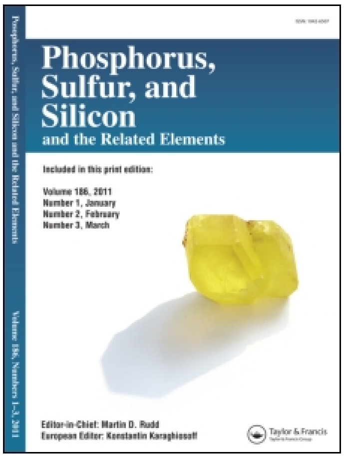

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The Synthesis and Characterization of 2-Amino-3-methylpyridinium Dihydrogenmonophosphate: $(C_6H_9N_2)H_2PO_4$

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The Synthesis and Characterization of 2-Amino-3-methylpyridinium Dihydrogenmonophosphate: $(C_6H_9N_2)H_2PO_4$

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A new crystal of 2-amino-3-methylpyridinium dihydrogenmonophosphate has been prepared and characterized by X-ray crystallography, thermal analysis, and impedance and NMR spectroscopies. This compound crystallizes in the triclinic space group $P\bar{1}$ *with* $a = 7.343(2)$ Å, $b = 7.987(2)$ Å, $c = 8.116(4)$ Å, $\alpha = 77{,}62(3)^\circ$, $\beta = 77{,}74(3)^\circ$, $\gamma = 87{,}03(2)^\circ$, $V = 454.3\ (3)$ Å^3, *and* $Z = 2$. *The crystal structure was solved and refined to* $R = 0.030$ *with 1602 independent reflections. The atomic arrangement can be described as* $(H_2PO_4^-)_n$ *polymeric chains anchoring the 2-amino-3-methylpyridinium cations through short hydrogen bonds. All ring atoms of the organic entity are coplanar. The exocyclic N atom is an electron receiving center, which is consistent with features of imino resonance evidenced by bond lengths and angles. Solid state* ^{31}P, ^{13}C, *and* ^{15}N *CP-MAS-NMR spectroscopies are in agreement with the X-ray structure. Ab initio calculations allow the attribution of carbons and nitrogen to the independent crystallographic sites.*

Keywords Crystal structure; dihydrogenomonophosphate; impedance spectroscopy; nuclear magnetic resonance; X-ray diffraction

INTRODUCTION

In recent years, the organic monophosphates were studied due to the possibility of their application in different areas of chemistry.[1] These materials are generally prepared at r.t. conditions by the reaction of

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organic amines with phosphoric acid. In the organic-cation monophosphates, hydrogen bonds influence both the alignment and spacing of the nearest-neighbors inorganic ribbons,[2] chains,[3,4] or layers[5,6] and take part in the stability and cohesion of these compounds. In order to investigate the influence of hydrogen bonds on chemical and structural features, we report in this work the chemical preparation and structural investigation of a new organic-cation dihydrogenomonophosphate $(2\text{-NH}_2\text{-3-CH}_3\text{C}_5\text{H}_3\text{NH})\text{H}_2\text{PO}_4$. Its characterization by solid state NMR spectroscopy, thermal analysis, infrared spectroscopy, and conductivity experiments are also reported.

RESULTS AND DISCUSSION

Structure Description

Structural determination shows that the title compound crystallizes in the triclinic space group $P\overline{1}$. The final atomic coordinates and thermal parameters of all atoms are given in Table I. Interatomic distances,

TABLE I Final Atomic Coordinates and Beq for Non-Hydrogen Atoms

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{eq}(\text{Å}^2)$
P	0.97376(4)	0.06283(4)	0.24276(4)	0.03124(11)
O(1)	0.9046(2)	−0.10881(13)	0.21716(13)	0.0538(3)
O(2)	1.16833(13)	0.0253(1)	0.29072(12)	0.0481(3)
O(3)	0.99877(13)	0.19550(11)	0.07817(12)	0.0404(3)
O(4)	0.83618(13)	0.11200(13)	0.39070(12)	0.0451(3)
N(1)	0.5615(2)	0.33712(13)	0.3335(1)	0.0365(3)
N(2)	0.7752(2)	0.5055(1)	0.1261(2)	0.0462(3)
C(1)	0.6017(2)	0.4840(2)	0.2167(2)	0.0329(3)
C(2)	0.4583(2)	0.6079(2)	0.1966(2)	0.0381(3)
C(3)	0.2851(2)	0.5680(2)	0.2962(2)	0.0505(4)
C(4)	0.2481(2)	0.4128(2)	0.4142(2)	0.0561(4)
C(5)	0.3896(2)	0.2994(2)	0.4313(2)	0.0457(4)
C(6)	0.4988(2)	0.7745(2)	0.0718(2)	0.0498(4)
H(1)	0.9554	−0.1339	0.1030	0.075
H(2)	1.1619	−0.0358	0.4129	0.063
H(3)	0.8573	0.4158	0.1310	0.032
H(4)	0.8207	0.6067	0.0600	0.032
H(5)	0.6659	0.2573	0.3520	0.044
H(6)	0.383(3)	0.180(2)	0.504(3)	0.059
H(7)	0.1234	0.3839	0.4846	0.064
H(8)	0.1806	0.6528	0.2801	0.057
H(9)	0.3853	0.8338	0.0647	0.086
H(10)	0.5849	0.8369	0.1091	0.032
H(11)	0.5498	0.7601	−0.0274	0.032

Estimated SDS are given in parentheses.

