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Bis(guanidinium) 5-sulfosalicylate monohydrate

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
R factor = 0.046
wR factor = 0.140
Data-to-parameter ratio = 8.3

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

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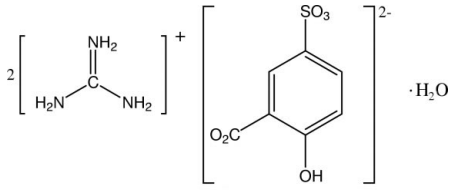
The crystal structure of the hydrated proton-transfer compound hydrate of 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid) with guanidine, $2CH_6N_3^+\cdot C_7H_4O_6S^{2-}\cdot H_2O$, reveals the presence of an extensively hydrogen-bonded three-dimensional network polymer in which all proton donor and acceptor atoms on the two guanidine cations, the dianionic sulfosalicylate anion and the water molecule are utilized. The structure is significantly different chemically and structurally from that of the previously reported anhydrous guanidinium sulfosalicylate compound $CH_6N_3^+\cdot C_7H_5O_6S^-$.

Comment

The acid strength of aromatic sulfonic acids ensures that the formation of proton-transfer compounds will result from their reaction with most Lewis bases. Furthermore, the sulfonate group provides three available O atoms as proton-accepting centres for hydrogen-bonding associations, enhancing the utility of sulfonates for supramolecular assembly. The structures of the guanidinium salts of a number of sulfonates including aromatic types have been determined because of their potential as optical materials (Russell *et al.*, 1994*a*,*b*). This property arises through a combination of the trigonal symmetry of the guanidinium cation with that of the sulfonate group, giving assembly into two-dimensional hydrogen-bonded sheet structures which may be extended through interlayer linkages *via* the third sulfonate O atom into three-dimensional network polymers.

3-Carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid, 5-SSA) has the additional interactive carboxylic acid and phenolic functional substituent groups which lend themselves to secondary *n*-dimensional hydrogen-bonding extension. Furthermore, 5-SSA is able to protonate water and several hydrate structures of the acid have been reported: the dihydrate (Attig & Mootz, 1977; Aliev *et al.*, 1995), the deuterated dihydrate (Attig & Williams, 1977), the trihydrate (Attig & Mootz, 1977), and the pentahydrate (Merschenz-Quack & Mootz, 1990). Many of these have protonated polyaqua species, such as the $H_7O_3^+$ cation species of the trihydrate (Mootz & Fayos, 1970). The only reported structures of Lewis base 5-SSA proton-transfer compounds are with aniline (an anhydrate) (Bakasova *et al.*, 1991), theophylline (a monohydrate) (Madarasz *et al.*, 2002), trimethoprim (a dihydrate) (Raj *et al.*, 2003), and guanidine (GU), a 1:1 anhydrate (Zhang *et al.*, 2004). In addition, we have also determined the structures of the proton-transfer compounds of 5-SSA with a set of bicyclic heteroaromatic Lewis bases (Smith *et al.*, 2004). These are with quinoline: quinolinium 5-sulfosalicylate trihydrate; with 8-hydroxyquinoline: 8-hydroxyquinolinium 5-sulfo-

salicylate monohydrate; with 8-aminoquinoline: 8-aminoquinolinium 5-sulfosalicylate dihydrate; and with quinaldic acid, the adduct structure quinolinium-2-carboxylic acid–5-sulfosalicylate-quinoline-2-carboxylic acid (1/1). We also prepared a compound with guanidine which is a (2:1) hydrate, reported here: $2(GU)^{+}\cdot(5\text{-}SSA)^{2-}\cdot H_2O$, (I), which is significantly different both chemically and structurally from the Zhang *et al.* (2004) structure.



(I)

The structure of (I) shows the presence of a dianionic $(5\text{-}SSA)^{2-}$ species, arising from the deprotonation of both the sulfonate and the carboxylic acid groups (Fig. 1). As expected with guanidinium salts, there is extensive hydrogen bonding, in this case involving all potential H-atom donors of the GU^{+} cation in 14 interactions to all sulfonate O atoms, both carboxylate O atoms, the phenolic O atom and the water O-atom acceptor sites of the $(5\text{-}SSA)^{-}$ anions (Table 1). However, no cyclic $R_2^2(8)$ N—H(guanidine)···O(sulfonate) interactions are present such as are found in the previously reported $(GU)^{+}\cdot(5\text{-}SSA)^{-}$ structure (Zhang *et al.*, 2004), where a short O—H···O(carboxyl) linkage [2.611 (2) Å] is also found. The result in (I) is a three-dimensional network polymer structure (Fig. 2).

The usual intramolecular Ophenol)···O(carboxyl) hydrogen bond is present [O···O = 2.518 (3) Å] in the 5-SSA anion; this distance compares with 2.601 (2) Å in the 1:1 compound (Zhang *et al.*, 2004).

Experimental

The synthesis of the title compound, (I), was carried out by heating, under reflux, 1 mmol quantities of 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid, 5-SSA) and guanidinium carbonate in 50 ml of 50% ethanol–water for 10 min. After concentration to *ca* 30 ml, partial room-temperature evaporation of the hot-filtered solution gave large colourless flat prisms of (I) (m.p. 478.5–484.1 K).

