

IR Vibration and Characterization of All L–Arginine Chlorides

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Abstract. The reaction of L–arginine with hydrochloric acid (HCl) in water solvent at 0–33°C temperature was investigated in detail in this study. In total, five compounds were successfully obtained and identified, of which L–Arg·HCl (P1), L–Arg·HCl (P2₁), L–Arg·HCl·H₂O (P2₁), L–Arg·2HCl·H₂O (P2₁2₁2₁) were known, and L–Arg·2HCl (new) crystal was a novel finding in this study. The conditions for the formation of all compounds were described in this study. Moreover, we present and compare the FT–IR ATR spectra and other properties of all obtained crystals from the L–Arg+HCl+H₂O and L–Arg+HBr+H₂O systems. The novel compound L–Arg·2HCl (new) compound contains two double–charged crystallographically independent argininium (L–Arg²⁺) cations and four chloride ions in a unit cell.

Keywords: L–arginine halides, chloride, dichloride, bromide, dibromide, IR spectra

1. Introduction

The salts of optically active L–amino acids, in particularly L–arginine, crystallize in enantiomorphous space groups P2₁2₁2₁, P2₁, P1 and very rarely in others. These space groups being acentric allow displaying nonlinear optical (NLO) and piezoelectric properties, while polar P2₁ and P1 groups, also pyroelectric effect. Search and investigation of L–arginine (L–Arg) salts is interesting both with respect to discovering crystals with above–mentioned properties and to investigating structural features and formation mechanisms. The systematic investigations of L–arginine salts as objects related to proteins began from the study of halides at the beginning of the sixties. Mazumder and Srinivasan [1] investigated the structures of L–Arg·HCl (P2₁), L–Arg·HCl·H₂O (P2₁), L–Arg·HBr·H₂O (P2₁) with space group P2₁ and showed that the last two are isomorphous. L–Arg·HCl (P2₁) as promising NLO materials were recognized by Davydov et al. [2]. The authors [3] obtained another L–Arg·HCl (P1) compound and determined a crystal structure having a triclinic structure. Later on, issues of growth and study of various properties of halides of single charged L–arginine cation were elucidated in [4–14]. The crystals of L–Arg·HCl·H₂O (P2₁), L–Arg·HBr·H₂O (P2₁) were studied by IR spectroscopy [5–9]. FT–IR ATR spectrum of L–Arg·HCl·H₂O (P2₁) was presented in [5, 6]. It is not however clear from [7] that the spectrum of L–Arg·HCl·H₂O (P2₁) or the spectrum of L–Arg·HCl (P2₁) is given. FT–IR ATR spectrum of L–Arg·HBr·H₂O (P2₁) was presented in [8]. The authors [9] claim to have studied the L–Arg·HBr crystal, but all data, including the FT–IR ATR spectrum, are consistent with the L–Arg·HBr·H₂O (P2₁) crystal data. The spectrum of L–Arg·HCl (P1) crystal was not described in the literature. The authors [15–17] discovered a whole class of salts with a double charged L–Arg²⁺ arginine cation, including halides. The structure of crystalline salts of L–Arg²⁺ cation has essential distinctions from the structure of crystals with L–Arg⁺ cation, which may

manifest also in physical properties. In [15] presented IR spectra of L-Arg·2HBr·H₂O (P1) and L-Arg·2HCl·H₂O (P₂₁2₁2₁) compounds registered with nujol. In [17] study was the determination of crystal structures of L-Arg·2HBr·H₂O (P1) and L-Arg·2HCl·H₂O (P₂₁2₁2₁), and comparison with each other halides. Crystal L-Arg·2HBr·H₂O (P1) has good pyroelectric properties, the parameter of which ($\gamma/\varepsilon=6.8 \mu\text{Cm}^{-2}\text{K}^{-1}$) is comparable to the parameter of the known TGS crystal ($\gamma/\varepsilon=11 \mu\text{Cm}^{-2}\text{K}^{-1}$). However, the temperature dependence of the pyroelectric coefficient allows the L-Arg·2HBr·H₂O (P1) crystal to be used over a wider temperature range (up to 345 K) compared to the TGS crystal (up to 322 K) [17]. L-Arg·2HCl·H₂O (P₂₁2₁2₁) crystal does not have good pyroelectric properties like L-Arg·2HBr·H₂O (P1) because they are not isostructural.

