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cis-Diaquabis(quinoline-2-carboxylato-κ^2N,O)-iron(II)–quinoline-2-carboxylic acid–water (2/1/2)

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In the title compound, $[Fe(C_{10}H_7NO_3)_2(H_2O)_2]_2\cdot C_{10}H_7NO_3\cdot 2H_2O$, two *cis*-diaquabis(quinoline-2-carboxylato)iron(II) molecules, one free quinoline-2-carboxylic acid molecule and two water molecules are present in the asymmetric unit. In the complex, the central Fe^{II} ion has a distorted octahedral coordination geometry, involving two N and two O atoms of the two bidentate organic ligands, together with two aqua O atoms in a *cis* configuration.

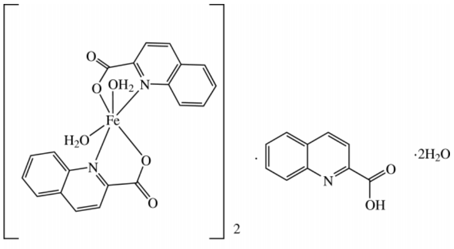
Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.008 Å
R factor = 0.045
wR factor = 0.174
Data-to-parameter ratio = 16.3

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

Comment

Quinoline-2-carboxylic acid is a tryptophan metabolite (Martell & Smith, 1974). Crystal strutures of its metal complexes have been determined with Cu^{II} (Haendler, 1986), Mn^{II} (Haendler, 1996; Okabe & Koizumi, 1997), Fe^{II}, Co^{II} (Okabe & Makino, 1998, 1999), Ni^{II} (Odoko *et al.*, 2001) and V^{IV} (Okabe & Muranishi, 2002). The iron complex improves the Fenton oxidation reaction by Fenton's reagent ($FeSO_4\cdot 7H_2O$ and H_2O_2) (Shul'pin, 2002), acting as a co-catalyst. Although the Fe^{II} complex has already been structurally characterized as *trans*-diaquabis(2-quinolinecarboxylato-*N,O*)iron(II)–ethanol–water (1/2/2) (Okabe & Makino, 1998), the structure of the Fe^{II} complex in a *cis* configuration has now also been determined as the title mixed solvate, (I).



(I)

The structure of the complex is shown in Fig. 1, and selected geometric parameters are listed in Table 1. Two *cis*-diaquabis(quinoline-2-carboxylato)iron(II) molecules, one free quinoline-2-carboxylic acid molecule and two water molecules are present in the asymmetric unit. The structures of the two independent complex molecules are almost the same. The bidentate organic ligands in each complex are nearly perpendicular to each other [N1—Fe1—N2 = 93.5 (1)° and N3—Fe2—N4 = 95.7 (1)°]. In each complex, the central Fe^{II} ion is coordinated by two N and two O atoms of the two organic ligands and by two aqua O atoms, in a distorted octahedral geometry. The ligand atoms are coordinated in a *cis* configuration. This *cis* configuration is quite different from *trans*-diaquabis(2-quinolinecarboxylato)iron(II) (Okabe & Makino, 1998), in which the quinoline rings of the two ligands lie in the same plane. The carboxyl groups of the ligands are

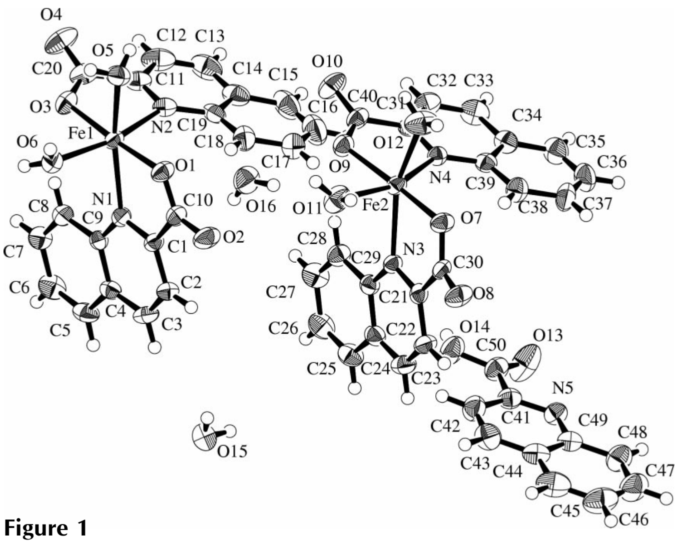


Figure 1
*ORTEP*II (Johnson, 1976) drawing of the title compound, with the atomic numbering scheme. Ellipsoids for non-H atoms are drawn at the 50% probability level.

