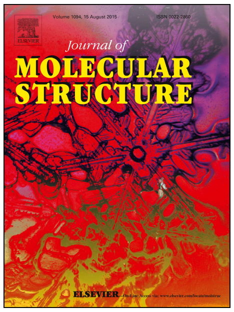

L-Alanine halogenides with *L*-alanine *L*-alaninium dimeric cation

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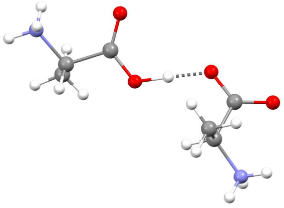

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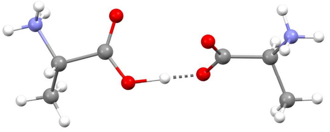

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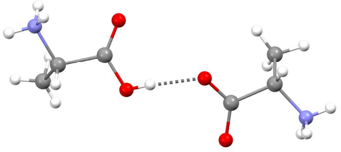
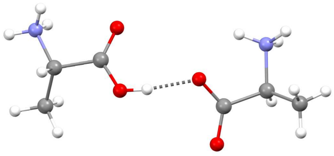


type D



L-Alanine halogenides with *L*-alanine *L*-alaninium dimeric cation

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Abstract

Crystalline salts *L*-alanine *L*-alaninium chloride (**I**), *L*-alanine *L*-alaninium bromide (**II**) and *L*-alanine *L*-alaninium iodide (**III**) were obtained, which have dimeric cations in the structure. The salts crystallize in the monoclinic crystal system with the space group $P2_1$ (Z=4). *L*-alanine···*L*-alaninium dimers are realized *via* rather short O–H···O hydrogen bonds between carboxyl and carboxylate groups with the O···O distances equal to 2.421(2), 2.423(2) Å in (**I**), 2.437(10), 2.413(8) Å in (**II**) and 2.421(5), 2.442(5) Å in (**III**) at 200K. The salts (**I**) and (**II**) are isotypic, while the salt (**III**) has different packing so the structure is distinct. The infrared and Raman spectra and the crystal structures of these compounds are discussed. Besides, we obtained for the first time a new simple salt *L*-alaninium iodide.

Keywords: L-alanine L-alaninium dimeric cation, hydrogen bond, structure, vibrational spectra

1. Introduction

Formation of salts has been extensively investigated for a range of amino acids [1]. A particular type of salt includes dimeric ($A\cdots A^+$) cations composed of one A zwitterion and one A^+ cation tightly connected by a strong O–H···O hydrogen bond. With a singly charged anion X^-, such cations form a unique series of $(A\cdots A^+)X^-$ salts. Their preparation is, however, not straightforward; considerable efforts must often be spent determining the optimal, often non-stoichiometric composition of the initial solution, as stoichiometric ratios do not ensure synthesis of the desired salt (or indeed of any salt at all) [2-4]. Among the known salts of the amino acid alanine, simple salts prevail over the salts with dimeric cations.

The first known salt of alanine with (alanine···alaninium) dimeric cation was 2*L*-Ala·HNO_3 obtained in 2001 by Silva et al. [5], although the system *L*-alanine–HNO_3–water had been studied previously and only (*L*-AlaH)NO_3 was obtained [6]. Alanine moieties have

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the only conformation, where N1, C2, C1 atoms and O atoms of the carboxyl(ate) group are *ca*. in the same plane, and the O-C1-C2-C3 torsion angles close to –60° and 120°. However, the mutual arrangement of zwitterionic and cationic alanine moieties in the dimeric cation can be distinct, and is characterized by the several angles presented in Scheme 1 and Table 1 (one can also use angles <CCO$_H$O and <O$_H$OCC instead of <OCO$_H$O and <O$_H$OCO). In this case, carboxyl and carboxylate groups are *ca*. in the same plane. We designate this type of dimeric cation as type-A (Fig. 1).

Later 2*L*-Ala·HNO$_3$ was investigated as NLO crystal [7,8]. Inelastic neutron scattering and Raman spectra of 2*L*-Ala·HNO$_3$ were investigated at different temperatures and the distinctions were discussed in view of the structure [9].

The second salt 2*L*-Ala·H$_3$PO$_3$·H$_2$O was obtained and characterized (crystal structure, piezoelectric and pyroelectric behavior) by Pankova and coauthors [10-12]. Here, alanine and alaninium moieties are arranged otherwise. Carboxyl and carboxylate groups are *trans* oriented and <CO$_H$OC equals to –154°. Oxygen atoms, those forming the dimeric cation *via* O–H···O hydrogen bond of 2.530(2) Å, are *trans* positioned to the N atoms of NH$_3$ groups and the corresponding OCCN torsion angles equal to 168° and 164°. Chronologically, we denote this conformation of the cation as type-B. Types A and B differ in the angles <O$_H$OCO and <O$_H$OCC (see Table 1).

The salt *L*-alanine *L*-alaninium triiodide was synthesized while trying to obtain *L*-alaninium iodide from a solution containing excess of HI [13, 14]. It also forms dimeric cations of type-B.

The next halogenide *D*-alanine *D*-alaninium bromide was obtained by Fischer [15] not directly, but as an unplanned product of a reaction of *D*-alanine with 2,3-dibromosuccinic acid. The main distinction of *D*-alanine *D*-alaninium dimer from the dimers of type-A and type-B is the *gauche*-orientation of carboxyl and carboxylate groups when the angle <CO$_H$OC equals to –87°. It represents a further type of dimers – type-C.

With picric acid at least two salts of 2:1 ratio were obtained, one of which is an anhydrous sample based on vibrational spectra [16], and the second one is a monohydrate 2*L*-Ala·picric acid·H$_2$O structurally confirmed in [17]. In the structure of *L*-alanine *L*-alaninium picrate monohydrate alanine moieties form the fourth type of alanine dimers called type-D by us. The type-D is closer to the type-B. The only distinction is that in this type of dimeric cation the alanine moiety forms a dimer *via* oxygen atom, which is in the *cis*-position to the NH$_3$ group, unlike to previously mentioned types of dimeric cations, where it is *trans*-positioned.

Alanine dimers of type-D also exist in the structure of *L*-AlaH·(*L*-Ala··*L*-AlaH)SiF$_6$·H$_2$O [18].

We published preliminary data on obtaining of *L*-alanine *L*-alaninium chloride and *L*-alanine *L*-alaninium bromide in [16].

In the present work, we have focused on detailed results of investigation of the halogenide systems *L*-Ala–HCl–H$_2$O, *L*-Ala–HBr–H$_2$O and *L*-Ala–HI–H$_2$O. We obtained salts with dimeric cation in all three systems. Preparation of the 2*L*-Ala·HI was possible using stabilized hydriodic acid, bearing in mind previous experience in [13,14], where the hydriodic acid without stabilizer undergoes a partial oxidation resulting in the formation of an I_3^- anion and the corresponding salt (*L*-Ala···*L*-Ala$^+$)I_3^-. Besides, we have managed to obtain the *L*-alaninium iodide.

2. Experimental

2.1. Synthesis and crystal growth

As initial reagents we used *L*-alanine (≥98%, TLC) and hydriodic acid (57% w/w, distilled, stabilized with <1.5% hypophosphorous acid, 99.95%) from “Sigma-Aldrich” Chem. Co., and hydrochloric (32% w/w, chemically pure grade) and hydrobromic (40.5% w/w, ultrapure grade) acids from “Reakhim” Co. All compounds have been obtained at room temperature by evaporation of aqueous solutions containing non-stoichiometric ratios of solved components: *L*-alanine and hydrochloric, hydrobromic or hydriodic acid. From 2:1 M-ratio first *L*-alanine bulk crystals are formed, and then the needles of 2*L*-Ala·HCl (or 2*L*-Ala·HBr, or 2*L*-Ala·HI). By collecting and weighting *L*-alanine crystals, we calculated that the 2*L*-Ala·HCl (or 2*L*-Ala·HBr, or 2*L*-Ala·HI) starts to form from *ca*. 1.4:1 M-ratio, which we tried and confirmed experimentally. From 1:1 M-ratio using HCl or HBr, a mixture of salts 2*L*-Ala·HCl and *L*-Ala·HCl (2*L*-Ala·HBr and *L*-Ala·HBr) is formed. Thus, to obtain pure *L*-Ala·HCl and *L*-Ala·HBr crystals we used solutions with 1:1.5 M-ratio of components, i.e. with excess of hydrochloric or hydrobromic acid. To obtain *L*-Ala·HI the 1:1 M-ratio was used. Alanine used for preparation in experiments taken from 1 to 2g.

2.2. Crystal structure determination

Suitable single crystals of the title compounds were manually selected and checked for irregularities under the microscope. Well-developed crystals were mounted on glass needles with laboratory grease. Single-crystal X-ray intensity data were obtained at 200K (Oxford Cryosystems Cryostream 600 resp. 800 Plus) by a measurement on a Enraf Nonius Kappa CCD diffractometer, sealed tube, equipped with a graphite monochromator and monocapillary optics using Mo-K$_\alpha$ (λ = 0.71073 Å) radiation for 2*L*-Ala·HCl or on a Bruker APEXII diffractometer equipped with a CCD area detector and an Incoatec Microfocus Source IµS (30 W, multilayer mirror, Mo-K$_\alpha$) for 2*L*-Ala·HBr and 2*L*-Ala·HI. The structures were solved using direct methods; subsequent difference Fourier syntheses and least-squares refinements yielded the positions of the remaining atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters, hydrogen atoms with isotropic displacement parameters. The hydrogen atoms were treated as riding on their parent atoms, except for the hydrogen atoms of the oxygen and nitrogen atoms. All calculations were performed using Enraf Nonius or Bruker instrument software (APEX3 software suite) and the SHELX97 program package [19-21].

