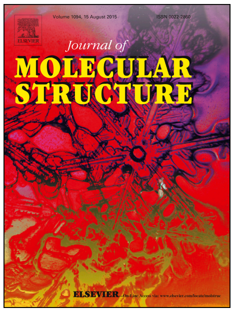

Halogenides of β-alanine

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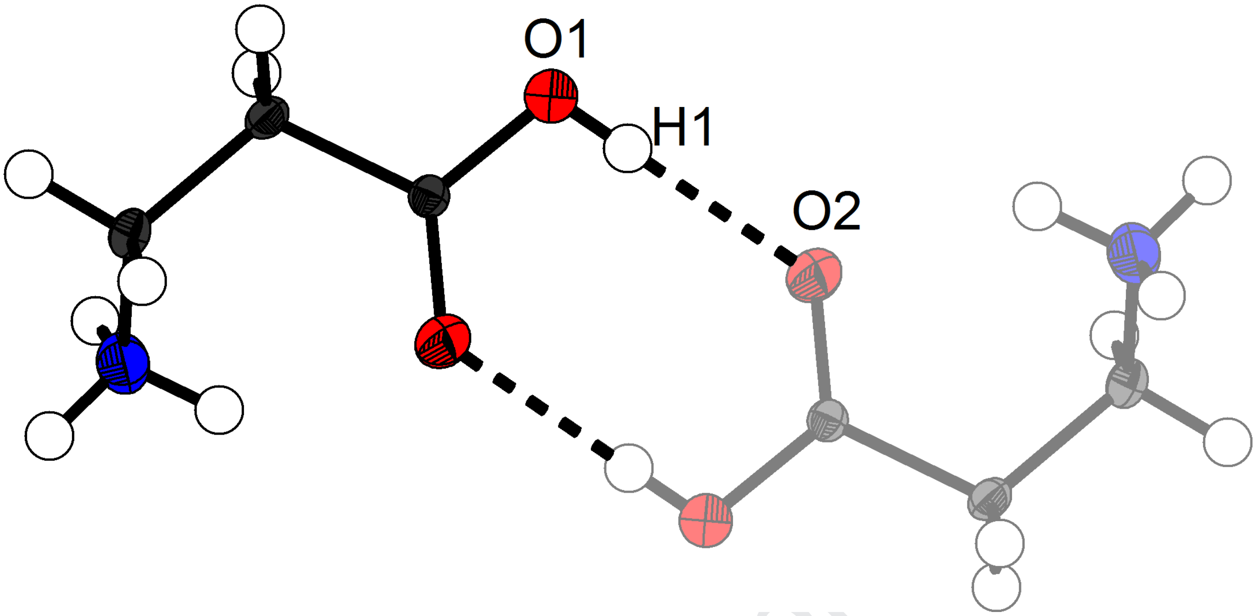
Credit authorship contribution statement

A.M. Petrosyan: Conceptualization, Writing - original draft, Review & editing.
G. Giester: Investigation, Formal analysis,Writing - review & editing.
M. Fleck: Formal analysis, Visualization, Writing - review & editing.
V.V. Ghazaryan: Investigation, Visualization, Writing - review & editing.


O1
H1
O2

Halogenides of β-alanine

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Abstract

The following halogenides of β-alanine: β-Ala·HF (I), β-Ala·HCl (II), β-Ala·HBr (III), β-Ala·HI (IV), 2β-Ala·HBr (V) and 2β-Ala·HI (VI) have been synthesized and characterized structurally and by vibrational spectroscopy. The salts (I-III) are simple salts A^+X^- but are not isostructural. The salt (IV) of the type of $(A^+\cdots A^+)(X^-)_2$ comprises a centrosymmetric dimeric dication. The isotypic salts (V), (VI) belong to the type $(A^+\cdots A)X^-$ with centrosymmetric dimeric cations and strong hydrogen bonds.

Keywords: salts of β-alanine; crystal structure; dimeric cations; vibrational spectra

1. Introduction

Reactions of amino acids with inorganic and organic acids may lead to the formation of various types of salts, when a proton transfer takes place from an acid to an amino acid [1]. In addition to simple compounds with definite cation and anion as well as mixed salts with different cations and anions there is a certain class with various types of dimeric cations.

The majority of studied halogenides of amino acids are chlorides. However, investigation of other halogenides is also of interest and they may differ significantly from chlorides. Fluorine, chlorine, bromine and iodine atoms vary by their electronegativity (by Pauling scale: 3.98, 3.16, 2.96 and 2.66, respectively [2]). Ionic radii of fluoride, chloride, bromide and iodide anions are also different: i.e. 1.19, 1.67, 1.82 and 2.06, respectively (in Å by Shannon [3]). As can be seen by both characteristics, the anions chloride and bromide are closest to each other. Therefore, chlorides and bromides are usually isostructural. Iodides are often not isostructural with chlorides and bromides, while fluorides as a rule are not isostructural with other halogenides (see section 13.2 in Ref. [4]).

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For nonstandard and achiral β-alanine various simple salts of (A^+X^-) type (*e.g.* (β-AlaH)(H_2PO_4) [5]) as well as with ($A^+\cdots A^+$)(X^-)$_2$ (*e.g.* (β-AlaH$\cdots\beta$-AlaH)(NO_3)$_2$) [6]) and ($A^+\cdots A$)X^- (*e.g.* (β-AlaH$\cdots\beta$-Ala)(NO_3)) [7]) types with dimeric cations are known, where A and A^+ (or AH) are amino acids in zwitterionic and protonated cationic states, respectively, and X^- is an anion. There is some information also concerning halogenides of β-alanine. Ennan et al. [8] studied reactions of some amino acids including β-alanine with hydrofluoric acid. For comparison they obtained also respective hydrochlorides. Based on the presence of a strong and broad absorption band in the 700–2000 cm^{-1} region in the infrared spectrum of β-alanine·HF and the absence of this band in the spectrum of the respective chloride they concluded that β-alanine·HF contains the $(F\text{-}H\text{-}F)^-$ group, and also a β-alaninium cation and zwitterionic β-alanine, which are connected with the anion by hydrogen bonds according to the following scheme: $^-OOC\text{-}CH_2\text{-}CH_2\text{-}NH_3^+\cdot(F\text{-}H\text{-}F)^-\cdot{}^+H_3N\text{-}CH_2\text{-}CH_2\text{-}COOH$. In [1] it was supposed that formation of a dimeric cation according to the scheme: (β-$Ala^+\cdots\beta$-Ala)$(F\text{-}H\text{-}F)^-$ is also possible. However, structure determination was necessary to confirm or reject these suppositions. Godzisz et al. [9] obtained crystals of 2β-Ala·HCl and performed a detailed structural and vibrational and ^{13}C solid-state NMR spectroscopic investigation. According to [9] the 2β-Ala·HCl salt crystallizes in the centrosymmetric space group $C2/c$ and consists of a (β-AlaH$\cdots\beta$-Ala) dimeric cation formed by a symmetric $O\cdots H\cdots O$ hydrogen bond with an $O\cdots O$ distance equal to 2.4729(17) Å at 298K. In view of this centrosymmetric hydrogen bond the authors determined the crystal structure of the 2β-Ala·HCl salt at 100 K hoping to find a phase transition, but none was observed in this temperature range. In [10], among other 20 salts it was reported on existence of 2β-Ala·HBr crystals without detailed structural and vibrational spectroscopic data because of limited scope of the paper.

In the present study we report new results on structures and vibrational spectra of β-Ala·HF (**I**), β-Ala·HCl (**II**), β-Ala·HBr (**III**) β-Ala·HI (**IV**), 2β-Ala·HBr (**V**) and 2β-Ala·HI (**VI**) and we continue the systematic investigation of the role of amino acids in the issue of isostructurality of their halogenides [11].

2. Experimental

2.1. Sample preparation

As initial reagents we used β-alanine from “Armbiotechnology” Institute (provided by Dr. A.E. Aghajanyan), hydrofluoric acid (45%, ultrapure grade), hydrochloric (32%, chemically pure grade) and hydrobromic (40.5%, ultrapure grade) acids from “Reakhim“ Co., and hydriodic acid (57% w/w, distilled, stabilized with <1.5% hypophosphorous acid, 99.95%) from “Sigma-Aldrich” Chem. Co. Crystals of titled compounds were obtained from aqueous solution containing stoichiometric quantities of β-alanine and the respective acid by slow evaporation at room temperature. A typical amount of β-alanine taken was 1 g and the volumes of the final solutions were 6 ml approximately. Small polyethylene beakers were used for preparation of solutions. Only for *β*-alanine.HBr (**III**) silica gel was used as an absorber to crystallize hygroscopic crystals.

