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Piperazine-1,4-diium bis(3-carboxy-4-hydroxybenzenesulfonate) dihydrate

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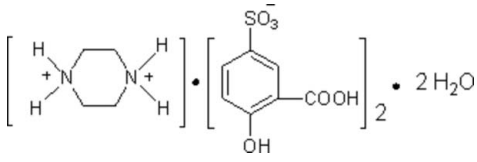
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.003 Å; R factor = 0.035; wR factor = 0.104; data-to-parameter ratio = 11.1.

The asymmetric unit of the title compound, $C_4H_{12}N_2^{2+}\cdot 2C_7H_5O_6S^-\cdot 2H_2O$, comprises one-half of the piperazine-1,4-diium cation, which lies across an inversion centre, a 3-carboxy-4-hydroxybenzenesulfonate anion and a water molecule. An extensive network of intermolecular O—H···O and N—H···O hydrogen bonds links the cations and anions in alternating rows down the b axis.

Related literature

For information on the role of water in self-assembly processes, see: Smith *et al.* (2007). For reference structural data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_4H_{12}N_2^{2+}\cdot 2C_7H_5O_6S^-\cdot 2H_2O$
M_r = 558.52
Triclinic, $P\overline{1}$
a = 6.8980 (13) Å
b = 7.2012 (14) Å
c = 12.800 (2) Å
α = 100.280 (3)°
β = 93.084 (3)°
γ = 111.459 (3)°
V = 577.31 (19) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 294 (2) K
0.24 × 0.20 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.930, T_{max} = 0.947
2992 measured reflections
2016 independent reflections
1786 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.104
S = 1.04
2016 reflections
182 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O3^{i}	0.82	1.90	2.690 (2)	160
O4—H4···S1^{i}	0.82	2.96	3.5926 (16)	136
N1—H1A···O7^{ii}	0.914 (9)	1.803 (10)	2.715 (3)	175 (2)
N1—H1B···O3^{iii}	0.907 (10)	2.006 (12)	2.895 (2)	166 (2)
N1—H1B···S1^{iii}	0.907 (10)	2.874 (19)	3.6176 (17)	140 (2)
O7—H7A···O3^{iv}	0.848 (10)	1.938 (13)	2.750 (2)	160 (3)
O7—H7A···S1^{iv}	0.848 (10)	2.998 (13)	3.781 (2)	154 (2)
O6—H6···O5	0.82	1.91	2.630 (2)	147
O7—H7B···O2	0.849 (10)	1.863 (10)	2.710 (2)	175 (3)

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2001); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2414).

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  doi:10.1107/S1600536807057856

supplementary materials

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Piperazine-1,4-diium bis(3-carboxy-4-hydroxybenzenesulfonate) dihydrate

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Comment

3-carboxy-4-hydroxy benzene sulfonate also known as 5-sulfosalicylic acid (SSA) has six potential donor sites in the three substituent groups (the sulfonic acid, the carboxylic acid and the phenolic groups), and it can form mono-, di- and trianionic ligand species through deprotonation. The presence of the numerous oxygen atoms in three substituent groups usually results in hydrogen-bonding associations, and the self-assembly process of crystallization often requires the incorporation of water molecules in the structures (Smith *et al.* 2007).

We report here the synthesis and structure of piperazine-1,4-diium 3-carboxyl-4-hydroxyl benzene sulfonate monohydrate, (I), Fig. 1 which was obtained from a solution of 2-hydroxy-5-sulfobenzoic acid and piperazine. Bond distances and angles in (I) are normal (Allen *et al.*, 1987). The asymmetric unit of the title compound comprises one half of the piperazine-1,4-diium cation, which lies about an inversion centre, a 3-carboxy-4-hydroxybenzenesulfonate anion and a water solvate. In the crystal structure molecules were interlinked by hydrogen bonds, Table 1, involving oxygen atoms from the sulfonate and carboxylate groups of the 5-sulfosalicylate, and the nitrogen atoms of the piperazinediium cation. The water molecules function as a bridge between two anions and a cation producing a three-dimensional hydrogen-bonded framework structure. The hydroxyl group of the 5-sulfosalicylate forms an intramolecular O6—H6···O5 hydrogen bond but is not involved in the crystal packing.

