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Search for molecular crystals with NLO properties: 5-Sulfosalicylic acid with nicotinamide and isonicotinamide

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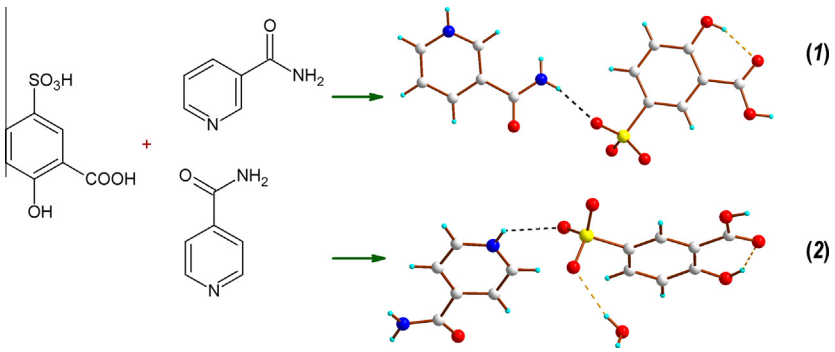
HIGHLIGHTS

- Novel salts **1–2** of nicotinamide and isonicotinamide with 5-sulfosalicylic acid are prepared.
- These salts are characterized by X-ray and IR studies as well as SGH measurements.
- Salts **1** and **2** crystallize in *Pca*2$_1$ and *Pbca* space groups, respectively.
- Crystal structure analysis revealed different structural hydrogen-bonded motifs to distinguish **1** and **2**.
- Salt 1 shows relatively efficient second harmonic frequency generation.

GRAPHICAL ABSTRACT



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ABSTRACT

Two proton transfer hydrogen-bonded complexes of 5-sulfosalicylic acid (3-carboxy-4-hydroxybenzenesulfonic acid, 5-SSA) with the aromatic amides: nicotinamide (NA) and isonicotinamide (INA), are characterized by X-ray diffraction and spectroscopic studies. In the crystal structures of nicotinamidium 3-carboxy-4-hydroxybenzenesulfonate, **1**, and isonicotinamidium 3-carboxy-4-hydroxybenzenesulfonate monohydrate, **2**, the ions are linked into three dimensional frameworks by a combination of O–H···O, N–H···O and C–H···O hydrogen bonds and cation–anion π–π stacking interactions. The hydrogen-bonding behavior of the pyridine N atom is different in the two crystals, bonding to a sulfonate O atom of anion in **2** but to a carbonyl O atom of cation in **1**. The complex **1** shows relatively efficient second harmonic frequency generation.

Introduction

The last decades have witnessed a tremendous interest in molecular materials and soft condensed matter [1]. An important class of molecular materials is the nonlinear optically active (NLO) crystals [2–4]. The discovery of new materials exhibiting nonlinear optical properties in the combination with desirable physical properties (optical transparency, thermal, optical and mechanical stability) continues to be an important goal in nonlinear optics. Essential applications of these materials lie in the areas of optical signal processing, as well as storage and other information processing tasks [4].

Relatively recently, a very efficient new approach has been developed for obtaining new molecular materials with NLO

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properties [5,6]. The method is based on acid–base hydrogen bond interactions and molecular recognition. A molecular crystal is build from an inorganic or organic acid and an organic base (chromophore molecule). It is assumed that the acid part is responsible for favorable mechanical and thermal properties, due to strong hydrogen bond interactions which stabilize the crystal lattice [6]. The organic part, due to its relatively high hyperpolarizability value, is mainly responsible for nonlinear optical properties of the crystal [4]. Perhaps it would be interesting to notice that the hydrogen bond also plays a important role in the creation of non-centrosymmetric structures of crystals [7] and contributes to the molecular quadratic hyperpolarizability of such systems [8–11].

We previously characterized the molecular complexes of amides (nicotinamide and isonicotinamide) with 3-nitrophenol [12]. Both complexes do not involve proton transfer, but reveal features to distinguish the co-crystals. The primary direct N(pyridine)···H–O(hydroxyl) hydrogen bonding is found in the isonicotinamide co-crystal. On the contrary, the nicotinamide co-crystal contains O(hydroxyl)–H···O(carboxyl) and N(amine)–H···N(pyridine) hydrogen bonds and also shows relatively efficient second harmonic frequency generation [12].

In the present paper we have replaced 3-nitrophenol by very strong 5-sulfosalicylic acid which contains five O–H bonds in three substituent groups (the sulfonic, carboxylic and phenolic groups), and it may give mono-, di- or tri-anionic ligand species through deprotonation, and may be useful to build potentially optical materials. Furthermore with deprotonation of sulfonic group, the three oxygen atoms provide an additional set of potential acceptor sites for hydrogen bonding associations. With these adducts three-dimensional hydrogen bonding network are common, although cation–cation or cation–anion aromatic ring π–π interactions are rare. The self-assembly process of crystallization often requires the incorporation of water molecules in these structures [13–16].

