Crystal structure of mono-β-alanine hydrochloride

Crystal structure of mono-β-alanine hydrochloride has been studied by single crystal X-ray diffraction. The compound crystallizes in the orthorhombic system. The space group is \( \text{Pbca} \), with the following lattice constants: \( a = 9.7414(5) \) Å, \( b = 7.4671(6) \) Å, \( c = 16.5288(11) \) Å, \( V = 1202.31(14) \) Å\(^3\), \( Z = 8 \). The asymmetric unit contains one β-alanine 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 \( ^+\text{NH}_3 \) groups and, also, between \( ^+\text{NH}_3 \) groups and \( \text{Cl}^- \) anions. Fourier transform infrared spectrum of β-alanine 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 1400–1500 cm\(^{-1} \) [10] for β-alanine hydrochloride (β-ALA·HCl). Therefore, the main aim of this work was to study the crystal structure of β-ALA·HCl and its vibrational properties in the wider range of frequencies.

Experimental

The single crystals and the polycrystalline powder of β-ALA·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 0.5×0.5×0.5 mm³ were hand-picked, carefully dried by filter paper and left in the desiccator under P₂O₅ 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 P₂O₅.

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 monochromator 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 F² 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 (–CH₂–) were placed at calculated positions (C–H = 0.97 Å) and treated as riding on their parent atoms, with Uiso(H) values set at 1.2–1.5 Ueq(C). The rest of the H atoms (i.e. those corresponding to –NH₃⁺ and –COOH groups) were found from difference Fourier maps and constrained with N–H ≤ 1.03 Å (similar to ammonia) and O–H ≤ 0.98 Å, 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.

| Empirical formula | C₃H₈NO₂Cl |
|-------------------|------------|
| a                 | 9.7414(5) Å |
| b                 | 7.4671(6) Å |
| c                 | 16.5288(11) Å |
| V                 | 1202.31(14) Å³ |
| Z                 | 8 |
| D (calc.)         | 1.387·10³ kg·m⁻³ |
| Crystal system    | orthorhombic |
| Space group       | Pbca |
| Mᵣ               | 125.55 |

Table 1

### Basic crystallographic data, data collection and refinement parameters

| Empirical formula | C₃H₈NO₂Cl |
|-------------------|------------|
| a                 | 9.7414(5) Å |
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| Crystal system    | orthorhombic |
| Space group       | Pbca |
| Mᵣ               | 125.55 |

| | |
|---|---|
| Cell parameters from 1876 reflections, θ = 4.165–29.036 |
| T | 293 K |
| μ(Mo Ka) | 0.534 mm⁻¹ |
**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{\(\text{NH}_3\text{CH}_2\text{CH}_2\text{COOH}\)}\)) 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 Å, 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 Å) with the clos-
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 | x        | y        | z        | Ueq * / Å² |
|-----------|----------|----------|----------|------------|
| Cl1       | 0.5755(6)| 0.1443(9)| 0.4026(3)| 0.0481(3)  |
| N1        | 0.8957(2)| 0.2305(3)| 0.4402(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)| 0.3711(14)| 0.0453(6)  |
| C2        | 1.0566(2)| 0.1977(4)| 0.3249(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)| 0.3636(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)  |

\[ *U_{eq} = \frac{1}{2} \sum_i \sum_j U_{ij} a_i^* a_j \]

Table 3
Atomic displacement parameters

| Atom site | U₁₁ / Å² | U₂₂ / Å² | U₃₃ / Å² | U₁₂ / Å² | U₁₃ / Å² | U₂₃ / Å² |
|-----------|----------|----------|----------|----------|----------|----------|
| 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

| 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 |
|-----------------|-------|-------|
| O1–C1–O2       | 124.2(2) |
| O1–C1–C2       | 125.2(2) |
| O2–C1–C2       | 110.6(2) |
| N1–C3–C2       | 112.4(2) |
| N1–C3–H3A      | 109.1 |
| C2–C3–H3A      | 109.1 |
| N1–C3–H3B      | 109.1 |
| C2–C3–H3B      | 109.1 |
| H3A–C3–H3B     | 107.9 |
| C1–O2–H2       | 115.3(3) |
| C3–N1–H1A      | 112.7(19) |

| Torsion angles, ° | Angle      | Value |
|-------------------|------------|
| O1–C1–C2–C3      | –6.3(4)    |
| O2–C1–C2–C3      | 175.3(2)   |

| Angle | Value |
|-------|-------|
|       |       |
|       |       |
|       |       |
|       |       |
|       |       |
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

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

Mono-β-alanine hydrochloride was found to crystallize in the orthorhombic space group \( \text{Pbca} \) 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 addition, \(\text{–NH}_3^+\) groups of the one half layer form hydrogen bonds with the closest \(\text{Cl}^-\) 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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\[
\begin{array}{|c|c|}
\hline
\text{\( \nu, \text{cm}^{-1} \)} & \text{Assignment} \\
\hline
1587 & \delta_0(\text{NH}_3^+) \\
1572 & \delta_0(\text{NH}_3^+) \\
1493 & \delta_0(\text{NH}_3^+) \\
1473 & \delta_0(\text{CH}_2) \\
1402 & \nu(\text{C}=\text{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}=\text{C}), \rho(\text{NH}_3^+) \\
1130 & \rho(\text{NH}_3^+) \\
1100 & \rho(\text{NH}_3^+) \\
1086 & \nu(\text{C}=\text{C}) \\
1053 & \nu(\text{C}=\text{N}) \\
953 & \rho(\text{NH}_3^+) \\
912 & \rho(\text{NH}_3^+) \\
860 & \nu(\text{C}=\text{C}) \\
831 & \nu(\text{C}=\text{N}), \nu(\text{C}=\text{C}) \\
800 & \rho(\text{CH}_2) \\
636 & \delta(\text{COO}) \\
567 & \omega(\text{COO}) \\
509 & \tau(\text{NH}_3^+) \\
\hline
\end{array}
\]
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