Experimental

2-hydroxy-5-sulfobenzoic acid (2.18 g, 10 mmol) and piperazine (0.86 g, 10 mmol) were dissolved in warm H_2O (20 ml). Crystals of the title compound were obtained by slow evaporation of this solution.

Refinement

The H atoms of the water molecule and those on the N atoms were located in difference Fourier maps; their the parameters were freely refined. All other H atoms were positioned geometrically and refined using a riding model, with O—H = 0.82 Å for hydroxy H atoms, C—H = 0.93 Å for aromatic H atoms, and 0.97 Å for methylene H atoms, respectively, and with U_{iso}(H) = 1.5Ueq(O) for hydroxy and U_{iso}(H) = 1.2Ueq(C) for aromatic and methylene H atoms.

Figures

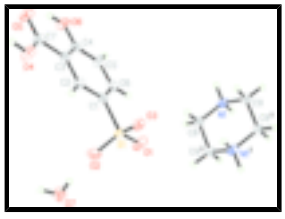


Fig. 1. The molecular structure of (I) with 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitary radii. [Symmetry code; (i) 1 − *x*, −*y*, 1 − *z*.]

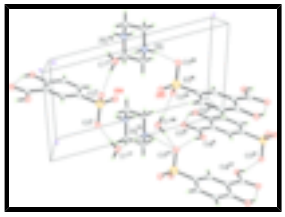


Fig. 2. The crystal packing of (I) showing the O—H···O and N—H···O hydrogen bonds (dashed lines). [Symmetry codes: (i) 1 − *x*, 1 − *y*, 1 − *z*; (ii) 1 − *x*, 2 − *y*, 2 − *z*; (iii) 1 + *x*, *y*, *z*; (iv) 1 + *x*, 1 + *y*, *z*; (v) 1 − *x*, 2 − *y*, 1 − *z*; (vi) *x*, 1 + *y*, *z*; (vii) 1 − *x*, − *y*, 1 − *z*]

Piperazine-1,4-diium bis(3-carboxy-4-hydroxybenzenesulfonate) dihydrate

Crystal data

$C_4H_{12}N_2^{2+}\cdot 2C_7H_5O_6S^-\cdot 2H_2O$	$Z = 1$
$M_r = 558.52$	$F_{000} = 292$
Triclinic, $P\overline{1}$	$D_x = 1.607$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 6.8980$ (13) Å	Cell parameters from 2045 reflections
$b = 7.2012$ (14) Å	$\theta = 3.1$–$26.3°$
$c = 12.800$ (2) Å	$\mu = 0.31$ mm^{-1}
$\alpha = 100.280$ (3)°	$T = 294$ (2) K
$\beta = 93.084$ (3)°	Block, colourless
$\gamma = 111.459$ (3)°	0.24 × 0.20 × 0.18 mm
$V = 577.31$ (19) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	1786 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.021$
$T = 294$(2) K	$\theta_{max} = 25.0°$
φ and ω scans	$\theta_{min} = 1.6°$
Absorption correction: multi-scan (SADABS;Bruker, 2000)	$h = -8\rightarrow 8$
$T_{min} = 0.930$, $T_{max} = 0.947$	$k = -8\rightarrow 5$
2992 measured reflections	$l = -13\rightarrow 15$
2016 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.035$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.104$	$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 0.226P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$

