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**(a) Cover Page**

**Pseudo-Merohedral Twinning in the Structure of the Hydrated 1:1 Proton-Transfer Compound of 5-Sulfosalicylic Acid with 4-Aminopyridine.**

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**(b) Index Abstract**

**Pseudo-Merohedral Twinning in the Structure of the Hydrated 1:1 Proton-Transfer Compound of 5-Sulfosalicylic Acid with 4-Aminopyridine.**

by *Graham Smith*

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The structure determination of the three-dimensional hydrogen-bonded structure of the 1:1 proton-transfer hydrate salt of 5-sulfosalicylic acid (3-carboxy-4-hydroxybenzenesulfonic acid) with 4-aminopyridine has revealed pseudo-merohedral twinning with four cations, four anions and six water molecules of solvation in the asymmetric unit.

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**Figure for insertion in Index Abstract: (SSAPAPYIA.TIF)**

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**(c,d). Title: Authors and Affiliations**

**Title**

Pseudo-Merohedral Twinning in the Structure of the Hydrated 1:1 Proton-Transfer Compound of 5-Sulfosalicylic Acid with 4-Aminopyridine.

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**Abstract**

The structure of the pseudo-merohedrally twinned crystal of the 1:1 proton-transfer compound of 5-sulfosalicylic acid (3-carboxy-4-hydroxybenzenesulfonic acid) with 4-aminopyridine: 4-aminopyridinium 3-carboxy-4-hydroxybenzenesulfonate sesquihydrate has been determined at 180 K and the hydrogen-bonding pattern is described. Crystals of the compound are monoclinic with space group  $P2_1/c$ , with unit cell dimensions  $a = 35.2589(8)$ ,  $b = 7.1948(1)$ ,  $c = 24.5851(5)$  Å,  $\beta = 110.373(2)^\circ$ , and  $Z = 16$ . The monoclinic asymmetric unit comprises four cation-anion pairs and six water molecules of solvation with only the pyridinium cations having pseudo-symmetry as a result of inter-cation aromatic ring  $\pi$ - $\pi$  stacking effects. Extensive hydrogen bonding gives a three-dimensional framework structure.

**Key Words:** 5-sulfosalicylic acid; proton-transfer compound; pseudo-merohedral twinning; hydrogen bonding.

**Running Title:**

4-aminopyridinium 3-carboxy-4-hydroxybenzenesulfonate sesquihydrate

# **Merohedral Twinning in the Structure of the Hydrated 1:1 Proton-Transfer Compound of 5-Sulfosalicylic Acid with 4-Aminopyridine.**

by

Graham Smith\*

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## **Introduction**

The utility of 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid, 5-SSA) for the formation of stable 1:1 and to a lesser extent 1:2 crystalline salts with nitrogen Lewis bases has been recognized for some time, particularly those with the aromatic amines [1-4]. With these compounds three-dimensional hydrogen-bonded framework structures are common, often incorporating water molecules of solvation but only occasionally are cation-cation or cation-anion aromatic ring  $\pi$ - $\pi$  interactions present. A large number of such compounds have been prepared and crystallographically characterized, the most common being the simple monocyclic aromatic and heteroaromatic Lewis base salts, e.g. 4-*X*-substituted anilines (*X* = F, Cl, Br [5], CO<sub>2</sub>H [6]), 3-aminobenzoic acid [7], 3-methoxyaniline [8], 4-(2-hydroxyethyl)aniline [9], benzylamine (1:2) [10], pyrazine [11], the substituted pyrimidines, 2-aminopyrimidine [12], 2-amino-4,6-dimethylpyrimidine [13] and 2,6-diamino-4-oxopyrimidine [14], and the substituted pyridines, 2-hydroxypyridine [12], 2-aminopyridine (1:1) [12] and (1:2) [15], 3-aminopyridine [16], 4-carboxypyridine [17], 2,6-dimethylpyridine [18], 4-(hydrazinocarbonyl)pyridine [19], 2-amino-5-methylpyridine [20] and 2-amino-5-chloropyridine [21]. However, the structure of the 1:1 salt of 5-SSA

with 4-aminopyridine has never been reported. We obtained good crystals of this compound as a hydrate, 4-aminopyridinium 3-carboxy-4-hydroxybenzenesulfonate sesquihydrate, the title compound (**1**) from a 1:1 stoichiometric reaction in 50% ethanol-water. X-ray diffraction data acquired at 180 K presented difficulties, resisting satisfactory structure solution in the higher symmetry orthorhombic unit cell suggested by the data collection and reduction routines. Subsequent transformation to a larger but lower-symmetry monoclinic cell and recognition of the presence of a form of merohedral twinning in the crystal gave both satisfactory structure solution and refinement.

### **Experimental**

*Preparation.* The title compound **1** was synthesized by heating together under reflux for 10 min., 1 mmol quantities of 5-sulfosalicylic acid (3-carboxy-4-hydroxybenzenesulfonic acid) and 4-aminopyridine in 50 mL of 50% ethanol-water. After concentration to *ca.* 30 mL, partial room temperature evaporation of the hot-filtered solution gave colourless well-formed crystal prisms, m.p. 252 °C.

