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Tris(1,10-phenanthroline-κ^2N,N')iron(II) squarate octahydrate

Ibrahim Uçar,* Hümeyra Paşaoĝlu, Orhan Büyükgüngör and Ahmet Bulut

Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayís University, TR-55139 Kurupelit-Samsun, Turkey

Correspondence e-mail: iucar@omu.edu.tr

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In the title compound, $[Fe(C_{12}H_8N_2)_3](C_4O_4)\cdot 8H_2O$ or $[Fe(phen)_3]sq\cdot 8H_2O$, where phen is 1,10-phenanthroline and sq is the squarate dianion $(C_4O_4)^{2-}$, the Fe^{II} centre has a distorted octahedral coordination geometry comprising six N atoms from the three bidentate chelating phen ligands. An extensive three-dimensional network of $O_{water}—H\cdots O$, $O_{water}—H\cdots O_{water}$ and $C—H\cdots O$ hydrogen-bonding interactions is responsible for crystal stabilization.

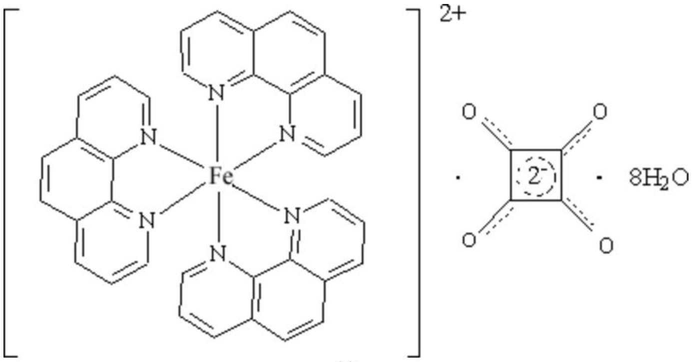
Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.003 Å
R factor = 0.041
wR factor = 0.113
Data-to-parameter ratio = 14.8

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

Comment

Many workers from a variety of scientific disciplines are interested in the crystal design and engineering of multi-dimensional arrays and networks containing metal ions as nodes. From the viewpoint of crystal engineering, squaric acid is a useful tool for constructing crystalline architectures because of its rigid, planar four-membered ring framework and its proton-donating and accepting capabilities for hydrogen bonding (Reetz *et al.*, 1994; Bertolasi *et al.*, 2001; Zaman *et al.*, 2001; Mathew *et al.*, 2002; Uçar *et al.*, 2005). In addition, mixed-ligand metal complexes of 1,10-phenanthroline (phen) and its substituted derivatives continue to attract attention because this ligand plays an important role in biological systems, such as the binding of small molecules to DNA (Xu *et al.*, 2002; Macias *et al.*, 2003; Mudasir *et al.*, 2003). 1,10-Phenanthroline has also been used extensively as a ligand in both analytical and preparative coordination chemistry (Idriss *et al.*, 1980; Koch & Ackermann, 1992; Lorenzo *et al.*, 1998; Shabir & Forrow, 2003).



(I)

In our ongoing research on squaric acid, we have synthesized some mixed-ligand metal complexes of squaric acid and their structures have been reported (Bulut *et al.*, 2004; Uçar *et al.*, 2004). In this context, the title mixed-ligand complex, (I), of iron(II) squarate with phen has been prepared and its crystal structure is reported here.