TABLE II Main Interatomic Distances (Å) and Angles (°) in the (2-NH_2-3-$CH_3C_5H_3NH$)H_2PO_4 Atomic Arrangement

P	O(1)	O(2)	O(3)	O(4)
		PO_4 Tetrahedron		
O (1)	1.556(1)	2.497(2)	2.515(2)	2.453(2)
O (2)	106.70(9)	1.557(1)	2.471(2)	2.512(2)
O (3)	110.78(7)	107.83(8)	1.500(1)	2.525(2)
O (4)	106.60(8)	110.30(8)	114.38(6)	1.504(1)
O(1)-H(1) = 0.98 Å			P-O(1)-H(1) = 114.0°	
O(2)-H(2) = 1.00 Å			P-O(2)-H(2) = 113.5°	
		[2-NH_2-3-$CH_3C_5H_3NH$]$^+$ Cation		
N(1)-C(1)	1.342(2)		C(1)-N(1)-C(5)	123.3(2)
N(2)-C(1)	1.328(2)		N(2)-C(1)-N(1)	117.8(2)
C(1)-C(2)	1.418(2)		N(2)-C(1)-C(2)	123.4(2)
C(2)-C(3)	1.366(3)		N(1)-C(1)-C(2)	118.7(2)
C(3)-C(4)	1.394(3)		C(3)-C(2)-C(1)	117.4(2)
C(4)-C(5)	1.352(3)		C(1)-C(2)-C(6)	120.3(2)
N(1)-C(5)	1.351(2)		C(3)-C(2)-C(6)	122.3(2)
C(2)-C(6)	1.490(2)		C(2)-C(3)-C(4)	122.2(2)
			C(5)-C(4)-C(3)	118.5(2)
			N(1)-C(5)-C(4)	119.9(2)

Estimated SD are given in parentheses.

bond angles, and hydrogen bonding scheme are given in Tables II and III respectively. This atomic arrangement has no special features, as most of its characteristics are comparable to those of numerous previously described organic-cation phosphates.[5,7]

Figure 1 shows the ORTEP plot of the structure including the atom's labelling and their vibrational ellipsoids at 40% probability. The crystal structure consists of one phosphate anion and one organic cation. The atomic arrangement of this salt contains $(H_2PO_4^-)_n$ polymeric chains anchoring the 2,3–picoline cations through short hydrogen bonds. The projection of this arrangement is depicted in Figure 2.

TABLE III The Hydrogen-Bond Scheme in (2-NH_2-3-$CH_3C_5H_3NH$)H_2PO_4

O(N)—H··· O	O(N)—H (Å)	H··· O (Å)	O(N)··· O (Å)	O(N)—H··· O(°)
O1—H(1) O3	0.98	1.61	2.582(2)	168.7
O2—H(2) O4	1.00	1.58	2.577(2)	172.8
N1—H(5) O4	0.99	1.69	2.680(2)	176.7
N2—H(3) O3	0.91	2.07	2.949(2)	160.3
N2—H(4) O3	0.90	2.08	2.958(2)	162.6

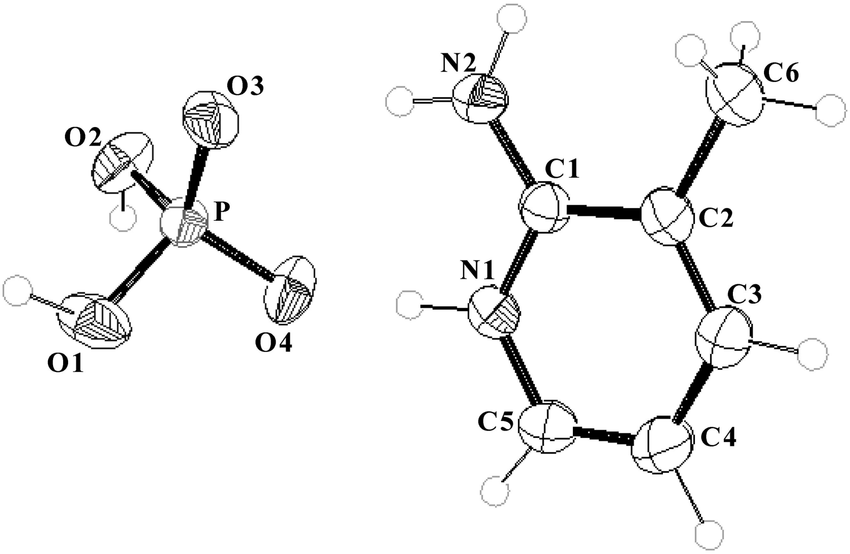


FIGURE 1 Asymmetric unit of (2-NH_2-3-$CH_3C_5H_3NH$)H_2PO_4. Thermal ellipsoids are shown at 40% probability.

