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Crystal structure of mono- β -alanine hydrochloride

Crystal structure of mono- β -alaninium chloride has been studied by single crystal X-ray diffraction. The compound crystallizes in the orthorhombic system. The space group is *Pbca*, with the following lattice constants: $a = 9.7414(5) \text{ \AA}$, $b = 7.4671(6) \text{ \AA}$, $c = 16.5288(11) \text{ \AA}$, $V = 1202.31(14) \text{ \AA}^3$, $Z = 8$. The asymmetric unit contains one β -alaninium cation ($^+\text{NH}_3\text{CH}_2\text{CH}_2\text{COOH}$) and one chloride anion. The structure was shown to consist of layers stacked along the c -axis and connected with each other by weak van der Waals forces. Each layer consists of two halves linked by hydrogen bonds between carbonyl and NH_3^+ groups and, also, between NH_3^+ groups and Cl^- anions. Fourier transform infrared spectrum of β -alaninium chloride was recorded and analyzed. The spectroscopic results were found to support the conclusions of the structural study.

Keywords: β -alanine; amino acids; X-ray diffraction; FTIR

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Introduction

β -alanine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{COOH}$, is the simplest and the only naturally occurring β -amino acid participating (as a constituent of carnosine and anserine dipeptides as well as pantothenic acid) in some important biochemical processes in muscle and brain tissues of mammals, including humans [1]. The crystal structure of β -alanine and some of its derivatives has already been studied [1–9]. However, this is not the case for the simplest salts of β -alanine such as halides which

can be considered as promising precursors for the development of new hybrid organic-inorganic materials. To the best of our knowledge, the vibrational spectra of these compounds also have not been reported yet, except in the narrow range of $1400\text{--}1500 \text{ cm}^{-1}$ [10] for β -alanine hydrochloride ($\beta\text{-ALA}\cdot\text{HCl}$). Therefore, the main aim of this work was to study the crystal structure of $\beta\text{-ALA}\cdot\text{HCl}$ and its vibrational properties in the wider range of frequencies.

Experimental

The single crystals and the polycrystalline powder of $\beta\text{-ALA}\cdot\text{HCl}$ were prepared by the following technique. 3.5 ml of concentrated hydrochloric acid, HCl, (mass

fraction 36 wt. %, purity >99.99 wt.%), were combined with solution of 3.54 g of β -alanine (purity >98 wt.%) in 20 ml of distilled water. The resulting solution

was evaporated to the final volume of 10 ml and left for cooling and crystallization in the Petri dish for several days. After this, the crystals of β -ALA·HCl were filtered out using glass filter. The largest crystals with the size up to $0.5 \times 0.5 \times 0.5 \text{ mm}^3$ were hand-picked, carefully dried by filter paper and left in the desiccator under P_2O_5 for 24 h. The precipitate containing smaller crystals was washed with small amount of acetone (purity >99 wt.%), dried under vacuum at 100°C for 3–4 h, carefully powdered using an agate mortar and pestle and stored in the desiccator under P_2O_5 .

IR spectra of the powdered sample of β -ALA·HCl were recorded at room temperature in the range from 400 cm^{-1} to 3500 cm^{-1} using Nicolet 6700 FTIR spectrometer (Thermo Scientific, USA) equipped with diamond Smart Orbit ATR sampling accessory.

X-ray data for β -ALA·HCl single crystal were collected using four-circle diffractometer Xcalibur Sapphire3 (Oxford Diffraction Limited, UK) equipped with fine-focus sealed Mo tube, graphite mono-

chromator and Sapphire3 CCD plate detector. The crystal structure of β -ALA·HCl was solved by direct methods as implemented in SHELXS-97 program [11] and refined by the full matrix least squares method on all F^2 data using the SHELXL-97 programs [12]. The non-hydrogen atoms were refined anisotropically, by means of the full-matrix least squares procedure. The hydrogen atoms of the methylene groups ($-\text{CH}_2-$) were placed at calculated positions ($\text{C}-\text{H} = 0.97 \text{ \AA}$) and treated as riding on their parent atoms, with $U_{\text{iso}}(\text{H})$ values set at $1.2-1.5 U_{\text{eq}}(\text{C})$. The rest of the H atoms (i.e. those corresponding to $-\text{NH}_3^+$ and $-\text{COOH}$ groups) were found from difference Fourier maps and constrained with $\text{N}-\text{H} \leq 1.03 \text{ \AA}$ (similar to ammonia) and $\text{O}-\text{H} \leq 0.98 \text{ \AA}$, and their displacement factors were refined isotropically. The basic crystallographic data and details of the measurement and refinement are summarized in Table 1. A list of the observed and calculated structural factors and the anisotropic displacement factors is available in Supplementary.

