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Hydrogen bonding in two ammonium salts of 5-sulfosalicylic acid: ammonium 3-carboxy-4-hydroxybenzenesulfonate monohydrate and triammonium 3-carboxy-4-hydroxybenzenesulfonate 3-carboxylato-4-hydroxybenzenesulfonate

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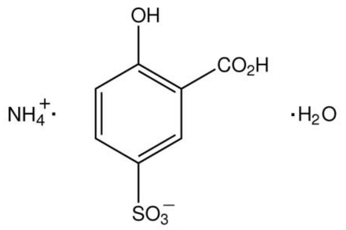
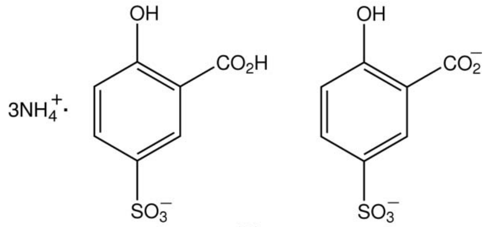
The structures of two ammonium salts of 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid, 5-SSA) have been determined at 200 K. In the 1:1 hydrated salt, ammonium 3-carboxy-4-hydroxybenzenesulfonate monohydrate, $\mathrm{NH_4^+\cdot C_7H_5O_6S^-\cdot H_2O}$, (I), the 5-SSA$^-$ monoanions give two types of head-to-tail laterally linked cyclic hydrogen-bonding associations, both with graph-set $R^4_4(20)$. The first involves both carboxylic acid $\mathrm{O-H\cdots O_{water}}$ and water $\mathrm{O-H\cdots O_{sulfonate}}$ hydrogen bonds at one end, and ammonium $\mathrm{N-H\cdots O_{sulfonate}}$ and $\mathrm{N-H\cdots O_{carboxy}}$ hydrogen bonds at the other. The second association is centrosymmetric, with end linkages through water $\mathrm{O-H\cdots O_{sulfonate}}$ hydrogen bonds. These conjoined units form stacks down *c* and are extended into a three-dimensional framework structure through $\mathrm{N-H\cdots O}$ and water $\mathrm{O-H\cdots O}$ hydrogen bonds to sulfonate O-atom acceptors. Anhydrous triammonium 3-carboxy-4-hydroxybenzenesulfonate 3-carboxylato-4-hydroxybenzenesulfonate, $\mathrm{3NH_4^+\cdot C_7H_4O_6S^{2-}\cdot C_7H_5O_6S^-}$, (II), is unusual, having both dianionic 5-SSA^{2-} and monoanionic 5-SSA$^-$ species. These are linked by a carboxylic acid $\mathrm{O-H\cdots O}$ hydrogen bond and, together with the three ammonium cations (two on general sites and the third comprising two independent half-cations lying on crystallographic twofold rotation axes), give a pseudo-centrosymmetric asymmetric unit. Cation–anion hydrogen bonding within this layered unit involves a cyclic $R^3_3(8)$ association which, together with extensive peripheral $\mathrm{N-H\cdots O}$ hydrogen bonding involving both sulfonate and carboxy/carboxylate acceptors, gives a three-dimensional framework structure. This work further demonstrates the utility of the 5-SSA$^-$ monoanion for the generation of stable hydrogen-bonded crystalline materials, and provides the structure of a dianionic 5-SSA^{2-} species of which there are only a few examples in the crystallographic literature.

Comment

3-Carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid, 5-SSA) is a very strong acid which is capable of protonating water, and the structures of a number of pseudopolymorphic hydrates are known, namely the dihydrate and trihydrate (Mootz & Fayos, 1970; Attig & Mootz, 1977), and the pentahydrate (Merschenz-Quack & Mootz, 1990). Protonated polyaqua species have been found in these structures, *e.g.* $\mathrm{H_7O_3^+}$ in the trihydrate (Mootz & Fayos, 1970). 5-SSA has proved to be a useful acid for the formation of stable crystalline salts with Lewis bases (Bakasova *et al.*, 1991; Raj *et al.*, 2003; Smith *et al.*, 2005, 2006, 2011; Smith & Wermuth, 2008, 2009; Smith, Wermuth & Healy, 2004; Smith, Wermuth & White, 2004). Because no structures of ammonium salts of 5-SSA have been reported, we attempted to prepare 1:1 and 1:2 salts for crystallographic analysis. Both 1:1 and 1:0.5 reactions with ammonium carbonate gave the monohydrated 1:1 salt $\mathrm{NH_4^+\cdot 5\text{-}SSA^-\cdot H_2O}$, (I), but a suitable



(I)



(II)

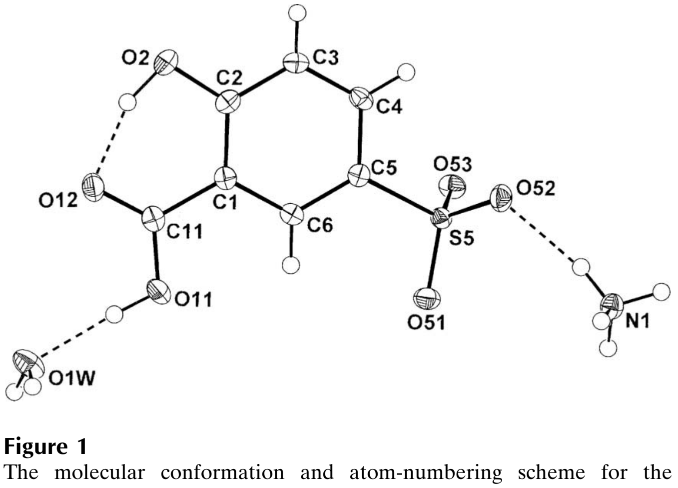


Figure 1
The molecular conformation and atom-numbering scheme for the 5-SSA$^-$ monoanion, the ammonium cation and the solvent water molecule in (I). Inter-species hydrogen bonds are shown as dashed lines and displacement ellipsoids are drawn at the 50% probability level.

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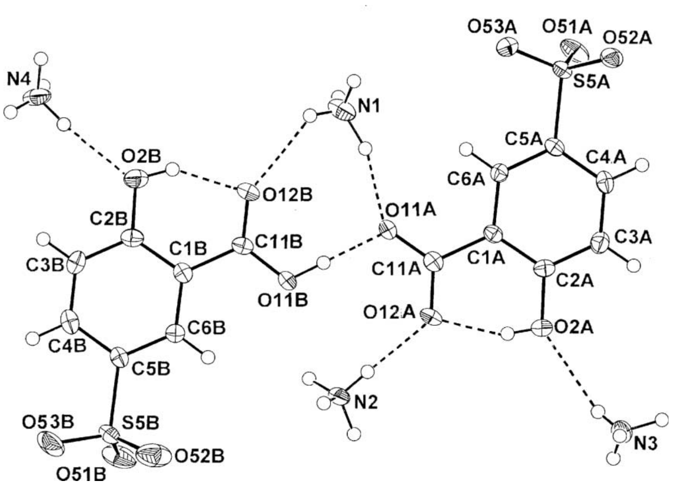

Figure 2

The molecular conformation and atom-numbering scheme for the 5-SSA^{2-} dianion (*A*), the 5-SSA$^-$ monoanion (*B*), the two ammonium cations on general sites (centred at N1 and N2) and the two ammonium cations (N3 and N4) lying on twofold rotation axes in the asymmetric unit of (II). Inter-species hydrogen bonds are shown as dashed lines and displacement ellipsoids are drawn at the 50% probability level.

crystalline 1:2 salt could not be obtained, even with ammonia. However, the 1:1 stoichiometric reaction of 5-SSA with piperidine-4-carboxamide (isonipecotamide) did not give the expected proton-transfer salt of that Lewis base but instead gave the unusual ammonium salt of 5-SSA, $3NH_4^+\cdot5\text{-SSA}^{2-}\cdot5\text{-SSA}^-$, (II), the ammonium ion presumably being derived from the hydrolysis of the amide by 5-SSA. The structures of both (I) and (II) (Figs. 1 and 2) are reported here.

