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Crystal Structure, (^{31}P , ^{13}C) MAS-NMR, IR Spectroscopy and Thermal Investigations of 2,6-Dimethylanilinium Dihydrogenmonophosphate Monohydrate

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Crystal Structure, (^{31}P , ^{13}C) MAS-NMR, IR Spectroscopy and Thermal Investigations of 2,6-Dimethylanilinium Dihydrogenmonophosphate Monohydrate

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Chemical preparation, crystal structure, thermal analysis, IR absorption, and NMR studies are given for a new hybrid organic-inorganic compound, the (2,6-dimethylanilinium) dihydrogenophosphate monohydrate $[\text{C}_8\text{H}_{12}\text{N}]\text{H}_2\text{PO}_4\cdot\text{H}_2\text{O}$. This compound crystallizes in a triclinic $P\bar{1}$ unit-cell, with $a = 7.392(5)$ Å, $b = 8.323(3)$ Å, $c = 10.306(5)$ Å, $\alpha = 95.769(4)^\circ$, $\beta = 102.642(3)^\circ$, $\gamma = 113.498(2)^\circ$, $V = 554.88(5)$ Å³, and $Z = 2$. Its crystal structure is determined and refined to $R = 0.040$ with 1942 independent reflections. The atomic arrangement can be described by inorganic layers built by H_2PO_4^- anions, and H_2O molecules with which the organic molecules perform different interactions to form a stable 3D network. Solid state ^{31}P and ^{13}C CP-MAS-NMR spectroscopies are in agreement with the X-ray structure.

Keywords Hydrogen bonds; layered compound; IR spectroscopy; NMR spectroscopy; X-ray diffraction

INTRODUCTION

Inorganic-organic hybrid materials have attracted intensive interest owing to their enormous variety of intriguing structural topologies and their fascinating properties, as well as their great potential application in many fields, such as catalysis, medicine, sorption, conductivity, magnetism, and photochemistry.^{1–14} In this field, an important advance is

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made in the design and synthesis of organic cation phosphates modified by various organic molecules and synthesis procedure. As a result, a large number of organic cation phosphates containing aniline molecule and its derivatives has been reported.^{15,16} As shown by several works on this type of materials, water molecules also play an important role for their structure cohesion and stability.¹⁷

In the present article, we report the synthesis and crystal structure of a new organic-cation dihydrogenmonophosphate $[\text{C}_8\text{H}_{12}\text{N}]\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$. Its characterization by solid state NMR, IR spectroscopy, and thermal analysis are also reported.

RESULTS AND DISCUSSION

Crystal Structure

Final atomic coordinates and anisotropic displacement thermal parameters (B_{eq}) of all non-hydrogen atoms are given in (Table I). The geometrical configuration of the asymmetric unit, $[\text{C}_8\text{H}_{12}\text{N}]\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, is shown in an Ortep drawing (Figure 1). The atomic arrangement of this compound can be described as a typical inorganic layers organisation.

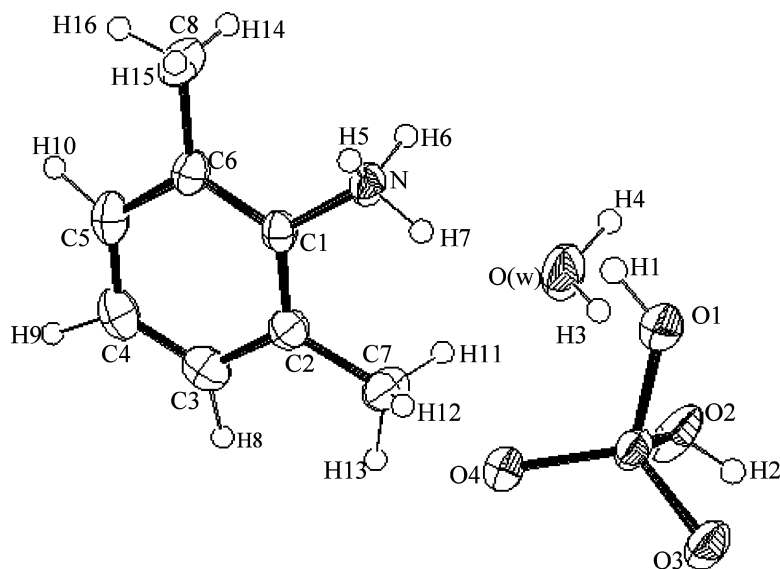


FIGURE 1 ORTEP drawing of the molecular structure of $[\text{C}_8\text{H}_{12}\text{N}]\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ with displacement ellipsoids drawn at the 45% probability level and H atoms shown small spheres of arbitrary radii.