Table 1

Basic crystallographic data, data collection and refinement parameters

Empirical formula	$\text{C}_3\text{H}_8\text{NO}_2\text{Cl}$
<i>a</i>	$9.7414(5) \text{ \AA}$
<i>b</i>	$7.4671(6) \text{ \AA}$
<i>c</i>	$16.5288(11) \text{ \AA}$
<i>V</i>	$1202.31(14) \text{ \AA}^3$
<i>Z</i>	8
<i>D</i> (calc.)	$1.387 \cdot 10^3 \text{ kg} \cdot \text{m}^{-3}$
Crystal system	orthorhombic
Space group	<i>Pbca</i>
M_r	125.55
Cell parameters from 1876 reflections, $\theta = 4.165-29.036$	
<i>T</i>	293 K
$\mu(\text{Mo } K\alpha)$	0.534 mm^{-1}

$F(000)$	528
Crystal dimensions and shape, color	$0.45 \times 0.35 \times 0.25 \text{ mm}^3$ prism, colorless
Data collection	
Diffractometer and radiation used	Xcalibur Sapphire3, Mo $K\alpha$, $\lambda = 0.71073 \text{ \AA}$
Scan technique	$\omega - 2\theta$
θ Range	$3.65^\circ - 30.91^\circ$
Index ranges	$-11 \leq h \leq 13$, $-10 \leq k \leq 10$, $-22 \leq l \leq 22$
Absorption correction	multi-scan, CrysAlisPro 1.171.39.38a (Rigaku Oxford Diffraction, 2017). Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm
T_{\min} , T_{\max}	0.75985, 1.00000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7329, 1573, 1124
R_{int}	0.0315
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0669, 0.1724, 1.003
No. of reflections	1573
No. of parameters	80
No. of restraints	0
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ ($e \cdot \text{\AA}^{-3}$)	0.311, -0.335

Results and discussion

β -ALA·HCl, as indicated in Table 1, crystallizes in the orthorhombic space group $Pbca$ with eight formula units per elementary cell. The refined atomic coordinates and atomic displacement parameters are given in Tables 2 and 3, and the bond lengths and angles are summarized in Table 4. The asymmetric unit of β -ALA·HCl contains one β -alaninium cation ($^+\text{NH}_3\text{CH}_2\text{CH}_2\text{COOH}$) and one chloride anion. The arrangement of these species in the elementary cell is shown in Fig. 1. The crystal structure may be considered as consisting of double layers connected with each other by weak van der Waals

forces and stacked along the c -axis, as can be seen in Fig. 2. Each double layer consists of two halves which are mirror images of each other. They are shifted against each other along the a -axis by about one half of the translation. As a result, the $-\text{C}=\text{O}$ groups of the one half layer are almost directly facing the $-\text{NH}_3^+$ groups of the other half layer. Therefore, the two halves of the double layer are linked together by the hydrogen bonds, whose length varies from 2.680 to 2.998 \AA , formed by $-\text{C}=\text{O}$ and $-\text{NH}_3^+$ groups. In addition, $-\text{NH}_3^+$ groups of the one half layer form hydrogen bonds (length 2.613 \AA) with the clos-

est Cl⁻ anions of the other half layer. This is drawn in greater details in Fig. 3. Furthermore, each half layer itself is stabilized by the multidirectional hydrogen bonds between the Cl⁻ anions, on the one side, and both the closest -NH₃⁺ groups (length 2.546 Å) and the -OH part of the carboxyl group (-C(=O)OH) (length 2.316 Å), on the other, as seen in Fig. 4. There is also

an intramolecular hydrogen bond (length 2.548 Å) between the -NH₃⁺ and -C=O groups of the same β-alaninium cation.

IR spectrum of β-ALA·HCl is shown Fig. 5. The observed vibrational bands were tentatively assigned on the basis of the comparison with published IR spectra of β-alanine [13], β-ALA·HNO₃ [5] and 2(β-ALA)·HCl [9].

