organic compounds

Pyrazinediium bis(3-carboxy-4-hydroxy-benzenesulfonate) dihydrate

Jia-Rong Wang,[a]* Ze-Hui Yang,[a] Chun-Hai Liu[b] and Ling-Lan Li[a]

[a]College of Chemical Engineering, Ningbo University of Technology, Ningbo, Zhejiang 315016, People's Republic of China, and [b]Hunan Jiuzhitang Co. Ltd, Changsha, Hunan 410008, People's Republic of China
Correspondence e-mail: jr_wang@126.com

Pyrazine and 5-sulfosalicylic acid crystallize from a methanol solution containing water as the title salt, $C_4H_6N_2^{2+} \cdot 2C_7H_5O_6S^- \cdot 2H_2O$. The pyrazinediium cation sits on an inversion center. The component ions and water molecules are linked by intermolecular O—H···O, N—H···O and C—H···O hydrogen bonds into layers running parallel to the $(10\bar{2})$ plane.

Related literature

For related literature, see: Smith *et al.* (2004, 2005); Meng *et al.* (2008).
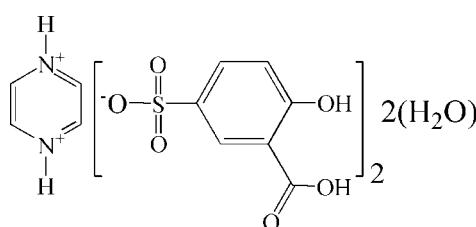
Experimental

Crystal data

$C_4H_6N_2^{2+} \cdot 2C_7H_5O_6S^- \cdot 2H_2O$
$M_r = 552.48$
Triclinic, $P\bar{1}$
$a = 6.7887$ (5) Å
$b = 6.9256$ (6) Å
$c = 13.0349$ (10) Å
$\alpha = 100.663$ (7)°
$\beta = 97.761$ (9)°
$\gamma = 107.735$ (9)°
$V = 561.52$ (9) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.32$ mm^{-1}
$T = 298$ (2) K
$0.20 \times 0.10 \times 0.08$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{min} = 0.929$, $T_{max} = 0.975$

5286 measured reflections
2412 independent reflections
1977 reflections with $I > 2\sigma(I)$
$R_{int} = 0.064$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.131$
$S = 1.08$
2412 reflections
178 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8···O6	0.93	2.40	3.273 (3)	156
C9—H9···O6^i	0.93	2.41	3.240 (3)	149
C6—H6···O1^{ii}	0.93	2.49	3.249 (2)	139
N1—H1B···O7	0.87 (3)	1.71 (3)	2.580 (3)	176 (3)
O7—H7A···O5	0.83 (3)	1.84 (3)	2.659 (2)	171 (3)
O7—H7B···O4^i	0.83 (3)	1.81 (3)	2.631 (3)	172 (3)
O3—H3A···O2	0.83 (3)	1.92 (3)	2.625 (2)	143 (3)
O1—H1A···O5^{ii}	0.82 (3)	1.92 (3)	2.719 (2)	163 (3)

Symmetry codes: (i) $x, y - 1, z$; (ii) $-x, -y + 1, -z + 1$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 2001; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

References

Bruker (2001). *SAINT-Plus* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Meng, X.-G., Xiao, Y.-L., Wang, Z.-L. & Liu, C.-L. (2008). *Acta Cryst.* C**64**, o53–o57.
Sheldrick, G. M. (1997). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Smith, G., Wermuth, U. D. & Healy, P. C. (2005). *Acta Cryst.* C**61**, o555–o558.
Smith, G., Wermuth, U. D. & White, J. M. (2004). *Acta Cryst.* C**60**, o575–o581.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supporting information

Pyrazinediium bis(3-carboxy-4-hydroxybenzenesulfonate) dihydrate

Jia-Rong Wang, Ze-Hui Yang, Chun-Hai Liu and Ling-Lan Li

S1. Comment

5-sulfosalicylic acid is strong organic acid (pKa = 2.85) which can release its sulfonic acid H to Lewis base N atoms, forming 1:1 molecular adducts in general (Smith *et al.*, 2004 and 2005). In order to gain more insight into these analogues, we have recently prepared an organic salt containing 5-H_2SSA, whose crystal structure is reported here.