It is known that salts of L-arginine can exist in various polymorphic modifications. We assume that their isostructural types also exist. Although L-arginine halides (HBr, HCl) have been thoroughly studied by a number of researchers, so far there has been no report of obtaining L-Arg·2HCl·H₂O (P1) crystal to isostructure L-Arg·2HBr·H₂O (P1), or their anhydrous types. Therefore, in this paper, we have investigated L-Arg+HCl+H₂O system in detail in order to obtain the crystals above.

2. Experimental part

As initial reagents we used L-arginine (L-Arg, 98%) purchased from “Sigma” and hydrochloric acid (HCl) “VWR Chemicals”, analytical reagent), which is 37%, $\rho=1,18 \text{ g/cm}^3$ solution. We investigated in more detail the reaction of L-arginine with hydrochloric acid (HCl) in water media at 0–33°C temperature. The main difficulty in crystallization of L-Arginine chlorides is connected to very high solubility in water. For this reason, the solutions were placed in a silica gel with a closed vessel at 0–4°C temperature. 66 (33×2) solutions were prepared in L-Arg:mHCl molar ratio, where $m=1\div 9$ and changes by 0.25 steps. The materials were weighed on a “KERN ADJ 200–4” scale with an accuracy of 0.0001. The pH of the solutions was determined by “pH–673M” and “HI 2211” pH-meters. Attenuated total reflection Fourier transform infrared (FT–IR ATR) spectra were registered using “Perkin–Elmer Spectrum Two FT–IR” spectrometer with ZnSe prism (4000–450 cm^{-1} , single reflection accessory, ATR distortion is corrected, number of scans: 32, resolution: 4 cm^{-1}). For the study of thermal properties, we used a “Boëtius” type microscope with the heating stage (with 20°C up to 350°C intervals).

3. Results and discussion

3.1 Conditions for obtaining compounds

The crystals L-Arg·HCl (P1), L-Arg·HCl (P₂₁) and L-Arg·HCl·H₂O (P₂₁) are formed from aqueous solutions at a temperature of 0–33°C in the molar ratio L-Arg:mHCl, where $m = 1\div 1.25$, which corresponds to the $\text{pH} = 7.5\text{--}2.5$ (see Fig. 1). The crystal L-Arg·HCl (P₂₁) is formed from a solution in the molar ratio L-Arg:mHCl, where $m=1\div 1.2$ ($\text{pH}=7.75\div 3.5$), at a temperature of 0–4 or 20–33°C. The solutions were placed in a silica gel with a closed vessel at 0–4°C. L-Arg·HCl (P₂₁) crystals repeat their crystallization at 0–4°C and become L-Arg·HCl (P1) at 18–33°C by fast evaporation. The crystal L-Arg·HCl·H₂O (P₂₁) is formed from a solution in the molar ratio 1:1.1 at 10–30°C by slow evaporation. The authors [5] report that single crystals of L-arginine hydrochloride monohydrate were successfully grown at ambient temperature (28.5°C) from its aqueous solution ($\text{pH}=5.4$) by slow evaporation. As shown in the Fig. 1, the current study and the authors of [5] indicate the same conditions for the formation of the L-Arg·HCl·H₂O (P₂₁) crystal. The 1·1 and 1·2 crystal mixture is formed from a solution in the molar ratio L-Arg:mHCl, where $m=1.25\div 1.75$ ($\text{pH}=2.55\div 1.48$). The crystal L-Arg·2HCl·H₂O (P₂₁2₁2₁) is formed from a solution in the molar ratio L-Arg:mHCl, where $m=1.75\div 2.25$ ($\text{pH}=1.48\div 0.44$) at 10–33°C by slow evaporation. The crystal L-Arg·2HCl (new) is formed from a solution in the molar ratio L-

Arg:mHCl, where $m=2.5\div 9$, and the pH value in that range has a negative sign (see Fig. 1). The crystal L-Arg·2HCl (new) is formed at a temperature of 0–33°C by fast evaporation.