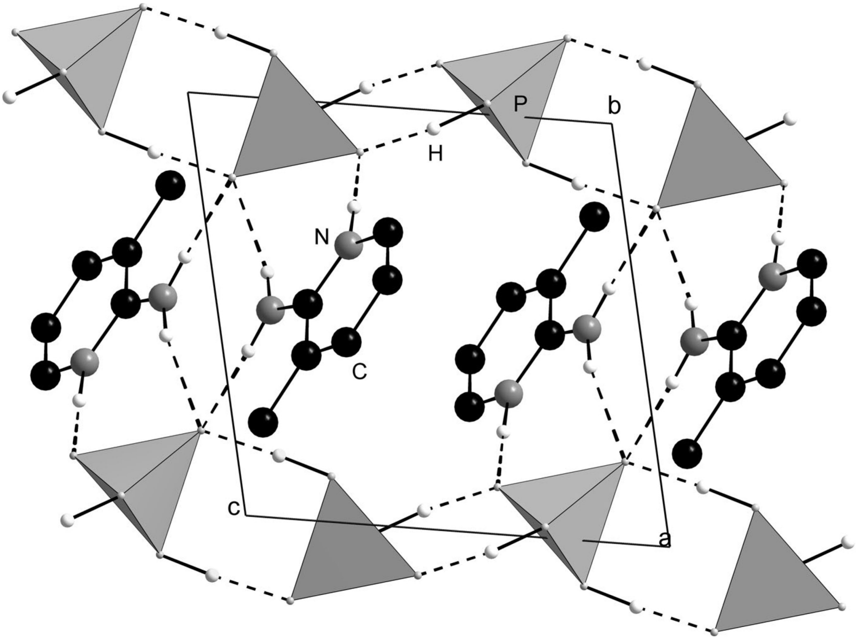


FIGURE 2 A projection of the structure of (2-NH_2-3-$CH_3C_5H_3NH$)H_2PO_4 along the a axis. A polyhedral representation is used for the PO_4 tetrahedron.

Chains of phosphate anions are made up from $H_2PO_4^-$ units, themselves interconnected by strong hydrogen bonds to build $(H_2PO_4^-)_n$ infinite chains extending along the c direction. Every chain is built up via short hydrogen bonds that connect P—OH groups to P=O groups (donor–acceptor distance: 2.582(2) Å and 2.577(2) Å). These chains are themselves interconnected by a means of N—H··· O hydrogen bonds originating from the 2-amino-3-methylperidinium cation. The organic cations established both ionic interactions and hydrogen bonds with the inorganic skeleton and formed thick layers (Figure 2). The Van der Waals contacts created between these latters gave rise to a three-dimensional network in the structure and added stability to this compound.

An examination of the $H_2PO_4^-$ geometry (Table II) shows two kinds of P—O distances. The largest ones [1.556 (1) and 1.557 (1) Å] can be attributed to P—OH distances; the shortest ones [1.500 (1) and 1.504 (1) Å] correspond to the phosphorus atom doubly bonded to the oxygen atom (P=O). The average values of the P—O distances and the O—P—O angles are 1.529 Å and 109.43°, respectively. These values are in good agreement with those observed in such anions in other dihydrogenomonophosphates.[7]

The geometrical features of the 2-amino-3methylperidinium cation are similar to those observed in the structure of 2-amino-3-methylpyridinium ortho-phthalate[8] and 2-amino-5-methylpyridinium tetrachlorozincate.[9]

The atoms C1, C2, C3, C4, C5, and N1 of the pyridinium ring of the title compound have a good coplanarity, and they form a conjugated plane with an average deviation of 0.0046 Å. The mean value of C—C and N—C bond lengths are 1.382 and 1.346 Å, which are between that of a single bond and a double bond and which agree with those in the literature.[8] Furthermore, the bond length of N2—C1 [1.328(2) Å] is slightly shorter than those of N1—C1 [1.342(2) Å] and N1—C5 [1.351(2) Å]; the bond lengths of C2—C1 [1.418(2) Å] and C3—C4 [1.394(3) Å] are considerably larger than those of C2—C3 [1.366(3) Å] and C4—C5 [1.352(3) Å]. The sum of the angles around N1 is 359.9°. All these features of the bond length and angle are consistent with the imino resonance (Figure 3)[8] and suggest a great contribution from such resonance to the title compound. The N2—C1 [1.328(2) Å] is approximately equal to the C=N double bond length, which indicates that the atom N2 of the imino group must be sp^2 hybridized. The distance C2—C6 [1.490(3) Å] clearly indicates a single bond. The C—N—C angles of pyridine are very sensitive to protonation.[10,11] A pyridinium cation always possesses an expanded angle of C—N—C in comparison with the parent pyridine. The angle of C(1)—N(1)—C(5) [123.3 (2)] is consistent with the type of

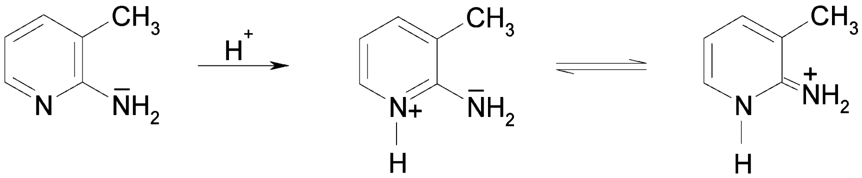


FIGURE 3 A resonance shown in the 2-NH_2-3-$CH_3C_5H_3NH^+$ cation.

pyridinium cation. The hydrogen atom H (N1), which is deprived from its parent, attaches the nitrogen atom.

NMR Results

The ^{31}P MAS NMR spectrum of the crystalline monophosphate (2-NH_2-3-$CH_3C_5H_3NH$)H_2PO_4 is shown in Figure 4 and is in good agreement with the X-ray structure. Indeed, it exhibits a single resonance peak corresponding to only one crystallographic site. The chemical shift value (1.5 ppm) agrees with those corresponding to monophosphates (between -10 and $+5$ ppm).[12–18] Recording the spectrum with high-power proton decoupling (Figure 5) induces a decrease of the width for the signal ($\Delta\nu_{1/2}$ = 200 Hz versus $\Delta\nu_{1/2}$ = 550 Hz). This proves that phosphorus atoms are close to protons. A further proof of this is obtained by 2D HETCOR ^{31}P-^{1}H NMR. When the 2D spectrum is recorded with a short