It was interesting to check the possibility to associate the sulfonate groups to nicotinamide and isonicotinamide. This work deals with the synthesis, crystal structure, spectroscopic studies and optical characterization of new one proton transfer compounds, namely nicotinamidium 3-carboxy-4-hydroxybenzenesulfonate, **1**, and isonicotinamidium 3-carboxy-4-hydroxybenzenesulfonate monohydrate, **2**.

Experimental

Synthesis

Nicotinamide (NA), isonicotinamide (INA) and 5-sulfosalicylic acid (5-SSA) are commercial reagents from Fluka. Reagents and solvents were used as purchased without further purification. The target compounds were prepared by dissolving a 1:1 ratio of 5-SSA (0.213 g) and, respectively, NA and INA (0.100 g) in 10 ml of methanol–water mixture (1:2) and heated to dissolve the solid. When the solutions became homogeneous, they were cooled and crystals of nicotinamidium 3-carboxy-4-hydroxybenzenesulfonate, **1**, and isonicotinamidium 3-carboxy-4-hydroxybenzenesulfonate monohydrate, **2**, were obtained by slow evaporation. Elemental analysis, IR spectra and X-ray structural investigations confirmed the chemical formulae of the title compounds. **1**: $C_{13}H_{12}N_2O_7S$ found C, 45.93; H, 3.48; N, 8.17; S, 9.76%; **2**: $C_{13}H_{14}N_2O_8S$ found C, 43.43; H, 3.86; N, 7.89; S, 8.94%.

X-ray data collection

Details of data collections, analyses and refinements for the studied crystals are given in Table 1. The crystallographic measurements for **1** and **2** were performed on a Xcalibur PX four-circle diffractometer with Onyx (for **1**) or Ruby (for **2**) CCD camera. The intensity data were collected at 100(2) and 90(2) K, respectively for **1** and **2**, using graphite-monochromatized Mo K_α radiation (λ = 0.71073 Å). Data collection, cell refinement, and data reduction and analysis were carried out with the Xcalibur PX software (CrysAlis PRO) [17].

Table 1
Crystal data and structure refinement for salts **1** and **2**.

	1	**2**
Empirical formula	$C_{13}H_{12}N_2O_7S$	$C_{13}H_{14}N_2O_8S$
Moiety formula	$C_6H_7N_2O^+ \cdot C_7H_5O_6S^-$	$C_6H_7N_2O^+ \cdot C_7H_5O_6S^- \cdot H_2O$
Formula weight (g)	340.31	358.32
Temperature (K)	100(2)	90(2)
λ (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	$Pca2_1$	$Pbca$
Unit cell dimensions (Å, °)	a = 16.141(7)	a = 13.457(3)
	b = 6.720(2)	b = 12.651(3)
	c = 12.628(5)	c = 16.790(4)
Volume (Å^3)	1369.7(9)	2858.4(12)
Z	4	8
Absorption coefficient (mm^{-1})	0.279	0.277
Calculated density ($mg\ m^{-3}$)	1.650	1.665
$F(000)$	704	1488
Crystal size (mm)	0.45 × 0.25 × 0.14	0.26 × 0.24 × 0.09
θ range (°)	4.9–35.0	2.86–28.78
Index ranges	$-26 \leqslant h \leqslant 20$	$-17 \leqslant h \leqslant 15$
	$-9 \leqslant k \leqslant 8$	$-17 \leqslant k \leqslant 10$
	$-20 \leqslant l \leqslant 14$	$-21 \leqslant l \leqslant 13$
Collected reflections	15,436	8385
Unique reflections, R_{int}	4257, 0.044	3303, 0.022
Observed reflections [$I > 2\sigma(I)$]	3097	2782
Parameters	223	238
Goodness-of-fit on F^2	1.001	1.029
R_1 [$I > 2\sigma(I)$]	0.0389	0.0337
wR_2 [all data]	0.0726	0.0870
Largest diff. peak and hole (e Å^{-3})	0.37 and −0.53	0.38 and −0.45

The structures were solved by direct methods using the SHELXS-97 program [18] and refined on F^2 by full-matrix least squares with anisotropic thermal parameters for all non-H atoms using SHELXL-97 [18]. All H atoms were found in difference Fourier maps and were refined isotropically. In the final refinement cycles, the C-bonded H atoms were positioned geometrically and treated as riding atoms, with C–H = 0.95 Å, and with $U_{iso}(H) = 1.2U_{eq}(C_{aryl})$. The N- and O-bonded H atoms were refinement with $U_{iso}(H) = 1.2U_{eq}(N)$ and 1.5 $U_{eq}(O)$, respectively.

Complete crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre; CCDC reference numbers 968379-968380. These data 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; e-mail: deposit@ccdc.cam.uk).