In (I), the 1:1 hydrated ammonium salt of 5-SSA (Fig. 1), the 5-SSA$^-$ monoanion is involved in six intermolecular hydrogen-bonding associations, four with the ammonium cation and two with the water molecule, which acts both as a bridge between sulfonate O-atom acceptors and as an acceptor in the carboxylic acid O—H···O hydrogen bond (Table 1). The 5-SSA$^-$ monoanions give two types of head-to-tail lateral cyclic hydrogen-bonding dimeric associations, through both carboxylic acid O—H···O$_{\text{water}}$ and water O—H···O$_{\text{sulfonate}}$ hydrogen bonds at one end, and through N—H···O$_{\text{sulfonate}}$ and N—H···O$_{\text{carboxy}}$ hydrogen bonds at the other. Both of these conjoined units have graph-set $R_4^4(20)$ (Etter *et al.*, 1990; Bernstein *et al.*, 1995) and form stacks down *c*, and they are extended into a three-dimensional framework structure through N—H···O and water O—H···O hydrogen bonds to sulfonate O-atom acceptors (Fig. 3). Among these are examples of $R_4^4(12)$ and $R_4^3(10)$ cyclic associations.

In salt (II), the asymmetric unit (Fig. 2) contains a 5-SSA^{2-} dianion (*A*), a 5-SSA$^-$ monoanion (*B*) and three ammonium cations. Two of these (centred at N1 and N2) occupy general positions, while the third comprises two independent half-cations (N3 and N4) lying on crystallographic twofold rotation axes. The anions are close to being coplanar [dihedral angle between the *A* and *B* benzene rings = 8.04 (10)°] and associate head-to-head through a strong carboxylic acid O—H···O$_{\text{carboxylate}}$ hydrogen bond. The hydrogen-bonded cation–anion asymmetric unit is pseudo-centrosymmetric and features an inter-anion cyclic hydrogen-bonding association involving atom N1 [graph set $R_3^2(8)$; Table 2]. A related conjoined association involving atom N2 [N2—H22···O11*B*: N···O = 2.909 (3) Å and N—H···O = 108°] is also present. Extensive peripheral hydrogen bonding and N—H···O

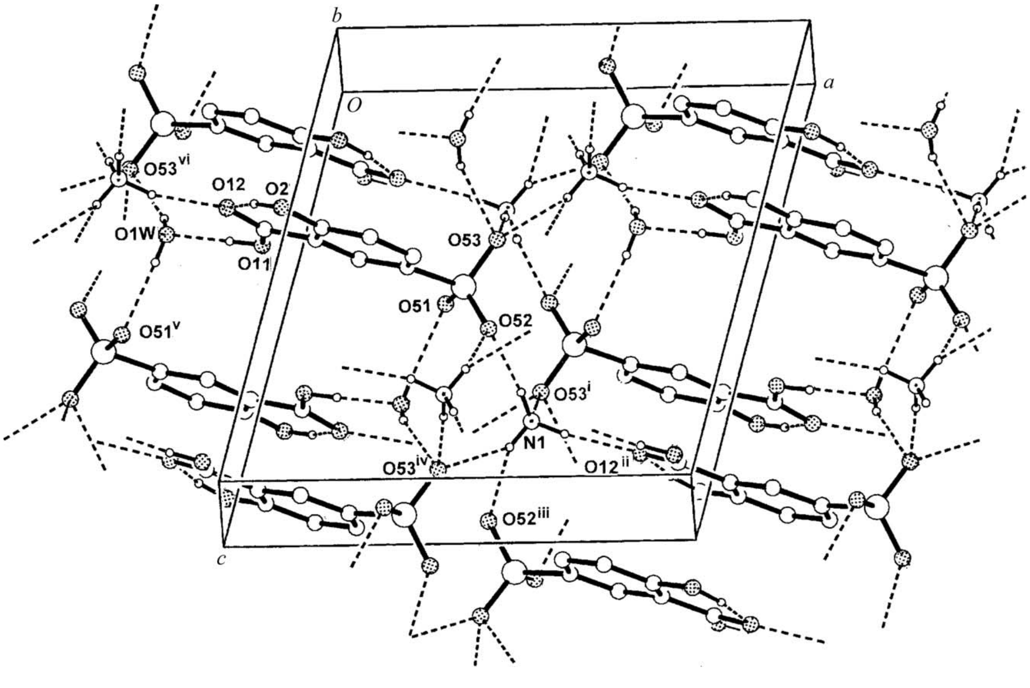

Figure 3

A perspective view of the three-dimensional hydrogen-bonded framework structure of (I). Hydrogen-bonding associations are shown as dashed lines and non-associative H atoms have been omitted. For symmetry codes, see Table 1.

