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Published

2006

Journal Title

Acta crystallographica. Section E, Structure reports online

DOI

[10.1107/S1600536806017090](https://doi.org/10.1107/S1600536806017090)

Downloaded from

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Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Editors: **W. Clegg** and **D. G. Watson**

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3-Methoxyanilinium 3-carboxy-4-hydroxybenzenesulfonate dihydrate

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Received 8 May 2006

Accepted 9 May 2006

Key indicators

Single-crystal X-ray study

T = 297 K

Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$

R factor = 0.037

wR factor = 0.129

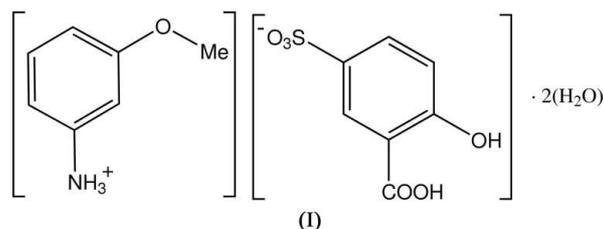
Data-to-parameter ratio = 8.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The 1:1 proton-transfer compound of *m*-anisidine with 5-sulfosalicylic acid, 3-methoxyanilinium 3-carboxy-4-hydroxybenzenesulfonate dihydrate, $\text{C}_7\text{H}_{10}\text{NO}^+ \cdot \text{C}_7\text{H}_5\text{O}_6\text{S}^- \cdot 2\text{H}_2\text{O}$, 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* = F, Cl, Br) (Smith *et al.*, 2005a), *X* = CO₂H (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 (*m*-anisidine, MANIS) in 50% ethanol–water, *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 ($Cg \cdots Cg$) = 3.676 (3) Å and inter-plane dihedral angle α , = 4.9 (5)°], and their associative functional groups lying essentially parallel to the 2₁ 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.

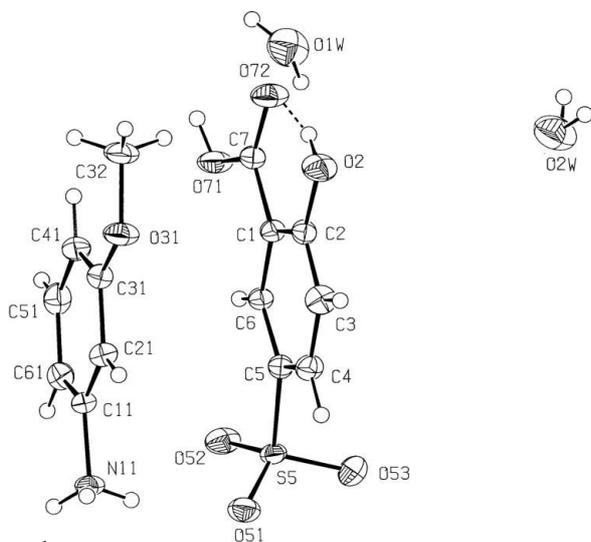


Figure 1
The asymmetric unit of (I). Displacement ellipsoids are drawn at the 40% probability level. The intramolecular hydrogen bond is shown as a dashed line.

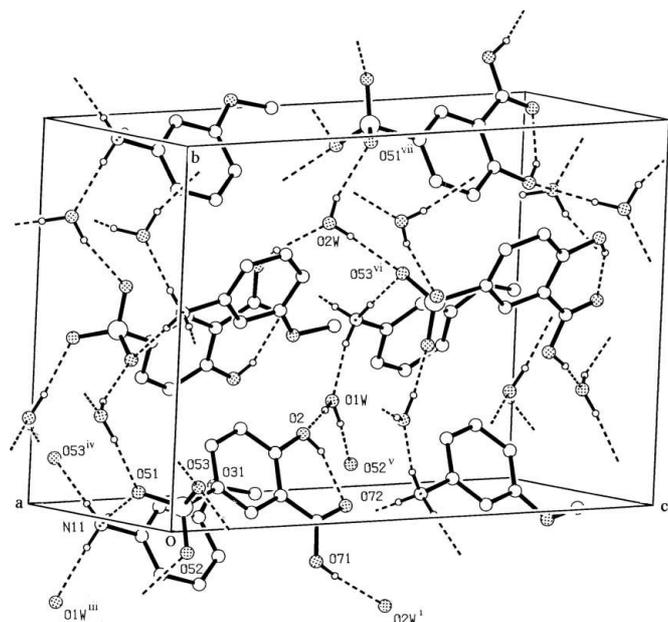


Figure 2
A perspective view of the packing of (I) in the unit cell, showing hydrogen-bonding associations as dashed lines. For symmetry codes see Table 1.

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

C₇H₁₀NO⁺·C₇H₅O₆S[−]·2H₂O
M_r = 377.37
 Orthorhombic, *Pna*2₁
a = 7.1911 (6) Å
b = 12.1574 (12) Å
c = 18.7595 (12) Å
V = 1640.1 (2) Å³

Z = 4
D_x = 1.528 Mg m^{−3}
 Mo *K*α 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)
*T*_{min} = 0.899, *T*_{max} = 0.964
 2366 measured reflections

1943 independent reflections
 1462 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.022
 θ_{max} = 27.5°
 3 standard reflections
 frequency: 150 min
 intensity decay: 0.9%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.037
wR (*F*²) = 0.129
S = 0.84
 1943 reflections
 226 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 2.5948P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.002
 Δρ_{max} = 0.28 e Å^{−3}
 Δρ_{min} = −0.35 e Å^{−3}
 Absolute structure: Flack (1983)
 Flack parameter: −0.13 (14)

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O2—H2···O72	0.78 (7)	1.88 (7)	2.593 (5)	153 (8)
O71—H71···O2W ⁱ	0.86 (6)	1.84 (6)	2.649 (7)	157 (6)
N11—H11A···O51	0.84 (7)	2.09 (8)	2.910 (6)	166 (7)
N11—H11A···O72 ⁱⁱ	0.84 (7)	2.52 (8)	2.791 (5)	100 (6)
N11—H11B···O1W ⁱⁱⁱ	0.86 (8)	1.95 (8)	2.797 (7)	170 (5)
N11—H11C···O53 ^{iv}	0.92 (8)	2.02 (8)	2.937 (6)	178 (10)
O1W—H11W···O2	0.93 (9)	2.12 (9)	3.048 (7)	174 (9)
O1W—H12W···O52 ^v	0.87 (9)	1.98 (9)	2.811 (6)	161 (7)
O2W—H21W···O53 ^{vi}	0.90 (8)	1.90 (8)	2.804 (7)	180 (10)
O2W—H22W···O51 ^{vii}	0.86 (9)	2.08 (8)	2.911 (6)	161 (7)

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

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 *U*_{iso}(H) values fixed at 1.2*U*_{eq}(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*.

The School of Science, Griffith University and the School of Physical and Chemical Sciences, Queensland University of Technology are thanked for financial assistance.

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