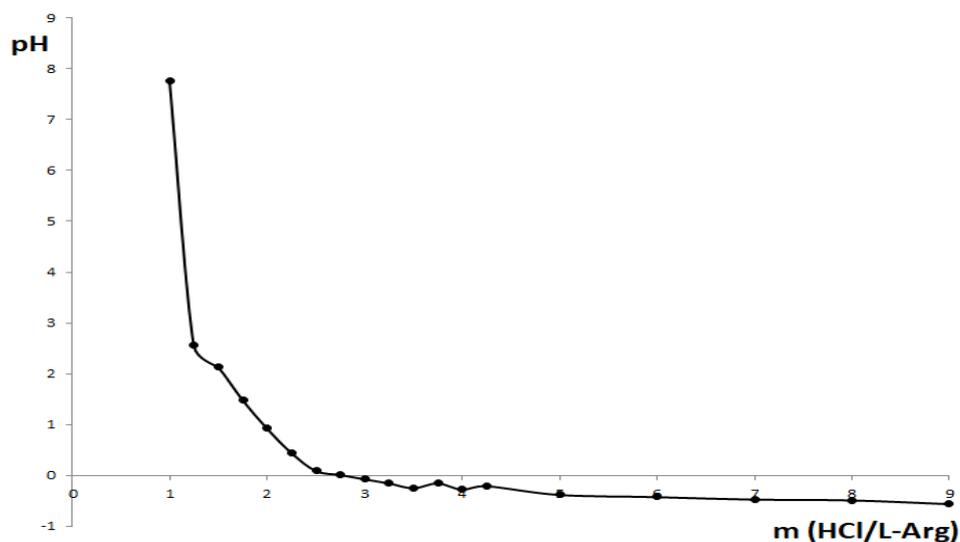


Fig. 1. The curve of pH dependence on L-Arg:mHCl molar ratio, where $m=1\div 9$, changes by 0.25 steps.

3.2 Thermal properties

In the literature, the melting point ranges from 216 to 240°C for L-Arg·HCl (P1) and L-Arg·HCl (P2₁). We have studied the thermal properties of all crystals by a “Boëtius” microscope with a heating stage.

Oddly enough, both crystals L-Arg·HCl (P2₁) and L-Arg·HCl (P1) melt with decomposition at the same temperature of 220°C. The L-Arg·HCl·H₂O (P2₁) crystal loses water at 98°C and melts at 222°C and L-Arg·2HCl·H₂O (P2₁2₁2₁) crystal melts at 65°C and loses water at 135°C. The L-Arg·2HCl (new) crystal melts at 120°C, and decomposes at 250°C.

