# CrystEngComm



# PAPER



**Cite this:** *CrystEngComm*, 2015, **17**, 4143

# Rare stoichiometry of carboxyl-carboxylate benzbetaine complexes: *in vitro versus in silico*†

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The first betaine–mineral acid complex of 3:2 stoichiometry, as well as a 1:1 complex common for this class of compounds, has been obtained. Crystalline [di-(3-trimethylammonium-benzoic acid)–(3-trimethylammonium-benzoate)]diiodide (1) is the only betaine–mineral acid 3:2 complex obtained so far. Two concomitant polymorphs of this 3:2 complex, 1-I and 1-II, have been isolated and characterized by X-ray diffraction and FTIR spectroscopy. Polymorphs 1-I, of monoclinic space group  $P2_1/c$ , and 1-II, of orthorhombic space group Pccn, have very similar lattices and aggregates of one zwitterionic molecule and two cations O–H···O bonded into a 3-membered catemeric carboxyl–carboxylate–carboxyl interval, but polymorph 1-II dissolves better in methanol than 1-I. Alternative hypothetical aggregates of 3-trimethylammonium-benzoate hydroiodide 1:1, 2:1 and 3:2 complexes optimized at the B3LYP/6-31G-(d,p) level of theory suggest that the betaine-to-acid 3:2 stoichiometry is favoured at the stage of small cluster aggregation and not due to the complex crystal packing preferences.

Accepted 19th April 2015 DOI: 10.1039/c5ce00054h

Received 9th January 2015,

www.rsc.org/crystengcomm

# Introduction

The carboxylic acid aggregates have been extensively investigated for decades due to their basic significance in chemical sciences, practice and manifold applications.<sup>1</sup> The H-bonding patterns of neutral carboxylic acid groups are often considered as the most predictable ones. In most cases molecules with the COOH group aggregate into dimers, described by the graph set  $R_2^2(8)$ ,<sup>2</sup> while much less frequent are chains, so called catemers, described by the graph set C(4). Also other aggregates of the carboxylic acid are possible, like tetra- or hexamers. Our survey of monocarboxylic acids in the Cambridge Structural Database (CSD - version November 2013)<sup>3</sup> revealed 3449 R<sub>2</sub><sup>2</sup>(8) dimers, 408 C(4) catemers, one 3-membered cyclamer,<sup>4</sup> seventeen 4-membered cyclamers and two 6-membered cyclamers.<sup>5,6</sup> However, equally important finite OH…O bonded catemeric intervals of carboxyl-carboxylate groups have been studied much less and no rules describing their aggregation have been reported. There are three groups of compounds containing the carboxyl and carboxylate

groups: neutral organic acids, their salts, and zwitterionic molecules, like amino acids and betaines.<sup>7</sup> In the salts of



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<sup>†</sup> Electronic supplementary information (ESI) available: Detailed experiment and structure description, atomic coordinates and equivalent isotropic displacement parameters, selected bond lengths, bond angles and torsion angles, hydrogen bonds and shortest contact distance (Tables S1–S8), the reciprocal space projections for the diffraction patterns, comparison of the aggregates and crystal structures by their superposition, the differential scanning calorimetry diagram, and the X-ray powder diffraction diagrams (Fig. S1–S6). For ESI and crystallographic data in CIF and other electronic format, see DOI: 10.1039/c5ce00054h

organic acids, if one carboxyl group is deprotonated, the most common aggregation type is a dimer, but H-bonded aggregates built of three, four or more carboxyl-carboxylate units are also possible. Such aggregates require only one cation to balance the charge equal to -1 and it is independent of the number of acid units in the aggregate (Scheme 1).<sup>8-11</sup> Our survey of the CSD aimed at identifying the interval aggregates of carboxylic and carboxylate groups with cationic counter-ions yielded 1815 dimers, 206 trimers and 32 tetramers.