TABLE I Final Atomic Coordinates and B_{eq} (\AA^2) for all Atoms in $[\text{C}_8\text{H}_{12}\text{N}]\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$

Atoms	x	y	z	B_{eq}
P(1)	0.06515(7)	0.77922(6)	−0.00326(5)	0.031
O(3)	0.1917(2)	0.6845(2)	−0.0356(2)	0.039
O(1)	−0.0275(2)	0.8220(2)	−0.1398(1)	0.045
O(4)	0.1765(2)	0.9460(2)	0.1066(1)	0.038
N(1)	−0.3999(2)	1.1109(2)	0.2211(2)	0.034
O(2)	−0.1230(2)	0.6479(2)	0.0392(2)	0.054
C(1)	−0.3261(3)	1.2065(2)	0.3643(2)	0.031
C(6)	−0.3280(3)	1.3729(3)	0.3901(2)	0.036
C(2)	−0.2571(3)	1.1293(3)	0.4660(2)	0.037
C(5)	−0.2516(3)	1.4660(3)	0.5252(2)	0.046
C(8)	−0.4063(4)	1.4521(3)	0.2786(2)	0.051
C(7)	−0.2663(4)	0.9448(3)	0.4367(3)	0.053
C(3)	−0.1818(3)	1.2274(3)	0.5989(2)	0.049
C(4)	−0.1782(4)	1.3949(3)	0.6279(2)	0.050
O(w)	−0.3983(3)	0.7951(2)	0.1051(2)	0.062
H(1)	−0.07688	0.89724	−0.13353	0.050
H(2)	−0.13660	0.54361	0.03304	0.050
H(3)	−0.33699	0.74643	0.08243	0.050
H(4)	−0.53489	0.72917	0.05073	0.050
H(5)	−0.37048	1.01390	0.20563	0.050
H(6)	−0.33200	1.18010	0.16780	0.050
H(7)	−0.54740	1.05150	0.18520	0.050
H(8)	−0.13879	1.15520	0.66730	0.050
H(9)	−0.12900	1.48479	0.72900	0.050
H(10)	−0.28290	1.57620	0.54130	0.050
H(11)	−0.40530	0.85110	0.38970	0.050
H(12)	−0.18000	0.94649	0.38070	0.050
H(13)	−0.20190	0.91260	0.52581	0.050
H(14)	−0.53250	1.38490	0.23679	0.050
H(15)	−0.32150	1.48469	0.23549	0.050
H(16)	−0.40680	1.56247	0.30705	0.050

Estimated standard deviations are given in parentheses.

These layers, built by H_2PO_4^- anions and H_2O molecules, are parallel to the (a, b) planes and centered at $z = 0$ (Figure 2). The organic cations are located in the space delimited by the successive inorganic layers with which they perform ionic and hydrogen bonds (Figure 3). Two of the four P—O bonds in the H_2PO_4^- tetrahedron have short lengths ranging from 1.500 Å to 1.509 Å, while the remaining two have lengths ranging from 1.565 Å to 1.571 Å (Table II). The two shorter P—O bonds in the present crystal may have partial double-bond character while the longer bonds are attributed to P—OH bonds. The O—P—O and the HO—P—OH angles