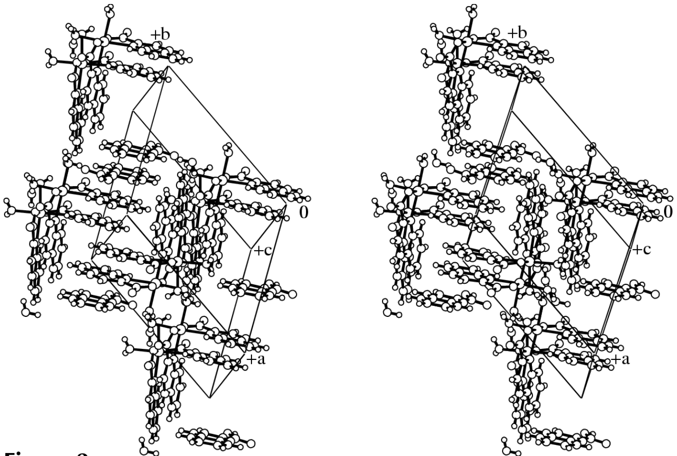


Figure 2
A stereoview of the molecular packing of (I).

ionized. The organic ligands and the central Fe^{II} ion form five-membered rings in a slightly distorted manner, as reflected by the torsion angles [O1—C10—C1—N1 = −1.5 (5), O3—C20—C11—N2 = −16.1 (8), O7—C30—C21—N3 = −13.3 (5) and O9—C40—C31—N4 −10.1 (7)°]. Five-membered ring formation is usually observed in the metal complexes of quinoline-2-carboxylic acid (Okabe & Makino, 1999). The ligand—Fe distances are a little different from each other: Fe—O(carboxylate) = 2.025 (3)–2.080 (4) Å, Fe—N = 2.209 (3)–2.290 (3) Å and Fe—O(water) = 2.122 (5)–2.190 (3) Å. These values are somewhat different from those in the *trans* complex: Fe—O(carboxylate, *trans*) = 2.087 (1) Å, Fe—N(*trans*) = 2.270 (1) Å and Fe—O(water, *trans*) = 2.131 (1) Å. These *cis* and *trans* configurations of Fe^{II} complexes of quinoline-2-carboxylic acid should influence differently the metal—H_2O_2 binding interaction in the Fenton reaction (Shul'pin, 2002).

In the crystal packing, shown in Fig. 2, quinoline rings of the complex and the free quinoline-2-carboxylic acid stack alternately. The Fe^{II} complex, the free quinoline-2-carboxylic acid and the water molecule are linked to each other by a hydrogen-bonding network, as shown in Table 2.

Experimental

Purple plate-shaped crystals were obtained by slow evaporation from a mixture of quinoline-2-carboxylic acid and $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ (4:1) dissolved in water.

Crystal data

$[Fe(C_8H_8NO_2)_2(H_2O)_2]_2{\cdot}$-$C_{10}H_7NO_2{\cdot}2H_2O$
$M_r = 1081.59$
Triclinic, $P\bar{1}$
$a = 12.662$ (3) Å
$b = 13.438$ (3) Å
$c = 16.340$ (3) Å
$\alpha = 97.20$ (2)°
$\beta = 101.94$ (2)°
$\gamma = 117.79$ (1)°
$V = 2326.0$ (10) Å^3

$Z = 2$
$D_x = 1.544$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12.7$–14.3°
$\mu = 0.71$ mm^{-1}
$T = 296.2$ K
Plate, purple
0.30 × 0.20 × 0.10 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.844$, $T_{max} = 0.932$
11146 measured reflections
10701 independent reflections
4869 reflections with $I > 2\sigma(I)$

