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Two salts of 5-sulfosalicylic acid and 3-aminopyridine

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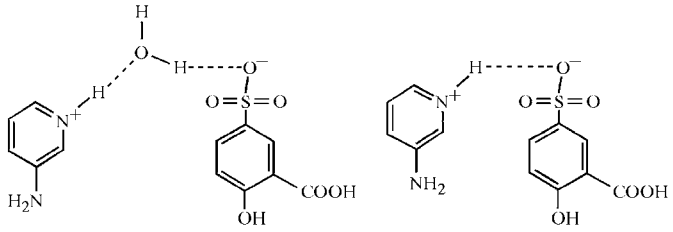
5-Sulfosalicylic acid (5-SSA) and 3-aminopyridine (3-APy) crystallize in the same solvent system, resulting in two kinds of 1:1 proton-transfer organic adduct, namely 3-aminopyridinium 3-carboxy-4-hydroxybenzenesulfonate monohydrate, $C_5H_7N_2^+\cdot C_7H_5O_6S^-\cdot H_2O$ or 3-APy·5-SSA·H_2O, (I), and the anhydrous adduct, $C_5H_7N_2^+\cdot C_7H_5O_6S^-$ or 3-APy·5-SSA, (II). Both compounds have extensively hydrogen-bonded three-dimensional layered polymer structures, with interlayer homo- and heterogeneous π–π interactions in (I) and (II), respectively.

Comment

Recently, much attention has been devoted to the design and synthesis of supramolecular architectures assembled *via* various weak noncovalent interactions, such as hydrogen bonds, π–π stacking and C—H$\cdots\pi$ interactions (Remenar *et al.*, 2003; Aakeröy *et al.*, 2001; Sokolov *et al.*, 2006). 5-Sulfosalicylic acid, 5-SSA, is a particularly strong organic acid which is capable of protonating N-containing heterocycles and other Lewis bases (Smith *et al.*, 2004, 2005, 2005*a*,*b*, 2006; Smith, 2005; Muthiah *et al.*, 2003; Raj *et al.*, 2003; Fan *et al.*, 2005; Wang & Wei, 2007). As part of our research programme aiming to gain further insight into hydrogen-bonding interactions involving 3-aminopyridine (3-APy) and 5-SSA, the present work has been undertaken. Two types of organic salts are formed from the same mixed solution of 3-APy and 5-SSA. We report here the molecular and supramolecular structures of 3-aminopyridinium 5-sulfosalicylate monohydrate, (I), and 3-aminopyridinium 5-sulfosalicylate, (II).



Similar to the analogous organic adducts reported by Smith and co-workers, the H atoms are transferred from the sulfonic acid group to the pyridine N atoms in both compounds (Fig. 1). One solvent water molecule is included in the molecular structure of (I), which acts as a linkage between 3-APy cations and 5-SSA anions. There is no solvent molecule in (II) (Fig. 1), although methanol and water were both present in the mixed solution of 3-Apy and 5-SSA. The monohydrate, (I), consists of one 3-APy anion, one 5-SSA anion and a solvent water molecule, with $Z' = 1$. However, the anhydrous structure of (II) has $Z' = 2$, with two 3-APy–5-SSA pairs in the selected asymmetric unit which are not related by any symmetry operation of the space group $P2_1/n$. Although the origin of these contrasting Z' values in the two compounds is largely unambiguous, the higher Z' structure of (II) may be a metastable relic of fast-growing crystal nuclei (Das *et al.*, 2006; Anderson & Steed, 2007), and this conclusion is perhaps justified by the much higher yield of the brown crystals of (I) than of the pale-yellow crystals of (II).

