Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Tris(1-cyclopropyl-6-methyl-2-(*N*-methylaminocarbonyl)-4-oxo-1,4-dihydropyridin-4-olato)iron(III) dimethylformamide sesquisolvate dihydrate

Tim F. Tam,[a]* Regis Leung-Toung,[a] Yingsheng Wang,[a] Michael Spino[a] and Alan J. Lough[b]*

[a]Medicinal Chemistry Department, ApoPharma Inc., 400 Ormont Drive, Weston, Ontario, Canada M9L 1N9, and [b]Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 3H6

Correspondence e-mail: ttam@apotex.ca, alough@chem.utoronto.ca

Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.005 Å
Some non-H atoms missing
R factor = 0.062
wR factor = 0.176
Data-to-parameter ratio = 19.0

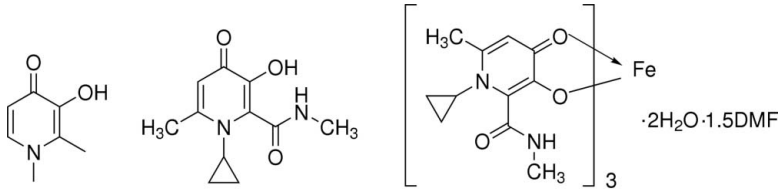
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 27 October 2005
Accepted 4 November 2005
Online 16 November 2005

In the crystal structure of the title compound, $[Fe(C_{11}H_{13}N_2O_3)_3]\cdot1.5C_3H_7NO\cdot2H_2O$, the Fe^{III} ion is six-coordinated in a distorted octahedral configuration consisting of six donor O atoms from three bidentate ligands. The Fe complex crystallizes with two molecules of water and one and a half molecules of dimethylformamide (DMF). The three aminocarboxy groups ($CONHCH_3$) are all rotated out of the planes of their respective pyridinone rings. Intermolecular O—H···O and N—H···O hydrogen bonds contribute to the stabilization of the crystal structure.

Comment

For background information and related references regarding the title compound, (I), see Tam *et al.* (2005). The single-crystal X-ray structures of several iron–pyridinone complexes have been reported (Charalambous *et al.*, 1988; Clarke *et al.*, 1992; Xiao *et al.*, 1992). We report here the structure of (I), an iron(III) complex of 1-cyclopropyl-3-hydroxy-6-methyl-2-*N*-methylaminocarbonyl-1,4-dihydropyridin-4-one (Apo6619).



(I)

The structure of (I) is shown in Fig. 1. The Fe^{III} ion is six-coordinate, with a distorted octahedral configuration consisting of six donor O atoms from three deprotonated Apo6619 ligands. The six Fe—O bond distances range from 1.972 (2) to 2.0637 (18) Å, while the short (keto C═O) and long (phenolic C—O) bond lengths of the chelating C—O groups indicate that some keto character has been retained in the complex (Table 1).

There are geometric differences among the three deprotonated Apo6619 ligands in Fe complex (I). The amide groups of all three ligands are rotated out of the planes of their respective pyridinone rings, giving dihedral angles of −120.9 (3), −131.4 (3) and 160.3 (3)° for N2—C16—C21—N5, N3—C27—C32—N6 and N1—C5—C10—N4, respectively. The C—C bond lengths linking the amide groups to the pyridinone rings and the amide carbonyl (C═O) bond lengths in the ligands of the Fe^{III} complex have clearly retained their C—C single-bond length and their C═O double-bond length characters (Table 1). Only one of the amide NH groups is

involved in an intramolecular N—H···O_p (p = phenolic) hydrogen bond, while the other two form intermolecular N—H···O_w (w = water) hydrogen bonds (Table 2). The amide groups do not appear to be involved in electron delocalization/resonance stabilization of the pyridinone rings of the title complex in the solid state.

Experimental

A solution of 6.0 *N* NaOH (3.34 ml, 20.0 mmol) was added to a suspension of Apo6619 (4.45 g, 20.0 mmol) (Tam *et al.*, 2003) in deionized water (30 ml) at room temperature. To the resulting clear orange–red solution was added dropwise a solution of $FeCl_3·6H_2O$ (1.77 g, 6.60 mmol) dissolved in deionized water (4 ml). The mixture was stirred at room temperature for 6 d. The resulting red solid was filtered, washed with deionized water and acetone, then air-dried. Suitable crystals for X-ray structure determination were obtained by recrystallization from wet dimethylformamide (5% H_2O) and toluene (1:4 ratio, *v*/*v*).

Crystal data

$[Fe(C_{11}H_{13}N_2O_3)_3]·1.5C_3H_7NO·2H_2O$
M_r = 865.23
Triclinic, $P\overline{1}$
a = 11.9319 (8) Å
b = 14.3968 (9) Å
c = 15.3024 (9) Å
α = 116.811 (3)°
β = 108.353 (3)°
γ = 95.164 (4)°
V = 2141.6 (2) Å^3
Z = 2
D_x = 1.342 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20782 reflections
θ = 2.6–26.6°
μ = 0.42 mm^{-1}
T = 150 (1) K
Plate, red
0.22 × 0.21 × 0.10 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.805, T_{max} = 0.949
20782 measured reflections
9756 independent reflections
6632 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 27.6°
$h = -15 \rightarrow 14$
$k = -18 \rightarrow 18$
$l = -16 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.176
S = 1.12
9756 reflections
514 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0906P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0061 (15)

Table 1
Selected geometric parameters (Å, °).