Betaines and amino acids are zwitterions with a positively charged nitrogen atom and negatively charged carboxylate group.<sup>7</sup> The best known and most common are their baseacid hydrogen-bonded aggregates of 1:1 stoichiometry. The base molecule is protonated and the carboxyl group is hydrogen bonded to an anion (COOH…anion). There are 318 such structures of betaine salts deposited with the CSD. The next most frequently represented are the aggregates of stoichiometry 2:1, where the protonated betaine interacts by COOH…OOC hydrogen bond with the zwitterion. Such a homoconjugated cationic dimer is stabilized also by electrostatic forces between itself and the counter-anion. There are 32 such salts deposited with the CSD. There are no complexes of stoichiometry 3:2 and no betaines forming O-H…O bonded complexes of different stoichiometries with the same acid.

The group of compounds 2-, 3- and 4-(trimethylammonium)benzoates (benzbetaines), their esters, hydrates and salts with halogen anions,<sup>12–20</sup> is particularly important due to their biochemical significance as well as applications in the pharmaceutical and the nutrition industries. Of the trimethylammonium benzoates, the adducts with halides in the ratios 1:1 (ref. 12, 15, 20) and 2:1 (ref. 18) have been obtained (Scheme 2). Their structures were studied by diffraction, spectroscopy and theoretical methods. Recently, we have studied the structures of



**Scheme 2** Examples of trimethylammonium derivatives: (a) 4-trimethylammonium benzoate;<sup>16</sup> (b) 4-trimethylammonium benzoic acid chloride;<sup>15</sup> (c) bis(4-trimethylammonium-benzoate)hydrogen iodide;<sup>18</sup> and (d) [di-(3-trimethylammonium-benzoic acid)–(3-trimethylammonium-benzoate)]diiodide (this work).

4-trimethylammonium-benzoic acid chloride,<sup>15</sup> 4-trimethylammonium-benzoite hydrate,<sup>16</sup> methyl-4-trimethylammonium-benzoic acid iodide,<sup>17</sup> bis(4-trimethylammonium-benzoate) hydroiodide hydrate<sup>18</sup> and methyl ester of 3-trimethylammonium benzoic acid iodide.<sup>19</sup> Tadros and Sakla<sup>20</sup> showed the connection between the quaternization of dimethylamino-



Fig. 1 The symmetry-independent unit in (a) polymorphs 1-I and 1-II of [di-(3-trimethylammonium-benzoic acid)–(3-trimethylammonium benzoate)]diiodide and (b) 3-trimethylammonium-benzoic acid iodide (2). The hydrogen bonds have been marked by cyan dashed lines. Thermal ellipsoids have been drawn at the 50% probability level.

benzoic acid in an excess of methyl iodide in methanol and the temperature and time of the reaction, as well as the position of the dimethylamino group at the benzoic acid ring.

To the best of our knowledge no bis(3-trimethylammonium-benzoate) hydrohalide 2:1 salts have been obtained until now. Also, no salts in the zwitterion : anion 3 : 2 ratio, or any of higher stoichiometries described by the general formula n:(n-1), were found in the CSD. Thus the structure of [di-(3-trimethylammonium-benzoic acid)-(3-trimethylammonium-benzoate)]diiodide (1) presented in this work is the first example of the 3:2 aggregate. In the reiterated attempts to change the ratio of this complex we found that 1 exists in two polymorphic forms, 1-I and 1-II (Fig. 1). They have been studied by single-crystal X-ray diffraction, thermal DSC analysis, FTIR spectroscopy and DFT calculations. The main objects of our concern were the O-H…O catemeric interval aggregates of carbonyl and carboxylate groups in the zwitterionic type compounds. The 1:1 complex 3-trimethylammonium-benzoic acid iodide has the expected O-H…I bonded structure.

