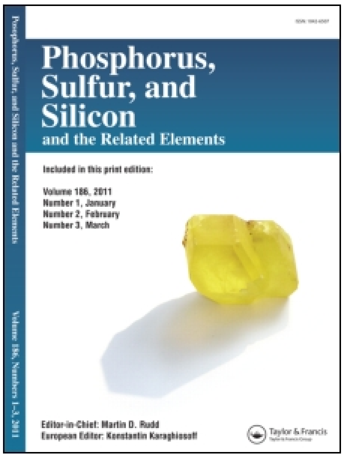

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Characterization of a New Monophosphate $(C_6H_6NCl_2)(H_2PO_4)$ with an Interesting Chlorine-Mediated Framework

R. Kefi[a]; C. Ben Nasr[a]; F. Lefebvre[b]
[a] Laboratoire de chimie des Matériaux, Faculté des Sciences de Bizerte, Zarzouna, Tunisie [b] Laboratoire de Chimie Organométallique de Surface (LCOMS), Ecole Supérieure de Chimie Physique Electronique, Villeurbanne Cedex, France

To cite this Article Kefi, R. , Nasr, C. Ben and Lefebvre, F.(2007) 'Synthesis and Characterization of a New Monophosphate $(C_6H_6NCl_2)(H_2PO_4)$ with an Interesting Chlorine-Mediated Framework', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 9, 2053 — 2068

To link to this Article: DOI: 10.1080/10426500701370300
URL: http://dx.doi.org/10.1080/10426500701370300

Phosphorus, Sulfur, and Silicon, 182:2053–2068, 2007

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500701370300

Synthesis and Characterization of a New Monophosphate $(C_6H_6NCl_2)(H_2PO_4)$ with an Interesting Chlorine-Mediated Framework

R. Kefi
C. Ben Nasr
Laboratoire de chimie des Matériaux, Faculté des Sciences de Bizerte, Zarzouna, Tunisie

F. Lefebvre
Laboratoire de Chimie Organométallique de Surface (LCOMS),
Ecole Supérieure de Chimie Physique Electronique,
Villeurbanne Cedex, France

Chemical preparation, crystal structure, and NMR spectroscopy of a new monophosphate with 2,3-dichloroanilinium cation are given. This new compound crystallizes in the monoclinic system, with the space group P21/n and the following parameters: $a = 11.031\ (6)$, $b = 6.007(3)$, $c = 15.227(2)$ Å $\beta = 98.98(4)$, $V = 996.73(3)$ Å^3, and $Z = 4$. The crystal structure has been determined and refined to $R = 0.048$ and $R_w = 0.1317$ using 2030 independent reflections. The structure can be described as clusters that aggregate with six organic molecules, resulting in a $(1\ 0\ \bar{1})$ two dimensional sheet, and formation of arrays in three dimensions, via various interactions (H-bonds, electrostatic, Van der Waals). In addition, C—Cl$\cdots\pi$ interactions are observed as a consequence of the chlorine atom being flanked by two phenyl rings of the neighboring molecules. The structure has also short intermolecular Cl$\cdots$Cl interactions [type I, Cl$\cdots$Cl = 3.380(1) Å, C—Cl$\cdots$Cl′ = 132.26°]. This compound has also been investigated by IR, thermal analysis, and solid-state ^{13}C and ^{31}P MAS NMR spectroscopy combined with Ab Initio calculations.

Keywords Ab Initio calculations; hydrogen bonds; inorganic layer; IR spectroscopy; NMR spectroscopy; X-ray diffraction

INTRODUCTION

Among the various categories of phosphates, monophosphates are the most numerous, not only because they were the first to be investigated, but also because they are the most stable and therefore the only

Received February 1, 2007; accepted March 14, 2007.

Address correspondence to C. Ben Nasr, Laboratoire de chimie des Materiaux, Faculte des Sciences de Bizerte, Zarzouna 7021, Tunisie. E-mail: cherif.bennasr@fsb.rnu.tn

phosphates to be found in nature. These compounds have been of great interest over recent years from both academic and industrial points of view,[1] due to their wide structural and compositional diversities. Among these materials, organic phosphates are particularly interesting. It has been found that the hydrogen bonds and the nature of organic molecules seem to determine the molecular organization of these compounds as to build infinite anionic networks with various geometries: ribbons,[2] chains,[3] two-dimensional networks,[4] and three-dimensional networks.[5] In order to study the influence of hydrogen bonds on the chemical and structural features, we report and discuss the results of a structural investigation concerning a new organic-cation monophosphate $(C_6H_6NCl_2)(H_2PO_4)$. This molecule has also been characterized by IR spectroscopy, differential thermal analysis, ^{31}P and ^{13}C solid state MAS NMR spectroscopy combined with Ab Initio calculations and ionic conductivity.

RESULTS AND DISCUSSION

Structure Description

Molecular structure of the monophosphate is displayed in Figure 1 and the crystallographic data are listed in Table I. The final atomic

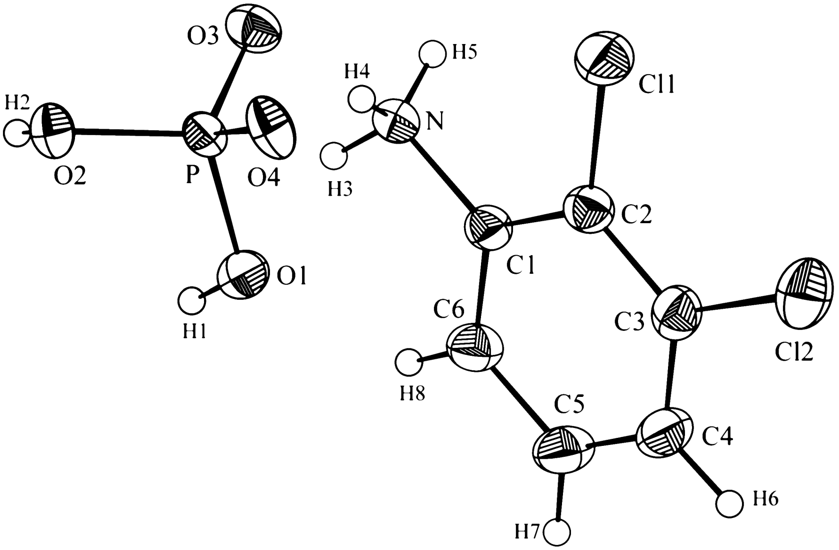

FIGURE 1 ORTEP representation of the asymmetric unit of the $(C_6H_6NCl_2)(H_2PO_4)$.