The crystallographic data as well as details of the measurements are listed in Table 2. 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. 1556749-1556751.

2.3. Vibrational spectra

Attenuated total reflection Fourier-transform infrared spectra (FTIR ATR) were registered by a Nicolet 5700 spectrometer using Smart Performer single-reflection ATR accessory (ZnSe prizm, Happ-Genzel apodization, corrected for ATR distortion, number of scans 32, resolution 4 cm^{-1}). Nujol mull technique used to register part of the IR spectrum in the region 600–400 cm^{-1} (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 at room temperature with resolution 4 cm^{-1}. Number of scans and laser power at the sample were 256 and 0.44W for (**I**), 384 and 0.44W for (**II**), 512 and 0.37W for (**III**), 256 and 0.35W for (**IV**), 256 and 0.36W for (**V**) and 256 and 0.32W for (**VI**).

3. Results and discussion

3.1. Molecular and crystal structures

The salts 2*L*-Ala·HCl, 2*L*-Ala·HBr and 2*L*-Ala·HI crystallize in the monoclinic crystal system with the space group $P2_1$, Z=4 (see Table 2). The structures of 2*L*-Ala·HCl and 2*L*-Ala·HBr are isotypic but differ from 2*L*-Ala·HI as already recognizable from the unit cell parameters (Table 2). Let us start from the structure of 2*L*-Ala·HCl. The unit cell contains two (*L*-Ala···*L*-Ala$^+$) dimeric cations and two chloride anions in the asymmetric unit (Fig. 2). Bond lengths and valence angles are normal (see Table S1 in supporting material). The C–O lengths are changed, which is expected and the reason of which is the rather short O–H···O hydrogen bond between the carboxyl group of alaninium moiety and the carboxylate group of zwitterionic alanine moiety. Thus, in the *L*-Ala(A)···*L*-Ala(B)$^+$ and *L*-Ala(C)···*L*-Ala(D)$^+$ two dimeric cation’s distances of O–H···O hydrogenbonds equal to 2.421(2) Å and 2.423(2) Å, respectively (for 2*L*-Ala·HBr they have lengths of 2.437(10) Å and 2.413(8) Å). The dimeric cations in the structure are of type-C (Fig. 1). Carboxyl and carboxylate groups are at an angle to each other, so the CO_HOC angles, passing O–H···O hydrogen bond, are equalto 78° and 75° (in 2*L*-Ala·HBr 91° and 87°). One can name it as a *gauche*-conformation. Characteristic torsion angles of dimeric cations are listed in Table 1. In contrast to the type-C, in the types-A and B, carboxyl and carboxylate groups are almost coplanar having *trans*-conformation and $<CO_HOC$ tends to 180°. Somewhat other situation is in the type-D, where $<CO_HOC = –126°$. In the *L*-alaninium cations of *L*-alanine compounds, NH_3^+ and OH groups are in some cases located side by side [23,24], but are commonly located in the opposite sides as in the known types of dimeric cations of *L*-alanine. As concerns to zwitterionic *L*-alanine,

the oxygen atom forming dimeric cation and the amino group mainly are oppositely directed. The only exception is type-D, where they are neighboring. The difference between type-A and type-B may be characterized with <O_HOCO angle.

The crystal 2*L*-Ala·HCl has a layered structure. Layers are arranged perpendicular to the *b*-axis (Fig. 3). Since methyl groups are located at the outer sides of the layers, no hydrogen bond i.e. no strong interaction exists between layers, so the crystal has cleavage. In the layers, one can distinguish the chains built with *L*-Ala(A)···*L*-Ala(B)$^+$ dimeric cations and Cl1 anions serially connected with N1A–H12A···Cl1···H12B–N1B hydrogen bonds (see details of all H-bonds in Table 3). The angle between the chain orientation and the c-axis is 43°. Such chains are located parallel to each other in the same plane parallel (010) and are interconnected with N1A–H13A···Cl1 and N1B–H13B···Cl1 hydrogen bonds, thus forming “semilayers” (Fig. 4). Fully identical chains and network exist between *L*-Ala(C)···*L*-Ala(D)$^+$ dimeric cations and Cl2 anions, thus forming a second “semilayer”. In this case chain-forming hydrogen bonds are N1C–H12C···Cl2 and N1D–H12D···Cl2, and the interconnections are N1C–H13C···Cl2 and N1D–H13D···Cl2. The directions of the previous and the later chains are *ca*. perpendicular in projection onto (010) and are at an angle equal to 86°. The structural layers of the crystal are formed from these two “semilayers” linked from one hand with N–H···O type hydrogen bonds N1A–H11A···O2C and N1C–H11C···O2A between zwitterionic *L*-Ala(A) and *L*-Ala(C) moieties, and from the other hand with N–H···Cl type hydrogen bonds N1B–H11B···Cl2 and N1D–H11D···Cl1 attracting *L*-Ala(B)$^+$ and *L*-Ala(D)$^+$ cationic moieties. This type of semilayers was called as S1 type hydrogen bonded sheets in [25] and also found in some salts of other amino acids. Comparison of the crystal structures of 2*L*-Ala·HBr obtained by us (or 2*L*-Ala·HCl, which is isotypic) and 2*D*-Ala·HBr obtained by A. Fischer [15] showed, that the structural layers are similar, but they are different in arrangement in between (see Fig.5). In the structure of 2*L*-Ala·HBr the layers alternately are arranged oppositely, while in the structure of 2*D*-Ala·HBr they are unidirectional. Although symmetries are the same, there are one dimeric cation and a bromide anion in the asymmetric unit of 2*D*-Ala·HBr and Z=2. Possibly, the difference in preparation method leads to the formation of different structures. It is interesting to note, that the crystal structure of 2*L*-Ala·HBr is less compact (D_{calc}=1.553 gcm^{-3} at 296K), than that of 2*D*-Ala·HBr (D_{calc}=1.561 gcm^{-3} at 299K). Examining *L*-Ala(A) and *L*-Ala(B) couple in the structure of 2*L*-Ala·HI, on the assumption of C-O bonds lengths one can conclude that the H-atom of the carboxyl group should be attached to the (B) moiety, however it is close to (A) and we have *L*-Ala(B)···*L*-Ala(A)$^+$ dimeric cation instead of *L*-Ala(A)···*L*-Ala(B)$^+$ in 2*L*-Ala·HCl and 2*L*-Ala·HBr. Ignoring this, one can say that 2*L*-Ala·HI also consists of similar layers, which is a result of identical hydrogen bonds (see Tables 3-5). So, three different crystal structures are observed which crystallize in the same symmetry group and are built by corresponding structural blocks (layers).

3.2. Infrared and Raman spectra

The vibrational spectra of 2*L*-Ala·HCl (**I**), 2*L*-Ala·HBr (**II**) and 2*L*-Ala·HI (**III**) are shown in the Figs. 6-8, and the spectra of *L*-Ala·HCl (**IV**), *L*-Ala·HBr (**V**) and *L*-Ala·HI (**VI**) are presented in the Figs. 9-11 for comparison. The wavenumbers of peaks and their assignments are listed in Tables 6 and 7.

A detailed investigation of the spectra of (**I**, **II**, **III**) in comparison with those of (**IV**, **V**, **VI**) shows several differences. In the high frequency region one can expect the observation of N–H, C–H and O–H stretching vibrations of NH_3^+, CH_3, CH and COOH groups. It is true for the 1:1 compounds (**IV**, **V**, **VI**) but not in the case of 2:1 compounds with dimeric cation (**I**, **II**, **III**). As is noted above, in the structure of (**I**), (**II**) and (**III**) the OH of the carboxylic group are engaged in the rather strong O–H···O hydrogen bond, thus the stretching mode of O–H occurs not in the region of N–H stretching vibrations, but in the low frequency region centered at *ca*. 800 cm^{-1}. This value is in good agreement with the correlation between ν(OH) and R(O···O) [26]. Therefore, the baseline of the **R** spectra of (**I**), (**II**) and (**III**) is curved around that region (1700-400 cm^{-1}). It is easy to see, that in the same region of the IR spectra of (**IV**), (**V**) and (**VI**) the baseline is straight. So, one can find the ν(CH) vibrational modes as strong Raman lines in the regions 3019-2885 cm^{-1} for (**I**), 3013-2884 cm^{-1} for (**II**) and 3010-2883 cm^{-1} for (**III**). Nearby medium-intensity lines are caused by ν(NH) vibrations, which have their counterparts in the IR spectra in the form of strong bands (3062, 3030, 2926 in Fig. 6 and 3071, 3025, 2913 cm^{-1} in Fig. 7 and 3072, 2902 cm^{-1} in Fig. 8) overlapping ν(CH) weak bands. One more feature of the spectra arises because of strong hydrogen bond in a dimeric cation. Such strong hydrogen bond leads to change of covalent bond lengths in carboxyl and carboxylate groups (see Table S1 in supporting material) which in turn leads to decreasing of stretching vibration frequency of carboxylic C=O in comparison with “free” carboxyl groups of 1:1 samples. The ν(C=O) vibration, which appears as a strong band with peaks 1718 cm^{-1} in *L*-Ala·HCl (Fig.9), and 1719 cm^{-1} in *L*-Ala·HBr (Fig.10) and 1728, 1716 cm^{-1} in *L*-Ala·HI (Fig.11), is shifted to the lower frequency region and observed as a broad band at 1673 cm^{-1} in 2*L*-Ala·HCl (Fig.5), 1667 cm^{-1} in 2*L*-Ala·HBr (Fig.7) and 1666 cm^{-1} in 2*L*-Ala·HI (Fig.8), overlapped with $\nu_{as}(COO^-)$ vibrations. Characterization of some further peaks can be seen in Tables 6 and 7.