2016 reflections	$\Delta\rho_{max}$ = 0.29 e Å^{-3}
182 parameters	$\Delta\rho_{min}$ = −0.33 e Å^{-3}
6 restraints	Extinction correction: SHELXL, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.056 (7)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.18428 (7)	0.46867 (7)	0.70639 (4)	0.0325 (2)
O1	0.3025 (3)	0.4558 (3)	0.61877 (12)	0.0540 (5)
O2	0.0505 (3)	0.5810 (3)	0.69897 (13)	0.0549 (5)
O3	0.0567 (2)	0.2658 (2)	0.72449 (10)	0.0366 (4)
O4	0.1360 (2)	0.7404 (3)	1.09825 (12)	0.0498 (4)
H4	0.0971	0.7675	1.1564	0.075*
O5	0.4490 (3)	0.8749 (3)	1.19742 (12)	0.0526 (4)
O6	0.7792 (2)	0.9051 (3)	1.09761 (12)	0.0512 (4)
H6	0.7159	0.9232	1.1484	0.077*
N1	0.7087 (3)	0.0786 (3)	0.55348 (14)	0.0383 (4)
C1	0.3649 (3)	0.5961 (3)	0.82344 (15)	0.0304 (4)
C2	0.2889 (3)	0.6465 (3)	0.91627 (15)	0.0308 (4)
H2	0.1452	0.6130	0.9160	0.037*
C3	0.4238 (3)	0.7473 (3)	1.01111 (15)	0.0307 (4)
C4	0.6405 (3)	0.8012 (3)	1.00941 (16)	0.0353 (5)
C5	0.7156 (3)	0.7501 (3)	0.91494 (18)	0.0405 (5)
H5	0.8594	0.7859	0.9140	0.049*
C6	0.5800 (3)	0.6470 (3)	0.82266 (17)	0.0367 (5)
H6A	0.6315	0.6112	0.7597	0.044*
C7	0.3409 (3)	0.7940 (3)	1.11070 (16)	0.0364 (5)
C8	0.5938 (3)	0.2154 (3)	0.54583 (17)	0.0402 (5)
H8A	0.6926	0.3507	0.5437	0.048*
H8B	0.5224	0.2265	0.6085	0.048*
C9	0.5640 (3)	−0.1322 (3)	0.55349 (17)	0.0383 (5)
H9A	0.4917	−0.1324	0.6164	0.046*
H9B	0.6435	−0.2184	0.5560	0.046*

O7	0.0665 (3)	0.9051 (3)	0.61474 (14)	0.0545 (4)
H1A	0.779 (3)	0.077 (4)	0.4952 (11)	0.048 (7)*