TABLE I Crystal Data and Experimental Parameters Used for the Intensity Data Collection Strategy and Final Results of the Structure Determination

I. Crystal data	
Formula: ($C_6NH_6Cl_2$)(H_2PO_4)	$F_w = 261.10$
Crystal system: monoclinic	
a = 11.031(6), b = 6.007(3), c = 15.227(2) Å β = 98.98(4)°, V = 996.73(3) Å^3. Z = 4	Space group : P21/n
Refinement of unit-cell parameters with $\rho_{\text{cal.}}$ = 1.813 g·cm^{-3}	25 reflection (7° < θ < 10°) $F(000) = 576.00$
Linear absorption factor : μ (Ag Kα) = 0.801 cm^{-1}	Morphology : prism
Crystal size (mm) : 0.34 × 0.26 × 0.20	Color : transparent
II. Intensity measurements	
Temperature : 293.2 K	Wavelenght : MoK_α(0.7107 Å)
Diffractometer : Enraf-Nonius MACH 3	Scan mode: ω - 2θ
Monochromator : graphite plate	Theta range : 2.71 – 27.43°
Measurement area: (± *h. k. l*)	$h_{\text{max.}} = 12; k_{\text{max.}} = 7; l_{\text{max.}} = 19$
Number of scanned reflections	2276 ($R_{\text{int.}} = 0.057$)
Number of independent reflections	2030
Orientation and control reflections	−2 −8 −5 and −2 8 −5
III. Structure determination	
Program used : SHELX-97[29]	Determination: direct methods
All the hydrogen atoms were located from difference	
Absorption correction: Analytical[30]	Tmin = 0.7950, Tmax = 0.8561
Fourier maps. They are not refined.	
Unique reflections included: (2030(I >2 $^\sigma$))	Refined parameters : 140
Weighting scheme: σ	$R = 0.048$; $R_w = 0.1317$
Residual Fourier density: −0.64 Å^3<ρ 0.08 Å^3	Goodness-of-fit on F^2: 1.081
Drawings made with Diamond[31]	Largest shift/error = 0.052

coordinates of all atoms and their equivalent isotropic temperature factors U(eq) are given in Table II. The main geometrical features of the different entities are reported in Table III.

Figure 2 displays the crystal structure viewed along the **a** direction. This projection shows that the atomic arrangement of this compound is built up by $(H_4P_2O_8)^{2-}$ clusters. Each cluster aggregates with six organic molecule, resulting in $(1\ 0\ \bar{1})$ two dimensional sheets (Figure 3). Arrays are finally formed in three dimensions via various interactions (H-bonds, electrostatic, van der Waals).

The detailed geometry of the $H_2PO_4^-$ anion indicates that the P=O bonds are significantly shorter [1.534(1)–1.495(2) Å] than the P—OH bonds [1.572(4)–1.545(8) Å]. It is well known that P—OH distances are,

TABLE II Final Atomic Coordinates and U(eq) in $(C_6H_6NCl_2)(H_2PO_4)$. Esd are Given in Parentheses

Atoms	x	y	z	U(eq) (Å^2)
Cl(1)	0.63164(6)	0.28120(12)	0.37109(5)	0.0490(2)
Cl(2)	0.39799(8)	0.20240(13)	0.46366(5)	0.0546(2)
P(1)	0.06902(5)	0.25836(9)	0.59067(4)	0.02759(19)
O(1)	−0.05210(15)	0.1354(3)	0.60521(12)	0.0398(4)
O(2)	0.07827(16)	0.2452(3)	0.49055(11)	0.0329(4)
O(3)	0.05084(16)	0.5013(3)	0.61676(11)	0.0390(4)
O(4)	0.17673(14)	0.1518(3)	0.64685(11)	0.0362(4)
N(1)	0.61709(16)	0.6868(3)	0.25468(12)	0.0296(4)
C(1)	0.51017(19)	0.6442(4)	0.29724(14)	0.0304(4)
C(2)	0.5073(2)	0.4600(4)	0.35248(14)	0.0331(5)
C(3)	0.4044(2)	0.4256(4)	0.39319(15)	0.0375(5)
C(4)	0.3063(2)	0.5718(5)	0.37888(17)	0.0436(6)
C(5)	0.3099(2)	0.7507(4)	0.3232(2)	0.0447(6)
C(6)	0.4121(2)	0.7885(4)	0.28192(18)	0.0396(5)
H(1)	−0.0630	0.0057	0.5772	0.082(13)
H(2)	0.093(3)	0.117(6)	0.477(2)	0.049
H(3)	0.597(2)	0.806(4)	0.2174(19)	0.030(6)
H(4)	0.6271	0.5614	0.2252	0.057(9)
H(5)	0.6824	0.7247	0.2918	0.043(8)
H(6)	0.2348	0.5447	0.4097	0.071(11)
H(7)	0.2424	0.8548	0.3146	0.040(7)
H(8)	0.4123	0.9203	0.2460	0.058(9)

