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Iron(II) hydrazinium sulfate

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The title compound, poly[[dihydraziniumiron(II)]-di-μ-sulfato-κ^4O:O'], $[Fe(SO_4)_2(N_2H_5)_2]_n$, contains fairly regular *trans*-FeN_2O_4 octahedra. The Fe atoms (site symmetry $\overline{1}$) are bridged by pairs of sulfate groups into infinite [100] chains, which are cross-linked by a network of N—H···O hydrogen bonds. $Fe(N_2H_5)_2(SO_4)_2$ is isostructural with its zinc, chromium(II) and cadmium-containing analogues.

Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(N–N) = 0.004 Å
R factor = 0.032
wR factor = 0.076
Data-to-parameter ratio = 11.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The divalent-metal–hydrazinium sulfates of general formula $M(N_2H_5)_2(SO_4)_2$, where M = Cr, Mn, Fe, Co, Ni, Cu, Zn and Cd can be readily prepared by reacting a salt of the respective metal with hydrazinium sulfate in dilute sulfuric acid (Hand & Prout, 1966), although this method usually results in a microcrystalline product. Recently, we described the single-crystal structure of $Cd(N_2H_5)_2(SO_4)_2$ (Srinivasan *et al.*, 2006) and we now report the isostructural title compound, (I), $Fe(N_2H_5)_2(SO_4)_2$. The compounds $Zn(N_2H_5)_2(SO_4)_2$ (Prout & Powell, 1961) and $Cr(N_2H_5)_2(SO_4)_2$ (Parkins *et al.*, 2001) also share the same stucture.

Compound (I) contains *trans*-FeN_2O_4 octahedra (Fig. 1), in which the N atom is part of a hydrazinium ($N_2H_5^+$) cation. The Fe atoms (site symmetry $\overline{1}$) are connected by pairs of sulfate groups into infinite chains that propagate in [100]. The intra-chain Fe···Fe separation in (I) is equal to the *a* unit-cell dimension, *i.e.* 5.3306 (3) Å. The two distinct Fe—O bond lengths in (I) are similar (Table 1) and do not show the gross differences seen in the chromium and zinc analogues.

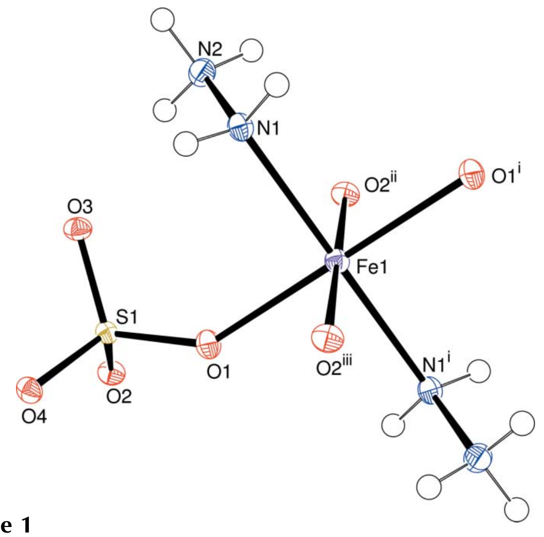

Figure 1
The asymmetric unit of (I) expanded to show the iron coordination (50% displacement ellipsoids; arbitrary spheres for the H atoms). Symmetry codes: (i) $-x, -y, -z$; (ii) $x - 1, y, z$; (iii) $1 - x, -y, -z$.

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The iron–sulfate chains in (I) are cross-linked by N—H$\cdots$O hydrogen bonds (Table 2), resulting in the same hydrogen-bonding network seen in the other analogues noted above. A well defined trifurcated N2—H3*C*$\cdots$(O,O,O) interaction occurs (mean bond angle about H3*C* = 107.3°).

