Bis(guanidinium) 5-sulfosalicylate monohydrate

The crystal structure of the hydrated proton-transfer compound hydrate of 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid) with guanidine, \( 2\text{C}_8\text{H}_7\text{N}_5^+\cdot\text{C}_7\text{H}_4\text{O}_6\text{S}_2^2\cdot\text{H}_2\text{O} \), 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 \( \text{CH}_6\text{N}_3^+\cdot\text{C}_7\text{H}_5\text{O}_6\text{S}^- \).

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., 1994a, 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 polyaquaspecies, such as the \( \text{H}_3\text{O}_{\text{aq}}^+ \) 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-
The structure of (I) shows the presence of a dianionic (5-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-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)$^+$⋅(5-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-hydroxybenzene-sulfonic 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.

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**Crystal data**

$2\text{CH}_6\text{N}_3^+\cdot\text{C}_7\text{H}_4\text{O}_6\text{S}_2^{2-}\cdot\text{H}_2\text{O}$

$M_r = 354.35$

Orthorhombic, $P_{2_1}2_12_1$

$a = 12.030$ (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

$\theta = 12.5$–17.4$^\circ$

$\mu = 0.25$ mm$^{-1}$

$T = 295$ (2) K

Prism, colourless

$0.45 	imes 0.35 	imes 0.30$ mm

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

$w = 1/\left[\sigma^2(F^2) + (0.1P)^2 + 2.556P\right]$

where $P = (F^2 + 2F_2)/3$

$\Delta(\sigma)_{\text{max}} = 0.015$

$\Delta_{\text{free}} = 0.44$ e Å$^{-3}$

$\Delta_{\text{free}} = -0.45$ e Å$^{-3}$

Extinction correction: SHELXL97

Extinction coefficient: 0.059 (4)

Absolute structure: Flack (1983), 79 Friedel pairs

Flack parameter = 0.1 (2)
The authors acknowledge financial support from the School of Physical and Chemical Sciences (Queensland University of Technology) and Griffith University.

References


Table 1

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Symmetry codes: (i) 1+x, y, z; (ii) 1−x, y−1/2, −1−z; (iii) x−1, 1/2−y, 1−z; (iv) −1−x, −y, 1/2+z; (v) 1/2+x, 1/2−y, 1−z; (vi) x, y, 1+z; (vii) y, 1−x, −1/2−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 $U_{eq}(H) = 1.2U_{eq}(C)$.