### Experimental

#### Syntheses

Preparation of [di-(3-trimethylammonium-benzoic acid)-(3-trimethylammonium-benzoate)]diiodide 1 (complex 3:2)

A solution of 3-dimethylamino-benzoic acid (2.56 g; 0.0155 M) in methanol (30  $\text{cm}^3$ ) and methyl iodide (1.47 g, 0.103 M) was stirred at 25 °C for 28 h. The crude product, 2.93 g, was filtered off, washed with a small amount of acetonitrile. [Di-(3-trimethylammonium-benzoic acid)-(3-trimethylammoniumbenzoate)]diiodide in the form of colourless crystals was separated. After recrystallization from an ethanol-acetonitrile (10:1) mixture, m.p. 191-192 °C, it was identified as 1, with a considerable content of polymorph 1-I. The filtrate was evaporated to half of the volume and the remaining crystals, mainly of 1-I, were filtered off, 0.05 g. From the filtrate evaporated to dryness, 1.01 g of the crystals of polymorph 1-II could be isolated and recrystallized from a mixture of acetonitrile-methanol (3:1), m.p. 188-189 °C, and then several of the picked crystals were identified as polymorph 1-II. This suggests that polymorph 1-II is more soluble in methanol than 1-I. The powder diffraction patterns of the products always contained a mixture of polymorphs 1-I and 1-II, and also of another compound that was later identified as the 1:1 complex (see below). The ratio of 1-I to 1-II is 3:1. NMR (DMSO-d<sub>6</sub>, ppm); <sup>1</sup>H: 3.68, CH<sub>3</sub>; 7.80, H(5); 8.13, H(6); 8.30, H(4); 8.41, H(2); <sup>13</sup>C: 56.38, CH<sub>3</sub>; 121.11, C(2); 125.10, C(6), 130.63, C(4); 130.67, C(5); 132.59, C(1); 147.40, C(3); 166.05, C(7). Analysis for C<sub>30</sub>H<sub>41</sub>N<sub>3</sub>O<sub>6</sub>I<sub>2</sub>, m.wt. 793.48; calc. %C, 45.41; %H, 5.20; %N, 5.30; found: %C, 45.23; %H, 4.95; %N, 5.18. All attempts to obtain one of the polymorphs from recrystallization resulted in concomitant polymorphs 1-I and 1-II.

Preparation of 3-trimethylammonium-benzoic acid iodide 2 (complex 1:1)

To a solution of 5 g (0.03 M) of 3-dimethylamino-benzoic acid in 30 ml of methanol, 3.3 g (0.031 M) of methyl iodide

was added and stirred at 25 °C for 35 h. The crude product was washed with acetonitrile. Yellow crystals were obtained, m.p. 211–213 °C. Analysis for  $C_{10}H_{14}NO_2I$ , m.wt. 309.13; calc. %C, 39.11; %H, 4.59; %N, 4.56; found: %C, 39.24; %H, 4.52; %N, 4.31.

We tried to obtain complexes of the 2:1 stoichiometry by increasing and reducing the acid concentration; however, all subsequent analyses of the precipitate showed that either 1:1 and 3:2 complexes were obtained or, in the excess of HI, esterification took place and the compound was converted to the methyl ester of 3-trimethylammonium benzoic acid iodide.<sup>19</sup>

#### Measurements

The single-crystal X-ray diffraction data of 3-trimethylammonium-benzoic acid iodide 1:1 complex 2 and [di-(3trimethylammonium-benzoic acid)-(3-trimethylammoniumbenzoate)]diiodide, polymorphs 1-I and 1-II, were measured using an Oxford Diffraction Excalibur EOS-CCD diffractometer. The structures were solved by direct methods and refined using SHELXL.<sup>21</sup> H atoms were located according to the ideal geometry (hydroxyl 0.82 Å, arene 0.93 Å, and methyl 0.96 Å). Anisotropic thermal parameters were refined for non-Hatoms, and isotropic Uiso parameters for H atoms were linked to  $U_{eq}$  of their carriers. The crystal data, details of data collections and structure refinements are given in Tables 1 and S1-S2<sup>†</sup> and the final atomic coordinates are in Tables S3 and S4 (ESI<sup>†</sup>). The crystal data have been deposited with the Cambridge Crystallographic Database Centre as supplementary publications CCDC 1041713 (polymorph 1-I), 1041714 (1-II) and 1056077 (2).

