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catena-Poly[diethylenetriaminium [ferrate(III)-tri-μ-sulfato-κ^6*O*:*O*′] monohydrate]

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Ferric sulfate reacts with diethylenetriamine in the presence of acid under hydrothermal conditions to form the title compound, $(C_4H_{16}N_3)[Fe(SO_4)_3]\cdot H_2O$. The six-coordinate ferrate trianion entity exists as a tri-μ_2-sulfate-bridged chain that propagates along the *c* axis of the monoclinic unit cell. The trication and uncoordinated water molecule connect the polyanionic chain into a three-dimensional network structure.

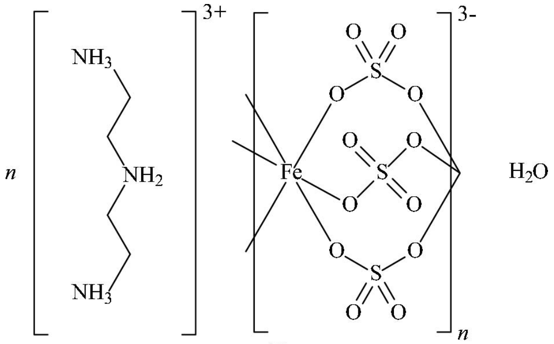
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
R factor = 0.044
wR factor = 0.109
Data-to-parameter ratio = 15.0

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

Comment

Iron(II) sulfate reacts with ethylenediamine to form ethylenediammonium tetraaquabissulfatoferrate(II) (Held, 2003). Under hydrothermal conditions, similar reactions yield ethylenediammonium(2+) trifluorosulfatoferrate(III) and ethylenediammonium(2+) bis[aquafluorosulfatoferrate(II)]. The polyanionic ferrate chains feature μ_3-bridging sulfate groups (Paul *et al.*, 2003). Triethylenetetraamine affords the analogous ferrate(II) that also features such bridging sulfate groups (Paul *et al.*, 2002). The F atom in the ferrates, which comes from other reagents used in the syntheses, also participates in bridging. Limited studies on the synthesis of anionic iron–sulfate frameworks have highlighted the influence of the amines, solvents and reaction conditions on the resulting product. The studies have also demonstrated how the fluoride anion functions as a mineralizing agent that is also incorporated into the polyanionic chain. The present study uses iron(III) sulfate as reagent.



(I)

Iron(III) sulfate reacts with diethylenetriamine under hydrothermal conditions to yield the title compound, (I) (Fig. 1). The Fe atom is linked to the O atoms of six sulfate groups in an octahedral geometry; the three sulfate groups link two adjacent Fe atoms, giving rise to a chain that propagates along the *c* axis of the monoclinic unit cell (Fig. 2).

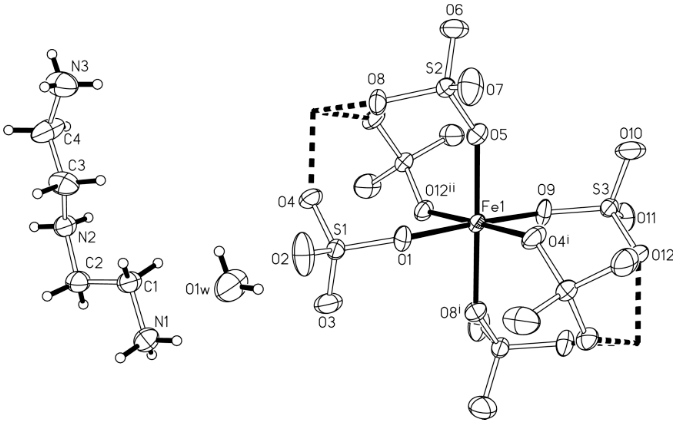


Figure 1
ORTEPII (Johnson, 1976) plot illustrating the coordination geometry of the Fe atom in $[C_4H_{16}N_3][Fe(SO_4)_3]\cdot H_2O$. Displacement ellipsoids are drawn at the 70% probability level and H atoms are drawn as spheres of arbitrary radii. Symmetry codes are those used in Table 1.

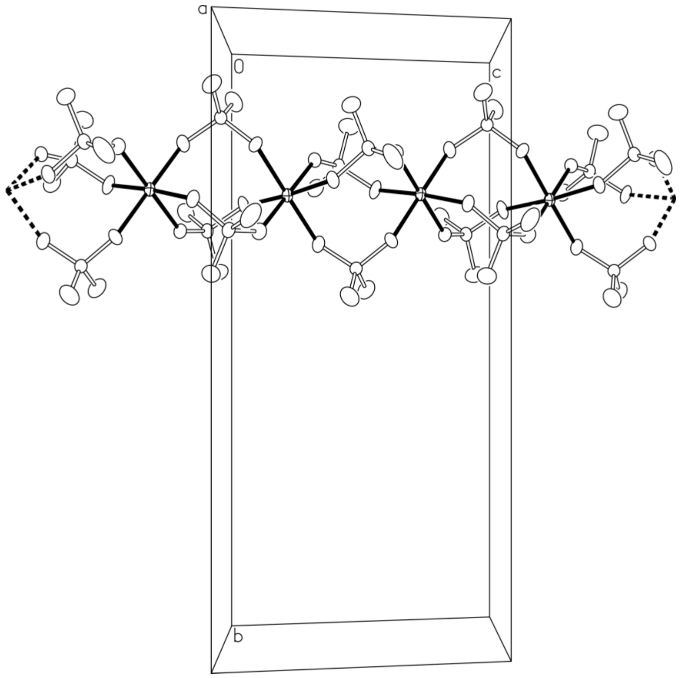


Figure 2
ORTEPII (Johnson, 1976) plot of the polycationic $[Fe(SO_4)_3]$ chain.