Table 2

Fractional atomic coordinates and isotropic or equivalent displacement parameters

Atom site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} [*] / Å ²
Cl1	0.57555(6)	0.14434(9)	0.40265(3)	0.0481(3)
N1	0.8957(2)	0.2305(3)	0.44022(12)	0.0470(5)
H1A	0.894(3)	0.369(5)	0.433(2)	0.068(9)
H1B	0.815(3)	0.203(4)	0.4584(19)	0.060(8)
H1C	0.952(3)	0.216(4)	0.472(2)	0.071(10)
C1	1.1833(2)	0.1496(3)	0.37117(14)	0.0453(6)
C2	1.0566(2)	0.1977(4)	0.32491(14)	0.0520(6)
H2A	1.0628	0.1459	0.2712	0.062
H2B	1.0532	0.3268	0.3188	0.062
C3	0.9247(2)	0.1359(4)	0.36360(17)	0.0507(7)
H3A	0.8494	0.1557	0.3263	0.061
H3B	0.9304	0.0083	0.3741	0.061
O1	1.18503(18)	0.0817(3)	0.43693(11)	0.0605(5)
O2	1.2945(2)	0.1964(3)	0.33036(12)	0.0645(6)
H2	1.357(4)	0.173(5)	0.349(2)	0.076(11)

$$*U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$$

Table 3

Atomic displacement parameters

Atom site	<i>U</i> ₁₁ / Å ²	<i>U</i> ₂₂ / Å ²	<i>U</i> ₃₃ / Å ²	<i>U</i> ₂₃ / Å ²	<i>U</i> ₁₃ / Å ²	<i>U</i> ₁₂ / Å ²
Cl1	0.0354(4)	0.0540(6)	0.0549(4)	0.0009(2)	0.00071(19)	0.0004(2)
C1	0.0397(11)	0.0542(16)	0.0418(11)	-0.0072(9)	0.0000(8)	0.0028(9)
C2	0.0393(11)	0.0741(19)	0.0426(11)	-0.0032(11)	-0.0012(8)	0.0078(10)
C3	0.0395(12)	0.057(2)	0.0559(14)	-0.0115(10)	-0.0057(9)	-0.0007(9)
O1	0.0486(10)	0.0808(15)	0.0522(10)	0.0070(9)	-0.0030(7)	0.0085(9)
O2	0.0358(9)	0.1009(18)	0.0567(10)	0.0063(10)	0.0010(8)	0.0041(9)
N1	0.0355(10)	0.0585(17)	0.0469(10)	-0.0009(8)	0.0005(8)	-0.0033(9)

The wide absorption band in the range 3300–2500 cm^{-1} is characteristic of stretching vibrations of the N–H and O–H groups, involved into the system of hydrogen bonds [5, 9]. Stretching vibrations of CH_2 are superimposed on top of the N–H and O–H bands [5, 9]. The weak bands observed from ~ 2650 to ~ 1850 cm^{-1} seem to correspond to the overtones and combination bands of the fundamental vibrations. The C=O stretching vibration is located

at about 1711 cm^{-1} , confirming the existence of the β -alaninium cation in the lattice of β -ALA·HCl. Interestingly, this absorption band, in fact, seems to be splitted with the second minimum lying at about 1722 cm^{-1} and a shoulder — at 1680 cm^{-1} . This may be related to the participation the C=O-groups in the hydrogen bonding.

The rest of the observed vibrational bands and their assignments are summarized in Table 5. In general, it can be

Table 4

Geometric parameters

Bond lengths, Å			
Bond	Value	Bond	Value
C1–O1	1.199(3)	O2–H2	0.71(4)
C1–O2	1.323(3)	N1–H1A	1.04(3)
C1–C2	1.496(3)	N1–H1B	0.87(3)
C3–N1	1.477(3)	N1–H1C	0.77(3)
C3–C2	1.507(3)	C2–H2A	0.9700
C3–H3A	0.9700	C2–H2B	0.9700
C3–H3B	0.9700		
Angles, °			
Angle	Value	Angle	Value
O1–C1–O2	124.2(2)	C3–N1–H1B	111(2)
O1–C1–C2	125.2(2)	H1A–N1–H1B	105(2)
O2–C1–C2	110.6(2)	C3–N1–H1C	112(3)
N1–C3–C2	112.4(2)	H1A–N1–H1C	103(3)
N1–C3–H3A	109.1	H1B–N1–H1C	113(3)
C2–C3–H3A	109.1	C1–C2–C3	114.4(2)
N1–C3–H3B	109.1	C1–C2–H2A	108.7
C2–C3–H3B	109.1	C3–C2–H2A	108.7
H3A–C3–H3B	107.9	C1–C2–H2B	108.7
C1–O2–H2	115(3)	C3–C2–H2B	108.7
C3–N1–H1A	112.7(19)	H2A–C2–H2B	107.6
Torsion angles, °			
Angle	Value	Angle	Value
O1–C1–C2–C3	–6.3(4)	N1–C3–C2–C1	67.5(3)
O2–C1–C2–C3	175.3(2)		