There are a half of a pyrazinediium cation, one each a 5-HSSA⁻ anion and a water molecule in the asymmetric unit. Similarly to analogous organic adducts reported by others (Meng *et al.*, 2008), the H atom is transferred from the sulfonic acid group to the pyrazine N atoms (Fig.1). Except for this, the other bond lengths and angles are usual.

By a combination of seven intermolecular hydrogen bonds (Table 1), these components are linked into a two-dimensional layers (Fig.2) running parallel to the (10$\bar{2}$) plane in the crystal.

Program *PLATON* (Spek, 2003) reports two distances indicating possible aromatic π-π stacking interactions between symmetry-center related benzene rings comprising atoms C1 to C6 in this crystal. Centroid distances between the closest symmetry-related benzene rings are 3.848 (2) and 4.239 (2) Å, respectively (symmetry codes: 1-x,1 -y, 1-z for the former one and 1-x, 2-y, 1-z for the latter one).

S2. Experimental

All the reagents and solvents were used as obtained without further purification. Equimolar amount of pyrazine (0.2 mmol, 16.0 mg) and 5-sulfosalicylic acid dihydrate (0.2 mmol, 50.8 g) were dissolved in 95% methanol (10 ml). The mixture was stirred for ten minutes at ambient temperature and then filtered. The resulting colorless solution was kept in air for two weeks. Plate shaped colorless crystals suitable for single-crystal X-ray diffraction analysis were grown by slow evaporation of the solvent.

S3. Refinement

H atoms bonded to C atoms were positioned geometrically with C–H = 0.93Å (aromatic) and refined in a riding mode [U_{iso}(H) = 1.2U_{eq}(aromatic C)]. H atoms bonded to N and O atoms were found in difference Fourier maps with N—H and O—H distances being refined freely [the refined distances are given in Table 1; U_{iso}(H)= 1.2U_{eq}(N) or 1.5U_{eq}(O)].
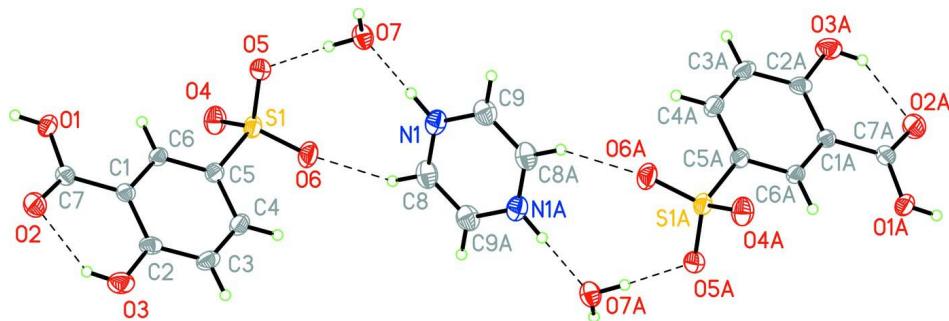
Figure 1

Molecular structure of the title salt showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H-bonds are shown in dashed lines. Symmetry code: (A) 2 - x, 1 - y, 2 - z.
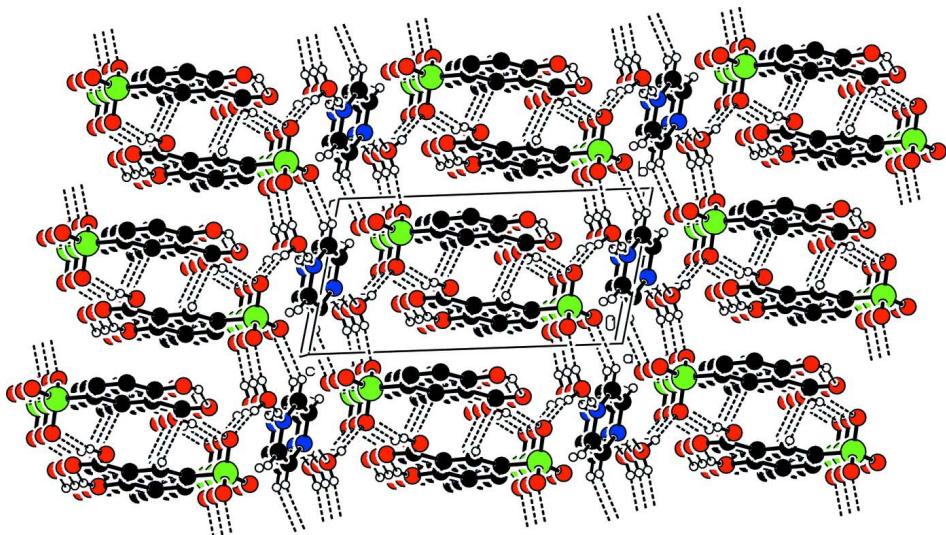
Figure 2