Spectroscopic measurements

The FT-IR powder spectra of both complexes were recorded on a Bruker IFS-88 spectrometer with a resolution of 2 cm^{-1} using samples in KBr pellets at room temperature.

SHG measurements

The quadratic NLO response of compounds **1** and **2** was evaluated by performing second harmonic generation (SHG) on powder

samples of **1** and **2** using the modified Kurtz–Perry method [19]. About 50 mg of compound is inserted into a sample holder, made of two Pyrex (25 × 75 × 1) mm microscope slides separated by a thin (0.3 mm thick) spacer. The corresponding space is filled with the NLO powder sandwiched between the two slides. A 1.064 μm fundamental laser beam is emitted by a Q-switched Nd^{3+};YAG nanosecond laser (SAGA from Thales Laser) at a 10 Hz repetition rate. A Schott RG 1000 filter is used to filter out any remaining visible light from the IR incident laser beam. The second harmonic signal at 532 nm is detected by a photomultiplier (Hamamatsu) and its intensity is measured on an oscilloscope screen. The SHG signal must be compared to a reference nonlinear material, here a urea powder.

Results and discussion

Crystal structures

*Nicotinamidium 3-carboxy-4-hydroxybenzenesulfonate – **1***

Compound **1** exists as an organic–organic salt, the H atom of sulfonic group being transferred to the pyridine N atom (Fig. 1). Surprisingly, there is no solvent molecule in **1**. The structures of 5-SSA salts usually incorporate at least one solvent molecule and only few anhydrous compounds are known [13,20,21]. Deprotonation of sulfonic group was confirmed by comparing the S–O (1.456(1), 1.474(2) and 1.457(1) Å) bond lengths (Table 2). The hydroxyl and carboxyl groups of 5-SAA^- lie approximately in the ring plane of anion with deviations of 0.023(3) and −0.051(3) Å for atoms O31 and O21, respectively. The protonation of the cation is confirmed by C–N bond distances (1.333(3) and 1.346(3) Å) and the C–N–C (123.2(2)°) bond angle (Table 2). The pyridine rings of the nicotinamidium are slightly distorted from planarity with the largest deviations from an aromatic ring plane occurring for the atom C4 (−0.016(2) Å). The carboxamide group is twisted with respect to the aromatic ring; the dihedral angle between the carboxamide group and the pyridine ring plane is 19.9(4)°. Nicotinamidium cation (NA^+) adopts a *syn* conformation with the heterocyclic N and amide N atoms located on the same side of the cation [torsion angle C2–C3–C7–N7 is −21.0(3)° (Table 2)]. A similar conformation has been observed in the previously described nicotinamide-nitrophenol complex [12], and also in other complexes with NA [22–24].

Each NA^+ is connected to an adjacent NA^+ *via* N1–H1···O7^{ii} hydrogen bonds, between the pyridine hetero N and the carbonyl O atoms, to form a C(6) chain along the *c*-axis (shown as ball-and-stick style) [25]. Similarly, adjacent 5-SSA^- ions are joined via O21–H20···O51^{i} hydrogen bonds, to give an infinite C(8) chain running down the *a*-axis (shown as sticks) (Fig. 2a). Cation–cation chains (C(6)) are alternated with anion–anion chains (C(8)), and are linked into a three-dimensional network by N7–H71···O61 and N7–H72···O41^{iii} hydrogen bonds formed between the carboxyamide groups of cation and the sulfonate O atoms of anions (Table 3 and Fig. 2b).

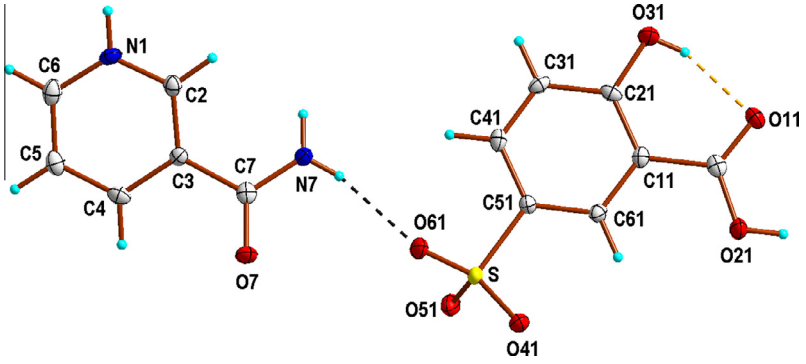

Fig. 1. The molecular structure of **1**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Table 2
Selected geometric parameters (Å, °) for salts **1–2**.

