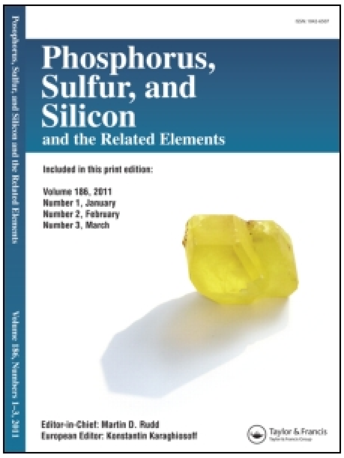

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# Synthesis and Characterization of Two New Compounds: $N(C_2H_4NH_3)_3(H_2TO_4)(HTO_4)\cdot 2H_2O$ (T = P, As)

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# Synthesis and Characterization of Two New Compounds: $N(C_2H_4NH_3)_3(H_2TO_4)(HTO_4)\cdot 2H_2O$ (T = P, As)

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*The synthesis and structures of two new compounds with the general formula $N(C_2H_4NH_3)_3(H_2TO_4)(HTO_4)\cdot 2H_2O$ (T = P, As) are reported. They crystallize with triclinic unit cells and are isotropic. We determined the structure of phosphate salt. The following unit cell parameters were found: a = 9.886(4), b = 9.308(2), c = 10.140(3) Å, $\alpha$ = 109.38(2), $\beta$ = 108.83(3), $\gamma$ = 74.40(3)°, V = 819.2(5) $Å^3$, and $\rho_{cal.} = 1.537\ g \cdot cm^{-3}$. The crystal structure was solved with a final R = 0.042 for 3748 with I >3$\sigma$ I). The space group is P-1 and Z = 2. The atomic arrangement can be described as a three-dimensional network of hydrogen bonds made up from $H_nPO_4^{3-n}$ (n = 1, 2) anions and $H_2O$ molecules between which are trapped the tris(2-ammoniumethyl)amine cations. Solid-state $^{13}C$ and $^{31}P$ MAS-NMR spectroscopies are in agreement with X-ray structure. Ab initio calculations allow the attribution of the phosphorus signals to the independent crystallographic sites.*

**Keywords** Crystal structure; nuclear magnetic resonance; organic cation monophosphate; X-ray diffraction

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Crystallographic Data for the structure reported in this article have been deposited into the Cambridge Crystallographic Data Center as supplementary publication No. 260135. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB 12EZ, UK. E-mail: deposit@ccdc.cam.ac.uk.

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## INTRODUCTION

Organic phosphoric complexes have been widely studied due to their many practical and potential uses in various fields, such as bimolecular sciences, catalysis, fuel cell, liquid crystal-material developers, and quadratic nonlinear optics.[1–6] Among these complexes, monophosphate salts of ethylendiamine[7–9] and diethylentriamine have been described.[10] Until now, the monohydrogenmonophosphate $[NH_3(CH_2)_2NH_2(CH_2)_2NH_2(CH_2)_2NH_3](HPO_4)_2{\cdot}2H_2O$ is the only monophosphate complex of triethylentetraamine known.[11] The present work is devoted to a detail structure of the $N(C_2H_4NH_3)_3(H_2PO_4)(HPO_4){\cdot}2H_2O$ compound obtained by the reaction of tris(2-aminoethyl)amine with monophosphoric acid. The characterization by $^{13}C$ and $^{31}P$ solid-state NMR spectroscopy is also reported.

## RESULTS AND DISCUSSION

### Description of the Structure

Final atomic coordinates and thermal parameters are given in Table I. Those of hydrogen atoms were also determined but are not given in