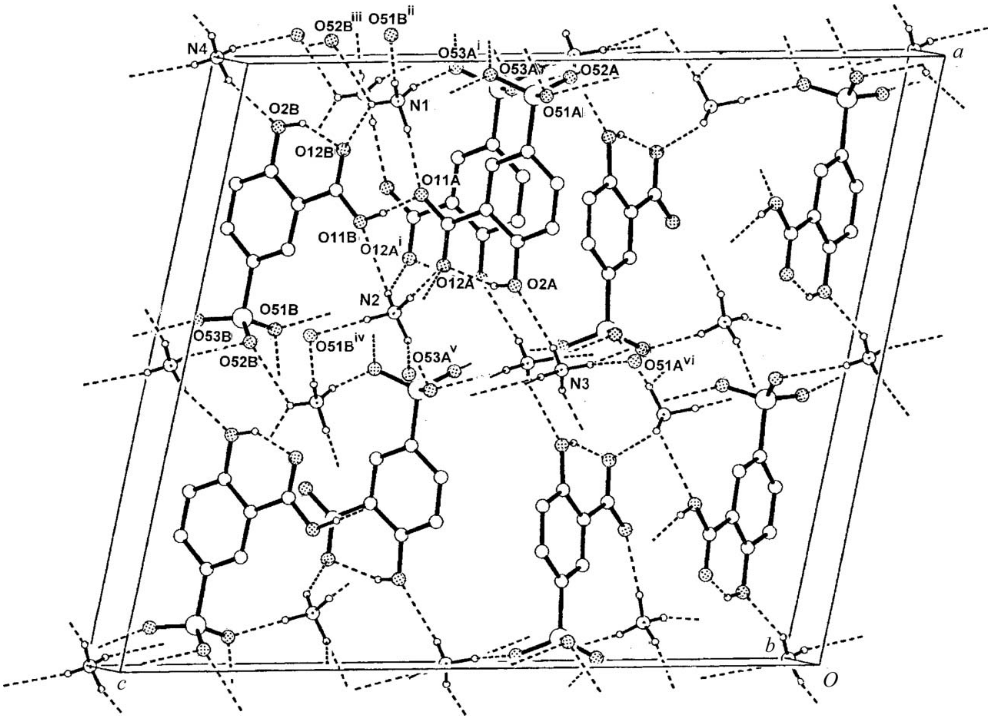

Figure 4

The three-dimensional hydrogen-bonded framework structure of (II) in a perspective view down the *b*-axial direction of the unit cell. Hydrogen-bonding associations are shown as dashed lines and non-associative H atoms have been omitted. For symmetry codes, see Table 2.

interactions involving the ammonium anions and both sulfonate and carboxy/carboxylate O-atom acceptors gives a three-dimensional framework structure (Fig. 4).

The 5-SSA$^-$ monoanions and 5-SSA^{2-} dianions in (I) and (II) have features which are commonly found in other structures of both the parent acid and its anions (Attig & Mootz, 1977; Smith, Wermuth & White, 2004). In these, the carboxylic acid group is essentially coplanar with the benzene ring, due largely to the cyclic (*S*6) motif generated by the short intramolecular phenolic O—H$\cdots$O$_{carboxy}$ hydrogen bond. In (I), the C2—C1—C11—O11 torsion angle is −175.28 (13)°, and in (II) the corresponding angles are −178.22 (19) (*A*) and −177.44 (19)° (*B*). A second feature common to most 5-SSA structures is the relatively short intramolecular aromatic C—H$\cdots$O interaction with one O atom of the sulfonate group, resulting in its lying close to the plane of the benzene ring [C$\cdots$O contacts and C—C—S—O torsion angles of 2.9242 (19) Å and −13.37 (14)°, respectively, in (I), 2.930 (3) Å and 20.9 (2)°, respectively, in anion *A* of (II), and 2.910 (3) Å and −23.3 (2)°, respectively, in anion *B* of (II)]. These values compare with values of, for example, 2.9480 (18) Å and −14.41 (14)°, and 2.884 (3) Å and −6.0 (2)° in the hydroxylamine and morpholine (monohydrate) salts, respectively (Smith *et al.*, 2011).

The work presented here further demonstrates the utility of the 5-SSA$^-$ monoanion, in particular for the generation of stable hydrogen-bonded crystalline materials, as well as providing an example of a structure having a dianionic 5-SSA^{2-} species, of which there are few occurrences in the crystallographic literature.

Experimental

Compound (I) was synthesized by heating together 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid, 1 mmol) and $(NH_4)_2CO_3$ (either 0.5 mmol or 1 mmol) in water (30 ml) for 10 min. Colourless flat prisms were obtained after total room-temperature evaporation of the solvent over a period of several months. Compound (II) was obtained as the product from the attempted preparation of a salt of 5-sulfosalicylic acid with the Lewis base 4-carbamoylpiperidine (isonipecotamide). Isonipecotamide (1 mmol) and 5-sulfosalicylic acid (1 mmol) in methanol (50 ml) were heated under reflux for 10 min and, after concentration to *ca* 30 ml, total room-temperature evaporation of the hot-filtered solution gave a viscous product containing a small quantity of colourless crystals of (II), from which a specimen was cleaved for the X-ray analysis.

Hydrated salt (I)

Crystal data

$NH_4^+ \cdot C_7H_5O_6S^- \cdot H_2O$
$M_r = 253.23$
Monoclinic, $P2_1/c$
$a = 11.8476$ (3) Å
$b = 7.2879$ (2) Å
$c = 12.1343$ (3) Å
$\beta = 105.018$ (3)°

$V = 1011.94$ (5) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.34$ mm^{-1}
$T = 200$ K
0.30 × 0.22 × 0.12 mm

Data collection

Oxford Gemini-S CCD area-detector diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010)
$T_{min} = 0.970$, $T_{max} = 0.980$

6550 measured reflections
1986 independent reflections
1681 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$

Table 1
Geometry of hydrogen-bonds and other interactions (Å, °) for (I).

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
N1—H1*A*···O53$^{\rm i}$	0.94 (2)	1.96 (2)	2.8881 (18)	173 (2)
N1—H1*B*···O12$^{\rm ii}$	0.92 (2)	1.99 (2)	2.861 (2)	156.2 (19)
N1—H1*C*···O52$^{\rm iii}$	0.86 (2)	2.40 (2)	3.0230 (19)	129.3 (18)
N1—H1*C*···O53$^{\rm iv}$	0.86 (2)	2.25 (2)	2.9703 (19)	140.7 (19)
N1—H1*D*···O52	0.92 (2)	1.98 (2)	2.8825 (19)	169 (2)
O2—H2···O12	0.99 (3)	1.67 (3)	2.6092 (17)	158 (3)
O11—H11···O1*W*	0.89 (2)	1.78 (2)	2.6706 (18)	177 (2)
O1*W*—H11*W*···O51$^{\rm v}$	0.76 (2)	2.04 (2)	2.7985 (18)	177 (3)
O1*W*—H12*W*···O53$^{\rm vi}$	0.83 (2)	2.26 (2)	3.0591 (18)	160 (2)

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

Table 2
Geometry of hydrogen-bonds and other interactions (Å, °) for (II).

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
O2*A*—H2*A*···O12*A*	0.80 (3)	1.79 (2)	2.536 (2)	155 (2)
O2*B*—H2*B*···O12*B*	0.87 (3)	1.78 (3)	2.554 (2)	146 (3)
O11*B*—H11*B*···O11*A*	0.92 (3)	1.65 (3)	2.564 (2)	175 (3)
N1—H11···O53*A*$^{\rm i}$	0.91	1.95	2.841 (2)	168
N1—H12···O51*B*$^{\rm ii}$	0.90	1.94	2.823 (3)	168
N1—H13···O11*A*	0.96	2.01	2.917 (2)	156
N1—H14···O12*B*	0.84	2.19	2.831 (2)	133
N1—H14···O52*B*$^{\rm iii}$	0.84	2.31	2.773 (2)	115
N2—H21···O51*B*$^{\rm iv}$	0.96	1.90	2.846 (3)	171
N2—H22···O11*B*	0.97	2.45	2.909 (2)	108
N2—H22···O12*A*$^{\rm i}$	0.97	2.52	3.418 (2)	153
N2—H23···O12*A*	0.86	1.93	2.794 (2)	177
N2—H24···O53*A*$^{\rm v}$	0.96	2.43	2.810 (2)	103
N3—H31···O2*A*	0.88	2.23	2.9753 (18)	143
N3—H32···O51*A*$^{\rm vi}$	0.98	1.93	2.848 (3)	155
N3—H32···O52*A*$^{\rm vii}$	0.98	2.47	2.9901 (16)	113
N4—H41···O2*B*	0.85	2.10	2.906 (2)	156
N4—H42···O52*B*$^{\rm viii}$	0.81	2.15	2.891 (2)	152

