

(12,17-Diethoxycarbonyl-2,3,6,7,- 11,18-hexamethylcorrphycen- ato- $\kappa^4 N$)iodoiron(III) chloroform solvate

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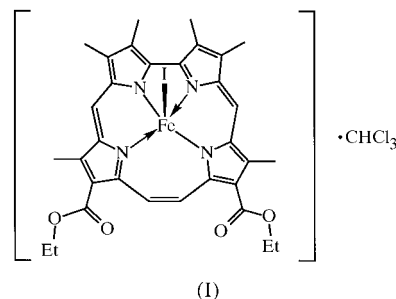
The title complex, (diethyl 3,4,8,15,19,20-hexamethyl-21,22,23,24-tetraazopentacyclo[16.2.1.1^{2,5}.1^{7,11}.1^{14,17}]tetracosal(20),2(22),3,5,7,9,11,13(24),14,16,18-undecaene-9,14-dicarboxylate- $\kappa^4 N$)iodoiron(III) chloroform solvate, $[\text{Fe}(\text{C}_{32}\text{H}_{32}\text{N}_4\text{O}_4)\text{I}]\cdot\text{CHCl}_3$, shows an almost planar arrangement of the corrphycene moiety with a slightly distorted trapezoidal pyramidal core; the Fe^{III} atom is 0.416 (1) Å from the plane of the C_{20}N_4 system. The $\text{Fe}-\text{N}$ distances are 2.049 (3), 2.044 (3), 2.079 (3) and 2.075 (3) Å. The solvated chloroform forms a $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond [$\text{C}\cdots\text{O}$ 3.107 (10) Å] to an adjacent carbonyl O atom. This is the first X-ray structure analysis of a corrphycenatoiron(III) derivative.

Comment

Corrphycene is one of the porphyrin family and it is transcribed as [18]porphyrin-(2.1.0.1). Although the structures of various metalcorrphycenes have been reported [Sessler *et al.*, 2000; there are two descriptions, including *ORTEP* drawings, of iron(III) corrphycene, but detailed structural data are not available], little is known about the structure of iron corrphycene. In this paper, we describe the first example of an X-ray crystallographic analysis of the iron(III) corrphycene complex, (I).

The molecular structure of (I) with the atom-numbering scheme is shown in Fig. 1. One of the ethoxycarbonyl groups is disordered. On the other hand, the other ethoxycarbonyl group adopts an ordered structure because it is involved in a $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond with an adjacent chloroform molecule [$\text{C}33\cdots\text{O}2$ 3.119 (11) Å]. The corrphycene ring exhibits an almost planar structure where the shifts of the peripheral 24 atoms from the least-squares plane of the C_{20}N_4 corrphycenate core are within 0.059 (4) Å. The central N_4 cavity shows trapezoidal geometry, with $\text{N}1\cdots\text{N}2$ 2.464 (4), $\text{N}2\cdots\text{N}3$

2.805 (5), $\text{N}3\cdots\text{N}4$ 3.308 (5) and $\text{N}4\cdots\text{N}1$ 2.811 (5) Å. Thus, the surface area within the N_4 coordinating core is 8.015 Å², which is smaller than the corresponding area of iron porphyrins, *cf.* 8.123 Å² in both $[\text{Fe}(\text{OEP})\text{Cl}]$ and $[\text{Fe}(\text{TPP})\text{I}]$ [OEP is the dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin



[Cambridge Structural Database (Version 5.20; Allen & Kennard, 1993) reference code TOYRUU (Senge, personal deposition)] and TPP is the dianion of *meso*-tetraphenylporphyrin (Hatano & Scheidt, 1979)}. The axial $\text{Fe}-\text{I}$ bond distance is 2.600 (1) Å, which is longer than that reported for $[\text{Fe}(\text{TPP})\text{I}]$ of 2.55 Å. The $\text{Fe}-\text{N}$ bond distances for direct-linked pyrroles, 2.044 (3) and 2.049 (3) Å, are slightly shorter than those for etheno-bridged pyrroles, 2.080 (3) and 2.075 (3) Å; the average $\text{Fe}-\text{N}$ bond distance is 2.07 Å in both $[\text{Fe}(\text{OEP})\text{Cl}]$ and $[\text{Fe}(\text{TPP})\text{I}]$. The deviation of the central Fe^{III} atom from the least-squares plane of the C_{20}N_4 core, 0.416 (1) Å, is significantly smaller than that of $[\text{Fe}(\text{TPP})\text{I}]$,