concluded that the character of the measured IR-spectrum of β -ALA·HCl, indicating the compound containing

β -alaninium cations involved in hydrogen bonds, is in agreement with the results of the structural study.

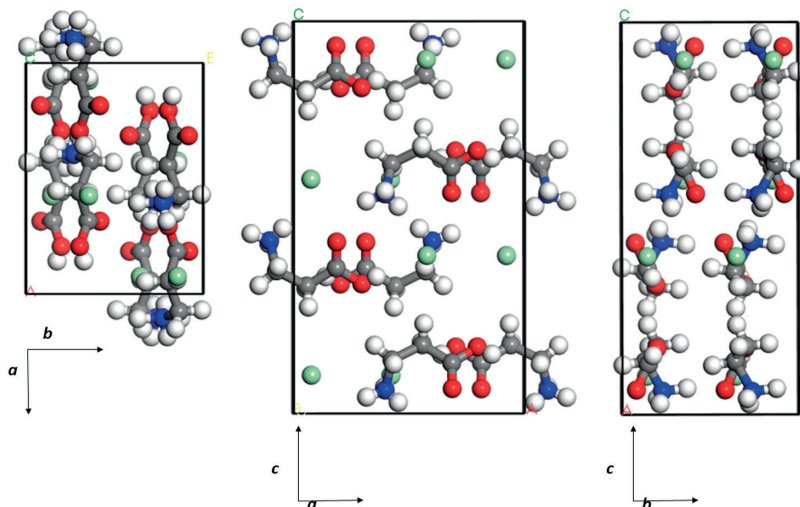


Fig. 1. The elementary cell of β -ALA·HCl in three projections. White balls — H, red balls — O, grey balls — C, blue balls — N, green balls — Cl

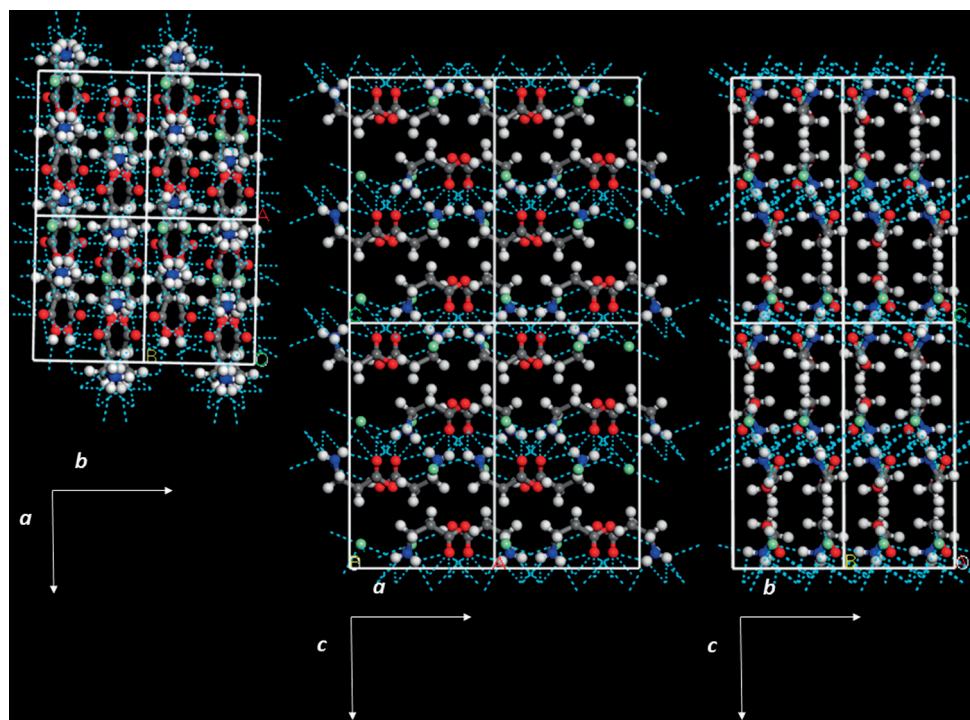


Fig. 2. The structure of the β -ALA·HCl in three projections with hydrogen bonds indicated as dashed blue lines and clearly seen stacking of double layers along the c -axis. Color interpretation is the same as in Fig. 1

