

Mamiko Odoko\* and  
Nobuo OkabeFaculty of Pharmaceutical Sciences, Kinki  
University, Kowakae 3-4-1, Higashiosaka,  
Osaka 577-8502, JapanCorrespondence e-mail:  
odoko@phar.kindai.ac.jp

## Key indicators

Single-crystal X-ray study  
 $T = 296$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
 $R$  factor = 0.037  
 $wR$  factor = 0.116  
Data-to-parameter ratio = 16.5For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>. $\mu$ -Oxo- $\kappa^2\text{O}:\text{O}$ -bis[bis(1,10-phenanthroline- $\kappa^2\text{N},\text{N}'$ )-  
(sulfato- $\kappa\text{O}$ )iron(III)] octahydrate

In the crystal structure of the title binuclear iron(III) complex,  $[\text{Fe}_2^{\text{III}}\text{O}(\text{SO}_4)_2(\text{C}_{12}\text{H}_8\text{N}_2)_4]\cdot 8\text{H}_2\text{O}$ , the Fe atoms are connected by an O atom, which lies on a twofold axis. Each Fe atom is also coordinated by four N atoms of two 1,10-phenanthroline ligands and one O atom of a sulfate ion, resulting in a distorted octahedral geometry. The  $\text{Fe}\cdots\text{Fe}$  separation is 3.5552 (21) Å and the  $\text{Fe}-\text{O}-\text{Fe}$  bridge angle is 172.81 (12)°. The crystal packing is stabilized by a network of  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds.