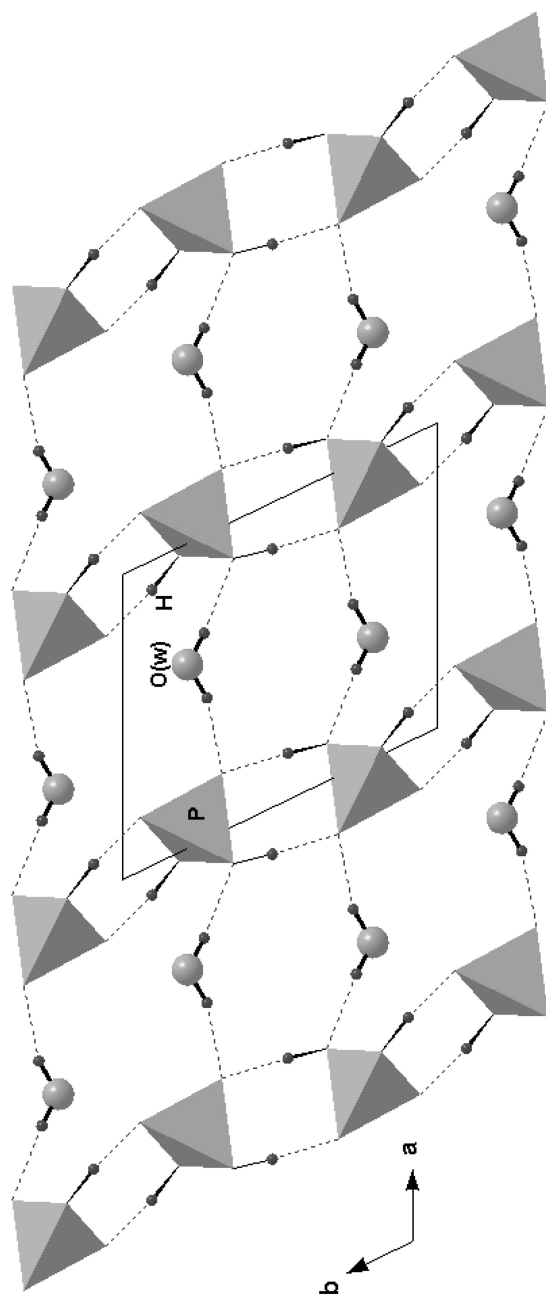


FIGURE 2 Projection along the c axis of the inorganic layer in the $[\text{C}_8\text{H}_{12}\text{N}][\text{H}_2\text{PO}_4] \cdot \text{H}_2\text{O}$ structure.

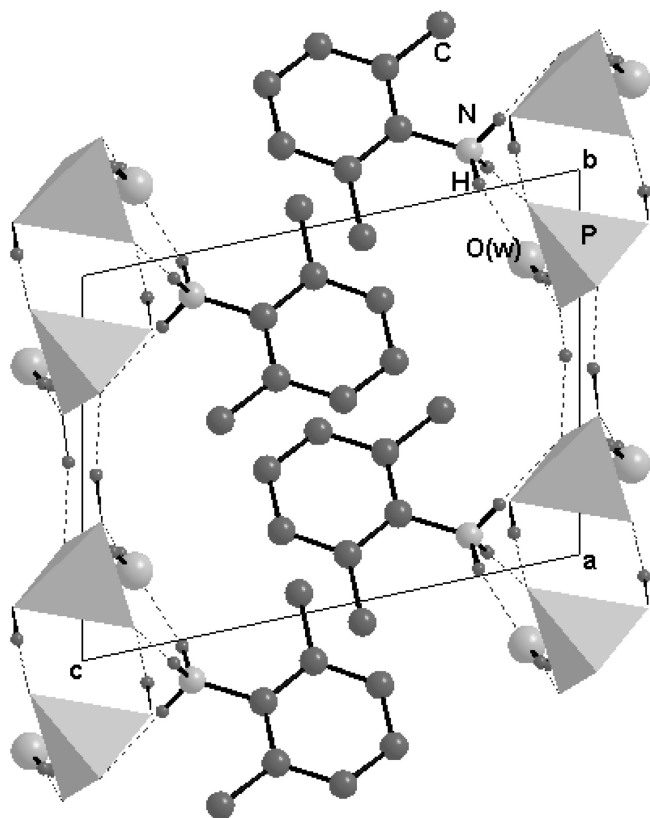


FIGURE 3 Projection along the *a* axis of the atomic arrangement of $[\text{C}_8\text{H}_{12}\text{N}]\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$.

range from $106.20(9)^\circ$ to $116.10(8)^\circ$. They are in good agreement with that observed in such anions in other similar phosphates.^{15,16}

The H_2PO_4^- groups are connected by strong hydrogen bonds to develop infinite chains in the \bar{b} direction. Water molecules of the structure link the successive chains to give rise to infinite layers parallel to the (*a*, *b*) plane. As far as the organic groups are concerned, each one establishes another kind of $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds, with the inorganic layers involving the three hydrogen atoms of the NH_3 group. These atoms are bonded to one water molecule and two H_2PO_4^- anions. Thus, this atomic arrangement exhibits three types of hydrogen bonds (Table III). The first hydrogen bonds of type $[\text{O}-\text{H} \cdots \text{O}]$, involving two short contacts with $\text{H} \cdots \text{O}$ values are 1.76 \AA and 1.78 \AA , connect PO_4 tetrahedron

