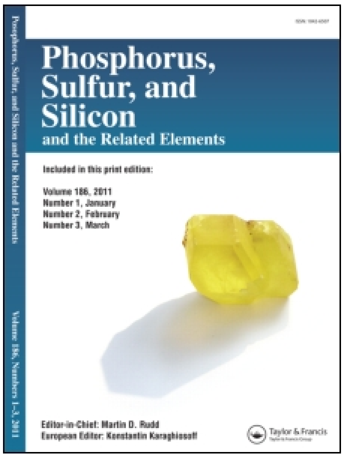

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Chemical Preparation, Spectroscopic Study and Crystal Structure of DL 2-Ammoniumbutyric Dihydrogenmonophosphate ({\rm CH_3CH_2CHCOOH)(H_2PO_4)^{\hbox{\bf --}}}\vspace*{-2pt}\break\hspace*{-26pt}|\hspace*{26pt}\break\hspace*{-24pt}{^{\bm +}}{\rm NH_3}\hspace*{24pt}}

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CHEMICAL PREPARATION, SPECTROSCOPIC STUDY AND CRYSTAL STRUCTURE OF DL 2-AMMONIUMBUTYRIC DIHYDROGENMONOPHOSPHATE

$$(CH_3CH_2\underset{\substack{| \\ {}^{+}NH_3}}{C}HCOOH)(H_2PO_4)^-$$

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Crystals of DL 2-ammoniumbutyric dihydrogenmonophosphate were obtained by evaporating an aqueous solution containing equimolar quantities of DL 2-amino butyric and orthophosphoric acids. IR and NMR spectrometry studies has been investigated and confirmed by X-ray single crystal diffraction results. The title compound is monoclinic, space group $P2_1/c$, unit cell dimensions $a = 10.5450(3)$ Å, $b = 10.0486(3)$ Å, $c = 8.9526(4)$ Å, $\beta = 111.769(5)^\circ$. Using 1,303 reflections with $I > 3\sigma(I)$ measured on CAD4 Mach 3 diffractometer, the crystal structure was solved by direct methods and was refined by least squares full matrix procedures to $R = 0.038$. The main feature of this structure consists of an alternate stacking of $H_2PO_4^-$ tetrahedral sheets and $NH_3C_3H_6COOH^+$ cation layers. The $H_2PO_4^-$ groups are associated to form infinite chains $[(H_2PO_4)n]^{n-}$. The crystal structure is stabilized by a three-dimensional network of strong hydrogen bonds.

Keywords: Hybrid; hydrogen bonding; phosphate; x-ray diffraction

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The supplementary material has been sent to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, deposition N°. CCDC 167871 and can be obtained by contacting the CCDC.

INTRODUCTION

The number of hybrid materials has been rapidly growing owing to their applications in medicine and material science. Organic-inorganic hybrid compounds are of intensive interest in the field of new materials chemistry as these materials can exhibit synergetic properties such as electrical, magnetic and optical properties[1] and are excellent model of certain essential features of the amino acids-phosphate interactions in several biological systems.[2–6]

This article is part of systematic investigation on organic-inorganic hybrid materials including amino acids and various mineral acids. The formation of the $(H_2PO_4^-)_n$ polyanion in hybrid compound interest inorganic and chemists investigating in new materials with optical properties and biological or pharmacological drugs.[7–10] Hybrid material described here contains different organic electron donors and the structural study of $H_2PO_4^-$ anions is fascinating by a great diversity of interactions; it shows clearly the strong and various hydrogen bonds between anions and cations.

RESULTS AND DISCUSSION

Infrared Study

The IR absorption spectrum of DL 2-ammoniumbutyric dihydrogenmonophosphate is reported in Figure 1. It exhibits broad bands of absorption between 3525.6 and 2414.7 cm^{-1} which corresponds to the following valence vibrations:

- The bands at 3425.3 and 3363.6 cm^{-1} are attributed to an associated carboxylic acid.
- The valence vibration bands ν_{NH_3} appears in the form of strong and broad bands with multiple peaks between 3363.6 and 2500 cm^{-1}.
- Broad bands due to P—OH vibration are present between 2750 and 2550 cm^{-1}.
- The bands observed at 3024.2, 2993.3 and 2854.5 cm^{-1} correspond respectively to the valence vibrations ν_{-CH_3}, ν_{-CH_2} and ν_{-CH}.