Experimental

The reaction of hydrazine monohydrate ($N_2H_4 \cdot H_2O$; 0.50 g, 10 mmol) and ethyl bromoacetate (1.671 g, 10 mmol) in 5 ml of dry ethanol resulted in the formation of a white solid containing hydrazinium bromide and ethyl hydrazinoacetate, as reported earlier (Srinivasan *et al.*, 2006). This white solid (0.236 g) was dissolved in water (30 ml) and mixed with an aqueous solution (30 ml) of $FeSO_4 \cdot 7H_2O$ (0.278 g, 1 mmol) and a few drops of conc. H_2SO_4. The resulting clear solution, with a pH of 2, was concentrated over a water bath to 20 ml and kept for crystallization at room temperature. After three days, many block-shaped light-green crystals of (I) had formed. These were recovered by filtration, washed with cold water and dried in air.

Crystal data

$[Fe(SO_4)_2(N_2H_5)_2]$
$M_r = 314.08$
Triclinic, $P\overline{1}$
$a = 5.3306$ (3) Å
$b = 5.8205$ (3) Å
$c = 7.3835$ (4) Å
$\alpha = 92.034$ (3)°
$\beta = 103.313$ (3)°
$\gamma = 99.237$ (3)°
$V = 219.41$ (2) Å^3
$Z = 1$
$D_x = 2.377$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 2.23$ mm^{-1}
$T = 120$ (2) K
Lath, pale green
0.05 × 0.02 × 0.01 mm

Data collection

Nonius KappaCCD diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{\min} = 0.897$, $T_{\max} = 0.978$
3957 measured reflections
1004 independent reflections
911 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.043$
$\theta_{\max} = 28.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.076$
$S = 1.12$
1004 reflections
90 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0127P)^2 + 0.6538P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.58$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—O1	2.109 (2)	Fe1—N1	2.184 (2)
Fe1—O2$^{\rm i}$	2.147 (2)		
S1—O1—Fe1	142.94 (13)	S1—O2—Fe1$^{\rm ii}$	128.85 (12)

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

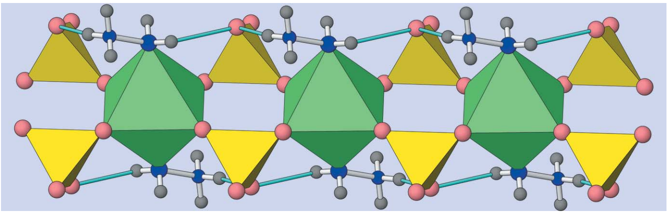

Figure 2
Polyhedral view of a fragment of the chain structure of (I). Colour key: Fe octahedra green, S tetrahedra yellow, O pink, N blue, H grey. The H$\cdots$O portions of the hydrogen bonds are coloured light blue.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
N1—H1*A*$\cdots$O3$^{\rm iii}$	0.82 (4)	2.37 (4)	3.070 (3)	143 (3)
N1—H1*B*$\cdots$O4$^{\rm iv}$	0.82 (4)	2.12 (4)	2.867 (3)	151 (4)
N2—H2*A*$\cdots$O4$^{\rm iii}$	0.88 (4)	1.96 (4)	2.799 (3)	160 (4)
N2—H2*B*$\cdots$O3	0.80 (4)	2.02 (4)	2.769 (4)	156 (4)
N2—H2*C*$\cdots$O2$^{\rm v}$	0.82 (4)	2.51 (4)	2.849 (3)	106 (3)
N2—H2*C*$\cdots$O2$^{\rm iv}$	0.82 (4)	2.32 (4)	3.011 (4)	141 (4)
N2—H2*C*$\cdots$O1$^{\rm vi}$	0.82 (4)	2.45 (4)	3.073 (3)	133 (4)

Symmetry codes: (iii) $-x+1, -y, -z+1$; (iv) $x-1, y-1, z$; (v) $-x+1, -y, -z$; (vi) $x, y-1, z$.

The H atoms were located in difference maps and their positions and $U_{\rm iso}$ values were freely refined.