	1	2		1	2
Cation			*Anion*		
N1–C2	1.333 (3)	1.342 (2)	S–O41	1.4560 (14)	1.4567 (11)
N1–C6	1.346 (3)	1.340 (2)	S–O51	1.4736 (15)	1.4798 (11)
C2–C3	1.383 (3)	1.375 (2)	S–O61	1.4567 (14)	1.4464 (11)
C3–C4	1.394 (3)	1.395 (2)	S–C51	1.773 (2)	1.770 (2)
C4–C5	1.393 (3)	1.397 (2)	O11–C71	1.225 (2)	1.228 (2)
C5–C6	1.376 (3)	1.380 (2)	O21–C71	1.320 (3)	1.324 (2)
C3–C7/C4–C7	1.507 (3)	1.514 (2)	O31–C21	1.345 (2)	1.344 (2)
C7–O7	1.236 (2)	1.232 (2)	C11–C21	1.399 (3)	1.412 (2)
C7–N7	1.330 (2)	1.328 (2)	C11–C71	1.485 (2)	1.482 (2)
N1–C2–C3	119.9 (2)	119.67 (14)	O11–C71–O21	123.5 (2)	122.31 (14)
C2–N1–C6	123.2 (2)	122.59 (14)	O21–C71–C11	114.5 (2)	114.65 (12)
O7–C7–N7	123.7 (2)	124.29 (14)	O31–C21–C11	123.2 (2)	123.76 (13)
N7–C7–C3/N7–C7–C4	117.5 (2)	117.50 (14)	O31–C21–C31	117.0 (2)	116.53 (13)
O7–C7–C3/O7–C7–C4	118.8 (2)	118.21 (13)	S–C51–C61	119.4 (2)	121.32 (12)
C2–C3–C7–O7/C5–C4–C7–O7	158.3 (2)	165.75 (14)	O31–C21–C11–C71	−1.2 (3)	−0.5 (2)
C4–C3–C7–O7/C3–C4–C7–O7	−17.7 (3)	−12.1 (2)	O41–S–C51–C61	23.9 (2)	17.30 (14)
C2–C3–C7–N7/C5–C4–C7–N7	−21.0 (3)	−13.4 (2)	O51–S–C51–C61	−95.9 (2)	−101.38 (13)
C4–C3–C7–N7/C3–C4–C7–N7	163.0 (2)	168.77 (13)	O61–S–C51–C61	144.5 (2)	139.08 (12)

