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People's Republic of ChinaCorrespondence e-mail:
yunlongfu@dns.sxtu.edu.cn**Key indicators**Single-crystal X-ray study
 $T = 273$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.033
 wR factor = 0.085
Data-to-parameter ratio = 11.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**Piperazinium(2+) hexaaquairon(II) bis(sulfate)**

In the crystal structure of the title compound, $(\text{C}_4\text{H}_{12}\text{N}_2)^+[\text{Fe}(\text{H}_2\text{O})_6](\text{SO}_4)_2$, hydrogen bonds link the piperazinium cation, the hexaaquairon(II) cation and the sulfate anions into a three-dimensional network. The $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and piperazinium cations each lie on a centre of symmetry.

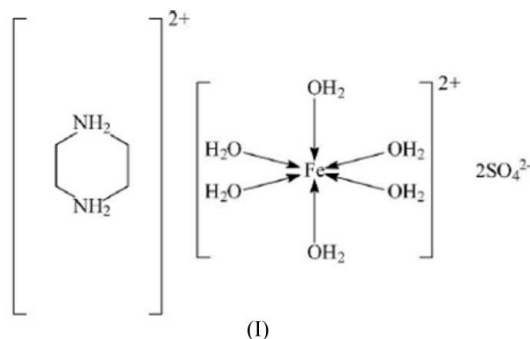
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Comment

This report describes a study of the reactions of iron(II) sulfate and piperazine under solvothermal conditions. We have previously described a 4,4-bipyridine salt of hexaaquairon(II) sulfate, accompanied by two uncoordinated water molecules (Fu *et al.*, 2005). A similar reaction with *N,N*-dimethylformamide (DMF) as solvent and piperazine as diamine yielded the title compound, (I) (Fig. 1), although DMF was not incorporated into the crystal structure. The compound can be regarded as a double salt of piperazinium sulfate and hexaaquairon(II) sulfate.



The $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $\text{C}_4\text{H}_{12}\text{N}_2^{2+}$ cations and the sulfate anions interact through hydrogen bonds (Table 2), forming a three-dimensional network. The organic cation and the Fe atom each lie on an inversion centre. There are only four examples in the literature of a hexaaquametal sulfate salt having an organic piperazine cation. The structures of piperazinium hexaaquacobalt(II) bis(sulfate) (Pan *et al.*, 2003) and piperazinium hexaaquanickel(II) bis(sulfate) (Meng *et al.*, 2004) are similar to that of the title compound, but hemi(piperazinium) hexaaquaaluminium(III) bis(sulfate) tetrahydrate (Bataille, 2003) and piperazinium hexaaquazinc(II) bis(sulfate) (Rekik *et al.*, 2005) have additional hydrogen-bond interactions with uncoordinated water molecules.

Experimental

Iron(II) sulfate heptahydrate (0.278 g, 1 mmol) was dissolved in DMF (7 ml) with constant stirring. A drop of concentrated sulfuric

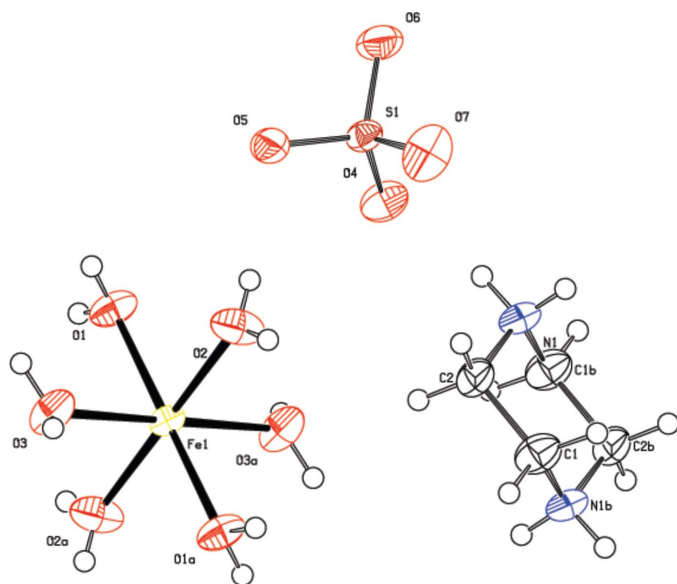


Figure 1
A plot of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (a) $-x, -y + 1, -z + 1$; (b) $-x, -y + 1, -z + 2$.]

