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# $\beta$ -Alaninium picrate: A new salt with di- $\beta$ -alaninium dimeric cation

## M. Fleck<sup>a</sup>, V.V. Ghazaryan<sup>b</sup>, A.M. Petrosyan<sup>b,\*</sup>

<sup>a</sup> Institute of Mineralogy and Crystallography, University of Vienna, Althanstr. 14, A-1090 Vienna, Austria <sup>b</sup> Institute of Applied Problems of Physics, NAS of Armenia, 25 Nersessyan Str., 0014 Yerevan, Armenia

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#### 1. Introduction

One of the topics of our current research is the family of salts of amino acids with  $A \cdots A^+$  dimeric cation with short hydrogen bonds [1–5], where A and  $A^+$  are amino acids in zwitter-ionic and singly charged state respectively. There are two types of such salts, depending on the valency of the anion, i.e.,  $(A \cdots A^+) \cdot X^-$  (this encompasses the vast majority of such salts known to date, see [4] and references therein) and  $2(A \cdots A^+) \cdot Y^{2-}$  [6,7]. In addition to said  $(A \cdots A^+)$  type dimeric cations, there are two types of salts with dimeric  $(A^+ \cdots A^+)$  type cation:  $(A^+ \cdots A^+) \cdot 2X^-$  [8–11] and  $(A^+ \cdots A^+) \cdot Y^{2-}$  [12–16]. In all these salts, the amino acid is  $\beta$ -alanine, thus  $A^+$  is the  $\beta$ -alaninium cation (an overview of these compounds with some data is given in Table 1).

It is interesting to note that  $\beta$ -alanine  $\beta$ -alaninium picrate obtained and investigated in Ref. [17] is perhaps the first example of the 2(A···A<sup>+</sup>)·2X<sup>-</sup> type salts. Vibrational spectra of this crystal have been investigated in Ref. [18]. According to the authors of Refs. [17,18] crystals of  $\beta$ -alanine  $\beta$ -alaninium picrate were obtained by evaporation from aqueous solution containing equimolar quantities of  $\beta$ -alanine and picric acid. Recently another paper was published [19], which is devoted to the growth and characterization of "novel bis  $\beta$ -alanine picrate". It does not contain quotations of previous works on  $\beta$ -alanine  $\beta$ -alaninium picrate [17,18]. The grown crystal of "bis  $\beta$ -alanine picrate" (see Fig. 1 in Ref. [19]) contains colorless parts, which shows that it cannot be picrate or picric acid, because in this case it must be homogeneously yellow. Infrared spectrum

## ABSTRACT

 $\beta$ -Alaninium picrate crystallizes in the form of yellow columns, in the triclinic system (space group  $P\overline{1}$ , Z = 2). The asymmetric unit contains one  $\beta$ -alaninium cation and one picrate anion. Nevertheless, the unit cell comprises a dimeric centrosymmetric  $\beta$ -Ala<sup>+</sup>... $\beta$ -Ala<sup>+</sup> cation and two picrate anions. The O···O distance (2.636(2) Å) in the dimeric cation is among the shortest distances of known salts with A<sup>+</sup>...A<sup>+</sup> type dimeric cations. The infrared and Raman spectra are shown and discussed. A comparison of known crystals with  $\beta$ -Ala<sup>+</sup>... $\beta$ -Ala<sup>+</sup> cations is presented, which shows that four different types can be distinguished. © 2012 Elsevier B.V. All rights reserved.

of "bis  $\beta$ -alanine picrate" corresponds well to the IR spectrum of  $\beta$ -alanine, although the unit cell parameters are not in good agreement with those of  $\beta$ -alanine [20]. In this context it should be mentioned another paper on an alleged *L*-alanine compound, which in fact is *L*-alanine, namely, "Synthesis, growth and material characterization of bis *L*-alanine triethanol amine (BLATEA) single crystals grown by slow evaporation technique" [21]. No crystal and molecular structure is reported, while unit cell parameters, powder XRD pattern and IR spectrum correspond well to respective characteristics of *L*-alanine with the exception of that the IR spectrum contains additional absorption band at 3408.18 cm<sup>-1</sup> caused probably by absorbed water due to hygroscopicity of KBr.