2.2. Crystal structure determination and refinement

Small fragments of the title compounds with homogeneous extinction were were manually selected, mounted on glass capillaries with laboratory grease and used for single crystal X-ray data collections: sample (V) was measured at room temperature on an Enraf Nonius Kappa CCD diffractometer (sealed tube, equipped with a graphite monochromator + monocapillary optics using Mo-K_α radiation) at a crystal-detector distance of 30 mm, 0.5° scan width.

All other compounds were investigated at 200 K on a Bruker APEXII diffractometer equipped with a CCD area detector, an Incoatec Microfocus Source IµS (30 W, multilayer mirror, Mo-K_α) and an Oxford Cryosystems Cryostream 800 Plus LT device. Several sets of phi- and omega-scans with 2° scan width were collected at a crystal-to-detector distance of 40 mm up to 65° 2ϴ full sphere. The absorption was corrected in all cases by the evaluation of multi-scans. Reflection data were processed with the Nonius program package DENZO-SMN [12] for (V) or otherwise within the Bruker APEX3 software suite [13]. The crystal structures were solved by direct methods and refined by full-matrix least-squares techniques (Shelx-97 [14].

Non-hydrogen atoms were refined with independent anisotropic displacement parameters, hydrogen atoms with isotropic displacement parameters. All hydrogen atoms were treated as riding on their parent atoms, i.e. fixing distances and angles but allowing free rotation.

Selected crystal parameters as well as a summary on the data collections and structure refinements are given in Tables 1 and 7, selected bond lengths and valence and torsion angles in Tables 2 and 8. Details of the hydrogen bonding systems are compiled in Tables 3-6 and 9-10. Further crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033), citing the title of this paper and the CCDC nos. 1967057 (**I**), 1967058 (**II**), 1967470 (**III**), 1967060 (**IV**), 776234 (**V**) and 1967059 (**VI**).

2.3. Vibrational spectra

Attenuated total reflection Fourier-transform infrared spectra (FTIR ATR) were registered by a Nicolet 5700 spectrometer (ZnSe prism, Happ-Genzel apodization, ATR distortion is corrected, number of scans 32, resolution 4 cm^{-1}). Part of the IR spectrum in the region 500–400 cm^{-1} was taken from FTIR spectra registered with Nujol mull (number of scans 32, resolution 2 cm^{-1}).

Fourier-transform Raman spectra were registered by a NXR FT-Raman Module of a Nicolet 5700 spectrometer. Number of scans and laser power at the sample were 512 and 0.43 W (**I**), 512 and 0.18 W (**IV**), 256 and 0.44 W (**V**) and 1024 and 0.18 W. (**VI**).

3. Results and discussion

*3.1. β-Alaninium fluoride (**I**)*

The salt (**I**) crystallizes in the monoclinic system with space group $P2_1/c$. The asymmetric unit contains one formula unit, that is, one *β*-alaninium cation and one fluoride anion (Fig. 1).

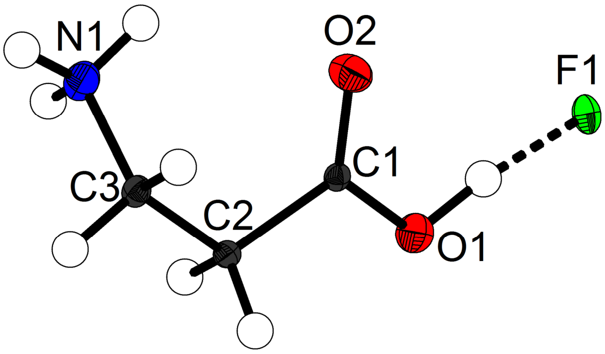


Fig. 1. Molecular structure of *β*-alaninium fluoride (**I**).

So, neither the scheme $^{-}OOC\text{-}CH_2\text{-}CH_2\text{-}NH_3^{+}\cdot(F\text{-}H\text{-}F)^{-}\cdot{}^{+}H_3N\text{-}CH_2\text{-}CH_2\text{-}COOH$ [8] nor the scheme (*β*-Ala$^{+}\cdots$*β*-Ala)(F-H-F)$^{-}$ [1] was confirmed. The salt can be described as of $A^{+}X^{-}$ simple type, that is (*β*-AlaH)F. Selected bond lengths and angles are presented in Table 2. These values are usual for the *β*-alaninium cation and agree with respective values of *β*-Ala·HCl (**II**), *β*-Ala·HBr (**III**) and *β*-Ala·HI (**IV**) (Table 2). The torsion angles O1C1C2C3 and C1C2C3N1 define the arrangements of carboxyl and amino groups (Table 2). The conformation of the *β*-alaninium cation in the structure of (**I**) is *gauche(+)*. Hydrogen bond parameters in the structure of (**I**) are shown in Table 3. The carboxyl group and the fluoride ion form an O1-H1···F1 hydrogen bond with an O···F distance equal to 2.4027(9) Å. The NH_3^{+} group forms three N-H···F hydrogen bonds: N1-H11···F1, N1-H12···F1 and N1-H13···F1 (Table 3). There are also short contacts: C3-H32···F1 (with distances H32···F1 and C3···F1 equal to 2.41 and 3.402(1) Å, respectively), N1-H12···O2 and N1-H11···O2 (the last one is intramolecular), which may be considered as weak hydrogen bonds.

The O1-H1···F1 hydrogen bond is not record-breakingshort but still rather short for O-H···F type hydrogen bonds. For comparison, in the structure of glycine hydrogen fluoride [15] there are four glycinium cations three of which form O-H···F hydrogen bonds with O···F distances equal to 2.436(1) Å, 2.446(1) Å and 2.476(1) Å, while in the structure of *L*-leucinium fluoride monohydrate [16] this O···F distance measures 2.441(1) Å.

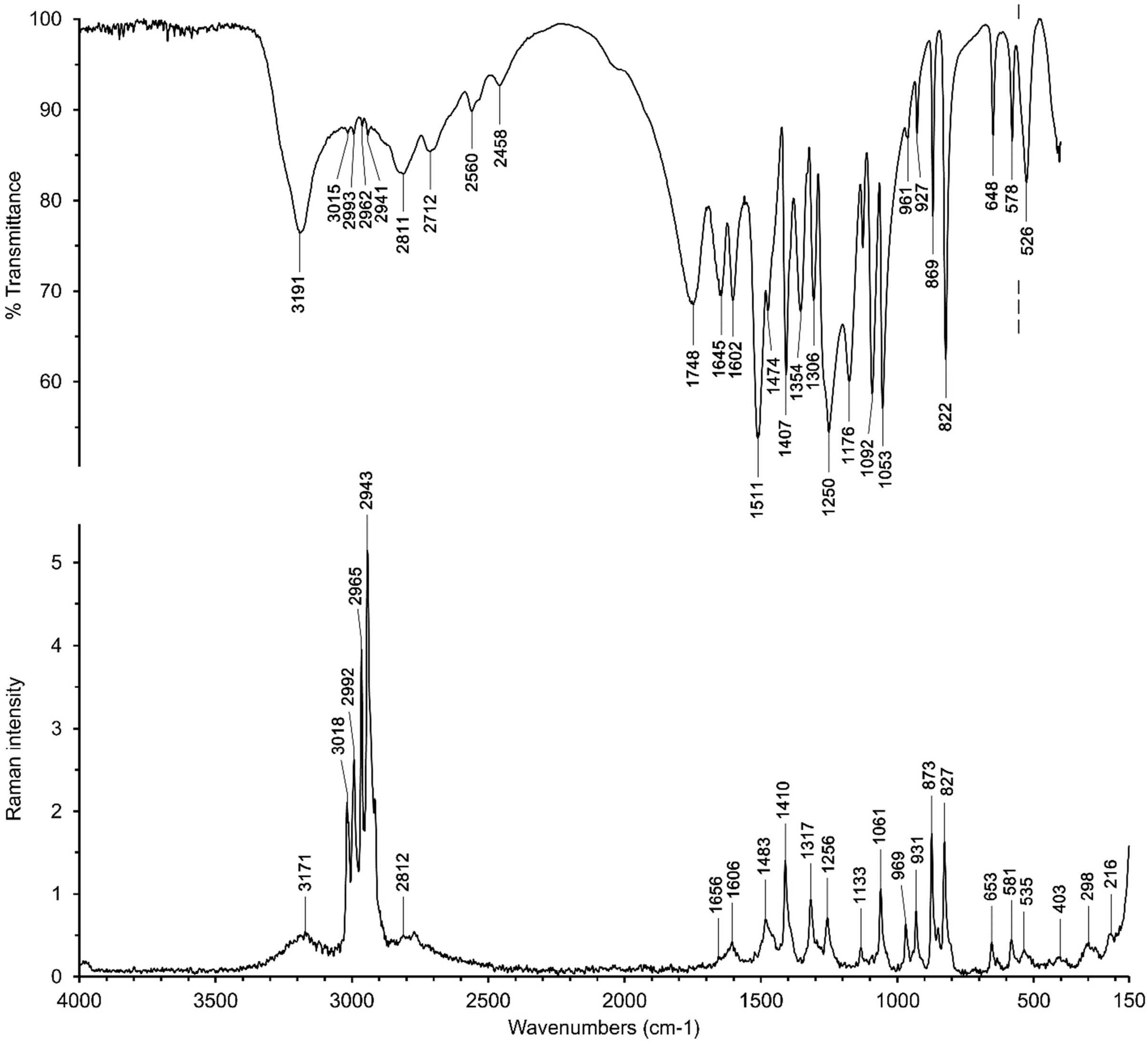


Fig. 2. Infrared and Raman spectra of *β*-alaninium fluoride (**I**).