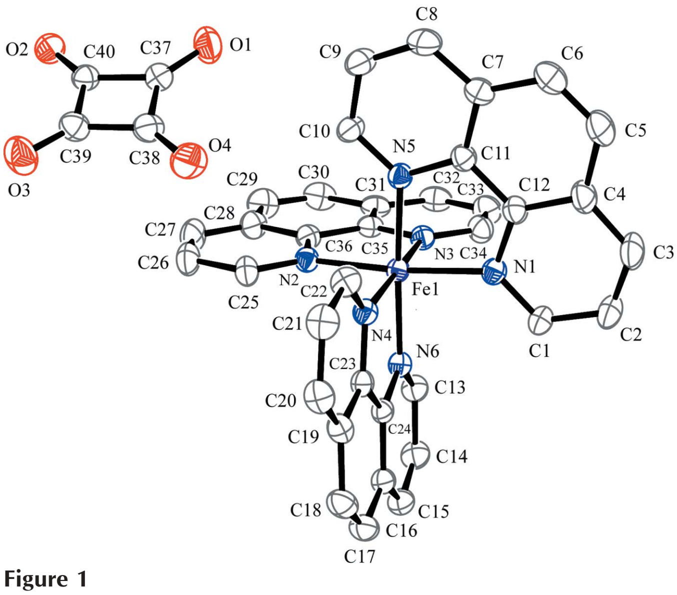


Figure 1
A view of the constituent ions of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Phenanthroline H atoms and water molecules have been omitted for clarity.

The asymmetric unit of (I) contains an $[\mathrm{Fe(phen)_3}]^{2+}$ complex cation, an uncoordinated squarate dianion ($C_4O_4^{2-}$) and eight water molecules (Fig. 1). The $\mathrm{Fe^{II}}$ ion of (I) is bonded to three bidentate phen ligands through their N atoms in a distorted octahedral geometry. The Fe1—N bond distances range from 1.9710 (16) to 1.9803 (16) Å, and are in agreement with those observed in other $[\mathrm{Fe(phen)_3}]^{2+}$ complexes (Koh *et al.*, 1994; Hoshina *et al.*, 2000; Odoko & Okabe, 2004). The angles subtended at the Fe atom by the phen ligands are 82.57 (7), 82.80 (7) and 82.71 (6)°, in agreement with those reported for other phen-containing $\mathrm{Fe^{II}}$ complexes (Deng *et al.*, 2001; Zhang *et al.*, 2004). All the N—Fe1—N bond angles (Table 1) deviate significantly from the ideal values of 90 or 180° because of the constrained geometry of the phen ring systems.

The crystal packing in (I) is formed by intermolecular hydrogen-bonding interactions (Fig. 2). The eight solvent water molecules link the squarate dianions to each other through these hydrogen-bonding interactions (see Table 2 for details). The complex cation and squarate dianion are also linked to each other *via* C—H···O hydrogen bonds.

Experimental

Squaric acid (0.57 g, 5 mmol) was dissolved in water (25 ml), neutralized with NaOH (0.40 g, 10 mmol) and added to a hot solution of $\mathrm{FeCl_2{\cdot}H_2O}$ (0.724 g, 5 mmol) dissolved in water (50 ml). The mixture was refluxed at 333 K for 12 h and then cooled to room temperature. The yellow crystals which formed were filtered off and washed with water and ethanol, and dried *in vacuo*. A solution of 1,10-phenanthroline (0.540 g, 3 mmol) in methanol (50 ml) was added dropwise with stirring to a suspension of $\mathrm{FeSq{\cdot}2H_2O}$ (0.204 g, 1 mmol) in water (50 ml). The resulting dark-red solution was refluxed for 2 h and then cooled to room temperature. After a few days, well formed red crystals were selected for X-ray studies.

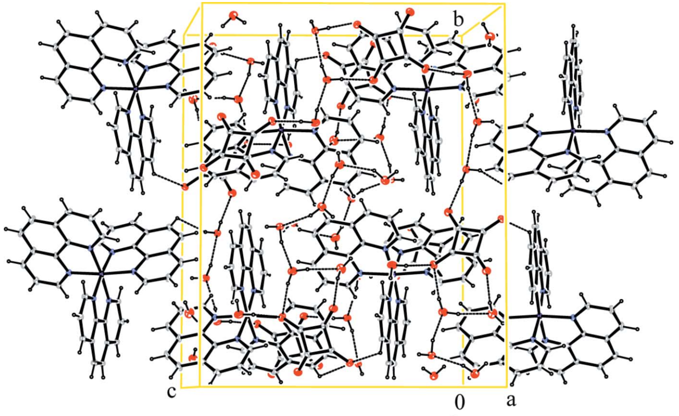


Figure 2
The crystal packing of (I), viewed down the *a* axis. Dashed lines indicate hydrogen bonds.