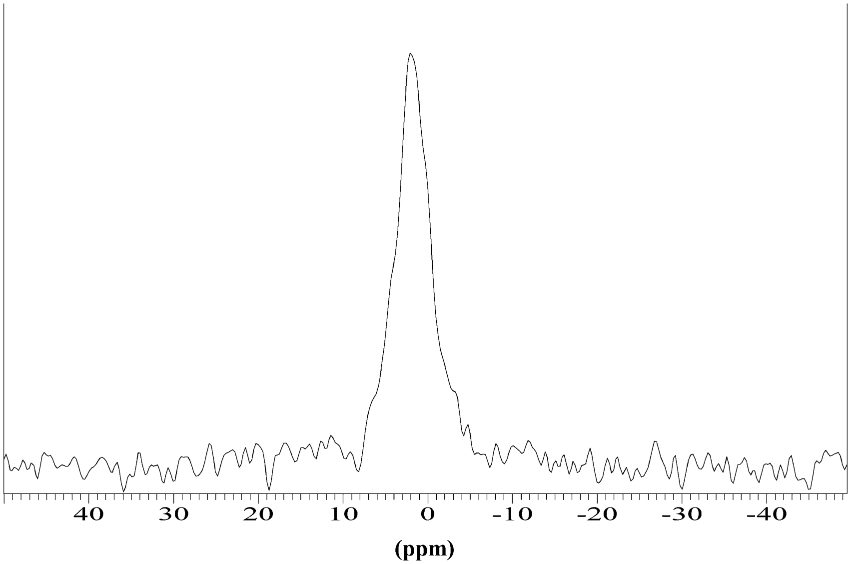


FIGURE 4 The ^{31}P MAS-NMR spectrum of (2-NH_2-3-$CH_3C_5H_3NH$)H_2PO_4.

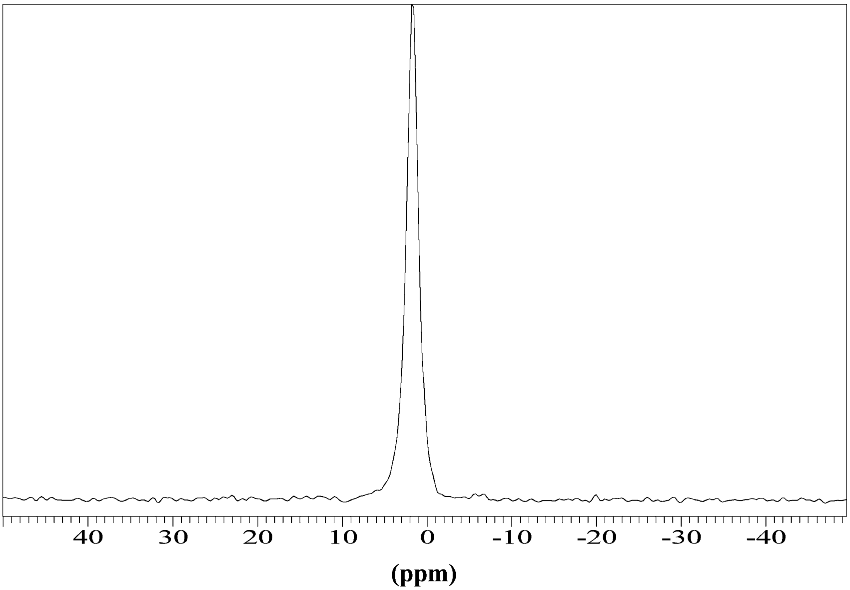


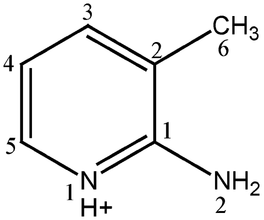
FIGURE 5 The ^{31}P MAS with a high decoupling NMR spectrum of $(2\text{-}NH_2\text{-}3\text{-}CH_3C_5H_3NH)H_2PO_4$.

contact time (typically 200 μs), a correlation is obtained between phosphorus and acidic protons linked to it (Figure 6). In contrast, when a large contact time (typically 5 ms) is used, the phosphorus atom shows a correlation with most protons of the solid including those of the organic moiety, due to spin diffusion (Figure 7).

The ^{13}C CP-MAS-NMR spectrum of crystalline dihydrogenmonophosphate $(2\text{-}NH_2\text{-}3\text{-}CH_3C_5H_3NH)H_2PO_4$ is given in Figure 8. The spectrum contains 6 resonances corresponding to the 6 carbon atoms of the organic cation. This result proves the presence of only one organic moiety in the asymmetric unit of the compound, which agrees with the X-ray diffraction data. To assign NMR components to the different carbon atoms, we have calculated the chemical shifts of the organic entity by use of the Ab initio method (at the B3LYP/6-31+G* level). The obtained results are gathered in Table IV. The carbon atoms are labelled as depicted in Scheme 1.

As δ_{iso} is the absolute chemical shift and relative chemical shifts, such as those measured experimentally, that corresponds to the difference $\delta_{exp} = \delta_{ref} - \delta_{iso}$, we can propose the attribution regrouped in Table IV.

Figure 9 shows the ^{15}N CP-MAS-NMR spectrum of the title compound. This spectrum is in good agreement with the X-ray structure.



SCHEME 1

Indeed, it exhibits two resonances at −227 and −316 ppm corresponding to the two crystallographically independent nitrogen atoms. The use of Ab intio calculations gives the following calculated chemical shifts values: δ_{iso} (N1) = 132.3 ppm and δ_{iso} (N2) = 202.6 ppm. From these theoretical calculations, we can conclude that N1 should be less shielded than N2. This allows us to propose that the signal at −227 ppm corresponds to N1 and that at −316 ppm corresponds to N2.