TABLE II Main Interatomic Distances (Å) and Bond Angles (°) in the Inorganic Entities of [C₈H₁₂N]H₂PO₄·H₂O

P	O (1)	O (2)	O (3)	O(4)
O (1)	1,565(16)	2;5085(24)	2,4602(25)	2,5181(17)
O (2)	106,20(9)	1,5718(17)	2,5236(26)	2,4777(17)
O (3)	106,26(6)	109,93(8)	1,5099 (18)	2,5542(22)
O (4)	110,45(8)	107,49(9)	116,10(8)	1,5003(12)
	O(1)–H(1)	=0,8448(1)	P–O(1)–H(1)	=116,45(3)
	O(2)–H(2)	=0,8274(2)	P–O(2)–H(2)	=115,37(9)
	O(w)–H(3)	=0.7735(15)		
	O(w)–H(4)	= 0.9397(17)		

Estimated standard deviations are given in parentheses.

so as to build [H₂PO₄]_n[–] chains. The short distance between two successive phosphorus atoms in the chain, P···P = 4.153 Å, is a strong indication that the [H₂PO₄]_n[–] can be considered as a macroanion,¹⁸ as would be expected in other compounds.¹⁹ The second hydrogen bonds of type [O(w)–H···O] are responsible of the cohesion between successive chains to build inorganic layers parallel to the (a, b) planes. The last hydrogen bonds of type N–H···O, connect the organic cations C₈H₉NH₃⁺ to the inorganic layers.

An examination of the organic moiety geometrical features shows that the atoms C1, C2, C3, C4, C5, and C6 of the phenyl ring have a good coplanarity, and they form a conjugated plane with average deviation of 0.0018 Å. The mean value of C–C bond lengths is 1.3877 Å, which is between that of a single bond and a double bond, and is comparable to those in other substituted benzene.²⁰ Furthermore, the distances

TABLE III Hydrogen-bond Scheme in [C₈H₁₂N]H₂PO₄·H₂O

D–H··· A	D–H(Å)	H··· A(Å)	D··· A(Å)	D–H··· A(°)
O1–H1··· O4	0.84	1.76	2.605(2)	175
O2–H2··· O3	0.83	1.78	2.602(2)	171
O(w)–H3··· O2	0.77	2.15	2.9212(3)	171
O(w)–H4··· O3	0.94	1.89	2.779(3)	157
N1–H5··· O(w)	0.92	1.91	2.782(2)	156
N1–H6··· O3	0.92	2.05	2.962(2)	175
N1–H7··· O4	0.96	1.82	2.777(2)	176

Estimated standard deviations are given in parentheses.

C2-C7, C6-C8 and C1-N1 of 1.5069(35), 1.5020(35), and 1.4746(25) Å, respectively, indicate three single bonds (Table IV).

It is interesting to compare the studied crystal with the substituted anilinium analogs: 2,4-dimethylanilinium dihydrogenphosphate¹⁵ and 2,5-dimethylanilinium dihydrogenphosphate.¹⁶ These anhydrous substituted anilinium crystallize at room temperature in the monoclinic ($P2_1/c$) and in orthorhombic ($P2_12_12_1$) space groups, respectively. Despite the difference between the space groups in these compounds, the distances and angles in studied compounds are quite similar to those observed in $[2,4-(\text{CH}_3)_2\text{C}_6\text{H}_3\text{NH}_3]\text{H}_2\text{PO}_4$ ¹⁵ and $[2,5-(\text{CH}_3)_2\text{C}_6\text{H}_3\text{NH}_3]\text{H}_2\text{PO}_4$.¹⁶ In addition, the encapsulation of a solvent molecule in the 2,6-DMAP structure increases the number of hydrogen bonds, and the cohesion if compared to those in 2,4-DMAP and 2,5-DMAP structures. So, it should be concluded that the organic molecule seems to play a key role in directing the final structure of this kind of materials. Furthermore, the change of the CH_3 group position leads to novel structure, which could not be obtained in another way.