Infrared and Raman spectra of (**I**) are shown in Fig. 2. Knowledge of the crystal structure makes it possible to interpret the vibrational spectra. The presence of a broad absorption band superimposed with peaks in the 2000-900 cm^{-1} interval is due to the stretching mode of the O-H group of the *β*-alaninium cation in an O-H···F strong hydrogen bond. Such a band is absent in the spectra of (**II**), (**III**) and (**IV**) (see below). So, peaks in high-frequency region are caused by stretching modes of NH_3^+ and CH_2 groups. The H11 atom of the NH_3^+ group forms weaker hydrogen bonds. Therefore, the absorption peak at 3191 cm^{-1} we assigned to stretching vibration of the N1-H11 bond. The H12 atom of the NH_3^+ group forms stronger hydrogen bonds and the absorption band at 2811 cm^{-1} is assigned to stretching vibration of the N1-H12 bond. The H13 atom of the NH_3^+ group forms the strongest hydrogen bond N1-H13···F1 and the absorption band at 2712 cm^{-1} is assigned to stretching vibration of the N1-H13 bond. Their positions are in good agreement with a ν(NH) *vs*. d(N···F) correlation [17]. Weak peaks at 3015, 2993, 2962 and 2941 cm^{-1} are assigned to ν(CH) which is confirmed by respective peaks in the Raman spectrum. Here 3018, 2992 cm^{-1} and 2965, 2943 cm^{-1} are assigned to ν_{as}(CH) and ν_s(CH), respectively. Peaks at 2560 and 2458 cm^{-1} we assign to overtone and combination tones. In the range 2000-400 cm^{-1} there are some characteristic peaks of the *β*-alaninium cation. They are assigned based on [18]. The presence of an absorption band at 1748 cm^{-1} testifies the presence of a COOH group (ν(C=O)). The peaks at 1645, 1602 cm^{-1} are assigned to asymmetric, an absorption band at 1511 cm^{-1} to symmetric deformation vibrations of the NH_3^+ group; peaks at 1474, 1407, 1354 and 1306 cm^{-1} to deformation vibrations of CH_2 groups, the band at 1250 cm^{-1} to ν(C-OH), the band at 1053 cm^{-1} to ν(C-N) and peaks at 869, 822 cm^{-1} to ν(C-C).

*3.2. β-Alaninium chloride (**II**)*

The salt (**II**) crystallizes in the orthorhombic system with space group *Pbca* (Table 1) and therefore is not isostructural with (**I**). Although *β*-alaninium fluoride (**I**) and *β*-alaninium chloride (**II**) are not isostructural and have different symmetries, they have some common features. The asymmetric unit of (**II**) also contains one formula unit, that is, one *β*-alaninium cation and one chloride anion (Fig. 3). It too can be described as of A^+X^- simple type, that is (*β*-AlaH)Cl.

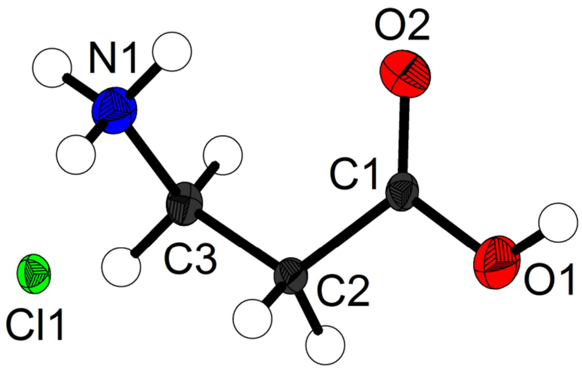


Fig. 3. Asymmetric unit of *β*-alaninium chloride (**II**).

The intramolecular bond lengths and angles of (**II**) and also the conformation (Table 2) are similar to that of (**I**). The conformation of the *β*-alaninium cation in the structure of (**II**) also is *gauche(+)*. Hydrogen bond parameters in the structure of (**II**) are listed in Table 4. The carboxyl group forms an O1-H1···Cl1 hydrogen bond with an O··Cl distance equal to 3.007(2) Å. The NH_3^+ group forms three N-H···Cl hydrogen bonds: N1-H11··Cl1, N1-H12···Cl1 and N1-H13···Cl1 (Table 4). Due to similar conformation ofthe *β*-alaninium cation here also an intramolecular contact N1-H13···O2 is present. There are three short C-H···Cl contacts: C2-H21···Cl1 (with H21···Cl1 and C2···Cl1 2.84 and 3.678(2) Å, respectively), C3-H31···Cl1(with H31···Cl1 and C3···Cl1 2.93 and 3.449(2) Å, respectively) and C3-H32···Cl1 (with H32···Cl1 and C3···Cl1 2.71 and 3.699(2) Å, respectively), which can be considered as weak hydrogen bonds. In the structures of chlorides of amino acids, the O···Cl distances in O-H···Cl hydrogen bonds are *ca*. 3.0 Å. Shorter hydrogen bonds were observed in the structures of two forms of betainium chloride: 2.955(2) Å [19] and 2.946(3) Å [20]. Therefore, in the structure of (**II**) the O1-H1···Cl1 hydrogen bond should be considered as common in contrast to (**I**), where the respective O1-H1···F1 hydrogen bond is significantly shorter than usual O-H···F hydrogen bonds.

The infrared and Raman spectra of (**II**) are shown in Fig. 4. In this case, broad absorption bands in the region 2000-400 cm^{-1} are absent. So, in the high-frequency region in addition to stretching vibrations of N-H and C-H bonds also a vibration of the O-H group is expected. In the spectrum of (**II**) ν(OH) for O-H···Cl hydrogen bond with O···Cl distance equal to 3.0 Å is expected at *ca*. 2920 cm^{-1} according to correlation [17]. The absorption peak at 3165 cm^{-1} and Raman-line at 3170 cm^{-1} we assign to a weaker hydrogen bonded N-H group. The ν(CH) vibrations of CH_2 groups are better seen in the Raman spectrum at 3018, 2989, 2950, 2930 cm^{-1}. Other expected peaks of *β*-alaninium cation are observed in the region 1800-500 cm^{-1}.

