

Bis(tetrahydrofuran- κ O)(*meso*-5,10,15,20-tetraisopropylporphyrinato- κ^4 N)iron(III) perchlorate

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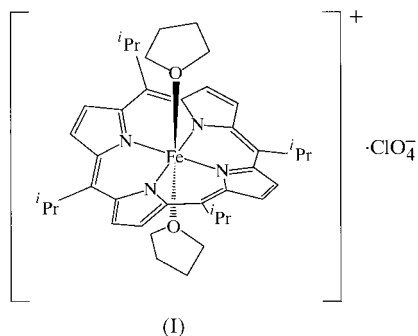
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The title complex, $[\text{Fe}(\text{C}_{32}\text{H}_{36}\text{N}_4)(\text{C}_4\text{H}_8\text{O})_2]\text{ClO}_4$, shows an S_4 -ruffled porphyrin ring, where the maximum deviation of the *meso*-carbon from the least-squares plane of the $[\text{Fe}(\text{C}_{20}\text{N}_4)]$ core is as high as 0.675 (9) Å. This is the highest class of deviation among S_4 -ruffled iron(III) porphyrin complexes. The average Fe– N_p bond distance is 1.967 (12) Å (N_p denotes an N atom of the equatorial ligand).

Comment

Metalloporphyrins with non-planar structures are essential in understanding the role and functions of haemoproteins with a deformed porphyrin ring (Finzel *et al.*, 1984; Hobbs & Shelton, 1995; Ikeue *et al.*, 2000). In this paper, we describe the molecular structure of the title complex, (I), which shows the presence of a highly deformed porphyrin ring.



The molecular structure of (I) with the atom-numbering scheme is shown in Fig. 1. The porphyrin ring exhibits an S_4 -ruffled structure, where the shifts of the *meso*-C atoms C5, C10, C15 and C20 from the least-squares plane of the $[\text{Fe}(\text{C}_{20}\text{N}_4)]$ porphyrinato core are -0.675 (9), 0.623 (8), -0.579 (8) and 0.640 (8) Å, respectively. The ruffling dihedral angles of the two pairs of diagonal pyrroles, 37.4 (7) and 38.3 (7)°, are much larger than those in $[\text{Fe}(\text{TETP})(\text{thf})_2]\text{ClO}_4$

[22.3 (1) and 21.2 (1)°; Ohgo *et al.*, 1999; TETP is the dianion of *meso*-tetraethylporphyrin and thf is tetrahydrofuran].

Both thf rings in (I) are parallel to the $C_{\text{meso}}-\text{Fe}-C_{\text{meso}}$ axis and are perpendicular to each other [$\text{C}5\cdots\text{Fe}1-\text{O}1-\text{C}33$ 1.4 (4), $\text{C}10\cdots\text{Fe}1-\text{O}2-\text{C}40$ 8.5 (4), $\text{C}40-\text{O}2-\text{O}1-\text{C}33$ 96.5 (7) and $\text{C}37-\text{O}2-\text{O}1-\text{C}36$ 79.5 (7)°]. One of the two coordinated thf molecules shows a bent form, which is well illustrated by the $\text{Fe}1-\text{O}2-\text{C}40-\text{C}39$ and $\text{Fe}1-\text{O}2-\text{C}37-\text{C}38$ torsion angles of 124.4 (6) and -124.1 (7)°, respectively. In contrast, the other thf molecule shows a planar form; the $\text{Fe}1-\text{O}1-\text{C}33-\text{C}34$ and $\text{Fe}1-\text{O}1-\text{C}36-\text{C}35A$ torsion angles are -173.6 (4) and -163.7 (15)°, respectively. This difference in the coordination structure of the thf molecules is ascribed to the crystal packing in the direction normal to the porphyrin ring.

The Fe– N_p bond distances of (I) [average 1.967 (12) Å] are significantly shorter than those of other bis(thf) complexes, such as $[\text{Fe}(\text{TETP})(\text{thf})_2]\text{ClO}_4$ [average 2.006 (3) Å], $[\text{Fe}(\text{TPP})(\text{thf})_2]\text{ClO}_4$ [average 2.016 (3) Å; Chen *et al.*, 1998; TPP is the dianion of *meso*-tetraphenylporphyrin] and $[\text{Fe}(\text{OEP})(\text{thf})_2]\text{ClO}_4$ [1.994 Å; Masuda *et al.*, 1982; OEP is the dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin]. The average deviation of the *meso*-C atoms from the least-squares plane of the porphyrin ring is well known as an index of the degree of deformation. In the case of (I), it is 0.68 Å, which is much larger than the corresponding values in $[\text{Fe}(\text{TPP})(\text{thf})_2]\text{ClO}_4$ (0.01 Å) and $[\text{Fe}(\text{OEP})(\text{thf})_2]\text{ClO}_4$ (0.03 Å). In addition, there