Crystal data

$[\mathrm{Fe(C_{12}H_8N_2)_3}](\mathrm{C_4O_4})\cdot 8\mathrm{H_2O}$
$M_r = 852.63$
Monoclinic, $P2_1/c$
$a = 10.9285\ (6)$ Å
$b = 21.3431\ (7)$ Å
$c = 16.8988\ (8)$ Å
$\beta = 98.804\ (4)°$
$V = 3895.4\ (3)$ Å^3
$Z = 4$

$D_x = 1.454$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5187 reflections
$\theta = 1.7$–$27.8°$
$\mu = 0.46$ mm^{-1}
$T = 297\ (2)$ K
Block, red
0.31 × 0.25 × 0.19 mm

Data collection

Stoe IPDS-2 diffractometer
ω scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
$T_{\min} = 0.734$, $T_{\max} = 0.932$
42766 measured reflections
8612 independent reflections

5723 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.050$
$\theta_{\max} = 27.2°$
$h = -13 \rightarrow 14$
$k = -27 \rightarrow 27$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.113$
$S = 0.96$
8612 reflections
583 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0679P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0023 (3)

Table 1
Selected geometric parameters (Å, °).

N1—Fe1	1.9791 (16)	N4—Fe1	1.9735 (16)
N2—Fe1	1.9710 (16)	N5—Fe1	1.9803 (16)
N3—Fe1	1.9721 (16)	N6—Fe1	1.9773 (16)
N2—Fe1—N3	82.80 (7)	N4—Fe1—N1	91.48 (7)
N2—Fe1—N4	93.58 (7)	N6—Fe1—N1	93.46 (7)
N3—Fe1—N4	174.11 (7)	N2—Fe1—N5	93.37 (7)
N2—Fe1—N6	90.91 (7)	N3—Fe1—N5	91.43 (7)
N3—Fe1—N6	92.67 (6)	N4—Fe1—N5	93.43 (7)
N4—Fe1—N6	82.71 (6)	N6—Fe1—N5	174.41 (7)
N2—Fe1—N1	173.69 (7)	N1—Fe1—N5	82.57 (7)
N3—Fe1—N1	92.45 (7)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5A···O12^{i}	0.84 (2)	2.13 (2)	2.878 (4)	149 (2)
O5—H5B···O6	0.84 (2)	1.91 (2)	2.731 (3)	163 (2)
O6—H6A···O7^{ii}	0.86 (2)	1.97 (2)	2.816 (3)	166 (2)
O6—H6B···O10^{iii}	0.89 (2)	1.81 (2)	2.677 (3)	166 (2)
O7—H7A···O1^{ii}	0.82 (2)	2.01 (2)	2.811 (3)	166 (3)
O7—H7B···O2	0.82 (2)	1.92 (2)	2.737 (2)	169 (2)
O8—H8A···O3	0.85 (2)	1.88 (2)	2.722 (3)	173 (2)
O8—H8B···O7	0.82 (2)	2.02 (2)	2.832 (3)	169 (2)
O9—H9B···O3	0.89 (2)	1.94 (3)	2.782 (4)	157 (7)
O9—H9A···O11^{iv}	0.86 (2)	2.53 (6)	3.147 (5)	129 (6)
O10—H10A···O4	0.84 (2)	1.94 (2)	2.745 (3)	160 (2)
O10—H10B···O9	0.85 (2)	1.95 (2)	2.786 (4)	165 (2)
O11—H11A···O4	0.87 (2)	1.86 (2)	2.720 (3)	173 (2)
O11—H11B···O8^{v}	0.82 (2)	2.00 (2)	2.808 (3)	170 (2)
O12—H12A···O5^{vi}	0.83 (2)	1.96 (2)	2.775 (4)	168 (2)
O12—H12B···O11^{vi}	0.88 (2)	2.13 (2)	2.771 (3)	129 (2)
C20—H20···O2^{v}	0.93	2.57	3.267 (3)	132

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

H atoms attached to C atoms were placed at calculated positions (C—H = 0.93 Å) and were allowed to ride on the parent atom [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)]. Other H atoms were located in a difference map and were refined with the O—H and H···H distances restrained to 0.85 (2) and 1.37 (2) Å, respectively; the isotropic displacement parameters were refined for H9A and H9B and set equal to 1.5 times $U_{\rm eq}$(O) for the remaining atoms.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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