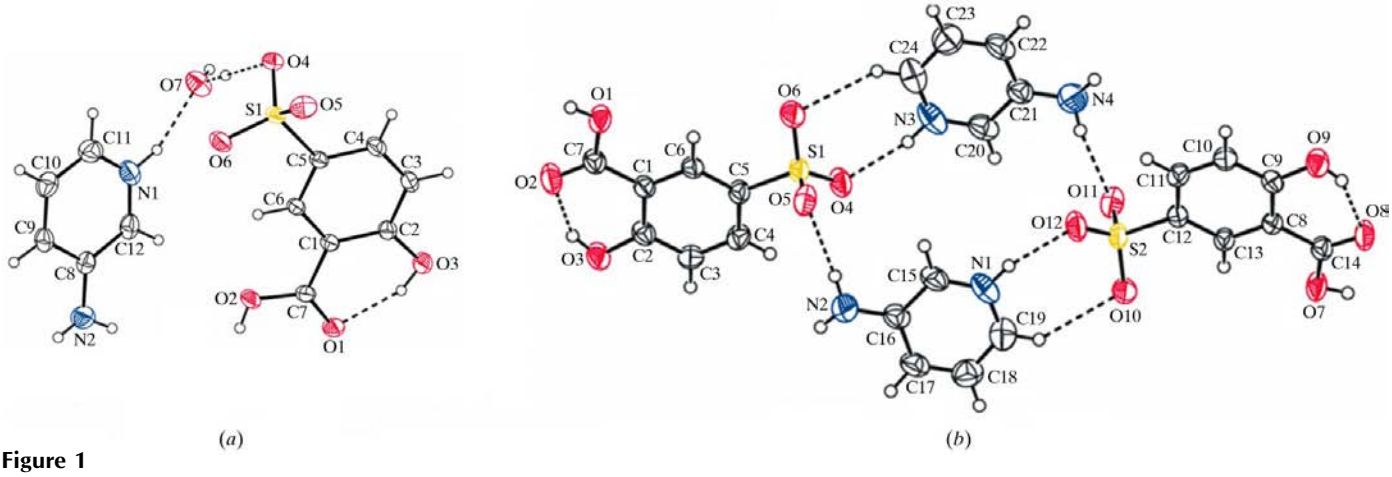


Figure 1
The molecular structures of (*a*) (I) and (*b*) (II), showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

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Maybe owing to the difference in hydrogen bonds involving the sulfonate group, the conformation of the sulfonate groups with respect to the benzene rings is different in the two structures. In (I), the plane defined by three sulfonate O atoms is almost perpendicular to the attached benzene ring, with a dihedral angle of 89.6 (1)° and with the closest distance of the three O atoms to the benzene ring being only about 0.134 Å. However, the corresponding angles and distances in (II) are 83.2 (1)° and *ca* 0.387 Å for the anion containing atom S1, and 86.8 (1)° and *ca* 0.570 Å for the anion containing atom S2.

In the crystal structures of both compounds, the molecules are linked into three-dimensional frameworks by a combination of O—H···O, N—H···O and C—H···O hydrogen bonds and π–π stacking interactions. In (I), the supramolecular structure can be readily analysed in terms of simple substructures.

In the first of these substructures, water atom O7 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* atoms H7*A* and H7*B*, respectively, to sulfonate atoms O4 at (x, y, z) and O5 at ($1 + x$, y, z), respectively, so forming a $C_1^2(6)$ (Bernstein *et al.*, 1995) chain running parallel to the [100] direction and generated by translation. Similarly, carboxyl atom O2 in the molecule at (x, y, z) acts as another hydrogen-bond donor, *via* atom H2, to atom O4 at (x, $1 + y$, z), forming a $C(8)$ chain running parallel to the [010] direction. The three O—H···O hydrogen bonds together generate a simple two-dimensional substructure lying in the (001) plane (Fig. 2).

The second substructure is formed by a combination of one C—H···O and three N—H···O hydrogen bonds. Pyridine atom N1 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* atom H1, to water atom O7 in the same asymmetric unit, so forming a finite zero-dimensional substructure. Amine atom N2 acts as a bifurcated hydrogen-bond donor, *via* atoms H2*A* and H2*B*, to sulfonate atoms O4 at (x, $1 + y$, z) and O6 at ($-x$, $2 - y$, $2 - z$), respectively, so linking the adjacent (001) framework into a further two-dimensional sheet running parallel to the (001) direction (Fig. 3) which lies in the domain of $0.331 < z < 1.669$. In the two-dimensional substructure, another weak nonclassical hydrogen bond, C10—H10···O5 [C···O = 3.332 (3) Å and C—H···O = 158 (3)°], and a π–π stacking interaction between adjacent symmetry-related pyridine rings [centroid-to-centroid separation = 3.722 (1) Å and interplanar spacing = 3.412 (1) Å; symmetry code: $-x + 1$,