A strong absorption $\nu_{C=O}$ around 1712.7 cm^{-1} confirms the presence of the carboxylic groups. Various valency and bending vibration bands whose both position, between 1300–900 and 600–400 cm^{-1}, are typical of dihydrogenmonophosphate anions.

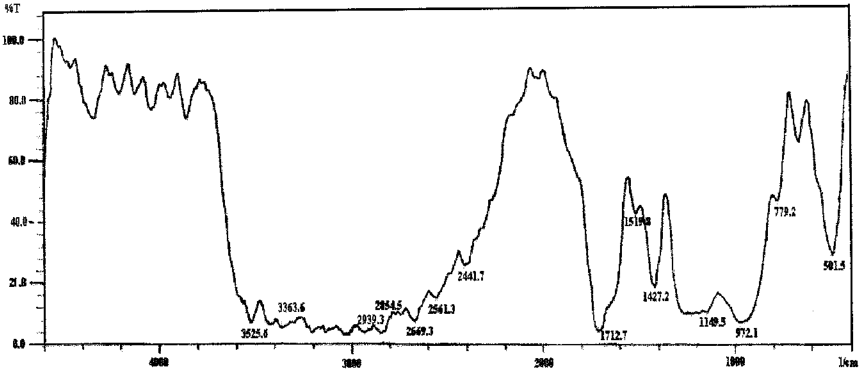

FIGURE 1 IR spectra of $(NH_3C_3H_6COOH)^+(H_2PO_4)^-$.

NMR Spectrometry

NMR ^{1}H spectrum. We see in Figure 2 that the NMR^{1}H spectrum of $(NH_3C_3H_6COOH)^+(H_2PO_4)^-$ is characterized by the presence of the following peaks:

- triplet of the protons of the methyl group coupled with $-CH_2$ appears toward 1 ppm.
- multiplet of $-CH_2$ coupled with $-CH_3$ and $-CH$ appears in the field 1.6–1.8 ppm.

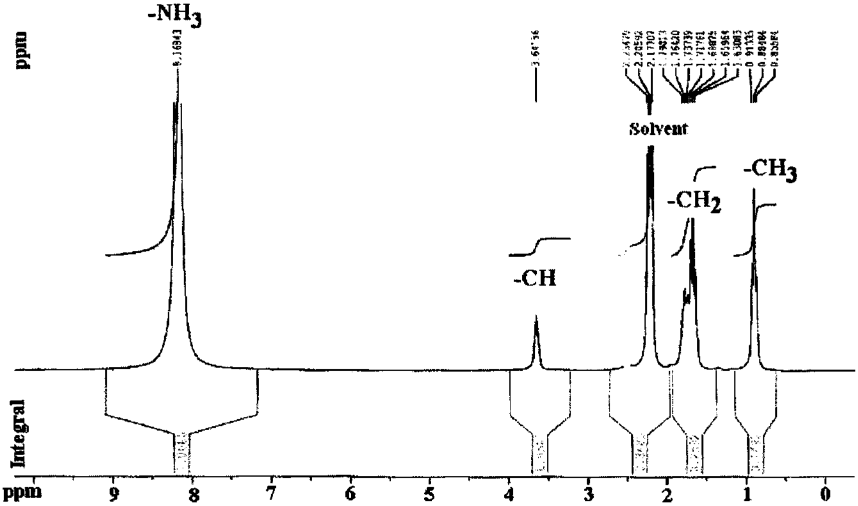

FIGURE 2 NMR ^{1}H spectrum of $(NH_3C_3H_6COOH)^+(H_2PO_4)^-$.

- triplet of the proton of —CH located toward 3.64 ppm.
- singlet of the three protons of ammonium group appears at 8.168 ppm.

We carried out spectra of NMR ^{13}C and ^{31}P for studying the carboxylic and phosphate groups.

NMR ^{13}C spectrum. Examination of the NMR ^{13}C spectrum of $(NH_3C_3H_6COOH)^+(H_2PO_4)^-$ (Figure 3) reveals in particular the signals of resonance located at 20.332, 23.974, and 33.160 ppm which correspond to $-CH_3$, $-CH_2$ and —CH respectively. The peak of resonance located at 174.784 ppm characterizes the quaternary carbon of the carboxylic group.