3.3 FT-IR ATR Spectra

All compounds were registered and identified by FT-IR ATR spectra (see Fig. 2, 3). Wavenumbers (in cm^{-1}) and assignment of peaks in FT-IR ATR spectra are given in Table 1. We present and compare the FT-IR ATR spectra of all obtained crystals from the L-Arg+HCl/HBr+H₂O systems in order to clarify ambiguities in the literature. The compounds L-Arg·HCl (P1) [3] and L-Arg·HCl·H₂O (P2₁) [6] have two crystallographically independent arginium (L-Arg⁺) cations in the unit cell as found by X-ray analysis. IR spectra do not easily allow to visualize of two crystallographically independent arginium (L-Arg⁺) cations (see Fig. 2) due to the fact that the characteristic bands for (COO⁻) and for (NH₃⁺), (NH₂) groups are in the same range. But (L-Arg²⁺) cation has a typical absorption band around 1700 cm^{-1} (see Fig. 3) and in the IR spectrum of the compound L-Arg·2HCl (new) two typical absorption bands at 1731 and 1714 cm^{-1} exist (see Fig. 3c, Table 1). In the FT-IR spectra of L-Arg·2HCl·H₂O (P2₁2₁2₁) (1512 cm^{-1}) and L-Arg·2HBr·H₂O (P1) (1525 cm^{-1}) a characteristic deformation band of the NH₃⁺ group, present in all amino acids, appears at 1520 cm^{-1} . The FT-IR spectrum of L-Arg·2HCl has an absorption band with two peaks at 1530 and 1513 cm^{-1} . A detailed study of the Raman spectrum of the L-Arg·HCl·H₂O (P2₁) crystal [18] showed that the lines at about 1100 cm^{-1} belong to NH₃···O (where O belongs to the COOH groups of another molecule) and NH₃···Cl hydrogen bonds. In the IR spectrum of L-Arg·2HCl (new), the absorption band at 1280–950 cm^{-1} is very different from the spectra of other chlorides of L-arginine, which is also due to the presence of hydrogen bonds of (NH₃···O) and (NH₃···Cl) between two arginine cations and four Cl⁻ ions. The FT-IR spectrum of L-Arg·2HBr·H₂O (P1) contains an absorption band with an unusually high frequency of 3605 cm^{-1} (3607 cm^{-1} [17]), which should be assigned confidently to $\nu(\text{O-H})$

stretching vibrations of a water molecule. In the case of L-Arg·2HCl·H₂O, the absorption band of a water molecule is at 3119 cm⁻¹.