IR Absorption Spectroscopy

Although IR spectroscopy is one of the major physical methods for investigating molecular structure, we have recorded the IR spectrum

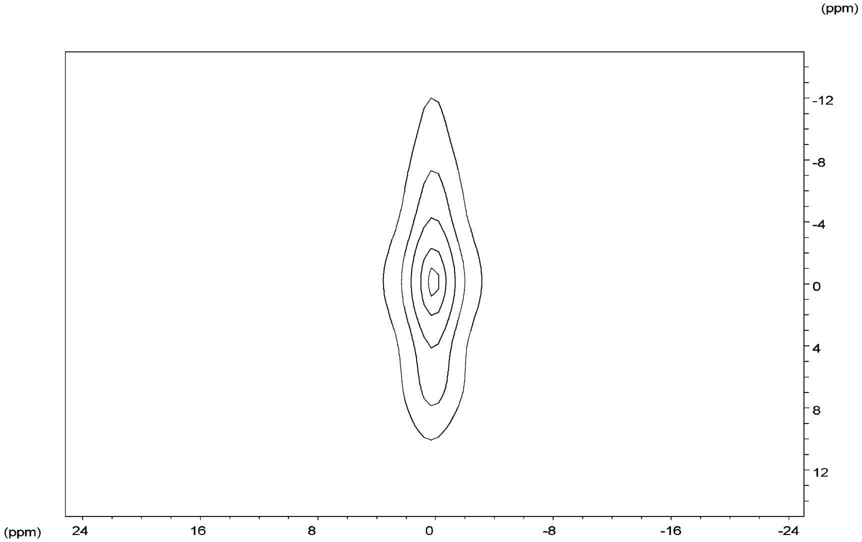


FIGURE 6 The two-dimensional ^{31}P–H CP-MAS RMN spectrum of (2-NH$_2$-3-CH$_3$C$_5$H$_3$NH)H$_2$PO$_4$ for a short contact time (200 μs).

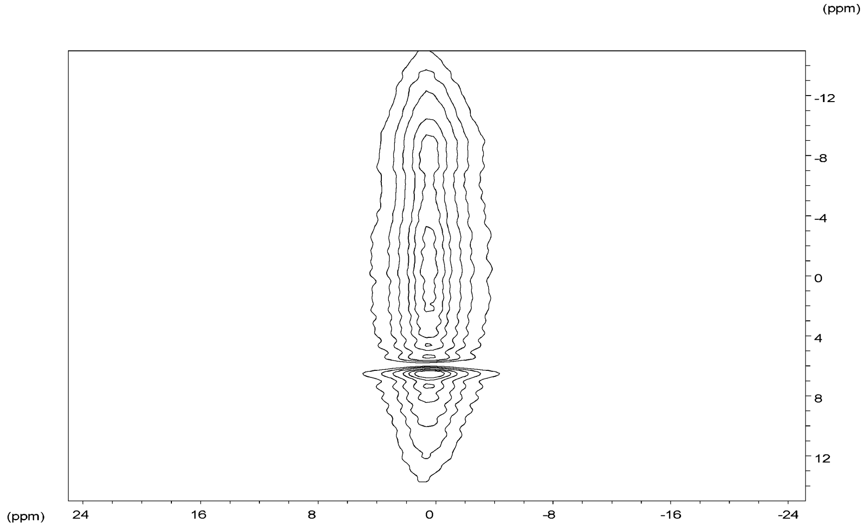


FIGURE 7 A two-dimensional ^{31}P–H CP-MAS RMN spectrum of $(2\text{-}NH_2\text{-}3\text{-}CH_3C_5H_3NH)H_2PO_4$ for a large contact time (5 ms).

of the dihydrogenomonophosphate $(2\text{-}NH_2\text{-}3\text{-}CH_3C_5H_3NH)H_2PO_4$ (Figure 10). To assign IR peaks to vibrational modes, we have examined the modes and frequencies in similar compounds.[19] The broad bands between 3500 and 2300 cm^{-1} correspond to the stretching of the organic and hydroxyl groups [ν(N—H), ν(C—H), and ν(O—H) of P—OH groups]. The vibrations between 1650 and 1200 cm^{-1} are assigned to bending

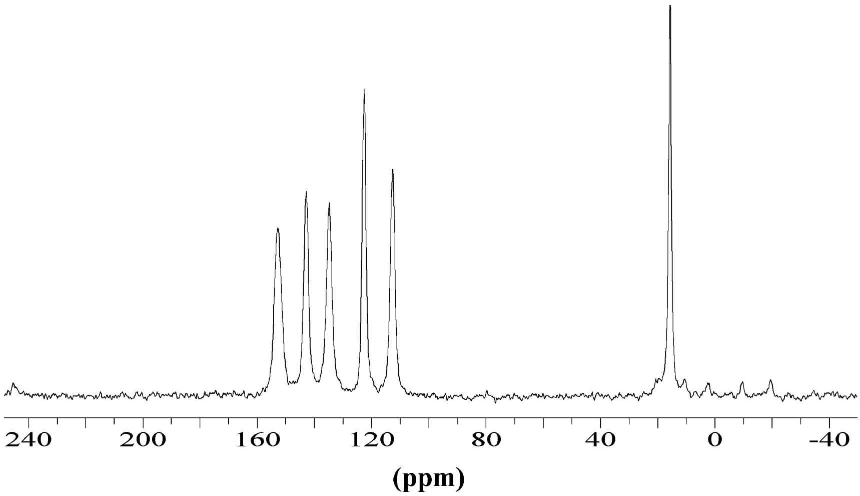


FIGURE 8 The ^{13}C CP-MAS NMR spectrum of $(2\text{-}NH_2\text{-}3\text{-}CH_3C_5H_3NH)H_2PO_4$.