4. Conclusions

L-alanine *L*-alaninium chloride, *L*-alanine *L*-alaninium bromide and *L*-alanine *L*-alaninium iodide are salts with a (*L*-Ala···*L*-Ala$^+$) dimeric cation and crystallize in the monoclinic space group $P2_1$. The O···O distances of O–H···O hydrogen bonds in dimeric cations are among shortest found in likewise salts and equal to 2.421(2), 2.423(2) Å in 2*L*-Ala·HCl, 2.437(10), 2.413(8) Å in 2*L*-Ala·HBr, and 2.421(5), 2.442(5) Å in 2*L*-Ala·HI. A bit shorter distances of dimers’ hydrogen bond have only two salts of amino acids, namely (*L*-Trp···*L*-Trp$^+$)·$HgCl_3^-$ with 2.41(2) Å O···O distance [27] and (*L*-Pro···*L*-Pro$^+$)·NO_3^- with 2.414(3) Å O···O distance [28]. However, for (*L*-Trp···*L*-Trp$^+$)·$HgCl_3^-$ the measurement accuracy is low. 2*L*-Ala·HCl and 2*L*-Ala·HBr are isotypic, while 2*L*-Ala·HI has different structure. In spite of this, the crystal structures consist of similar structure moieties.

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Table 1. Types of conformations of *L*-alanine *L*-alaninium dimeric cations in the structures of known salts and torsion angles (in °) for specification.

	<O*CCN ψ^1(*L*-AlaH)	<OCO$_H$O	<CO$_H$OC	<O$_H$OCO	<O*CCN ψ^1(*L*-Ala)	Ref.
type-A						
(*L*-Ala···*L*-AlaH)NO$_3$	156	–12	173	168	159	[5]
type-B						
(*L*-Ala···*L*-AlaH)H$_2$PO$_3$·H$_2$O	168	–3	–154	–11	164	[11]
(*L*-Ala···*L*-AlaH)I$_3$	–171	4	162	0	–179	[14]
	–166	0	170	1	166	
type-C						
(*L*-Ala···*L*-AlaH)Cl	–179	–2	78	–6	178	this work
	–176	4	75	–9	173	
(*L*-Ala···*L*-AlaH)Br	–178	–3	91	–9	175	this work
	–177	0	87	–10	174	
(*L*-Ala···*L*-AlaH)I	177	–6	106	–11	175	this work
	–179	–3	100	–10	172	
(*D*-Ala···*D*-AlaH)Br **	–179	–2	87	–9	176	[15]
type-D						
(*L*-Ala···*L*-AlaH)picrate·H$_2$O	178	–4	–126	–28	–16	[17]
L-AlaH·(*L*-Ala···*L*-AlaH)SiF$_6$·H$_2$O	–177	12.8	–160	31	–20	[18]

* taken oxygen atom which forms dimeric O–H···O hydrogen bond.

** there are given inverted values of *D*-alanine to be easy comparable with *L*-alanine samples.

Table 2. Crystal data and details of the refinement for *L*-alanine *L*-alaninium chloride (**I**), *L*-alanine *L*-alaninium bromide (**II**), *D*-alanine *D*-alaninium bromide [15] and *L*-alanine *L*-alaninium iodide (**III**).

	(**I**)	(**II**)	[15]	(**III**)
Formula	$C_3H_7NO_2\cdot C_3H_8NO_2\cdot Cl$	$C_3H_7NO_2\cdot C_3H_8NO_2\cdot Br$	$C_3H_7NO_2\cdot C_3H_8NO_2\cdot Br$	$C_3H_7NO_2\cdot C_3H_8NO_2\cdot I$
M_r	214.65	259.11	259.11	306.10
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$	$P2_1$
a (Å)	5.0763(10)	5.1817(10)	9.485(4)	11.6812(4)
b (Å)	19.268(4)	18.821(4)	5.1678(6)	5.2997(2)
c (Å)	10.909(2)	11.173(2)	11.258(2)	19.4133(6)
α(°)	90.00	90.00	90.00	90.00
β(°)	90.43(3)	90.235(1)	92.97(3)	103.369(2)
γ(°)	90.00	90.00	90.00	90.00
V(Å^3), Z	1067.0(4), 4	1089.6(4), 4	551.087, 2	1169.25(7), 4
D_{calc}(gcm^{-3})	1.336	1.579	1.561	1.739
μ(Mo K_α) (cm^{-1})	0.347	3.762		2.729
F(000)	456	528		600
T(K)	200(2)	200(2)	299	200(2)
hkl range	-7/7, -29/28, -16/16	-7/7, -26/26, -14/15		-17/17, -8/8, -29/29
Reflections measured	14543	14672		42047
Reflections unique	7676	5284		8835
Data with ($F_o > 4\sigma(F_o)$)	6420	3329		7544
R_{int}	0.0272	0.0709		0.0322
Parameters refined	249	251		250
Flack parameter [21]	-0.004(16)	0.038(11)		0.001(10)
$R(F)$* (for $F_o > 4\sigma(F_o)$)	0.0338	0.0524		0.0327
$wR(F^2)$* (all reflections)	0.0481	0.0996		0.0412
Weighting parameters a / b	0.035 / 0.104	0.025 / 0.000		0.013 / 1.237
$\Delta\rho_{fin}$ (max/min) [e Å^{-3}]	0.235 / -0.198	1.058 / -1.047		1.077 / -1.675
CCDC no.	1556749	1556750	629449	1556751

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

Table 3. Hydrogen bonds parameters for *L*-alanine *L*-alaninium chloride (in Å and °).

D–H···A	D–H	H···A	D···A	<DHA
O1B–H1B···O1A^{i}	1.03(3)	1.40(3)	2.421(2)	170(3)
O1D–H1D···O1C	1.07(3)	1.37(3)	2.423(2)	165(3)
N1A–H11A···O2C	0.91	1.90	2.779(2)	162
N1A–H12A···Cl1^{ii}	0.91	2.38	3.2793(19)	170
N1A–H13A···Cl1^{iii}	0.91	2.48	3.3678(18)	167
N1B–H11B···Cl2	0.91	2.36	3.2662(18)	174
N1B–H12B···Cl1^{iv}	0.91	2.39	3.2776(19)	165
N1B–H13B···Cl1	0.91	2.34	3.248(2)	177
N1C–H11C···O2A^{i}	0.91	1.91	2.778(2)	160
N1C–H12C···Cl2^{i}	0.91	2.35	3.254(2)	172
N1C–H13C···Cl2	0.91	2.48	3.378(2)	168
N1D–H11D···Cl1^{iii}	0.91	2.34	3.2500(18)	177
N1D–H12D···Cl2^{iii}	0.91	2.38	3.2664(19)	164

N1D–H13DC···Cl2^{ii}	0.91	2.33	3.240(2)	173

Symmetry codes: (i) x–1, y, z; (ii) x, y, z+1; (iii) x+1, y, z+1; (iv) x+1, y, z.

Table 4. Hydrogen bonds parameters for *L*-alanine *L*-alaninium bromide (in Å and °).

D–H···A	D–H	H···A	D···A	<DHA
O1B–H1B···O1A^{i}	0.89(3)	1.63(6)	2.437(10)	149(9)
O1D–H1D···O1C	0.90(3)	1.66(7)	2.413(8)	139(9)
N1A–H11A···O2C	0.91	1.89	2.765(9)	161
N1A–H12A···Br1^{ii}	0.91	2.48	3.388(9)	175
N1A–H13A···Br1^{iii}	0.91	2.61	3.491(8)	162
N1B–H11B···Br2	0.91	2.52	3.419(7)	168
N1B–H12B···Br1^{iv}	0.91	2.54	3.314(8)	160
N1B–H13B···Br1	0.91	2.49	3.397(6)	176
N1C–H11C···O2A^{i}	0.91	1.91	2.786(9)	154
N1C–H12C···Br2^{i}	0.91	2.50	3.396(6)	167
N1C–H13C···Br2	0.91	2.58	3.484(8)	170
N1D–H11D···Br1^{iii}	0.91	2.48	3.388(7)	173
N1D–H12D···Br2^{iii}	0.91	2.53	3.411(6)	165
N1D–H13DC···Br2^{ii}	0.91	2.48	3.390(8)	174

Symmetry codes: (i) x–1, y, z; (ii) x, y, z+1; (iii) x+1, y, z+1; (iv) x+1, y, z.

Table 5. Hydrogen bonds parameters for *L*-alanine *L*-alaninium iodide (in Å and °).