in general, longer than P—O distances, and they increase as the strength of the O—H· · ·O hydrogen bond increases, that is as the O· · ·O distance decreases. Moreover, it is also rather well established that in response to an increase of the P—OH bond lengths, the remaining P=O bonds of a PO_4 group tend to shorten. Decreases in the $O_A\cdots O_D$ distance are also accompanied by a decrease in the difference between the H—O_D and H· · ·O_A distances, and there is a tendency for very strong hydrogen bonds to be symmetric (where O_D and O_A are donor and acceptor oxygen atoms, respectively, in the O_D—H· · ·OA bond).[6,7] In our investigation of $(C_6H_6NCl_2)(H_2PO_4)$ structure, the use of correlations between P—OH, P=O, and O· · ·O distances proved to be a powerful tool for identifying donor and acceptor oxygen atoms. Hydrogen bonding has a key role in linking the template molecules with the clusters made by H_2PO_4 moieties. All the D(donor)-H· · ·A(acceptor) hydrogen bonds are listed in Table III, with an upper limit of 1.97 Å for H· · ·A distances and a lower limit of 148° for the D—H· · ·A bond angles. This atomic arrangement with medium (between 1.82 and 1.97 Å) O(P)—H· · ·O distances involving two H· · ·O contacts ensures the cohesion between the PO_4 tetrahedra to build the clusters, whereas three N—H· · ·O hydrogen bonds

TABLE III Interatomic Distances (Å) and Bond Angles (°) in $(C_6H_6NCl_2)(H_2PO_4)$. Esd are Given in Parentheses

The PO_4 tetrahedron				
P	O(1)	O(2)	O(3)	O(4)
O(1)	1.572(4)	2.517(2)	2.468(2)	2.507(2)
O(2)	107.65(10)	1.545(8)	2.517(2)	2.520(2)
O(3)	105.19(10)	109.61(9)	1.534(1)	2.520(2)
O(4)	109.58(10)	111.93(10)	112.54(10)	1.495(2)
O(1)-H(1) = 0.88 Å			P-O(1)-H(1) = 113.54°	
O(2)-H(2) = 0.82 Å			P-O(2)-H(2) = 109.47°	
$(C_6H_6NCl_2)^+$ group				
Cl(1)-C(2)	1.730(2)		C(6)-C(1)-C(2)	120.72
Cl(2)-C(3)	1.726(3)		C(6)-C(1)-N(1)	118.92
N(1)-C(1)	1.454(3)		C(2)-C(1)-N(1)	120.32
C(1)-C(6)	1.377(3)		C(4)-C(5)-C(6)	120.62
C(1)-C(2)	1.393(3)		C(1)-C(6)-C(5)	119.42
C(5)-C(4)	1.374(4)		C(3)-C(2)-C(1)	118.92
C(5)-C(6)	1.393(4)		C(3)-C(2)-Cl(1)	121.06
C(2)-C(3)	1.391(3)		C(1)-C(2)-Cl(1)	120.01
C(3)-C(4)	1.385(4)		C(4)-C(3)-C(2)	120.62
			C(4)-C(3)-Cl(2)	118.89
			C(2)-C(3)-Cl(2)	120.53
			C(5)-C(4)-C(3)	119.72
Hydrogen bonds				
O(N)—-H···O	O(N)—H	H—O	O(N)—O	O(N)—H—O
O(1)-H(1)···O(2)	0.89	1.82	2.703(3)	173
O(2)-H(2)···O(1)	0.83	1.97	2.703(3)	148
N(1)-H(3)···O(3)	0.92	1.93	2.824(2)	166
N(1)-H(4)···O(4)	0.89	1.89	2.758(2)	164
N(1)-H(5)···O(4)	0.87	1.84	2.701(2)	168

(with H···O values in the range 1.84–1.93 Å) connect the clusters and the organic ligands.

The calculated average values of distortion indices corresponding to the different angles and distances in the PO_4 tetrahedra [DI(OPO) = 0.018; DI(PO) = 0.014 and DI(OO) = 0.005], exhibit a pronounced distortion of the PO distances and OPO angles if compared to OO distances; so the phosphate group can be considered as a rigid regular arrangement of oxygen atoms, with the P atom displaced from their centroid.[8] As expected, O=P=O angle (112.54°) are significantly bigger than O—P—O angles with an OH group involved therein (average 109.07°). The O—P—O angle with two OH residues is again significantly smaller (107.65°). These geometrical features have also been noted in other crystal structures.[9,10]

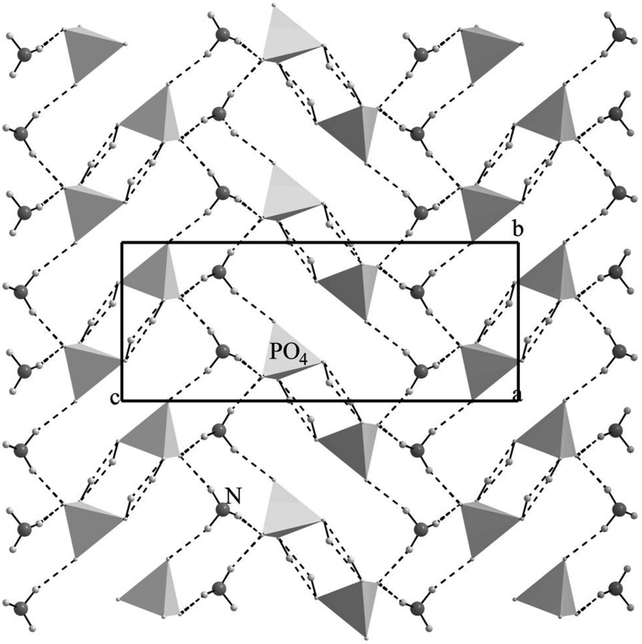

FIGURE 2 Projection of $(C_6H_6NCl_2)(H_2PO_4)$ structure in the plane (a, c).

Interactions involving the chlorine atoms seem to play a dominant role in the crystallization of the present compound. Although interactions involving halogens restrict the number of possible modes of packing, it seems difficult to have a predictive approach of the structure.