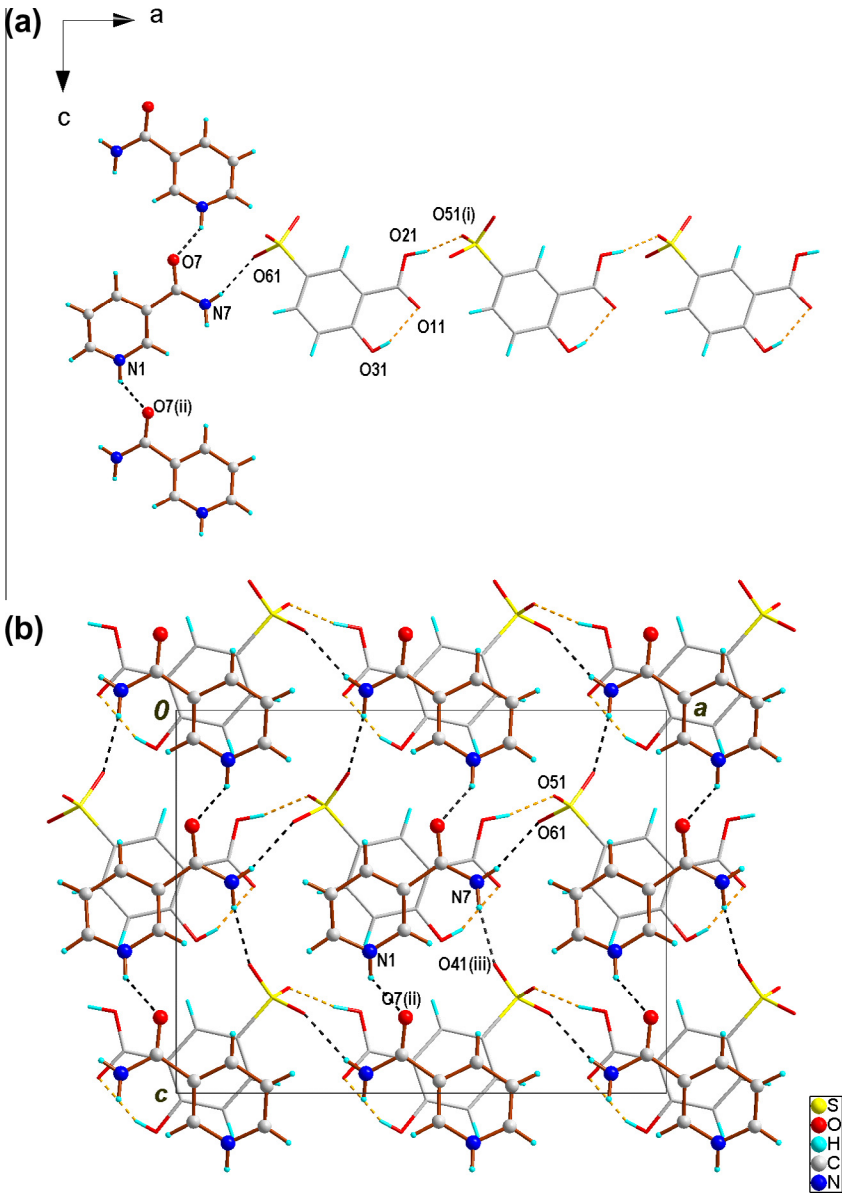

Fig. 2. A packing diagram of **1** viewed down the *b*-axis, showing anion–anion and cation–cation interactions via O–H···O (orange dashed lines) and N–H···O hydrogen bonds (black dashed lines), respectively in (a), and showing 3D architecture of the crystal. Symmetry codes are given in Table 3. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 3
Hydrogen-bond geometry for **1** (Å, °).

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	D–H···A
O21–H20···O51^{i}	0.89 (2)	1.71 (2)	2.591 (2)	167 (2)
O31–H30···O11	0.77 (2)	1.89 (3)	2.611 (2)	156 (3)
N1–H1···O7^{ii}	0.89 (2)	1.90 (2)	2.662 (2)	143 (2)
N7–H71···O61	0.78 (2)	2.10 (2)	2.864 (2)	166 (2)
N7–H72···O41^{iii}	0.88 (3)	1.99 (3)	2.866 (3)	170 (2)
C2–H2···O41^{iii}	0.95	2.56	3.339 (3)	140
C5–H5···O11^{iv}	0.95	2.41	3.186 (2)	139
C61–H61···O31^{v}	0.95	2.53	3.258 (3)	133

Symmetry codes: (i) $x + 1/2, -y + 1, z$; (ii) $-x + 1, -y, z + 1/2$; (iii) $-x + 3/2, y, z + 1/2$; (iv) $x - 1, y, z$; (v) $-x + 2, -y + 1, z - 1/2$.

The three-dimensional framework is interlinked by weak C–H···O hydrogen bonding interactions (Table 3), and stack down the *b*-axis, the alternating cation–anion–cation separation indicating π–π interactions. The distances between the centroids of N1–C6 ring at (*x*, *y*, *z*) and C11–C61 rings at ($x - 1/2$, $-y$, z) and ($x - 1/2$, $-y + 1$, z) are 3.458(3) and 3.756 Å, with the an interplanar spacing of 3.254(2) and 3.280(2) Å, and a centroid offset of 1.17 and 1.83 Å, respectively. The angle between the planes of these rings is 5.76(5)°.

*Isonicotinamidium 3-carboxy-4-hydroxybenzenesulfonate monohydrate - **2***

Contrary to **1**, complex **2** crystallizes as a monohydrate (Fig. 3). The C–N (1.342(2) and 1.340(2) Å) and S–O bond distances (1.457(1), 1.480(1) and 1.446(1) Å) indicate that the pyridine N atom of INA is protonated and the sulfonic group of 5-SSA is deprotonated. The hydroxyl and carboxyl groups of 5-SAA^{-} ion deviate from the benzene ring plane, with deviations of 0.042(3), −0.077(3) and 0.087(3) Å for atoms O31, O21 and O11, respectively. The pyridine ring of INA^{+} ion is nearly planar; the largest deviation from an aromatic ring plane occur for atom N1 (−0.006(2) Å). The carboxamide group is twisted with respect to

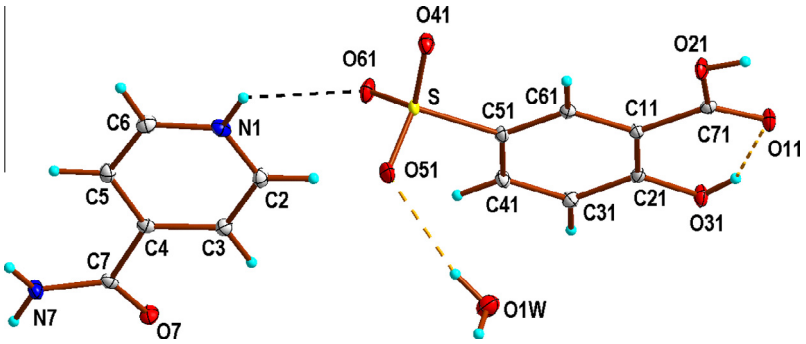

Fig. 3. The molecular structure of **2**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