D–H···A	D–H	H···A	D···A	<DHA
O1A–H1A···O1B^{i}	1.11(6)	1.54(6)	2.421(5)	131(4)
O1D–H1D···O1C	1.05(10)	1.49(9)	2.442(5)	148(6)
N1A–H11A···O2C	0.91	1.89	2.753(4)	157
N1A–H12A···I1^{ii}	0.91	2.71	3.611(6)	169
N1A–H13A···I1	0.91	2.76	3.658(6)	168
N1B–H11B···I2	0.91	2.74	3.620(3)	162
N1B–H12B···I1^{iii}	0.91	2.80	3.628(6)	152
N1B–H13B···I1^{iv}	0.91	2.70	3.605(6)	172
N1C–H11C···O2A^{ii}	0.91	1.96	2.764(5)	147
N1C–H12C···I1^{ii}	0.91	2.77	3.623(5)	157
N1C–H13C···I1	0.91	2.75	3.664(6)	177
N1D–H11D···I1	0.91	2.76	3.641(3)	163
N1D–H12D···I2^{v}	0.91	2.78	3.630(5)	155
N1D–H13D···I2^{vi}	0.91	2.70	3.609(6)	175

Symmetry codes: (i) x, y–1, z; (ii) x, y+1, z; (iii) x+1, y, z; (iv) x+1, y+1, z; (v) x–1, y–1, z; (vi) x–1, y, z

Table 6. Wavenumbers (in cm^{-1}) and assignment of peaks in IR and Raman spectra of *L*-alanine *L*-alaninium chloride (**I**), *L*-alanine *L*-alaninium bromide (**II**), *L*-alanine *L*-alaninium iodide (**III**)

I		**II**		**III**		Assignment
IR	Raman	IR	Raman	IR	Raman	
3062;3030	3094;3019;3	3071;3025	3097;3013;3	3072	3096	ν(NH) NH_3^+

	009;2999		002			
2969	2984;2971;2944;2885	2969;	2985;2971;2943;2884	2970;2938	3010;2988;2971;2939	ν(CH) CH, CH_3
2926		2913		2902	2917;2883	ν(NH) NH_3^+
	2732		2729		2730	ν(OH) COOH
2695;2605;2474		2686;2589;2460		2683;2573;2469		Combi
1980	1978	1940	1947	1866	1885	Combi
1673	1681	1667	1676	1666	1670	ν(C=O) and $\nu_{as}(COO^-)$
1593;1581	1597	1596;1575	1606;1577	1595;1569	1570	$\delta_{as}(NH_3^+)$
1504		1494				
1483	1486sh	1474		1489		$\delta_s(NH_3^+)$
1464;1409	1460;1416	1409	1458;1418	1466;1414	1456	$\delta_{as}(CH_3)$
1371	1375	1369	1374	1366	1372	$\delta_s(CH_3)$
1341	1347	1339	1343	1338	1343	
1307	1307	1303	1306		1302	δ(CH)
		1256		1252		$\rho(CH_3)$
1211	1214	1208	1204	1201	1202	δ(COH)
1129;1113	1136;1116	1121;1111	1127;1113	1108	1110	$\rho(NH_3^+)$
1001	997	995	993	990	988	
948		942		947		
	919		918		916	
855		852		851		
828	834	826	834	819	834	ν(CN)
768;758	762	768;757	761	768;754	759	
612;600	616	612;593	619	615;583	620;589sh	δ(COO)
					569	
508		506		502;483		
429	423	425	416	419	411	
	406		404			
	377;336;195		361;327;198		356sh;322	

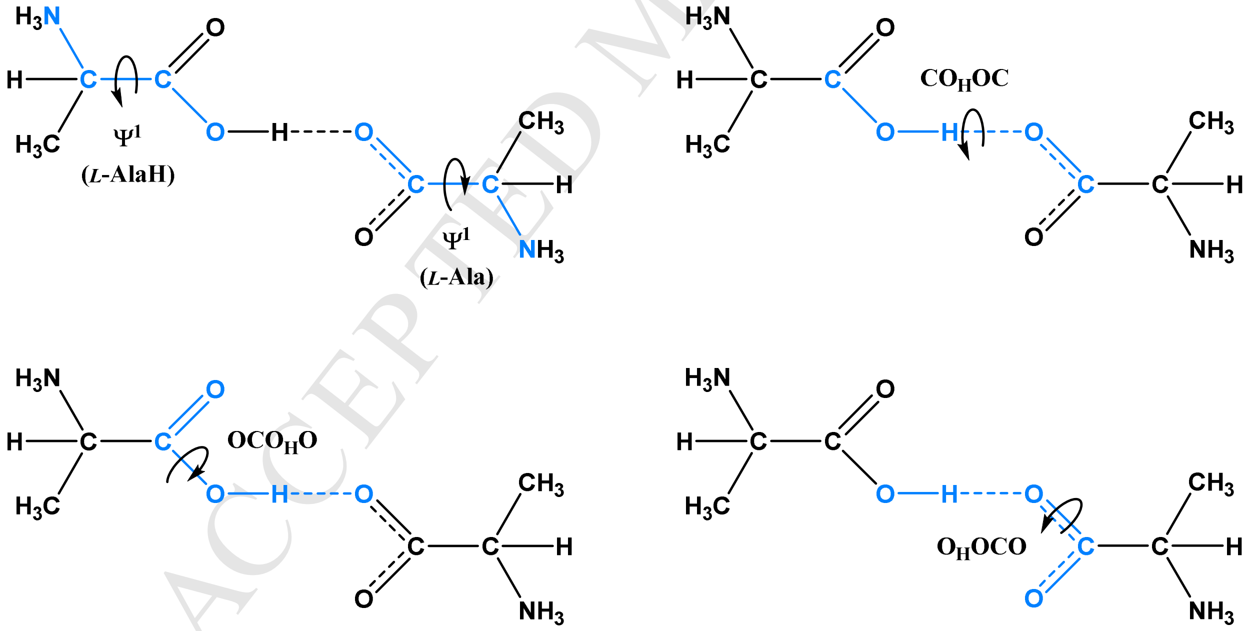
combi-combination, overtone, sh-shoulder, s-symmetric, as-asymmetric, ν-stretching, δ-deformation, ρ-rocking.

Table 7. Wavenumbers (in cm^{-1}) and assignment of peaks in IR and Raman spectra of *L*-alaninium chloride (**IV**), *L*-alaninium bromide (**V**) and *L*-alaninium iodide (**VI**).

IV		**V**		**VI**		Assignment
IR	Raman	IR	Raman	IR	Raman	
3213sh;3199;3166	3202;3163	3202;3156;2971;2912		3143;3109;3039;2994	3117;3050;3031;3024;3011;3000	ν(NH) NH_3^+
2963;2915;2888	3016;2991;2964;2951;2928;2917sh;2898		3017;2993;2963;2948;2897		2950;2945;2932;2896	ν(CH) CH, CH_3
2838	2840		2927;2917	2918		ν(NH) NH_3^+
2801			2793			ν(OH) COOH
2717;2792;2648;2627;2580;2538;2496;2465	2746;2720;2697;2658;2626;2581;2542;2504;2467	2701;2609;2567;2523;2483;2452	2746;2612;2571	2688;2597;2561;1546;2471;2456;2398	2758	Combi
1968	1973	1933	1933	1903		Combi
		1734sh	1738sh			Combi
1718	1724	1719	1725	1728;1716	1740;1719	ν(C=O)
1606;1582	1584	1600;1574	1600;1576	1584;1572	1589;1574;1555	$\delta_{as}(NH_3^+)$
1530		1519				
1493	1495	1485	1485	1484	1481	$\delta_s(NH_3^+)$

1469;1418	1471;1458;1432;1424	1466;1413	1457;1419	1461sh;1455;1406	1455;1412	$\delta_{as}(CH_3)$
1382	1385	1381	1385	1383	1388	$\delta_s(CH_3)$
1349	1352	1344	1347	1335	1335	
1316	1316	1309	1311	1298;1289	1316	δ(CH)
				1254		$\rho(CH_3)$
1234	1240	1222	1229	1210	1215	δ(COH)
1197	1199	1193	1196	1185	1194	$\rho(CH_3)$
1139;1114	1143;1118	1128;1112	1132;1116	1108	1121;1111;1091	$\rho(NH_3^+)$
1008	1010	1001	1004	993	996	
976	981	971	976	976	977	
	955					
919	921	916	919	913	915;894;872;861;849	
846	848					
813	816	817	818	806	810	ν(CN)
		792	798		789	
770				765	774	
738	740	731	734	698	712;695	
613	615	609	611	609	614	δ(COO)
520	522	515	518		516	
	402		396;361		308;379	
	338;277;179		331;274;206		321;280	

combi-combination, overtone, sh-shoulder, s-symmetric, as-asymmetric, ν-stretching, δ-deformation, ρ-rocking.



Scheme 1. Illustration of selected torsion angles in *L*-alanine *L*-alaninium dimer.

