metal-organic compounds

Chloro(3,6,13,16-tetraethyl-2,7,12,-17-tetramethylporphycenato-$\kappa^4 N$)-iron(III) chloroform solvate

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The X-ray crystallographic analysis of the title complex, chloro[3,10,13,20-tetraethyl-4,9,14,19-tetramethylpentacyclo-[16.2.1.1^{2,5}.1^{8,11}.1^{12,15}]tetracosa-2,4,6,8(23),9,12,14,16,18(21),-19-decaene]iron(III) chloroform solvate, [Fe($C_{33}H_{37}N_4$)-Cl]·$CHCl_3$, reveals a twisted macrocyclic framework with a slightly distorted rectangular pyramidal core, where the deviation of the central Fe^{III} atom from the least-squares plane of the $C_{20}N_4$ core is 0.594 (1) Å. Some important bond distances are as follows: Fe—N 2.019 (3), 2.026 (3), 2.028 (3) and 2.034 (3) Å; Fe—Cl 2.232 (1) Å.

Comment

Porphycene, known as the first porphyrin isomer (Vogel *et al.*, 1987), has attracted much attention because of its possible use as a sensitizer for photodynamic therapy (PDT). Elucidation of the structural features of iron porphycene complexes is quite important, not only for reconsidering the role of the Fe atom in natural porphyrins from a distinctly structural viewpoint, but for explaining their novel physicochemical properties. Among the complexes containing the porphycenatoiron
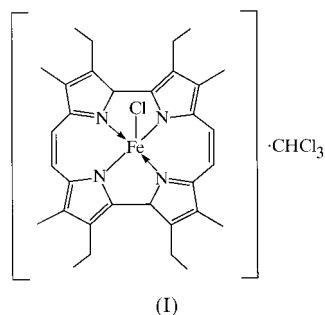
unit, only a few examples, such as σ-bonded aryliron porphycenes and μ-oxo-iron porphycene dimers have been crystallographically analysed (Kadish *et al.*, 1998; Lausmann *et*

al., 1994). In this paper, we describe the first example of an X-ray crystallographic analysis of a chloroiron(III) porphycene complex, (I), which is necessary for structural comparison with widely used chloroiron(III) porphyrin complexes.

The porphycene ring (Fig. 1) exhibits a slightly twisted structure, where the shifts of the 24 peripheral atoms from the least-squares plane of the $C_{20}N_4$ porphycenate core range from 0.011 to 0.391 (4) Å. The deformation pattern looks like a hybrid of the ruffled and saddled structures frequently observed in porphyrin complexes (Ma *et al.*, 1998). The C atoms which show a large deviation from the $C_{20}N_4$ plane are C3, C9, C13, and C19, with deviations of 0.347 (4), −0.301 (4), 0.391 (4) and 0.234 (4) Å, respectively. The axial Fe—Cl bond distance is 2.232 (1) Å, which is not significantly different from that reported for the similarly β-substituted porphyrin complex [Fe(OEP)Cl] of 2.23 Å [OEP is the dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin; Senge, M. O. (1997), data taken from the Cambridge Structural Database (Allen & Kennard, 1993)]. The peripheral ethyl groups take an $\alpha\beta\alpha\beta$ conformation to avoid steric repulsion at the directly linked pyrrole rings. While the average Fe—N bond distance in [Fe(OEP)Cl] is 2.07 Å, those of (I) are much shorter, with values of 2.019 (3), 2.026 (3), 2.028 (3) and 2.034 (3) Å. The central N_4 cavity has a rectangular geometry, with a long side of 2.944 (4) Å and a short side of 2.579 (4) Å. Thus, the surface
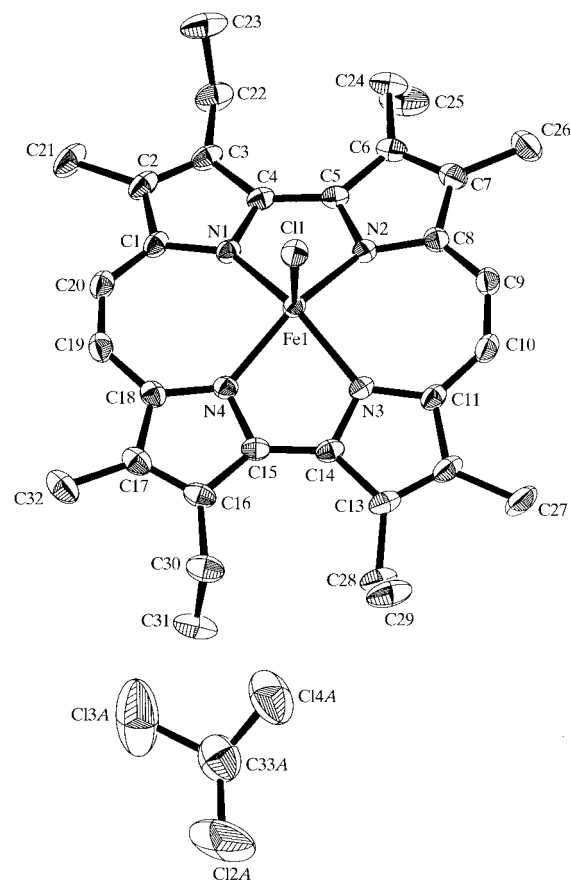