$R_{int} = 0.054$
$\theta_{max} = 27.5°$
$h = -16 \rightarrow 14$
$k = 0 \rightarrow 17$
$l = -21 \rightarrow 21$
3 standard reflections every 150 reflections intensity decay: 0.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.174$
$S = 0.84$
10701 reflections
658 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—O1	2.025 (3)	Fe2—O7	2.043 (3)
Fe1—O3	2.061 (4)	Fe2—O9	2.080 (4)
Fe1—O5	2.166 (4)	Fe2—O11	2.190 (3)
Fe1—O6	2.173 (3)	Fe2—O12	2.122 (5)
Fe1—N1	2.248 (5)	Fe2—N3	2.265 (4)
Fe1—N2	2.290 (3)	Fe2—N4	2.209 (3)
O1—Fe1—O3	176.0 (2)	O9—Fe2—O12	93.7 (2)
O1—Fe1—O5	86.4 (2)	O9—Fe2—N3	106.9 (1)
O1—Fe1—O6	91.2 (1)	O9—Fe2—N4	76.0 (1)
O1—Fe1—N1	76.5 (2)	O11—Fe2—O12	92.2 (2)
O1—Fe1—N2	102.6 (1)	O11—Fe2—N3	91.3 (1)
O3—Fe1—O5	89.9 (2)	O11—Fe2—N4	161.1 (2)
O3—Fe1—O6	90.1 (1)	O12—Fe2—N3	159.3 (2)
O3—Fe1—N1	107.3 (2)	O12—Fe2—N4	87.4 (2)
O3—Fe1—N2	76.1 (1)	N3—Fe2—N4	95.7 (1)
O5—Fe1—O6	85.3 (1)	Fe1—O1—C10	120.8 (3)
O5—Fe1—N1	162.4 (1)	Fe1—O3—C20	119.0 (3)
O5—Fe1—N2	94.2 (1)	Fe2—O7—C30	119.0 (3)
O6—Fe1—N1	90.9 (1)	Fe2—O9—C40	118.4 (3)
O6—Fe1—N2	166.2 (1)	Fe1—N1—C1	110.8 (3)
N1—Fe1—N2	93.5 (1)	Fe1—N1—C9	131.2 (3)
O7—Fe2—O9	171.9 (1)	Fe1—N2—C11	109.9 (3)
O7—Fe2—O11	87.4 (1)	Fe1—N2—C19	132.1 (3)
O7—Fe2—O12	83.5 (2)	Fe2—N3—C21	110.7 (3)
O7—Fe2—N3	76.2 (1)	Fe2—N3—C29	131.9 (3)
O7—Fe2—N4	111.3 (1)	Fe2—N4—C31	112.6 (3)
O9—Fe2—O11	85.1 (1)	Fe2—N4—C39	128.9 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5A···O15$^{\mathrm{i}}$	0.83	2.02	2.801 (4)	158
O6—H6B···O15$^{\mathrm{ii}}$	0.82	1.92	2.731 (4)	167
O5—H5B···O3$^{\mathrm{iii}}$	0.82	2.12	2.910 (4)	162
O6—H6A···O4$^{\mathrm{iii}}$	0.83	1.99	2.760 (5)	154
O11—H11A···O13$^{\mathrm{iv}}$	0.92	1.95	2.854 (5)	166
O11—H11B···O10$^{\mathrm{v}}$	0.92	2.00	2.917 (5)	175
O14—H14···O10$^{\mathrm{vi}}$	0.83	1.87	2.675 (5)	169
O15—H15A···O8$^{\mathrm{vii}}$	0.84	1.87	2.704 (5)	170
O12—H12A···O5$^{\mathrm{v}}$	0.82	2.15	2.949 (5)	165
O15—H15B···N5$^{\mathrm{viii}}$	0.93	2.01	2.936 (5)	178
O12—H12B···O16$^{\mathrm{v}}$	0.82	1.94	2.757 (5)	170
O16—H16A···O11	0.92	2.15	3.071 (5)	178
O16—H16B···O2	0.89	1.83	2.722 (5)	178

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

All H atoms were located in a difference Fourier map. Those of the quinoline rings were then positioned geometrically and refined as riding, while those of the water molecules were fixed at the positions found in the map.

Data collection: *MSC/AFC* (Molecular Structure Corporation & Rigaku Corporation, 1999); cell refinement: *MSC/AFC*; data reduction: *teXsan* (Molecular Structure Corporation & Rigaku Corporation, 1999); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999) and *DIRDIF*94 (Beurskens *et al.*, 1992); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *teXsan*.

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