

## Ethylenediammonium bis(3-carboxy-4-hydroxybenzenesulfonate) tetrahydrate

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## Key indicators

Single-crystal X-ray study

T = 295 K

Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$ 

R factor = 0.044

wR factor = 0.143

Data-to-parameter ratio = 14.0

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

In the title compound,  $\text{C}_2\text{H}_{10}\text{N}_2^{2+} \cdot 2\text{C}_7\text{H}_5\text{O}_3\text{S}^- \cdot 4\text{H}_2\text{O}$ , the cation and anion interact with the water molecules to form a three-dimensional network. In the anion, the negative charge resides on the sulfonate group. The dication lies on a special position of site symmetry  $\bar{1}$ .

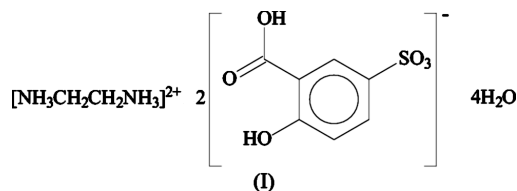
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## Comment

The guanidinium salt of 3-carboxy-4-hydroxybenzenesulfonic acid features an anion whose negative charge resides on the sulfonate group, the anion retaining the acid H atoms of the carboxyl and hydroxy groups. The three amino groups engage in extensive hydrogen-bonding interactions with the anion (Zhang *et al.*, 2004). In the title ethylenediammonium analogue, (I), because the dication lies on a special position of  $\bar{1}$  site symmetry, there are only three donor sites on the cation so the hydrogen-bonding interactions with the anion appear to be satisfied only with the inclusion of water molecules in the crystal structure (Fig. 1). Compound (I) crystallizes with four molecules of water for each dication. The three-dimensional network structure is stabilized by extensive hydrogen bonding (Table 2).



## Experimental

Copper diacetate hydrate (0.40 g, 2 mmol) and ethylenediamine (0.17 g, 3 mmol) were added to an aqueous solution of the sodium salt of 3-carboxy-4-hydroxybenzenesulfonic acid (0.72 g, 3 mmol). The solution was allowed to evaporate at room temperature and colorless crystals separated from the solution after a week. The compound was not a metal complex. Analysis calculated (found, %): C 33.80 (33.96), H 4.96 (4.89), N 4.93 (4.97).

## Crystal data

 $\text{C}_2\text{H}_{10}\text{N}_2^{2+} \cdot 2\text{C}_7\text{H}_5\text{O}_3\text{S}^- \cdot 4\text{H}_2\text{O}$  $M_r = 568.52$ Triclinic,  $P\bar{1}$  $a = 7.111 (1) \text{ \AA}$  $b = 7.140 (1) \text{ \AA}$  $c = 12.765 (3) \text{ \AA}$  $\alpha = 87.77 (3)^\circ$  $\beta = 75.86 (3)^\circ$  $\gamma = 77.36 (3)^\circ$  $V = 613.1 (2) \text{ \AA}^3$ 

Z = 1

 $D_x = 1.540 \text{ Mg m}^{-3}$ Mo  $K\alpha$  radiation

Cell parameters from 5480

reflections

 $\theta = 3.0\text{--}27.5^\circ$  $\mu = 0.30 \text{ mm}^{-1}$ 

T = 295 (2) K

Prism, colorless

0.39 × 0.26 × 0.19 mm

Data collection

Rigaku R-AXIS RAPID  
diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan  
(*ABSCOR*; Higashi, 1995)  
 $T_{\min} = 0.841$ ,  $T_{\max} = 0.946$   
6115 measured reflections

2793 independent reflections  
2394 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.014$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -9 \rightarrow 8$   
 $k = -9 \rightarrow 9$   
 $l = -16 \rightarrow 16$

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.044$   
 $wR(F^2) = 0.143$   
 $S = 1.10$   
2793 reflections  
199 parameters  
H atoms treated by a mixture of  
independent and constrained  
refinement

$w = 1/[\sigma^2(F_o^2) + (0.0958P)^2 + 0.0909P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.47 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.44 \text{ e } \text{\AA}^{-3}$

