

Two-dimensional hydrogen-bond network in bis[(ferrocenylmethyl)-dimethylammonium] sulfate pentahydrate

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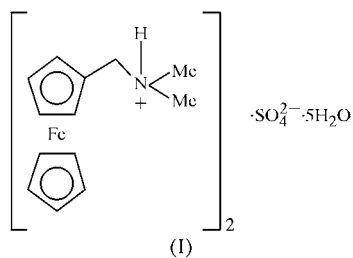
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In the title compound, $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_8\text{H}_{13}\text{N})]_2(\text{SO}_4) \cdot 5\text{H}_2\text{O}$, the Fe–C bond lengths lie in the range 2.021 (3)–2.047 (2) Å. Intermolecular N–H···O and O–H···O hydrogen bonds link the cations, sulfate anions and water molecules into a two-dimensional hydrogen-bonded network, which stabilizes the crystal packing.

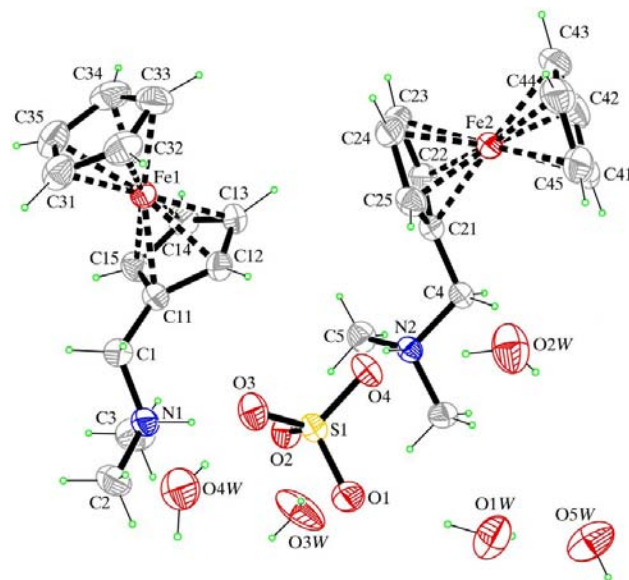
Comment

The hydrogen bond is the most versatile intermolecular interaction responsible for molecular aggregation in biological and material science (Sowerby *et al.*, 1996). Conventionally strong hydrogen bonds such as N–H···O, N–H···N and O–H···O have been extensively used in the area of supramolecular chemistry and crystal engineering. (Ferrocenylmethyl)dimethylamine, serving as an intermediate, plays an important role in the syntheses of many ferrocene derivatives (Rainer & Gottself, 1998). With this background and as a continuation of our previous studies of the N–H···O(NO_3^-) hydrogen bond in the (ferrocenylmethyl)dimethylammonium chloride salt (Guo *et al.*, 2006), we have now studied the N–H···O(SO_4^{2-}) hydrogen bond in the supramolecular system of the title ammonium salt, (I), and present the results here.

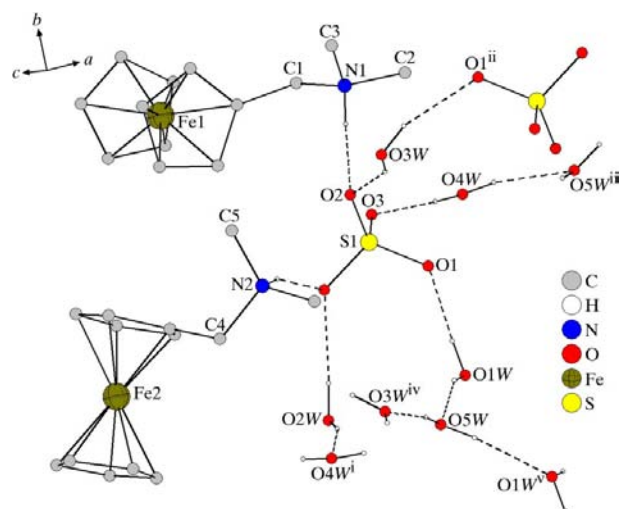


As shown in Fig. 1, the asymmetric unit of (I) consists of two monoprotonated ammonium ions, *viz.* $[(\text{C}_5\text{H}_5)\text{Fe1}(\text{C}_8\text{H}_{13}\text{N})]^+$ and $[(\text{C}_5\text{H}_5)\text{Fe2}(\text{C}_8\text{H}_{13}\text{N})]^+$, one sulfate anion and five unco-

