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# *catena*-Poly[piperazinium(2+) [ferrate(III)-$\mu$-hydroxo-$\kappa^2O$:$O$-di-$\mu$-sulfato-$\kappa^4O$:$O'$] dihydrate]

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**Key indicators**

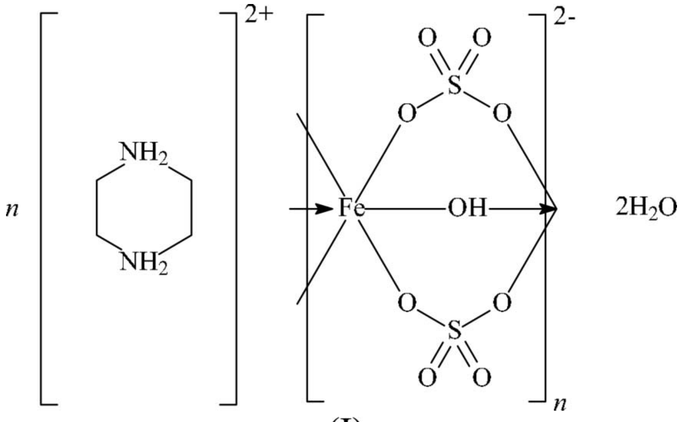
Single-crystal X-ray study
$T$ = 295 K
Mean $\sigma$(C–C) = 0.007 Å
Disorder in solvent or counterion
$R$ factor = 0.035
$wR$ factor = 0.134
Data-to-parameter ratio = 11.7

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

In the crystal structure of the polymeric title compound, $\{(C_4H_{12}N_2)[Fe(OH)(SO_4)_2]\cdot 2H_2O\}_n$, the anion exists as a linear chain whose two independent Fe$^{III}$ atoms both occupy special positions of $\overline{1}$ site symmetry. The two independent cations, which also lie on inversion sites, interact with the polyanionic chain and with the uncoordinated water molecules to form a tight-held three-dimensional network.

## Comment

This report continues previous studies on the reaction of ferric sulfate and amines under hydrothermal conditions; the polyanionic hydroxodisulfatoferrate(III) chain was obtained with the use of hexamethylenediamine (Fu *et al.*, 2005*a*) and ethylenediamine (Fu *et al.*, 2005*b*). The use of the diamine, piperazine, afforded the expected anion; the compound crystallizes as a dihydrate, (I) (Fig. 1).



(I)

The polyanionic chain is linear (Fig. 2), and the cations and uncoordinated water molecules link the chains into a three-dimensional network through hydrogen bonds (Table 2). The principal features, *e.g.* bond dimensions and repeat distance, of the chain are similar to those reported previously.

## Experimental

Ferric sulfate nonahydrate (1.68 g, 3.0 mmol) was dissolved in a water–ethanol mixture (1:1, *v*/*v*, 10 ml). Concentrated sulfuric acid (0.16 ml, 3 mmol) was added followed by piperazine (0.26 g, 3 mmol). The mixture was stirred briefly to form a homogeneous gel; the gel was transferred into a 15 ml Teflon-lined Parr bomb that was then heated 383 K for 48 h. Yellow crystals were isolated in about 80% yield (with respect to Fe).

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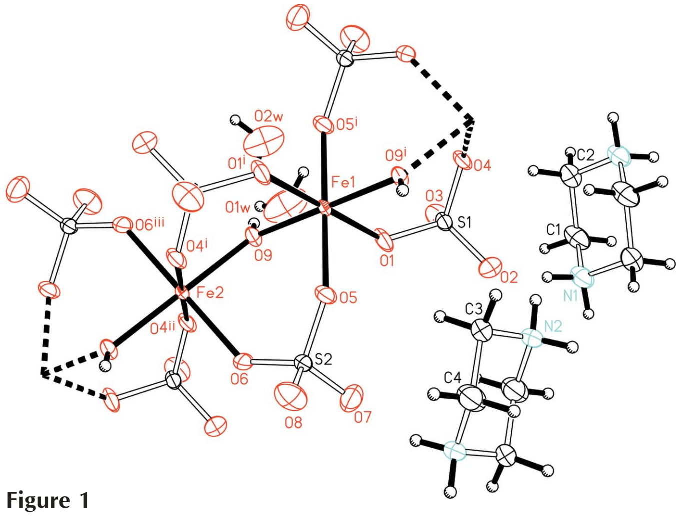

**Figure 1**
*ORTEPII* plot (Johnson, 1976) showing the atom-numbering scheme of (I). Displacement ellipsoids are drawn at the 50% probability level. Only one of the disordered water molecules is shown. The symmetry codes are as given in Table 1.