Concerning the directionality of the observed interchlorine contacts, all contacts shorter than 3.4 Å are symmetrical, in most cases having exact or approximate head-on directions, whereas those with distances between 3.4 and 4 Å are either symmetrical (type I) or asymmetrical (type II) contacts,[11,12] the asymmetrical ones being the majority. Considering the interchlorine atoms distances, it is obvious that there is an important Cl· · ·Cl interaction (type I) [d(Cl(2)-Cl(2)^i) 3.380(1) Å] (i = -x; -l-y; -z) with a value considerably less than the sum of the conventional isotropic van der Waals radii (which are about 3.52 Å for chlorine). It should also be pointed out that the C(5)-Cl(2)-Cl(2)^i θ angle is 132.26°. A Database analysis of halogen-halogen contacts showed that when the X· · ·X (X = halogen) contact distance is significantly lower than the van der Waals sum, the associated C—X· · ·X angles are clustered around 180 and 90°;[13] the C—Cl· · ·Cl angle observed is not particularly close to either cluster, and almost certainly its value is constrained by the

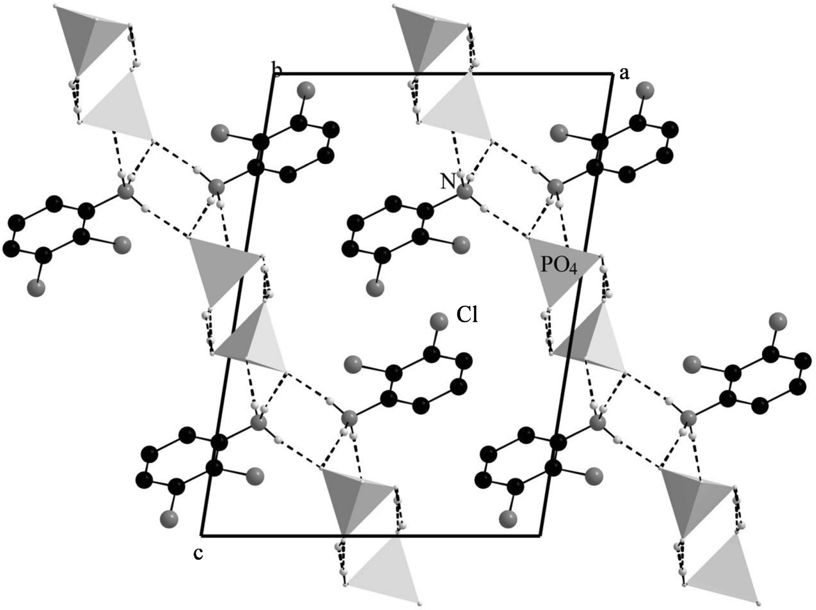

FIGURE 3 Polyhedral representation of the framework ($C_6H_6NCl_2$)(H_2PO_4), viewed down the **a** direction.

formation of N—H···O hydrogen bonds. The C—Cl···π[14] interactions are observed (Figure 4) as a consequence of the chlorine atom being flanked by two phenyl rings of the neighboring molecules.

As can be clearly seen on Figure 3, the two neighbouring anilinium rings, which are not connected by hydrogen bonding, stack each other by turns in a face to face mode. The centroid-centroid distance is 3.395(2) Å, less than 3.8 Å, the maximum value accepted for π-π interactions.[15] So, there is a π-π stacking interaction between the adjacent antiparallelly arrayed anilinium rings. Unlike some other examples in which π-π stacking interactions cause polar geometry,[16] the two anilinium rings are anti-parallel, due to the strong polar character of the 2,3-dichloroanilinium cation.

Regarding the organic cations arrangement, the protonated 2,3-dichloroanilinium is localized in the interdimer spacing, and it neutralizes the negative charge of the anionic part. Each organic entity is bounded to three different (H_2PO_4) groups belonging to two different dimeric units through three N—H···O hydrogen bonds. The organic molecule exhibits a regular spatial configuration with distances C—C, C—N, C—Cl and angles C—C—C, C—C—N, Cl—C—C comparable to those in other 2,3-dichloroanilinium compounds.[17,18] The mean value of the

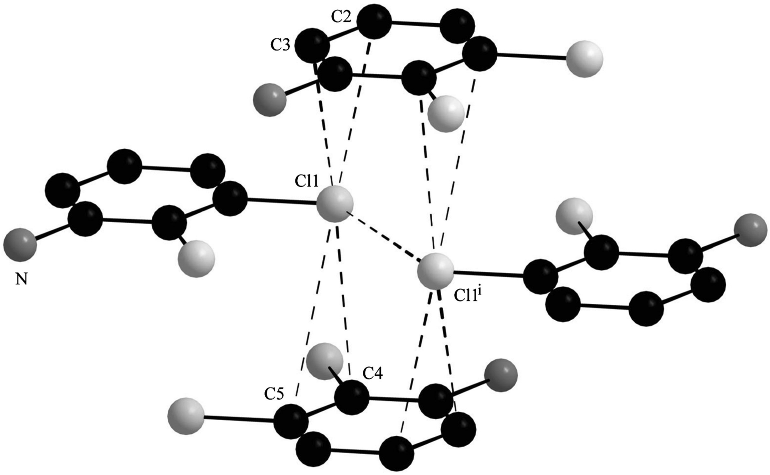

FIGURE 4 C—Cl···π and Cl···Cl contact in $(C_6H_6NCl_2)(H_2PO_4)$.

(C—C) length of benzene cycle is 1.385 Å, which is between single bond and double bond and agrees with that in benzene.[19] All the carbon atoms of the phenyl ring are coplanar with an average deviation of 0.006 Å. Furthermore, the N-C(1) (1.454(3) Å) distance clearly indicates a single bond.