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.080$
$S = 1.10$
1986 reflections
177 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.41$ e Å^{-3}

Salt (II)

Crystal data

$3\mathrm{NH_4}^+\cdot\mathrm{C_7H_4O_6S}^{2-}\cdot\mathrm{C_7H_5O_6S}^-$
$M_r = 487.48$
Monoclinic, *C*2
$a = 18.7682$ (8) Å
$b = 5.0027$ (2) Å
$c = 21.2122$ (10) Å
$\beta = 101.990$ (4)°

$V = 1948.20$ (15) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.35$ mm^{-1}
$T = 200$ K
0.35 × 0.20 × 0.15 mm

Data collection

Oxford Gemini-S CCD area-detector diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010)
$T_{\min} = 0.970$, $T_{\max} = 0.980$

6235 measured reflections
3804 independent reflections
3399 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.064$
$S = 0.96$
3804 reflections
293 parameters
1 restraint

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}
Absolute structure: Flack (1983), 1668 Friedel pairs
Flack parameter: 0.47 (5)

H atoms involved in hydrogen-bonding interactions were located by difference methods and their positional and isotropic displacement parameters were refined. However, in the final stages of the refinement of (II), all ammonium H atoms were allowed to ride on their parent atoms, with $U_{\rm iso}(\mathrm{H}) = 1.2U_{\rm eq}(\mathrm{N})$. Other H atoms were included in the refinement at calculated positions (C—H = 0.93 Å) and were also allowed to ride, with $U_{\rm iso}(\mathrm{H}) = 1.2U_{\rm eq}(\mathrm{C})$. For (II), the absolute structure parameter (Flack, 1983) was refined as the relative population of an inversion twin domain, with a resulting value of 0.47 (5) (1668 Friedel pairs), thus indicating an inversion twin with approximately equal domain populations.

For both compounds, data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 2012); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3289). Services for accessing these data are described at the back of the journal.

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supplementary materials

Acta Cryst. (2013). C**69**, 534-537 [doi:10.1107/S0108270113008846]

Hydrogen bonding in two ammonium salts of 5-sulfosalicylic acid: ammonium 3-carboxy-4-hydroxybenzenesulfonate monohydrate and triammonium 3-carboxy-4-hydroxybenzenesulfonate 3-carboxylato-4-hydroxybenzenesulfonate

Graham Smith and Urs D. Wermuth

(I) Ammonium 3-carboxy-4-hydroxybenzenesulfonate monohydrate

Crystal data

$NH_4^+\cdot C_7H_5O_6S^-\cdot H_2O$
M_r = 253.23
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 11.8476 (3) Å
b = 7.2879 (2) Å
c = 12.1343 (3) Å
β = 105.018 (3)°
V = 1011.94 (5) Å^3
Z = 4
F(000) = 528
D_x = 1.662 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4154 reflections
θ = 3.3–28.8°
μ = 0.34 mm^{-1}
T = 200 K
Plate, colourless
0.30 × 0.22 × 0.12 mm

Data collection

Oxford Gemini-S CCD area-detector diffractometer
Radiation source: Enhance (Mo) X-ray source
Graphite monochromator
Detector resolution: 16.077 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010)
T_{min} = 0.970, T_{max} = 0.980
6550 measured reflections
1986 independent reflections
1681 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 26.0°, θ_{min} = 3.3°
$h = -14\rightarrow14$
$k = -8\rightarrow8$
$l = -14\rightarrow14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.080
S = 1.10
1986 reflections
177 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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 $F^2 > \sigma(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S5	0.37799 (3)	0.25408 (5)	0.47006 (3)	0.0153 (1)
O2	−0.03102 (11)	0.74348 (15)	0.35866 (10)	0.0237 (3)
O11	−0.07816 (10)	0.17557 (16)	0.35930 (9)	0.0222 (3)
O12	−0.16178 (10)	0.45066 (16)	0.31543 (10)	0.0237 (4)
O51	0.34009 (10)	0.06649 (14)	0.48037 (9)	0.0218 (3)
O52	0.45827 (9)	0.32167 (15)	0.57398 (9)	0.0220 (3)
O53	0.42377 (10)	0.27654 (15)	0.36926 (9)	0.0204 (3)
C1	0.04430 (13)	0.4338 (2)	0.38498 (12)	0.0158 (4)
C2	0.05972 (14)	0.6246 (2)	0.38732 (12)	0.0176 (4)
C3	0.17155 (14)	0.6994 (2)	0.42016 (13)	0.0180 (5)
C4	0.26804 (14)	0.5877 (2)	0.44817 (13)	0.0180 (4)
C5	0.25331 (13)	0.3955 (2)	0.44433 (12)	0.0159 (4)
C6	0.14291 (13)	0.3203 (2)	0.41430 (12)	0.0166 (4)
C11	−0.07415 (13)	0.3551 (2)	0.35021 (12)	0.0173 (5)
N1	0.58883 (13)	0.0734 (2)	0.74498 (13)	0.0197 (4)
O1W	−0.29627 (11)	0.04628 (19)	0.31417 (12)	0.0282 (4)
H2	−0.096 (3)	0.655 (4)	0.337 (2)	0.081 (9)*
H3	0.18100	0.82620	0.42320	0.0220*
H4	0.34260	0.63830	0.46950	0.0220*
H6	0.13380	0.19350	0.41350	0.0200*
H11	−0.152 (2)	0.136 (3)	0.344 (2)	0.063 (8)*
H1A	0.583 (2)	−0.044 (3)	0.713 (2)	0.061 (7)*
H1B	0.6668 (19)	0.097 (3)	0.7774 (15)	0.031 (5)*
H1C	0.5567 (18)	0.071 (3)	0.8010 (18)	0.038 (6)*
H1D	0.555 (2)	0.163 (3)	0.6940 (19)	0.044 (6)*
H11W	−0.306 (2)	0.016 (3)	0.371 (2)	0.042 (7)*
H12W	−0.314 (2)	−0.039 (3)	0.267 (2)	0.055 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S5	0.0142 (2)	0.0158 (2)	0.0163 (2)	−0.0009 (2)	0.0047 (2)	0.0002 (2)
O2	0.0202 (6)	0.0203 (6)	0.0293 (6)	0.0053 (5)	0.0043 (5)	0.0033 (5)
O11	0.0173 (6)	0.0220 (6)	0.0269 (6)	−0.0055 (5)	0.0048 (5)	−0.0014 (5)
O12	0.0162 (6)	0.0271 (7)	0.0264 (6)	−0.0006 (5)	0.0028 (5)	−0.0007 (5)
O51	0.0224 (6)	0.0167 (6)	0.0275 (6)	−0.0015 (5)	0.0086 (5)	0.0022 (5)
O52	0.0180 (6)	0.0238 (6)	0.0209 (6)	0.0010 (5)	−0.0011 (5)	−0.0018 (5)
O53	0.0219 (6)	0.0204 (6)	0.0223 (6)	−0.0010 (5)	0.0120 (5)	0.0000 (4)