#### *Crystallography.*

A complete sphere of X-ray diffraction data was acquired for **1** at 180(2) K on an Oxford Diffraction Gemini-S Ultra CCD-detector diffractometer employing graphite crystal monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data collection and reduction was completed using CrysAlis CCD and CrysAlis RED [22] with data corrected for absorption (SADABS [23]). Only partial solution of the structure could be obtained from the diffraction data obtained under the original orthorhombic cell setting, using direct methods (SHELXS97 [24]).

The orthorhombic unit cell was transformed to the reported monoclinic cell having twice the volume and a solution was initially obtained in the space group  $P2_1$ , then subsequently in  $P2_1/c$  as reported in Table 1. A merohedral twin was recognized and accommodated in SHELXL97 [24] (operating within WinGX [25]), giving complete refinement, with anisotropic thermal parameters for all non-hydrogen atoms. The SHELXL97 BASF factor for the twin components was 0.4910. The atoms of cation F were found to have uncharacteristically large and irregular thermal parameters compared to those of the other cations and anions of the structure and were constrained using SIMU in SHELXL97. Hydrogen atoms potentially involved in hydrogen-bonding interactions were located by difference methods and their positional and isotropic thermal displacement parameters were refined. However, these atoms were constrained in the final cycles of refinement. Other hydrogen atoms were included in the refinement at calculated positions and treated as riding models. General crystallographic details are given in Table 1. The atom numbering scheme employed for the 5-SSA anion species (Fig. 1) follows the convention used in previous structural studies on 5-SSA proton-transfer compounds by our group [3, 5-10, 12].

**INSERT 1 Schematic of 1 is given here (SSAPAPY.eps)**

The basic chemical formula for **1**

## **Results and Discussion**

In the structure of compound **1** the asymmetric unit contains four independent 5-SSA anion species (A-D), four protonated 4-aminopyridine cation species (E-H) and six water molecules of solvation (O1W-O6W) (Fig. 1).

**INSERT 2 : Figure 1 (Atom numbering scheme for the cations, anions and water species in the asymmetric unit of 1) SSAPAPY1.TIF**

Protonation of the hetero-N of the pyridine rings occurs as expected for all 4-aminopyridine molecules, with subsequent formation of  $N^+H \dots O_{\text{water}}$  hydrogen-bonding interactions (Table 2). The amino H atoms of the cation also form hydrogen bonds with water molecules as well as with sulfonate O acceptors in bridges. Similarly the water molecules also act as donors in bridging sulfonate groups. The carboxyl groups of anions A and C give hydrogen bonds to water molecules O1W and O3W while those of anions B and D form hydrogen bonds with sulfonate O acceptors of anions A and C. Additional secondary hydrogen-bonding interactions, best seen in Figure 2, give structure extension into a three-dimensional framework (Fig. 3). Aromatic ring  $\pi$ - $\pi$  interactions also present between the cation pairs (E, F) and (G, H) [minimum ring centroid separations: C1E-C6E to C1F-C6F, 3.597(2) Å; C1G-C6G to C1H-C6H, 3.608(2) Å], giving stacking down the *b* axis in the unit cell.

**INSERT 3 and 4: Figure 2 (extension of the basic asymmetric unit of 1) (SSAPAPY2.TIF) and Figure 3 (packing of 1 in the unit cell) SSAPAPY3.TIF)**

The hydrogen-bonding environments of the donor centres of most of the independent cation and anion species in the structure are similar. Non-crystallographic mirror pseudo-symmetry involving the cation pairs (E, F) and (G, H) is apparent and would appear to contribute to the crystallographic twinning problems associated with the structure. The non-related water molecules further contribute to the problems.

With the 5-SSA anion species, the usual intramolecular phenolic O-H...O<sub>carboxyl</sub> hydrogen bonds are found [range 2.566(6) - 2.636(5) Å]. This association is consistent with the essential coplanarity of the carboxyl group and the parent benzene ring [torsion angle range for C2-C1-C11-O11: -177.9(3) - 179.9(3)°].

### **Conclusion**

Although the reason for the presence of pseudo-merohedral twinning in this compound is not understood, it must be considered unusual among the large number of ordered 1:1 and 1:2 compounds of 5-SSA with aromatic Lewis bases. With **1**, as with the other Lewis base salts of 5-SSA, the importance of water molecules of solvation as donors in inter-sulfonate hydrogen-bonding bridges is seen.

### **Supplementary material**

CCDC 765689 contains the supplementary crystallographic data for compound **1** from this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* [http://www.ccdc.cam.ac.uk/data\\_requestcif](http://www.ccdc.cam.ac.uk/data_requestcif) or by e-mailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

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**Table 1.** Crystal data for compound **1**.