**TABLE I Final Atomic Coordinates and Beq for Nonhydrogen Atoms**

| Atom | x (σ) | y (σ) | z (σ) | $B_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| P(1) | 0.19340(3) | 0.16694(4) | 0.83574(3) | 0.01848(6) |
| P(2) | 0.28984(3) | −0.02460(4) | 0.38344(3) | 0.01967(6) |
| O(3) | 0.05282(13) | 0.25000(16) | 0.19994(13) | 0.0495(3) |
| O(4) | 0.13600(15) | 0.49148(15) | 1.15895(14) | 0.0515(3) |
| O(5) | 0.40844(10) | −0.17456(11) | 0.39715(12) | 0.0343(2) |
| O(6) | 0.14658(9) | −0.06535(11) | 0.37255(9) | 0.0274(2) |
| O(7) | 0.33049(10) | 0.10610(11) | 0.51802(10) | 0.0311(2) |
| O(8) | 0.28429(10) | 0.01346(11) | 0.24722(9) | 0.0289(2) |
| O(9) | 0.16835(10) | 0.20443(11) | 0.69017(10) | 0.0300(2) |
| O(10) | 0.03407(9) | 0.20054(11) | 0.85276(10) | 0.0277(2) |
| O(W1) | 0.27626(10) | 0.27549(10) | 0.96188(10) | 0.0292(2) |
| O(W2) | 0.25899(9) | −0.00179(10) | 0.82318(10) | 0.0272(2) |
| N(1) | 0.54058(12) | −0.15784(13) | 0.80762(12) | 0.0244(2) |
| N(2) | 0.21647(14) | −0.18488(14) | 0.97377(13) | 0.0313(3) |
| N(3) | 0.09595(11) | −0.18266(12) | 0.56456(12) | 0.0236(2) |
| N(4) | 0.32947(11) | −0.38077(11) | 0.71845(11) | 0.0219(2) |
| C(1) | 0.54241(14) | −0.30757(16) | 0.69608(14) | 0.0278(3) |
| C(2) | 0.48727(14) | −0.42112(15) | 0.73430(15) | 0.0276(3) |
| C(3) | 0.31367(17) | −0.33747(17) | 0.96703(15) | 0.0349(3) |
| C(4) | 0.29065(16) | −0.44263(15) | 0.81379(15) | 0.0298(3) |
| C(5) | 0.09777(14) | −0.35056(15) | 0.53166(15) | 0.0278(3) |
| C(6) | 0.25154(15) | −0.43681(16) | 0.56650(14) | 0.0284(3) |

**TABLE II Main Interatomic Distances (Å) and Angles (°) in the $N(C_2H_4NH_3)_3(H_2PO_4)(HPO_4)\cdot 2H_2O$ Atomic Arrangement**

| | | | | |
|---|---|---|---|---|
| $P(1)O_4$ Tetrahedron | | | | |
| P(1) | O(7) | O(8) | O(9) | O(10) |
| O(7) | 1.555(12) | 2.441(18) | 2.537(17) | 2.413(17) |
| O(8) | 102.43(7) | 1.575(11) | 2.473(18) | 2.526(17) |
| O(9) | 112.46(7) | 107.23(7) | 1.496(12) | 2.518(16) |
| O(10) | 110.21(7) | 109.98(7) | 113.86(7) | 1.508(11) |
| O(7)-H(O7) = 0.79 Å | | | P(1)-O(7)-H(O7) = 121.0° | |
| O(8)-H(O8) = 0.89 Å | | | P(1)-O(8)-H(O8) = 115.6° | |
| $P(2)O_4$ Tetrahedron | | | | |
| P(2) | O(3) | O(4) | O(5) | O(6) |
| O(3) | 1.576(2) | 2.511(3) | 2.481(3) | 2.509(3) |
| O(4) | 108.37(11) | 1.520(2) | 2.505(3) | 2.517(3) |
| O(5) | 106.35(10) | 110.81(10) | 1.523(2) | 2.506(2) |
| O(6) | 108.31(11) | 111.87(10) | 110.91(10) | 1.519(2) |
| O(3)-H(O3) = 0.77 Å | | | P(2)-O(3)-H(O3) = 107.4° | |
| $[N(C_2H_4\ NH_3)_3]^{3+}$ Cation | | | | |
| N(1)-C(1) | 1.475(2) | | C(4)-N(4)-C(2) | 110.26(12) |
| N(2)-C(2) | 1.480(2) | | C(4)-N(4)-C(6) | 111.80(12) |
| N(3)-C(5) | 1.482(2) | | C(6)-N(4)-C(2) | 110.12(12) |
| N(4)-C(2) | 1.471(2) | | N(1)-C(1)-C(2) | 111.19(13) |
| N(4)-C(4) | 1.463(2) | | N(4)-C(2)-C(1) | 112.25(12) |
| N(4)-C(6) | 1.468(2) | | N(2)-C(3)-C(4) | 111.79(13) |
| C(1)-C(2) | 1.511(2) | | N(4)-C(4)-C(3) | 111.63(2) |
| C(3)-C(4) | 1.519(2) | | N(3)-C(5)-C(6) | 110.39(13) |
| C(5)-C(6) | 1.505(2) | | N(4)-C(6)-C(5) | 112.59(2) |

order to shorten the table. Interatomic distances, bonding angles, and the hydrogen bonding scheme are listed in Tables II and III, respectively.