H1B	0.802 (3)	0.129 (4)	0.6142 (10)	0.068 (8)*
H7A	0.092 (5)	1.019 (2)	0.6563 (17)	0.074 (10)*
H7B	0.063 (5)	0.808 (3)	0.6449 (19)	0.079 (10)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0353 (3)	0.0313 (3)	0.0238 (3)	0.0054 (2)	0.00128 (19)	0.00453 (19)
O1	0.0540 (9)	0.0603 (10)	0.0288 (8)	0.0014 (8)	0.0137 (7)	0.0040 (7)
O2	0.0631 (10)	0.0487 (9)	0.0510 (10)	0.0232 (8)	−0.0133 (8)	0.0082 (8)
O3	0.0381 (7)	0.0324 (7)	0.0271 (7)	0.0018 (6)	0.0016 (6)	0.0019 (5)
O4	0.0404 (9)	0.0569 (10)	0.0330 (8)	0.0032 (7)	0.0099 (6)	−0.0059 (7)
O5	0.0569 (10)	0.0558 (10)	0.0293 (8)	0.0104 (8)	−0.0054 (7)	−0.0026 (7)
O6	0.0372 (8)	0.0585 (10)	0.0429 (9)	0.0085 (7)	−0.0128 (7)	0.0004 (8)
N1	0.0303 (8)	0.0426 (10)	0.0324 (9)	0.0065 (8)	−0.0060 (7)	0.0032 (8)
C1	0.0311 (10)	0.0249 (9)	0.0295 (10)	0.0051 (8)	0.0019 (8)	0.0042 (7)
C2	0.0265 (9)	0.0264 (9)	0.0315 (10)	0.0025 (7)	0.0021 (7)	0.0031 (7)
C3	0.0320 (10)	0.0245 (9)	0.0291 (10)	0.0041 (8)	0.0005 (8)	0.0052 (7)
C4	0.0325 (10)	0.0285 (10)	0.0379 (11)	0.0051 (8)	−0.0059 (8)	0.0070 (8)
C5	0.0254 (9)	0.0421 (12)	0.0492 (12)	0.0077 (9)	0.0033 (9)	0.0095 (9)
C6	0.0333 (10)	0.0359 (11)	0.0378 (11)	0.0096 (9)	0.0088 (8)	0.0063 (9)
C7	0.0412 (11)	0.0280 (10)	0.0296 (10)	0.0036 (8)	0.0009 (8)	0.0024 (8)
C8	0.0429 (11)	0.0323 (10)	0.0371 (11)	0.0087 (9)	−0.0028 (9)	0.0012 (8)
C9	0.0394 (11)	0.0367 (11)	0.0358 (11)	0.0121 (9)	−0.0018 (9)	0.0074 (9)
O7	0.0682 (11)	0.0440 (10)	0.0561 (10)	0.0247 (9)	0.0157 (9)	0.0133 (9)