NMR Results

The ^{31}P and ^{13}C CP-MAS NMR spectra of the title compound are shown on Figures 5 and 6, respectively. The ^{31}P NMR spectrum is in full agreement with the X-ray structure and displays only one peak at 1.5 ppm. The position of this peak is also in agreement with a phosphate species, usually found between −20 and +10 ppm. Recording the spectrum at a low spinning rate (ca. 1 kHz) allows the observation of numerous spinning sidebands which, after simulation with the DMFIT software[20] allow, the obtention of parameters reflecting the anisotropy around the phosphorus atom, the axiality of the CSA tensor $(\delta_{33} - \delta_{iso})$, and the anisotropy of the CSA tensor $\eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{iso})$, δ_{11}, δ_{22} and δ_{33} being the principal components of the CSA tensor. The axiality is found to be −57 ppm while $\eta = 0.70$. It is then possible to compare these values to those obtained by theoretical calculation of the NMR parameters. By doing these calculations at the B3LYP/ $6 - 31 + G^*$ level and for the H_2PO_4 coordinates taken from the X-ray determination, the following values are obtained: Axiality −130 ppm and $\eta = 0.75$. There is a large discrepancy between the experimental and calculated axiality

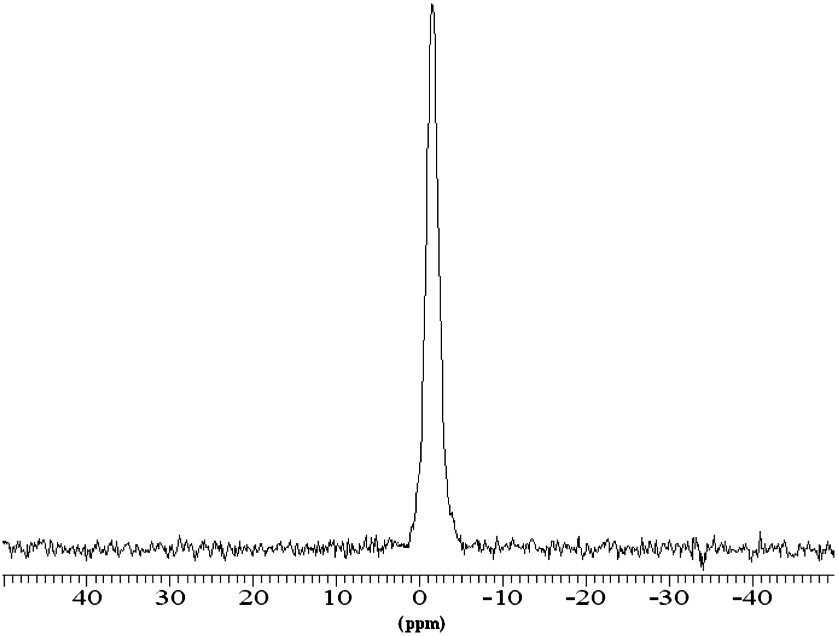

FIGURE 5 ^{31}P CP-MAS NMR spectrum of ($C_6H_6NCl_2$)(H_2PO_4).

parameters, probably due to the fact that the surrounding was not taken into account. On the other hand, the η parameter is well calculated.

The ^{13}C NMR spectrum shown on Figure 6 displays at least three resonances at 123, 130.5 and 138 ppm. An additional resonance can be suspected at ca. 143 ppm, but due to the bad signal to noise ratio (even if

TABLE IV Experimental and Calculated ^{13}C NMR Chemical Shifts

		Theoretical values (ppm)				
				4 organic groups*		
Carbon atom	Experimental (ppm)	No optimization	Optimization of protons	C-Cl–Cl	C-Cl–π	Full optimization
C1	123	112.2	114.2	113.0	114.2	118.9
C2	123	126.8	126.0	122.3	131.2	129.6
C3	138	143.1	141.5	135.6	141.4	144.7
C4	130.5	128.2	131.1	127.5	127.2	134.3
C5	130.5	119.7	123.0	126.1	121.6	125.7
C6	123	108.4	112.9	115.0	110.6	113.9

*C-Cl–Cl corresponds to the molecules interacting via these bonds while C-Cl–π corresponds to the two molecules above and below.

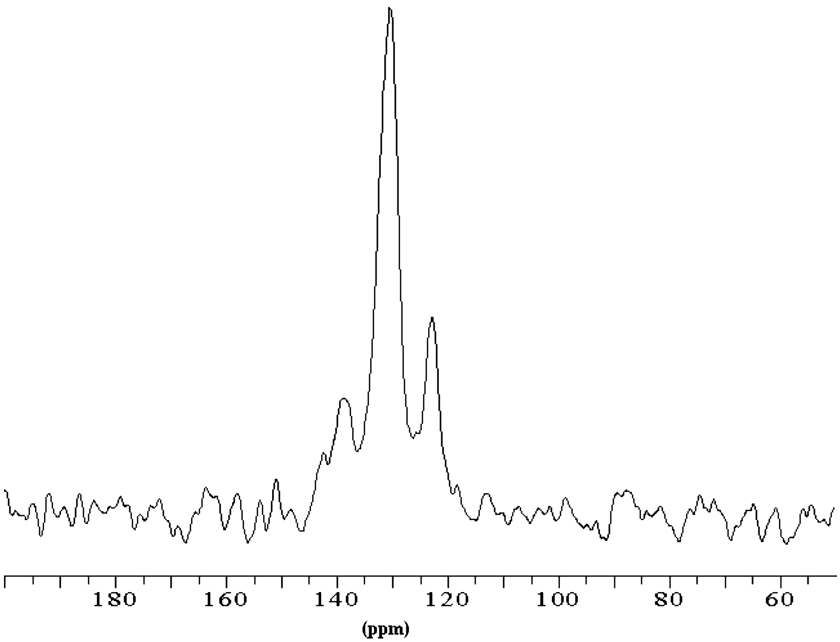

FIGURE 6 ^{13}C MAS NMR spectrum of $(C_6H_6NCl_2)(H_2PO_4)$.

