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Tris(1,10-phenanthroline-$\kappa^2 N,N'$)iron(III) trinitrate monohydrate

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In the title compound, $[Fe(C_{12}H_8N_2)_3](NO_3)_3 \cdot H_2O$, the Fe atom lies on a twofold rotation axis and is coordinated by three planar 1,10-phenanthroline ligands in a slightly distorted octahedral environment. One nitrate anion and the disordered water molecule also lie on twofold rotation axes. The crystal structure is stabilized by partial stacking and hydrogen-bonding interactions.

Comment

1,10-Phenanthroline (phen) molecules can stack with nucleo-bases to enhance complex formation with DNA, which is the principal target in the chemotherapy of tumors. Fe complexes containing phen have been studied for their ability to interact with DNA (Furtado *et al.*, 1997; Mudasir *et al.*, 2003). Few crystal structures of Fe^{3+} complexes of phen have been reported (Baker *et al.*, 1975), although there are many papers describing crystal structures containing $[Fe(phen)]^{2+}$ cations (Broomhead *et al.*, 1982; Che *et al.*, 1997; Deng *et al.*, 2001; Hoshina *et al.*, 2000; Koh *et al.*, 1994; Li *et al.*, 1993; Reiff *et al.*, 1983; Ronco *et al.*, 1986; Yan *et al.*, 2000; Zalkin *et al.*, 1973). In the present study, we synthesized the title compound, $[Fe(phen)_3]^{3+} \cdot 3NO_3^- \cdot H_2O$, and analyzed its crystal structure.

(I)
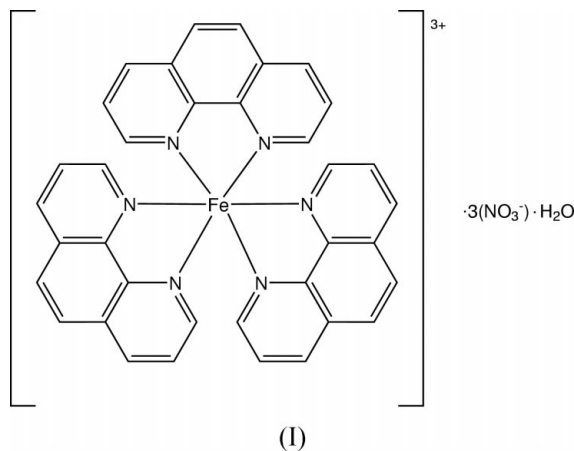
Fig. 1 shows a view of the $[Fe(phen)_3]^{3+}$ cation. The Fe atom, which lies on a twofold rotation axis, is coordinated by six N atoms of three phen ligands to form a distorted octahedral environment. The Fe1—N1 bond length, 1.988 (1) Å, is slightly longer than the other Fe—N bonds; the average Fe—N bond length is 1.976 Å, in agreement with previously reported results for the $[Fe(phen)_3]^{3+}$ cation (Baker *et al.*, 1975), ranging from 1.967 (8) to 1.980 (8) Å. The N—Fe—N bite angles are similar to those previously reported [82.8 (3)–83.1 (3)°]. Each phen ligand is planar, with mean deviations of
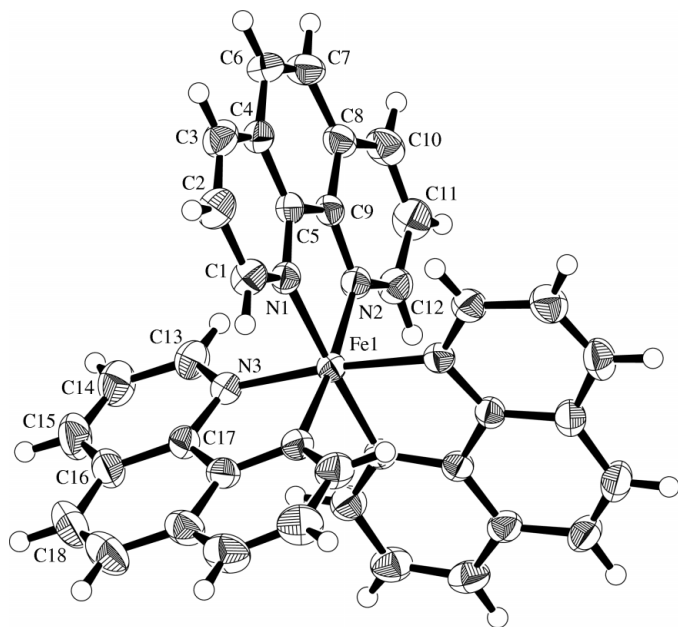
Figure 1
*ORTEP*II (Johnson, 1976) drawing of the $[Fe(phen)_3]^{3+}$ cation of (I). Displacement ellipsoids for non-H atoms are shown at the 50% probability level. Unlabeled atoms are related to labeled atoms by the symmetry operator $(-x, y, \frac{1}{2} - z)$.

0.036 [plane N1/C1–C12/N2] and 0.011 Å [plane N3/C13–C18/C13^i–C18^i/N3^i; symmetry code as in Table 1].

The crystal structure is stabilized by partial stacking interactions between the phen ligands of neighboring cations [C4···C7^{ii} and C7···C4^{ii} = 3.383 (7), C14···C15^{iii} and C15···C14^{iii} = 3.589 (3) Å; symmetry codes: (ii) $-x, -y, -z$; (iii) $-\frac{1}{2} - x, \frac{1}{2} - y, -z$; Fig. 2] and by O—H···O hydrogen-bonding interactions between the disordered water molecule (lying on a twofold axis) and nitrate anions (Table 2 and Fig. 3). One nitrate anion lies on a twofold rotation axis.