TABLE IV Calculated (δ_{iso}) and Experimental (δ_{exp}) Chemical Shifts of the Organic Group Carbon Atoms in (2-NH_2-3-$CH_3C_5H_3NH)H_2PO_4$

Carbon atoms	C1	C2	C3	C4	C5	C6
δ_{iso} (ppm)	47.2	86.5	46.7	91.7	68.2	186.7
δ corrected(*)	154.9	115.8	155.6	110.6	134.1	15.6
δ_{exp} (ppm)	142.7	122.4	152.7	112.6	134.7	15.6

(*)Theoretical chemical shift determined by calibrating the peak of the methyl carbon atom at 15.6 ppm.

and stretching modes [$\delta(NH^+)$ and $\nu(C{=}C)$]. The observed shoulder at 1260 cm^{-1} and the band at 830 cm^{-1} are assigned to the δ(P—O—H) in-plane bending and δ(P—O—H) out-of-plane bending modes.[20] Various valence and bending vibration bands between 1200 and 400 cm^{-1} are characteristic of a PO_4 tetrahedron.[19] In this case, the internal vibration analysis of the PO_4 tetrahedron gives 4 vibrational frequencies; 2 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 650–300 cm^{-1} ranges, respectively. Supplementary frequencies in the $\nu_s(PO_4)$ domain are attributed to bending modes $\delta(C_{aryl}—H)_{ip}$.[21]

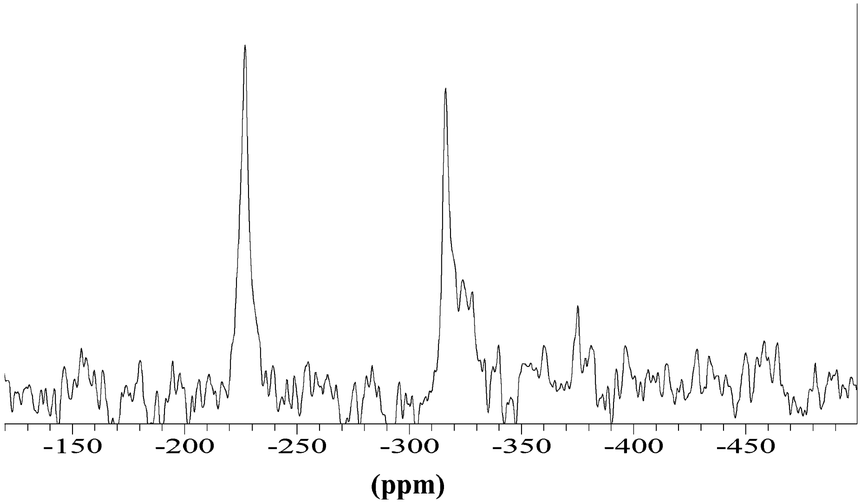


FIGURE 9 The ^{15}N CP-MAS NMR spectrum of (2-NH_2-3-$CH_3C_5H_3$ $NH)H_2PO_4$.

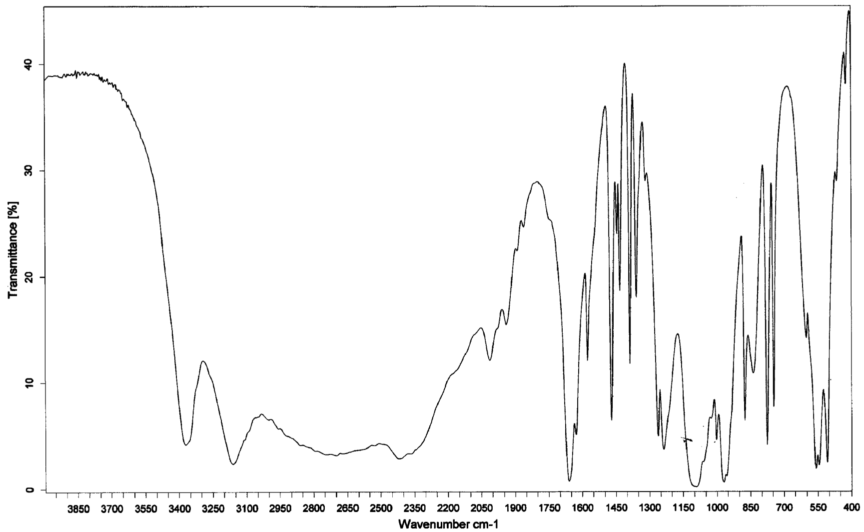


FIGURE 10 The IR absorption spectrum of $(2\text{-}NH_2\text{-}3\text{-}CH_3C_5H_3NH)H_2PO_4$.