Excerpt from the crystal structure showing the formation of the two-dimensional layers running parallel to the $[10\overline{2}]$ direction. Hydrogen bonds are shown as dashed lines. For the sake of clarity, H atoms not involved in the motif have been omitted from the drawing.

Pyrazinediium bis(3-carboxy-4-hydroxybenzenesulfonate) dihydrate

Crystal data

$C_4H_6N_2{}^{2+}\cdot2C_7H_5O_6S^-\cdot2H_2O$	$Z = 1$
$M_r = 552.48$	$F(000) = 286$
Triclinic, $P\overline{1}$	$D_x = 1.634$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 6.7887$ (5) Å	Cell parameters from 2269 reflections
$b = 6.9256$ (6) Å	$\theta = 1.6$–25.2°
$c = 13.0349$ (10) Å	$\mu = 0.32$ mm^{-1}
$\alpha = 100.663$ (7)°	$T = 298$ K
$\beta = 97.761$ (9)°	Plate, colourless
$\gamma = 107.735$ (9)°	$0.20 \times 0.10 \times 0.08$ mm
$V = 561.52$ (9) Å^3	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	5286 measured reflections
Radiation source: fine focus sealed Siemens Mo tube	2412 independent reflections
	1977 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.064$
0.3° wide ω exposures scans	$\theta_{max} = 27.0°$, $\theta_{min} = 1.6°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)	$h = -8{\rightarrow}8$
	$k = -5{\rightarrow}8$
	$l = -16{\rightarrow}16$
$T_{min} = 0.929$, $T_{max} = 0.975$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.045$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.131$	
$S = 1.08$	H atoms treated by a mixture of independent and constrained refinement
2412 reflections	
178 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0732P)^2 + 0.0236P]$
0 restraints	where $P = (F_o^2 + 2F_c^2)/3$
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} = 0.001$
	$\Delta\rho_{max} = 0.32$ e Å^{-3}
	$\Delta\rho_{min} = -0.51$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.4240 (3)	0.7285 (3)	0.48381 (14)	0.0311 (4)
C2	0.6433 (3)	0.7939 (3)	0.48820 (17)	0.0361 (5)
C3	0.7816 (3)	0.8439 (3)	0.58633 (18)	0.0439 (5)
H3	0.9265	0.8851	0.5895	0.053*
C4	0.7052 (3)	0.8328 (3)	0.67817 (17)	0.0425 (5)
H4	0.7985	0.8671	0.7432	0.051*
C5	0.4881 (3)	0.7704 (3)	0.67421 (15)	0.0338 (4)
C6	0.3486 (3)	0.7183 (3)	0.57800 (14)	0.0323 (4)
H6	0.2040	0.6762	0.5758	0.039*
C7	0.2761 (3)	0.6708 (3)	0.38006 (15)	0.0362 (5)
C8	0.9086 (4)	0.6243 (4)	0.96127 (19)	0.0543 (6)
H8	0.8459	0.7119	0.9346	0.065*
C9	0.8819 (4)	0.3018 (4)	0.99291 (18)	0.0511 (6)
H9	0.8012	0.1641	0.9884	0.061*
N1	0.7935 (3)	0.4275 (3)	0.95466 (13)	0.0466 (5)
H1B	0.658 (4)	0.377 (4)	0.928 (2)	0.056*
O1	0.0776 (2)	0.6158 (3)	0.38832 (11)	0.0484 (4)
H1A	−0.005 (5)	0.578 (5)	0.331 (2)	0.073*
O2	0.3328 (3)	0.6740 (3)	0.29528 (11)	0.0531 (4)
O3	0.7255 (3)	0.8128 (3)	0.40112 (14)	0.0523 (4)
H3A	0.633 (5)	0.788 (5)	0.348 (3)	0.078*
O4	0.2517 (3)	0.8910 (3)	0.79365 (12)	0.0535 (4)
O5	0.2546 (2)	0.5428 (2)	0.78053 (11)	0.0467 (4)
O6	0.5615 (3)	0.8329 (3)	0.88036 (11)	0.0522 (4)