ordinated water molecules. The two Fe atoms are bonded to the two five-membered carbon rings, with Fe1–C and Fe2–C bond lengths in the ranges 2.021 (3)–2.044 (2) and 2.015 (2)–2.048 (2) Å, respectively (Table 1). The rings C11–C15 and C31–C35 in $[(\text{C}_5\text{H}_5)\text{Fe1}(\text{C}_8\text{H}_{13}\text{N})]^+$ are nearly parallel, with a dihedral angle between their mean planes of 1.42°, while the two rings C21–C25 and C41–C45 in $[(\text{C}_5\text{H}_5)\text{Fe2}(\text{C}_8\text{H}_{13}\text{N})]^+$ have a dihedral angle of 3.17°. The two carbon rings in the two cations exhibit nearly eclipsed conformations, as is usually found in other ferrocene derivatives (Ye *et al.*, 2005; Todd *et al.*, 2006). In the structure of the SO_4^{2-} anion, the S–O bond distances [1.462 (1)–1.483 (1) Å] and O–S–O angles


Figure 1

A view of the components of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radii.


Figure 2

The structure of (I). Dashed lines indicate hydrogen bonds. The symmetry codes are as given in Table 2.

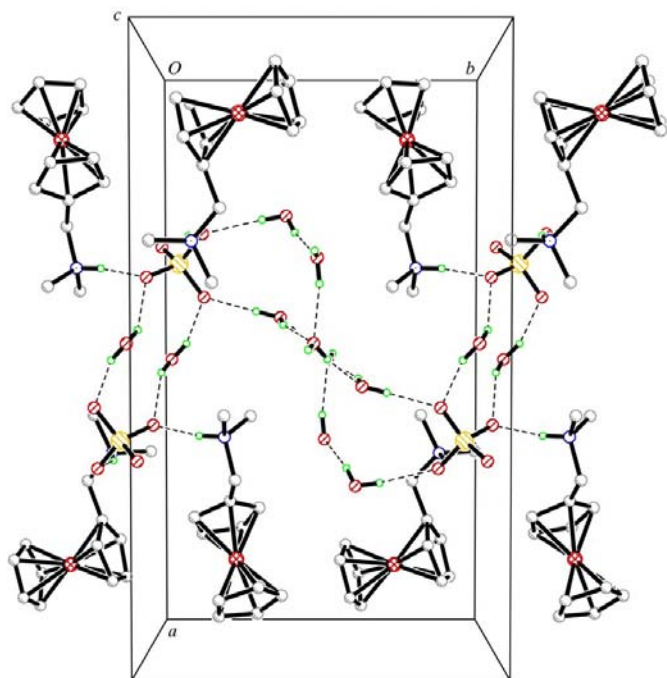


Figure 3

The two-dimensional hydrogen-bond network in (I). Intermolecular N—H...O and O—H...O hydrogen bonds are shown as dashed lines.

[108.23 (8)–110.96 (9)°] are close to the respective values for an ideal tetrahedral S-atom environment.

In the crystal structure of (I), classical intermolecular N—H...O and O—H...O hydrogen bonds are observed (Table 2 and Fig. 2), which link the two ammonium cations, one sulfate anion and five uncoordinated water molecules into a two-dimensional hydrogen-bonded network and stabilize the crystal packing (Fig. 3). It is noted that cations $[(C_5H_5)Fe1(C_8H_{13}N)]^+$ and $[(C_5H_5)Fe2(C_8H_{13}N)]^+$ both bond to the same SO_4^{2-} anion, which in turn bonds to the water molecules. The $D\cdots A$ distances and $D-H\cdots A$ angles in the N—H...O hydrogen bonds are 2.745 (2) and 2.757 (2) Å, and 168 and 158°, respectively, while those in O—H...O(SO_4^{2-}) hydrogen bonds lie in the ranges 2.754 (2)–2.884 (3) Å and 150 (3)–177 (3)°, respectively. Additionally, there is extensive hydrogen bonding between the water molecules, with O...O interatomic distances ranging from 2.697 (3) to 2.853 (3) Å (Table 2).