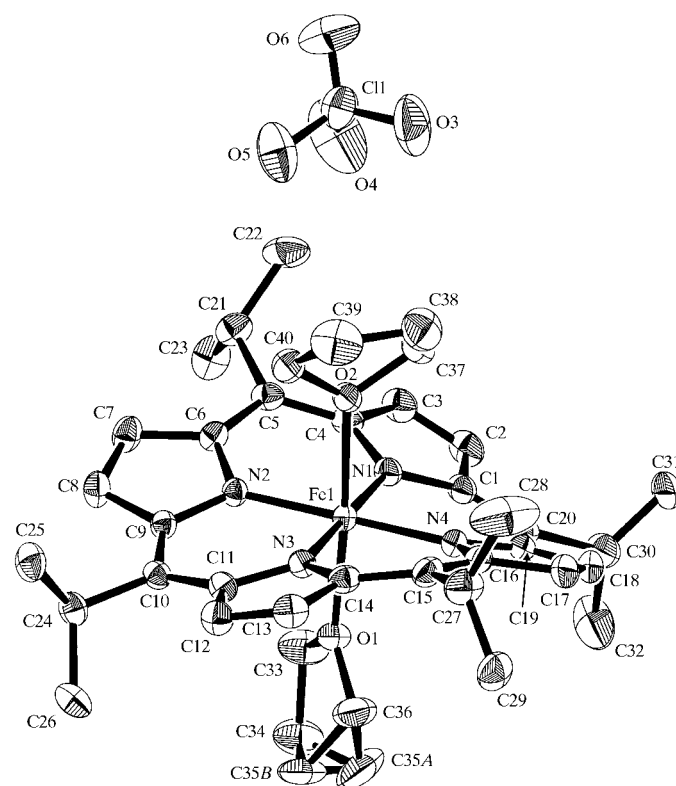


Figure 1
The molecular structure (ORTEP; Johnson, 1965) of (I) with the atomic numbering. Displacement ellipsoids are shown at the 30% probability level and H atoms have been omitted for clarity.

is a tendency for the more deformed complexes to have shorter Fe—N_p bonds, as in (I). These results suggest that (I) is one of the most highly deformed (porphyrinato)iron(III) complexes known to date.

Experimental

meso-Tetraisopropylporphyrin was prepared according to the procedure of Ema *et al.* (1994). Insertion of iron was carried out by refluxing *meso*-tetraisopropylporphyrin with FeCl₂·4H₂O in methanol–chloroform (1:3). The resulting chloroiron(III) complex was converted into the title complex, (I), by treatment with AgClO₄ in tetrahydrofuran solution. The solid thus obtained was recrystallized from tetrahydrofuran–heptane (3:1).

Crystal data

[Fe(C ₃₂ H ₃₆ N ₄)(C ₄ H ₈ O) ₂]ClO ₄	$D_x = 1.274 \text{ Mg m}^{-3}$
$M_r = 776.16$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 10.56 (10) \text{ \AA}$	$\theta = 14.36\text{--}15.56^\circ$
$b = 32.98 (15) \text{ \AA}$	$\mu = 0.488 \text{ mm}^{-1}$
$c = 11.64 (8) \text{ \AA}$	$T = 298 \text{ K}$
$\beta = 92.8 (7)^\circ$	Prismatic, brown
$V = 4048 (51) \text{ \AA}^3$	$0.5 \times 0.4 \times 0.2 \text{ mm}$
$Z = 4$	

Data collection

Rigaku AFC-5 diffractometer	$\theta_{\text{max}} = 27.53^\circ$
ω scans	$h = -13 \rightarrow 13$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$k = 0 \rightarrow 42$
$T_{\text{min}} = 0.819$, $T_{\text{max}} = 0.907$	$l = 0 \rightarrow 15$
9566 measured reflections	3 standard reflections every 100 reflections
9128 independent reflections	frequency: 50 min
4237 reflections with $I > 2\sigma(I)$	intensity decay: -0.72%
$R_{\text{int}} = 0.037$	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.063$	$w = 1/[\sigma^2(F_o^2) + (0.1329P)^2]$
$wR(F^2) = 0.215$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.911$	$(\Delta/\sigma)_{\text{max}} < 0.001$
9128 reflections	$\Delta\rho_{\text{max}} = 0.68 \text{ e \AA}^{-3}$
495 parameters	$\Delta\rho_{\text{min}} = -0.41 \text{ e \AA}^{-3}$

There is disorder in one of the two coordinated thf molecules, with site-occupancy factors for the disordered atoms, C35A and C35B, of 0.43 and 0.57, respectively. H atoms were refined using a riding model, with C—H distances of 0.96 Å for primary H, 0.97 Å for secondary and 0.93 Å for aromatic H atoms. H-atom U values were constrained to 1.2 times the equivalent isotropic U of the atoms to which they were 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: *TEXSAN*

Table 1

Selected geometric parameters (Å, °).

Fe1—N1	1.946 (14)	Fe1—N2	1.988 (9)
Fe1—N3	1.950 (14)	Fe1—O2	2.183 (19)
Fe1—N4	1.982 (9)	Fe1—O1	2.221 (19)
N1—Fe1—N3	179.45 (14)	N4—Fe1—N2	179.75 (14)
Fe1—O1—C36—C35A	−163.7 (15)	C11—C10—C24—H24	−171
Fe1—O1—C36—C35B	152.7 (8)	C16—C15—C27—H27	176
Fe1—O2—C37—C38	−124.1 (7)	C1—C20—C30—H30	−177
C4—C5—C21—H21	−165		

(Molecular Structure Corporation, 1992b); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); 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: OA1111). Services for accessing these data are described at the back of the journal.

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