Data collection: Collect (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor 1997); data reduction: *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor 1997) & *SORTAV* (Blessing 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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(I)

Crystal data

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Hall symbol: -P 1
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$c = 7.3835\ (4)$ Å
$\alpha = 92.034\ (3)°$
$\beta = 103.313\ (3)°$
$\gamma = 99.237\ (3)°$
$V = 219.41\ (2)$ Å^3

$Z = 1$
$F(000) = 160$
$D_x = 2.377$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 984 reflections
$\theta = 2.9–27.5°$
$\mu = 2.23$ mm^{-1}
$T = 120$ K
Lath, pale green
0.05 × 0.02 × 0.01 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (SADABS; Bruker, 2003)
$T_{\min} = 0.897$, $T_{\max} = 0.978$

3957 measured reflections
1004 independent reflections
911 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.043$
$\theta_{\max} = 28.0°$, $\theta_{\min} = 3.6°$
$h = -6 \rightarrow 6$
$k = -7 \rightarrow 7$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.076$
$S = 1.12$
1004 reflections
90 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
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0127P)^2 + 0.6538P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.58$ e Å^{-3}

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 $F^2 > \sigma(F^2)$ 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	$U_{\rm iso}$*/$U_{\rm eq}$
Fe1	0.0000	0.0000	0.0000	0.01099 (17)
S1	0.63302 (12)	0.24660 (11)	0.21899 (9)	0.00929 (18)
O1	0.3609 (4)	0.2280 (4)	0.0944 (3)	0.0142 (4)
O2	0.8223 (4)	0.2674 (3)	0.1024 (3)	0.0131 (4)
O3	0.6559 (4)	0.0411 (3)	0.3285 (3)	0.0130 (4)
O4	0.6932 (4)	0.4606 (3)	0.3470 (3)	0.0122 (4)
N1	0.0660 (5)	−0.1738 (5)	0.2599 (4)	0.0117 (5)
H1A	0.129 (7)	−0.079 (7)	0.350 (5)	0.017 (9)*
H1B	−0.077 (8)	−0.249 (7)	0.265 (5)	0.022 (10)*
N2	0.2501 (5)	−0.3342 (5)	0.2854 (4)	0.0144 (5)
H2A	0.281 (7)	−0.403 (7)	0.390 (6)	0.021 (10)*
H2B	0.391 (8)	−0.256 (7)	0.293 (6)	0.023 (10)*
H2C	0.188 (8)	−0.442 (7)	0.204 (6)	0.026 (11)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.0100 (3)	0.0120 (3)	0.0110 (3)	0.0012 (2)	0.0031 (2)	0.0007 (2)
S1	0.0085 (3)	0.0102 (3)	0.0094 (3)	0.0007 (2)	0.0033 (3)	0.0001 (3)
O1	0.0095 (9)	0.0156 (10)	0.0162 (10)	0.0006 (8)	0.0014 (8)	0.0011 (8)
O2	0.0136 (10)	0.0131 (10)	0.0141 (10)	0.0020 (8)	0.0063 (8)	0.0013 (8)
O3	0.0157 (10)	0.0118 (10)	0.0126 (10)	0.0017 (8)	0.0058 (8)	0.0024 (8)
O4	0.0151 (10)	0.0112 (10)	0.0105 (10)	0.0009 (8)	0.0048 (8)	−0.0015 (8)
N1	0.0079 (11)	0.0138 (12)	0.0136 (12)	0.0014 (10)	0.0033 (10)	0.0006 (10)
N2	0.0151 (13)	0.0145 (13)	0.0133 (13)	0.0034 (11)	0.0023 (11)	0.0012 (11)

Geometric parameters (Å, º)

Fe1—O1	2.109 (2)	S1—O1	1.513 (2)
Fe1—O1$^{\rm i}$	2.109 (2)	O2—Fe1$^{\rm iv}$	2.147 (2)
Fe1—O2$^{\rm ii}$	2.147 (2)	N1—N2	1.446 (4)
Fe1—O2$^{\rm iii}$	2.147 (2)	N1—H1A	0.82 (4)
Fe1—N1	2.184 (2)	N1—H1B	0.82 (4)
Fe1—N1$^{\rm i}$	2.184 (2)	N2—H2A	0.88 (4)
S1—O2	1.464 (2)	N2—H2B	0.80 (4)
S1—O3	1.473 (2)	N2—H2C	0.82 (4)
S1—O4	1.482 (2)		
O1—Fe1—O1$^{\rm i}$	180.0	O2—S1—O1	108.74 (12)
O1—Fe1—O2$^{\rm ii}$	87.04 (8)	O3—S1—O1	111.25 (12)