For further study of the  $\beta$ -alanine  $\beta$ -alaninium picrate crystal (we expected to find a phase transition at low temperatures) we have tried to reproduce this crystal. However, the infrared spectrum of crystals obtained from aqueous solution containing equimolar quantities differed from the spectrum shown in [18]. Subsequent crystal structure determination showed that the actual composition is 1:1, that is, the obtained crystal is  $\beta$ -alaninium picrate. Moreover, it turned out that  $\beta$ -alaninium picrate is a new member of the salts with ( $A^+ \cdots A^+$ ) type dimeric cation. In this paper, we describe the structure and vibrational spectra of  $\beta$ -alaninium picrate and compare it with other similar crystals.

#### 2. Experimental

#### 2.1. Synthesis and crystal growth

As initial reagents we used  $\beta$ -alanine purchased from Reanal (Hungary), and picric acid "pure" made in Poland. Elongated,



<sup>\*</sup> Corresponding author. Tel.: +374 10 241106; fax: +374 10 281861. *E-mail address:* apetros@iapp.sci.am (A.M. Petrosyan).

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Fig. 1. Spontaneously formed crystal of  $\beta$ -alaninium picrate.



Fig. 2. Molecular structure of  $\beta$ -alaninium picrate, with ellipsoids at the 50% probability level.



**Fig. 3.** Detail of the dimeric centrosymmetric  $\beta$ -Ala<sup>+</sup>... $\beta$ -Ala<sup>+</sup> cation. Hydrogen bonds shown as dashed lines. Notice that both molecules are symmetry related via the inversion center, which is in the middle of the dimeric unit.

transparent yellow crystals of  $\beta$ -alaninium picrate (Fig. 1) have been obtained by slow evaporation at room temperature from aqueous solution containing equimolar quantities of respective components. The same crystal was obtained also at 1.5:1 M ratio, while from stoichiometric 2:1 M ratio we were barely able to obtain the  $\beta$ -alanine  $\beta$ -alaninium picrate crystal described in [17,18].

#### 2.2. Crystal structure determination

For X-ray diffraction studies, a suitable single crystal sample of  $\beta$ -alaninium picrate with the size of approximately  $0.09 \times 0.05 \times 0.05 \text{ mm}^3$  was prepared by manually cutting a larger crystal and mounted on a thin glass needle with laboratory grease. The crystal was measured on a Bruker-Nonius Kappa diffractometer, equipped with a CCD area detector and employing graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). A full Ewald sphere was measured. The reflection data were collected and processed using the Bruker-Nonius program suites COLLECT, DENZO-SMN and related analysis software [22,23]. The structures were solved by direct methods and subsequent Fourier and difference Fourier syntheses, followed by full-matrix least-square refinements on  $F^2$ , using the program SHELX [24]. All non-hydrogen atoms have been refined



**Fig. 4.** Crystal structure of  $\beta$ -alaninium picrate, viewed along [010]. Notice the orientation of the picrate anions along ( $\overline{2}05$ ).



**Fig. 5.** Dimeric  $\beta$ -Ala<sup>+</sup>  $\cdots$   $\beta$ -Ala<sup>+</sup> cations in  $\beta$ -alaninium compounds  $\beta$ -Ala<sup>+</sup> NO<sub>3</sub><sup>-</sup> (type B), ( $\beta$ -Ala<sup>+</sup>)<sub>2</sub> BPDS<sup>2-</sup> (type C), ( $\beta$ -Ala<sup>+</sup>)<sub>2</sub> Snl<sup>2-</sup> (type D). For references see Table 1.

with anisotropic displacement parameter, the hydrogen atoms were located form the difference Fourier maps and refined without any restraints. Relatively high displacement parameters of the nitro groups' oxygen atoms suggested possible disorder of these groups. However, attempts to refine these atoms as disordered did not give better values, so we decided to use the model as presented here, although the relatively high residual electron density in the vicinity of the nitro groups resulted in rather high *R*-values. Crystallographic data and refinement details are given in Table 2.