O7	0.3909 (3)	0.2940 (3)	0.88232 (12)	0.0475 (4)
H7A	0.346 (5)	0.362 (5)	0.844 (2)	0.071*
H7B	0.340 (5)	0.169 (5)	0.849 (2)	0.071*
S1	0.38501 (8)	0.76139 (8)	0.79128 (3)	0.0378 (2)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0308 (9)	0.0259 (10)	0.0391 (9)	0.0108 (8)	0.0074 (8)	0.0115 (8)
C2	0.0321 (10)	0.0272 (10)	0.0533 (11)	0.0111 (8)	0.0152 (8)	0.0130 (9)
C3	0.0247 (10)	0.0414 (12)	0.0655 (13)	0.0105 (9)	0.0075 (9)	0.0150 (10)
C4	0.0325 (10)	0.0412 (12)	0.0495 (11)	0.0106 (9)	−0.0022 (9)	0.0113 (9)
C5	0.0319 (10)	0.0293 (10)	0.0391 (9)	0.0103 (8)	0.0030 (8)	0.0090 (8)
C6	0.0265 (9)	0.0316 (11)	0.0391 (9)	0.0101 (8)	0.0044 (7)	0.0103 (8)
C7	0.0369 (11)	0.0349 (11)	0.0396 (10)	0.0125 (9)	0.0085 (8)	0.0145 (8)
C8	0.0648 (16)	0.0550 (16)	0.0518 (13)	0.0315 (13)	0.0084 (11)	0.0173 (11)
C9	0.0617 (15)	0.0454 (14)	0.0481 (12)	0.0214 (12)	0.0105 (11)	0.0113 (10)
N1	0.0443 (10)	0.0565 (13)	0.0383 (9)	0.0203 (10)	0.0045 (8)	0.0073 (9)
O1	0.0322 (8)	0.0695 (12)	0.0376 (7)	0.0083 (8)	0.0005 (6)	0.0184 (7)
O2	0.0521 (9)	0.0701 (12)	0.0390 (8)	0.0189 (9)	0.0136 (7)	0.0176 (7)
O3	0.0404 (9)	0.0604 (11)	0.0606 (10)	0.0151 (8)	0.0235 (7)	0.0190 (8)
O4	0.0572 (10)	0.0634 (11)	0.0488 (8)	0.0343 (9)	0.0092 (7)	0.0126 (7)
O5	0.0447 (9)	0.0477 (10)	0.0400 (7)	0.0053 (7)	0.0014 (6)	0.0148 (7)
O6	0.0515 (9)	0.0557 (10)	0.0383 (7)	0.0133 (8)	−0.0093 (7)	0.0064 (7)
O7	0.0571 (10)	0.0444 (10)	0.0467 (8)	0.0238 (8)	0.0082 (7)	0.0152 (7)
S1	0.0369 (3)	0.0405 (3)	0.0328 (3)	0.0128 (2)	−0.0006 (2)	0.0074 (2)

Geometric parameters (Å, º)