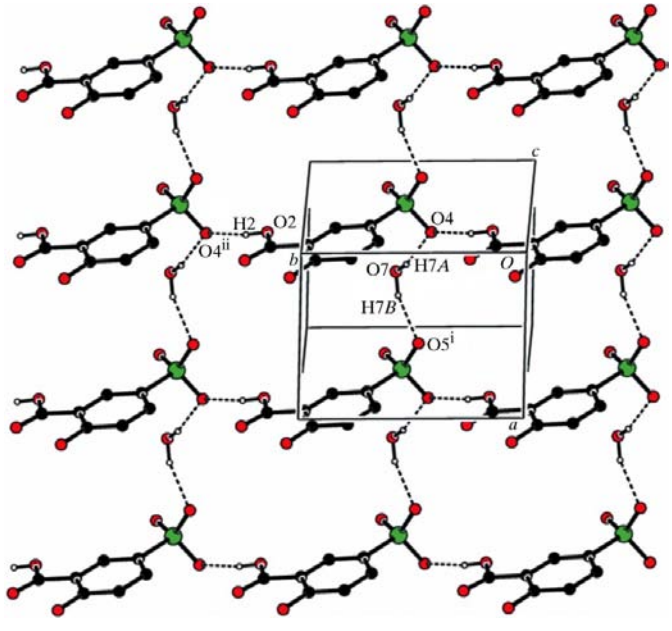

Figure 2
Part of the crystal structure of (I), showing the formation of the two-dimensional network in the (001) plane. Hydrogen bonds are shown as dashed lines. For the sake of clarity, the pyridinium cations and H atoms not involved in the motif have been omitted. [Symmetry codes: (i) $1 + x$, y, z; (ii) x, $1 + y$, z.]

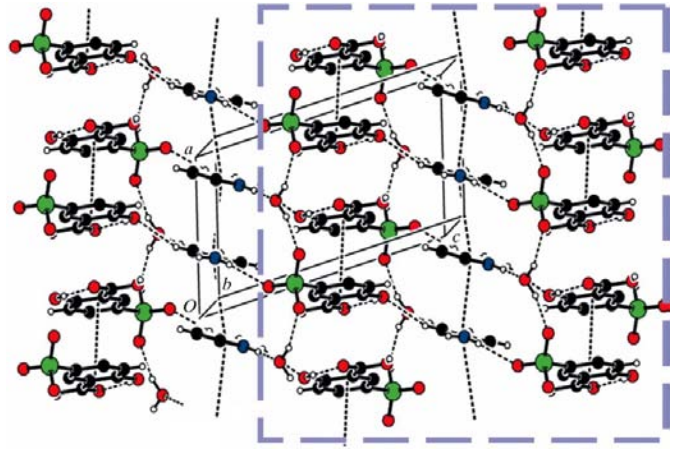

Figure 3
Part of the crystal structure of (I), showing the formation of the three-dimensional network built from hydrogen bonds and π–π interactions (dashed lines). The outlined area shows the (001) framework linked by N2—H···O2/O6 hydrogen bonds.

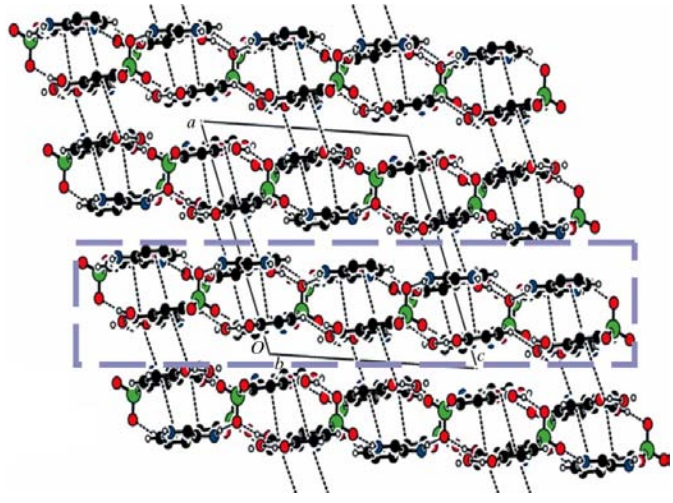

Figure 4
Part of the crystal structure of (II), showing the formation of the three-dimensional network. Hydrogen bonds and π–π interactions are shown as dashed lines. The outlined area shows the (100) network.

