

## Chloro(2,3,7,8,12,13,17,18-octaethylporphyrinato)iron(III)

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The molecular structure of the title compound,  $[\text{Fe}(\text{C}_{36}\text{H}_{44}\text{N}_4)\text{Cl}]$ , was determined by single-crystal X-ray diffraction at 130 K. The compound is characterized by an average Fe—N bond length of 2.071 (2) Å and an Fe—Cl bond length of 2.231 (1) Å.

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## Key indicators

Single-crystal X-ray study

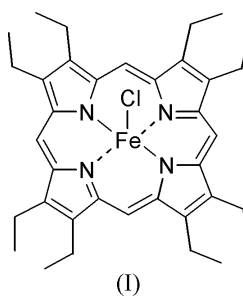
 $T = 126$  KMean  $\sigma(\text{C}-\text{C}) = 0.004$  Å $R$  factor = 0.048 $wR$  factor = 0.137

Data-to-parameter ratio = 18.9

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

## Comment

Pentacoordinated iron(III) porphyrins derived from the 2,3,7,8,12,13,17,18-octaethylporphyrin macrocycle (OEP) are widely used as biomimetic models for heme function (Wyllie & Scheidt, 2002). Many of these compounds are derived from or related to the title compound, (I) (Senge, 1996, 2000*a*). Compound (I) is an archetypal high-spin iron–porphyrin and has served as a reference compound in several recent studies (*e.g.* Kalish *et al.*, 2002; Senge, 2000*b*). Although briefly mentioned in reviews (Scheidt, 2000; Senge, 2000*a*), a crystal structure had not been published previously. Compound (I) has been shown to cocrystallize with  $\text{C}_{60}$  to form  $\text{C}_{60}\cdot\text{ClFe}^{\text{III}}(\text{OEP})\cdot\text{CHCl}_3$  crystals (Olmstead *et al.*, 1999). Despite a close contact (2.75 Å) between the porphyrin and the fullerene, the core structural parameters are very similar to those in the present structure. However, differences are found in the orientation of the ethyl side chains. In the present structure (Fig. 1), five neighboring ethyl groups point towards one side and three to the other side of the porphyrin ring plane.



The structure of the isolated porphyrin is characterized by a pentacoordinated iron center, with an average Fe—N bond length of 2.071 (2) Å and an Fe—Cl bond length of 2.231 (1) Å (Table 1). The Fe atom is displaced by 0.494 (1) Å from the mean plane of the 24 core atoms. These values differ only marginally from data given in the review by Scheidt (2000) (2.063 and 2.065 Å for the Fe—N bonds and 0.46 and 0.52 Å for the iron displacement). These are typical for a high-spin iron(III) complex. The macrocycle shows only minor deviations from planarity. The overall degree of distortion ( $\Delta$  = average deviation of the 24 macrocycle atoms from their

least-squares plane) is 0.045 (1) Å. The largest displacements from this plane are observed for atoms C3 and C13 [0.100 (1) and 0.137 (1) Å, respectively]. The compound forms very weak  $\pi$ - $\pi$  aggregates of the aromatic systems. With a mean plane separation of 4.02 (1) Å and a lateral shift of the metal centers of 6.87 (2) Å, this compound falls into Group W (Scheidt, 2000).

### Experimental

Compound (I) was prepared from the free base 2,3,7,8,12,13,17,18-octaethylporphyrin following standard procedures (Buchler, 1975) and was crystallized from CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH.

#### Crystal data

[Fe(C<sub>36</sub>H<sub>44</sub>N<sub>4</sub>)Cl]  
*M<sub>r</sub>* = 624.05  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>/*c*  
*a* = 15.045 (9) Å  
*b* = 22.154 (12) Å  
*c* = 9.972 (5) Å  
 $\beta$  = 106.05 (4)°  
*V* = 3194 (3) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.298 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 42 reflections  
 $\theta$  = 18–22°  
 $\mu$  = 0.59 mm<sup>-1</sup>  
*T* = 126 (2) K  
 Parallelepiped, blue  
 0.53 × 0.30 × 0.25 mm

#### Data collection

Siemens R3m/V diffractometer  
 $\omega$  scans  
 Absorption correction: refined from  $\Delta F$  (*XABS2*; Parkin *et al.*, 1995)  
*T<sub>min</sub>* = 0.787, *T<sub>max</sub>* = 0.867  
 7953 measured reflections  
 7331 independent reflections  
 5419 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.032  
 $\theta_{\max}$  = 27.5°  
*h* = -19 → 18  
*k* = 0 → 28  
*l* = 0 → 12  
 2 standard reflections every 198 reflections  
 intensity decay: none

#### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.048  
*wR* (*F*<sup>2</sup>) = 0.137  
*S* = 1.06  
 7331 reflections  
 387 parameters  
 H-atom parameters constrained

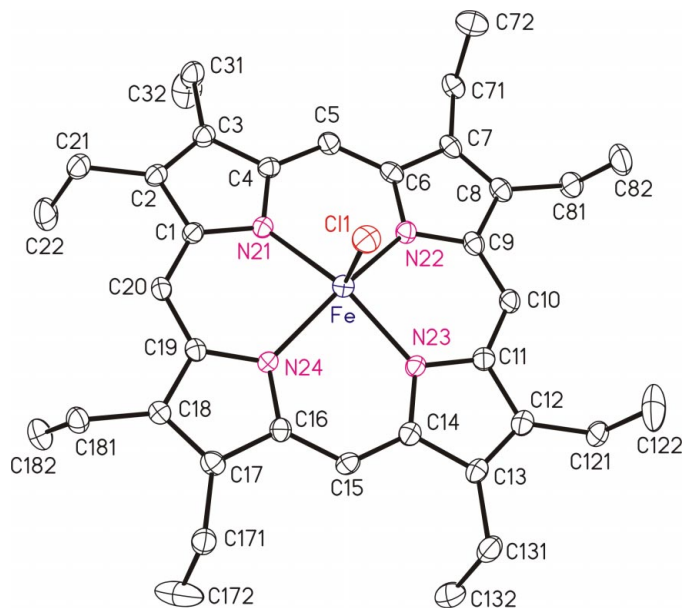
$w = 1/[\sigma^2(F_o^2) + (0.0678P)^2 + 1.2711P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.41 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.77 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Fe–N23	2.066 (2)	Fe–N22	2.078 (2)
Fe–N24	2.067 (2)	Fe–Cl1	2.2312 (12)
Fe–N21	2.074 (2)		
N23–Fe–N24	87.57 (9)	N21–Fe–N22	86.86 (9)
N23–Fe–N21	153.41 (8)	N23–Fe–Cl1	101.94 (8)
N24–Fe–N21	86.95 (8)	N24–Fe–Cl1	100.34 (7)
N23–Fe–N22	87.06 (9)	N21–Fe–Cl1	104.64 (7)
N24–Fe–N22	154.68 (9)	N22–Fe–Cl1	104.98 (7)

H atoms were positioned geometrically and constrained to ride on their parent atoms, with C–H distances in the range 0.95–0.99 Å, and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C) for methylene groups or *meso* H atoms and *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(C) for methyl groups.



**Figure 1**

A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

Data collection: *P3* (Siemens, 1995); cell refinement: *P3*; data reduction: *XDISK* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1995); software used to prepare material for publication: *SHELXL97*.

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