<b>Table 1</b> Space groups, $O \cdots O$ distances (Å) and C–C–C–N torsion angles (°) of $\beta$ -alaninium ( $\beta$ -Ala <sup>*</sup> ) compounds containing A <sup>*</sup> ···A <sup>*</sup> cations.				
#	Crystal	Space group	(00)	C—C—C—N
1	$\beta$ -Ala <sup>+</sup> picrate <sup>-</sup>	ΡĪ	2.636(2)	66.2(2)
2	$(\beta$ -Ala <sup>+</sup> ) <sub>2</sub> (BPDS) <sup>2-b</sup>	ΡĪ	2.690(2)	174.3(2)

1	β-Ala <sup>+</sup> picrate <sup>-</sup>	ΡĪ	2.636(2)	66.2(2)	а
2	$(\beta-Ala^+)_2 (BPDS)^{2-b}$	ΡĪ	2.690(2)	174.3(2)	[12]
3	$\beta$ -Ala <sup>+</sup> ClO <sub>4</sub> <sup>-</sup>	$P2_1/n$	2.726(4)	64.9(3)	[10]
4	$\beta$ -Ala <sup>+</sup> (FeCl <sub>4</sub> ) <sup>-</sup>	$P2_1/c$	2.640(5)	62.3(1)	[8]
5	$(\beta - Ala^{+})_{2}(SnI_{4})^{2-}$	$P2_1/c$	2.629(7); 2.646(7)	55.0(7); -61.7(7)	[15]
6	$\beta$ -Ala <sup>+</sup> oxalate <sup>-</sup> .0.5H <sub>2</sub> O	C2/c	2.750(2)	77.0(2)	[11]
7	$(\beta - Ala^{+})_{2}(Re_{2}Cl_{8})^{2-}$	C2/c	2.64(5)	69.8(12)	[16]
8	$(\beta-Ala^+)_2(CuCl_4)^{2-}$	I2/c	2.682(1)	67.5(1)	[13]
9	$(\beta-Ala^+)_2(CuBr_4)^{2-c}$	I2/c	2.704(1)	66.8(1)	[14]
10	$\beta$ -Ala <sup>+</sup> NO <sub>3</sub> <sup>-</sup>	$Pca2_1$	2.638(3); 2.643(3)	67.6(3); -70.0(4)	[9]

<sup>a</sup> This work.

<sup>b</sup> BPDS = biphenyl-4,4'-disulfonate.

<sup>c</sup> Note: The atomic position parameters x and y of C3 given in the CIF (CSD Refcode CAYPOH) differ from that in the publication and are erroneous.

Table	2
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Crystal data and details of the refinement for  $\beta$ -alaninium picrate.

Formula	C <sub>9</sub> H <sub>10</sub> N <sub>4</sub> O <sub>9</sub>
M <sub>r</sub>	318.21
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	4.5764(9)
b (Å)	12.060(2)
c (Å)	12.291(3)
α (°)	104.72(3)
β(°)	97.69(3)
γ (°)	95.83(3)
V (Å <sup>3</sup> )	643.6(2)
Ζ	2
$D_{\text{calcd}} (\text{g cm}^{-3})$	1.642
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	0.149
F(000)	328
T (K)	296(2)
hkl range	±6, -17/16, ±18
Reflections measured	5959
Reflections unique	4344
Data with $F_{\rm o} > 4\sigma$ ( $F_{\rm o}$ )	2953
R <sub>int</sub>	0.017
Parameters refined	240
$R(F)^{\rm a}$ (for $F_{\rm o} > 4\sigma(F_{\rm o})$	0.069
$R(F)^{a}$ (all reflections)	0.0995
$wR(F^2)^a$ (all reflections)	0.177
Weighting parameters <i>a</i> / <i>b</i>	0.048/0.379
$\Delta  ho_{ m fin}$ (max/min) (e Å <sup>-3</sup> )	0.880/-0.637

The CCDC data set 864240 contains supplementary crystallographic data for  $\beta$ -alaninium picrate. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

<sup>a</sup>  $R1 = \Sigma ||F_0| - |F_c||\Sigma |F_0|$ ,  $wR2 = [\Sigma w(F_0^2 - F_c^2)^2 / \Sigma wF_0^4]^{1/2}, w = 1/[\sigma^2(F_0^2) + (a \times P)^2 + b \times P], P = (F_0^2 + 2F_c^2)/3.$ 

#### 2.3. Vibrational spectroscopy

Fourier-transform Raman spectra were registered by a NXP FT-Raman Module of a Nicolet 5700 spectrometer (number of scans: 512, laser power at the sample: 0.16 W, resolution  $4 \text{ cm}^{-1}$ ) at room temperature. The same spectrometer was used for measuring attenuated total reflection Fourier-transform infrared spectra (FTIR ATR) (ZnSe prism, 4000–500 cm<sup>-1</sup>, Happ-Genzel apodization, ATR distortion is corrected, number of scans 32, resolution  $4 \text{ cm}^{-1}$ ). Part of the IR spectrum in the region 500–400 cm<sup>-1</sup> were taken from FTIR spectra registered with Nujol mull (4000–400 cm<sup>-1</sup>, number of scans 32, resolution 2 cm<sup>-1</sup>).