$-y+2, -z+2$] further consolidate the supramolecular structure. It is noteworthy that the π–π stacking interaction in (I) is homogeneous (Fig. 3): 3-APy cations stack only on top of 3-APy cations, and 5-SSA anions stack only on top of 5-SSA anions [centroid-to-centroid separation = 4.075 (1) Å and interplanar spacing *ca* 3.574 (1) Å; symmetry code: $1-x, 2-y, 1-z$]. Through these weak π–π interactions between the sulfonate benzene rings and a C12—H12···O3 hydrogen bond [C···O = 3.230 (2) Å and C—H···O = 129 (1)°], a three-dimensional network is formed (Fig. 3).

In the crystal structure of (II), the arrangement of the two sulfosalicylate anions and two aminopyridinium cations in the asymmetric unit is pseudocentrosymmetric. No further symmetry element was found by ADDSYMM in *PLATON* (Spek, 2003). By a combination of a series of X—H···O (X = C, N or O) hydrogen bonds and π–π stacking interactions, the anions and cations are also linked into a three-dimensional network, which can be readily analysed in terms of two simple substructures.

In the first substructure, the combined action of the 14 hydrogen bonds (Table 2) suffices to generate a two-dimensional network running parallel to the (100) direction (Fig. 4). In more detail, amino atom N2 at (x, y, z) acts as a dual hydrogen-bond donor to sulfonate atoms O5 at (x, y, z) and O6 at ($\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$), and atom N4 at ($x$, y, z) acts as a dual hydrogen-bond donor to sulfonate atoms O10 at ($\frac{1}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$) and O11 at ($x$, y, z), so forming two discrete one-dimensional $C_2^2(6)$ chains running parallel to the [010] direction (Bernstein *et al.*, 1995). By comparison, in both (I) and (II), the amino N atoms in the 3-APy cations form hydrogen bonds to sulfonate O atoms. However, the hydrogen-bonding behaviour of the pyridine N atom is completely different in the two compounds, bonding to a sulfonate O atom in (II) but to a water O atom in (I).

Adjacent [010] chains in (II) are interconnected by the remaining hydrogen bonds, producing a simple two-dimensional network running parallel to the (100) direction, and this is further consolidated by π–π stacking interactions (see below). However, unlike the one-dimensional chains formed in (II), the hydrogen bonding in (I) involving amino N2—H···O interactions forms an $R_4^2(12)$ ring only.

For convenience, we denote the benzene ring in (II) containing atom C1 as *A*, the benzene ring containing atom C8 as *B*, the pyridine ring containing atom N1 as *C* and the pyridine ring containing atom N3 as *D*. It is noteworthy that the two-dimensional network is consolidated by π–π stacking interactions between benzene ring *A* and pyridine ring *D* [centroid-to-centroid separation = 3.832 (1) Å and interplanar spacing *ca* 3.527 (1) Å; symmetry code: $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$], and between benzene ring *B* and pyridine ring *C* [centroid-to-centroid separation *ca* 3.727 (1) Å and interplanar spacing *ca* 3.517 (1) Å; symmetry code: $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$]. An analysis using the program *PLATON* (Spek, 2003) indicates that, in the supramolecular structure of (II), adjacent two-dimensional networks are linked by another π–π interaction into a three-dimensional framework (Fig. 4). In detail, benzene ring *B* at (x, y, z) is almost parallel to pyridine ring *D* in the same asymmetric unit, with a dihedral angle of *ca* 6.72 (1)°, a ring centroid separation of 3.707 (1) Å and an interplanar spacing of *ca* 3.506 (1) Å. Unlike (I), the π–π stacking interactions in (II) are heterogeneous (Fig. 4): pairs of 3-APy cations alternate with pairs of 5-SSA anions. The origin of the different π–π stacking patterns in these two compounds may be the effect of the incorporated solvent water molecule in (I), which can facilitate the formation of hydrogen-bonding interactions to a greater extent than any other solvent.

Experimental

All reagents and solvents were used as obtained without further purification. Equivalent molar quantities of 3-aminopyridine (1 mmol, 0.094 g) and 5-sulfosalicylic acid dihydrate (1 mmol, 0.254 g) were dissolved in 95% methanol (20 ml). The mixture was stirred for 10 min at ambient temperature and then filtered. The resulting light-brown solution was kept in air for two weeks. Brown crystals of (I) and pale-yellow crystals of (II) suitable for single-crystal X-ray diffraction analysis were grown by slow evaporation of the solution at the bottom of the vessel. Crystals of (I) and (II) were isolated manually according to the difference in colour and shape.