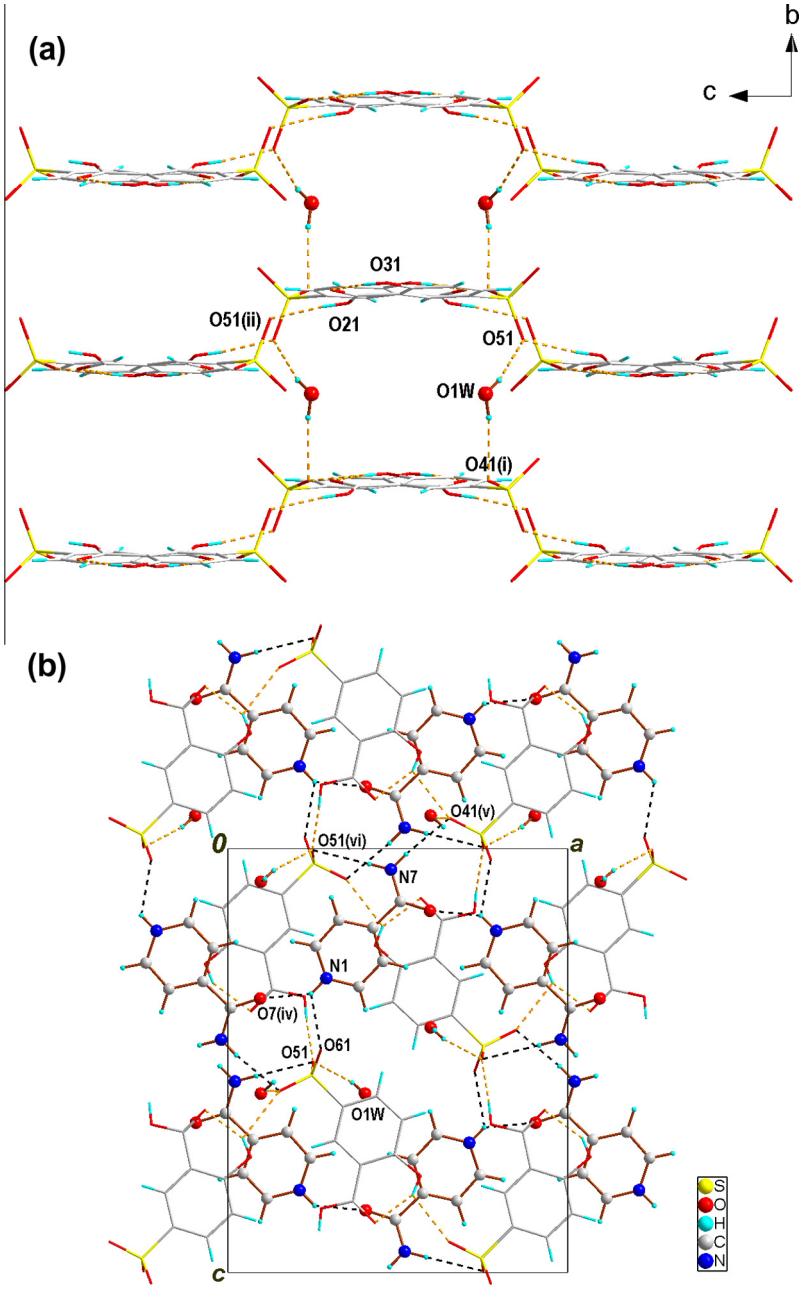

Fig. 4. A packing diagram of **2** viewed down the *a*-axis, showing anions and water molecules organized via O–H···O hydrogen bonds (orange dashed lines) in (a), and viewed down the *b*-axis, showing 3D architecture of the crystal, formed by O–H···O (orange dashed lines) and N–H···O hydrogen bonds (black dashed lines) in (b). Symmetry codes are given in Table 4. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 4
Hydrogen-bond geometry for **2** (Å, °).

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	D–H···A
O1W–H1W···O51	0.82 (2)	2.18 (2)	2.989 (2)	168 (2)
O1W–H2W···O41^{i}	0.81 (2)	2.18 (2)	2.985 (2)	171 (2)
O21–H20···O51^{ii}	0.86 (2)	1.81 (2)	2.664 (2)	174 (2)
O31–H30···O11	0.82 (2)	1.88 (2)	2.612 (2)	149 (2)
O31–H30···O41^{iii}	0.82 (2)	2.37 (2)	2.868 (2)	120 (2)
N1–H1···O61	0.86 (2)	2.25 (2)	2.834 (2)	125 (2)
N1–H1···O7^{iv}	0.86 (2)	2.05 (2)	2.756 (2)	138 (2)
N7–H71···O41^{v}	0.85 (2)	2.24 (2)	3.091 (2)	174 (2)
N7–H72···O51^{vi}	0.89 (2)	2.54 (2)	3.410 (2)	166 (2)
C2–H2···O61	0.95	2.38	2.920 (2)	116
C61–H61···O31^{vii}	0.95	2.56	3.453 (2)	157

Symmetry codes: (i) $-x+1/2, y-1/2, z$; (ii) $-x+1/2, -y+1, z+1/2$; (iii) $x+1/2, y, -z+3/2$; (iv) $x-1/2, y, -z+1/2$; (v) $x+1/2, y, -z+1/2$; (vi) $-x+1/2, -y+1, z-1/2$; (vii) $x-1/2, y, -z+3/2$.

the aromatic ring; the dihedral angle between the carboxamide group and pyridine ring plane is 12.8(3)°.