Compound	<b>1</b>
CCDC reference	765689
Melting point (°C)	252
Molecular formula	C <sub>12</sub> H <sub>15</sub> N <sub>2</sub> O <sub>6.5</sub> S
<i>M</i> <sub>r</sub>	339.32
Temperature (K)	180(2)
Wavelength (λ)	0.71073
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	35.2589(8)
<i>b</i> (Å)	7.1948(1)
<i>c</i> (Å)	24.5851(5)
β (°)	110.373(2)
<i>V</i> (Å <sup>3</sup> )	5846.6(2)
<i>Z</i>	16
<i>D</i> <sub>c</sub> (g cm <sup>-3</sup> )	1.542
μ (mm <sup>-1</sup> )	0.263
<i>F</i> (000)	2832
Instrument	Oxford Diffraction CCD
Reflections total, θ <sub>max</sub> (°)	48263, 25.0
Crystal size (mm)	0.30 x 0.20 x 0.08
Collection range:	
<i>h</i>	-40 to 40
<i>k</i>	-8 to 8
<i>l</i>	-29 to 28
Reflections (independent)	9953
Reflections [ <i>F</i> <sup>2</sup> >2 σ( <i>F</i> <sup>2</sup> )]	8416
<i>R</i> <sub>int</sub>	0.0207
<i>R</i> 1 <sup>a</sup> [ <i>F</i> <sup>2</sup> >2σ( <i>F</i> <sup>2</sup> )]	0.0439
<i>wR</i> 2 <sup>a</sup> (all data)	0.1350
<i>S</i> <sup>a</sup>	1.05
<i>n</i> <sub>p</sub>	939
Transmission factors (max/min)	0.980/0.910
Residuals: Δ <sub>max./min</sub> (eÅ <sup>-3</sup> )	0.467/-0.292

$$^a R1 = (\sum |F_o| - |F_c|) / \sum |F_o|; wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}; S = \{\sum [w(F_o^2 - F_c^2)^2] / (n-p)\}^{1/2}.$$

**Table 2.** Hydrogen-bonding interactions ( $\text{\AA}/^\circ$ ) for **1**

D-H...A	D-H	H...A	D...A	$\angle$ DH..A
N1E-H1E...O2W	0.87	1.98	2.841(6)	179
N1F-H1F...O2W <sup>i</sup>	0.86	1.98	2.818(5)	165
N1G-H1G...O4W	0.90	1.94	2.831(5)	179
N1H-H1E...O4W <sup>ii</sup>	0.85	2.01	2.813(5)	159
N41E-H41E...O1W	0.86	2.25	3.039(9)	152
N41E-H42E...O52D	0.79	2.18	2.942(6)	161
N41F-H41F...O53B	0.89	1.92	2.810(5)	178
N41F-H42F...O51D	0.89	2.08	2.972(5)	180
N41G-H41G...O3W <sup>iii</sup>	0.94	2.25	3.153(6)	162
N41G-H42G...O51B <sup>iv</sup>	0.87	2.17	2.982(5)	156
N41H-H41H...O52B	0.90	1.98	2.880(5)	179
N41H-H42H...O53D <sup>v</sup>	0.95	1.91	2.848(5)	172
O11A-H11A...O3W	0.93	1.71	2.641(5)	173
O11B-H11B...O52A <sup>i</sup>	0.84	1.81	2.646(5)	179
O11C-H11C...O1W	0.91	1.71	2.611(5)	178
O11D-H11D...O52C <sup>vi</sup>	0.98	1.66	2.623(4)	168
O2A-H2A...O12A	0.84	1.89	2.606(5)	142
O2B-H2B...O12B	0.85	1.79	2.636(5)	180
O2C-H2C...O12C	0.83	1.74	2.566(6)	180
O2D-H2D...O12D	0.80	1.81	2.610(5)	179
O1W-H11W...O52B	0.84	1.97	2.815(8)	178

O1W-H12W...O51B <sup>iv</sup>	0.83	1.97	2.800(9)	178
O2W-H21W...O53A <sup>i</sup>	0.83	2.01	2.785(5)	156
O2W-H22W...O6W	0.90	1.81	2.662(5)	157
O3W-H31W...O52D	0.94	1.86	2.757(5)	160
O3W-H32W...O51D <sup>iv</sup>	0.89	1.91	2.789(5)	180
O4W-H41W...O5W <sup>iv</sup>	0.90	1.77	2.669(6)	179
O4W-H42W...O53C <sup>vii</sup>	0.81	1.99	2.802(6)	178
O5W-H51W...O52C	0.74	2.08	2.767(5)	155
O5W-H52W...O51C <sup>vii</sup>	0.90	1.87	2.778(5)	175
O6W-H61W...O51A	0.94	1.94	2.764(5)	145
O6W-H62W...O52A <sup>viii</sup>	0.86	1.93	2.783(5)	173

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

## Figures

**Figure 1.** Atom numbering scheme for the four 5-SSA anions (A-D), the four 4-aminoanilinium cations (E-H) and the six water molecules of solvation (O1W-O6W) in the asymmetric unit of **1**. Inter-species hydrogen bonds are shown as dashed lines and non-hydrogen atoms are shown as 30% probability ellipsoids [26].

**Figure 2.** Hydrogen-bonding extensions of the basic repeating unit (shown as dashed lines) in the structure of **1**. For symmetry codes, see Table 2.

**Figure 3.** A view of the three-dimensional hydrogen-bonded structure of **1** in the unit cell, looking down the *b* cell direction.