(I)

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.

area within the N_4-coordination core, 7.593 Å^2, is much smaller than the corresponding area of [Fe(OEP)Cl], 8.123 Å^2. Because of the smaller surface area in (I), the deviation of the central Fe^{III} atom from the $C_{20}N_4$ plane of 0.594 (1) Å is significantly larger than in [Fe(OEP)Cl] (0.495 Å). The larger deviation should affect the electronic state of the Fe atom. In fact, complex (I) is determined to be the spin-admixed $S = \frac{5}{2}, \frac{3}{2}$ complex on the basis of the *SQUID* measurement in our preliminary work; $\mu_{eff} = 5.23\ \mu_B$ at 300 K (Ohgo *et al.*, 2001). This result is in sharp contrast to the case in [Fe(OEP)Cl], which displays a quite pure high-spin $S = \frac{5}{2}$ state. In conclusion, the present study has revealed that the unique cavity geometry of porphycene stabilizes the admixed intermediate spin state even in a chloroiron(III) complex.

Experimental

3,6,13,16-Tetraethyl-2,7,12,17-tetramethylporphycene was synthesized according to the literature method of Vogel *et al.* (1993) from ethyl 4-ethyl-3,5-dimethylpyrrole-2-carboxylate as starting material. This porphycene is a positional isomer of etioporphycene, reported by Vogel *et al.* (1993). Insertion of iron was carried out according to Adler *et al.* (1970) to afford the title chloroiron(III) complex.

Crystal data

$[Fe(C_{33}H_{37}N_4)Cl]\cdot CHCl_3$	$D_x = 1.381$ Mg m^{-3}
$M_r = 687.32$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 20 513
$a = 14.722\ (1)$ Å	reflections
$b = 10.225\ (1)$ Å	$\theta = 0.9–27.5°$
$c = 22.319\ (2)$ Å	$\mu = 0.81$ mm^{-1}
$\beta = 100.35\ (1)°$	$T = 298$ K
$V = 3305.1\ (6)$ Å^3	Prismatic, purple
$Z = 4$	$0.2 \times 0.2 \times 0.2$ mm

Data collection

Rigaku R-AXIS RAPID Imaging Plate diffractometer	5436 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.049$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$\theta_{max} = 27.5°$
	$h = -19 \rightarrow 17$
$T_{min} = 0.849$, $T_{max} = 0.851$	$k = -13 \rightarrow 10$
19 098 measured reflections	$l = -27 \rightarrow 28$
7514 independent reflections	Intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1119P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.070$	$\quad + 1.7054P]$
$wR(F^2) = 0.205$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} < 0.001$
7514 reflections	$\Delta\rho_{max} = 0.77$ e Å^{-3}
415 parameters	$\Delta\rho_{min} = -0.47$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.025 (2)

Table 1
Selected geometric parameters (Å, °).

Fe1—N4	2.019 (3)	Fe1—N1	2.034 (3)
Fe1—N3	2.026 (3)	Fe1—Cl1	2.2316 (10)
Fe1—N2	2.028 (3)		
N4—Fe1—N3	79.10 (12)	N4—Fe1—N1	93.15 (12)
N4—Fe1—N2	150.13 (11)	N3—Fe1—N1	149.33 (12)
N3—Fe1—N2	93.16 (12)	N2—Fe1—N1	78.83 (12)

There is disorder in the solvent $CHCl_3$ molecule. The site-occupation factors for the disordered groups (*A* and *B*) are 0.50 each. H atoms were refined using a riding model. The positional parameters of the H atoms were constrained to have C—H distances of 0.96 Å for primary, 0.97 Å for secondary, and 0.93 Å for aromatic H atoms. H-atom U_{eq} values were constrained to 1.2 times the U_{iso} of the atoms to which they were attached (1.5 for methyl groups).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992*a*); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992*b*); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SV* (Nemoto & Ohashi, 1993); software used to prepare material for publication: *SHELXL*97.

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