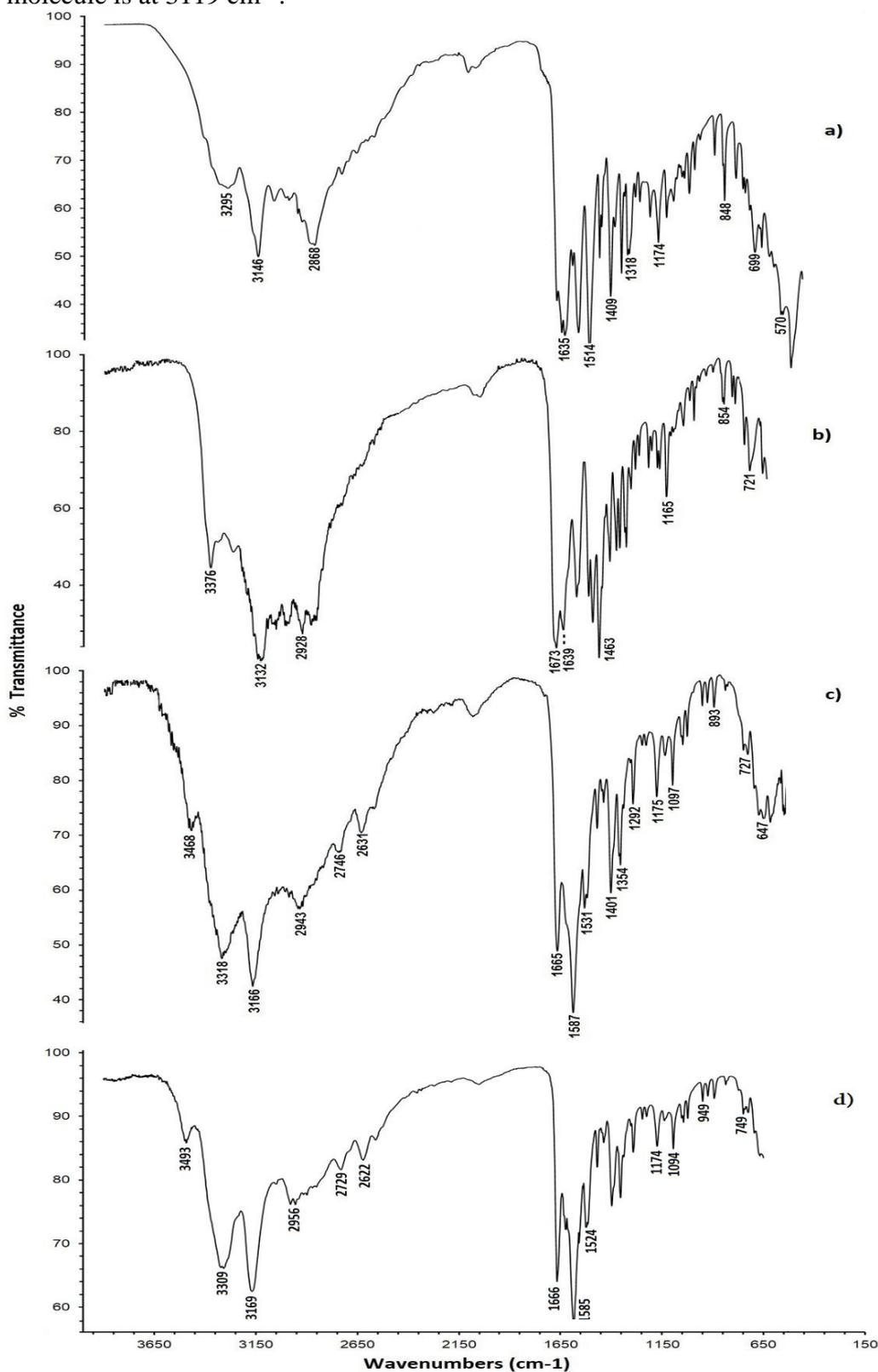


Fig. 2. FT-IR spectra of a) L-Arg-HCl (P₂₁), b) L-Arg-HCl (P₁), c) L-Arg-HCl·H₂O (P₂₁), d) L-Arg-HBr·H₂O.

There is no absorption band of the water molecule in the spectrum of FT-IR spectrum of L-Arg·2HCl (new). From FT-IR spectra discussion, we can claim the compound L-Arg·2HCl

(new) contains crystallographically independent two double-charged arginium cations and four Cl⁻ ions in the unit cell.

An X-ray study of L-Arg·HCl·H₂O (P₂₁) and L-Arg·HBr·H₂O (P₂₁) crystals showed that the crystals are isostructural [1]. We see their IR spectra are very similar, too (see Fig. 2 c, d). Unlike the L-Arg·2HCl (new) crystal, which has two doubly charged arginine cations in the unit cell.