the spectrum corresponds to 24 h acquisition), it is difficult to conclude. As six unequivalent carbon atoms were found by X-ray diffraction the attribution of the different NMR signals could be difficult. We have then undertaken *Ab Initio* calculations in order to help these attributions and by comparison between experimental and theoretical data to improve the X-ray determination by a more precise location of protons. Various calculations were made:

- calculation of the chemical shifts by taking the coordinates deduced from X-ray data (Table II);
- calculation of the chemical shifts after optimization of the positions of the protons;
- calculation of the chemical shifts for an entity composed of four organic groups where hydrogen atoms were located at the positions determined by optimization. This calculation was made in order to determine what was the effect of the interactions between organic groups. The four groups were chosen in such a way that two of them were in interaction by C—Cl—Cl bonds while the two others, one above and the other below, mimic the C—Cl—π interactions; and

- calculation of the chemical shifts after full optimization of the organic group. This calculation will give an indication of the interactions in the solid.

The absolute chemical shifts substracted from that of tetramethylsilane leading then values which could be compared to experimental ones. The results are given in Table IV with the proposed attributions (the carbon atoms are labelled as in Figure 1 and Table II). As it can be seen, the chemical shifts are highly sensitive not only to the positions of protons (optimization of the positions gives more realistic C—H and N—H distances, around 1.08 Å) but also to the interactions between molecules, as variations of 5 ppm are observed for the two types of organic molecules in the model. It is then relatively difficult to propose unambiguous attributions for the various signals. More precise periodic calculations with all molecules of the unit cell should be necessary to conclude. However, this can be correlated to the high relaxation delays which show that the crystal is highly rigid.

IR Absorption Spectroscopy

As infrared spectroscopy is a classical physical method for the investigation of the molecular structure, we have recorded the IR spectrum of the dihydrogenmonophosphate ($C_6H_6NCl_2$)(H_2PO_4) (Figure 7). To assign

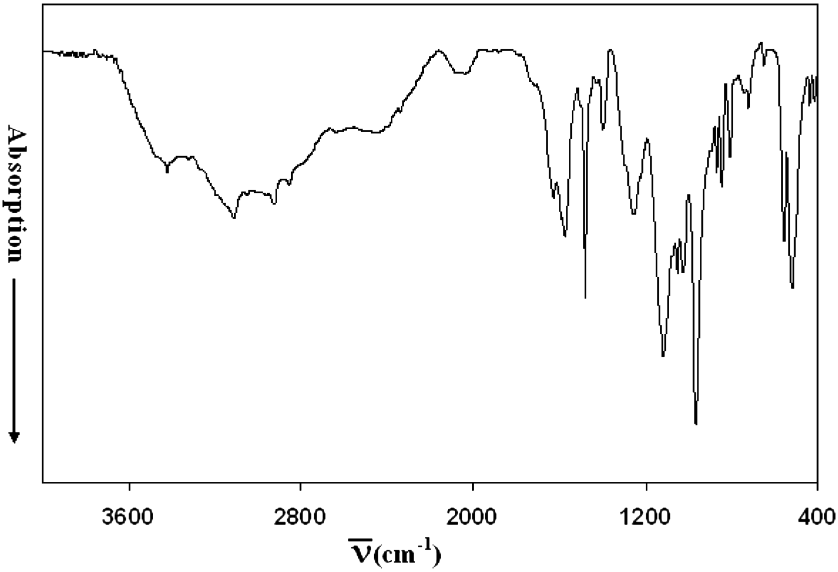

FIGURE 7 IR absorption spectrum of ($C_6H_6NCl_2$)(H_2PO_4).

the IR peaks to vibrational modes, we have examined the modes and frequencies in similar compounds.[21] Broad bands in the 3200–1800 cm^{-1} region correspond to the valence vibrations of N—H and O—H groups interconnected by a system of hydrogen bonds in the crystal.[22] The presence of the NH_3 group in the compound is confirmed also by an "indicator band" at 2053 cm^{-1}.[23,24] The stretching vibration bands of the C—H groups, observed between 3200 and 2600 cm^{-1}, are almost overlapped by the bands of the stretching N—H and O—H vibrations. Frequencies in the range 1630–1570 cm^{-1} are assigned to C=C stretching as well as the NH_3 bending. The bands in the 811–655 cm^{-1} range can be attributed to $\gamma(C_{aryl}—H)$ and $\gamma(C_{aryl}—C_{aryl})$.[25] Various valence and bending vibration bands between 1200 and 400 cm^{-1} are characteristic of a PO_4 tetrahedron.[21] In this range, the unperturbed PO_4 tetrahedron, with point group symmetry Td, gives four vibrational frequencies at 938, 420, 1017, and 567 cm^{-1} for $\upsilon(A_1)$, $\upsilon_2(E)$, $\upsilon_3(F_2)$, and $\upsilon_4(F_2)$, respectively.[26] However, the observed bands in the spectrum at 1120 and 1054 cm^{-1} can be attributed to the stretching vibrations, asymmetric and symmetric, of PO_2 atomic group, while those at 968 and 871 cm^{-1} correspond to the $P(OH)_2$ atomic groups of $H_2PO_4^-$ anion.[27] The splitting of the F_2 stretching mode of PO_4 into three components at 1120, 1045, and 972 cm^{-1} corroborates the symmetry lowering of H_2PO_4 in the solid state. On the other hand, the lower frequencies are related to the bending modes of H_2PO_4 group. In fact, the bands at 1267 and 1234 cm^{-1} correspond to in-plane bending δ(P—O—H), while the out-of-plane bending vibrations γ(P—O—H) are observed at 848 and 811 cm^{-1}. Bands at 653, 559, and 524 cm^{-1} correspond respectively to the rocking $\rho(PO_2)$, waging $\omega(PO_2)$, and bending δ(OHPOH).[28] The two bands at 441 and 433 cm^{-1} can be assigned to the distortion $\tau(PO_2)$, and the bending δ(O—P—O) vibrations.[28]

Thermal Analysis

The two curves corresponding to Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) in argon are shown in Figure 8. The DTA curve shows a series of weak peaks in a wide temperature range [430–623 K]. The most important one appears at about 451 K, and corresponds to a melting transformation. The TGA curve shows a continuous weight loss in all this temperature area. So, the corresponding phenomena could be interpreted by $H_2PO_4^-$ condensation, which starts at about 476 K, and a $[C_6H_5NCl_2]^+$ degradation leading to viscous matter of polyphosphoric acids with a carbon black residue.