#### 3. Results and discussion

#### 3.1. Molecular and crystal structure of $\beta$ -alaninium picrate

The molecular structure of  $\beta$ -alaninium picrate comprises  $\beta$ alaninium cations and picrate anions in a 1:1 ratio, in contrast to

Hydrogen bond parameters for  $\beta$ -alaninium picrate (in Å and °).

D—H···A	D—H	$H{\cdot}{\cdot}{\cdot}A$	$D{\cdots}A$	<dha< th=""></dha<>
N1A—H11A…O1B	0.87(4)	2.01(4)	2.821(3)	155(3)
N1A—H12A…O1B	0.91(3)	1.96(3)	2.850(2)	165(2)
N1A—H13A…O2A	0.90(3)	2.23(3)	2.888(2)	129(2)
O1A—H1A…O2A	0.89(2)	1.76(2)	2.636(2)	168(5)

#### Table 4

Selected interatomic distances and angles in  $\beta$ -alaninium picrate (in Å and °).

Distance		Angle	
01A-C1A	1.309(2)	02A-C1A-01A	123.5(2)
02AC1A	1.221(2)	02A-C1A-C2A	122.3(2)
C1A–C2A	1.499(3)	01A-C1A-C2A	114.2(2)
C2A–C3A	1.513(3)	C1A-C2A-C3A	114.0(2)
C3A-N1A	1.492(2)	N1A-C3A-C2A	112.9(2)
O1B-C1B	1.255(2)	O1B-C1B-C2B	124.9(2)
C1B-C2B	1.449(2)	O1B-C1B-C6B	123.9(2)
C1B-C6B	1.452(3)	C2B-C1B-C6B	111.3(2)
C2B-C3B	1.376(3)	C3B-C2B-C1B	124.7(2)
C2B-N1B	1.458(2)	C3B-C2B-N1B	116.1(2)
C3B-C4B	1.383(3)	C1B-C2B-N1B	119.2(2)
C4B-C5B	1.384(3)	C2B-C3B-C4B	118.9(2)
C4B-N2B	1.448(3)	C3B-C4B-C5B	121.4(2)
C5B-C6B	1.370(3)	C3B-C4B-N2B	119.6(2)
C6B—N3B	1.459(2)	C5B-C4B-N2B	119.0(2)
N1B-O3B	1.212(2)	C6B-C5B-C4B	119.1(2)
N1B-O2B	1.226(2)	C5B-C6B-C1B	124.7(2)
N2B-O5B	1.218(3)	C5B-C6B-N3B	115.7(2)
N2B-O4B	1.219(2)	C1B-C6B-N3B	119.6(2)
N3B-06B	1.158(3)		
N3B-07B	1.228(3)		

the expected 2:1 ratio. All atoms are located on general positions in the triclinic unit cell (Fig. 2). Although the name of the species somehow suggests that the  $\beta$ -alaninium cation is connected to the picrate anion, this is not the case. In contrast, two crystallographically related  $\beta$ -alaninium molecules are connected to each other via two symmetry-equivalent O-H...O type hydrogen bonds. Thus, although no atom of the crystal is located on a special position, the dimeric cation does display point symmetry 1 (Fig. 3). Nevertheless, there is some connection between the dimeric units (which carry two positive charges) and the picrate units, namely via N-H···O type hydrogen bonds (Table 3). It is interesting to notice that these bonds only connect to one of the seven oxygen atoms of the picrate anion, viz. to the deprotonated O1B atom. This fact also is expressed in the rather large values of the displacement parameters of the other oxygen atoms of the picrate anion - a fact that is responsible for the high residual electron density found around the nitro groups of the picrate anion (see Section 2).

Refs.



**Fig. 6.** Schematic depiction of structure types arranged by geometries and symmetries in dimeric  $\beta$ -Ala<sup>+</sup>... $\beta$ -Ala<sup>+</sup> cations in  $\beta$ -alaninium compounds. Symmetry centers are depicted as circles. Most  $\beta$ -alaninium compounds belong to type A. The structure type with trans-oriented molecules without inversion symmetry (drawn in gray) is theoretical, i.e. has not been found in any crystal.