The FTIR spectra of 1 and 2 were measured using the KBr disks on a Bruker IFS 66v/S instrument, with a resolution of 2 cm<sup>-1</sup>. The spectra were recorded by accumulation of 64 scans. The NMR spectra of 1 were recorded using a Varian VNMRS-400 spectrometer operating at 402.6435 and 101.2440 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively. The spectra were measured in DMSO-d<sub>6</sub> relative to an internal standard of TMS. The thermal analysis of 1-I was performed with a DSC THASS XP-10

Table 1 Selected crystal data of complex 3:2, polymorphs 1-I and 1-II, and complex 1:1 (2) of 3-trimethylammonium-benzoate with hydroiodic acid (*cf.* Tables S1–S2 in the ESI)

|   | 1-I                     | 1-II                    | 2  |
|---|-------------------------|-------------------------|--|
| Formula weight                              | $C_{30}H_{41}I_2N_3O_6$ | $C_{30}H_{41}I_2N_3O_6$ | C <sub>10</sub> H <sub>14</sub> INO <sub>2</sub> |
| Crystal system                              | Monoclinic              | Orthorhombic            | Monoclinic                                       |
| Space group                                 | $P2_1/c$                | Pccn                    | $P2_1/n$   |
| Unit cell dimensions                        |                         |                         |  |
| a (Å)                                       | 18.7965(10)             | 37.3738(17)             | 8.1929(2)  |
| b (Å)                                       | 13.9047(8)              | 13.9167(11)             | 11.3278(3)                                       |
| c (Å)                                       | 12.8843(6)              | 12.8674(7)              | 13.1285(3)                                       |
| β   | 96.010(4)°              | 90°                     | 105.735(3)°                                      |
| Volume (Å <sup>3</sup> )                    | 3348.9(3)               | 6692.6(7)               | 1172.76(5)                                       |
| Ζ   | 4                       | 8                       | 4  |
| Calculated density<br>(g cm <sup>-3</sup> ) | 1.574                   | 1.575                   | 1.739  |

calorimeter. The sample with a mass of 6.3 mg was stored in an  $Al_2O_3$  crucible in helium atmosphere and the rate of temperature change was 10 °C min<sup>-1</sup>.

#### **DFT calculations**

The DFT calculations were performed with the GAUSSIAN 09 program package.<sup>22</sup> The calculations employed the B3LYP exchange–correlation functional, which combines the hybrid exchange functional of Becke<sup>23,24</sup> with the gradient-correlation functional of Lee *et al.*<sup>25</sup> and the split-valence polarized 6-31G(d,p) basis set.<sup>26</sup> The 6-31G(d,p) basis set by Glukhovtsev *et al.*<sup>29</sup> for iodine has been acquired from the EMSI Basis Set Library.<sup>27,28</sup> The geometries in polymorphs 1-I and 1-II and in complex 2 were used as starting models for the structure optimizations. All calculated IR frequencies are positive, consistent with the minimum energies of the optimized structures.

#### Discussion

#### Crystal structure

The crystals of [di-(3-trimethylammonium-benzoic acid)–(3-trimethylammonium-benzoate)]diiodide, **1**, are composed of two 3-(trimethylammonium)-benzoic acid cations (A and C), one 3-(trimethylammonium)-benzoate zwitterion (B) and two iodide anions (Fig. 1). Cations A and C are joined to both oxygen atoms of the carboxylate group of zwitterion B by two non-equivalent hydrogen bonds,  $O(1)-H(1)\cdots O(11)$  and  $O(21)-H(21)\cdots O(12)$  (Fig. 1). The crystals of polymorph 1-I are monoclinic, with space group  $P2_1/c$ , while those of 1-II are orthorhombic, with space group Pccn (Table 1).