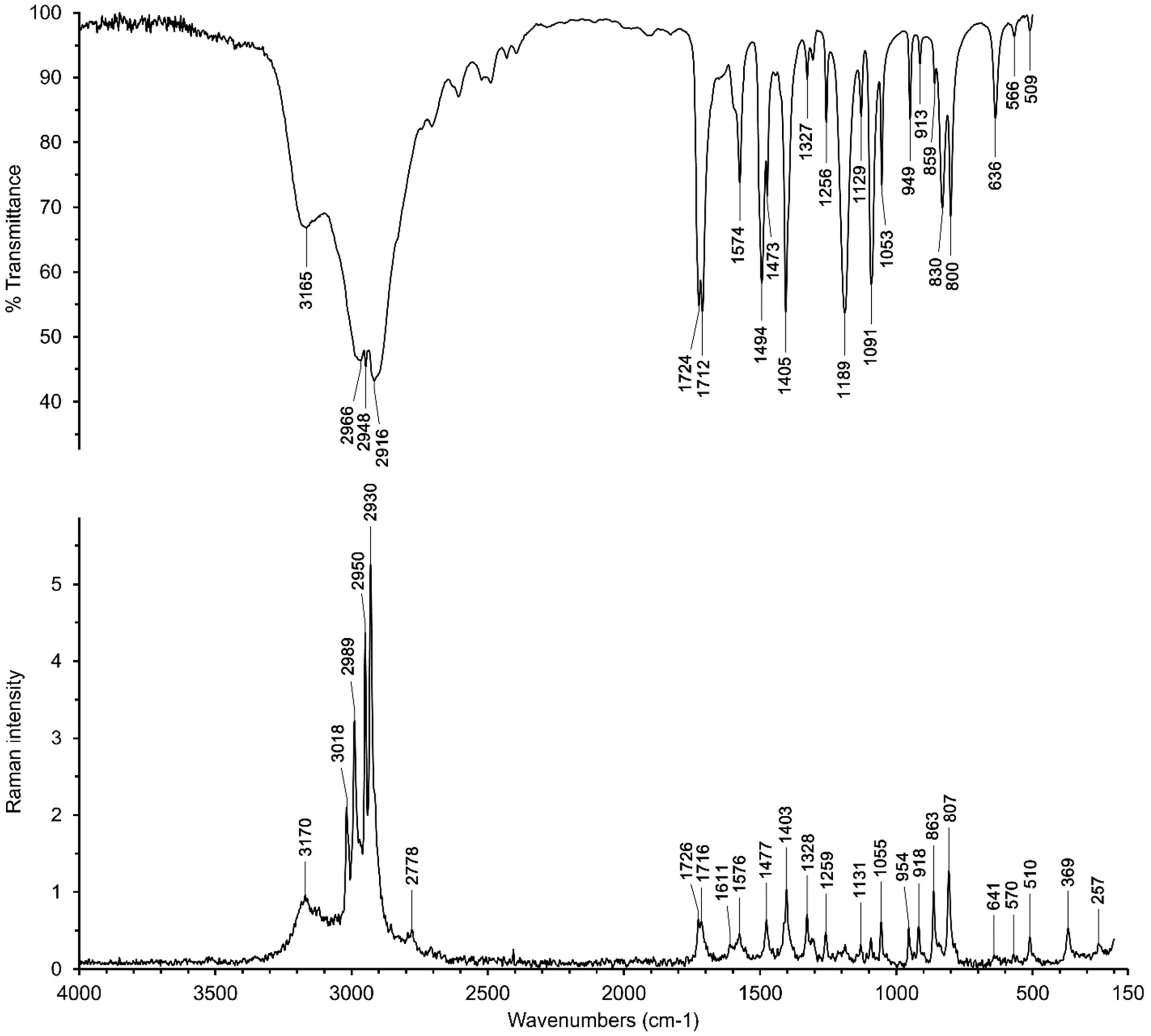


Fig. 4. Infrared and Raman spectra of β-alaninium chloride (**II**).

*3.3. β-Alaninium bromide (**III**)*

Crystals of β-alaninium bromide (**III**) are more hygroscopic compared to those of β-alaninium chloride (**II**). The salt (**III**) crystallizes in the monoclinic system with space group $P2_1/c$ (Table 1) and therefore it is not isostructural with (**II**). The space group is the same for (**III**) and (**I**), however, already comparison of unit cell parameters shows that both are not isostructural. The asymmetric unit of (**III**) also contains one formula unit, that is, one β-alaninium cation and one bromide anion (Fig. 5). It can be described as the A^+X^- simple type, too, that is, (β-AlaH)Br.

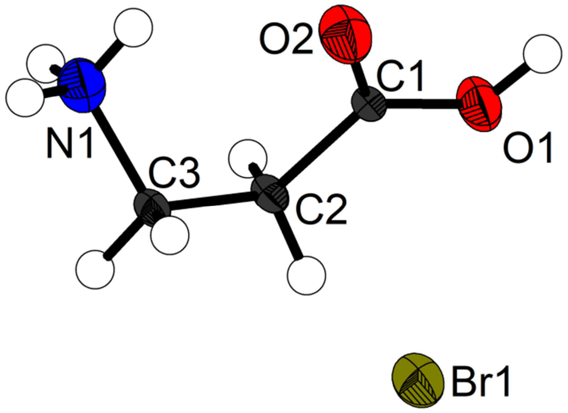


Fig. 5. Asymmetric unit of β-alaninium bromide (**III**).

The intramolecular bond lengths and angles of (**III**) and the conformation (Table 2) are like those of (**I**) and (**II**). The conformation of the β-alaninium cation in the structure of (**III**) also is *gauche(+)*.

Hydrogen bond parameters in the structure of (**III**) are shown in Table 5. The carboxyl group forms an O1-H1···Br1 hydrogen bond with the bromideion with an O···Br distance equal to 3.2119(14) Å. The NH$_3^+$ group forms two N-H···Br hydrogen bonds: N1-H11··Br1 (-x+2, -y+1, -z+1) and N1-H12···Br1 (-x+1, -y+1, -z+1) and one N1-H13···O2 (-x+2, -y+1, -z+1) hydrogen bond (Table 5). The atom H11 has an additional contact N1-H11···Br1 (-x+1, -y+1, -z+1) on the level of strong van der Waals interaction. Due to similar conformation of the β-alaninium cation here also an intramolecular contact N1-H13···O2 ispresent. In the structure there is a short C3-H32···Brl contact (with H32···Br1 and C3···Br1 2.98 and 3.660(2) Å respectively), which can be considered as a weak hydrogen bond.

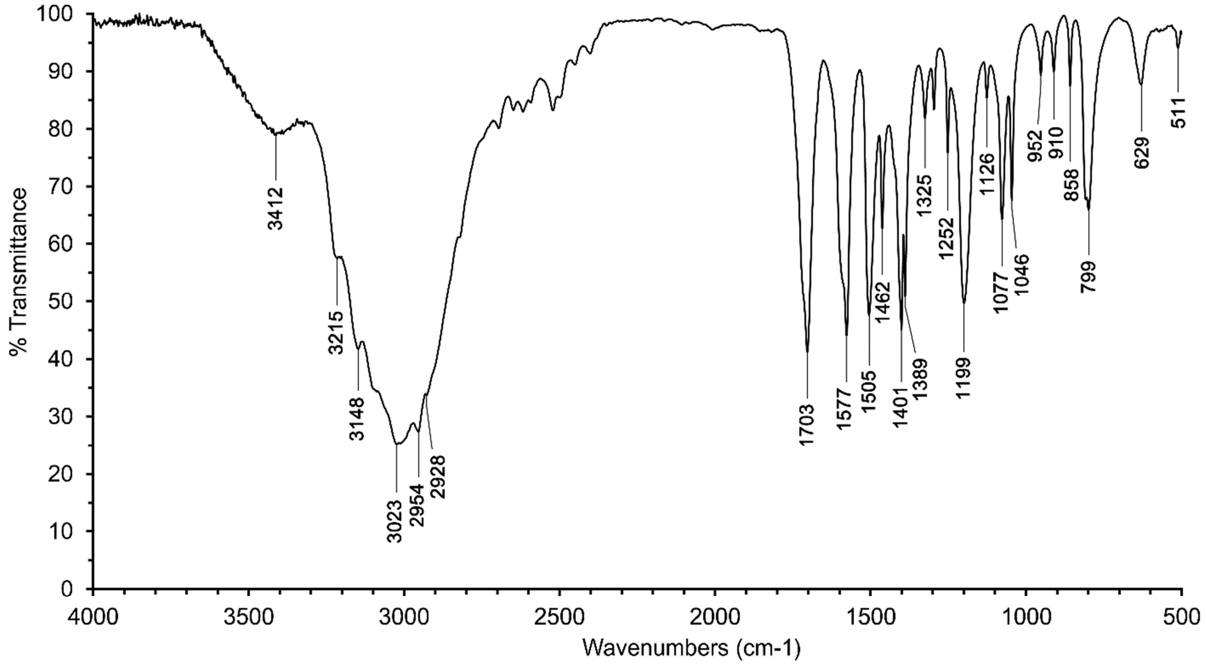


Fig. 6. Infrared spectrum of β-alaninium bromide (**III**).

Infrared spectrum of (III) is shown in Fig. 6. Raman spectrum of (**III**) was not registered because of its hygroscopic nature, even registration of its IR spectrum was difficult.

The peak at 3412 cm^{-1} in the spectrum of (**III**) is caused by absorption of hygroscopic water. The strong absorption band with peaks at 3215, 3148, 3023, 2954, 2928 cm^{-1} is caused by ν(NH), ν(OH) and ν(CH) vibrations of NH_3^+, COOH and CH_2 groups. A slight shift of the absorption band is due to the lower electronegativity of bromine compared with chlorine. Characteristic and expected peaks of the β-alaninium cation are observed in the region 1800-500 cm^{-1}.

The crystals (**I**, **II**, **III**) not being isostructural, nevertheless, form the same A^+X^- simple type and the remarkable difference between their infrared spectra is caused by strong O-H···F and usual O-H···Cl, O-H···Br hydrogen bonds.

*3.4. β-Alaninium iodide (**IV**)*

The salt (**IV**) crystallizes in the monoclinic system with space group $P2_1/n$ (Table 1). The asymmetric unit of (**IV**) also contains one formula unit, that is, one β-alaninium cation and one iodide anion.

