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Key indicators

Single-crystal X-ray study
T = 150 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.047
wR factor = 0.126
Data-to-parameter ratio = 16.9

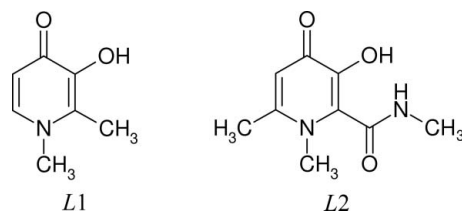
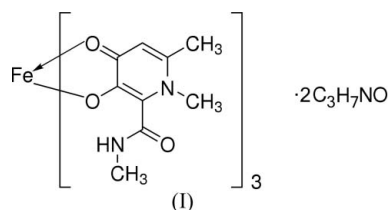
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

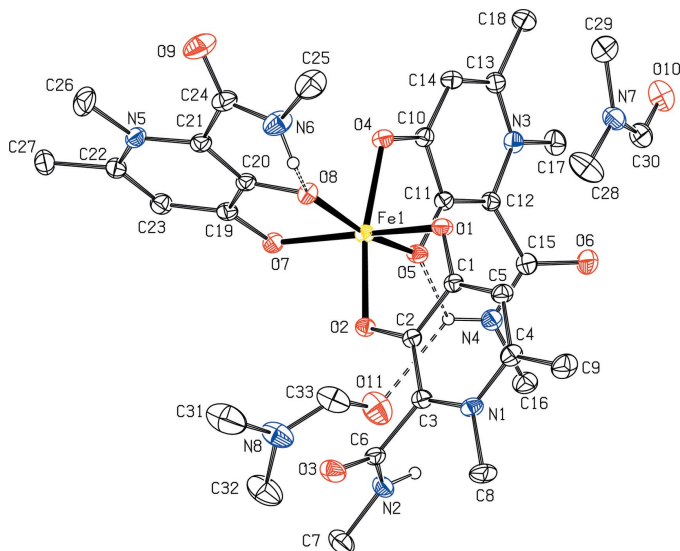
Tris(2-*N*-methylaminocarbonyl-3-hydroxy-1,6-dimethyl-1,4-dihydro-4-pyridinonato)iron(III) dimethylformamide disolvate

In the crystal structure of the title compound, $\text{Fe}(\text{C}_9\text{H}_{11}\text{N}_2\text{O}_3)_3 \cdot 2\text{C}_3\text{H}_7\text{NO}$, the Fe^{III} ion is six-coordinate with a distorted octahedral configuration consisting of six donor O atoms from three bidentate ligands. Two of the amide NH groups are involved in intramolecular $\text{N}-\text{H} \cdots \text{O}_p$ (p = phenolic) hydrogen bonds, while the third is involved in forming centrosymmetric dimers *via* intermolecular $\text{N}-\text{H} \cdots \text{O}_p$ hydrogen bonds.

Comment

Iron chelation therapy is now a mainstay for the treatment of human conditions of iron overload, *e.g.* transfusion-dependent β -thalassaemia (Cohen *et al.*, 2004). At present, the bidentate 1,2-dimethyl-3-hydroxy-4-pyridinone ligand (*L1*; also known as CP20, deferiprone or Ferriprox) is the only oral iron chelator drug approved (in 48 countries) for β -thalassaemic patients (Tam *et al.*, 2003). However, *L1* undergoes extensive metabolism in the liver, and more than 85% of the administered drug is recovered in the urine as the inactive 3-O-glucuronide. Hence, information on the structure of the ligand (*L*), as well as of the FeL_3 chelate, is important for the design of new bidentate Fe^{III} -sequestering agents with better pharmacokinetic profiles. The single-crystal X-ray structures of $\text{Fe}(\text{L}1)_3$ (Charalambous *et al.*, 1988; Clarke *et al.*, 1992) and $M(\text{L}1)_3$ ($M = \text{Al}$ and Ga ; Nelson *et al.*, 1988) have been reported previously. We report here the structure of the title compound, (I), an iron(III) complex of a related ligand, 2-*N*-methylaminocarbonyl-3-hydroxy-1,6-dimethyl-1,4-dihydro-4-pyridinone (*L2*).




Figure 1

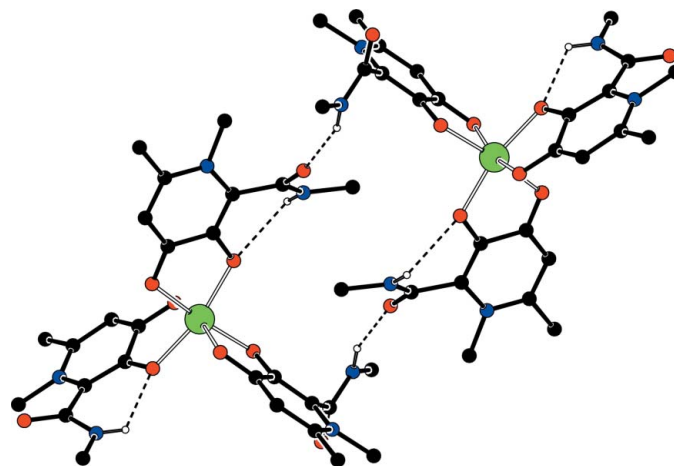
View of (I), showing 30% probability displacement ellipsoids (arbitrary spheres for the H atoms involved in hydrogen bonds; other H atoms have been omitted). Dashed lines indicate the hydrogen bonds.

with a distorted octahedral configuration consisting of six donor O atoms from three bidentate ligands. There is a difference in the Fe—O bond lengths (Table 1), with three (Fe—O2,O5,O8) being significantly shorter than the other three (Fe—O1,O3,O7). In addition, the short and long bond distances (Table 1) for the chelating C—O groups indicate that some ketonic character has been retained in the complex.