Geometric parameters (Å, °)

S1—O1	1.4310 (16)	C2—H2	0.9300
S1—O2	1.4419 (17)	C3—C4	1.403 (3)
S1—O3	1.4713 (14)	C3—C7	1.460 (3)
S1—C1	1.7640 (19)	C4—C5	1.384 (3)
O4—C7	1.314 (3)	C5—C6	1.372 (3)
O4—H4	0.8200	C5—H5	0.9300
O5—C7	1.221 (2)	C6—H6A	0.9300
O6—C4	1.345 (2)	C8—C9^{i}	1.504 (3)
O6—H6	0.8200	C8—H8A	0.9700
N1—C9	1.481 (3)	C8—H8B	0.9700
N1—C8	1.485 (3)	C9—C8^{i}	1.504 (3)
N1—H1A	0.914 (9)	C9—H9A	0.9700
N1—H1B	0.907 (10)	C9—H9B	0.9700
C1—C2	1.368 (3)	O7—H7A	0.848 (10)
C1—C6	1.393 (3)	O7—H7B	0.849 (10)
C2—C3	1.391 (3)		
O1—S1—O2	115.38 (11)	O6—C4—C3	121.52 (19)
O1—S1—O3	111.98 (9)	C5—C4—C3	119.85 (18)

O2—S1—O3	108.58 (10)	C6—C5—C4	120.59 (18)
O1—S1—C1	107.58 (10)	C6—C5—H5	119.7
O2—S1—C1	106.66 (9)	C4—C5—H5	119.7
O3—S1—C1	106.12 (8)	C5—C6—C1	119.82 (19)
C7—O4—H4	109.5	C5—C6—H6A	120.1
C4—O6—H6	109.5	C1—C6—H6A	120.1
C9—N1—C8	111.79 (16)	O5—C7—O4	122.67 (19)
C9—N1—H1A	109.3 (15)	O5—C7—C3	124.08 (19)
C8—N1—H1A	107.1 (15)	O4—C7—C3	113.26 (16)
C9—N1—H1B	109.5 (17)	N1—C8—C9^{i}	110.16 (16)
C8—N1—H1B	109.5 (17)	N1—C8—H8A	109.6
H1A—N1—H1B	109.7 (14)	C9^{i}—C8—H8A	109.6
C2—C1—C6	120.10 (18)	N1—C8—H8B	109.6
C2—C1—S1	118.23 (14)	C9^{i}—C8—H8B	109.6
C6—C1—S1	121.67 (15)	H8A—C8—H8B	108.1
C1—C2—C3	120.86 (18)	N1—C9—C8^{i}	109.94 (16)
C1—C2—H2	119.6	N1—C9—H9A	109.7
C3—C2—H2	119.6	C8^{i}—C9—H9A	109.7
C2—C3—C4	118.76 (18)	N1—C9—H9B	109.7
C2—C3—C7	120.57 (17)	C8^{i}—C9—H9B	109.7
C4—C3—C7	120.67 (17)	H9A—C9—H9B	108.2
O6—C4—C5	118.62 (18)	H7A—O7—H7B	115.9 (17)
O1—S1—C1—C2	172.95 (15)	C7—C3—C4—C5	178.02 (18)
O2—S1—C1—C2	48.60 (18)	O6—C4—C5—C6	−178.95 (19)
O3—S1—C1—C2	−67.04 (17)	C3—C4—C5—C6	0.0 (3)
O1—S1—C1—C6	−6.4 (2)	C4—C5—C6—C1	1.1 (3)
O2—S1—C1—C6	−130.77 (17)	C2—C1—C6—C5	−0.8 (3)
O3—S1—C1—C6	113.59 (17)	S1—C1—C6—C5	178.56 (15)
C6—C1—C2—C3	−0.5 (3)	C2—C3—C7—O5	177.08 (19)
S1—C1—C2—C3	−179.92 (14)	C4—C3—C7—O5	−2.2 (3)
C1—C2—C3—C4	1.6 (3)	C2—C3—C7—O4	−3.0 (3)
C1—C2—C3—C7	−177.75 (17)	C4—C3—C7—O4	177.72 (18)
C2—C3—C4—O6	177.61 (17)	C9—N1—C8—C9^{i}	−57.5 (2)
C7—C3—C4—O6	−3.1 (3)	C8—N1—C9—C8^{i}	57.3 (2)
C2—C3—C4—C5	−1.3 (3)		

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···O3^{ii}	0.82	1.90	2.690 (2)	160
O4—H4···S1^{ii}	0.82	2.96	3.5926 (16)	136
N1—H1A···O7^{iii}	0.914 (9)	1.803 (10)	2.715 (3)	175 (2)
N1—H1B···O3^{iv}	0.907 (10)	2.006 (12)	2.895 (2)	166 (2)
N1—H1B···S1^{iv}	0.907 (10)	2.874 (19)	3.6176 (17)	140 (2)
O7—H7A···O3^{v}	0.848 (10)	1.938 (13)	2.750 (2)	160 (3)

O7—H7A···S1^{v}	0.848 (10)	2.998 (13)	3.781 (2)	154 (2)
O6—H6···O5	0.82	1.91	2.630 (2)	147
O7—H7B···O2	0.849 (10)	1.863 (10)	2.710 (2)	175 (3)

Symmetry codes: (ii) −*x*, −*y*+1, −*z*+2; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) *x*+1, *y*, *z*; (v) *x*, *y*+1, *z*.