The crystals of polymorphs 1-I and 1-II can be distinguished by their morphology (Fig. 2). In their structures, the positions and orientations of the complex aggregates are very similar and the main difference is in the location of the 3-trimethylammonium group of the zwitterion (Fig. 3).



**Fig. 2** Crystals of [di-(3-trimethylammonium-benzoic acid)-(3-trimethylammonium-benzoate)]diiodide: (a) polymorph **1-I** and (b) polymorph **1-II.** Apart from these pure forms of concomitant polymorphs **1-I** and **1-II,** their twin-like agglomerates also were formed, with the "twinning plane" (010) (see Fig. S1†).



Fig. 3 Superimposed OH···O bonded aggregates and anions of [di-(3trimethylammonium-benzoic acid)–(3-trimethylammoniumbenzoate)]diiodide in polymorph 1-I (green) and polymorph 1-II (yellow). The superimposed aggregates viewed from other directions are shown in the ESI Fig. S2 and S3.†

The structure of 1:1 complex 2 is built of OH…I bonded ionic pairs (Fig. 1); the O…I distance is 3.446(6) Å. The next shortest interionic bonds are all longer than the sum of the van der Waals radii, except  $C(5)H(5)\cdots O(2')$  (symmetry code 1.5 - x, -0.5 + y, 1.5 - z), with a  $H(5)\cdots O(2')$  distance of 2.476 Å shorter than the sum of van der Waals radii according to Bondi by 0.274 Å.

The dimensions of units A, B and C (see Fig. 1) in both polymorphs 1-I and 1-II are consistent within standard deviations (Tables S5–S6 in the ESI<sup>†</sup>).

The presence of the COOH groups, in polymorphs 1-I and 1-II, in cations A and C is confirmed by C-OH bonds longer than 1.300(6) Å and by C=O bonds shorter than 1.204(6) Å. In zwitterion B, the C(17)-O(1) and C(17)-O(2) bond lengths are 1.255(10) and 1.240(11) Å in polymorph 1-I, and 1.256(6) and 1.243(6) Å in polymorph 1-II, respectively. The dimensions of hydrogen bonds O(1)-H(1)···O(11) and O(21)-H(21)···O(12) linking cations A and C with zwitterion B, are very similar, in polymorph 1-I of 2.529(9) and 2.533(9) Å, and also similar in polymorph 1-II of 2.493(5) and 2.549(5) Å, respectively (Table S7<sup>†</sup>). The aggregates are surprisingly similar in their shape, too (Fig. 3): the planes fitted to cations A and C are inclined to the plane of zwitterion B by 40.70° and 44.21° in 1-I, and 41.21° and 45.86° in 1-II, respectively. Likewise, the lattices (Table 1) of polymorphs 1-I and 1-II are surprisingly similar, including the *a*-parameter, which is almost exactly two times longer in 1-II than in 1-I (Fig. 4a and b). The superposition of both structures shown in Fig. S5† illustrates the differences mainly associated with the orientation of the nearly identical aggregates (Fig. 3), as can be seen in the position of trimethylammonium groups between Fig. 4a and b.

The iodide anions are located close to the nitrogen atom of zwitterion B in the structures of both polymorphs; however the N(11)…I(2) distances of 4.435(7) in 1-I and 4.433(4)Å in 1-II are somewhat longer than the N(11)…I(1) distances of 4.374(8) and 4.375(5)Å, respectively (Table S8†). Additionally, the hydrogen atoms of the methyl groups interact with the iodide anions as well as with the ring protons at the *para*-position. These interatomic distances vary from 3.900 to 3.968 Å (Table S7 in the ESI†).