The asymmetric unit of the structure consists of two phosphate anions with a different acidity degree, two water molecules, and one organic cation: tris(2-ammoniumethyl)amine (Figure 1). All atoms forming these entities occupy the general positions in the unit cell. The atomic arrangement of tris(2-ammoniumethyl)amine mono-and dihydrogenmonophosphate dihydrate shows polyanions resulting from the aggregation of $H_nPO_4^{3-n}$ (n = 1,2) and $H_2O$ molecules through strong hydrogen bonds as to form a three-dimensional network (Figure 2). The organic cation stabilizes the crystal structure by establishing both ionic interactions and hydrogen bonds with the inorganic skeleton (Figure 3). The presence of a three-dimensional hydrogen bondings network between mineral anions and organic cations has been observed in biological systems such as phenylethylamines-ATP, phenylethylamines-GTP, and phenylethylamines-PIB complexes.[12]

**TABLE III Hydrogen-Bond Scheme in $N(C_2H_4NH_3)_3(H_2PO_4)(HPO_4)\cdot 2H_2O$**

| O(N)-H···O | O(N)-H (Å) | H···O (Å) | O(N)···O (Å) | O(N)-H···O(°) |
|---|---|---|---|---|
| O8-H(5)···O4 | 0.89(3) | 1.70(3) | 2.580(2) | 176.1(2) |
| O7-H(6)···O5 | 0.79(2) | 1.76(2) | 2.531(2) | 168.4(2) |
| O3-H(7)···O5 | 0.77(2) | 1.86(2) | 2.514(2) | 173.9(2) |
| N1-H(8)···O9 | 0.85(2) | 1.97(2) | 2.800(2) | 162.5(2) |
| N1-H(9) O6 | 0.88(2) | 1.88(2) | 2.735(2) | 163.3(1) |
| N1-H(10)···O10 | 0.86(2) | 1.93(2) | 2.800(2) | 176.5(1) |
| N2-H(11)···O6 | 0.89(2) | 1.87(2) | 2.759(2) | 173.3(2) |
| N2-H(12)···O10 | 0.82(2) | 2.00(2) | 2.818(2) | 170.2(2) |
| N2-H(13)···OW(1) | 0.95(2) | 1.86(2) | 2.773(2) | 160.6(2) |
| N3-H(14)···O10 | 0.83(2) | 2.04(2) | 2.847(2) | 163.3(2) |
| N3-H(15)···O4 | 0.89(2) | 1.87(2) | 2.751(2) | 167.8(2) |
| N3-H(16)···O4 | 0.90(2) | 2.03(2) | 2.911(2) | 163.9(1) |
| OW(1)-H(3)···O6 | 0.77(3) | 1.99(3) | 2.756(2) | 169.1(3) |
| OW(1)-H(4)···OW(2) | 0.83(2) | 1.95(3) | 2.781(3) | 174.4(2) |
| OW(2)-H(1)···O9 | 0.79(2) | 2.00(2) | 2.753(2) | 160.4(2) |
| OW2-H(2)···O8 | 0.71(2) | 2.26(2) | 2.926(2) | 156.3(2) |

Chains of phosphate anions are made up from $H_2PO_4^-$ and $HPO_4^{2-}$ units, themselves interconnected by strong hydrogen bonds as to build infinite chains running along the **a** direction. Every chain is built up through short hydrogen bonds that connect P—OH to P=O groups (donor–acceptor: 2.5143(18), 2.5319(8), 2.5804(18) Å). Between these chains, two water molecules, crystallographically independent, come to