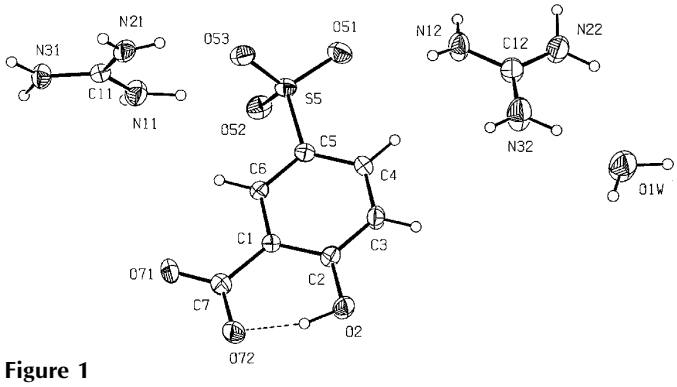


Figure 1
The molecular configuration and atom-naming scheme for (I). Displacement ellipsoids are drawn at the 30% probability level.

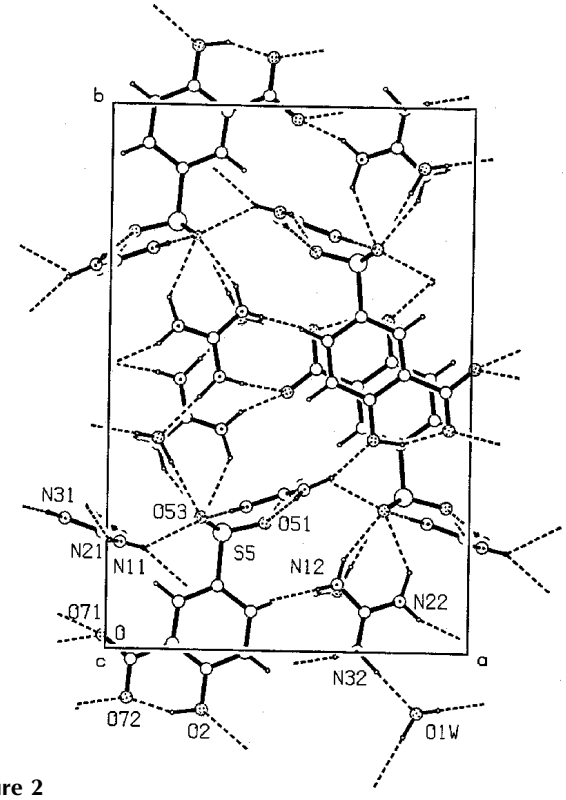


Figure 2
Perspective view of the packing of (I) in the unit cell, viewed down *a*, showing hydrogen-bonding associations as broken lines.

Crystal data

$2CH_6N_3^{+}\cdot C_7H_4O_6S^{2-}\cdot H_2O$
M_r = 354.35
Orthorhombic, $P2_12_12_1$
a = 12.030 (3) Å
b = 18.010 (5) Å
c = 7.290 (2) Å
V = 1579.5 (7) Å^3
Z = 4
D_x = 1.490 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 12.5–17.4°
μ = 0.25 mm^{-1}
T = 295 (2) K
Prism, colourless
0.45 × 0.35 × 0.30 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (*TEXSAN for Windows*; Molecular Structure Corporation, 1999)
T_{min} = 0.895, T_{max} = 0.928
2428 measured reflections
2173 independent reflections
1644 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 27.5°
$h = -6 \rightarrow 15$
$k = 0 \rightarrow 23$
$l = -3 \rightarrow 9$
3 standard reflections
every 150 reflections
intensity decay: 0.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.140
S = 0.90
2173 reflections
261 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 2.556P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.015
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.059 (4)
Absolute structure: Flack (1983), 79 Friedel pairs
Flack parameter = 0.1 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O72	0.98 (6)	1.62 (6)	2.518 (3)	152 (5)
O1W—H1A···O72^{i}	0.90 (10)	2.11 (10)	3.008 (7)	179 (9)
O1W—H1B···O53^{ii}	0.93 (11)	2.13 (11)	3.055 (7)	180 (8)
N11—H11A···O53	0.81 (7)	2.29 (7)	3.018 (7)	151 (6)
N11—H11B···O51^{iii}	0.90 (5)	2.19 (5)	3.089 (7)	180 (5)
N12—H12A···O72^{iv}	0.90 (4)	2.09 (4)	2.987 (7)	179 (5)
N12—H12B···O52^{v}	0.89 (5)	2.17 (5)	3.006 (6)	157 (4)
N21—H21A···O52^{vi}	0.83 (5)	2.52 (5)	3.127 (6)	131 (5)
N21—H21A···O2^{iv}	0.83 (5)	2.34 (5)	3.031 (6)	141 (5)
N21—H21B···O51^{vii}	0.89 (6)	2.21 (6)	3.003 (7)	149 (5)
N22—H22A···O71^{i}	0.90 (7)	1.94 (7)	2.801 (6)	159 (6)
N22—H22B···O52^{v}	1.00 (9)	2.22 (9)	3.043 (7)	139 (7)
N31—H31A···O53^{vii}	0.99 (7)	1.87 (6)	2.860 (6)	174 (6)
N31—H31B···O52^{iii}	0.96 (7)	1.91 (7)	2.873 (7)	179 (8)
N32—H32A···O1W	0.94 (9)	1.93 (9)	2.871 (8)	180 (8)
N32—H32B···O71^{iv}	0.81 (7)	2.06 (8)	2.826 (8)	157 (8)
C4—H4···O51	0.95	2.59	2.953 (5)	103

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

All H atoms involved in hydrogen-bonding interactions (those on the guanidinium cation and on the water molecule) were located by difference methods and their positional and isotropic displacement parameters were refined. Others were included in the refinement at calculated positions (C—H = 0.95 Å) as riding atoms, with U_{iso}(H) = 1.2U_{eq} (C).

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: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON for Windows* (Spek, 1999); software used to prepare material for publication: *PLATON* for Windows.

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