C1	0.0158 (8)	0.0191 (8)	0.0132 (7)	−0.0004 (7)	0.0053 (6)	−0.0001 (6)
C2	0.0213 (8)	0.0193 (8)	0.0130 (7)	0.0025 (7)	0.0061 (6)	0.0018 (6)
C3	0.0222 (8)	0.0148 (8)	0.0175 (8)	−0.0017 (7)	0.0061 (6)	0.0006 (6)
C4	0.0182 (8)	0.0202 (8)	0.0164 (7)	−0.0054 (7)	0.0059 (6)	0.0004 (6)
C5	0.0165 (8)	0.0183 (8)	0.0135 (7)	0.0009 (6)	0.0051 (6)	0.0004 (6)
C6	0.0180 (8)	0.0164 (8)	0.0160 (7)	−0.0023 (7)	0.0054 (6)	−0.0011 (6)
C11	0.0177 (8)	0.0231 (9)	0.0116 (7)	−0.0014 (7)	0.0045 (6)	−0.0013 (6)
N1	0.0173 (8)	0.0218 (8)	0.0203 (7)	0.0014 (6)	0.0055 (6)	0.0002 (6)
O1W	0.0304 (7)	0.0332 (8)	0.0222 (7)	−0.0139 (6)	0.0089 (6)	−0.0017 (6)

Geometric parameters (Å, º)

S5—O51	1.4545 (11)	N1—H1A	0.94 (2)
S5—O52	1.4546 (11)	N1—H1C	0.86 (2)
S5—O53	1.4700 (12)	C1—C11	1.473 (2)
S5—C5	1.7615 (16)	C1—C6	1.400 (2)
O2—C2	1.354 (2)	C1—C2	1.402 (2)
O11—C11	1.3149 (19)	C2—C3	1.392 (2)
O12—C11	1.2304 (19)	C3—C4	1.373 (2)
O2—H2	0.99 (3)	C4—C5	1.411 (2)
O11—H11	0.89 (2)	C5—C6	1.377 (2)
O1W—H12W	0.83 (2)	C3—H3	0.9300
O1W—H11W	0.76 (2)	C4—H4	0.9300
N1—H1B	0.92 (2)	C6—H6	0.9300
N1—H1D	0.92 (2)		
O51—S5—O52	113.01 (6)	O2—C2—C3	117.15 (13)
O51—S5—O53	111.40 (7)	O2—C2—C1	122.61 (15)
O51—S5—C5	107.57 (7)	C1—C2—C3	120.24 (14)
O52—S5—O53	112.60 (7)	C2—C3—C4	120.57 (14)
O52—S5—C5	106.59 (7)	C3—C4—C5	119.52 (15)
O53—S5—C5	105.11 (7)	S5—C5—C6	120.62 (11)
C2—O2—H2	99.4 (19)	C4—C5—C6	120.31 (14)
C11—O11—H11	111.0 (14)	S5—C5—C4	118.96 (12)
H11W—O1W—H12W	110 (2)	C1—C6—C5	120.32 (14)
H1A—N1—H1C	108 (2)	O11—C11—C1	114.58 (13)
H1A—N1—H1D	114 (2)	O12—C11—C1	122.31 (14)
H1B—N1—H1D	112 (2)	O11—C11—O12	123.12 (14)
H1C—N1—H1D	110 (2)	C2—C3—H3	120.00
H1B—N1—H1C	105.4 (19)	C4—C3—H3	120.00
H1A—N1—H1B	108 (2)	C3—C4—H4	120.00
C6—C1—C11	120.87 (13)	C5—C4—H4	120.00
C2—C1—C11	120.10 (14)	C1—C6—H6	120.00
C2—C1—C6	119.02 (14)	C5—C6—H6	120.00
O51—S5—C5—C4	170.43 (11)	C2—C1—C11—O11	−175.28 (13)
O51—S5—C5—C6	−13.37 (14)	C2—C1—C11—O12	4.8 (2)
O52—S5—C5—C4	48.96 (13)	C6—C1—C11—O11	5.8 (2)
O52—S5—C5—C6	−134.84 (12)	C6—C1—C11—O12	−174.16 (14)
O53—S5—C5—C4	−70.76 (13)	O2—C2—C3—C4	−178.65 (14)

O53—S5—C5—C6	105.45 (13)	C1—C2—C3—C4	1.5 (2)
C6—C1—C2—O2	179.07 (13)	C2—C3—C4—C5	−0.5 (2)
C6—C1—C2—C3	−1.0 (2)	C3—C4—C5—S5	175.28 (12)
C11—C1—C2—O2	0.1 (2)	C3—C4—C5—C6	−0.9 (2)
C11—C1—C2—C3	179.98 (14)	S5—C5—C6—C1	−174.81 (11)
C2—C1—C6—C5	−0.4 (2)	C4—C5—C6—C1	1.3 (2)
C11—C1—C6—C5	178.61 (13)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O53^{i}	0.94 (2)	1.96 (2)	2.8881 (18)	173 (2)
N1—H1*B*···O12^{ii}	0.92 (2)	1.99 (2)	2.861 (2)	156.2 (19)
N1—H1*C*···O52^{iii}	0.86 (2)	2.40 (2)	3.0230 (19)	129.3 (18)
N1—H1*C*···O53^{iv}	0.86 (2)	2.25 (2)	2.9703 (19)	140.7 (19)
N1—H1*D*···O52	0.92 (2)	1.98 (2)	2.8825 (19)	169 (2)
O2—H2···O12	0.99 (3)	1.67 (3)	2.6092 (17)	158 (3)
O11—H11···O1*W*	0.89 (2)	1.78 (2)	2.6706 (18)	177 (2)
O1*W*—H11*W*···O51^{v}	0.76 (2)	2.04 (2)	2.7985 (18)	177 (3)
O1*W*—H12*W*···O53^{vi}	0.83 (2)	2.26 (2)	3.0591 (18)	160 (2)
C3—H3···O51^{vii}	0.93	2.53	3.3049 (19)	140
C4—H4···O52^{viii}	0.93	2.56	3.387 (2)	148
C6—H6···O11	0.93	2.43	2.741 (2)	100
C6—H6···O51	0.93	2.54	2.9242 (19)	105

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1; (ii) *x*+1, −*y*+1/2, *z*+1/2; (iii) −*x*+1, *y*−1/2, −*z*+3/2; (iv) *x*, −*y*+1/2, *z*+1/2; (v) −*x*, −*y*, −*z*+1; (vi) −*x*, *y*−1/2, −*z*+1/2; (vii) *x*, *y*+1, *z*; (viii) −*x*+1, −*y*+1, −*z*+1.