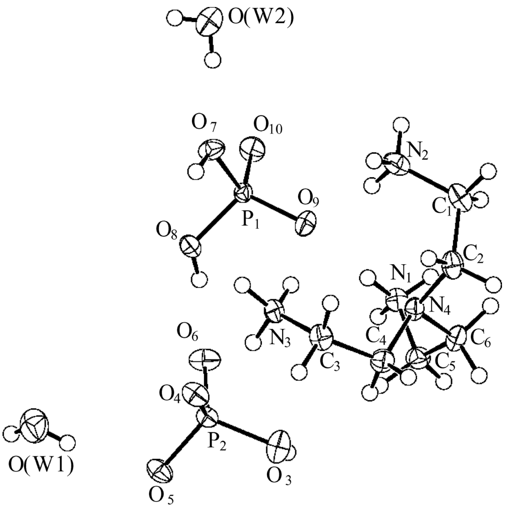

**FIGURE 1** Asymmetric unit of $N(C_2H_4NH_3)_3(H_2PO_4)(HPO_4)\cdot 2H_2O$.

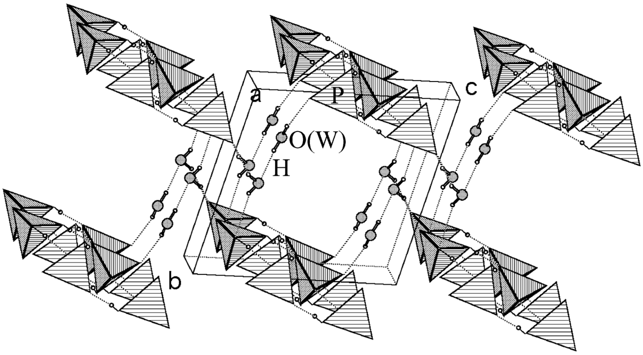

**FIGURE 2** Perspective view of the three-dimensional arrangement of the inorganic entity in $N(C_2H_4NH_3)_3(H_2PO_4)(HPO_4)\cdot 2H_2O$.

be attached through OH· · ·O strong hydrogen bonds in order to perform the three-dimensional cohesion of the structure (Figure 2).

This uncommon richness in hydrogen bonds is a phenomenon rarely observed in simple organic or mineral compounds; it could be used as a structural model and mime for some reaction mechanisms of the chemical processes in biological media.

Selected bond lengths and angles are listed in Table II. Both of the P atoms are coordinated with oxygen atoms with average P—O distances

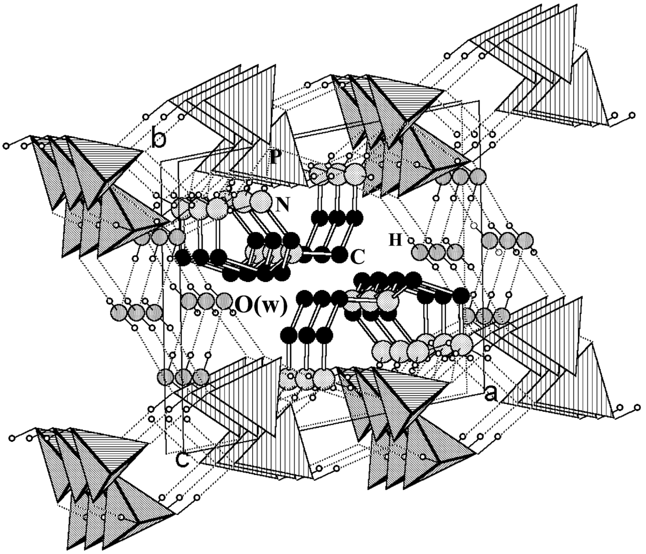

**FIGURE 3** Perspective view of the three-dimensional arrangement in $N(C_2H_4NH_3)_3(H_2PO_4)(HPO_4)\cdot 2H_2O$.

of 1.534 Å. The O—P—O bond angles are close to the expected tetrahedral angle of 109.4°. One hydrogen position for each of the oxygens O(3), O(7), and O(8) has been observed in the difference Fourier maps. Thus, P(1)-O(7), P(1)-O(8), and P(2)-O(3) have distances of 1.555(12), 1.575(11), and 1.576(2) Å, respectively, corresponding to P-OH units. These values are comparable to the reported data.[7–10]

