Chloro(2,3,7,8,12,13,17,18-octaethyl-porphyrinato)iron(III)

The molecular structure of the title compound, [Fe(C_{36}H_{44}N_{4})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.

Comment

Pentacoordinated iron(III) porphyrins derived from the 2,3,7,8,12,13,17,18-octaaethylporphyrin 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, 2000a). 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, 2000b). Although briefly mentioned in reviews (Scheidt, 2000; Senge, 2000a), a crystal structure had not been published previously. Compound (I) has been shown to cocrystallize with C_{60} to form C_{60}ClFe^{III}(OEP)·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 (Δ = 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 π–π 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 CH2Cl2/CH3OH.

#### Crystal data

[Fe(C36H44N4)Cl]  

\[ M_r = 624.05 \]

Monoclinic, \( P_2_1/c \)  

\[ a = 15.045 (9) \text{ Å} \]  

\[ b = 22.154 (12) \text{ Å} \]  

\[ c = 9.972 (5) \text{ Å} \]  

\[ \beta = 106.05 (4)^\circ \]  

\[ V = 3194 (3) \text{ Å}^3 \]  

\[ Z = 4 \]

#### Data collection

Siemens R3m/V diffractometer  

\( \omega \) scans  

Absorption correction: refined from \( F^2 \)  

\( \Delta F \) (XABS2; Parkin et al., 1995)  

7953 measured reflections  

7331 independent reflections  

5419 reflections with \( I > 2\sigma(I) \)

#### Refinement

Refinement on \( F^2 \)  

\[ R_{\text{int}} = 0.032 \]  

\( \theta_{\text{max}} = 27.5^\circ \]  

\( h = -19 \rightarrow 18 \]  

\( k = 0 \rightarrow 28 \]  

\( l = 0 \rightarrow 12 \]  

2 standard reflections  

every 198 reflections  

intensity decay: none

#### Table 1

Selected geometric parameters (Å, °).

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<th>Bond</th>
<th>Distance (Å)</th>
<th>Bond</th>
<th>Distance (Å)</th>
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<td>Fe–N22</td>
<td>2.078 (2)</td>
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<tr>
<td>Fe–N24</td>
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<td>Fe–Cl</td>
<td>2.2312 (12)</td>
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<td>2.074 (2)</td>
<td>N21–Fe–N24</td>
<td>87.57 (9)</td>
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<tr>
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<td>N22–Fe–Cl1</td>
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### References


Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*, University of Göttingen, Germany.