acid (0.06 ml, 1 mmol) was added, followed by piperazine (0.086 g, 1 mmol). The final mixture was placed in a 15 ml Teflon-lined Parr bomb, which was heated at 383 K for 2 d. The bomb was cooled and opened to reveal pale-green block-shaped crystals in about 40% yield with respect to Fe.

Crystal data

$(C_4H_{12}N_2)[Fe(H_2O)_6](SO_4)_2$
 $M_r = 444.22$
 Monoclinic, $P2_1/n$
 $a = 7.8345$ (6) Å
 $b = 9.3814$ (8) Å
 $c = 11.0965$ (9) Å
 $\beta = 91.2840$ (10)°
 $V = 815.37$ (11) Å³
 $Z = 2$
 $D_x = 1.809$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 2.8$ – 27.0 °
 $\mu = 1.25$ mm⁻¹
 $T = 273$ (2) K
 Block, pale green
 $0.18 \times 0.15 \times 0.14$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{min} = 0.806, T_{max} = 0.844$
 4636 measured reflections
 1763 independent reflections
 1679 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.021$
 $\theta_{max} = 27.0$ °
 $h = -8 \rightarrow 10$
 $k = -10 \rightarrow 11$
 $l = -10 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.085$
 $S = 1.10$
 1763 reflections
 155 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0439P)^2 + 0.5012P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.63$ e Å⁻³
 $\Delta\rho_{min} = -0.36$ e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.026 (2)

Table 1

Selected geometric parameters (Å, °).

Fe1—O2	2.0894 (18)	Fe1—O3	2.1273 (18)
Fe1—O1	2.1253 (16)		
O2—Fe1—O1	87.49 (8)	O2—Fe1—O3	90.95 (8)
O2 ⁱ —Fe1—O1	92.51 (8)	O1—Fe1—O3	88.04 (7)
O2—Fe1—O3 ⁱ	89.05 (8)	O1 ⁱ —Fe1—O3	91.96 (7)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H12 ⁱⁱ ···O7 ⁱⁱ	0.88 (5)	2.43 (4)	3.080 (3)	131 (3)
N1—H12 ⁱⁱ ···O6 ⁱⁱ	0.88 (5)	2.10 (5)	2.953 (3)	165 (3)
O3—H6 ⁱⁱⁱ ···O6 ⁱⁱⁱ	0.86 (4)	1.91 (4)	2.757 (2)	167 (3)
N1—H11 ^{iv} ···O7	0.89 (4)	2.54 (4)	3.065 (3)	119 (3)
O2—H4 ^v ···O5	0.73 (3)	2.04 (3)	2.768 (3)	174 (3)
O1—H1 ^v ···O5 ⁱⁱⁱ	0.79 (4)	1.94 (4)	2.733 (2)	175 (3)
O1—H2 ^v ···O6 ^{iv}	0.87 (4)	1.94 (4)	2.783 (3)	164 (3)
O3—H5 ^v ···O7 ^v	0.80 (3)	1.90 (4)	2.695 (3)	173 (3)
O2—H3 ^{vi} ···O4 ^{vi}	0.80 (4)	1.91 (4)	2.698 (3)	165 (3)

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

H atoms were located in difference Fourier maps and were refined with distance restraints of O—H = N—H = 0.85 (1) Å and C—H = 0.95 (1) Å; their displacement parameters were refined freely.

Data collection: SMART (Bruker, 2002); cell refinement: SAINT; data reduction: SAINT (Bruker, 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: SHELX97.

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