In the crystal structure of **2**, each adjacent 5-SSA^{-} ions are joined *via* O21–H20···O51^{ii} hydrogen bonds. These ions are further organized into corrugated layers *via* other O31–H30···O41^{iii} hydrogen bonds formed between the hydroxyl groups and the sulfonate O41 atoms. The molecule is involved in hydrogen bonds with atoms O51 and O41 of two different of 5-SSA^{-} ions of adjacent layers (O1W–H1W···O51 and O1W–H2W···O41^{i}) (Fig. 4a). The role of water molecule in the overall hydrogen-bonding pattern of the O–H···O interactions in **2** displays similarities to the previously reported salts by Meng et al. [15]. Cations (shown as ball-and-stick style) and anions (shown as sticks) are linked to each other by the N–H···O hydrogen bonds. The pyridine atom N1 acts as a bifurcated hydrogen-bond donor to the carbonyl atom O7 of INA^{+} and the sulfonate atom O61 of 5-SSA^{-} (N1–H1···O7^{iv} and N1–H1···O61). Similarly, the amine atom N7 is involved in bifurcated hydrogen bonds from sulfonate atoms O41 and O51 of two different 5-SSA^{-} ions (N7–H71···O41^{v} and N7–H72···O51^{vi}). In this way, a three-dimensional network is created (Fig. 4b and Table 4).

Additional stabilization is provided by weak C–H···O hydrogen bonds (Table 4) and also cation–anion π–π stacking interactions. The distance between the centroids of N1–C6 ring at (x, y, z) and C11–C61 rings at $(x, -y+3/2, z-1/2)$ is 3.530(3) Å, and the interplanar spacing and the centroid offset are 3.243(3) and 1.39 Å, respectively. The angle between the planes of these rings is 1.02(3)°.

Infrared spectra

The IR spectra of the studied complexes are presented in Figs. 5 and 6. As can be seen in both complexes a large absorption is observed in the ~1860–3600 cm^{-1} range, though with different profiles in two salts. In this region one expects to find an absorption coming from stretching vibrations of *v*(X–H) modes engaged in medium strong hydrogen bond of O–H···O, N^{+}–H···O^{-} and C–H···O types. The origin of the observed broad absorption with a complex structure in the infrared region of hydrogen-bonded solids has been widely discussed in the literature [26,27]. It is well established that in solids the main band shaping mechanism of the v(XH) band is phonon coupling effects, i.e. a strongly anharmonic coupling mechanism between the high-frequency hydrogen stretching vibration and the low-frequency lattice phonons. However in many cases one should expect also a Fermi resonance interaction between the fundamental vibration v(X–H) and the overtones or combination tones of intramolecular vibrations, leading to the substructure of bands. The detailed assignment of the spectra in lower frequency region is difficult and will be the subject of a separate paper, on the use of DFT calculations.

SHG properties

The studied crystals consist of complex π electronic molecular hydrogen-bonded systems with the electron donor–acceptor groups. Due to hydrogen bond interactions and proton transfer, one should expect some changes of molecular quadratic hyperpolarizabilities of the interacting molecules [28]. For example the calculated molecular hyperpolarizabilities for nicotinamide and

