

$\mu$ -Oxo-di- $\mu$ -sulfato-bis[aqua(1,10-phenanthroline- $\kappa^2N,N'$ )iron(III)] tetrahydrate

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Key indicators

Single-crystal X-ray study  
 T = 291 K  
 Mean  $\sigma(C-C)$  = 0.004 Å  
 R factor = 0.036  
 wR factor = 0.100  
 Data-to-parameter ratio = 14.7

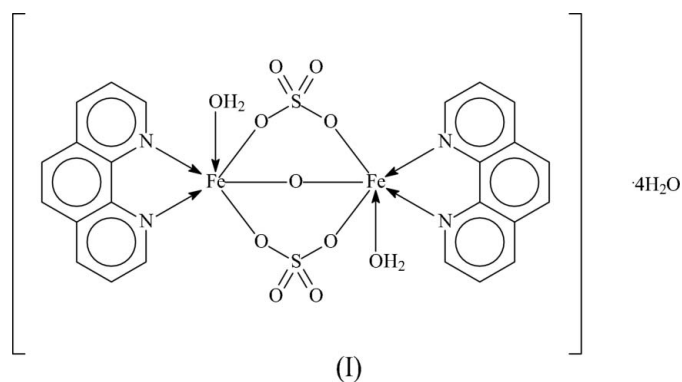
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The two aqua(1,10-phenanthroline)iron(III) parts of the title compound,  $[Fe_2O(SO_4)_2(C_{12}H_8N_2)_2(H_2O)_2] \cdot 4H_2O$ , are linked through one oxo and two sulfate bridges. Both metal centres show octahedral coordination, in which the three O atoms that are involved in bridging occupy the *fac* sites. Hydrogen bonds link adjacent dinuclear complexes into a three-dimensional network.

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Comment

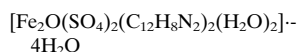
Octahedral transition metal complexes with an odd number of electrons for the metal are known to undergo temperature- and pressure-induced spin crossover, and iron(III) complexes with bidentate N-donor ligands (e.g. 1,10-phenanthroline, phen) are the most extensively studied (Chu *et al.*, 2001; MacLean *et al.*, 2003; Wang *et al.*, 2006). For iron(III) sulfate, a  $\mu$ -oxo complex is known; this octahydrate has two bis(1,10-phenanthroline)(sulfato-O)iron(III) parts connected through the oxo bridge (Odoko & Okabe, 2005). A similar synthesis has yielded the title tetrahydrate, (I). However, the two aqua(1,10-phenanthroline)iron(III) parts of (I) are connected through a  $\mu$ -oxo as well as through two sulfate groups (Fig. 1). The three O atoms that are involved in bridging occupy *fac* sites. Adjacent molecules are linked by hydrogen bonds (Table 2) into a three-dimensional network.



Experimental

1,10-Phenanthroline (0.35 g, 2.0 mmol) dissolved in ethanol (15 ml) was mixed with iron(III) sulfate (0.28 g, 1.0 mmol) dissolved in 95% ethanol (10 ml). The mixture was set aside. After one week, red crystals of (I) separated from the solution (yield 80%). The water in the structure possibly comes from the air as the reaction was carried out in the open.

## Crystal data


 $M_r = 788.32$ 

 Triclinic,  $P\bar{1}$ 
 $a = 8.7682 (7) \text{ \AA}$ 
 $b = 12.253 (1) \text{ \AA}$ 
 $c = 14.736 (1) \text{ \AA}$ 
 $\alpha = 103.289 (1)^\circ$ 
 $\beta = 100.135 (1)^\circ$ 
 $\gamma = 93.053 (1)^\circ$ 
 $V = 1509.5 (2) \text{ \AA}^3$ 
 $Z = 2$ 
 $D_x = 1.734 \text{ Mg m}^{-3}$ 

 Mo  $K\alpha$  radiation

 $\mu = 1.18 \text{ mm}^{-1}$ 
 $T = 291 (2) \text{ K}$ 

Block, red

 $0.26 \times 0.22 \times 0.18 \text{ mm}$ 

## Data collection

Bruker APEX-II area-detector diffractometer

 $\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

 $T_{\min} = 0.749, T_{\max} = 0.816$ 

12825 measured reflections

6747 independent reflections

 5205 reflections with  $I > 2\sigma(I)$ 
 $R_{\text{int}} = 0.020$ 
 $\theta_{\text{max}} = 27.5^\circ$ 

## Refinement

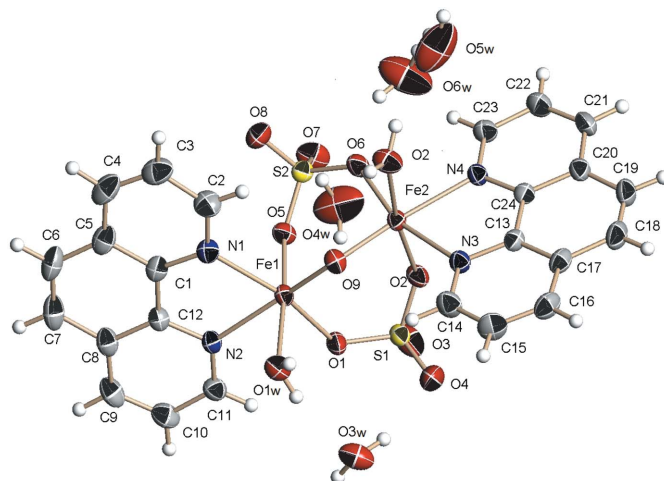
 Refinement on  $F^2$ 
 $R[F^2 > 2\sigma(F^2)] = 0.036$ 
 $wR(F^2) = 0.100$ 
 $S = 1.03$ 