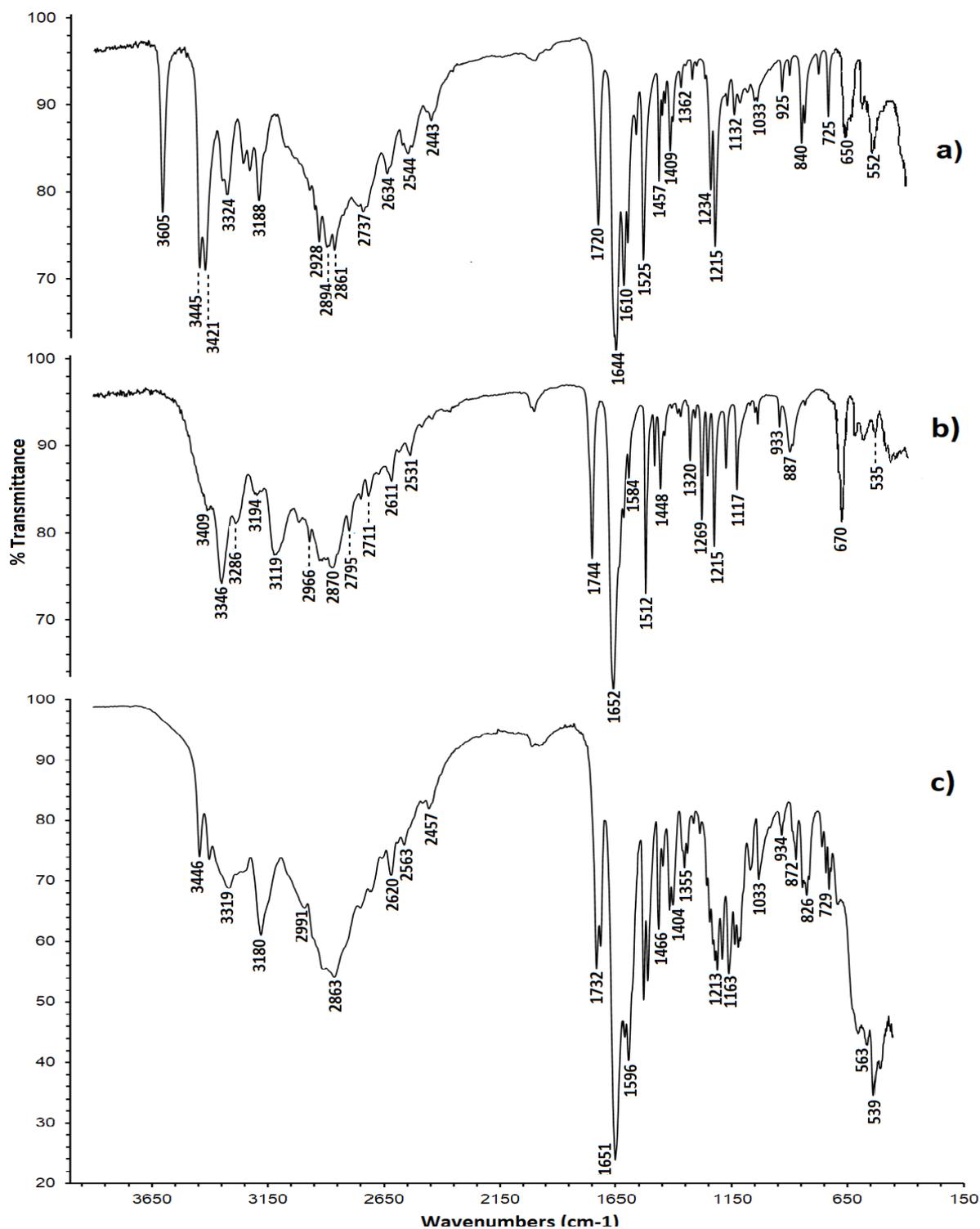


Fig. 3. FT-IR ATR spectra of a) L-Arg·2HBr·H₂O (P1), b) L-Arg·2HCl·H₂O (P₂₁2₁2₁), and c) L-Arg·2HCl (new).

Table 1. Wavenumbers (in cm⁻¹) and assignment of peaks in FT-IR ATR spectra I) L-Arg·HCl (P1), II) L-Arg·HCl (P₂₁), III) L-Arg·HCl·H₂O (P₂₁), IV) L-Arg·2HCl·H₂O (P₂₁2₁2₁) and V) L-Arg·2HCl (new) crystals.

