3-Methoxyanilinium 3-carboxy-4-hydroxybenzenesulfonate dihydrate
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The 1:1 proton-transfer compound of \textit{m}-anisidine with 5-sulfosalicylic acid, 3-methoxyanilinium 3-carboxy-4-hydroxybenzenesulfonate dihydrate, \( \text{C}_7\text{H}_10\text{NO}^+\cdot\text{C}_7\text{H}_5\text{O}_6\text{S}^-\cdot2\text{H}_2\text{O} \), is a three-dimensional framework structure built from hydrogen-bonding interactions involving the aminium group of the cation, the two water molecules of solvation and the sulfonate, carboxylate and phenolic substituent groups of the anion.

Comment

A number of 1:1 proton-transfer compounds of 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid, 5-SSA) with aniline-type Lewis bases have been reported: with aniline (Bakasova et al., 1991), the 4-\( X \)-substituted anilines (\( X = \text{F}, \text{Cl}, \text{Br} \)) (Smith et al., 2005a), \( X = \text{CO}_2\text{H} \) (Smith et al., 2005b), 3-aminobenzoic acid (Smith, 2005), and 1,4-phenylenediamine (Smith et al., 2005). In the majority of these structures, 1:1 proton-transfer compounds are formed and are usually hydrates. The structure of the compound formed from the reaction of 5-SSA with 3-methoxyaniline (\textit{m}-anisidine, MANIS) in 50\% ethanol–water, \textit{viz.} 3-methoxyanilinium 5-sulfosalicylate dihydrate, (I), reported here, also shows this common trend.

In (I), the MANIS cation, the 5-SSA anion and the two water molecules of solvation (Fig. 1) form a three-dimensional hydrogen-bonded framework structure (Fig. 2). The cation and anion pairs in the asymmetric unit have assembled with their benzene rings essentially parallel [ring centroid separation \( (C_g\cdot\cdot\cdot C_g) = 3.676 \ (3) \text{ Å} \) and inter-plane dihedral angle \( \alpha = 4.9 \ (5) \)\], and their associative functional groups lying essentially parallel to the 2\textsubscript{1} screw axis of the unit cell. The two water molecules of solvation (O1W and O2W) lie in layers between these end groups and serve as donors for hydrogen-bonding associations with O-atom acceptors from three separate sulfonate groups, as well as one from a phenol group (Table 1). The water molecules also act as acceptors for an aminium H atom and the carboxylic acid H atom. The other aminium protons are also associated with either sulfonate O-atom acceptors or the carboxyl O-atom acceptor of the anion species, giving a three-dimensional framework structure.
The asymmetric unit of (I). Displacement ellipsoids are drawn at the 40% probability level. The intramolecular hydrogen bond is shown as a dashed line.

The 5-SSA anions have the usual intramolecular O—H(phenol)· · ·O(carboxyl) hydrogen bond [2.593 (5) Å] with the carboxylic acid group lying essentially in the plane of the benzene ring [torsion angle C2—C1—C7—O71 = −171.6 (5)°]. The methoxy group of the MANIS cation is also essentially coplanar with the benzene ring [torsion angle C21—C31—O31—C32 = 177.7 (5)°].

Experimental
The title compound, (I), was synthesized by heating 1 mmol quantities of 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid) and 3-methoxyaniline (m-anisidine) in 50% ethanol–water (50 ml) for 10 min under reflux. After concentration to ca 30 ml, total room-temperature evaporation of the hot-filtered solution gave pale-brown prisms of (I).