IR Spectroscopy

The infrared absorption spectrum (Fig. 4) of the title compound $[\text{C}_8\text{H}_{12}\text{N}]\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ shows the vibration bands of 2,6-dimethylanilinium cation, H_2PO_4^- anion and H_2O molecule. To assign the IR

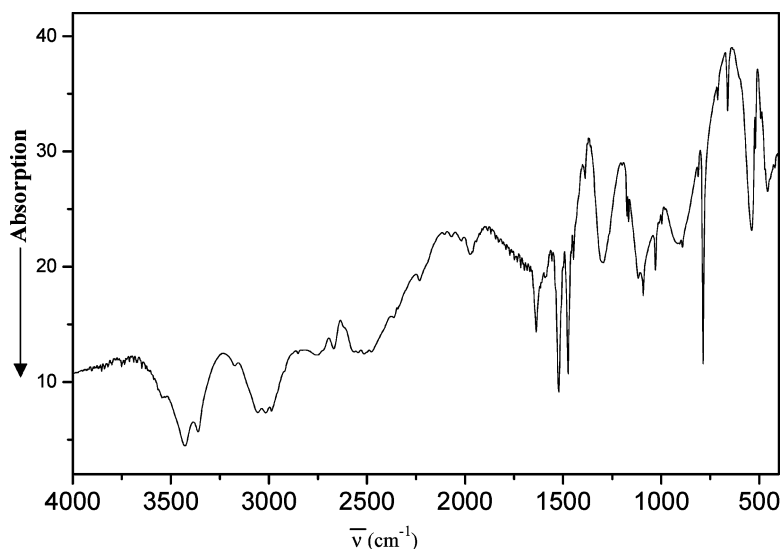


FIGURE 4 IR spectrum of $[\text{C}_8\text{H}_{12}\text{N}]\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$.

peaks to vibrational modes, we have examined the modes of frequencies in similar compounds.²¹ So, the broad bands between 3500 and 2300 cm^{-1} correspond to the stretching vibrations of the organic cation [$\nu(\text{N-H})$ and $\nu(\text{C-H})$] and $\nu(\text{O-H})$ of P-OH groups. Bands in the 1620–1200 cm^{-1} region correspond to the valence vibrations of C=C and C-N groups. Between 1200 and 400 cm^{-1} various valence and bending vibration band are characteristic of the monophosphate group.²² Indeed, the internal vibration analysis of the PO_4 tetrahedron gives four vibrational frequencies, two stretching modes ν_s and ν_{as} (respectively symmetric and asymmetric), and two bending modes δ_s and δ_{as} . These vibrations are expected in the 1200–800 cm^{-1} and 650–400 cm^{-1} ranges,²³ respectively. Supplementary frequencies in $\nu_s(\text{PO}_4)$ domain are attributed to bending modes $\delta(\text{C}_{\text{aryl}}-\text{H})_{\text{ip}}$.²⁴

Thermal Analysis

Two curves of thermal analysis (DTA and TGA) carried under flowing drying argon atmosphere are given in Figure 5. The DTA curve shows that the monophosphate undergoes a series of thermal accidents. The first one, observed at 347 K, is accompanied by a weight loss (TGA

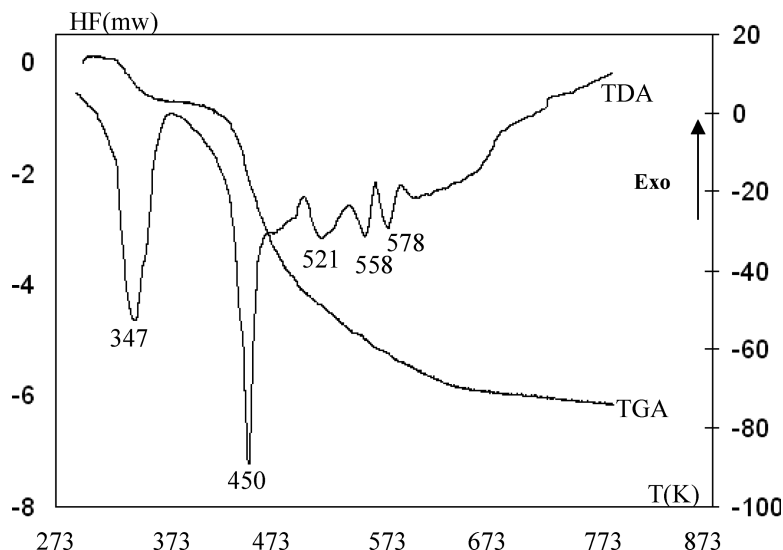


FIGURE 5 DTA and TGA curves of $[\text{C}_8\text{H}_{12}\text{N}]\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ at rising temperature.