Selected intramolecular bond lengths as well as valence and torsion angles of (**IV**) are provided in Table 2. However, the structure of (**IV**) differs from the structures of (**I**, **II**, **III**). Hydrogen bond parameters in the structure of (**IV**) are shown in Table 6. In this case the carboxyl group of the β-alaninium cation does not form hydrogen bond with an anion. Instead, two β-alaninium cations combine to a centrosymmetric β-alaninium$\cdot\cdot\beta$-alaninium dimeric cation (Fig. 7), where the O···O distance of O1-H1···O2 hydrogen bond is equal to 2.6540(16) Å.

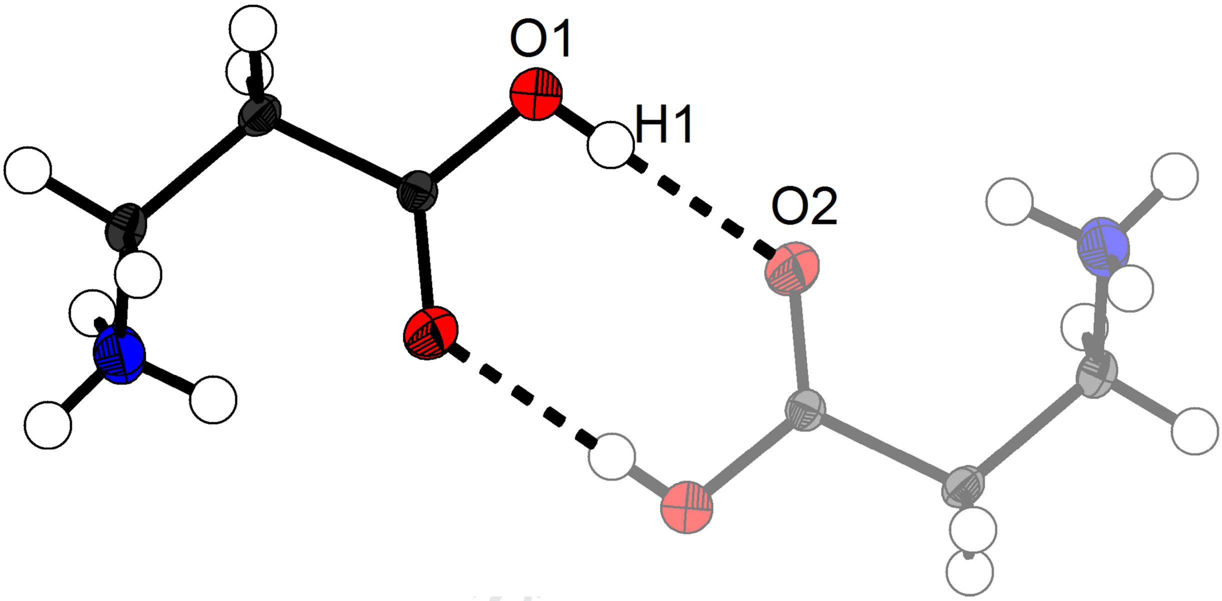


Fig. 7. Dimeric β-alaninium…β-alaninium cation in the structure of β-alaninium iodide (**IV**).

The conformation of the β-alaninium cation in this case is *gauche(-)*. There is an intermolecular N1-H13···O2 contact, too, which can be considered as weak hydrogen bond. The iodide anion forms two N-H···I type hydrogen bonds: N1-H12···I1(x, y, z) and weak N1-H11···I1 (-x+1/2, y-1/2, -z+1/2). So, the salt β-Ala·HI (**IV**) is one more salt of the $(A^+\cdots A^+)(X^-)_2$ type and thus differs significantly from the crystals (**I**, **II**, **III**). Most of known salts with $(A^+\cdots A^+)$ type cation are salts of β-alanine [1]. In [21] four types of β-Ala$^+\cdot\cdot\beta$-Ala$^+$ dimeric cations (A, B, C, D) were distinguished. Two of them are centrosymmetric and other two are noncentrosymmetric. The first A-type is characterized by a centrosymmetric arrangement of two β-alaninium cations in *gauche* conformation. The B-type looks like the A-type, but there is no inversion center. This type is represented by (β-AlaH$\cdot\cdot\beta$-AlaH)$(NO_3)_2$) [6]. The C-type is characterized by centrosymmetric *trans*-oriented β-alaninium cations, and in the D-type two amino ends of both *gauche*-oriented β-alaninium cations are facing in the same direction and therefore this type also is noncentrosymmetric. Consequently, the dimeric cation in the crystal (**IV**) belongs to the A-type.

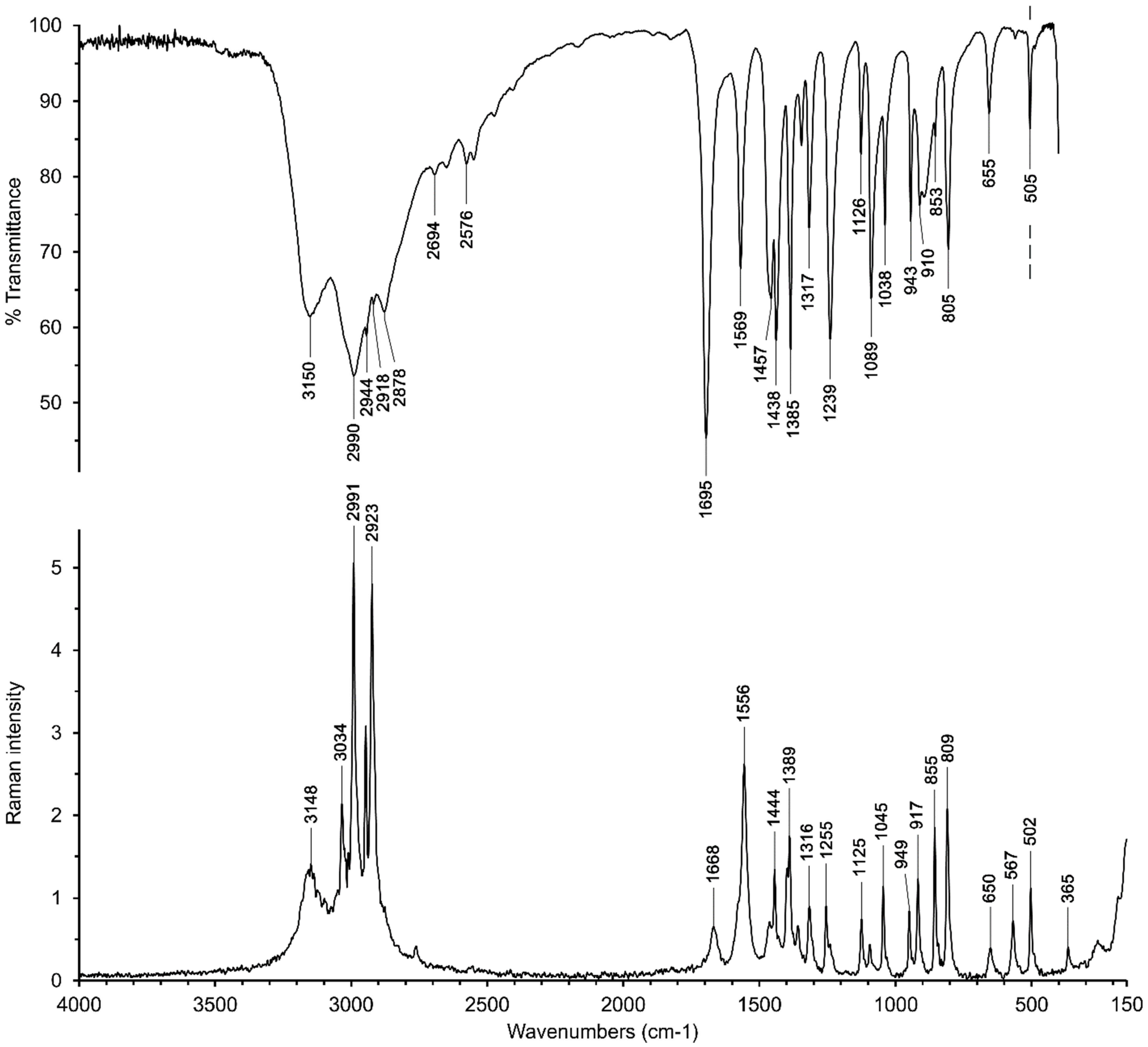


Fig. 8. Infrared and Raman spectra of *β*-alaninium iodide (**IV**).

Vibrational spectra of (**IV**) are shown in Fig. 8. For ν(OH) the position at *ca*. 3000 cm^{-1} is expected for the O-H···O hydrogen bond with an O···O distance of 2.654 Å according to the correlation between ν(OH) and O···O distance [22]. So, the absorption band centered at 2990 cm^{-1} is caused by ν(NH), ν(OH) and ν(CH) vibrations of NH_3^+, COOH and CH_2 groups. The absorption peak at 3150 cm^{-1} and a Raman-line at 3148 cm^{-1} are caused by ν(NH) of the NH_3^+ group in the weaker hydrogen bond N1-H13···O2. Theν(CH) vibrations of CH_2 groups are better seen in the Raman spectrum at 3034, 2991, 2947, 2923 cm^{-1}. Other expected peaks of *β*-alaninium cation are observed in the region 1800-500 cm^{-1}.