The amide groups of all three ligands are rotated out of the planes of the respective pyridinone rings to which they are bonded, giving dihedral angles of -102.5 (3), -135.3 (3) and 146.6 (3) $^\circ$ for C2—C3—C6—O3, C11—C12—C15—O6 and C20—C21—C24—O9, respectively. The largest out-of-plane rotation for the amide group containing N2 facilitates the formation of an intermolecular N—H...O hydrogen bond linking molecules into centrosymmetric dimers (Fig. 2), creating $R_2^2(24)$ rings (Bernstein *et al.*, 1995), while the NH groups of the other two amide groups are involved in intramolecular N—H...O hydrogen bonds, one of which is also involved in the formation of an N—H...O hydrogen bond to one dimethylformamide solvent molecule (see Table 2 for hydrogen-bond geometries). There are also numerous weak C—H...O interactions present in the crystal structure of (I), with H...O distances ranging from 2.17 to 2.59 Å, but these are not discussed in detail here.

Experimental

The ligand (2.15 g, 11.0 mmol) (Tam & Li, 2002) was dissolved in a $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ buffer solution (100 ml, pH 9.7), and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.988 g, 3.67 mmol) was added. The mixture was stirred at room temperature for a few days. The resulting red solid was collected by filtration, and was recrystallized from a mixture of CH_2Cl_2 and ethyl acetate. Suitable crystals of (I) for X-ray structure determination were obtained by recrystallization from wet DMF and diethyl ether.


Figure 2

View of an N—H...O hydrogen-bonded (dashed lines) centrosymmetric dimer of $\text{Fe}(\text{L}2)_3$ molecules in (I). Colour codes: green Fe, red O, blue N and black C. H atoms not involved in hydrogen bonding have been omitted.

Crystal data

$\text{Fe}(\text{C}_9\text{H}_{11}\text{N}_2\text{O}_3)_3 \cdot 2\text{C}_3\text{H}_7\text{NO}$
 $M_r = 787.64$
 Triclinic, $P\bar{1}$
 $a = 11.1137$ (2) Å
 $b = 13.0414$ (3) Å
 $c = 13.8382$ (3) Å
 $\alpha = 79.1515$ (10) $^\circ$
 $\beta = 68.8106$ (10) $^\circ$
 $\gamma = 79.7017$ (9) $^\circ$
 $V = 1823.18$ (7) Å 3

$Z = 2$
 $D_x = 1.435$ Mg m $^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 24188 reflections
 $\theta = 2.9$ – 27.5 $^\circ$
 $\mu = 0.48$ mm $^{-1}$
 $T = 150$ (1) K
 Block, red
 $0.10 \times 0.06 \times 0.04$ mm

Data collection

Bruker–Nonius KappaCCD diffractometer
 φ scans and ω scans with κ offsets
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)
 $T_{\min} = 0.910$, $T_{\max} = 0.982$
 24188 measured reflections

8323 independent reflections
 6063 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.062$
 $\theta_{\text{max}} = 27.5$ $^\circ$
 $h = -14 \rightarrow 14$
 $k = -16 \rightarrow 16$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.126$
 $S = 1.01$
 8323 reflections
 492 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 0.7105P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.55$ e Å $^{-3}$
 $\Delta\rho_{\text{min}} = -0.49$ e Å $^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0071 (13)

Table 1
 Selected bond lengths (Å).

Fe1—O2	1.9801 (15)	C1—O1	1.295 (3)
Fe1—O5	2.0071 (16)	C2—O2	1.321 (3)
Fe1—O8	2.0121 (16)	C10—O4	1.290 (3)
Fe1—O1	2.0342 (16)	C11—O5	1.316 (3)
Fe1—O7	2.0367 (16)	C19—O7	1.298 (3)
Fe1—O4	2.0483 (16)	C20—O8	1.315 (3)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2–H2A \cdots O6 ⁱ	0.88	1.96	2.797 (3)	158
N4–H4A \cdots O11	0.88	2.32	2.946 (3)	128
N4–H4A \cdots O5	0.88	2.41	2.860 (3)	112
N6–H6A \cdots O8	0.88	2.03	2.615 (3)	123

Symmetry code: (i) $-x, -y + 1, -z + 1$.

All H atoms were placed in calculated positions, with C–H distances ranging from 0.95 to 0.98 Å and N–H = 0.88 Å. They were included in the refinement in the riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ or $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{methyl carrier})$.

Data collection: *COLLECT* (Nonius, 2003); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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