NMR ^{31}P spectrum. We observe on Figure 4 the NMR ^{31}P spectrum of $(NH_3C_3H_6COOH)^+(H_2PO_4)^-$; it exhibits one peak at 17.49 ppm which characterizes the phosphorus atom not coupled in the $H_2PO_4^-$ group.

Crystal Structure Determination

The unit cell dimensions have been refined by a least square method using the angular data of 25 independent reflections. The Lorenz and polarization correction has been applied. The crystal structure solved by direct methods in the space group $P2_1/c$ using SIR program.[11]

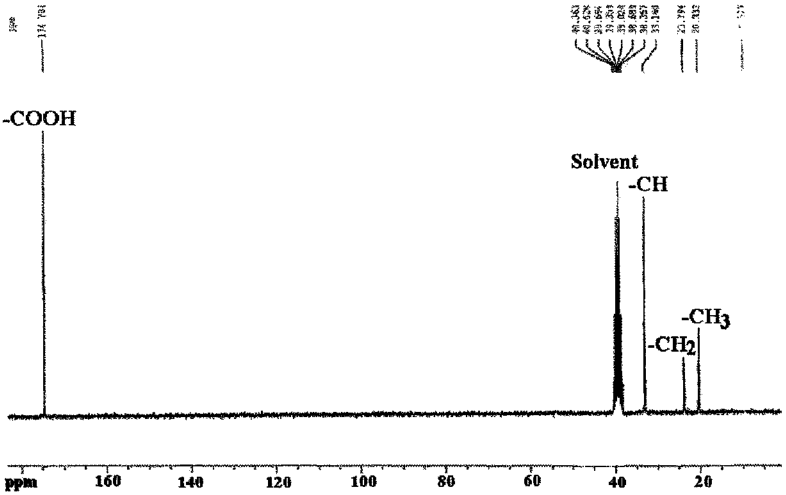

FIGURE 3 NMR ^{13}C spectrum of $(NH_3C_3H_6COOH)^+(H_2PO_4)^-$.

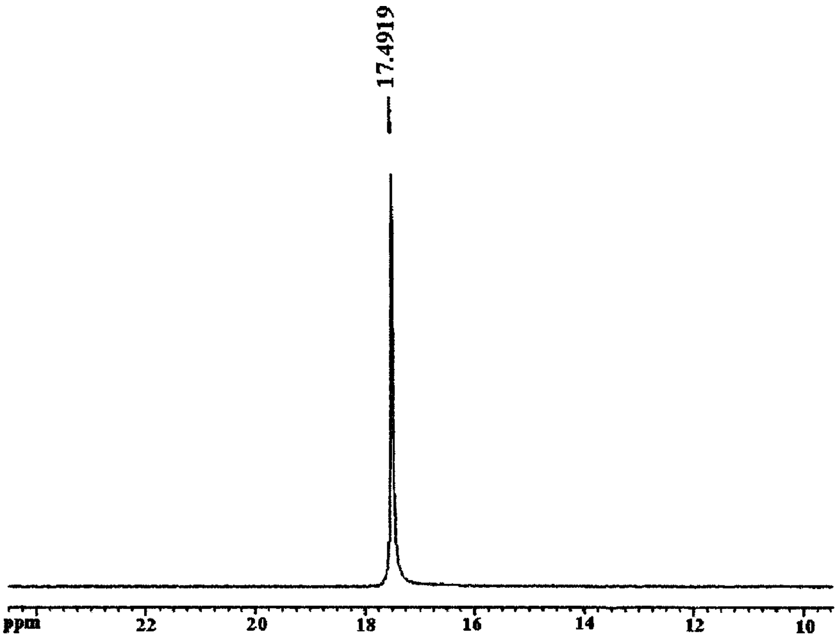

FIGURE 4 NMR ^{31}P spectrum of $(NH_3C_3H_6COOH)^+(H_2PO_4)^-$.

All Hydrogen atoms are located on a difference Fourier map. Final refinement cycles using 1303 reflections with $I > 3\sigma(I)$ converged with $R = 0.038$, $wR = 0.052$ and $S = 1.022$. Atomic scattering factors from International Tables for X-ray crystallography (1974, vol IV). The Table I summarizes experimental conditions used during the intensity data collection.

STRUCTURE DESCRIPTION

Numbering scheme used in the crystal analysis is shown in Figure 5.