The amine used in the present study, tris(2-aminoethyl)amine, has three terminal nitrogen atoms, all of which are protonated. So, the amine molecules are arranged as to form three talons of a claw. The tris(2-ammoniumethyl)amine cations interact through hydrogen bonding with the double-bonded oxygens as well as with the hydroxyl oxygens (Figure 3). Table II reports the principal geometrical features of a $[N(C_2H_4\ NH_3)_3]^{3+}$ cation. The C—C and C—N bond lengths vary from 1.505(2) to 1.519(2) Å and 1.471(2) to 1.482(2) Å, respectively. They are close to those observed in $[NH_3(CH_2)_2NH_2(CH_2)_2NH_2(CH_2)_2NH_3](HPO_4)_2$: (1.5097(13) to 1.5110(13) and 1.4758(12) to 1.4872(12), respectively).[11]

Table III shows that only the N1, N2, and N3 nitrogen atoms of the ethylammonium groups are involved in hydrogen bondings. The failure of the basic central trialkylamine to participate in hydrogen bonding is probably due to the steric effect caused by the three ethylammonium groups around the title nitrogen atom.

## NMR Results

Figure 4 shows the proton-decoupled $^{31}P$ MAS NMR spectrum of crystalline hydrogenmonophosphate $N(C_2H_4NH_3)_3(H_2PO_4)(HPO_4)\cdot 2H_2O$. This spectrum is in good agreement with the X-ray structure. Indeed, it exhibits two resonances at −0.3 and 4.3 ppm, corresponding to two crystallographically unequivalent phosphorus. These chemical shift values agree well with those of monophosphates (between −10 and +5 ppm, depending on the compound).[13–19] The attribution of NMR components to the phosphorus atoms P1 and P2 was done by using Ab initio calculations. For this purpose, the chemical shifts of the two phosphorus atoms P1 and P2 in the two $PO_4$ tetrahedra were calculated. The results are depicted as follows:

$$P1\delta_{iso} = 295.1 \text{ ppm} \quad \Delta\delta = 112.6 \text{ ppm} \quad \eta = 0.17$$

$$P2\delta_{iso} = 291.6 \text{ ppm} \quad \Delta\delta = 79.4 \text{ ppm} \quad \eta = 0.20$$

$\delta_{iso}$ is the absolute chemical shift. As relative chemical shifts, such as those measured experimentally, correspond to the difference: $\delta_{exp} = \delta_{ref} - \delta_{iso}$, we can conclude from these theoretical calculations that P2 should be less shielded than P1. This allows us to propose that the

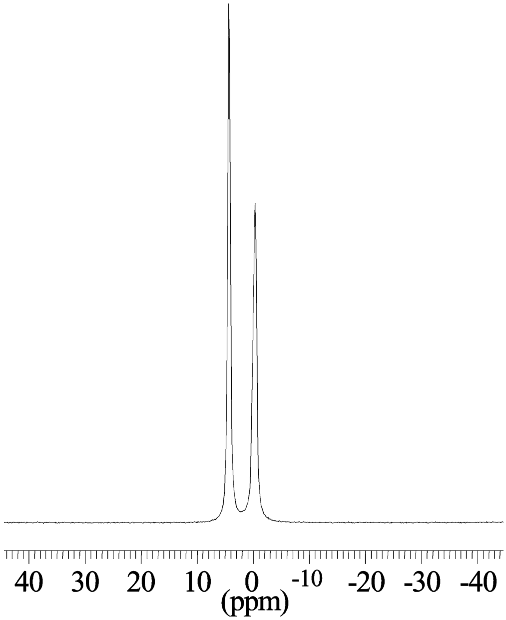

**FIGURE 4** $^{31}P$ MAS-NMR spectrum of crystalline $N(C_2H_4NH_3)_3(H_2PO_4)(HPO_4)\cdot 2H_2O$.

signal at −0.3 ppm corresponds to P1 and that the signal at 4.3 ppm corresponds to P2. In the two cases, the asymmetry parameter $\eta$ is different from zero, indicating that the local symmetry of the tetrahedra is lower than $T_d$.

The $^{13}C$ CP MAS spectrum of the as-synthesized hydrogenmonophosphate displays five different signals at 32.3, 33.3, 33.7, 47.3, and 48.2, with relative intensities 1:1:1:2:1 (Figure 5). This spectrum is in good agreement with the X-ray structure, which shows six crystallographically inequivalent carbons. The first three signals are assigned to the three $CH_2$ groups in $\alpha$ position of $NH_3^+$ (C1, C4, and C6). The two other signals, in a 1:2 ratio, are attributed to the three other $CH_2$ groups (C2, C3, and C5). This signal multiplicity is in good agreement with the X-ray structure as only one organic molecule is found in the asymmetric unit cell (Figure 1).