(II) Triammonium 3-carboxy-4-hydroxybenzenesulfonate 3-carboxylato-4-hydroxybenzenesulfonate

Crystal data

$3NH_4^+ \cdot C_7H_4O_6S^{2-} \cdot C_7H_5O_6S^-$
M_r = 487.48
Monoclinic, *C*2
Hall symbol: C 2y
a = 18.7682 (8) Å
b = 5.0027 (2) Å
c = 21.2122 (10) Å
β = 101.990 (4)°
V = 1948.20 (15) Å^3
Z = 4

F(000) = 1016
D_x = 1.662 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 4309 reflections
θ = 3.3–28.6°
μ = 0.35 mm^{-1}
T = 200 K
Prism, colourless
0.35 × 0.20 × 0.15 mm

Data collection

Oxford Gemini-S CCD area-detector diffractometer
Radiation source: Enhance (Mo) X-ray source
Graphite monochromator
Detector resolution: 16.077 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010)
T_{min} = 0.970, T_{max} = 0.980

6235 measured reflections
3804 independent reflections
3399 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 26.0°, θ_{min} = 3.3°
h = −20→22
k = −6→6
l = −26→22

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.064$
$S = 0.96$
3804 reflections
293 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0372P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Absolute structure: Flack (1983), 1668 Friedel pairs
Flack parameter: 0.47 (5)

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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 $F^2 > \sigma(F^2)$ 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}
S5B	0.57238 (3)	0.85320 (10)	0.88754 (3)	0.0237 (2)
O2B	0.88602 (8)	0.6623 (4)	0.90275 (9)	0.0307 (6)
O11B	0.73560 (8)	0.1825 (3)	0.78231 (8)	0.0241 (5)
O12B	0.85187 (8)	0.2752 (3)	0.82377 (8)	0.0296 (6)
O51B	0.55039 (9)	1.0130 (4)	0.82910 (9)	0.0412 (6)
O52B	0.53507 (9)	0.6018 (4)	0.88215 (10)	0.0499 (7)
O53B	0.56776 (10)	0.9980 (5)	0.94496 (9)	0.0510 (7)
C1B	0.76141 (12)	0.5330 (4)	0.85860 (11)	0.0197 (7)
C2B	0.81332 (12)	0.6960 (4)	0.89824 (10)	0.0209 (7)
C3B	0.79130 (12)	0.8985 (4)	0.93500 (11)	0.0247 (7)
C4B	0.71836 (12)	0.9423 (5)	0.93189 (11)	0.0242 (7)
C5B	0.66613 (12)	0.7820 (4)	0.89291 (10)	0.0195 (7)
C6B	0.68730 (11)	0.5788 (4)	0.85716 (10)	0.0205 (7)
C11B	0.78613 (11)	0.3196 (4)	0.81982 (10)	0.0199 (7)
S5A	0.95259 (3)	−0.89285 (10)	0.62625 (3)	0.0186 (2)
O2A	0.63906 (8)	−0.6322 (4)	0.58388 (8)	0.0289 (5)
O11A	0.78318 (8)	−0.2015 (3)	0.72237 (7)	0.0228 (5)
O12A	0.66852 (8)	−0.2910 (3)	0.67398 (8)	0.0301 (6)
O51A	0.98105 (9)	−0.7701 (3)	0.57438 (8)	0.0326 (6)
O52A	0.95508 (8)	−1.1831 (3)	0.62381 (7)	0.0256 (5)
O53A	0.98664 (8)	−0.7920 (3)	0.68988 (8)	0.0281 (5)
C1A	0.76202 (11)	−0.5447 (4)	0.64253 (11)	0.0180 (6)
C2A	0.71172 (11)	−0.6871 (4)	0.59609 (10)	0.0196 (7)
C3A	0.73507 (12)	−0.8908 (5)	0.56095 (11)	0.0238 (7)
C4A	0.80832 (12)	−0.9517 (4)	0.57040 (11)	0.0207 (7)

C5A	0.85886 (11)	−0.8110 (4)	0.61511 (10)	0.0181 (7)
C6A	0.83560 (11)	−0.6089 (4)	0.65088 (10)	0.0178 (6)
C11A	0.73660 (12)	−0.3307 (4)	0.68218 (10)	0.0195 (7)
N1	0.93692 (10)	−0.1249 (4)	0.78033 (9)	0.0309 (6)
N2	0.58715 (9)	0.1316 (4)	0.70855 (9)	0.0243 (6)
N3	0.50000	−0.8115 (5)	0.50000	0.0225 (8)
N4	1.00000	0.9029 (6)	1.00000	0.0312 (9)
H2B	0.8928 (15)	0.536 (6)	0.8762 (14)	0.050 (9)*
H3B	0.82590	1.00390	0.96160	0.0300*
H4B	0.70370	1.07950	0.95590	0.0290*
H6B	0.65230	0.47090	0.83190	0.0250*
H11B	0.7513 (16)	0.049 (7)	0.7586 (16)	0.078 (12)*
H2A	0.6370 (13)	−0.506 (5)	0.6065 (12)	0.030 (8)*
H3A	0.70140	−0.98650	0.53100	0.0290*
H4A	0.82380	−1.08800	0.54660	0.0250*
H6A	0.86960	−0.51500	0.68090	0.0210*
H11	0.95760	−0.01030	0.75620	0.0370*
H12	0.96770	−0.25720	0.79650	0.0370*
H13	0.89030	−0.20350	0.76240	0.0370*
H14	0.93010	−0.03740	0.81210	0.0370*
H21	0.57660	0.07340	0.74860	0.0290*
H22	0.61630	0.29430	0.71460	0.0290*
H23	0.61260	0.00450	0.69680	0.0290*
H24	0.54010	0.14480	0.68010	0.0290*
H31	0.53500	−0.69410	0.51290	0.0270*
H32	0.50980	−0.92950	0.46590	0.0270*
H41	0.96300	0.81290	0.98120	0.0380*
H42	0.98700	1.00450	1.02500	0.0380*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S5B	0.0234 (3)	0.0249 (3)	0.0242 (3)	0.0085 (2)	0.0083 (2)	−0.0002 (2)
O2B	0.0188 (8)	0.0416 (11)	0.0317 (10)	0.0003 (7)	0.0054 (7)	−0.0052 (8)
O11B	0.0209 (8)	0.0224 (9)	0.0290 (10)	0.0040 (6)	0.0055 (7)	−0.0070 (7)
O12B	0.0182 (9)	0.0327 (10)	0.0381 (11)	0.0068 (7)	0.0063 (7)	−0.0075 (7)
O51B	0.0356 (10)	0.0560 (12)	0.0334 (11)	0.0220 (8)	0.0106 (8)	0.0178 (9)
O52B	0.0290 (9)	0.0331 (9)	0.0894 (16)	−0.0010 (9)	0.0165 (9)	0.0103 (11)
O53B	0.0407 (11)	0.0816 (14)	0.0327 (11)	0.0227 (10)	0.0120 (9)	−0.0196 (10)
C1B	0.0235 (12)	0.0189 (12)	0.0170 (12)	0.0034 (8)	0.0052 (9)	0.0024 (8)
C2B	0.0179 (12)	0.0257 (11)	0.0202 (12)	0.0009 (9)	0.0067 (10)	0.0050 (9)
C3B	0.0288 (13)	0.0244 (13)	0.0198 (12)	−0.0050 (9)	0.0024 (9)	−0.0033 (9)
C4B	0.0346 (13)	0.0186 (11)	0.0205 (13)	0.0024 (9)	0.0083 (10)	−0.0007 (9)
C5B	0.0239 (12)	0.0180 (12)	0.0173 (12)	0.0024 (9)	0.0058 (9)	0.0001 (9)
C6B	0.0188 (11)	0.0208 (11)	0.0214 (12)	0.0007 (9)	0.0031 (9)	−0.0011 (9)
C11B	0.0180 (12)	0.0195 (11)	0.0230 (12)	0.0021 (9)	0.0062 (9)	0.0025 (10)
S5A	0.0177 (3)	0.0164 (2)	0.0234 (3)	0.0021 (2)	0.0084 (2)	0.0012 (2)
O2A	0.0172 (8)	0.0331 (10)	0.0345 (10)	0.0036 (7)	0.0013 (7)	−0.0084 (9)
O11A	0.0222 (8)	0.0224 (8)	0.0243 (9)	0.0030 (6)	0.0059 (7)	−0.0071 (7)
O12A	0.0180 (9)	0.0354 (9)	0.0371 (11)	0.0082 (7)	0.0064 (8)	−0.0104 (8)