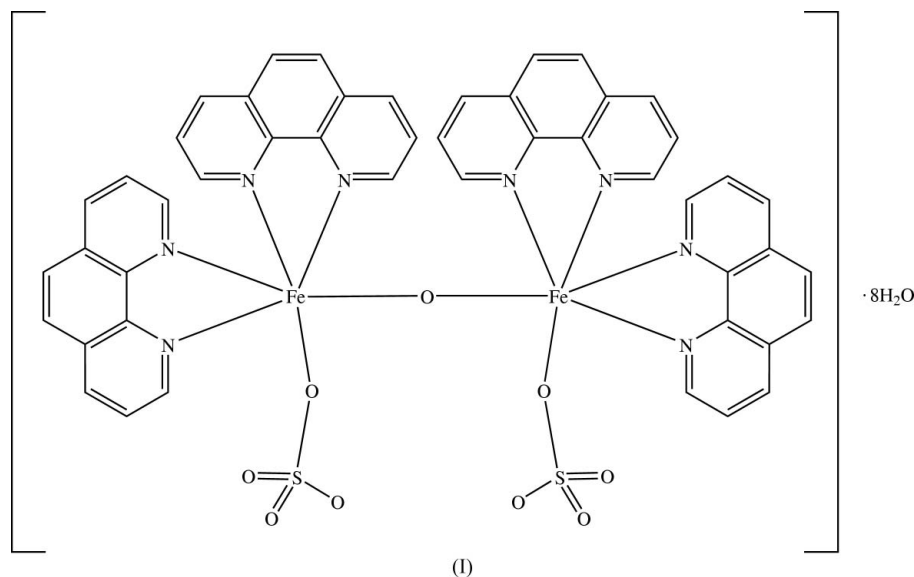
Received 25 January 2005

Accepted 21 February 2005

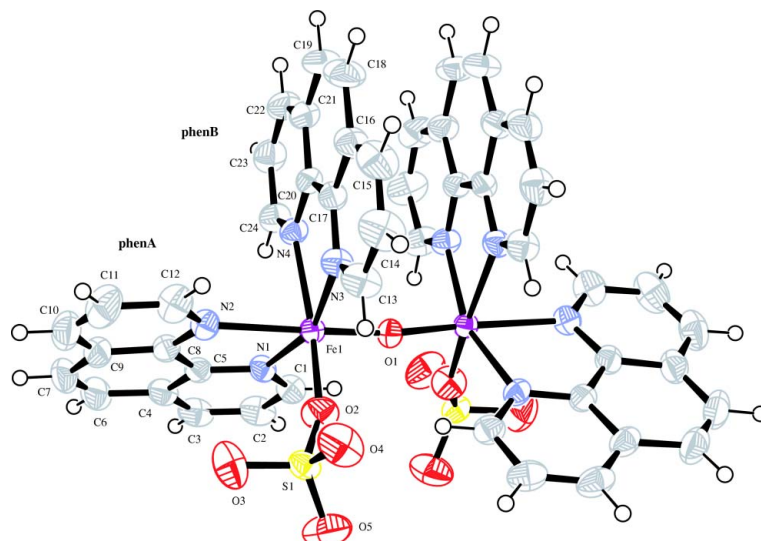
Online 26 February 2005

## Comment

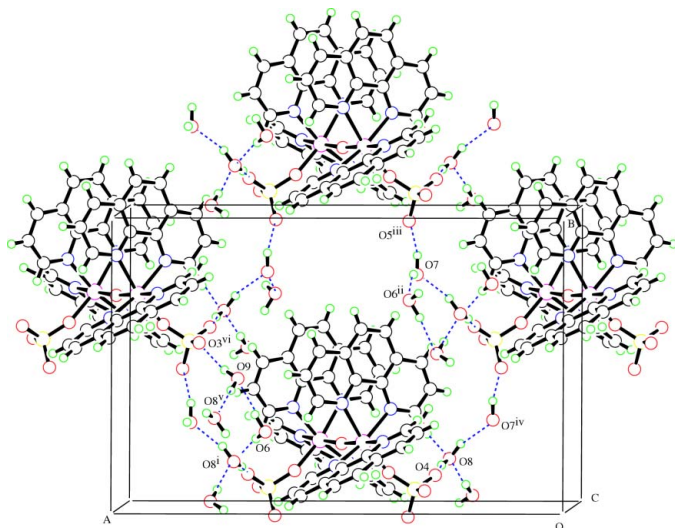
1,10-Phenanthroline (phen) can intercalate between nucleobases, and thus its derivatives and metal complexes have been studied as possible anticancer agents. Fe–phen complexes have been studied for their abilities to interact with DNA (Furtado *et al.*, 1997; Li *et al.*, 2002; Mudasir *et al.*, 2003). In order to clarify the coordination mode of Fe and phen, we have prepared and characterized  $[\text{Fe}^{\text{III}}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{NO}_3)_3\cdot\text{H}_2\text{O}$  (Odoko *et al.*, 2004). In the present study, we have synthesized another  $\text{Fe}^{\text{III}}$  complex,  $[\text{Fe}_2^{\text{III}}(\text{OSO}_3)_2(\text{C}_{12}\text{H}_8\text{N}_2)_4(\mu\text{-O})]\cdot 8\text{H}_2\text{O}$ , (I), and determined its crystal structure.



In the crystal structure of (I) (Fig. 1), the two Fe atoms are bridged by an O atom, which lies on a twofold axis. Two phen molecules (phenA and phenB) coordinate to the Fe atom as bidentate ligands, and one O atom of a sulfate ion binds at the position *cis* to the oxo bridge, resulting in a distorted octahedral environment for Fe. The sulfate ions are orientated on opposite sides of the complete molecule (Fig. 1), presumably for steric reasons. Intramolecular  $\pi$ – $\pi$  stacking interactions


**Figure 1**

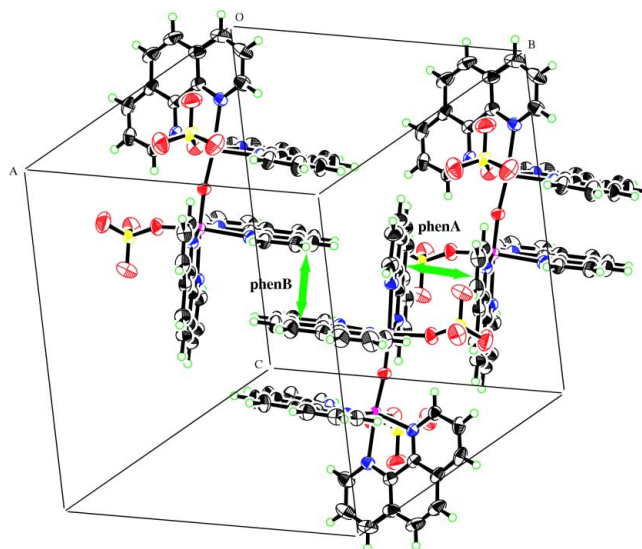
A view of the complex in (I). Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary radii. Unlabelled atoms are related to labelled atoms by the symmetry operator  $1 - x, y, \frac{1}{2} - z$ .