*3.5. β-Alaninium β-alanine bromide (**V**) and β-alaninium β-alanine iodide (**VI**)*

β-Alaninium *β*-alanine bromide (**V**) and *β*-Alaninium *β*-alanine iodide (**VI**) are isotypic with *β*-alaninium *β*-alanine chloride [9], they crystallize in space group *C*2/*c* with four formula units in the unit cell (Table 7). The asymmetric unit contains half of a formula unit, both the center of the dimeric cation and the halogenide anion are on special positions (an inversion center or a twofold axis, respectively). In Fig. 9 the centrosymmetric dimeric cation and the bromide anion are shown.

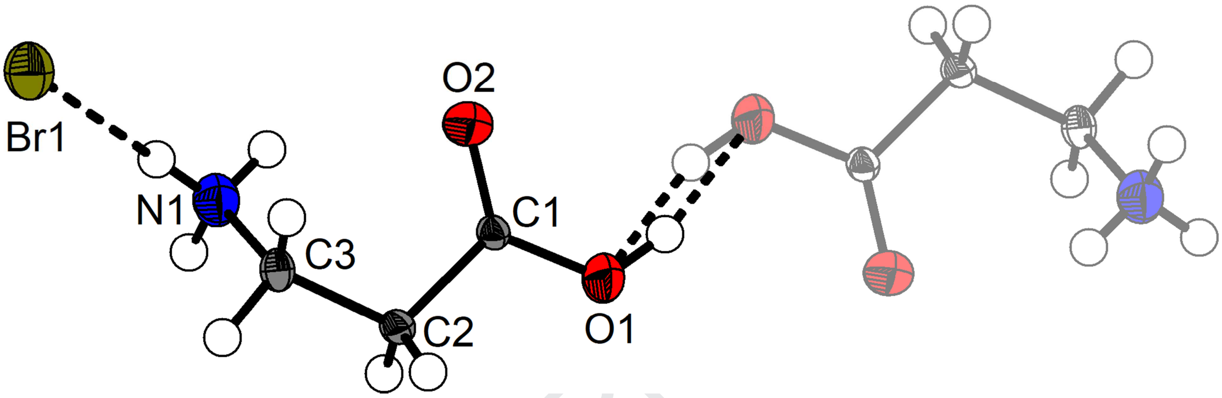


Fig. 9. Molecular structure of *β*-Alaninium *β*-alanine bromide (**V**). Both bromide anion and the center of the dimeric cation are on special positions.

In Table 8 selected bond lengths and angles in the structures of (**V**) and (**VI**) are listed. Evidently, these values are quite similar for both crystals. The conformation of *β*-alaninium cations in the structures of (**V**) and (**VI**) also is *gauche(+)*. Hydrogen bonds parameters in the structures of (**V**) and (**VI**) are shown in Tables 9 and 10. Additionally there are short contacts C3-H32···Br1 in (**V**) and C3-H31···I1, C3-H32···I1 in (**VI**) with distances H32···Br1 (2.94 Å), C3···Br1 (3.903 Å), H31···I1 (3.14 Å), C3···I1 (4011 Å), H32···I1 (3.15 Å), C3···I1 (3.881 Å), which can be considered as weak hydrogen bonds. In the model proposed for *β*-alaninium *β*-alanine chloride [9] the proton lies on the inversion center, while in our model for (**V**) and (**VI**) H1 was favored on a general, half-occupied position, symmetrically related by the center of inversion. Neutron diffraction analysis of the proton position would be necessary to determine which of these models is more reliable. The O···O dstances in centrosymmetric dimeric cations of (**V**) and (**VI**) are equal to 2.4723(17) and 2.461(2) Å, respectively, which are well comparable with 2.4729(17) Å in *β*-alaninium *β*-alanine chloride [9].

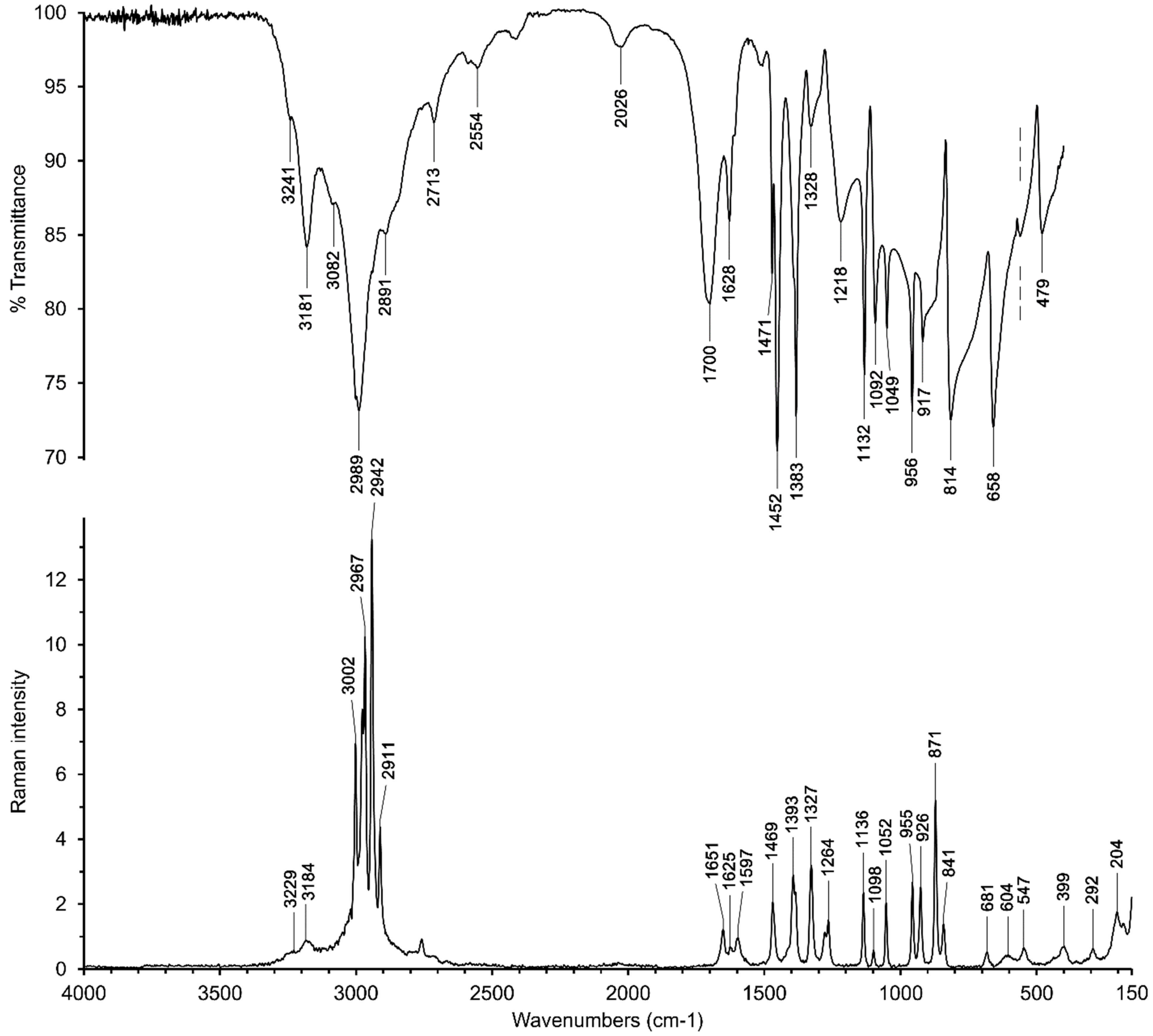


Fig. 10. Infrared and Raman spectra of β-alaninium β-alanine bromide (**V**).

Vibrational spectra of (**V**) and (**VI**) are shown in Figs. 10 and 11, respectively. They are very similar and with that of β-alaninium β-alanine chloride [9]. In the high-frequency region only stretching vibrations ν(NH) and ν(CH) of NH_3^+ and CH_2 groups are expected. Stretching vibrations ν(CH) are better seen in the Raman spectra, which are superimposed with bands caused by ν(NH). According to the correlation between the stretching vibration of O-H bonds ν(OH) (in cm^{-1}) and the R(O···O) distance (in Å) [22] strong O-H··O hydrogen bonds in the region 2.44–2.58 Å are characterized by a linear dependence, which is possible to reflect as ν(OH)=11250R-26876 [23]. For crystals (**V**) and (**VI**) with O···O distances equal to 2.4723(17) Å (at 296 K) and 2.461(2) Å (at 200 K) the expected value for ν(OH) of (V) is 940±20 cm^{-1} and 810±20 cm^{-1} for (VI). These values are in good agreement with absorption bands observed in Figs 16, 17 in the region 1500-400 cm^{-1} centered at *ca.* 850 cm^{-1}.