C1—C6	1.398 (3)	C8—N1	1.329 (3)
C1—C2	1.408 (3)	C8—C9^i	1.363 (4)
C1—C7	1.478 (2)	C8—H8	0.9300
C2—O3	1.341 (3)	C9—N1	1.329 (3)
C2—C3	1.397 (3)	C9—C8^i	1.363 (4)
C3—C4	1.373 (3)	C9—H9	0.9300
C3—H3	0.9300	N1—H1B	0.87 (3)
C4—C5	1.395 (3)	O1—H1A	0.82 (3)
C4—H4	0.9300	O3—H3A	0.83 (3)
C5—C6	1.380 (2)	O4—S1	1.4556 (17)
C5—S1	1.766 (2)	O5—S1	1.4721 (15)
C6—H6	0.9300	O6—S1	1.4421 (14)
C7—O2	1.220 (2)	O7—H7A	0.83 (3)
C7—O1	1.310 (2)	O7—H7B	0.83 (3)
C6—C1—C2	119.40 (17)	O1—C7—C1	113.11 (16)
C6—C1—C7	120.76 (17)	N1—C8—C9^i	120.2 (2)
C2—C1—C7	119.84 (17)	N1—C8—H8	119.9
O3—C2—C3	118.37 (18)	C9^i—C8—H8	119.9

O3—C2—C1	122.21 (19)	N1—C9—C8[i]	119.6 (2)
C3—C2—C1	119.41 (18)	N1—C9—H9	120.2
C4—C3—C2	120.51 (19)	C8[i]—C9—H9	120.2
C4—C3—H3	119.7	C8—N1—C9	120.2 (2)
C2—C3—H3	119.7	C8—N1—H1B	122.3 (17)
C3—C4—C5	120.19 (19)	C9—N1—H1B	117.4 (18)
C3—C4—H4	119.9	C7—O1—H1A	113 (2)
C5—C4—H4	119.9	C2—O3—H3A	111 (2)
C6—C5—C4	120.25 (18)	H7A—O7—H7B	107 (3)
C6—C5—S1	118.43 (15)	O6—S1—O4	114.02 (10)
C4—C5—S1	121.30 (15)	O6—S1—O5	111.78 (9)
C5—C6—C1	120.23 (17)	O4—S1—O5	109.60 (10)
C5—C6—H6	119.9	O6—S1—C5	107.54 (10)
C1—C6—H6	119.9	O4—S1—C5	106.61 (9)
O2—C7—O1	123.31 (18)	O5—S1—C5	106.90 (9)
O2—C7—C1	123.58 (18)		
C6—C1—C2—O3	−177.99 (18)	C6—C1—C7—O2	−179.0 (2)
C7—C1—C2—O3	2.2 (3)	C2—C1—C7—O2	0.8 (3)
C6—C1—C2—C3	1.1 (3)	C6—C1—C7—O1	1.0 (3)
C7—C1—C2—C3	−178.71 (18)	C2—C1—C7—O1	−179.17 (18)
O3—C2—C3—C4	178.12 (19)	C9[i]—C8—N1—C9	0.2 (4)
C1—C2—C3—C4	−1.0 (3)	C8[i]—C9—N1—C8	−0.2 (4)
C2—C3—C4—C5	0.3 (3)	C6—C5—S1—O6	−176.94 (15)
C3—C4—C5—C6	0.3 (3)	C4—C5—S1—O6	1.7 (2)
C3—C4—C5—S1	−178.24 (16)	C6—C5—S1—O4	−54.28 (18)
C4—C5—C6—C1	−0.2 (3)	C4—C5—S1—O4	124.33 (19)
S1—C5—C6—C1	178.39 (14)	C6—C5—S1—O5	62.88 (17)
C2—C1—C6—C5	−0.5 (3)	C4—C5—S1—O5	−118.51 (18)
C7—C1—C6—C5	179.32 (17)		

Symmetry code: (i) −x+2, −y+1, −z+2.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8···O6	0.93	2.40	3.273 (3)	156
C9—H9···O6[ii]	0.93	2.41	3.240 (3)	149
C6—H6···O1[iii]	0.93	2.49	3.249 (2)	139
N1—H1B···O7	0.87 (3)	1.71 (3)	2.580 (3)	176 (3)
O7—H7A···O5	0.83 (3)	1.84 (3)	2.659 (2)	171 (3)
O7—H7B···O4[ii]	0.83 (3)	1.81 (3)	2.631 (3)	172 (3)
O3—H3A···O2	0.83 (3)	1.92 (3)	2.625 (2)	143 (3)
O1—H1A···O5[iii]	0.82 (3)	1.92 (3)	2.719 (2)	163 (3)

Symmetry codes: (ii) x, y−1, z; (iii) −x, −y+1, −z+1.