Thermal Analysis

Two curves corresponding to DTA and TGA analysis in open air are given in Figure 11. The DTA curve shows that this dihydrogenmonophosphate undertakes two endothermic phenomena. The first peak occurs at 149°C and is accompanied by a weight loss obviously observed in the TGA curve. This weight loss corresponds to the removal

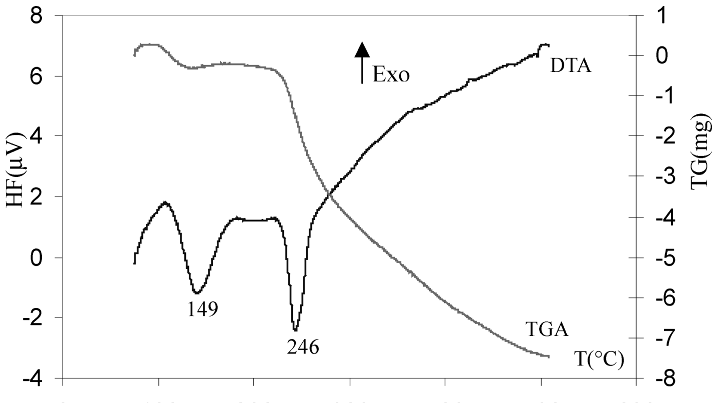


FIGURE 11 DTA and TGA curves of $(2\text{-}NH_2\text{-}3\text{-}CH_3C_5H_3NH)H_2PO_4$ at a rising temperature.

of a water molecule resulting from a dehydroxylation reaction due to the presence of terminal P—OH groups (% water: experimental 3.9, calculated 4.3). Then the TGA curve shows a continuous weight loss in the range 170–500°C characterized by an important peak at 246°C observed on the DTA curve. The corresponding phenomena could be interpreted by a $[2\text{-}NH_2\text{-}3\text{-}CH_3C_5H_3NH]^+$ degradation leading to a viscous matter of polyphosphoric acids with a carbon black residue.

Electrical Conductivity Measurements

Typical spectra were obtained by impedance spectroscopy measurements carried out in the temperature range 130–230°C, as shown in Figure 12. The total conductivity of samples has been obtained from the extrapolated intercept of the semicircle with the real axis at a low frequency. This intercept combines volume and grain boundary components of the total resistance (Figure 13) and shows the temperature dependence of the electrical conductivity, σ, of 2-amino-3-methylpyridinium dihydrogenmonophosphate. The increase of the conductivity as a function of temperature proves that this material has a nonmetal behavior.

If the carrier concentration remains constant throughout the temperature range measured, the Arrhenius diagram should be linear plotting

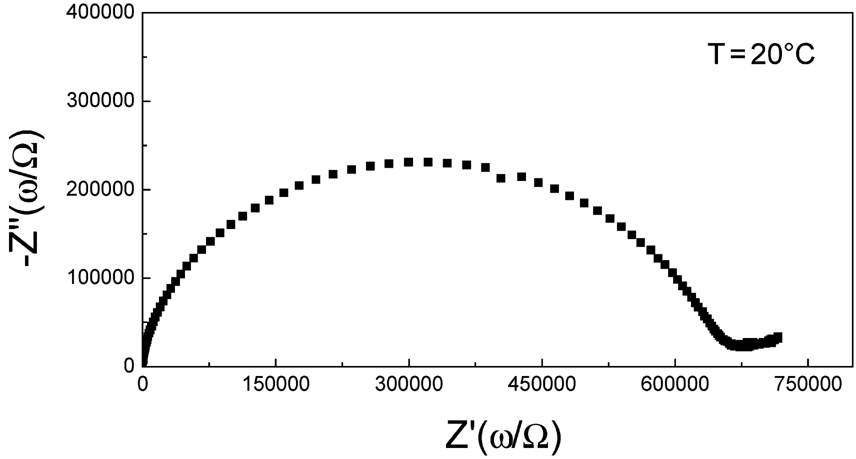


FIGURE 12 The typical impedance diagram obtained under air using symmetric cells for $(2\text{-}NH_2\text{-}3\text{-}CH_3C_5H_3NH)H_2PO_4$.

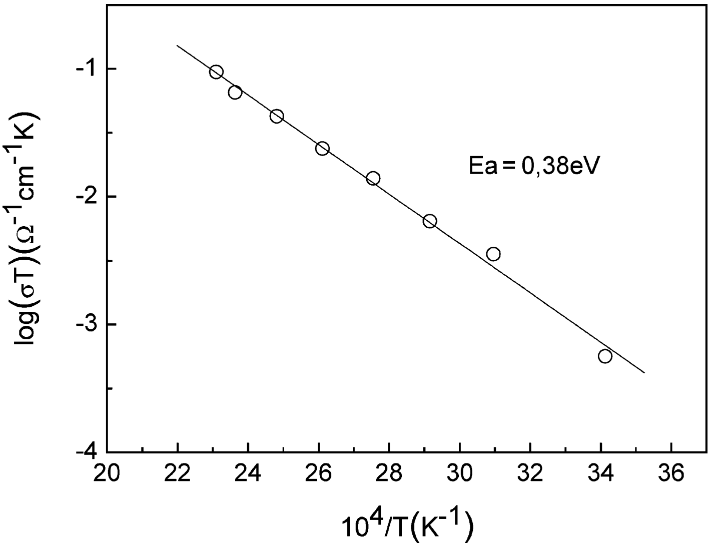


FIGURE 13 The temperature dependence of the conductivity of $(2\text{-}NH_2\text{-}3\text{-}CH_3C_5H_3NH)H_2PO_4$.

[log (σT) vs. $10^4/T$], following Eq. (1):

$$\sigma = \frac{A_0}{T}\exp\left(-\frac{E_a}{kT}\right) \tag{1}$$

where Ea is the activation energy and k and T are the Boltzman constant and the absolute temperature, respectively. The constant A_0 includes the carrier concentration as well as other material dependent parameters.[22,23] The Arrhenius plot shows that the activation energy is practically constant in the chosen temperature range, which can be explained by only one mechanism of conduction. The obtained value for the activation energy (0.38 eV) is relatively weak and is in favor of the electronical conductivity mechanism.