**Figure 2**

A view of the crystal packing of (I), showing hydrogen bonds (blue dashed lines) between cocrystallized water molecules and sulfate ions, and between water molecules. [Symmetry codes: (i)  $1 - x, y, \frac{1}{2} - z$ ; (ii)  $1 - x, 1 - y, -z$ ; (iii)  $x, 1 + y, z$ ; (iv)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (v)  $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$ ; (vi)  $\frac{1}{2} + x, \frac{1}{2} + y, z$ .]

exist between the two phenB molecules which face each other, with C...C contact distances ranging from 3.5212 (53) [C19...C19<sup>i</sup>; symmetry code (i):  $1 - x, y, \frac{1}{2} - z$ ] to 3.5629 (38) Å (C15...C23<sup>i</sup>).

Overall, this complex is similar to  $[\text{Fe}_2^{\text{III}}(\text{HL})_4(\text{OSO}_3)_2(\mu\text{-O})]$  [HL = 3-(2-pyridyl)pyrazole; Jones *et al.*, 1997], except for the orientations of the sulfate ligands. The Fe–N bond lengths in (I) range from 2.1320 (18) to 2.240 (2) Å, and the N–Fe–N bite angles are 75.64 (8) and 75.52 (9)° (Table 1). These values are comparable to those of other Fe–phen complexes, such as  $[\text{Fe}_2^{\text{III}}(\text{C}_{12}\text{H}_8\text{N}_2)_4\text{X}_2(\mu\text{-O})]$ , in which X = H<sub>2</sub>O (Plowman *et al.*, 1984) or Cl (Healy *et al.*, 1983). However, these values are significantly different from those found in our recent study of  $[\text{Fe}^{\text{III}}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{NO}_3)_3 \cdot \text{H}_2\text{O}$  (Odoko *et al.*,


**Figure 3**

A view of the crystal packing of (I), showing intermolecular  $\pi$ – $\pi$  stacking interactions (green arrows) between phen molecules. Water molecules have been omitted for clarity.

2004), in which the Fe–N bond lengths range from 1.968 (2) to 1.988 (1) Å, and the N–Fe–N bite angles are 82.43 (6) and 83.30 (7)°. The Fe–O–Fe<sup>i</sup> angle in (I) [172.81 (12)°] is larger than those of the H<sub>2</sub>O complex [155.1 (4)°] and Cl complex [161 (1)°], and the Fe...Fe separation in (I) [3.5552 (21) Å] is longer than that of the Cl complex (3.46 Å). These differences could be due to steric hindrance by the bulky sulfate ions attached to the Fe atoms.

The crystal structure of (I) is stabilized by O–H...O hydrogen bonds between cocrystallized water molecules and sulfate ions, and between water molecules (Table 2 and Fig. 2). In addition, intermolecular  $\pi$ – $\pi$  stacking interactions exist between phenA molecules, with contact distances ranging from 3.350 (3) [C1...C6<sup>viii</sup>; symmetry code (vii):  $1 - x, -y, -z$ ] to 3.578 (3) Å (C4...C4<sup>viii</sup>), and between phenB molecules,

ranging from 3.474 (3) [C21...C23<sup>ii</sup>; symmetry code (ii): 1 - x, 1 - y, -z] to 3.570 (3) Å (C22...C24<sup>ii</sup>) (Fig. 3), helping to stabilize the crystal packing

## Experimental

Red platelet crystals of (I) were obtained at room temperature by the slow evaporation of a mixture of a 50% (v/v) MeOH/water solution of 1,10-phenanthroline, iron(III) sulfate *n*-hydrate and succinic acid (molar ratio 1:1:1).

### Crystal data

[Fe <sub>2</sub> O(SO <sub>4</sub> ) <sub>2</sub> (C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>4</sub> ].8H <sub>2</sub> O	$D_x = 1.573 \text{ Mg m}^{-3}$
$M_r = 1184.78$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 19250 reflections
$a = 21.645 (8) \text{ \AA}$	$\theta = 3.1\text{--}27.5^\circ$
$b = 14.15 (1) \text{ \AA}$	$\mu = 0.75 \text{ mm}^{-1}$
$c = 16.48 (1) \text{ \AA}$	$T = 296.0 \text{ K}$
$\beta = 97.51 (3)^\circ$	Platelet, red
$V = 5004 (5) \text{ \AA}^3$	$0.30 \times 0.30 \times 0.10 \text{ mm}$
$Z = 4$	