Fig. 4 Structures of [di-(3-trimethylammonium-benzoic acid)-(3-trimethylammonium-benzoate)]diiodide complex 3:2 projected down the [y] and [z] axes in (a) polymorph 1-I and (b) polymorph 1-II, as well as (c) the structure of 3-trimethylammonium-benzoic acid iodide (2) complex 1:1. The hydrogen bonds have been shown as the cyan lines.

The structure of **1** is very similar in its interactions between the benzoic acid rings to that in the structure of potassium (benzo-15-crown-5) [3,5-dinitrobenzoate–(3,5-dinitrobenzoic acid)<sub>2</sub>].<sup>10</sup> The main difference between these structures is that catemeric interval **1** has positive charges located on the nitrogen atoms stabilized by two  $\Gamma$  anions, while that of 3,5-dinitrobenzoic acids has a negative charge at the carboxylate group of 3,5-dinitrobenzoate, stabilized by the K<sup>+</sup> cation.

The differential scanning calorimetry (DSC) diagram of 1 (Fig. S4, in the ESI†) contains only the exothermic peak at 190 °C. However, this peak clearly consists of two superimposed peaks that can be associated with the different melting points of 1-I and 1-II.

#### DFT calculations

Three models of the adducts of 3-trimethylammoniumbenzoic acid with iodide in ratios of 1:1(2'), 2:1(3) and 3:2(4) were optimized at the B3LYP/6-31G(d,p) level of theory and their structures are shown in Fig. 5. In the optimized structure 2', the electrostatic attraction between the positively charged nitrogen atom and the iodide anion significantly contributes to the aggregation energy, as indicated by a short  $N^+ \cdots I^-$  distance of 4.306 Å (Table S8 in the ESI†). This difference illustrates the competition between the OH $\cdots I$  hydrogen bond prevailing in the crystal and the electrostatic forces between the charged trimethylammonium group and the iodide anion in the optimized isolated complex.

Model 3 represents a hypothetical hydrogen-bonded complex of stoichiometry 2:1. The 3-trimethylammoniumbenzoic acid cation A and its zwitterion B are linked through the asymmetric and short COOH…OOC hydrogen bond of 2.503 Å (Table S7 in the ESI†). The N<sup>+</sup>…I<sup>-</sup> distance to cation A is slightly shorter than that to zwitterion B (Table S8 in the ESI†). The calculated energy of 3 is -8108.3556063 a.u. and its dipole moment is 10.64 D.



Fig. 5 Computed structures of the 1:1 (2'), 2:1 (3) and 3:2 (4-I and 4-II) complexes of 3-trimethylammonium-benzoic acid with hydroiodic acid.



Fig. 6 Solid-state FTIR spectra of (a) [di-(3-trimethylammonium-benzoate)]diiodide 1 and (b) trimethylammonium-benzoic acid iodide 2.

Model 4 corresponds to the aggregation in the crystals of 1, composed of two cations, a zwitterion and two iodide anions (Fig. 5). Two structures, 4-I and 4-II, have been optimized, from the starting models of aggregates in polymorphs 1-I and 1-II, respectively. The optimized model 4-I reproduces the aggregate well in crystal structure 1-I. The carboxylic groups of two 3-trimethylammonium-benzoic acid cations, A and C, interact with the carboxylate oxygen atoms of zwitterion B. The O(1)-H…O(11) and O(21)-H…O(12) distances in the theoretically optimized structure 4-I are 2.480 and 2.443 Å, respectively (Table S7†). The iodide anions are located on both sides of the zwitterion molecule; however they are closer to the nitrogen atoms of cations  $(N^+ \cdots I^-)$  distances are 4.357 and 4.323 Å, Table S8 in the ESI<sup>†</sup>) than to the nitrogen atom of the zwitterion  $(N^+ \cdots I^-)$  distances are 5.019 and 4.678 Å). The calculated energy of 4-I is -15622.6608034 a.u. and the dipole moment is 3.51 D. In model 4-II two cations of 3-trimethylammonium-benzoic acid, A and B, are linked by an asymmetric and medium strong O(1)-H···O(11) hydrogen bond of 2.585 Å. The so-formed dimer is linked to the 3-trimethylammonium-benzoate zwitterion C by the O(12)-H…O(21) hydrogen bond with a distance of 2.494 Å (Table S7 in the ESI<sup>†</sup>). The orientation of the carboxylic group is *cis* in cation A and trans in cation B. The benzoic acid moieties have  $N^+ \cdots I^-$  distances varying from 4.270 to 4.793 Å (Table S8 in the ESI<sup>†</sup>). The calculated energy of 4-II is -15 622.6660630 a.u. and the dipole moment is 7.60 D. The energy difference between 4-II and 4-I,  $\Delta E = 0.0052596$  a.u., indicates that structure 4-II is more stable by 13.8 kJ mol<sup>-1</sup>.