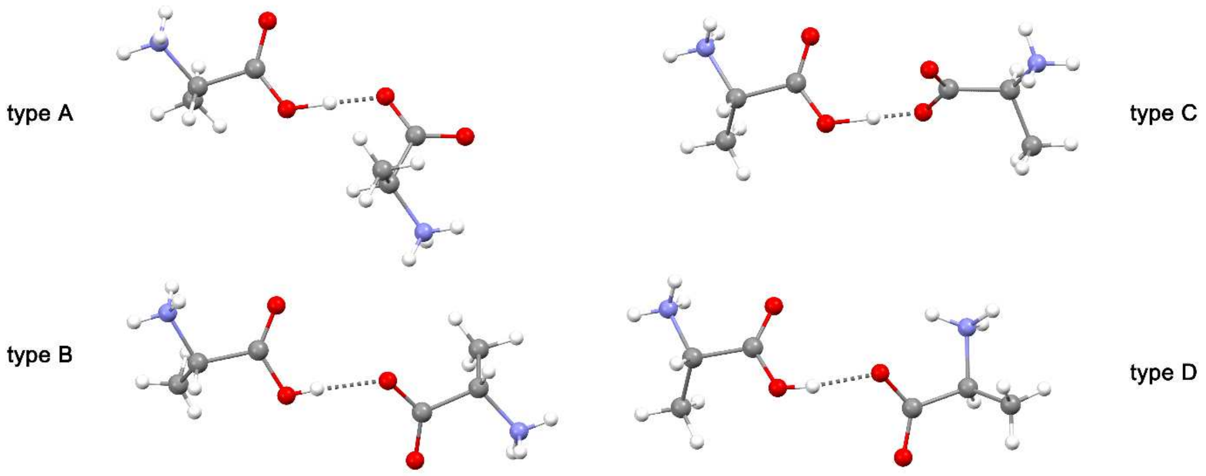
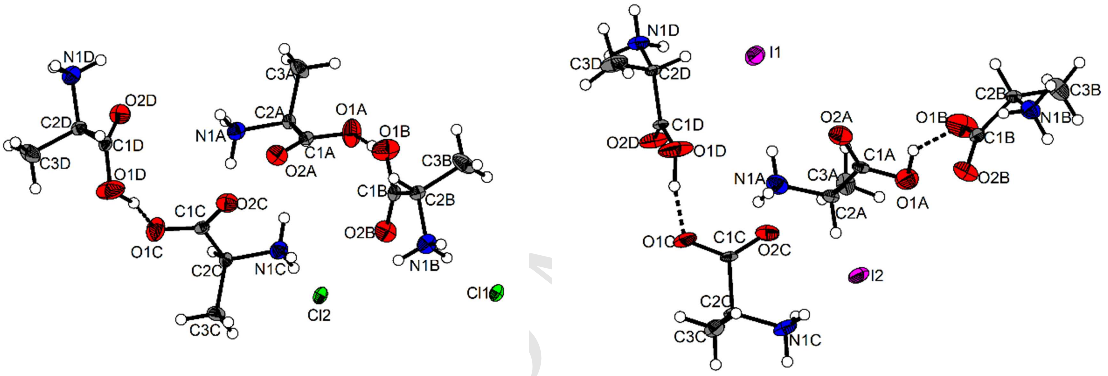


Fig. 1. *L*-alanine *L*-alaninium dimer types in the structures of known salts.



(a) **(b)**

Fig. 2. Asymmetric unit of *L*-alanine *L*-alaninium chloride (a) (note, that *L*-alanine *L*-alaninium bromide is isotypic) and *L*-alanine *L*-alaninium iodide (b).

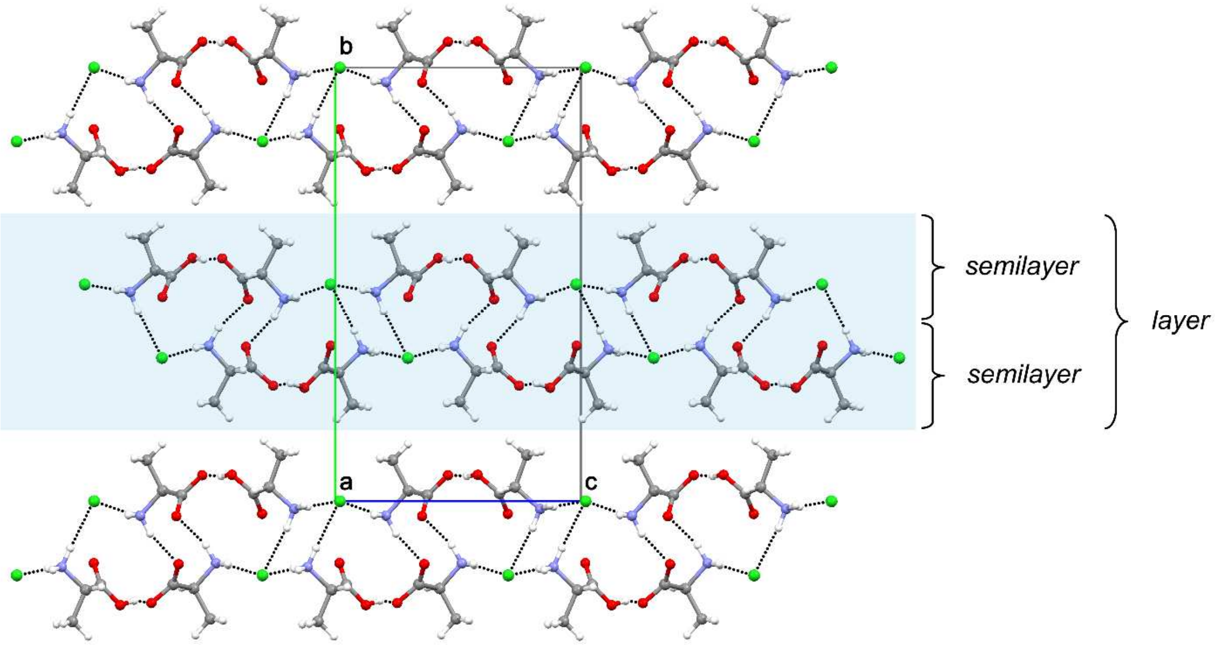


Fig. 3. Packing diagram of *L*-alanine *L*-alaninium chloride, viewed along [100].

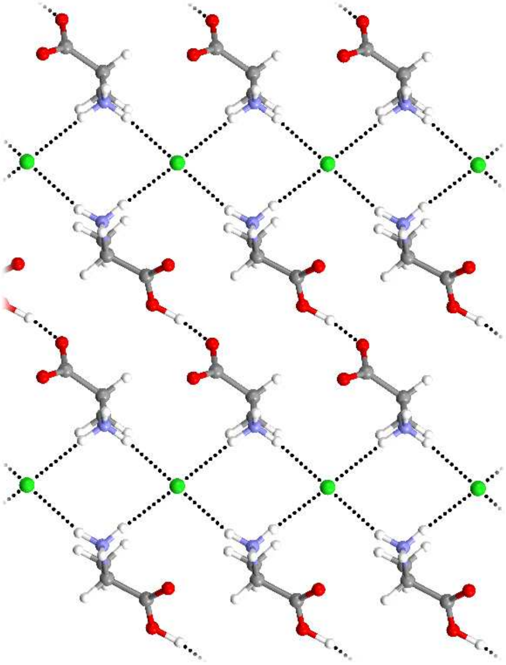
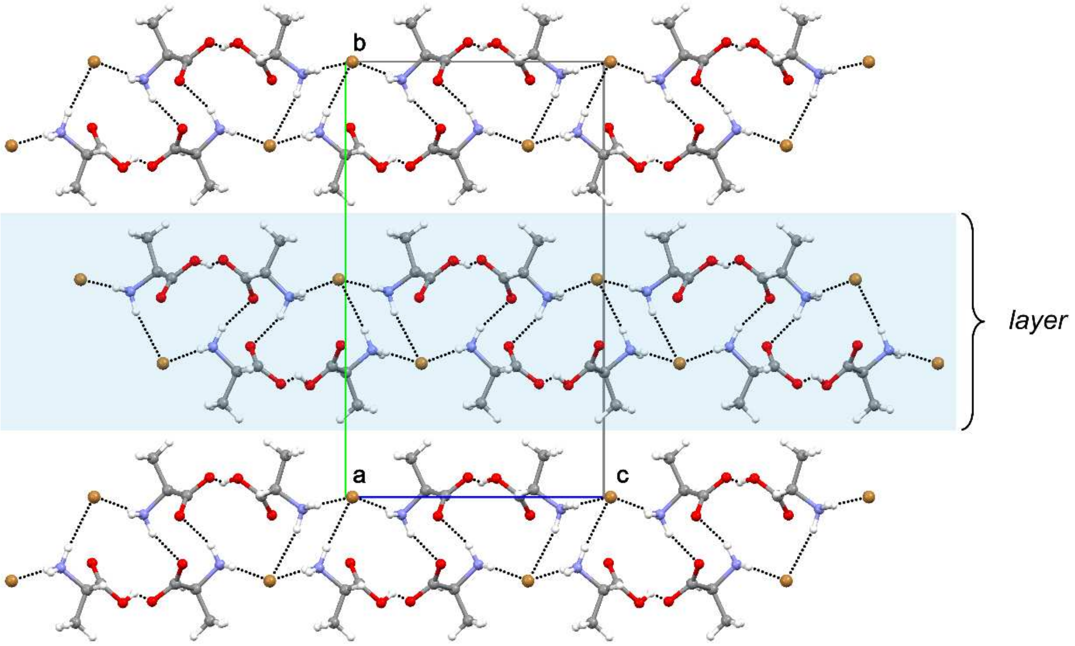
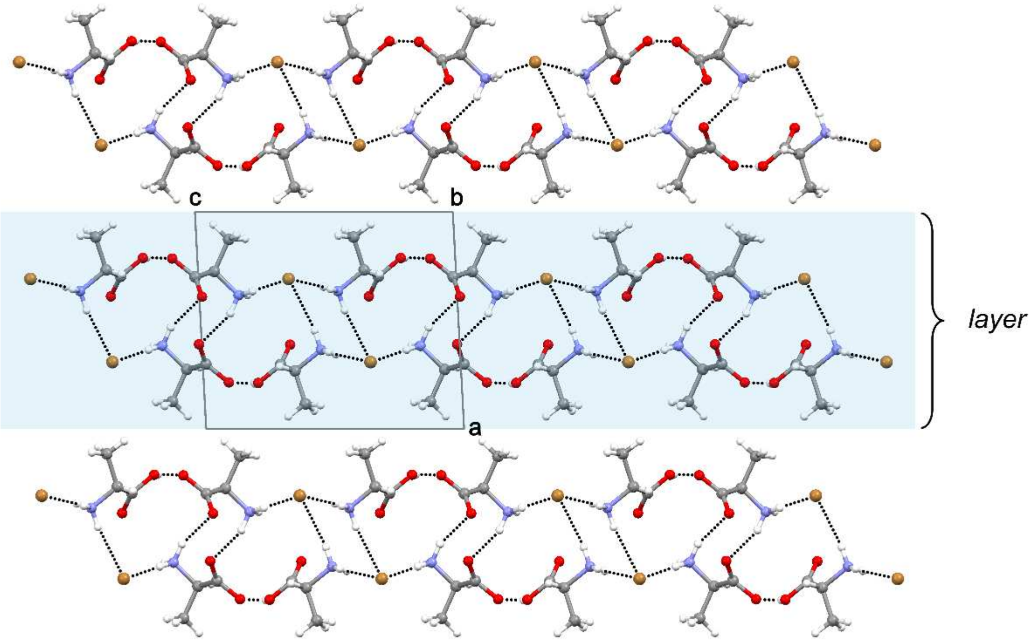