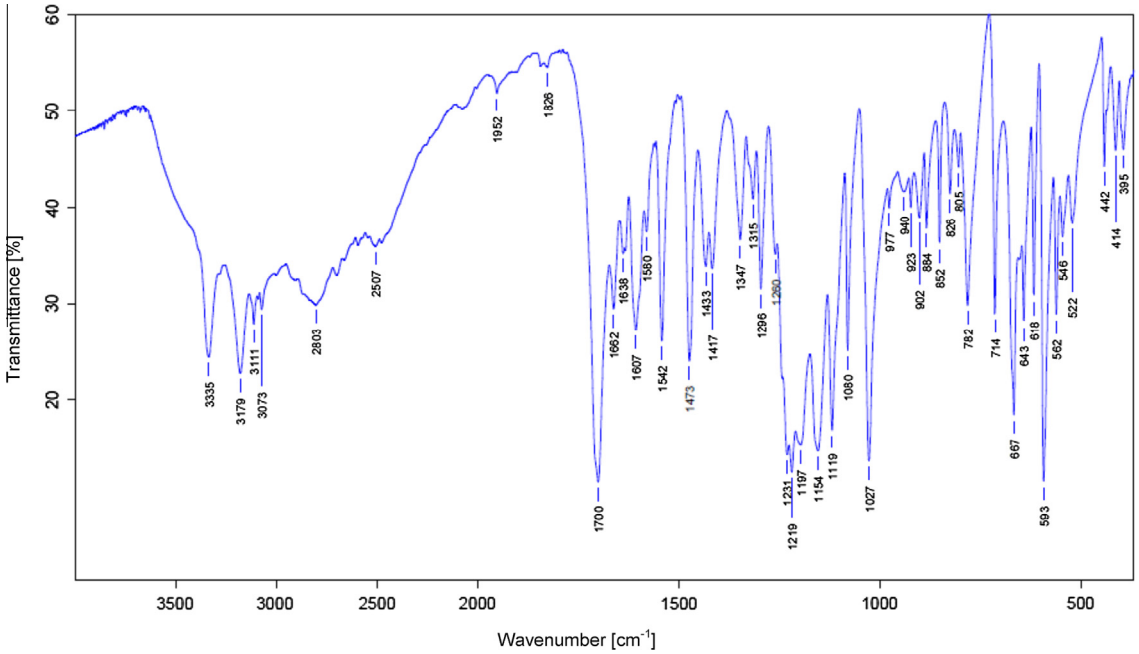

Fig. 5. Infrared spectrum of **1** in KBr pellet.

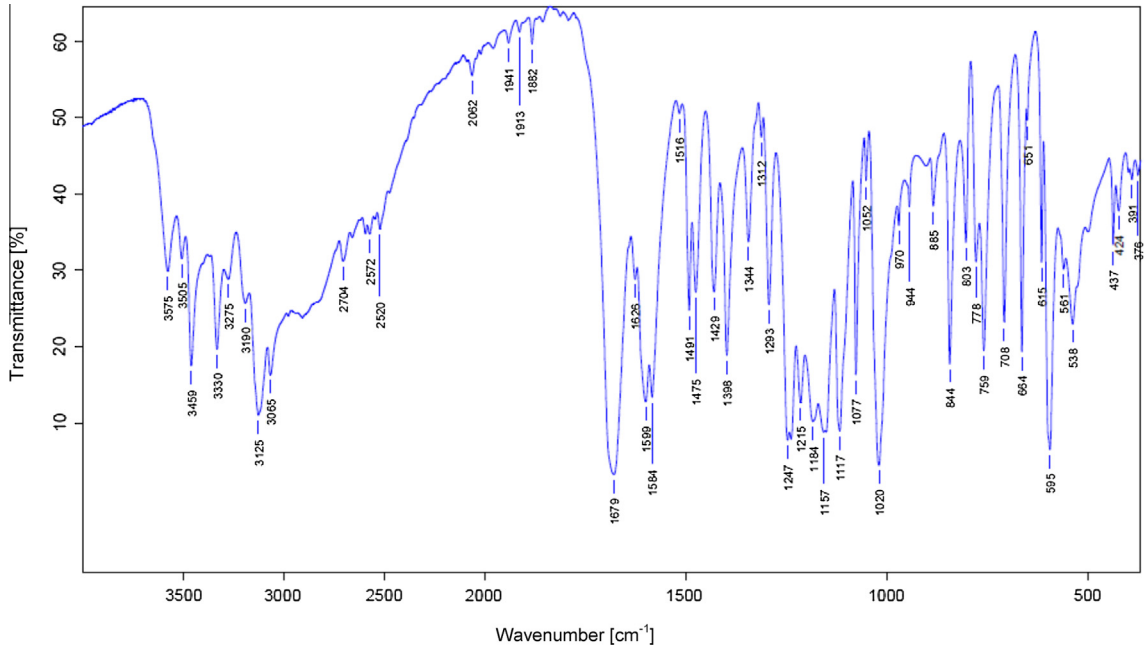

Fig. 6. Infrared spectrum of **2** in KBr pellet.

isonicotinamide are 1.81×10^{-30} and 0.74×10^{-30} esu respectively and their protonated species are 4.64×10^{-30} and 5.20^{-30} esu, respectively [29]. Complex **1** generates a second harmonic signal comparable to that from urea. This noticeable second harmonic response confirms the interest of H-bond complexes involving ionic molecules for the design and elaboration of novel nonlinear optical crystals with improved mechanical and crystal growth properties as compared to a single component of organic materials. Further studies should be focused on single crystal elaboration and nonlinear characterization.

Conclusions

Molecular hydrogen-bonded salts of nicotinamide and isonicotinamide with 5-sulfosalicylic acid have been characterized by X-ray diffraction, IR spectroscopic studies and the second harmonic generation measurements. Salt 1 crystallizes in non-centrosymmetric $Pca2_1$ space group, whereas salt 2 crystallizes in centrosymmetric *Pbca* space group. The crystal structure analysis showed that these hydrogen-bonded salts contain different structural hydrogen-bonded motifs. For instance, the hydrogen-bonding behavior of the pyridine N atom is different in the two crystals, bonding to a sulfonate O atom of anion in **2** but to a carbonyl O atom of cation in **1**. Additionally, the nicotinamidium 3-carboxy-4-hydroxybenzenesulfonate (**1**) shows relatively efficient second harmonic generation and is a promising material for frequency-doubling applications.

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