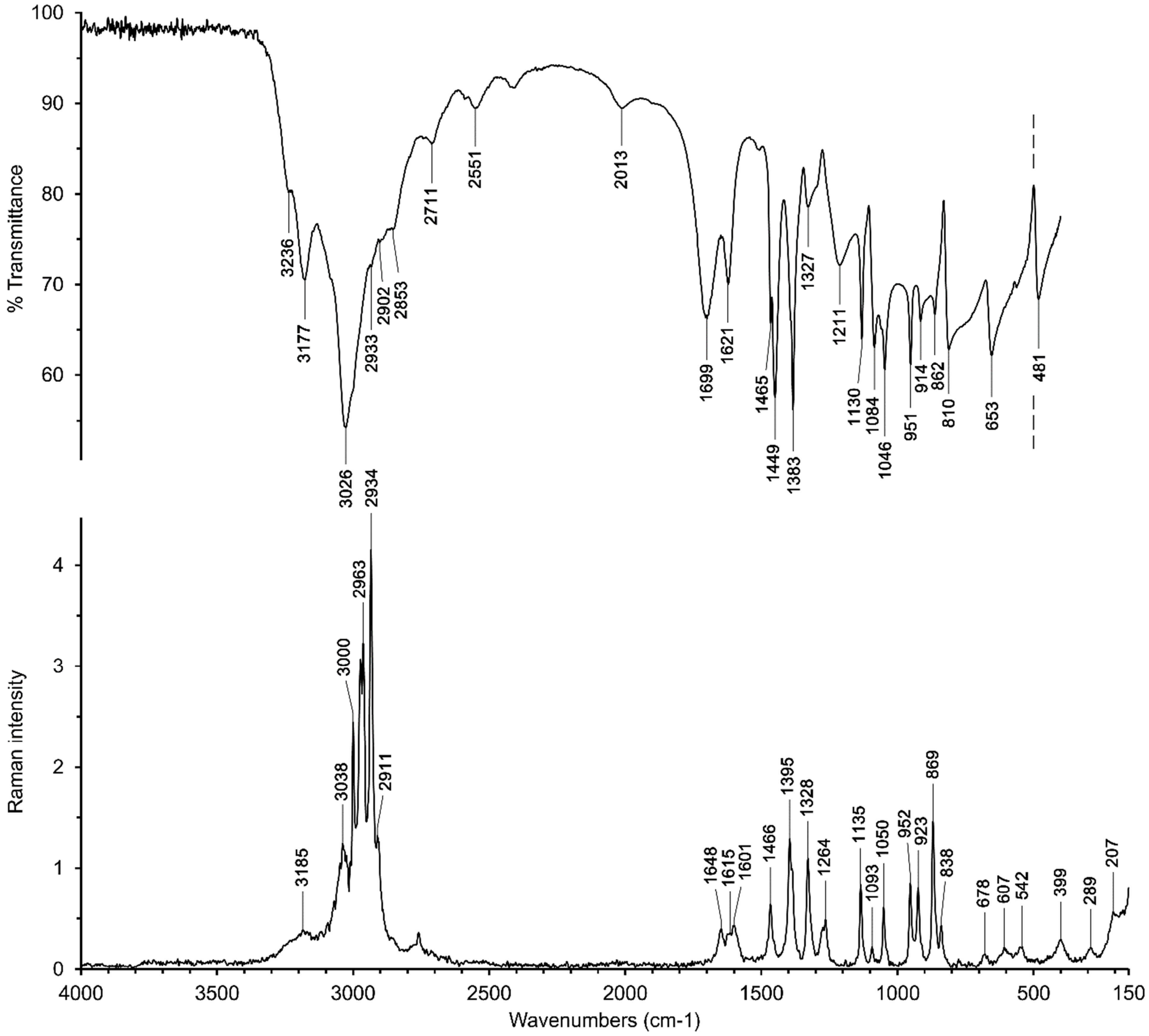
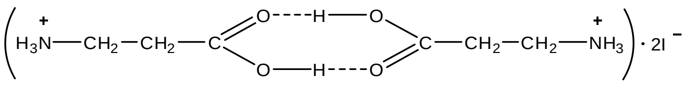


Fig. 11. Infrared and Raman spectra of *β*-alaninium *β*-alanine iodide (**VI**).

Conclusions

The salts *β*-alaninium fluoride (**I**), *β*-alaninium chloride (**II**), *β*-alaninium bromide (**III**) and *β*-alaninium iodide (**IV**) are not isostructural. The salts (**I-III**) are formed by simple type $A^{+}X^{-}$, where the carboxyl group forms a hydrogen bond with the respective anion. The salt (**IV**) is one more salt with a centrosymmetric *β*-alaninium···*β*-alaninium dimeric dication:



with an O···O hydrogen bond distance equal to 2.6540(16) Å.

The isotypic salts *β*-alaninium *β*-alanine bromide (**V**) and *β*-alaninium *β*-alanine iodide (**VI**) comprise centrosymmetric dimeric cations with strong hydrogen bonds with O···O distances equal to 2.4723(17) Å and 2.461(2) Å, respectively. The presence of strong hydrogen bonds in the structures of (**I**), (**V**) and (**VI**) is reflected in the infrared spectra.

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Table 1. Crystal data and details of the refinement for *β*-alaninium fluoride (**I**), *β*-alaninium chloride (**II**), *β*-alaninium bromide (**III**) and *β*-alaninium iodide (**IV**)

	(I)	**(II)**	**(III)**	**(IV)**
Formula	$C_3H_8FNO_2$	$C_3H_8ClNO_2$	$C_3H_8BrNO_2$	$C_3H_8INO_2$
M_r	109.10	125.55	170.01	217.00
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/c$	*Pbca*	$P2_1/c$	$P2_1/n$
a (Å)	8.268(2)	9.730(2)	5.6711(4)	6.735(1)
b (Å)	8.635(2)	7.412(2)	12.6980(8)	7.354(2)
c (Å)	6.759(1)	16.453(3)	8.9117(5)	13.327(3)
β(°)	96.46(3)		102.093(3)	96.86(3)
V(Å^3), Z	479.5(2), 4	1186.7(4), 8	627.50(7), 4	655.3(2), 4
Crystal size (mm^3)	0.3×0.3×0.1	0.3×0.2×0.075	0.5×0.2×0.1	0.4×0.25×0.15
D_{calc}(gcm^{-3})	1.511	1.405	1.800	2.199
μ(Mo K_α) (cm^{-1})	0.146	0.541	6.454	4.794
F(000)	232	528	336	408
T(K)	200(2)	200(2)	200(2)	200(2)
hkl range	±12, ±13, ±10	±14, ±11, ±25	±8, ±19, ±13	±10, ±11, ±20
Reflections measured	16435	36900	21217	21759
Reflections unique	1830	2258	2399	2507
Data with ($F_o > 2\sigma(F_o)$)	1627	2040	2029	2169
R_{int}	0.0457	0.0362	0.0545	0.0283
Parameters refined	68	75	70	69
$R(F)$* (for $F_o > 2\sigma(F_o)$)	0.0342	0.0485	0.0233	0.0161
$wR(F^2)$* (all reflections)	0.1017	0.1062	0.0504	0.0479
Weighting parameters a,b	0.048/0.122	0.018/1.268	0.0066/0.3553	0.018/0.453
$\Delta\rho_{fin}$ (max/min) [e Å^{-3}]	0.494/-0.249	0.373/-0.443	0.450/-0.481	0.840/-0.569

* $R1 = \Sigma \| |F_o| - |F_c| \| / \Sigma |F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$, $w = 1/[\sigma^2(F_o^2)+(a \times P)^2 + b \times P]$, $P = (F_o^2+2F_c^2)/3$

Table 2. Selected bond lengths (Å), valence and torsion angles (°) in β-alaninium fluoride (**I**), β-alaninium chloride (**II**), β-alaninium bromide (**III**) and β-alaninium iodide (**IV**).