## IR Absorption Spectroscopy

Although IR spectroscopy is one of the major physical methods for the investigation of molecular structures, we have studied the IR spectrum of crystalline hydrogenmonophosphate $N(C_2H_4NH_3)_3(H_2PO_4)(HPO_4)\cdot 2H_2O$, which is shown in Figure 6. To assign the IR

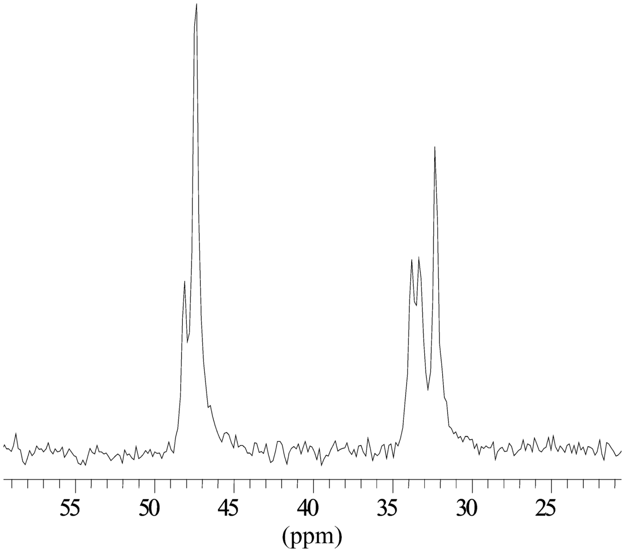

**FIGURE 5** $^{13}$C CP-MAS-NMR spectrum of crystalline $N(C_2H_4NH_3)_3(H_2PO_4)(HPO_4)\cdot 2H_2O$.

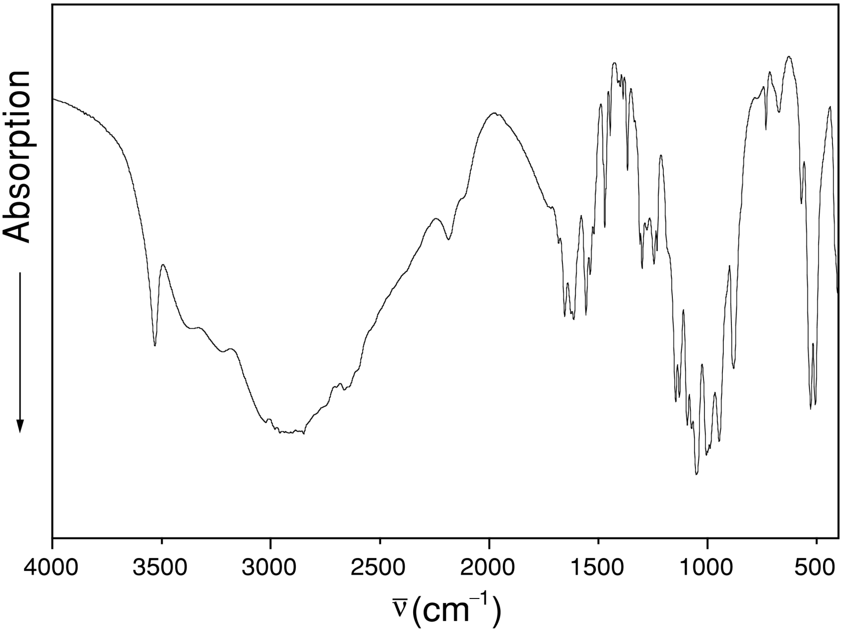

**FIGURE 6** IR spectrum of $N(C_2H_4NH_3)_3(H_2PO_4)(HPO_4)\cdot 2H_2O$.

peaks to vibrational modes, we examined the modes and frequencies observed in similar compounds.[20] Frequencies in the range 3600 and 2300 $cm^{-1}$ are attributed to the stretching of the organic and hydroxyl groups ($\nu$N—H, $\nu$C—H), and $\nu$(O—H) of $H_2O$ molecules and PO—H groups. The vibrations between 1650 and 1200 $cm^{-1}$ are assigned to bending modes ($\delta NH_3^+$, $\delta CH_2$). The various vibration bands between 1200 and 400 $cm^{-1}$ are characteristic of a monophosphate and correspond to valence and bending modes.[20] For example, the internal vibrations analysis of the $PO_4$ tetrahedron[21,22] shows that this group has four vibrational frequencies, two stretching modes of $\nu_s$ and $\nu_{as}$ (respectively symmetric and asymmetric), and two bending modes of $\delta_s$ and $\delta_{as}$. These vibrations are expected in the 1200–800 $cm^{-1}$ and 650–400 $cm^{-1}$ ranges, respectively.

