen phosphates, reveals the characteristic bands of phosphate anions and amine cations. TGA analysis shows that the thermal stability of this compound is poor. The ^{31}P MAS NMR spectroscopic study is consistent with the presence of seven phosphorus atoms in the framework.

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