curve). From this latter, we deduce a departure of the crystallization H_2O molecule (weight loss: calculated: 7.59%, experimental: 7.26%). The other DTA endothermic peaks, observed between 400 and 773 K, can be attributed to a simultaneous melting and degradation of the remaining anhydrous product. These phenomena, accompanied by a significant weight loss, lead to a consistent residue formed of polyphosphoric acid and black carbon.

NMR Spectroscopy

Figure 6 shows the proton decoupled ^{31}P MAS NMR spectrum of crystalline dihydrogenmonophosphate $[\text{C}_8\text{H}_{12}\text{N}]\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$. This spectrum agrees perfectly with the X-ray structure. Indeed, it

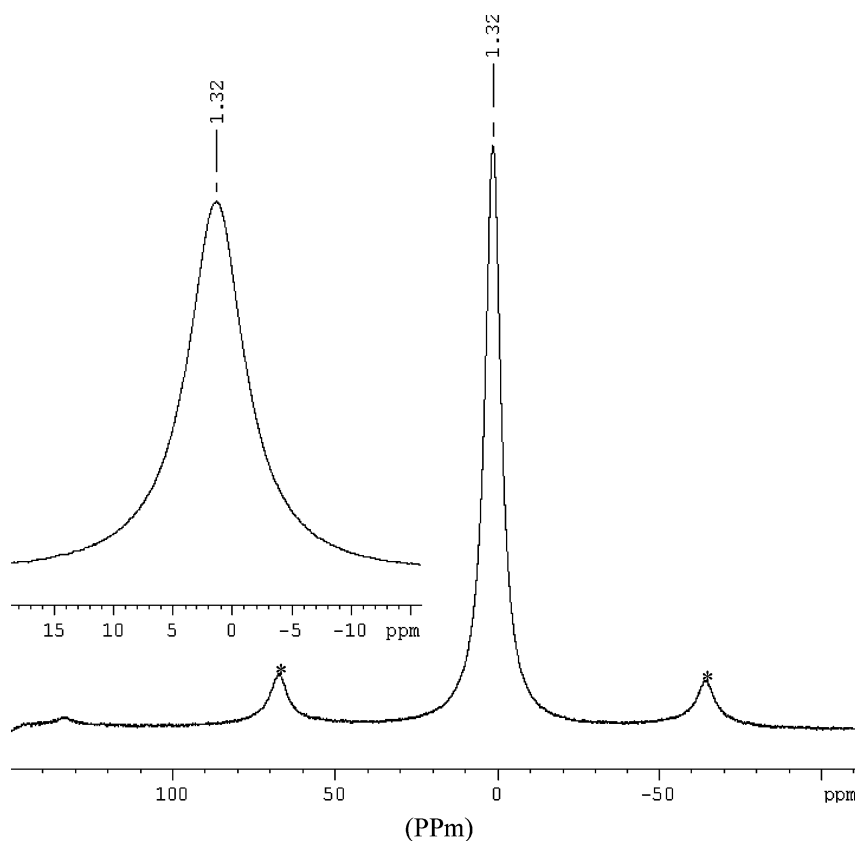


FIGURE 6 ^{31}P NMR spectrum of $[\text{C}_8\text{H}_{12}\text{N}]\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$. *Spinning side bands.