The ionic structure can be described as layers of $H_2PO_4^-$ groups alternating with layers of $NH_3C_3H_6COOH^+$ groups. The $H_2PO_4^-$ tetrahedron are connected through $OH\cdots O$ hydrogen bonds so that infinite chains of $[(H_2PO_4)_n]^{n-}$ are formed parallel to the b axis. A three-dimensional network of hydrogen bonds between anionic and cationic layers stabilizes the crystal structure.

TABLE I Crystal Data, Data Collection and Refinement Parameters

Crystal data	
$C_4H_{12}O_6NP$	Mo K_α radiation
Mr = 201.12	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25 reflections.
P 2_1/c	$\mu = 3.079$ cm^{-1}
a = 10.5450(3) Å	T = 293°K
b = 10.0486(3) Å	Colorless
c = 8.9526(4) Å	0.25 × 0.2 × 0.15 mm
$\beta = 111.769(5)°$	Z = 4
V = 881.0(1) $Å^3$	Dx = 1.52 g/cm^3
Data collection	
Enraf-Nonius Mach3 diffractometer	h = −11, 0 k = 0, 12
$\omega - 2\theta$ scans	l = −13, 13
2021 independent reflections	
θmax = 30°	
Refinement	
Refinement on F	$\Delta\rho_{max} = +0.413$ e/$Å^3$
R = 0.038	$\Delta\rho_{min} = -0.240$ e/$Å^3$
wR = 0.052	S = 1.022
1303 reflections (I > 3σ(I))	109 parameters

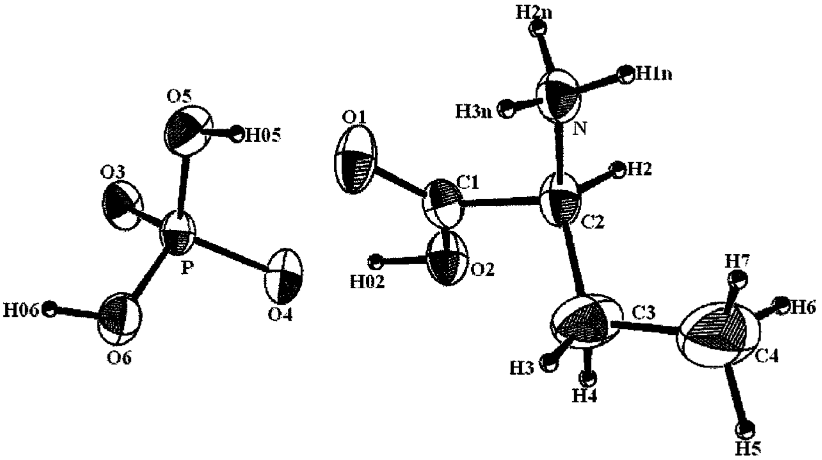

FIGURE 5 Ortep[12] view of $(NH_3C_3H_6COOH)^+(H_2PO_4)^-$.

The $H_2PO_4^-$ Anions

The geometrical features of the $H_2PO_4^-$ groups are quite regular and can be compared to those observed in similar structures,[13–16] as expected the two P—OH distances are significantly longer [P—O(5) = 1.566(2) Å and P—O(6) = 1.559(9) Å] than the other P—O distances [P—O(3) = 1.483(2) Å and P—O(4) = 1.521(2) Å]. The same evolution is also observed for the bond angles in the independent terahedra with three values of O—P—O angles:

- The shortest bond angle (HO—P—OH: 107.54(9)°) is observed for the nonterminal oxygen atoms.
- The intermediate mean value (⟨HO—P—O⟩: 108.67°) corresponding to the angles between terminal and non-terminal oxygen atoms.
- The bond angle involving only the terminal oxygen atoms is longer (O—P—O: 114.4(1)°).

Main interatomic distances and bond angles for $H_2PO_4^-$ groups are reported in Table II.

The Organic Cations

The organic cations are sandwiched between the anion layers formed by the phosphate groups, these cations appeared as carbonic chains prolonged according to the [001] direction.

The amino group is protonated by a phosphate hydrogen atom; the environment around the nitrogen atom is a distorted tetrahedron with a mean distances ⟨N—H⟩ of 0.933 Å and C—N of 1.486(3) Å.