### Data collection

Rigaku R-AXIS RAPID diffractometer	5762 independent reflections
$\omega$ scans	4674 reflections with $F^2 > 2\sigma(F^2)$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$R_{\text{int}} = 0.028$
$T_{\text{min}} = 0.610$ , $T_{\text{max}} = 0.928$	$\theta_{\text{max}} = 27.5^\circ$
24 059 measured reflections	$h = -28 \rightarrow 27$
	$k = -16 \rightarrow 18$
	$l = -21 \rightarrow 21$

### Refinement

Refinement on $F$	$w = 1/[\sigma^2(F_o^2) + (0.0707P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.116$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.12$	$\Delta\rho_{\text{max}} = 0.72 \text{ e \AA}^{-3}$
5762 reflections	$\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$
348 parameters	Extinction correction: none
H-atom parameters constrained	

**Table 1**

Selected geometric parameters (Å, °).

Fe1—O1	1.7811 (11)	Fe1—N3	2.152 (2)
Fe1—O2	1.9393 (19)	Fe1—N2	2.237 (2)
Fe1—N1	2.1320 (18)	Fe1—N4	2.240 (2)
O1—Fe1—O2	97.77 (8)	N1—Fe1—N2	75.64 (8)
O1—Fe1—N1	94.68 (7)	N3—Fe1—N2	89.41 (7)
O2—Fe1—N1	97.83 (9)	O1—Fe1—N4	91.27 (7)
O1—Fe1—N3	98.55 (7)	O2—Fe1—N4	168.56 (6)
O2—Fe1—N3	96.11 (9)	N1—Fe1—N4	88.36 (8)
N1—Fe1—N3	159.28 (7)	N3—Fe1—N4	75.52 (9)
O1—Fe1—N2	168.97 (5)	N2—Fe1—N4	83.30 (7)
O2—Fe1—N2	88.90 (7)	Fe1—O1—Fe1 <sup>i</sup>	172.81 (12)

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

**Table 2**

Hydrogen-bond geometry (Å, °).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O6—H6A...O9	0.96	1.99	2.925 (4)	164
O6—H6B...O8 <sup>i</sup>	0.98	1.88	2.812 (3)	158
O7—H7A...O6 <sup>ii</sup>	0.94	2.02	2.823 (4)	142
O7—H7B...O5 <sup>iii</sup>	0.93	1.79	2.696 (4)	164
O8—H8A...O7 <sup>iv</sup>	0.94	1.93	2.786 (3)	151
O8—H8B...O4	0.94	1.83	2.747 (3)	165
O9—H9A...O8 <sup>v</sup>	0.87	2.08	2.950 (4)	179
O9—H9B...O3 <sup>vi</sup>	0.98	1.91	2.847 (3)	158

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

H atoms, except those of water molecules, were placed in calculated positions, with  $C\text{---}H = 0.93 \text{ \AA}$ , and treated as riding, with  $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ . Those of water molecules were located in difference Fourier maps. Their positions were not refined and the constraint  $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(O)$  was applied.

Data collection: *PROCESS-AUTO* (Rigaku Corporation, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* and *CrystalStructure*.

## References

- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Furtado, F. A. C., Asad, N. R., Leitao, A. C. (1997). *Mut. Res.* **385**, 251–258.
- Healy, P. C., Skelton, B. W. & White, A. H. (1983). *Aust. J. Chem.* **36**, 2057–2064.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Jones, P. L., Jeffery, J. C., McCleverty, J. A. & Ward, M. D. (1997). *Polyhedron*, **16**, 1567–1571.
- Li, L., Song, G., Fang, G., Liu, L. & Cai, Z. (2002). *Hubei Daxue Xuebao, Ziran Kexueban*, **24**, 332–334.
- Mudasir, Wijaya, K., Yoshioka, N. & Inoue, H. (2003). *J. Inorg. Biochem.* **94**, 263–271.
- Rigaku Corporation (1998). *PROCESS-AUTO*. Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan.
- Rigaku/MS (2004). *CrystalStructure*. Version 3.6.0. Rigaku/MS, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
- Odoko, M. & Okabe, N. (2004). *Acta Cryst.* **E60**, m1822–m1824.
- Plowman, J. E., Locher, T. M., Schauer, C. K. & Anderson, O. P. (1984). *Inorg. Chem.* **23**, 3553–3559.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXL97*. University of Göttingen, Germany.