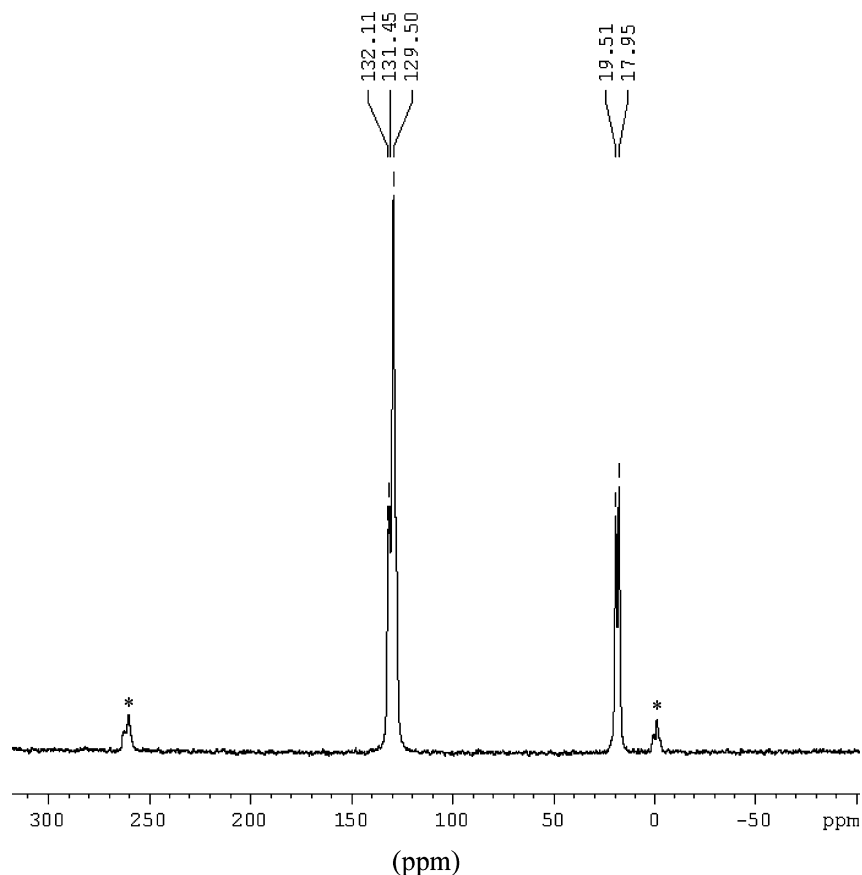


FIGURE 7 ^{13}C NMR spectrum of $[\text{C}_8\text{H}_{12}\text{N}] \text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$. *Spinning side bands.

exhibits only one resonance peak at 1.3 ppm, corresponding to the single phosphorus site which exists in the atomic arrangement. This chemical shift value is in full agreement with those of $(4\text{-C}_2\text{H}_5\text{-C}_6\text{H}_4\text{NH}_3)\text{H}_2\text{PO}_4$ ($\delta = 0.1$ ppm)²⁵ and $(\text{C}_6\text{H}_9\text{N}_2)\text{H}_2\text{PO}_4$ ($\delta = 1.5$ ppm).²⁶

Figure 7 shows the ^{13}C CP-MAS NMR spectrum of the title compound. The signals at 17.9 and 19.5 ppm correspond to the aliphatic carbon atoms C7 and C8 and prove the presence of only one organic entity in the asymmetric unit of the compound. The other signals at higher chemical shifts are related to the phenyl ring carbon atoms (C1, C2, C3, C4, C5, and C6).

TABLE IV Main Interatomic Distances (Å) and Bond Angles (°) in the Organic Entity of [C₈H₁₂N] H₂PO₄·H₂O

N(1)-C (1)	1,4746(25)	C(2)-C(1)-N(1)	119,65(2)
C(1)-C(6)	1,3902(31)	C(3)-C(1)-N(3)	117,13(2)
C (1)-C(2)	1,3903(31)	C(2)-C(1)-C(6)	123,21(2)
C(2)-C (3)	1,3893(29)	C(1)-C(2)-C(3)	117,55(2)
C(2)-C(7)	1,5069(35)	C(1)-C(2)-C(7)	122,39(2)
C(3)-C(4)	1,3844(40)	C(3)-C(2)-C(7)	120,05(2)
C(4)-C (5)	1,3765(37)	C(2)-C(3)-C(4)	120,72(2)
C(5)-C(6)	1,3956(28)	C(3)-C(4)-C(5)	120,32(2)
C(6)-C(8)	1,5020(35)	C(4)-C(5)-C(6)	121,06(2)
		C(5)-C(6)-C(8)	120,72(2)
		C(5)-C(6)-C(1)	117,11(2)
		C(8)-C(6)-C(1)	122,16(2)

Estimated standard deviations are given in parentheses.