Crystal data
C₇H₆NO₂⁻·C₇H₅O₆S⁻·2H₂O

Mᵣ = 377.37
Orthorhombic, Pna₂₁
a = 7.1911 (6) Å
b = 12.1574 (12) Å
c = 18.7595 (12) Å
V = 1640.1 (2) Å³

Z = 4
Dₐ = 1.528 Mg m⁻³
Mo Kα radiation
µ = 0.25 mm⁻¹
T = 297 (2) K
Prism, pale brown
0.44 × 0.30 × 0.15 mm

Data collection
Rigaku AFC-7R diffractometer
ω–2θ scans
Absorption correction: ψ scan
(TEXSAN for Windows; Molecular Structure Corporation, 1999)
Tmin = 0.899, Tmax = 0.964
2366 measured reflections

Refinement
Refinement on F²
wR(F²) = 0.037
S = 0.84
1943 independent reflections
226 parameters
H atoms treated by a mixture of independent and constrained refinement
w = 1/[σ²(Fo²) + (0.1P)² + 2.5948P]
where P = (Fo² + 2Fe²)/3
(Δ/σ)max = 0.002
Δρmax = 0.28 e Å⁻³
Δρmin = −0.35 e Å⁻³
Absolute structure: Flack (1983)
Flack parameter: −0.13 (14)

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

<table>
<thead>
<tr>
<th>D—H···A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
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<tbody>
<tr>
<td>O2—H2—O72</td>
<td>0.78 (7)</td>
<td>1.88 (7)</td>
<td>2.593 (5)</td>
<td>153 (3)</td>
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<tr>
<td>O71—H71—O28w</td>
<td>0.86 (6)</td>
<td>1.84 (6)</td>
<td>2.649 (7)</td>
<td>156 (7)</td>
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<tr>
<td>N11—H11A—O51</td>
<td>0.84 (7)</td>
<td>2.09 (8)</td>
<td>2.910 (6)</td>
<td>166 (7)</td>
</tr>
<tr>
<td>N11—H11A—O72w</td>
<td>0.84 (7)</td>
<td>2.52 (8)</td>
<td>2.791 (5)</td>
<td>100 (6)</td>
</tr>
<tr>
<td>N11—H11B—O11wiv</td>
<td>0.86 (8)</td>
<td>1.95 (8)</td>
<td>2.797 (7)</td>
<td>170 (7)</td>
</tr>
<tr>
<td>N11—H11C—O53wv</td>
<td>0.92 (8)</td>
<td>2.02 (8)</td>
<td>2.937 (6)</td>
<td>178 (10)</td>
</tr>
<tr>
<td>O1W—H11W—O52w</td>
<td>0.93 (9)</td>
<td>2.12 (9)</td>
<td>3.048 (7)</td>
<td>174 (9)</td>
</tr>
<tr>
<td>O1W—H11W—O53wv</td>
<td>0.87 (9)</td>
<td>1.98 (9)</td>
<td>2.811 (7)</td>
<td>161 (7)</td>
</tr>
<tr>
<td>O2W—H21W—O53wv</td>
<td>0.90 (8)</td>
<td>1.90 (8)</td>
<td>2.804 (7)</td>
<td>180 (10)</td>
</tr>
<tr>
<td>O2W—H22W—O53wv</td>
<td>0.86 (9)</td>
<td>2.08 (8)</td>
<td>2.911 (6)</td>
<td>161 (7)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) x, −y, −z; (ii) −x + 1, −y, −z; (iii) −x − 1, −y, −z; (iv) x + 1, y, −z; (v) −x + 1, −y, −z; (vi) x + 1, y, −z; (vii) −x + 1, −y, −z; (viii) x + 1, y, −z; (ix) −x − 1, −y, −z.

H atoms potentially involved in hydrogen-bonding interactions were located by difference methods and their positional and isotropic displacement parameters were refined. Other H atoms were included in the refinement in calculated positions (C—H = 0.95 Å), using a riding-model approximation, with Ueq(H) values fixed at 1.2Ueq(C). The absolute structure was determined without any Friedel pairs.

Data collection: MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1999); cell refinement: MSC/AFC Diffractometer Control Software; data reduction: TEXSAN for Windows (Molecular Structure Corporation, 1999); program(s) used to solve structure: SIR92 (Altomare et al., 1994); 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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References