Fe1—O5	1.972 (2)	O4—C13	1.293 (3)
Fe1—O3	2.0184 (18)	O5—C23	1.323 (3)
Fe1—O4	2.019 (2)	O6—C24	1.295 (3)
Fe1—O6	2.0298 (19)	O7—C10	1.251 (3)
Fe1—O2	2.0331 (19)	O8—C21	1.244 (3)
Fe1—O1	2.0637 (18)	O9—C32	1.249 (4)
O1—C1	1.313 (3)	C5—C10	1.485 (4)
O2—C2	1.291 (3)	C16—C21	1.513 (4)
O3—C12	1.315 (3)	C27—C32	1.495 (4)
N2—C16—C21—N5	−120.9 (3)	N1—C5—C10—N4	160.3 (3)
N3—C27—C32—N6	−131.4 (3)		

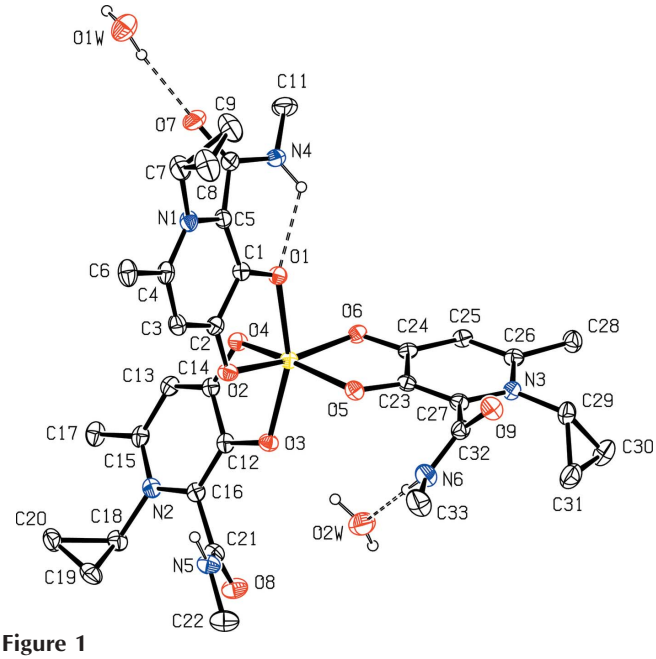


Figure 1
View of (I), showing 30% probability displacement ellipsoids (arbitrary spheres for the H atoms involved in hydrogen bonds; other H atoms have been omitted). Dashed lines indicate hydrogen bonds. The solvent dimethylformamide molecule is not shown.

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4A···O1	0.88	2.09	2.679 (3)	124
N5—H5A···O1W^{i}	0.88	2.15	2.912 (3)	144
N6—H6A···O2W	0.88	2.11	2.988 (4)	179
O1W—H1WA···O9^{ii}	0.84	2.03	2.857 (3)	168
O1W—H1WB···O7	0.84	2.06	2.890 (3)	170
O2W—H2WB···O3	0.84	2.11	2.936 (3)	170

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

All H atoms attached to carbon were placed in calculated positions, with C—H distances ranging from 0.95 to 1.00 Å and N—H = 0.88 Å. They were included in the refinement in a riding-motion approximation, with U_{iso}(H) = 1.2U_{eq} of the carrier atom, or 1.5U_{eq}(C) for methyl. The H atoms bonded to O atoms were placed in positions that gave theoretically ideal hydrogen bonds based on the most likely O···O contacts. They were then included in the refinement as riding atoms with O—H = 0.84 Å and U_{iso}(H) = 1.5U_{eq}O. During the refinement, areas of electron density were located in difference Fourier maps (close to inversion centers) that were assigned as additional DMF solvent molecules. The peak pattern of electron density suggested that the solvent molecule involved partial occupancy and was highly disordered; attempts to model the disorder were unsuccessful. In the final cycles of refinement, the contribution to electron density corresponding to the disordered DMF molecule was removed from the observed data using the SQUEEZE option in *PLATON* (Spek, 2003). The resulting data vastly improved the precision of the geometric parameters of the remaining structure. The contribution of an additional half-molecule of DMF has been included in the molecular formula. The carbonyl group of the DMF molecule, if present, would contribute to the hydrogen bonding, and would be available as a possible acceptor for H2WA. In the final difference map, the largest density peak is 1.30 Å from O1W.

Data collection: *COLLECT* (Nonius, 2003); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; 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*.

The authors acknowledge NSERC Canada and the University of Toronto for funding.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Charalambous, J., Dodd, A., McPartlin, M., Matondo, S. O. C., Pathirana, N. D. & Powell, H. R. (1988). *Polyhedron*, **7**, 2235–2237.
Clarke, E. T., Martell, A. E. & Reibenspies, J. (1992). *Inorg. Chim. Acta*, **196**, 177–183.
Nonius (2003). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (2001). *SHELXTL/PC*. Version 6.12 Windows NT Version. Bruker AXS Inc., Madison, USA.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Tam, T. F., Leung-Toung, R., Wang, Y., Spino, M., Williams, G. & Lough, A. J. (2005). *Acta Cryst.* E**61**, m2055–m2057.
Tam, T., Spino, M., Li, W., Wang, Y., Zhao, Y. & Shah, B. H. (2003). NZ Patent No. 529657.
Xiao, G., van der Helm, D., Hider, R. C. & Dobbin, P. S. (1992). *J. Chem. Soc. Dalton Trans.* pp. 3265–3271.