EXPERIMENTAL PART

Synthesis of [C₈H₁₂N]H₂PO₄·H₂O

The crystals of 2,6-dimethylanilinium dihydrogenphosphate monohydrate [C₈H₁₂N]H₂PO₄·H₂O were obtained from an aqueous solution containing 25 mmol, (3.025 g) of 2,6-dimethylaniline (Acros, 99%, d = 0.98) and 25 mmol (2.45 g) of monophosphoric acid H₃PO₄ (Acros, 85%, d = 1.7). The crystallization was performed in ambient conditions by slow evaporation of the solvent. Colorless crystals with suitable dimensions appear after some days (m = 7.6 g, yield = 70%). The produced chemical reaction is:



The obtained crystals are stable in air under normal conditions of temperature and hygrometry.

Investigation Techniques

X-Ray Diffraction

A suitable single crystal of the title compound was selected with a polarizing microscope and measured by a MACH3 Enraf–Nonius diffractometer operating with silver radiation ($\text{AgK}\alpha = 0.5608 \text{ \AA}$) for a structural determination. The unit-cell dimensions have been measured and refined using a set of 25 angle reflections. The structure was solved using the direct methods with the SHELXS-97 program.²⁷ The phosphorus atom site was first localized. The O, N, and C atom positions

TABLE V Crystal Data, Intensity Measurements Conditions and Structure Determination of $[\text{C}_8\text{H}_{12}\text{N}]\text{H}_2\text{PO}_4\cdot\text{H}_2\text{O}$

Empirical formula	$[\text{C}_8\text{H}_{12}\text{N}]\text{H}_2\text{PO}_4\cdot\text{H}_2\text{O}$
Formula weight	438.34
Crystal system	Triclinic
Space group	$\text{P}\bar{1}$
a	7.392(5) (Å)
b	8.323(3) (Å)
c	10.306(5) (Å)
α	95.769(4)°
β	102.642(3)°
γ	113.498(2)°
Z	2
V	554.88(2) Å ³
$\rho_{\text{cal.}}$	1.312 (g. cm ⁻³)
F(000)	232
$\mu(\text{AgK}\alpha)$	3.84 (cm ⁻¹)
Crystal size [mm]	0.95 × 0.75 × 0.60
Index ranges: $\pm h, \pm k, l$	$h_{\text{max.}} = 8, k_{\text{max.}} = 9, l_{\text{max.}} = 12$
Reflexions collected	3892
Independent reflexions	1942
R_{int}	0.011
Refined parameters	136
R [$I > 2\sigma(I)$]	0.0402
$R_{(w)}$	0.1130
Goodness-of-fit	1.15

were deduced from Fourier maps and distance consideration after refinement using the SHELXS-97 program.²⁸

The experimental conditions of data collection, the strategy followed for the structure determination and the final results are given in (Table V).

Crystallographic data (CIF) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data center as supplementary publication No. 636577. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB12EZ, U (Fax: +44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

Physical Measurements

The IR spectrum was recorded in the range 4000–400 cm⁻¹ with a spectrophotometer (Perkin-Elmer Spectrum 1000) using a sample dispersed in spectroscopically pure KBr pellet.

Thermal analysis was performed using the 'Thermal Analysis Instruments SDT2960' operating from room temperature up to 873 K at an average heating rate of $5^{\circ}\text{C}\cdot\text{min}^{-1}$ in flowing drying argon atmosphere.

NMR spectra were recorded on a Bruker DSX-300 spectrometer operating at 75.49 MHz for ^{13}C and 121.57 MHz for ^{31}P with a classical 4 mm probehead allowing spinning rates up to 10 kHz. ^{13}C and ^{31}P chemical shifts are given relative to tetramethylsilane and 85% H_3PO_4 , respectively (external references, precision 0.5 ppm). The ^{13}C spectrum was recorded by use of cross-polarization (CP) from protons (contact time 5 ms) and MAS. In all cases it was checked that there was a sufficient delay between the scans allowing a full relaxation of the nuclei.

CONCLUSION

The title compound was obtained by reaction of orthophosphoric acid with 2,6-dimethylaniline at r.t. It was characterized by various techniques. On the structural level, the atomic arrangement of this monohydrogenmonophosphate can be described by inorganic layers built by H_2PO_4^- anions and H_2O molecules. The organic cations are located in the space delimited by these layers. Solid-state ^{13}C and ^{31}P MAS NMR spectroscopies are in agreement with the X-ray structure. Upon heating, this organic cation monophosphate was stable until 347 K. After heating at 773 K, a viscous matter of polyphosphoric acids with a carbon black residue was obtained.

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