Fig. 1

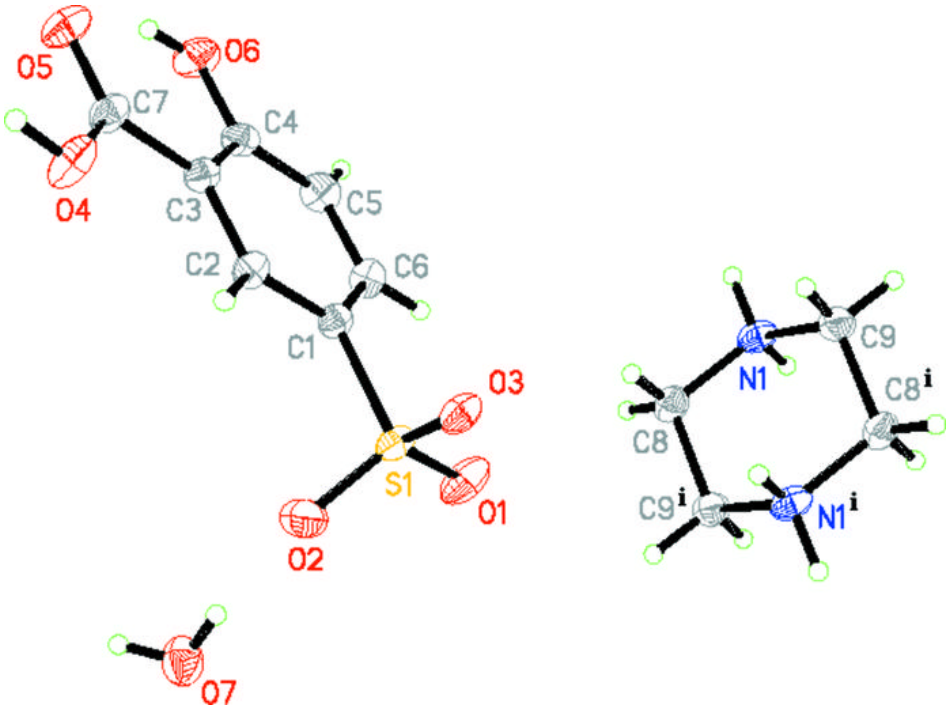
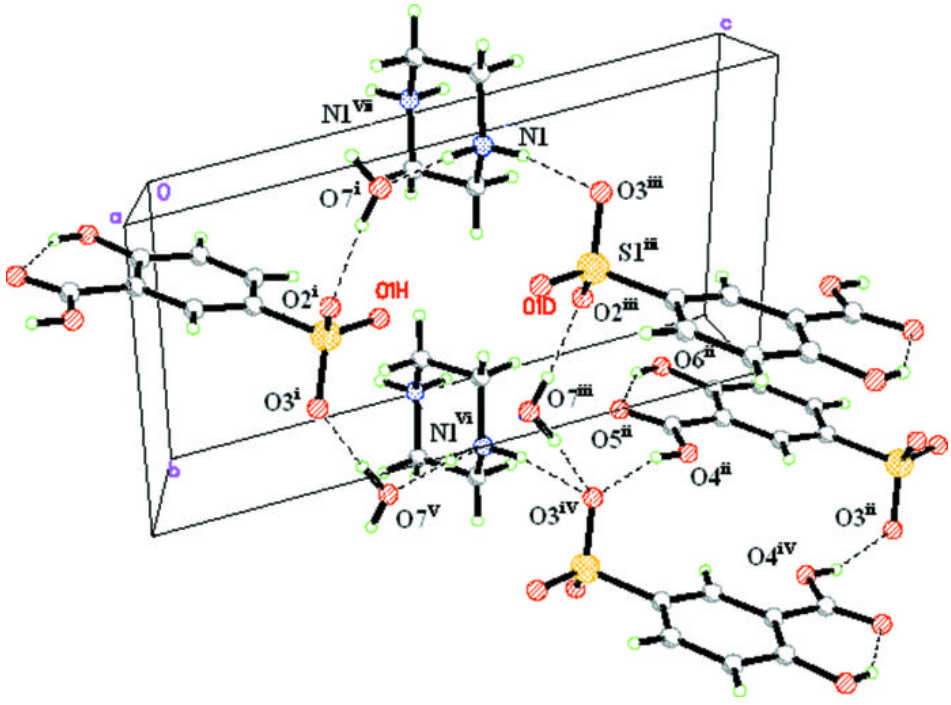


Fig. 2


c
O
a
b
N1vii
N1
O7i
O3iii
S1iii
O2i
O1H
O1D
O2iii
O6ii
O3i
O7iii
N1vi
O5ii
O4ii
O7v
O3iv
O3ii
O4iv