Compound (I)

Crystal data

$C_5H_7N_2^+\cdot C_7H_5O_6S^-\cdot H_2O$
M_r = 330.31
Triclinic, $P\overline{1}$
a = 7.1447 (4) Å
b = 8.4120 (5) Å
c = 12.3958 (7) Å
α = 80.285 (1)°
β = 74.434 (1)°
γ = 82.718 (1)°
V = 704.78 (7) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.27 mm^{-1}
T = 299 (2) K
0.25 × 0.20 × 0.20 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.924, T_{max} = 0.969
7356 measured reflections
2773 independent reflections
2507 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.146
S = 1.09
2773 reflections
220 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.66 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O7—H7A···O4	0.86 (3)	2.06 (3)	2.894 (2)	163 (3)
O3—H3A···O1	0.84 (3)	1.83 (3)	2.629 (2)	156 (3)
N1—H1···O7	0.89 (3)	1.87 (3)	2.723 (2)	160 (2)
C12—H12···O3^{i}	0.93	2.56	3.230 (2)	129
C10—H10···O5^{ii}	0.93	2.53	3.332 (3)	144
O7—H7B···O5^{iii}	0.88 (4)	1.94 (4)	2.781 (2)	158 (3)
N2—H2B···O6^{iv}	0.84 (3)	2.20 (3)	3.014 (3)	163 (3)
N2—H2A···O4^{v}	0.83 (3)	2.33 (3)	3.132 (3)	163 (3)
O2—H2···O4^{v}	0.83 (3)	1.84 (3)	2.6409 (18)	159 (3)

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

Compound (II)

Crystal data

$C_5H_7N_2^+\cdot C_7H_5O_6S^-$
M_r = 312.30
Monoclinic, $P2_1/n$
a = 13.9642 (10) Å
b = 12.8331 (9) Å
c = 15.7831 (11) Å
β = 114.957 (2)°
V = 2564.3 (3) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.28 mm^{-1}
T = 299 (2) K
0.10 × 0.04 × 0.02 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.972, T_{max} = 0.990
29389 measured reflections
6096 independent reflections
3596 reflections with $I > 2\sigma(I)$
R_{int} = 0.062

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.151
S = 1.01
6096 reflections
412 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O12	0.86 (3)	2.00 (3)	2.797 (3)	154 (3)
N3—H3A···O4	0.90 (3)	2.03 (3)	2.849 (3)	151 (3)
N2—H2A···O5	0.88 (3)	2.21 (4)	3.074 (4)	170 (3)
N2—H2B···O6^{i}	0.89 (3)	2.13 (3)	2.992 (3)	165 (3)
N4—H4B···O11	0.89 (3)	2.18 (4)	3.060 (4)	170 (3)
N4—H4A···O10^{ii}	0.88 (3)	2.07 (3)	2.940 (3)	175 (3)
O1—H1A···O11^{iii}	0.88 (3)	1.89 (3)	2.717 (3)	157 (3)
O7—H7A···O5^{iv}	0.88 (3)	1.81 (3)	2.646 (2)	159 (3)
O3—H3B···O2	0.88 (3)	1.82 (3)	2.608 (3)	148 (3)
O9—H9A···O8	0.81 (3)	1.89 (3)	2.610 (3)	148 (3)
C4—H4···O8^{v}	0.93	2.40	3.224 (3)	148
C11—H11···O2^{vi}	0.93	2.30	3.137 (3)	149
C19—H19···O10	0.93	2.60	3.376 (4)	142
C24—H24···O6	0.93	2.47	3.278 (4)	145

Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x, y, z-1$; (iv) $x, y, z+1$; (v) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (vi) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

For both (I) and (II), H atoms bonded to C atoms were positioned geometrically (C—H = 0.93 Å) and refined using a riding model [U_{iso}(H) = 1.2U_{eq}(C)]. H atoms bonded to N and water O atoms were found in a difference map and further refined with constraints of U_{iso}(H) = 1.2U_{eq}(N) and 1.5U_{eq}(O).

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3101). Services for accessing these data are described at the back of the journal.

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