The Differential Scanning Calorimetry (DSC) curve (Figure 9) exhibits the same thermal behaviour as observed in the DTA thermogram. The overall ΔH of fusion and the first dehydroxylation of $(H_4P_2O_8)^{2-}$,

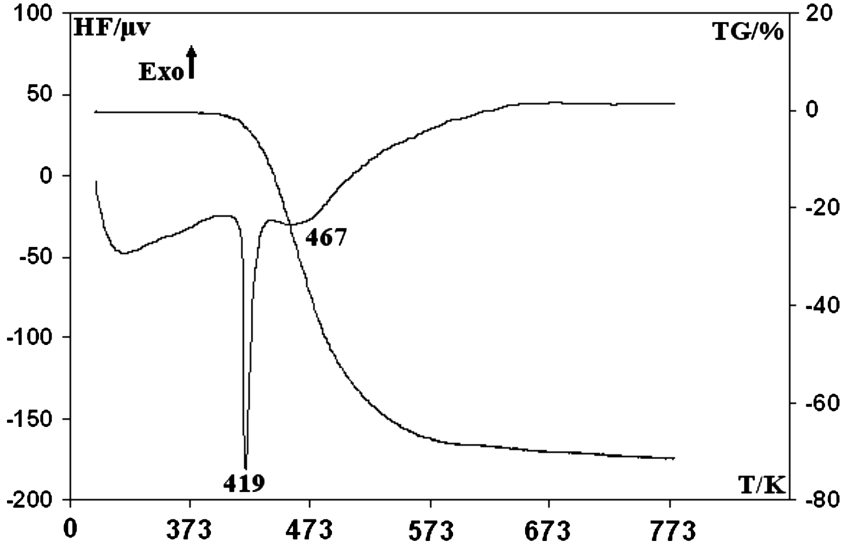

FIGURE 8 Thermal analysis (DTA and TG) under argon of $(C_6H_6NCl_2)(H_2PO_4)$.

in the region 381–573 K, is 467 J mol^{-1} calculated from the DSC curve. The resulting compound is a black liquid.

EXPERIMENTAL

Chemical Preparation

Crystals of the title compound, $(C_6H_6NCl_2)(H_2PO_4)$, were prepared by slowly addition at room temperature of 1.6 cm^3 of H_3PO_4 (85%, d =

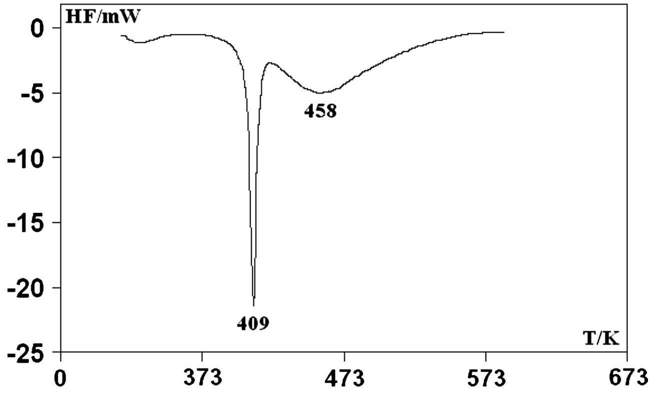

FIGURE 9 DSC curve under air condition of $(C_6H_6NCl_2)(H_2PO_4)$.

1.7) to an alcoholic solution containing 1.62 g of 2,3-dichloroaniline. A crystalline precipate was formed resulting from the following reaction:

After solubilization of the precipitate in water, the solution was slowly evaporated at room temperature during several days until the formation of transparent prismatic crystals with suitable dimensions for a crystallographic study. (2.75 g, 70% yield); m.p. 177–179°C; Anal. calcd. for $C_6H_8NPCl_2O_4$: C, 27.69; H, 3.07; N, 5.38; P, 11.92; Found: C, 27.98; H, 3.02; N, 5.14; P, 11.76. The crystals remain stable for months in normal conditions of temperature and humidity.

Investigation Techniques

X-ray Diffraction

A single crystal was used for X-ray measurements, with a MACH 3 Enraf Nonius diffractometer operating at 296 K with the wavelength $K\alpha(Mo) = 0.7107$ Å. The structure was solved by direct methods using the SIR92[29] program and refined by full matrix least-squares techniques based on F^2 using SHELX-L.[30] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms positions were located by difference-Fourier synthesis and not refined. The details of data collection, refinement and crystallographic data are summarized in Table I. The drawings were made with Diamond.[31]

Crystallographic Data (CIF) for the structure reported in this article have been deposited in to the Cambridge Crystallographic Data Center as supplementary publication No. 631018. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB 12EZ, UK (Fax: +44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

Physical Measurements

NMR spectroscopy. All NMR spectra were recorded on a Bruker DSX-300 spectrometer operating at 300 MHz for ^{1}H, 75.49 MHz for ^{13}C and 121.51 MHz for ^{31}P with a classical 4 mm probehead allowing spinning rates up to 10 kHz. ^{1}H and ^{13}C NMR chemical shifts are given relative to tetramethylsilane and ^{31}P ones relative to 85% H_3PO_4 (external references, precision 0.5 ppm). Both phosphorus and carbon spectra were recorded by use of cross-polarization from protons (contact time 5 ms). Indeed, the T_1 relaxation times of the various nuclei were found to be very long and for example, that of protons which is the shorter one, was so high that at least 600 s between two successive scans were necessary to achieve a quasi-full relaxation. This value was then taken for recording the ^{31}P and ^{13}C spectra. To determine the NMR chemical shifts of the atoms, *Ab initio* calculations were made with the Gaussian 98 software.[32]

IR spectroscopy. Infrared spectrum was recorded in the range 4000–400 cm^{-1} using a sample dispersed in spectroscopically pure KBr pellet.