I	II	III	IV	V	Assignment
		3318 (3328[6])	3119 (3119[17])		$\nu(\text{OH}) \text{H}_2\text{O}$
3376; 3266; 3132; 3057; 3007	3295; 3146; 3069	3468; 3166	3346; 3425; 3409; 3286; 3194; 3011	3445; 3403; 3317; 3179	$\nu(\text{NH}) \text{NH}_2$, NH_3^+
2928; 2884	2993; 2868	2943	2966; 2870;	2865	$\nu(\text{CH})$ CH , CH_2
2049	2734; 2661	2746; 2631; 2568, 2081	2795; 2744; 2711; 2611; 2579; 2531; 2481; 2436; 1994	2620; 2564; 2456; 2351; 1985	Overtones Combinational H-bond
			1744	1731; 1714	$\nu(\text{C}=\text{O})$
1673	1674	1665			$\nu_{\text{as}}(\text{COO}^-)$
1639; 1573	1635; 1567	1587	1652; 1607; 1582	1649; 1595	$\nu(\text{C}-\text{N})$ $\delta_{\text{as}}(\text{NH}_3^+)$ $\delta(\text{NH}_2)$
1514; 1494	1514	1531; 1519	1512	1530; 1513	$\delta_{\text{s}}(\text{NH}_3^+)$
1463; 1410	1464; 1454; 1409	1469; 1437; 1401	1473; 1448;	1466, 1448; 1405	(CH_2)
			1430	1416	$\nu(\text{C}-\text{O})\text{COOH}$
1378; 1361; 1329; 1306; 1284	1389; 1356; 1318; 1287	1354; 1339; 1292	1360; 1320; 1298	1354; 1316; 1288	$\omega(\text{CH}_2)$ $\tau(\text{CH}_2)$
1265; 1219; 1204; 1176; 1165; 1131; 1109; 995; 969	1265; 1215; 1174; 1134; 1099; 995; 969	1247; 1228 1175; 1134 1097; 995 951; 926	1269; 1244; 1215; 1164; 1117	1214; 1192; 1162; 1137; 1121	$\rho_{\text{r}}(\text{NH}_3^+)$ $\omega(\text{NH}_2^+)$ $\rho(\text{CH}_2)$
1047; 1016	1046; 1022	1055; 1047; 1025	1060; 1027	1070; 1035	$\nu(\text{C}-\text{N})$
			933	934	$\gamma(\text{OH}) \text{COOH}$
854; 447; 807; 792; 747; 721; 657	897; 856; 848; 791; 746; 665	893; 837; 748; 727; 647; 616	887; 822; 735; 630	877; 844; 835 825; 815; 759 742; 728; 691	$\nu(\text{C}-\text{C})$ $\gamma(\text{NH}_2)$
		672	670		$\nu_{\text{L}}(\text{H}_2\text{O})$
581; 574; 558; 543	570; 561; 521	565; 553; 548; 543	560; 480; 460	605; 567; 539; 512	$\rho(\text{NH}_2)$
ν - stretching, δ - deformation scissoring, ω - wagging, τ - twisting, ρ - rocking, γ - out-of-plane bending, ν_{L} - librational, s - symmetric, as - asymmetric					

L-Arg·2HCl·H₂O (P2₁2₁2₁) and L-Arg·2HBr·H₂O (P1) crystals each contain one doubly charged cation arginine (see Fig. 3). In contrast to appropriate isomorphous mono-halide monohydrates the crystals L-Arg·2HCl·H₂O (P2₁2₁2₁) and L-Arg·2HBr·H₂O (P1) are not isomorphous [17].

The IR spectra of L-Arg·2HCl (new) as well as L-Arg·2HCl·H₂O (P2₁2₁2₁) and L-Arg·2HBr·H₂O (P1) are also significantly different (see Fig. 3). According to the IR spectra, it can be argued that the L-Arg·2HCl (new) crystal is also not isostructural for the L-Arg·2HCl·H₂O (P2₁2₁2₁) and L-Arg·2HBr·H₂O (P1) crystals. The difference in the IR spectra shows that the crystals differ from each other in the interaction of cations, anions, and a water molecule.

3. Conclusions

Five compounds were obtained and identified from the L-Arg + HCl + aq system. We have succeeded in obtaining an anhydrous type of L-arginine dihydrochloride. We have shown that the number of cations in a unit cell is two for L-Arg·2HCl (new) crystal, which is same for L-Arg·HCl (P1), L-Arg·HCl·H₂O (P₂₁) and crystals. The crystals {L-Arg·HCl (P1), L-Arg·HCl (P₂₁), L-Arg·HCl·H₂O (P₂₁), L-Arg·2HCl·H₂O (P₂₁2₁2₁), L-Arg·HBr·H₂O (P₂₁), L-Arg·2HBr·H₂O (P1) and L-Arg·2HCl (new)} were considered fully studied by spectroscopic and thermal methods and the exact conditions for obtaining crystals are indicated.

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