The geometry of the organic molecules themselves is well within the range of the expected values (selected distances and angles are given in Table 4), with the exception of the hydrogen bond in the dimeric cation. The O···O distances may be divided into two groups. In one group (## 1, 4, 5, 7, 10) the O···O distances are relatively short (the mean value is 2.639 Å), while in second group (## 2, 3, 6, 8, 9) the O···O distances are longer (the mean value is 2.710 Å). Thus the value of the O···O distance in  $\beta$ -alaninium picrate (2.636(2) Å) is among the shortest distances in such A<sup>+</sup>···A<sup>+</sup> cations (see Table 1).

As far as the packing of the units is considered, the structure can be described as layers of picrate anions, with the amino acid moieties in the interstices (Fig. 4). The aromatic ring of the picrate anions lies in the plane ( $\overline{2}05$ ), although the nitro groups of N-atoms N1b and N3b are twisted out of this plane. The  $\beta$ -alaninium cations in between assume *gauche* conformation (torsion angle C1A-C2A-C3A-N1A equals 66.2(2)°) – the most common conformation when compared with related compounds (see Table 1 for values calculated from the CIFs of the listed species).

When comparing the structural properties of all known  $\beta$ -Ala<sup>+</sup> $\cdots\beta$ -Ala<sup>+</sup> dimers, we found four different types. The first type is that of  $\beta$ -alaninium picrate is characterized by a symmetric arrangement of two  $\beta$ -alaninium cations in *gauche* conformation (type A, Fig. 3). Another type is represented by  $\beta$ -Ala<sup>+</sup> NO<sub>3</sub>, in which there is no inversion center as in the above type, although the  $\beta$ -alaninium cations also assume *gauche* conformation and adopt a similar geometry (type B, Fig. 5). Since the inversion center is missing the four oxygen atoms are not coplanar, in the case of  $\beta$ -Ala<sup>+</sup> NO<sub>3</sub> the torsion angle O21–O22–O11–O12 equals –4.0°.

#### Table 5

Wavenumbers (in  $cm^{-1}$ ) and assignment of peaks in IR and Raman spectra of  $\beta$ -alaninium picrate.

IR	Raman	Assignment
	3373; 3358	
3261	3261	v(NH)
3176		
3079; 3039sh	3084; 3041	v(NH); v(CH)
2998; 2917; 2880	3008; 2951	v(CH); v(NH); v(OH)
2726; 2679		Sum tones
2590		Sum tone
2104; 2040		Sum tones
1687		СООН
1633; 1619	1652sh; 1633sh; 1620	v(C=C) ring
1588	1590	$\delta_{as}(NH_3^+)$
1564; 1557	1572; 1549	$v_{as}(NO_2)$
1523; 1487	1535sh; 1494	$\delta_{s}(NH_{3}^{+})$
1470; 1451	1481	$\delta(CH_2)$
1428	1433	$\delta(CH_2)$
1404	1407	$\omega(CH_2)$
1391	1392	
1362	1368	$\omega(CH_2)$
1331; 1320	1338; 1323	$v_{\rm s}({\rm NO}_2)$
1262	1279	v(C–O) phenolic
1241	1249	v(C—OH)
1165	1170	$\delta$ (CH) in-plane
1143	1155; 1146	$\rho(\text{NH}_3^+)$
1101; 1087	1090	v(CN)
1054	1057	v(CN)
960	963; 949	v(CC)
928	934	
913	918	
862	864	v(C—C)
828	827	$\delta(NO_2)$
790	813; 793	$\delta(CH)$ out-of-plane
745	753	
710	716	$\rho(CH_2)$
703sh	706	
582; 549; 522	551	
507; 437; 408	498; 408	
	370; 356; 332; 318	
	298; 202; 168	