EXPERIMENTAL

Chemical Preparation

The title compound was prepared according to Eq. (2):

$$2\text{-}NH_2\text{-}3\text{-}CH_3C_5H_3N + H_3PO_4 \longrightarrow (2\text{-}NH_2\text{-}3\text{-}CH_3C_5H_3NH)H_2PO_4 \tag{2}$$

by adding, in a crystallizoir, 1.7 mL (25 mmol) of concentrated monophosphoric acid (Fluka, 85% wt, d = 1.7) to a solution of acetone and distilled water (V/V) containing 2.5 mL (25 mmol) of 2-amino-3-methylpyridine (Acros, d = 1.07). The so-obtained solution was slowly evaporated at r.t. until the formation of single crystals of $(2\text{-}NH_2\text{-}3\text{-}CH_3C_5H_3NH)H_2PO_4$ (3.1 g, 60% yield), with suitable dimensions for crystallographic study. Analysis. calculated for $C_6H_{11}N_2PO_4$ (206 $g.mol^{-1}$): C, 34.95; H, 5.34; N, 13.59; P, 15.05. Found: C, 35.27; H, 5.44; N, 13.29; P, 15.04. The crystals are stable for months under normal conditions of temperature and humidity. The compound chemical formula was determined when resolving the crystal structure by X-ray diffraction.

Investigation Techniques

The title compound has been studied by various physico-chemical methods: X-ray diffraction, solid state NMR spectroscopy, infrared spectroscopy, thermal analysis, and electrical conductivity.

X-ray Diffraction

A single crystal was carefully selected under a polarizing microscope in order to perform its structural analysis by X-ray diffraction. Intensity data were collected on an Enraf-Nonius MACH3 automated four-circle diffractometer using graphite monochromated $MoK\overline{\alpha}$ radiation, $\lambda = 0.7107$ Å. The structure was solved by direct methods using the SIR92 program[26] and refined by full matrix least-squares techniques based on F using TeXsan.[27] The drawings were made with Diamond.[28] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms position was located by difference-Fourier synthesis and was not refined. Crystal data and experimental parameters used for the intensity data collection are summarized in Table V.

Crystallographic Data (CIF) for the structure reported in this article have been deposited into the Cambridge Crystallographic Data Center as supplementary publication No. 279241. 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 75.49 MHz for ^{13}C, 30.30 MHz for ^{15}N, and 121.57 MHz for ^{31}P with a classical 4-mm probehead allowing spinning rates up to 10 kHz. ^{13}C, ^{31}P, and ^{15}N NMR chemical shifts are given relative to tetramethylsilane, 85% H_3PO_4, and neat CH_3NO_2, respectively (external references. precision 0.5 ppm). The spectra (except

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

Empirical formula	$(2\text{-}NH_2\text{-}3\text{-}CH_3C_5H_3NH)H_2PO_4$
Formula weight	207.15
Crystal system	Triclinic
Space group	P-1
a	7.343(2) Å
b	7.987(2) Å
c	8.116(4) Å
α	77.62(3)°
β	77.74(3)°
γ	87.03(2)°
Z	2
V	454.3(3) $Å^3$
$\rho_{cal.}$	1.514 $g{\cdot}cm^{-3}$
F(000)	218
$\mu(AgK_{\overline{\alpha}})$	2.885 (cm^{-1})
Crystal size (mm)	0.60 × 0.30 × 0.25
Index ranges: ±h, ±k, l	$(h_{max} = \pm 8.\ k_{max} = \pm 9.\ l_{max} = 9)$
Collected reflections	1729
Independent reflections	1602
Unique reflections included	1440 $(I > 2.\sigma(I))$
R_{int}	0.01
Refined parameters	121
$R\ [I > 3.\sigma(I)]$	0.03
R_w	0.05
Goodness of fit	1.700

for phosphorus) were 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.

Infrared spectroscopy. Spectra were recorded in the range 4000–400 cm^{-1} with a Perkin-Elmer FTIR-1000 spectrophotometer using samples dispersed in spectroscopically pure KBr pellets.

Thermal behavior. Thermal analysis was performed using the multimodule 92 Setaram analyzer operating from r.t. up to 450°C at an average heating rate of 5°C/min.

Electrical conductivity. To measure electrical conductivity, we used impedance spectroscopy.[24,25] The impedance diagrams were recorded in the 5 Hz–13 MHz frequency range using a Hewlett Packard *HP 4192A* analyzer. To assure electrical contacts, the two parallel surfaces of the sample (having a cylindrical shape) were coated by a layer of silver paint. The platinum wires and the sample were held in contact by a weak mechanical pressure controlled by a screw/spring system and transmitted by an alumina rod.

CONCLUSION

$(2\text{-}NH_2\text{-}3\text{-}CH_3C_5H_3NH)H_2PO_4$ was prepared as single crystals at r.t. and characterized by various physico-chemical methods. On the structural level, the atomic arrangement of the title compound can be described by $(H_2PO_4^-)_n$ polymeric chains anchoring the organic cations through strong hydrogen bonds. Solid-state ^{31}P and ^{13}C NMR spectroscopy results are in agreement with those of the X-ray structure. Upon heating, this monophosphate was stable until 149°C K. After heating at 500°C, a viscous matter of polyphosphoric acids with a carbon black residue was obtained. The impedance spectroscopy measurements showed that the material has a nonmetal behaviour and an electronical conductivity mechanism.

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