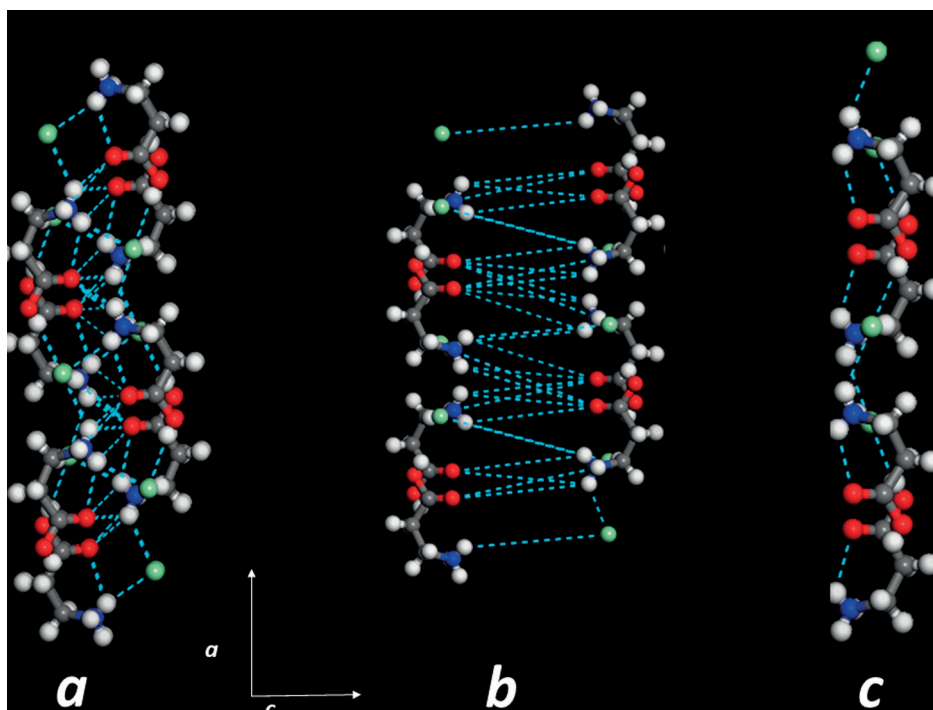


Fig. 3. The arrangement of the two halves of the double layer in the structure of β -ALA·HCl: (a) view along the b -axis; (b) hydrogen bonds between the halves of the layer; (c) the half of the double layer with intrinsic hydrogen bonds. Color interpretation is the same as in Fig. 1

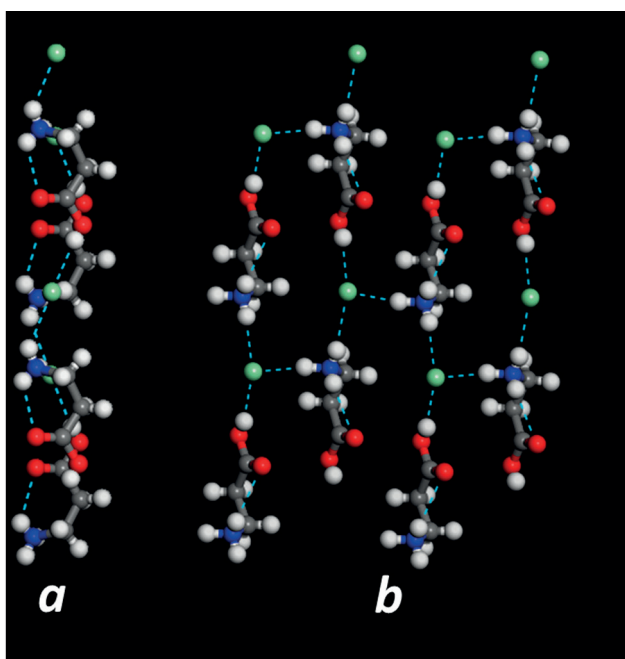


Fig. 4. Different views of the half layer with its intrinsic hydrogen bonds: (a) view along the b -axis as in Fig. 3; (b) projection on the ab -plane. Color interpretation is the same as in Fig. 1