6747 reflections

460 parameters

H atoms treated by a mixture of independent and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.0509P)^2 + 0.7248P]$ 

 where  $P = (F_o^2 + 2F_c^2)/3$ 
 $(\Delta/\sigma)_{\text{max}} = 0.001$ 
 $\Delta\rho_{\text{max}} = 0.72 \text{ e \AA}^{-3}$ 
 $\Delta\rho_{\text{min}} = -0.68 \text{ e \AA}^{-3}$ 

**Figure 1**

The structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

| $D-H \cdots A$            | $D-H$    | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|---------------------------|----------|--------------|--------------|----------------|
| $O6w-H6w1 \cdots O7$      | 0.85 (1) | 2.14 (1)     | 2.974 (4)    | 171 (4)        |
| $O6w-H6w2 \cdots O8^{iv}$ | 0.85 (1) | 2.01 (2)     | 2.840 (4)    | 168 (4)        |

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

**Table 1**

 Selected geometric parameters ( $\text{\AA}, ^\circ$ ).

|            |            |            |            |
|------------|------------|------------|------------|
| Fe1—O1     | 2.001 (2)  | Fe2—O2     | 2.057 (2)  |
| Fe1—O5     | 2.049 (2)  | Fe2—O6     | 2.004 (2)  |
| Fe1—O9     | 1.782 (2)  | Fe2—O2w    | 2.069 (2)  |
| Fe1—O1w    | 2.170 (2)  | Fe2—O9     | 1.792 (2)  |
| Fe1—N1     | 2.159 (2)  | Fe2—N3     | 2.160 (2)  |
| Fe1—N2     | 2.189 (2)  | Fe2—N4     | 2.185 (2)  |
| O1—Fe1—O5  | 88.46 (8)  | O2—Fe2—O6  | 91.34 (8)  |
| O1—Fe1—O9  | 101.07 (8) | O2—Fe2—O9  | 95.20 (8)  |
| O1—Fe1—O1w | 88.58 (8)  | O2—Fe2—O2w | 172.19 (8) |
| O1—Fe1—N1  | 86.82 (8)  | O2—Fe2—N3  | 90.52 (8)  |
| O1—Fe1—N2  | 161.01 (8) | O2—Fe2—N4  | 87.23 (7)  |
| O5—Fe1—O9  | 97.42 (8)  | O6—Fe2—O9  | 100.45 (8) |
| O5—Fe1—O1w | 172.32 (7) | O6—Fe2—O2w | 90.41 (9)  |
| O5—Fe1—N1  | 84.93 (8)  | O6—Fe2—N3  | 162.69 (8) |
| O5—Fe1—N2  | 92.33 (8)  | O6—Fe2—N4  | 87.10 (8)  |
| O9—Fe1—O1w | 90.10 (8)  | O9—Fe2—O2w | 91.97 (8)  |
| O9—Fe1—N1  | 97.42 (8)  | O9—Fe2—N3  | 96.52 (8)  |
| O9—Fe1—N2  | 167.57 (8) | O9—Fe2—N4  | 171.99 (8) |
| O1w—Fe1—N1 | 95.67 (8)  | O2w—Fe2—N3 | 85.58 (9)  |
| O1w—Fe1—N2 | 80.43 (8)  | O2w—Fe2—N4 | 85.25 (8)  |
| N1—Fe1—N2  | 75.71 (8)  | N3—Fe2—N4  | 75.81 (8)  |

**Table 2**

 Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ ).

| $D-H \cdots A$              | $D-H$    | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|-----------------------------|----------|--------------|--------------|----------------|
| $O1w-H1w1 \cdots O3w$       | 0.86 (1) | 2.02 (1)     | 2.850 (3)    | 164 (3)        |
| $O1w-H1w2 \cdots O3w^i$     | 0.85 (1) | 1.96 (1)     | 2.788 (3)    | 166 (3)        |
| $O2w-H2w1 \cdots O4w$       | 0.85 (1) | 1.82 (1)     | 2.658 (3)    | 171 (3)        |
| $O2w-H2w2 \cdots O5w$       | 0.83 (1) | 2.08 (2)     | 2.882 (5)    | 162 (3)        |
| $O3w-H3w1 \cdots O3^{ii}$   | 0.86 (1) | 1.95 (1)     | 2.809 (3)    | 177 (3)        |
| $O3w-H3w2 \cdots O4$        | 0.85 (1) | 1.98 (1)     | 2.801 (3)    | 162 (3)        |
| $O4w-H4w1 \cdots O7^{iii}$  | 0.85 (1) | 1.96 (1)     | 2.805 (4)    | 177 (4)        |
| $O4w-H4w2 \cdots O3^{iii}$  | 0.85 (1) | 2.16 (2)     | 2.948 (4)    | 155 (5)        |
| $O5w-H5w1 \cdots O7^{iv}$   | 0.86 (1) | 2.02 (3)     | 2.806 (4)    | 151 (5)        |
| $O5w-H5w2 \cdots O6w^{iii}$ | 0.87 (1) | 2.55 (6)     | 2.791 (5)    | 97 (4)         |

Carbon-bound H atoms were positioned geometrically, with  $C-H = 0.93 \text{ \AA}$ , and were included in the refinement in the riding-model approximation, with  $U(H) = 1.2U_{\text{eq}}(C)$ . Water H atoms were located in a difference Fourier map and were refined with distance restraints of  $O-H = 0.85 (1)$  and  $H \cdots H = 1.39 (1) \text{ \AA}$ . An alternative position of H5W2 at (0.520, 0.896, 1.083) would lead to better geometric parameters of the hydrogen bond. However, the  $H-O-H$  angle at O5W would then be too large ( $135^\circ$ ).

Data collection: SMART (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); 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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