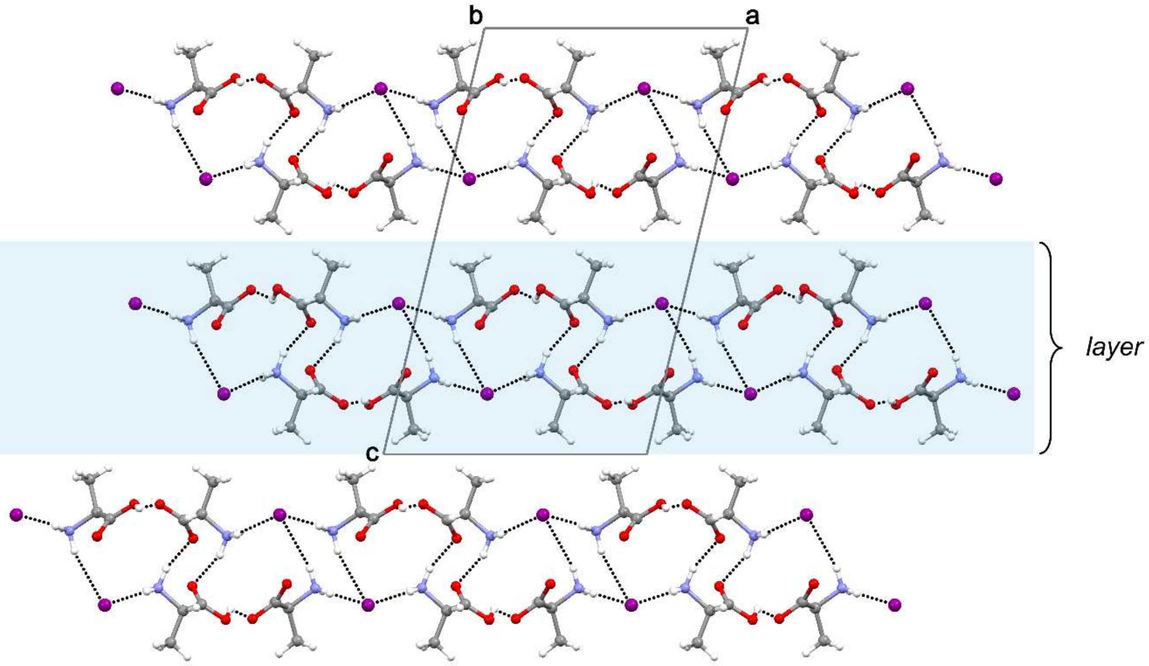
Fig. 4. H-bond network in semilayer of *L*-alanine *L*-alaninium chloride, viewed along [010].



L-alanine *L*-alaninium bromide



D-alanine *D*-alaninium bromide



L-alanine *L*-alaninium iodide

Fig. 5. Packing diagrams of *L*-alanine *L*-alaninium bromide, *D*-alanine *D*-alaninium bromide and *L*-alanine *L*-alaninium iodide. It is easy to see, that colored layers are similar.

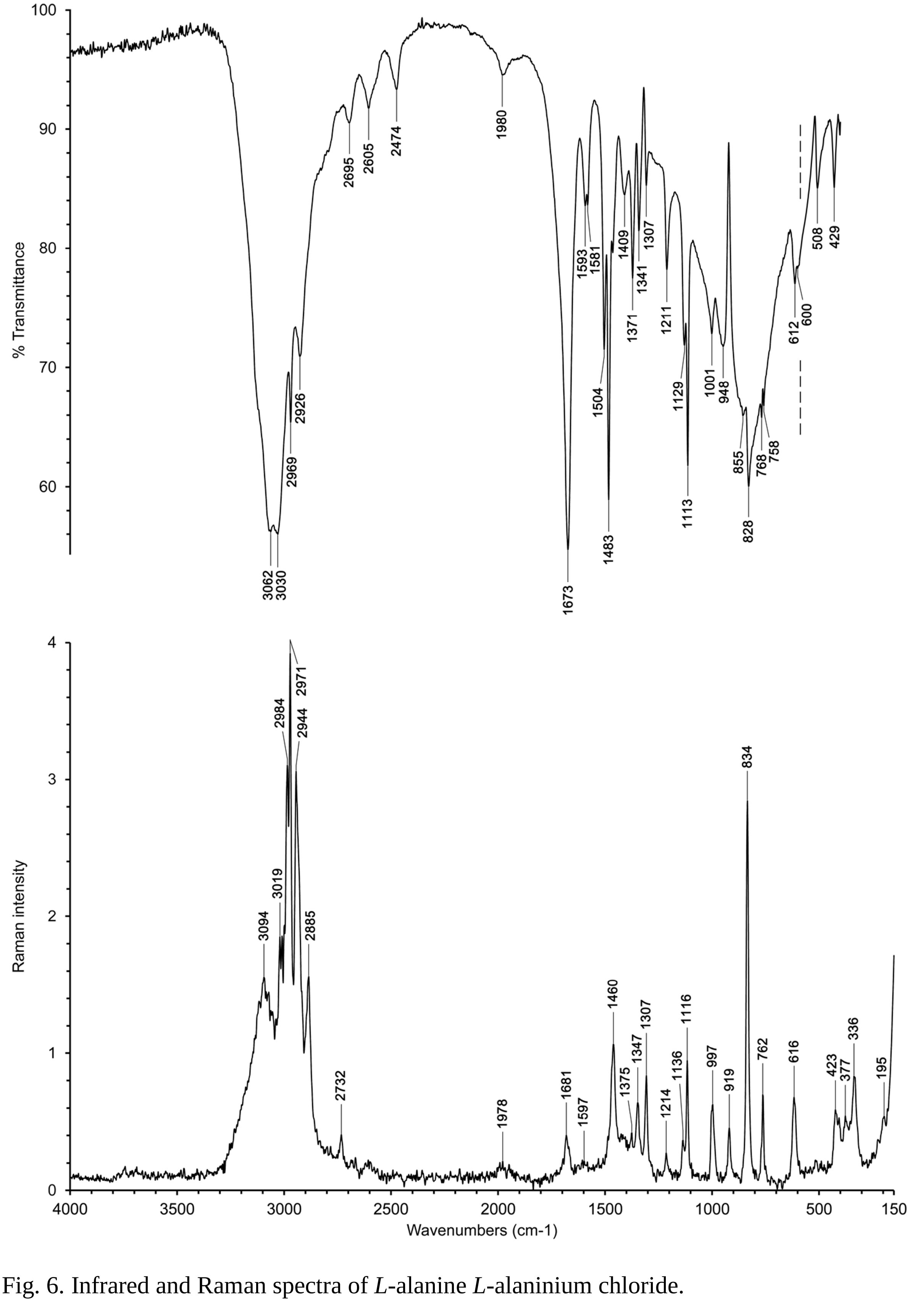


Fig. 6. Infrared and Raman spectra of *L*-alanine *L*-alaninium chloride.