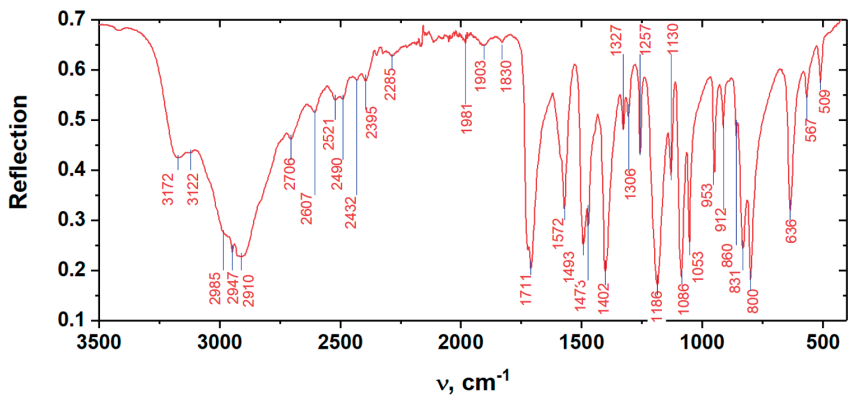


Fig. 5. IR spectrum of β -ALA·HCl at room temperature

Table 5

Vibrational bands observed in the IR-spectrum of β -ALA·HCl at room temperature

ν, cm^{-1}	Assignment
3421	$2 \times \nu(\text{C}=\text{O})$
3172	$\nu_s(\text{NH}_3^+), \nu_a(\text{CH}_2), \nu_s(\text{CH}_2), \nu(\text{N}-\text{H}\cdots\text{O}), \nu(\text{O}-\text{H}\cdots\text{Cl})$
3122	
3048	
3016	
2965	
2947	
2925–2902	
2854	
2834	
2706	
2607	
2521	
2490	
2432	
2395	
2285	
1981	
1903	
1830	
1722	$\nu_a(\text{C}=\text{O}), \nu_s(\text{C}=\text{O})$
1711	
1680	

ν , cm^{-1}	Assignment
1587	$\delta_a(\text{NH}_3^+)$
1572	$\delta_a(\text{NH}_3^+)$
1493	$\delta_s(\text{NH}_3^+)$
1473	$\delta_s(\text{CH}_2)$
1402	$\nu_s(\text{C-O})$
1394	$\delta(\text{CH}_2)$, $\omega(\text{CH}_2)$
1327	$\omega(\text{CH}_2)$
1306	$\tau(\text{CH}_2)$
1257	
1186	$\nu(\text{C-C})$, $\rho(\text{NH}_3^+)$
1130	$\rho(\text{NH}_3^+)$
1100	$\rho(\text{NH}_3^+)$
1086	$\nu(\text{C-C})$
1053	$\nu_s(\text{C-N})$
953	$\rho(\text{NH}_3^+)$
912	$\rho(\text{NH}_3^+)$
860	$\nu(\text{C-C})$
831	$\nu(\text{C-N})$, $\nu(\text{C-C})$
800	$\rho(\text{CH}_2)$
636	$\delta(\text{COO})$
567	$\omega(\text{COO})$
509	$\tau(\text{NH}_3^+)$

Conclusions

Mono- β -alanine hydrochloride was found to crystallize in the orthorhombic space group *Pbca* with eight formula units per elementary cell. The structure was shown to consist of double layers connected with each other by weak van der Waals forces and stacked along the *c*-axis. Each double layer, in turn, consists of two halves linked by hydrogen bonds between $-\text{C}=\text{O}$ and $-\text{NH}_3^+$ groups. In ad-

dition, $-\text{NH}_3^+$ groups of the one half layer form hydrogen bonds with the closest Cl^- anions of the other half layer. The results of the IR-spectroscopy were found to be consistent with these conclusions. The IR-active vibrational bands were identified and their preliminary assignment was carried out based on the comparison with similar compounds reported previously.

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