Experimental

Brown prismatic crystals of the title compound were obtained at room temperature by the slow evaporation of a DMF solution of 1,10-phenanthroline, iron(III) nitrate nonahydrate and malonic acid (molar ratio 1:1:1).

Crystal data

$[Fe(C_{12}H_8N_2)_3](NO_3)_3 \cdot H_2O$
$M_r = 800.50$
Monoclinic, $C2/c$
$a = 10.769$ (8) Å
$b = 24.58$ (2) Å
$c = 13.274$ (12) Å
$\beta = 103.00$ (3)°
$V = 3423$ (5) Å^3
$Z = 4$

$D_x = 1.553$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 716 reflections
$\theta = 3.1–27.4°$
$\mu = 0.52$ mm^{-1}
$T = 296.1$ K
Block, brown
$0.20 \times 0.20 \times 0.20$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (Higashi, 1995)
$T_{min} = 0.732, T_{max} = 0.904$
16 262 measured reflections

3869 independent reflections
2512 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 27.4°$
$h = -12 \rightarrow 13$
$k = -31 \rightarrow 31$
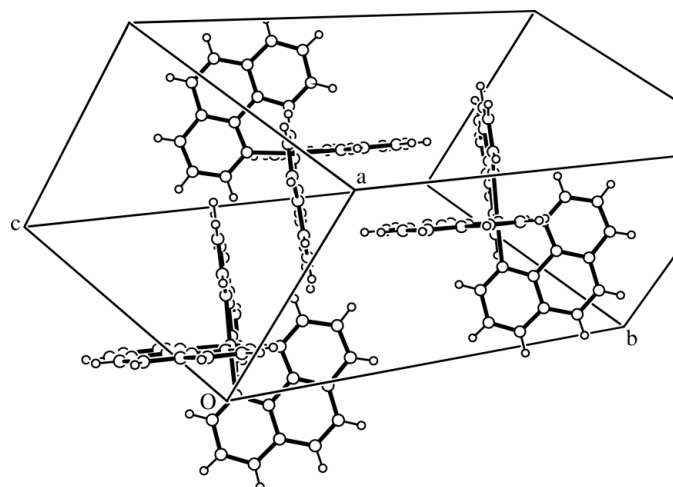$l = -17 \rightarrow 17$

Figure 2
View of the crystal packing, showing stacking of phen ligands.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.123$
$S = 1.02$
3869 reflections
256 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0811P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.71$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—N1	1.988 (1)	Fe1—N3	1.968 (2)
Fe1—N2	1.971 (2)		
N1—Fe1—N1^i	177.73 (7)	N2—Fe1—N2^i	89.39 (7)
N1—Fe1—N2	82.43 (6)	N2—Fe1—N3	93.89 (7)
N1—Fe1—N2^i	95.95 (6)	N2—Fe1—N3^i	173.95 (6)
N1—Fe1—N3	89.53 (6)	N3—Fe1—N3^i	83.30 (7)
N1—Fe1—N3^i	92.17 (6)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H13···O1^i	0.87	2.02	2.657 (4)	129
O6—H13···O2^i	0.87	2.38	3.053 (5)	135
O6—H14···O4^{ii}	0.89	2.24	3.067 (8)	154

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

H atoms, except those of water molecules, were placed in calculated positions, with C—H = 0.93 Å, and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$. Those of water molecules were located in a difference Fourier map and were then refined as riding with $U_{iso}(H) = 1.5_{eq}(O)$; one of these H atoms is disordered over two positions across the twofold rotation axis on which the water molecule lies, while the other lies on the axis.

Data collection: *PROCESS-AUTO* (Rigaku/MSC & Rigaku Corporation, 2004); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC & Rigaku Corporation, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997);

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molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *CrystalStructure*.

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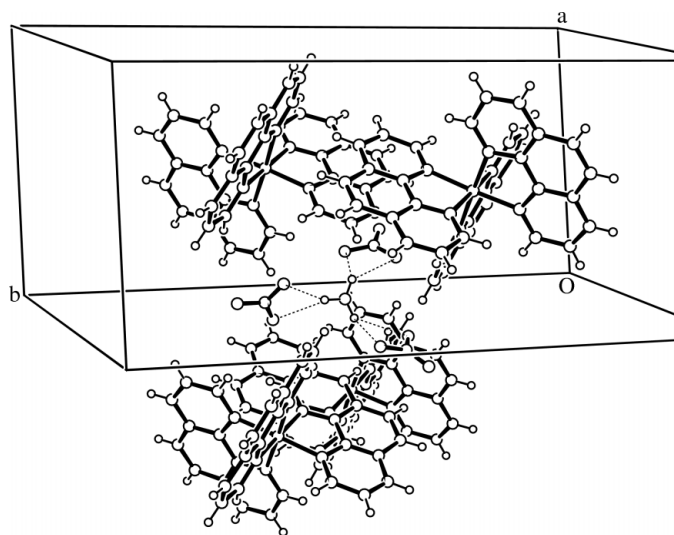
Figure 3
View of the crystal packing, showing hydrogen-bond interactions (dashed lines).

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