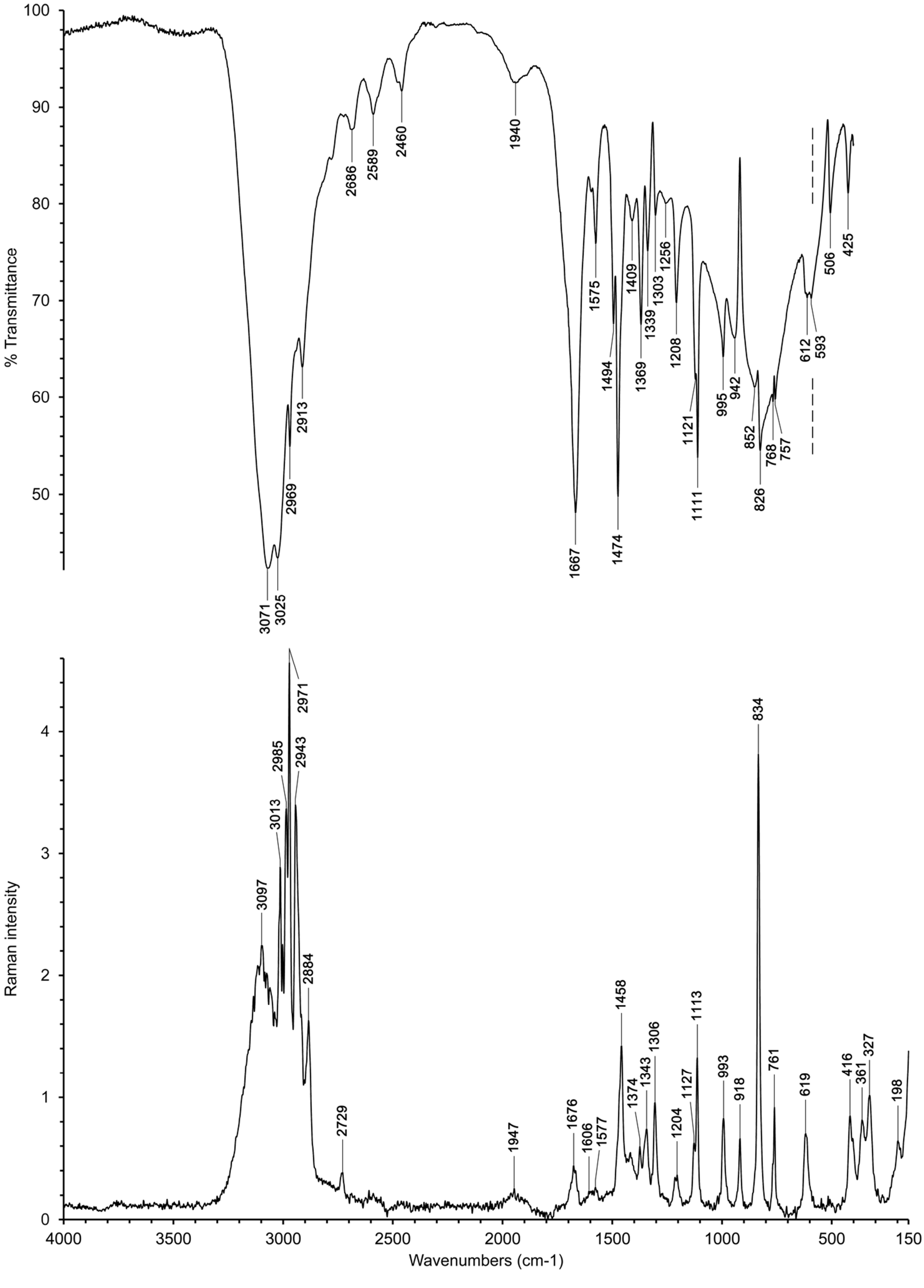


Fig. 7. Infrared and Raman spectra of *L*-alanine *L*-alaninium bromide.

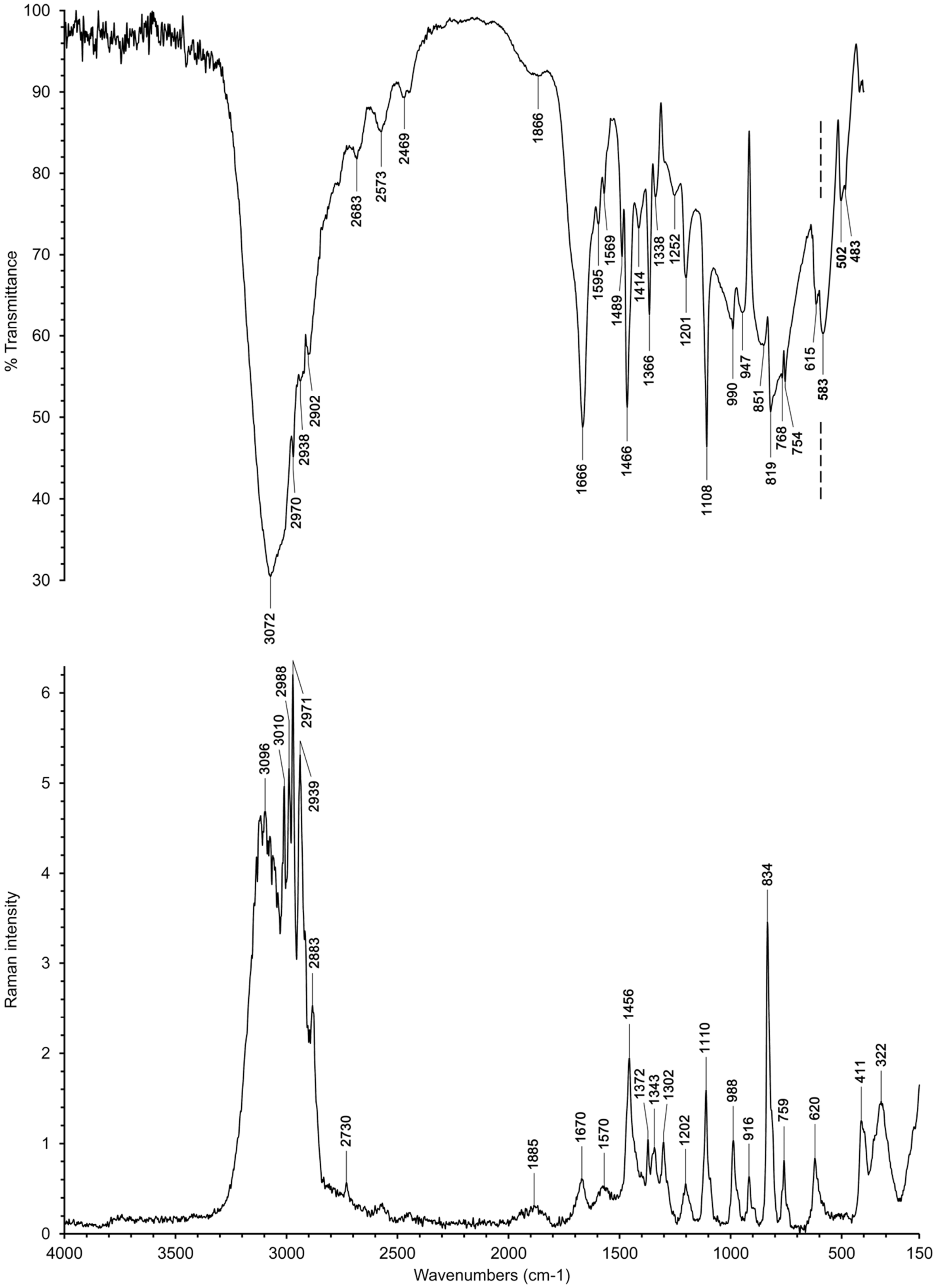


Fig. 8. Infrared and Raman spectra of *L*-alanine *L*-alaninium iodide.

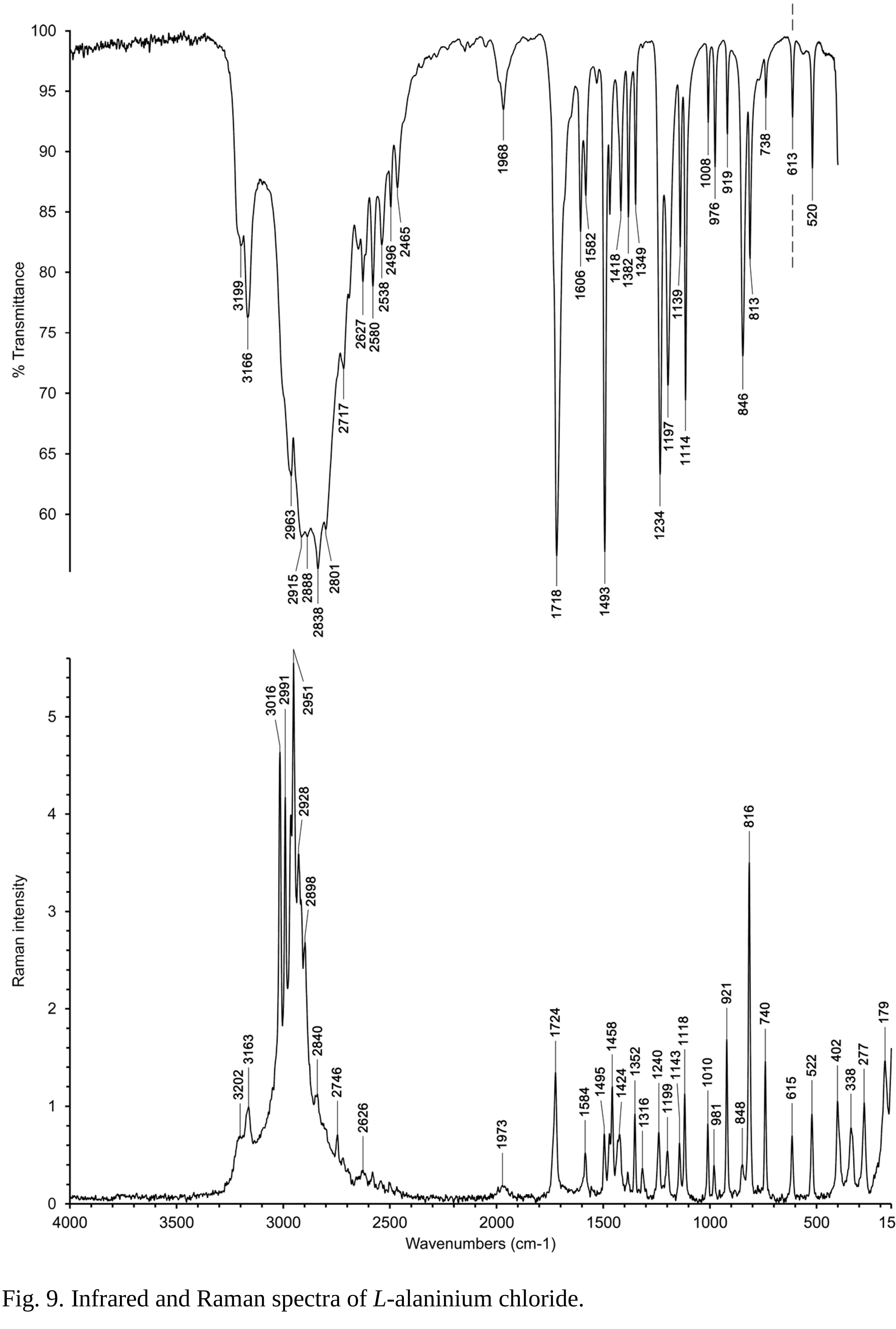


Fig. 9. Infrared and Raman spectra of *L*-alaninium chloride.