# FTIR spectra

The solid-state spectra of the polymorphs of [di-(3-trimethylammonium-benzoic acid)-(3-trimethylammonium-

benzoate)]diiodide (1-I and 1-II) are similar. The spectrum is shown in Fig. 6a. There are two broad absorptions in the spectrum: at 2480 cm<sup>-1</sup> attributed to the *v*O–H vibration of the bond engaged in the medium-strong O–H···O hydrogen bond and in the 1300–850 cm<sup>-1</sup> region centered at 1100 cm<sup>-1</sup>, which is typical of the O–H···O hydrogen bond shorter than 2.5 Å.<sup>30</sup> The  $v_{as}$ COO and *v*C=O vibrations appear at 1683 cm<sup>-1</sup>.

Fig. 6b shows the spectrum of trimethylammoniumbenzoic acid iodide (2). The strong and narrow band at  $1716 \text{ cm}^{-1}$  is attributed to the *v*COOH vibration.

## Conclusions

In the series of finite zwitterion:protonated-zwitterion carboxylate-carboxyl aggregates, a 3-membered interval of [di-(3trimethylammonium-benzoic acid)-(3-trimethylammoniumbenzoate)]diiodide complex (1), of stoichiometry 3:2, has been obtained for the first time. Complex 1 crystallizes as two polymorphs, at least. Also a 1:1 complex stoichiometry of 3-trimethylammonium-benzoate with hydroiodic acid was obtained in reiterated crystallizations of varied acidity solutions. The interval aggregates in the 3:2 complexes are stabilized by two short hydrogen bonds between the carboxylate and the carboxyl groups, as well as electrostatic forces between the iodide anions and the quaternary nitrogen atoms. The theoretically optimized structures of the 1:1 and 2:1 complexes are much less preferred energetically than the 3:2 complex; however the theoretically optimized 1:1 complex significantly differs in the interionic interactions from the experimentally determined structure, where OH…I bonds are formed. It shows that the energies calculated for isolated ionic aggregates can be irrelevant for predicting the complexes of different stoichiometries. Nonetheless, the synthesized 1:1 (2) and 3:2 (1-I and 1-II) complexes are the only complexes of different stoichiometries between a benzbetaine and a mineral acid deposited with the Cambridge Structural Database so far. It is still not clear how strongly this stoichiometry for specific stoichiometries of betaine complexes depends on the molecular structure of betaines themselves. Thus the understanding of these preferences still requires further investigation. The lattice dimensions of polymorphs 1-I and 1-II are remarkably similar, which result in some similarities in their powder-diffraction patterns (Fig. S5<sup>†</sup>). Complexes 1:1 and 3:2 are clearly distinguishable by their FTIR spectra, due to significantly different interactions in these structures.

# Acknowledgements

DFT calculations were performed at the Poznań Supercomputing and Networking Centre and supported in part by PL-Grid Infrastructure.

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