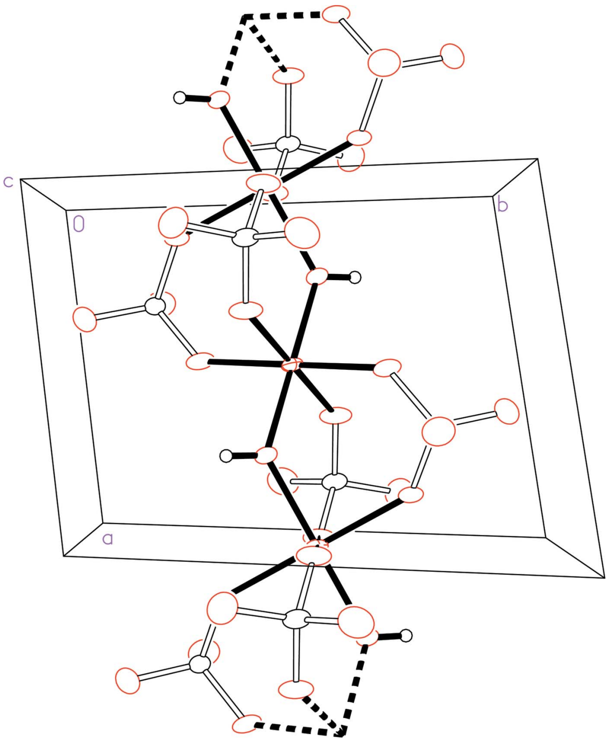

**Figure 2**
*ORTEPII* plot (Johnson, 1976) of the polyanionic [Fe(OH)(SO$_4$)$_2$] chain.

*Crystal data*

(C$_4$H$_{12}$N$_2$)[Fe(OH)(SO$_4$)$_2$]·2H$_2$O
$M_r$ = 389.17
Triclinic, $P\overline{1}$
$a$ = 7.0983 (6) Å
$b$ = 10.4690 (9) Å
$c$ = 10.5212 (9) Å
$\alpha$ = 60.421 (1)°
$\beta$ = 76.616 (1)°
$\gamma$ = 76.797 (2)°
$V$ = 655.4 (1) Å$^3$
$Z$ = 2
$D_x$ = 1.972 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 1907 reflections
$\theta$ = 2.3–28.1°
$\mu$ = 1.53 mm$^{-1}$
$T$ = 295 (2) K
Block, yellow
0.24 × 0.09 × 0.07 mm

*Data collection*

Bruker APEX area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.493, $T_{\max}$ = 0.901
3388 measured reflections
2264 independent reflections
2047 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.017
$\theta_{\max}$ = 25.0°
$h = -6 \rightarrow 8$
$k = -12 \rightarrow 11$
$l = -12 \rightarrow 12$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.134
$S$ = 1.22
2264 reflections
193 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0823P)^2 + 0.1835P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.71 e Å$^{-3}$
$\Delta\rho_{\min}$ = −0.69 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Fe1—O1 | 2.030 (3) | Fe2—O4$^{\rm ii}$ | 2.021 (2) |
| Fe1—O1$^{\rm i}$ | 2.030 (3) | Fe2—O4$^{\rm i}$ | 2.021 (2) |
| Fe1—O5 | 2.025 (2) | Fe2—O6 | 2.032 (2) |
| Fe1—O5$^{\rm i}$ | 2.025 (2) | Fe2—O6$^{\rm iii}$ | 2.032 (2) |
| Fe1—O9 | 1.956 (2) | Fe2—O9 | 1.964 (2) |
| Fe1—O9$^{\rm i}$ | 1.956 (2) | Fe2—O9$^{\rm iii}$ | 1.964 (2) |
| | | | |
| O1—Fe1—O5 | 91.7 (1) | O4$^{\rm ii}$—Fe2—O6 | 91.2 (1) |
| O1—Fe1—O5$^{\rm i}$ | 88.4 (1) | O4$^{\rm ii}$—Fe2—O6$^{\rm iii}$ | 88.8 (1) |
| O1—Fe1—O9 | 90.4 (1) | O4$^{\rm ii}$—Fe2—O9 | 89.7 (1) |
| O1—Fe1—O9$^{\rm i}$ | 89.6 (1) | O4$^{\rm ii}$—Fe2—O9$^{\rm iii}$ | 90.3 (1) |
| O5—Fe1—O9 | 89.6 (1) | O6—Fe2—O9 | 90.0 (1) |
| O5—Fe1—O9$^{\rm i}$ | 90.4 (1) | O6—Fe2—O9$^{\rm iii}$ | 90.0 (1) |

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x+1, y, z$; (iii) $-x+2, -y+1, -z+1$.

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O9—H9$o$···O1$w$ | 0.85 | 1.97 | 2.773 (4) | 158 |
| O1$w$—H1$w$1···O2$w$ | 0.85 | 2.16 | 2.657 (8) | 117 |
| O1$w$—H1$w$2···O2$w^{\rm iv}$ | 0.86 | 1.99 | 2.78 (1) | 152 |
| O1$w$—H1$w$1···O2$w$’ | 0.85 | 2.06 | 2.83 (1) | 150 |
| O2$w$—H2$w$1···O3$^{\rm iv}$ | 0.86 | 2.06 | 2.752 (8) | 137 |
| O2$w$—H2$w$2···O8$^{\rm v}$ | 0.86 | 1.97 | 2.717 (8) | 146 |
| O2$w$’—H2$w$3···O3$^{\rm iv}$ | 0.87 | 2.20 | 2.91 (1) | 139 |
| O2$w$’—H2$w$4···O8$^{\rm v}$ | 0.87 | 2.03 | 2.82 (1) | 149 |
| N1—H11···O2 | 0.90 | 1.98 | 2.835 (5) | 157 |
| N1—H12···O1$w^{\rm vi}$ | 0.90 | 2.09 | 2.909 (5) | 151 |
| N2—H21···O7$^{\rm vii}$ | 0.90 | 1.89 | 2.762 (4) | 163 |
| N2—H22···O2 | 0.90 | 2.17 | 2.852 (5) | 132 |

Symmetry codes: (iv) $-x+1, -y, -z+2$; (v) $x, y-1, z+1$; (vi) $-x+1, -y, -z+1$; (vii) $-x+1, -y+1, -z$.

One of the two water molecules is disordered over two positions; as the occupancy refined to nearly 0.5:0.5, the disorder was fixed at exactly 0.5:0.5. The water H atoms were placed at chemically sensible positions on the basis of hydrogen-bonding interactions, but they were not refined. Other H atoms were positioned geometrically [C—H = 0.97 Å and N—H = 0.90 Å; $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N)] and were included in the refinement in the riding-model approximation.

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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