Thermal analysis. Thermal analysis was performed using the "multimodule 92 Setaram analyzer" operating from room temperature up to 700 K at an average heating rate of 5°C min^{-1}.

CONCLUSION

The use of the 2,3-dichloroanilimium as organic cation in the phosphate matrix leads to a new hybrid compound of chemical formula $(C_6H_6NCl_2)$ (H_2PO_4) with an Interesting Chlorine-Mediated Framework. On the structural level, the atomic arrangement can be described as clusters that aggregate with six organic molecules. The compound cohesion is ensured by H-bonds, electrostatic, Van der Waals, $Cl\cdots Cl$ and $C{-}Cl\cdots\pi$ interactions. Solid-state ^{31}P and ^{13}C NMR spectroscopy results are in agreement with those of the X-ray structure. When heated, this monophosphate was stable until 451 K. By heating further, the important weight loss observed in the temperature range [451, 773 K] corresponds to the degradation of the organic entity and the $H_2PO_4^-$ condensation observed in the temperature range. These phenomena are confirmed by the obtained carbon residue at the end of the experience.

REFERENCES

[1] A. K. Cheetham, G. Férey, and T. Loiseau, *Angew. Chem. Int. Ed. Engl.*, **38,** 3268 (1999).
[2] L. Baouab and A. Jouini, *J. Solid State Chem.*, **141,** 343 (1988).
[3] M. T. Averbuch- Pouchot and A. Durif, *Acta Cryst.*, **C43,** 1894 (1987).
[4] M. T. Averbuch-Pouchot, A. Durif, and J. C. Guitel, *Acta Cryst.*, **C44,** 99 (1988).
[5] M. T. Averbuch-Pouchot, A. Durif, and J. C. Guitel, *Acta Cryst.*, **C45,** 421 (1989).
[6] M. Ichikawa, *Acta Cryst.*, **B43,** 23 (1986).
[7] I. Olovsoon, P.-G. Jonsson, In *Hydrogen Bonding*, P. Schuster, G. Sundel, C. Sandorty, Eds., (North Holland, Amesterdam, 1976) Vol II.
[8] W. H. Baur, *Acta Cryst.*, **B30,** 1195 (1974).
[9] L. Baouab, T. Guerfel, M. Soussi, and A. Jouini, *J. Chem. Cryst.*, **30,** 805 (2000).
[10] B. K. Aoki, K. Nagano, and Y. Iitaka, *Acta Cryst.*, **B27,** 11 (1971).
[11] G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids. Materials Science Monographs* (Elsevier, Amsterdam, 1989) Vol. 54.
[12] A. Dunand and R. Gerdil, *Acta Cryst.*, **B38,** 570 (1982).
[13] N. Ramasabbu, R. Parthasarathy, and P. Murray-Rust, *J. Am. Chem. Soc.*, **108,** 4308 (1986).
[14] M. D. Prasanna and T. N. Guru Row, *Cryst. Eng.*, **3,** 135 (2000).
[15] J. Janiak, *J. Chem. Soc., Dalton Trans.*, 3885 (2000).

[16] M. Ohkita, T. Suzuki, K. Nakatani, and T. Tsuji, *Chem. Lett.*, 988 (2001).
[17] L. Gray and P. G. Jones, *Z. Naturforsch. B. Chem. Sci.*, **57,** 73 (2002).
[18] R. Radinov, S. Shimova, and M. Khaimova, *Izvestiya po Khimiya*, **22,** 144 (1989).
[19] Z. J. Li, X. M. Chen, Z. X. Ren, Y. Li, X. A. Chen, and Z. T. Huang, *Chin. J. Struct. Chem.*, **16,** 311 (1997).
[20] D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J. O. Durand, B. Bujoli, Z. Gan, and G. Hoatson, *Magn. Reson. Chem.*, **40,** 70 (2002).
[21] H. NaïUli, T. Mhiri, and A. Daoud, *Int. J. Inorg. Mater.*, **3,** 393 (2001).
[22] I. Nemec, I. Cisarova, and Z. J. Micka, *J. Solid State Chem.*, **140,** 71 (1998).
[23] R. K. Khanna and M. Horak, *Spectrochim. Acta*, **22,** 1759 (1966).
[24] R. K. Khanna and M. Horak, *Spectrochim. Acta*, **22,** 1801 (1966).
[25] R. M. Silverstein, G. C. Bassler, and T. C. Morill, *Spectrometric Identification of Organic Compounds*, (Wiley, New York, 1974) 3rd Ed.
[26] K. Nakamoto, *IR and Raman Spectra of Inorganic and Coordinated Compounds* (Wiley-Interscience, New York, 1986).
[27] S. M. Haile, P. M. Calkins, and D. Boysen, *J. Solid State Chem.*, **139,** 373 (1998).
[28] A. Chtiuoi and A. Jouini, *J. Chem. Cryst.*, **34,** 43 (2004).
[29] J. Meulenaer and H. Tompa, *Acta Cryst.*, **19,** 1014 (1965).
[30] G. M. Sheldrick, SHELXS97 and SHELXL97. Program for Crystal Structure Solution and Refinement, University of Göttingen, Germany, 1997.
[31] K. Brandenburg, Diamond version 2.0 Impact GbR, Bonn, Germany, 1998.
[32] Gaussian 98, A.7., M. J. Frisch et al., Gaussian, Inc., Pittsburgh, PA, 1998.