TABLE II Main Geometrical Features of a PO_4 Tetrahedron as Observed in $(NH_3C_3H_6COOH)^+(H_2PO_4)^{-a}$

P	**O(3)**	**O(4)**	**O(5)**	**O(6)**
O(3)	**1.483(2)**	2.525(2)	2.475(2)	2.528(2)
O(4)	114.4(1)	**1.521(2)**	2.510(3)	2.446(2)
O(5)	108.44(9)	108.78(9)	**1.566(2)**	2.521(2)
O(6)	112.32(9)	105.14(9)	107.54(9)	**1.559(1)**

[a] The four P—O values are given along the diagonal, part of this table, the six O—O distances above the diagonal and the six O—P—O angles below the diagonal.

The carbon atom of the carboxylic group has a distorted sp^2 environment with the following distances and bond angles:

C—C: 1.509(3) Å C—C—O: 114.0(2)°
C—O: 1.288(3) Å C—C=O: 120.4(2)°
C=O: 1.224(3) Å O—C=O: 125.6(2)°

Hydrogen Bonding

The crystal structure is stabilized by a three-dimensional network of hydrogen bonding which connect anionic and cationic sheets.

Anion-anion interaction. Each $H_2PO_4^-$ group is connected by hydrogen bonds with its neighbour by relatively strong hydrogen bonds to build a two-dimensional network (see Figure 6).

A............H—B	A.....H (Å)	A...H—B (°)
O(4).......H(06)—O(6)	1.720(2)	169.4(1)

Anion-cation interactions. Layers of DL 2-ammoniumbutyric and dihydrogenmonophosphate are hydrogen bonded by three means:

- First: Two hydrogen atoms of the ammonium group are linked by hydrogen bonds with oxygen atoms of the phosphoric groups while the third is connected to an oxygen atom of the carboxylic group to form interionic bonds.

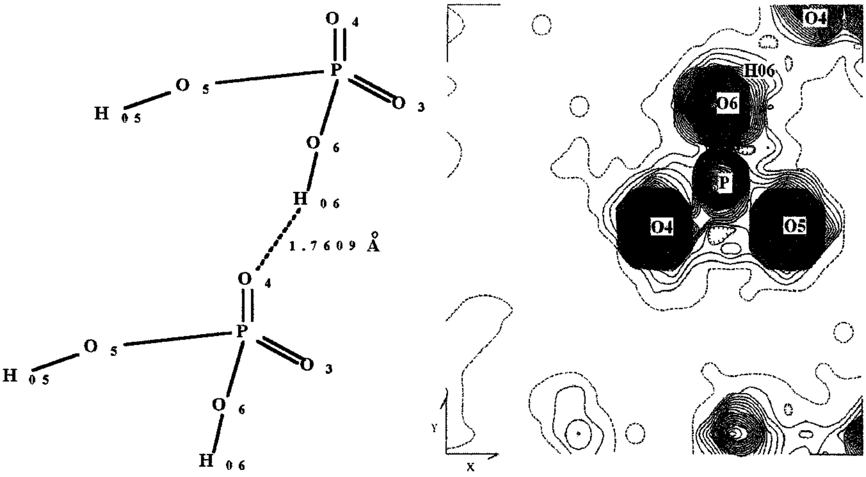

FIGURE 6 Anion-anion interaction via O(4) and H(06) in the section: O(4)—H(06)—O(6).

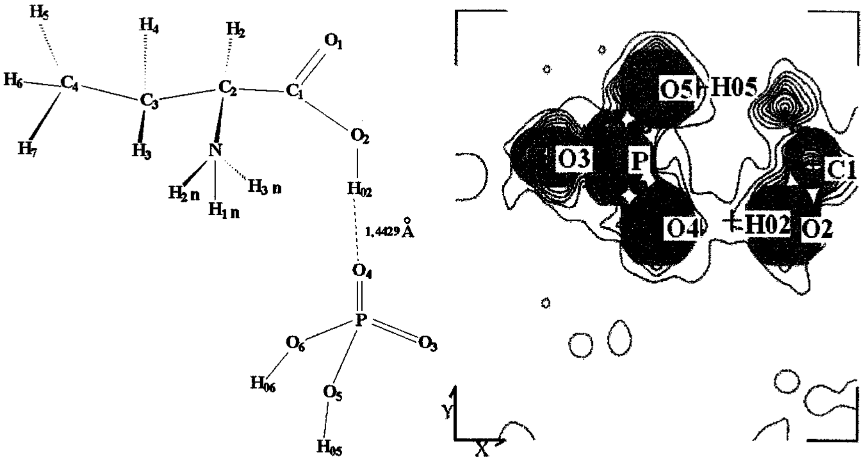

FIGURE 7 Anion-cation interaction via O(4) and H(02) in the section: O(4)—H(02)—O(2).