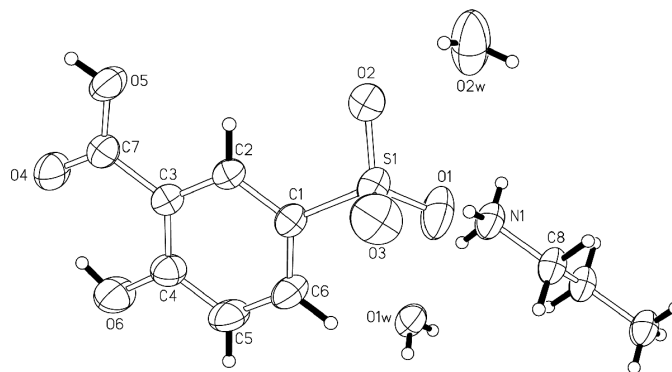


Figure 1  
*ORTEPII* (Johnson, 1976) plot of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

S1—O1	1.444 (2)	C1—C2	1.379 (2)
S1—O2	1.451 (2)	C1—C6	1.392 (3)
S1—O3	1.447 (2)	C2—C3	1.392 (2)
S1—C1	1.763 (2)	C3—C4	1.399 (3)
O4—C7	1.218 (2)	C3—C7	1.476 (2)
O5—C7	1.310 (2)	C4—C5	1.397 (3)
O6—C4	1.342 (3)	C5—C6	1.375 (3)
N1—C8	1.475 (2)	C8—C8 <sup>i</sup>	1.514 (4)
O1—S1—O2	113.4 (1)	C2—C3—C7	120.5 (2)
O1—S1—O3	110.3 (1)	C4—C3—C7	120.0 (2)
O1—S1—C1	107.5 (1)	O6—C4—C3	122.3 (2)
O2—S1—O3	111.1 (1)	O6—C4—C5	118.0 (2)
O2—S1—C1	106.4 (1)	C3—C4—C5	119.8 (2)
O3—S1—C1	107.9 (1)	C4—C5—C6	120.0 (2)
C2—C1—C6	120.0 (2)	C1—C6—C5	120.4 (2)
C2—C1—S1	119.6 (1)	O4—C7—O5	123.4 (2)
C6—C1—S1	120.4 (1)	O4—C7—C3	122.6 (2)
C1—C2—C3	120.3 (2)	O5—C7—C3	114.0 (2)
C2—C3—C4	119.5 (2)	N1—C8—C8 <sup>i</sup>	109.9 (2)

Symmetry code: (i)  $2 - x, -y, 1 - z$ .

Table 2

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1 <i>n</i> 1...O1	0.85 (3)	1.93 (3)	2.758 (3)	163 (3)
N1—H1 <i>n</i> 3...O3 <sup>ii</sup>	0.86 (3)	1.94 (3)	2.784 (3)	167 (2)
N1—H1 <i>n</i> 2...O1 <i>w</i>	0.85 (3)	2.09 (3)	2.908 (3)	161 (3)
O5—H5 <i>o</i> ...O1 <i>w</i> <sup>iii</sup>	0.86 (2)	1.81 (3)	2.656 (2)	170 (3)
O6—H6 <i>o</i> ...O4	0.85 (3)	1.82 (2)	2.598 (2)	151 (4)
O1 <i>w</i> —H1 <i>w</i> 1...O2 <i>w</i> <sup>iv</sup>	0.84 (3)	1.85 (3)	2.658 (3)	163 (4)
O1 <i>w</i> —H1 <i>w</i> 2...O2 <sup>v</sup>	0.85 (3)	2.00 (3)	2.848 (3)	175 (3)
O2 <i>w</i> —H2 <i>w</i> 1...O2	0.84 (3)	2.10 (3)	2.863 (3)	150 (5)
O2 <i>w</i> —H2 <i>w</i> 2...O3 <sup>vi</sup>	0.85 (2)	2.40 (2)	3.188 (3)	156 (4)

Symmetry codes: (ii)  $x, y - 1, z$ ; (iii)  $1 - x, 1 - y, 2 - z$ ; (iv)  $1 + x, y, z$ ; (v)  $1 + x, y - 1, z$ ; (vi)  $1 - x, 1 - y, 1 - z$ .

The O—H and N—H distances were restrained to 0.85 (1)  $\text{\AA}$  and the H...H distance to 1.35 (1)  $\text{\AA}$  for the acid and ammonium groups. The aliphatic, aromatic and methyl H atoms were placed in calculated positions [C—H = 0.93  $\text{\AA}$  (aromatic) and C—H = 0.97  $\text{\AA}$  (aliphatic), with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ , and C—H = 0.96  $\text{\AA}$ , with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  (methyl)], and were included in the refinement in the riding-model approximation.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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