## Thermal Analysis

Two curves corresponding to DTA and TGA analysis in open air are given in Figure 7. The DTA curve shows that this hydrogenmonophosphate undertakes a succession of endothermic phenomenon. The first peak occurs at 91.7°C and corresponds to the complete dehydration of the compound. It is accompanied with a weight loss obviously observed in the TGA curve. From this, we deduce a departure of two wa-

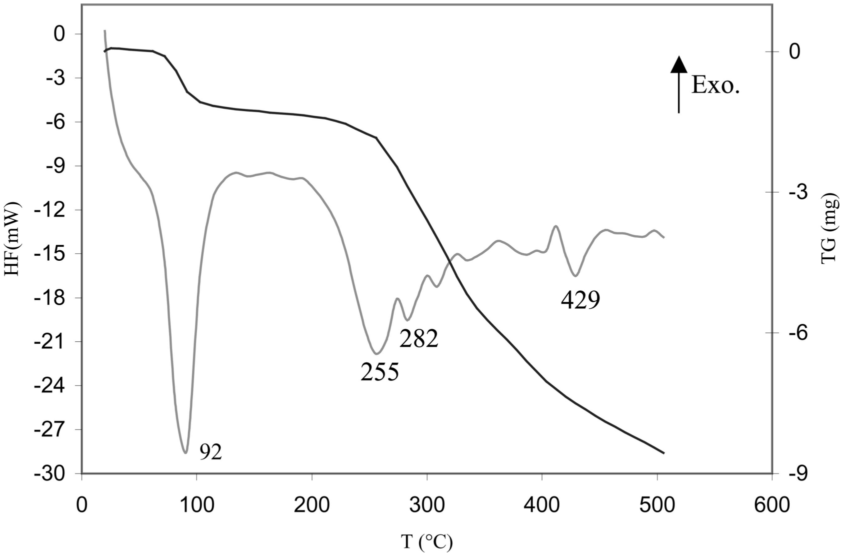

**FIGURE 7** DTA and TGA curves of $N(C_2H_4NH_3)_3(H_2PO_4)(HPO_4)\cdot 2H_2O$ at rising temperatures.

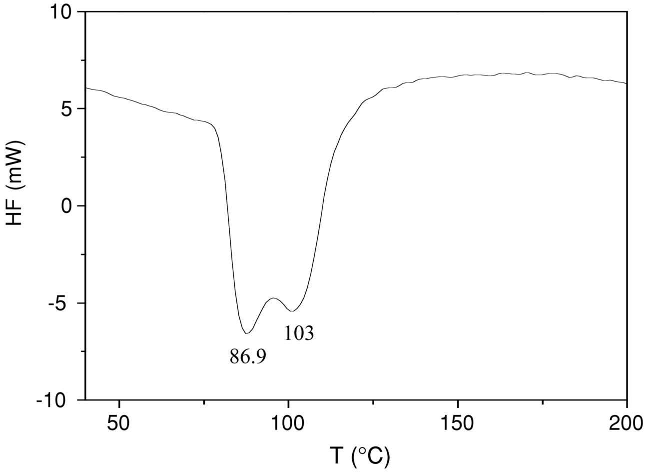

**FIGURE 8** DSC curve of $N(C_2H_4NH_3)_3(H_2PO_4)(HPO_4)\cdot 2H_2O$ at rising temperatures.

ter molecules (% water: experimental 9.1 and calculated 9.4). Then, the product undergoes a decomposition of the organic group over a wide temperature range (200–500°C). This is also confirmed by the significant weight loss observed in the TGA curve.

The DSC thermogram (Figure 8) reveals two endothermic peaks, which are detected at 86.9 and 103.0°C. Each one of these peaks corresponds to the dehydration of a water molecule. This result agrees with the X-ray diffraction one which shows the presence of two crystallographically independent water molecules. The dehydration enthalpies are $\Delta H_1 = 42.5$ and $\Delta H_2 = 55.7$ KJ·mol$^{-1}$, respectively.