A............H—B	A.....H (Å)	A...H—B (°)
O(3).......H(3N)–(N)	1.926(2)	169.7(1)
O(3).......H(1N)–(N)	1.855(1)	160.0(1)
O(2).......H(2N)–(N)	2.138(1)	159.9(1)

– Second: The carboxylic group is not deprotonated and its hydrogen is involved in the strongest interaction observed in this compound with the oxygen atom of the $H_2PO_4^-$ group (see Figure 7).

A............H—B	A.....H (Å)	A...H—B (°)
O(4).......H(02)—O(2)	1.449(2)	174.3(1)

– Third: The carboxylic oxygen atom O(1) is connected to the phosphoric group via a strong interaction (see Figure 8).

A............H—B	A.....H (Å)	A...H—B (°)
O(1).......H(05)—O(5)	1.787(2)	168.2(1)

EXPERIMENTAL

Chemical Preparation

Single crystals are prepared by slow evaporation at room temperature of a diluted aqueous solution containing DL 2-aminobutyric and

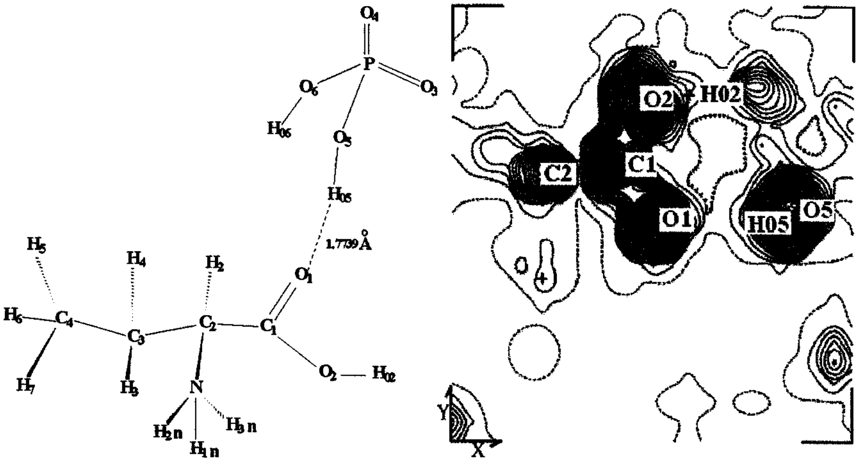

FIGURE 8 Anion-cation interaction via O(1) and H(05) in the section: O(1)—H(05)—O(5).

orthophosphoric acids in stoichiometric ratio, according to the following chemical reaction:

$$NH_2C_3H_6COOH + H_3PO_4 \longrightarrow [NH_3C_3H_6COOH]^+[H_2PO_4]^-$$

A few days later crystals grow as large colorless monoclinic prisms.

Infrared Spectrometry

Spectra were recorded in the range 4000–400 cm^{-1} with a Shimadzu FTIR 8000 SERIES spectrophotometer, using samples dispersed in spectroscopically pure KBr pellets.

NMR Spectrometry

The ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded with a Bruker Avance DPX 250 MHz spectrometer with TMS as an internal reference and DMSO as a solvent.

X-ray Diffraction

Single crystal diffraction patterns were registered with an automated four-circle Enraf Nonius Mach 3 diffractometer, graphite monochromator, using Mo-Kα radiation (λ = 0.71073 Å).

CONCLUSION

The IR, NMR, and single crystal X-ray diffraction study of the title compound reveals an ionic structure, the presence of infinite chains of hydrogen bonded dihydrogenmonophosphate anions where organic cations are sandwiched. The carboxylic group of the DL 2-aminobutyric acid is not ionised and its H atom is involved in a hydrogen bond with an O atom of $H_2PO_4^-$. The amino group is protonated by a phosphate H atom and all hydrogen atoms that are covalently bonded to anion, nitrogen, and oxygen atoms of cation base participate in a three-dimensional complex network of hydrogen bonding. Strong interactions between cations and anion sheets ensure the ionic structure cohesion. All $H \cdots O$ bonds which maintain the cohesion of this arrangement are characterized by relatively short distances, from 1.44 to 2.25 Å.

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