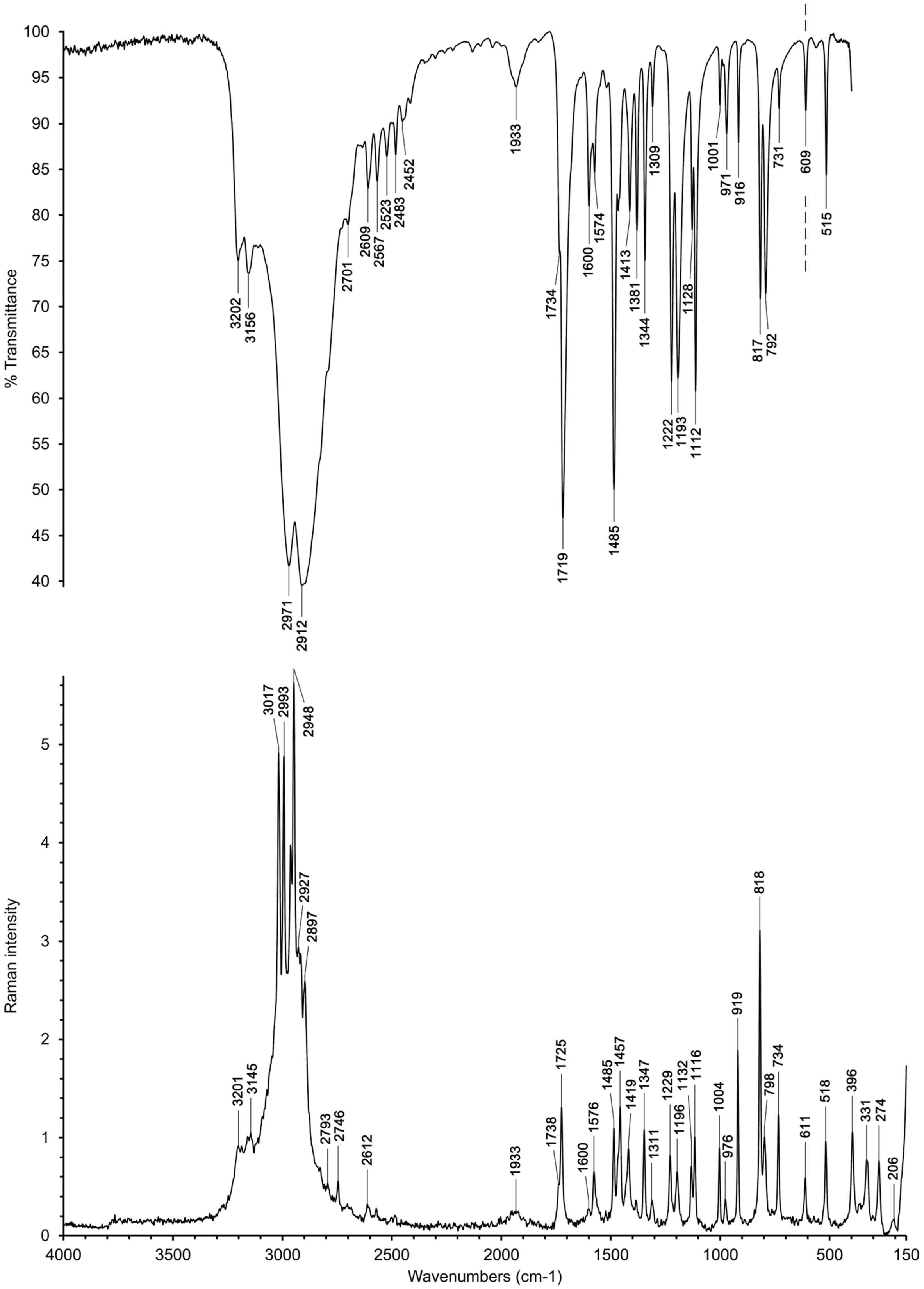


Fig. 10. Infrared and Raman spectra of *L*-alaninium bromide.

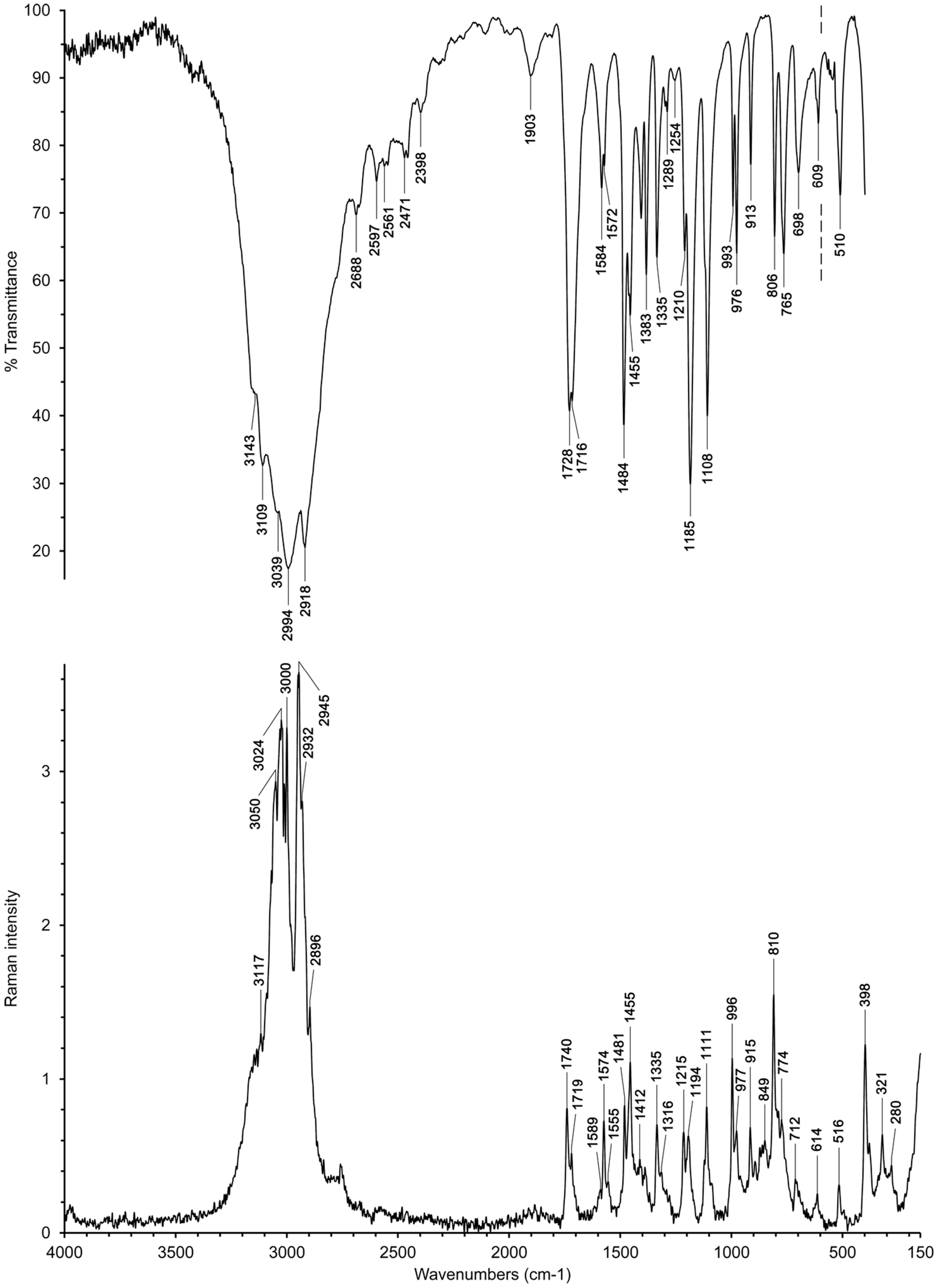


Fig. 11. Infrared and Raman spectra of *L*-alaninium iodide.

Highlights

Dimeric *L*-alanine *L*-alaninium cations are formed via short O-H···O hydrogen bonds

There are four known types of *L*-alanine *L*-alaninium dimeric cations

Three halogenides of *L*-alanine with dimeric cation are presented