## EXPERIMENTAL

### Chemical Preparation

The crystal of the title compound has been prepared according to the following chemical reaction:

$$N(C_2H_4NH_2)_3 + 2H_3TO_4 + 2H_2O \xrightarrow{T=P,\ As} N(C_2H_4NH_3)_3(H_2TO_4)(HTO_4)\cdot 2H_2O \qquad (1)$$

by mixing in a stoichiometric ratio a solution of orthophosphoric acid (85 wt.% $H_3PO_4$) with an aqueous solution of tris(2-amminoethyl)amine. After the reaction, the obtained solution is slowly evaporated at r.t. in order to allow the formation of $N(C_2H_4NH_3)_3(H_2PO_4)(HPO_4)\cdot 2H_2O$

crystals of suitable dimensions for X-ray structural analysis. The crystals are stable for a long time in normal conditions of temperature and hydrometry. The compound chemical formula was determined by solving its 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, and thermal analysis.

### 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 AgK$_{\bar{\alpha}}$ radiation, $\lambda = 0.5608$ Å. The structure was solved by direct methods using the SIR92 program[23] and was refined by full matrix least-squares techniques based on F using the TeXsan.[24] The drawings were made with the MolView.[25] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms position were located by difference-Fourier synthesis and refined. Crystal data and experimental parameters used for the intensity data collection are summarized in Table IV.

### Physical Measurements

*NMR Spectroscopy.* All NMR spectra were recorded on a Bruker DSX-300 spectrometer operating at 75.49 MHz for $^{13}$C and 121.51 MHz for $^{31}$P with classical 4-mm probehead allowing spinning rates up to 10 KHz. $^{13}$C NMR chemical shifts are given relative to tetramethylsiline and $^{31}$P ones are relative to 85% $H_3PO_4$ (external reference precision 0.5 ppm). Phosphorous spectra were recorded under classical MAS conditions while the carbon ones were recorded by the use of cross-polarization from protons (contact time 5 ms). To assign NMR components to the various carbons of the organic groups, ab initio calculations were performed with Gaussian 98 software.[15]

*Infrared Spectroscopy.* Spectra were recorded in the range of 4000–400 cm$^{-1}$ with a Perkin-Elmer FTIR spectrophotometer 1000 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 500°C at an average heating rate of 5°C/min.

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

| | |
|---|---|
| Empirical formula | $N(C_2H_4NH_3)_3(H_2PO_4)(HPO_4)\cdot 2H_2O$ |
| Formula weight | 379.26 |
| Crystal system | triclinic |
| Space group | P-1 |
| a | 9.886(4) Å |
| b | 9.308(2) Å |
| c | 10.140(3) Å |
| $\alpha$ | 109.38(2)° |
| $\beta$ | 108.83(3)° |
| $\delta$ | $\gamma = 74.40(3)°$ |
| Z | 2 |
| V | 819.2(5) Å$^3$ |
| $\rho_{\text{cal.}}$ | 1.537 g.cm$^{-3}$ |
| F(000) | 406 |
| $\mu$ (AgK$_{\bar{\alpha}}$) | 1.718 (cm$^{-1}$) |
| Crystal size [mm] | 0.04 × 0.03 × 0.025 |
| Index ranges: ± h, ± k, l | ($h_{max} = \pm 14$. $k_{max} = \pm 14$. $l_{max} = 15$) |
| Collected reflections | 6110 |
| Independent reflections | 5824 |
| Unique reflections included | 3748 [$I > 3.\sigma(I)$] |
| $R_{int}$ | 0.01 |
| Refined parameters | 199 |
| R ($I > 3.\sigma(I)$) | 0.042 |
| $R_w$ | 0.06 |
| Goodness of fit | 1.340 |

## Theoretical Calculations

In order to allow the attribution of the 31P NMR signals, ab initio calculations were performed using the Gaussian 98 software.[15] For this purpose, the coordinates of the two inequivalent $PO_4$ tetrahedra were used and the absolute chemical shift tensors were calculated by the B3LYP/6-311+G* method. The isotropic chemical shift, chemical shift anisotropy, and asymmetry parameter $\eta$ were then deduced from these data.

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