Compared with the reported fluoroferrates, the chain adopts a more regular motif as the bridging entities are all sulfate groups. The trication and uncoordinated water molecule connect the polyanionic chains into a three-dimensional network structure through hydrogen bonds (Table 2).

Experimental

Ferric sulfate nonahydrate (0.28 g, 0.5 mmol), diethylenetriamine (0.15 ml, 0.13 mmol), concentrated sulfuric acid (0.16 ml), water (6 ml), ethanol (5 ml) and glycol (7 ml) were placed in a Teflon-lined stainless steel bomb. The bomb was heated in an autoclave at 383 K for 4 d and then cooled to room temperature to furnish crystals of (I).

Crystal data

$(C_4H_{16}N_3)[Fe(SO_4)_3]\cdot H_2O$
$M_r = 468.24$
Monoclinic, $P2_1/c$
$a = 9.1329$ (8) Å
$b = 18.882$ (2) Å
$c = 8.8856$ (7) Å
$\beta = 103.264$ (1)°
$V = 1491.4$ (2) Å^3
$Z = 4$
$D_x = 2.085$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2096 reflections
$\theta = 2.3$–27.3°
$\mu = 1.51$ mm^{-1}
$T = 295$ (2) K
Rod, yellow
0.27 × 0.10 × 0.08 mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{\min} = 0.367$, $T_{\max} = 0.889$
8930 measured reflections
3369 independent reflections
2680 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\max} = 27.5°$
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 24$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.109$
$S = 1.03$
3369 reflections
225 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0532P)^2 + 0.8094P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.58$ e Å^{-3}
$\Delta\rho_{\min} = -0.44$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—O1	2.010 (2)	Fe1—O8$^{\rm i}$	2.024 (2)
Fe1—O4$^{\rm i}$	1.978 (2)	Fe1—O9	1.978 (2)
Fe1—O5	2.001 (2)	Fe1—O12$^{\rm ii}$	1.978 (2)
O1—Fe1—O4$^{\rm i}$	90.7 (1)	O4$^{\rm i}$—Fe1—O12$^{\rm ii}$	179.0 (1)
O1—Fe1—O5	92.8 (1)	O5—Fe1—O8$^{\rm i}$	178.9 (1)
O1—Fe1—O8$^{\rm i}$	86.2 (1)	O5—Fe1—O9	90.2 (1)
O1—Fe1—O9	175.9 (1)	O5—Fe1—O12$^{\rm ii}$	90.7 (1)
O1—Fe1—O12$^{\rm ii}$	88.5 (1)	O8$^{\rm i}$—Fe1—O9	90.8 (1)
O4$^{\rm i}$—Fe1—O5	89.8 (1)	O8$^{\rm i}$—Fe1—O12$^{\rm ii}$	89.6 (1)
O4$^{\rm i}$—Fe1—O8$^{\rm i}$	89.9 (1)	O9—Fe1—O12$^{\rm ii}$	88.7 (1)
O4$^{\rm i}$—Fe1—O9	92.2 (1)		

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1w—H1w1$\cdots$O3	0.85 (1)	2.06 (1)	2.904 (4)	176 (4)
O1w—H1w2$\cdots$O7$^{\rm ii}$	0.85 (1)	2.00 (2)	2.815 (4)	161 (6)
N1—H1n1$\cdots$O1w	0.86	2.19	2.909 (4)	141
N1—H1n2$\cdots$O11$^{\rm iii}$	0.86	1.99	2.779 (4)	152
N1—H1n3$\cdots$O8$^{\rm iv}$	0.86	2.13	2.971 (4)	166
N2—H2n2$\cdots$O2$^{\rm v}$	0.86	2.15	2.850 (4)	138
N2—H2n1$\cdots$O6$^{\rm vi}$	0.86	2.07	2.867 (4)	154
N3—H3n3$\cdots$O3$^{\rm vii}$	0.86	2.04	2.881 (4)	166
N3—H3n2$\cdots$O6$^{\rm ii}$	0.86	2.07	2.902 (4)	162
N3—H3n1$\cdots$O10$^{\rm viii}$	0.86	2.06	2.816 (4)	146

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

The C- and N-bound H atoms were placed at calculated positions (C—H = 0.97 Å and N—H = 0.86 Å) and were included in the refinement in the riding model approximation, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C,N). The water H atoms were located and refined isotropi-

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cally with distance restraints of O—H = 0.85 (1) Å and H···H = 1.39 (1) Å.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; 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: *SHELXL97*.

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