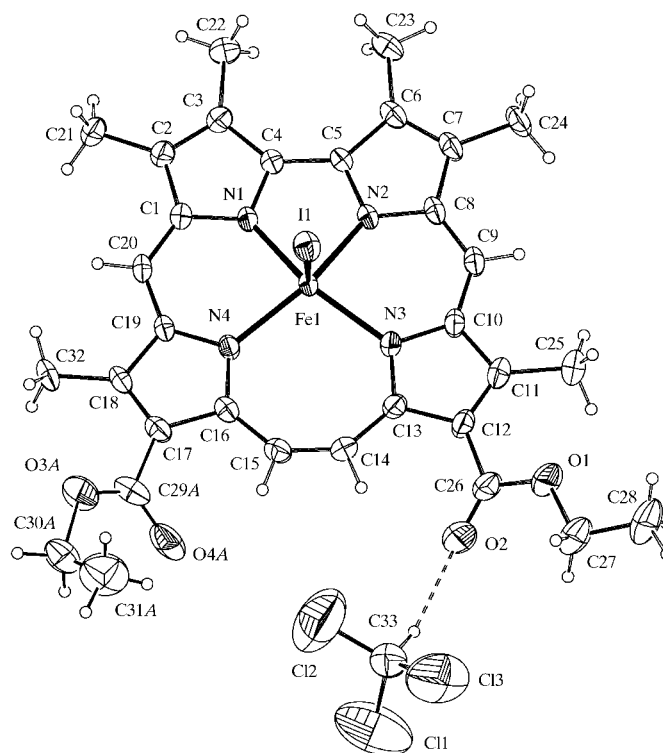


Figure 1

The molecular structure (*ORTEP*; Johnson, 1965) of the title compound with the atomic numbering. Displacement ellipsoids are shown at the 30% probability level and H atoms have been omitted for clarity.

0.526 Å. These results clearly demonstrate the difference in cavity geometry between the iron(III) corrphycene and the iron(III) porphyrin complexes.

Experimental

12,17-Bis(ethoxycarbonyl)-2,3,6,7,11,18-hexamethylcorrphycene was synthesized according to the method of Neya *et al.* (1998). Insertion of iron was carried out after Adler (Adler *et al.*, 1970). The chloro-iron(III) complex thus obtained was converted to the title complex by cleaving of the μ -oxo-bridged dimers (Maricondi *et al.*, 1969). The solid was recrystallized from chloroform solution.

Crystal data

[Fe(C ₃₂ H ₃₂ N ₄ O ₄)I]·CHCl ₃	Z = 2
$M_r = 838.73$	$D_x = 1.608 \text{ Mg m}^{-3}$
Triclinic, $P1$	Mo $K\alpha$ radiation
$a = 8.538 (2) \text{ \AA}$	Cell parameters from 25 reflections
$b = 14.114 (2) \text{ \AA}$	$\theta = 15.1\text{--}17.0^\circ$
$c = 15.648 (4) \text{ \AA}$	$\mu = 1.60 \text{ mm}^{-1}$
$\alpha = 106.040 (14)^\circ$	$T = 298 \text{ K}$
$\beta = 93.59 (2)^\circ$	Prismatic, purple
$\gamma = 104.964 (16)^\circ$	$0.5 \times 0.4 \times 0.1 \text{ mm}$
$V = 1732.5 (7) \text{ \AA}^3$	

Data collection

Rigaku AFC-7 diffractometer	$\theta_{\text{max}} = 27.5^\circ$
$\omega/2\theta$ scans	$h = 0 \rightarrow 11$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$k = -18 \rightarrow 17$
$T_{\text{min}} = 0.474$, $T_{\text{max}} = 0.852$	$l = -20 \rightarrow 20$
8460 measured reflections	3 standard reflections
7927 independent reflections	every 100 reflections
5539 reflections with $I > 2\sigma(I)$	frequency: 50 min
$R_{\text{int}} = 0.020$	intensity decay: 0.9%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0825P)^2 + 0.6822P]$
$R[F^2 > 2\sigma(F^2)] = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.150$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.88 \text{ e \AA}^{-3}$
7927 reflections	$\Delta\rho_{\text{min}} = -0.76 \text{ e \AA}^{-3}$
432 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

I1—Fe1	2.600 (1)	Fe1—N4	2.075 (3)
Fe1—N1	2.044 (3)	Fe1—N3	2.079 (3)
Fe1—N2	2.049 (3)		
N1—Fe1—N2	74.0 (1)	N1—Fe1—N3	152.1 (1)
N1—Fe1—N4	86.1 (1)	N2—Fe1—N3	85.6 (1)
N2—Fe1—N4	152.6 (1)	N4—Fe1—N3	105.6 (1)

There is a disorder in one of the two ethoxycarbonyl groups. The site-occupation factors for the disordered groups (*A* and *B*) are *A*:*B* = 0.50:0.50. H atoms were refined using a riding model. The positional parameters of the H atoms were constrained to have C—H distances

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
C33—H33 \cdots O2	0.98	2.20	3.107 (10)	154

of 0.96 Å for primary, 0.97 Å for secondary and 0.93 Å for aromatic H atoms. H-atom *U* values were constrained to 1.2 times U_{eq} of the atoms to which they are attached (1.5 for methyl groups).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992a); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software* and *TEXSAN* (Molecular Structure Corporation, 1992b); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SV* (Nemoto & Ohashi, 1993); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1624). Services for accessing these data are described at the back of the journal.

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