O51A	0.0340 (10)	0.0300 (9)	0.0412 (11)	0.0080 (7)	0.0250 (8)	0.0084 (8)
O52A	0.0232 (8)	0.0189 (7)	0.0340 (10)	0.0045 (7)	0.0044 (7)	0.0013 (7)
O53A	0.0197 (8)	0.0349 (9)	0.0286 (10)	−0.0009 (7)	0.0023 (7)	−0.0060 (7)
C1A	0.0188 (11)	0.0158 (10)	0.0205 (12)	0.0019 (9)	0.0069 (9)	0.0017 (9)
C2A	0.0181 (11)	0.0193 (11)	0.0208 (12)	0.0007 (9)	0.0024 (9)	0.0054 (9)
C3A	0.0282 (12)	0.0201 (11)	0.0206 (12)	0.0014 (10)	−0.0006 (9)	−0.0017 (10)
C4A	0.0288 (13)	0.0168 (12)	0.0164 (12)	0.0030 (8)	0.0045 (10)	−0.0015 (8)
C5A	0.0190 (12)	0.0178 (11)	0.0186 (12)	0.0037 (8)	0.0068 (9)	0.0027 (9)
C6A	0.0178 (10)	0.0167 (11)	0.0187 (11)	−0.0007 (8)	0.0031 (9)	−0.0015 (9)
C11A	0.0230 (12)	0.0174 (11)	0.0190 (12)	0.0016 (8)	0.0063 (9)	0.0026 (9)
N1	0.0260 (10)	0.0400 (12)	0.0290 (11)	0.0131 (9)	0.0107 (8)	0.0062 (10)
N2	0.0189 (9)	0.0225 (10)	0.0324 (11)	0.0049 (8)	0.0071 (8)	−0.0028 (9)
N3	0.0258 (15)	0.0197 (13)	0.0237 (15)	0.0000	0.0094 (12)	0.0000
N4	0.0114 (13)	0.062 (2)	0.0207 (15)	0.0000	0.0044 (11)	0.0000

Geometric parameters (Å, º)

S5B—O51B	1.461 (2)	N3—H32	0.9800
S5B—O52B	1.432 (2)	N3—H31	0.8800
S5B—O53B	1.435 (2)	N4—H41	0.8500
S5B—C5B	1.776 (2)	N4—H42	0.8100
S5A—O51A	1.4551 (18)	N4—H41^{ii}	0.8500
S5A—O52A	1.4541 (16)	N4—H42^{ii}	0.8100
S5A—O53A	1.4582 (17)	C1B—C11B	1.480 (3)
S5A—C5A	1.774 (2)	C1B—C6B	1.404 (3)
O2B—C2B	1.358 (3)	C1B—C2B	1.407 (3)
O11B—C11B	1.300 (3)	C2B—C3B	1.393 (3)
O12B—C11B	1.239 (3)	C3B—C4B	1.374 (3)
O2B—H2B	0.87 (3)	C4B—C5B	1.397 (3)
O11B—H11B	0.92 (3)	C5B—C6B	1.375 (3)
O2A—C2A	1.362 (3)	C3B—H3B	0.9300
O11A—C11A	1.265 (3)	C4B—H4B	0.9300
O12A—C11A	1.269 (3)	C6B—H6B	0.9300
O2A—H2A	0.80 (3)	C1A—C11A	1.499 (3)
N1—H13	0.9600	C1A—C6A	1.393 (3)
N1—H14	0.8400	C1A—C2A	1.408 (3)
N1—H12	0.9000	C2A—C3A	1.386 (3)
N1—H11	0.9100	C3A—C4A	1.382 (3)
N2—H22	0.9700	C4A—C5A	1.386 (3)
N2—H23	0.8600	C5A—C6A	1.388 (3)
N2—H24	0.9600	C3A—H3A	0.9300
N2—H21	0.9600	C4A—H4A	0.9300
N3—H32^{i}	0.9800	C6A—H6A	0.9300
N3—H31^{i}	0.8800		
O51B—S5B—O52B	111.44 (12)	S5B—C5B—C6B	120.59 (16)
O51B—S5B—O53B	112.82 (12)	C4B—C5B—C6B	120.2 (2)
O51B—S5B—C5B	105.41 (10)	S5B—C5B—C4B	119.15 (16)
O52B—S5B—O53B	113.34 (13)	C1B—C6B—C5B	120.5 (2)
O52B—S5B—C5B	106.89 (10)	O11B—C11B—C1B	116.60 (19)