O1^{i}—Fe1—O2^{ii}	92.96 (8)	O4—S1—O1	109.43 (12)
O1—Fe1—O2^{iii}	92.96 (8)	S1—O1—Fe1	142.94 (13)
O1^{i}—Fe1—O2^{iii}	87.04 (8)	S1—O2—Fe1^{iv}	128.85 (12)
O2^{ii}—Fe1—O2^{iii}	180.0	N2—N1—Fe1	118.02 (18)
O1—Fe1—N1	90.79 (9)	N2—N1—H1A	102 (3)
O1^{i}—Fe1—N1	89.21 (9)	Fe1—N1—H1A	111 (3)
O2^{ii}—Fe1—N1	95.14 (9)	N2—N1—H1B	107 (3)
O2^{iii}—Fe1—N1	84.86 (9)	Fe1—N1—H1B	107 (3)
O1—Fe1—N1^{i}	89.21 (9)	H1A—N1—H1B	112 (4)
O1^{i}—Fe1—N1^{i}	90.79 (9)	N1—N2—H2A	119 (3)
O2^{ii}—Fe1—N1^{i}	84.86 (9)	N1—N2—H2B	106 (3)
O2^{iii}—Fe1—N1^{i}	95.14 (9)	H2A—N2—H2B	101 (4)
N1—Fe1—N1^{i}	180.0	N1—N2—H2C	106 (3)
O2—S1—O3	109.79 (12)	H2A—N2—H2C	105 (4)
O2—S1—O4	107.99 (12)	H2B—N2—H2C	122 (4)
O3—S1—O4	109.57 (12)		

O2—S1—O1—Fe1	114.0 (2)	O3—S1—O2—Fe1^{iv}	24.58 (19)
O3—S1—O1—Fe1	−7.1 (3)	O4—S1—O2—Fe1^{iv}	143.99 (14)
O4—S1—O1—Fe1	−128.3 (2)	O1—S1—O2—Fe1^{iv}	−97.35 (16)
O2^{ii}—Fe1—O1—S1	124.1 (2)	O1—Fe1—N1—N2	−76.0 (2)
O2^{iii}—Fe1—O1—S1	−55.9 (2)	O1^{i}—Fe1—N1—N2	104.0 (2)
N1—Fe1—O1—S1	29.0 (2)	O2^{ii}—Fe1—N1—N2	−163.1 (2)
N1^{i}—Fe1—O1—S1	−151.0 (2)	O2^{iii}—Fe1—N1—N2	16.9 (2)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O3^{v}	0.82 (4)	2.37 (4)	3.070 (3)	143 (3)
N1—H1*B*···O4^{vi}	0.82 (4)	2.12 (4)	2.867 (3)	151 (4)
N2—H2*A*···O4^{v}	0.88 (4)	1.96 (4)	2.799 (3)	160 (4)
N2—H2*B*···O3	0.80 (4)	2.02 (4)	2.769 (4)	156 (4)
N2—H2*C*···O2^{iii}	0.82 (4)	2.51 (4)	2.849 (3)	106 (3)
N2—H2*C*···O2^{vi}	0.82 (4)	2.32 (4)	3.011 (4)	141 (4)
N2—H2*C*···O1^{vii}	0.82 (4)	2.45 (4)	3.073 (3)	133 (4)

Symmetry codes: (iii) −*x*+1, −*y*, −*z*; (v) −*x*+1, −*y*, −*z*+1; (vi) *x*−1, *y*−1, *z*; (vii) *x*, *y*−1, *z*.