The third type is realized in crystals of  $(\beta$ -Ala<sup>+</sup>)<sub>2</sub> biphenyl-4,4'disulfonate, which has centrosymmetrical dimers of trans-oriented  $\beta$ -alaninium cations (type C, Fig. 5). Finally, we found a fourth type, which is represented by  $(\beta$ -Ala<sup>+</sup>)<sub>2</sub> SnI<sub>4</sub>, where the two amino ends of both gauche-oriented cations are facing in the same direction (type D, Fig. 5). As in type B, the oxygen atoms are not coplanar, in  $(\beta$ -Ala<sup>+</sup>)<sub>2</sub> SnI<sub>4</sub> the torsion angle O3–O1–O2–O4 equals –8.2°. Theoretically, a fifth type is conceivable, namely with  $\beta$ -alaninium cations in trans-conformation, but without an inversion center. However, none of the crystals reported assumes this geometry. From all  $\beta$ -alaninium compounds containing  $\beta$ -Ala<sup>+</sup>... $\beta$ -Ala<sup>+</sup> cations, the majority (## 1, 3, 4, 6, 7, 8, 9 from Table 1) belongs to type A, i.e. has centrosymmetrical dimeric pairs in gauche-conformation. All other types have only one representative, viz. the one named above. A schematic overview of the geometries of these types is shown in Fig. 6.

#### 3.2. Vibrational spectra of $\beta$ -alaninium picrate

The IR and Raman spectra of  $\beta$ -alaninium picrate are shown in Fig. 7, wavenumbers and assignment of peaks are provided in Table 5. In the high-frequency region one expect to find bands caused by stretching vibrations of N–H, C–H and O–H bonds of NH<sub>3</sub><sup>+</sup>, CH<sub>2</sub>, OH groups of  $\beta$ -alaninium cation and CH groups of picrate anion. The absorption band at 3261 cm<sup>-1</sup> and respective Raman-line we assign to vibration of N1A–H13A bond, which forms weak hydrogen bond (see Table 3). The broad absorption band centered at 2917 cm<sup>-1</sup> and respective Raman lines in this region are caused



**Fig. 7.** Infrared and Raman spectra of  $\beta$ -alaninium picrate.

by vibrations of N1A-H11A and N1A-H12A bonds forming stronger hydrogen bonds as well as OH, CH<sub>2</sub> and CH groups. The observed positions of v(NH) and v(OH) correspond well to expected positions on the basis of respective correlations [25,26]. The picrate anion has some characteristic bands [3,5,18]. In the Raman spectrum these are the most intensive lines caused by vibrations of nitro group of picrate anion. The line at  $1549 \, \text{cm}^{-1}$  we assign to asymmetric stretching, the most intensive band with peaks at 1338 and 1323  $\text{cm}^{-1}$  to symmetric stretching and the line at 827 cm<sup>-1</sup> to deformation vibration of NO<sub>2</sub> groups. Respective bands in the IR spectrum are at 1564, 1557 cm<sup>-1</sup>( $v_{as}(NO_2)$ ), 1331, 1320 cm<sup>-1</sup> ( $v_s(NO_2)$ ) and 828 cm<sup>-1</sup> ( $\delta(NO_2)$ ). In addition, the IR spectrum comprises a characteristic band at 1262 cm<sup>-1</sup> caused by stretching vibration of the phenolic C-O bond and a band with peaks at 1633 and 1619 cm<sup>-1</sup> caused by stretching vibration of short C=C bonds in the ring. The IR spectrum also comprises a band at 1687 cm<sup>-1</sup>, which is not active in the Raman spectrum. We assign it to the COOH group. Similar bands were observed in the spectra of salts with  $(A \cdots A^{+})$  type dimeric cation with very short  $(O-H \cdots O)$  hydrogen bonds [4].

### 4. Conclusion

With this contribution we report a new crystal species,  $\beta$ -alaninium picrate, unexpectedly found in the system  $\beta$ -alanine + picric acid + H<sub>2</sub>O (in addition to the already known compound  $\beta$ -alanine  $\beta$ -alaninium picrate). We have characterized this novel species structurally and by infrared and Raman spectra. It belongs to the group of crystals that contain dimeric amino acid (A<sup>+</sup>···A<sup>+</sup>) cations. Comparison with other known similar salts showed that there are two groups of salts, i.e., with short and relatively long (O···O) distances. Furthermore, it was found that all these salts can be arranged into four structural types, according to conformation and symmetry of the dimers of  $\beta$ -alaninium cations.  $\beta$ -Alaninium picrate belongs to the group with short (O···O) distances and to the structure type A, with centrosymmetrical pairs of *gauche*-oriented  $\beta$ -alaninium cations, the group comprising the majority of known salts. Nevertheless, as some of these compounds have been determined some decades ago, it might be possible that of the type A species might in fact belong to type B, i.e. do not actually (but nearly) have inversion symmetry. Of course, only careful redetermination of these structures, ideally supported by physical evidence, can resolve this question.

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