	(**I**)	(**II**)	(**III**)	(**IV**)
C1-O1	1.3098(10)	1.325(2)	1.321(2)	1.3099(18)
C1-O2	1.2214(10)	1.211(2)	1.2052(19)	1.2237(16)
C1-C2	1.5081(11)	1.501(2)	1.503(2)	1.4978(19)
C2-C3	1.5129(11)	1.510(3)	1.515(2)	1.508(2)
C3-N1	1.4858(11)	1.489(2)	1.487(2)	1.490(2)
O2-C1-O1	124.72(7)	124.01(16)	123.72(14)	124.13(13)
O2-C1-C2	122.48(7)	124.76(16)	123.51(15)	121.58(13)
O1-C1-C2	112.81(7)	111.22(15)	112.77(14)	114.29(12)
C1-C2-C3	113.75(7)	114.38(15)	112.61(13)	112.67(12)
N1-C3-C2	112.17(7)	111.99(14)	111.09(13)	112.07(12)
O1-C1-C2-C3	-179.90(7)	174.9(1)	-171.26(15)	-173.4(1)
C1-C2-C3-N1	63.21(9)	66.5(2)	59.24(18)	-64.6(2)

Table 3. Hydrogen bonds parameters for β-alaninium fluoride (**I**) (in Å and °).

D-H···A	D-H	H···A	D···A	<DHA
O1-H1···F1	0.993(19)	1.415(19)	2.4027(9)	172.5(19)
N1-H11···F1^{i}	0.91	2.21	2.9605(10)	139
N1-H11···O2	0.91	2.35	2.9420(11)	122
N1-H12···F1^{ii}	0.91	2.12	2.8737(10)	140
N1-H12···O2^{iii}	0.91	2.29	2.845(11)	119
N1-H13···F1^{iv}	0.91	1.80	2.7007(11)	169

Symmetry code: (i) -x, y+1/2, -z+1/2; (ii) x, y+1, z; (iii) -x, y+1/2, -z+1/2; (iv) x, -y+3/2, z+1/2;

Table 4. Hydrogen bonds parameters for β-alaninium chloride (**II**) (in Å and °).

D-H···A	D-H	H···A	D···A	<DHA
O1-H1···Cl1^{i}	0.79(3)	2.22(3)	3.007(2)	172(3)
N1-H11···Cl1^{ii}	0.91	2.27	3.157(2)	165
N1-H12···O2	0.91	2.41	3.013(2)	124
N1-H12···Cl1	0.91	2.51	3.248(2)	139
N1-H13···O2^{iii}	0.91	2.55	3.135(2)	122
N1-H13···Cl1^{iv}	0.91	2.555	3.232(2)	132

Symmetry code: (i) x-1/2, -y+1/2, -z+1; (ii) –x+1, -y, -z+1; (iii) –x+1, -y+1, -z+1; (iv) x+1/2, -y+1/2, -z+1.

Table 5. Hydrogen bonds parameters for β-alaninium bromide (**III**) (in Å and °).

D-H···A	D-H	H···A	D···A	<DHA
O1-H1···Br1	0.78(3)	2.43(3)	3.2119(14)	173(3)
N1-H11···Br1^{i}	0.91	2.56	3.3469(13)	145

N1-H11···Br1^{ii}	0.91	2.98	3.368(1)	108
N1-H12···Br1^{iii}	0.91	2.46	3.3072(14)	156
N1-H13···O2^{i}	0.91	2.10	2.9177(17)	149
N1-H13···O2	0.91	2.34	2.910()	121

Symmetry code: (i) –x+2, -y+1, -z+1; (ii) -x+1, -y+1, -z+1; (iii) -x+1, -y+1, -z+1.

Table 6. Hydrogen bonds parameters for β-alaninium iodide (**IV**) (in Å and °).

D-H···A	D-H	H···A	D···A	<DHA
O1-H1···O2^{i}	0.77(3)	1.88(3)	2.6540(16)	178(3)
N1-H11···I1^{ii}	0.89	2.95	3.6540(14)	137
N1-H12···I1	0.89	2.72	3.5368(18)	153
N1-H13···O2	0.89	2.25	2.8648(17)	126

Symmetry code: (i) –x+2, -y+1, -z+1; (ii) -x+1/2, y-1/2, -z+1/2.

Table 7. Crystal data and details of the refinements for (β-alaninium…β-alanine) bromide (**V**) and (β-alaninium…β-alanine) iodide (**VI**). Some data of (β-alaninium…β-alanine) chloride [9] are provided for comparison.

	2β-Ala.HCl [9]	(**V**)	(**VI**)
Formula	$C_6H_{15}ClN_2O_4$	$C_6H_{15}BrN_2O_4$	$C_6H_{15}IN_2O_4$
M_r	214.65	259.11	306.10
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
a (Å)	19.938(4)	20.3113(4)	20.9592(7)
b (Å)	5.1990(10)	5.2250(1)	5.2698(2)
c (Å)	10.719(2)	10.8983(2)	11.0343(3)
β(°)	118.03(3)	117.971(1)	117.0470(10)
V(Å^3), Z	980.8(3), 4	1021.49(3), 4	1085.46(6), 4
Crystal size (mm^3)		0.43×0.4×0.3	0.30×0.20×0.075
D_{calc}(gcm^{-3})	1.454	1.685	1.873
μ(Mo K_α) (cm^{-1})	3.77	4.013	2.940
F(000)	456	528	600
T(K)	293(2)	296(2)	200(2)
hkl range	-25/26, -5/6, -13/14	-30/29, ±7, ±16	±32, ±8, ±16
Reflections measured	2829	7692	18435
Reflections unique	1143	1860	2073
Data with ($F_o > 2\sigma(F_o)$)		1758	2003
R_{int}	0.0376	0.0582	0.0196
Parameters refined	90	93	61
$R(F)$* (for $F_o > 2\sigma(F_o)$)	0.0286	0.0241	0.0144
$wR(F^2)$* (all reflections)	0.0769	0.0694	0.0457
Weighting parameters a, b	0.0380/0.5316	0.0451/0.0451	0.0281/0.6842
$\Delta\rho_{fin}$ (max/min) [e Å^{-3}]	0.21/-0.23	0.64/-0.58	0.83/-0.39

* $R1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$, $w = 1/[\sigma^2(F_o^2)+(a \times P)^2 + b \times P]$, $P = (F_o^2+2F_c^2)/3$

Table 8. Selected bond lengths (Å) and angles (°) in (β-alaninium…β-alanine) bromide (**V**) at 296 K and (β-alaninium…β-alanine) iodide (**VI**) at 200 K.

	(**V**)	(**VI**)
C1-O1	1.3070(13)	1.3095(13)
C1-O2	1.2238(14)	1.2280(13)
C1-C2	1.5148(14)	1.5131(15)
C2-C3	1.5112(15)	1.5145(16)
C3-N1	1.4884(16)	1.4922(16)
O2-C1-O1	123.54(9)	123.20(10)
O2-C1-C2	122.03(9)	122.25(10)
O1-C1-C2	114.42(9)	114.54(9)
C1-C2-C3	113.42(9)	113.08(9)
N1-C3-C2	111.9(1)	111.73(9)
O1-C1-C2-C3	170.4(1)	171.44(10)
C1-C2-C3-N1	63.00(13)	63.57(13)

Table 9. Hydrogen bonds parameters for (β-alaninium…β-alanine) bromide (**V**) (in Å and °) at 296 K.

D-H···A	D-H	H···A	D···A	<DHA
O1-H1···O1^{i}	0.865(18)	1.632(18)	2.4723(17)	163(4)
N1-H11···O2	0.85(2)	2.23(2)	2.8535(13)	131(2)
N1-H11···O1^{ii}	0.85(2)	2.46(3)	3.125(2)	136(2)
N1-H12···Br1^{iii}	0.87(2)	2.47(2)	3.2930(11)	158(2)
N1-H13···O1^{iv}	0.90(2)	1.96(2)	2.8588(15)	177(2)

Symmetry code: (i) -x+1/2, -y+1/2, -z+1; (ii) -x+1/2, y+1/2, -z+1/2; (iii) -x, -y+1, -z; (iv) x, -y, z-1/2.

Table 10. Hydrogen bonds parameters for (β-alaninium…β-alanine) iodide (**VI**) (in Å and °) at 200 K.

D-H···A	D-H	H···A	D···A	<DHA
O1-H1···O1^{i}	0.84	1.64	2.4613(18)	164
N1-H11···O2	0.91	2.21	2.8634(14)	128
N1-H11···O1^{ii}	0.91	2.37	3.0932(15)	136
N1-H12···I1^{iii}	0.91	2.70	3.5116(10)	150
N1-H13···O1^{iv}	0.91	1.93	2.8356(14)	176

Symmetry code: (i) -x+1/2, -y+1/2, -z+1; (ii) -x+1/2, y+1/2, -z+1/2; (iii) -x, -y+1, -z; (iv) x, -y, z-1/2.

Crystals of β-alaninium fluoride, chloride, bromide and iodide are not isostructural

β-alaninium iodide is a new salt with centrosymmetric ($A^+ \ldots A^+$) type dication

2β-Ala.HBr and 2β-Ala.HI are salts with ($A^+ \ldots A$) type dimeric cation

A.M. Petrosyan, G. Giester, V.V. Ghazaryan, M. Fleck, “Halogenides of β-alanine”

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.