O53B—S5B—C5B	106.30 (11)
O51A—S5A—C5A	108.15 (10)
O51A—S5A—O52A	112.02 (9)
O51A—S5A—O53A	113.25 (10)
O53A—S5A—C5A	105.98 (10)
O52A—S5A—O53A	111.55 (9)
O52A—S5A—C5A	105.32 (9)
C2B—O2B—H2B	108.9 (19)
C11B—O11B—H11B	116 (2)
C2A—O2A—H2A	102.5 (18)
H11—N1—H12	111.00
H12—N1—H13	108.00
H12—N1—H14	106.00
H11—N1—H13	120.00
H11—N1—H14	106.00
H13—N1—H14	105.00
H22—N2—H24	116.00
H23—N2—H24	111.00
H21—N2—H22	111.00
H22—N2—H23	109.00
H21—N2—H24	104.00
H21—N2—H23	105.00
H32—N3—H32^{i}	106.00
H31—N3—H32^{i}	114.00
H31^{i}—N3—H32	114.00
H31—N3—H32	113.00
H31—N3—H31^{i}	96.00
H31^{i}—N3—H32^{i}	113.00
C2B—C1B—C11B	119.5 (2)
C2B—C1B—C6B	118.57 (19)
C6B—C1B—C11B	121.96 (19)
O2B—C2B—C3B	117.5 (2)
C1B—C2B—C3B	120.5 (2)
O2B—C2B—C1B	122.05 (19)
C2B—C3B—C4B	119.8 (2)
C3B—C4B—C5B	120.4 (2)
O11B—C11B—O12B	122.44 (19)
O12B—C11B—C1B	120.96 (19)
C2B—C3B—H3B	120.00
C4B—C3B—H3B	120.00
H41—N4—H42^{ii}	111.00
H41—N4—H42	108.00
H41^{ii}—N4—H42	111.00
H41—N4—H41^{ii}	116.00
H41^{ii}—N4—H42^{ii}	108.00
H42—N4—H42^{ii}	102.00
C5B—C4B—H4B	120.00
C3B—C4B—H4B	120.00
C5B—C6B—H6B	120.00
C1B—C6B—H6B	120.00
C2A—C1A—C11A	120.56 (19)
C6A—C1A—C11A	121.06 (19)
C2A—C1A—C6A	118.37 (19)
C1A—C2A—C3A	120.5 (2)
O2A—C2A—C1A	122.02 (19)
O2A—C2A—C3A	117.50 (19)
C2A—C3A—C4A	120.0 (2)
C3A—C4A—C5A	120.4 (2)
S5A—C5A—C4A	119.53 (16)
S5A—C5A—C6A	120.75 (16)
C4A—C5A—C6A	119.7 (2)
C1A—C6A—C5A	120.97 (19)
O11A—C11A—O12A	123.22 (19)
O12A—C11A—C1A	117.62 (19)
O11A—C11A—C1A	119.2 (2)
C4A—C3A—H3A	120.00
C2A—C3A—H3A	120.00
C3A—C4A—H4A	120.00
C5A—C4A—H4A	120.00
C5A—C6A—H6A	120.00
C1A—C6A—H6A	119.00

O51B—S5B—C5B—C4B	96.72 (19)
O51B—S5B—C5B—C6B	−80.60 (19)
O52B—S5B—C5B—C4B	−144.60 (19)
O52B—S5B—C5B—C6B	38.1 (2)
O53B—S5B—C5B—C4B	−23.3 (2)
O53B—S5B—C5B—C6B	159.43 (19)
O53A—S5A—C5A—C6A	20.9 (2)
O52A—S5A—C5A—C4A	−40.39 (19)
O51A—S5A—C5A—C4A	79.54 (19)
O51A—S5A—C5A—C6A	−100.82 (18)
O52A—S5A—C5A—C6A	139.26 (17)
O53A—S5A—C5A—C4A	−158.72 (17)
C1B—C2B—C3B—C4B	−1.0 (3)
C2B—C3B—C4B—C5B	1.1 (3)
C3B—C4B—C5B—S5B	−177.43 (18)
C3B—C4B—C5B—C6B	−0.1 (3)
C4B—C5B—C6B—C1B	−1.1 (3)
S5B—C5B—C6B—C1B	176.24 (16)
C6A—C1A—C2A—O2A	−178.38 (19)
C6A—C1A—C2A—C3A	1.7 (3)
C11A—C1A—C2A—O2A	2.0 (3)
C11A—C1A—C2A—C3A	−177.9 (2)
C2A—C1A—C6A—C5A	−1.0 (3)
C11A—C1A—C6A—C5A	178.59 (19)

C6B—C1B—C2B—C3B	−0.2 (3)	C2A—C1A—C11A—O11A	−178.22 (19)
C6B—C1B—C2B—O2B	179.3 (2)	C2A—C1A—C11A—O12A	2.6 (3)
C6B—C1B—C11B—O11B	2.5 (3)	C6A—C1A—C11A—O11A	2.2 (3)
C6B—C1B—C11B—O12B	−177.0 (2)	C6A—C1A—C11A—O12A	−176.95 (19)
C11B—C1B—C2B—O2B	−0.7 (3)	O2A—C2A—C3A—C4A	178.7 (2)
C11B—C1B—C2B—C3B	179.81 (19)	C1A—C2A—C3A—C4A	−1.4 (3)
C2B—C1B—C6B—C5B	1.2 (3)	C2A—C3A—C4A—C5A	0.3 (3)
C11B—C1B—C6B—C5B	−178.8 (2)	C3A—C4A—C5A—S5A	−179.92 (18)
C2B—C1B—C11B—O11B	−177.44 (19)	C3A—C4A—C5A—C6A	0.4 (3)
C2B—C1B—C11B—O12B	3.0 (3)	S5A—C5A—C6A—C1A	−179.69 (16)
O2B—C2B—C3B—C4B	179.6 (2)	C4A—C5A—C6A—C1A	−0.1 (3)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2*A*—H2*A*···O12*A*	0.80 (3)	1.79 (2)	2.536 (2)	155 (2)
O2*B*—H2*B*···O12*B*	0.87 (3)	1.78 (3)	2.554 (2)	146 (3)
O11*B*—H11*B*···O11*A*	0.92 (3)	1.65 (3)	2.564 (2)	175 (3)
N1—H11···O53*A*^{iii}	0.91	1.95	2.841 (2)	168
N1—H12···O51*B*^{iv}	0.90	1.94	2.823 (3)	168
N1—H13···O11*A*	0.96	2.01	2.917 (2)	156
N1—H14···O12*B*	0.84	2.19	2.831 (2)	133
N1—H14···O52*B*^{v}	0.84	2.31	2.773 (2)	115
N2—H21···O51*B*^{vi}	0.96	1.90	2.846 (3)	171
N2—H22···O11*B*	0.97	2.45	2.909 (2)	108
N2—H22···O12*A*^{iii}	0.97	2.52	3.418 (2)	153
N2—H23···O12*A*	0.86	1.93	2.794 (2)	177
N2—H24···O53*A*^{vii}	0.96	2.43	2.810 (2)	103
N3—H31···O2*A*	0.88	2.23	2.9753 (18)	143
N3—H32···O51*A*^{viii}	0.98	1.93	2.848 (3)	155
N3—H32···O52*A*^{ix}	0.98	2.47	2.9901 (16)	113
N4—H41···O2*B*	0.85	2.10	2.906 (2)	156
N4—H42···O52*B*^{x}	0.81	2.15	2.891 (2)	152
C4*B*—H4*B*···O53*B*	0.93	2.55	2.910 (3)	104
C6*A*—H6*A*···O53*A*	0.93	2.57	2.930 (3)	103

Symmetry codes: (iii) *x*, *y*+1, *z*; (iv) *x*+1/2, *y*−3/2, *z*; (v) *x*+1/2, *y*−1/2, *z*; (vi) *x*, *y*−1, *z*; (vii) *x*−1/2, *y*+1/2, *z*; (viii) −*x*+3/2, *y*−1/2, −*z*+1; (ix) −*x*+3/2, *y*+1/2, −*z*+1; (x) −*x*+3/2, *y*+1/2, −*z*+2.