Experimental

A solution of $CuSO_4 \cdot 5H_2O$ (0.1248 g, 0.5 mmol) in methanol (10 ml) was added to a solution of (ferrocenylmethyl)dimethylamine (0.1213 g, 0.5 mmol) in methanol (10 ml). To this solution, dichloromethane (1.6 ml) was added dropwise, and the mixture was stirred for 2 h and then concentrated under vacuum to a volume of 10 ml. Red block-shaped crystals of (I) were obtained by slow evaporation of the solvent in air. Analysis found: C 46.8, H 7.2, N 4.7%; $C_{26}H_{46}Fe_2N_2O_9S$ requires: C 46.3, H 6.8, N 4.2%. FT-IR (KBr, ν , cm^{-1}): 3438 (ν_w), 2942 (w), 2645 (s), 2472 (w), 1707.9 (w), 1472.8 (ν_s), 1416.4 (w), 1381.2 (w), 1416.4 (w), 1116.3 (s), 1012.9 (w), 945.1 (w), 920.9 (w), 824.3 (w), 707.2 (w), 619.3 (ν_s), 501.2 (w), 486.4 (w).

Crystal data

$[Fe(C_5H_5)(C_8H_{13}N)]_2(SO_4) \cdot 5H_2O$
 $M_r = 674.42$
 Monoclinic, $P2_1/c$
 $a = 20.2187$ (14) Å
 $b = 11.5943$ (6) Å
 $c = 13.5435$ (9) Å
 $\beta = 93.106$ (3)°
 $V = 3170.2$ (3) Å³

$Z = 4$
 $D_x = 1.413$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 1.03$ mm⁻¹
 $T = 293$ (2) K
 Block, red
 $0.23 \times 0.16 \times 0.12$ mm

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (RAPID-AUTO; Rigaku, 1998)
 $T_{min} = 0.820$, $T_{max} = 0.884$

29485 measured reflections
 7269 independent reflections
 4691 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.048$
 $\theta_{max} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.067$
 $S = 1.01$
 7256 reflections
 401 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0198P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.32$ e Å⁻³
 $\Delta\rho_{min} = -0.43$ e Å⁻³

Table 1

Selected bond lengths (Å).

Fe1—C11	2.0238 (19)	Fe2—C41	2.015 (2)
Fe1—C33	2.027 (2)	Fe2—C21	2.0173 (18)
Fe1—C15	2.028 (2)	Fe2—C45	2.021 (3)
Fe1—C14	2.035 (2)	Fe2—C42	2.035 (2)
Fe1—C13	2.035 (2)	Fe2—C25	2.038 (2)
Fe1—C34	2.036 (2)	Fe2—C22	2.039 (2)
Fe1—C35	2.036 (2)	Fe2—C44	2.040 (2)
Fe1—C12	2.040 (2)	Fe2—C24	2.041 (2)
Fe1—C31	2.044 (2)	Fe2—C23	2.047 (2)
Fe1—C32	2.045 (2)	Fe2—C43	2.048 (2)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—HN1...O2	0.91	1.85	2.745 (2)	168
N2—HN2...O4	0.91	1.89	2.757 (2)	158
O1W—H1WA...O1	0.85 (2)	1.91 (2)	2.758 (3)	174 (3)
O1W—H1WB...O5W	0.84 (2)	2.06 (2)	2.847 (3)	158 (3)
O2W—H2WA...O4W ⁱ	0.83 (2)	2.05 (2)	2.853 (3)	162 (3)
O2W—H2WB...O4	0.83 (2)	2.07 (2)	2.884 (3)	167 (3)
O3W—H3WA...O1 ⁱⁱ	0.83 (2)	1.96 (2)	2.754 (2)	160 (3)
O3W—H3WB...O2	0.83 (2)	2.03 (2)	2.773 (2)	150 (3)
O4W—H4WB...O5W ⁱⁱⁱ	0.86 (2)	2.00 (2)	2.853 (3)	168 (3)
O4W—H4WA...O3	0.83 (2)	1.93 (2)	2.754 (2)	177 (3)
O5W—H5WB...O3W ^{iv}	0.81 (2)	1.90 (2)	2.697 (3)	171 (3)
O5W—H5WA...O1W ^v	0.81 (2)	1.95 (2)	2.745 (3)	168 (3)

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

The C-bound H atoms were positioned geometrically, with C—H = 0.98, 0.97 and 0.96 Å for those on cyclopentadienyl, methylene and methyl C atoms, respectively, and they were refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(methyl C)$. Atom H1N and H2N were positioned geometrically and allowed to ride on N1 and N2, respectively, with N—H = 0.91 Å and $U_{iso}(H) = 1.2U_{eq}(N)$. Water H atoms were located in a difference map and refined with O—H and H...H distance restraints of 0.85 (1) and 1.39 (1) Å, respectively, and with $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3015). Services for accessing these data are described at the back of the journal.

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