ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.690$, $T_{max} = 0.825$
23 653 measured reflections
3521 independent reflections (plus 3071 Friedel-related reflections)

$R_{int} = 0.025$
$\theta_{max} = 27.55°$
$h = -26 \rightarrow 32$
$k = -64 \rightarrow 63$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.047$
$S = 0.959$
6592 reflections
343 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.344$ e Å^{-3}
$\Delta\rho_{min} = -0.361$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.005 (9)

Table 1. *Selected geometric parameters (Å, °)*

Pd1—C3	2.120 (2)	N1—C4	1.288 (3)
Pd1—Cl3	2.3073 (6)	N1—C6	1.465 (3)
Pd1—Cl1	2.3369 (5)	C1—C2	1.508 (3)
Pd1—Cl2	2.3525 (5)	C2—C3	1.458 (3)
Ni1—N1	2.0005 (17)	C3—C4	1.466 (3)
Ni1—O1	2.0277 (15)	C4—C5	1.506 (3)
Ni1—Cl1	2.4919 (5)	C6—C6^{i}	1.510 (5)
O1—C2	1.250 (3)		
C3—Pd1—Cl3	87.49 (6)	O1—Ni1—Cl1^{i}	95.53 (4)
C3—Pd1—Cl1	91.24 (6)	N1—Ni1—Cl1	86.13 (5)
Cl3—Pd1—Cl1	178.38 (2)	O1—Ni1—Cl1	83.50 (4)
C3—Pd1—Cl2	173.95 (7)	Cl1^{i}—Ni1—Cl1	178.63 (3)
Cl3—Pd1—Cl2	92.05 (2)	Pd1—Cl1—Ni1	108.986 (19)
Cl1—Pd1—Cl2	89.317 (19)	C4—N1—Ni1	125.21 (15)
N1—Ni1—N1^{i}	84.56 (11)	C6—N1—Ni1	109.61 (14)
N1—Ni1—O1	92.04 (7)	C2—C3—C4	124.62 (19)
N1—Ni1—O1^{i}	176.33 (7)	C2—C3—Pd1	103.88 (14)
O1—Ni1—O1^{i}	91.40 (9)	C4—C3—Pd1	98.99 (14)
N1—Ni1—Cl1^{i}	94.89 (5)	N1—C4—C3	121.1 (2)

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, z$.

The H3 atom was refined isotropically, whereas other H atoms were placed in calculated positions and refined as riding atoms.

Data collection: *SMART* (Bruker, 1998). Cell refinement: *SMART* and *SAINT* (Bruker, 1998). Data reduction: *SAINT*. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *TEXSAN* (Molecular Structure Corporation/Rigaku Corporation, 1998). Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1087). Services for accessing these data are described at the back of the journal.

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(*meso*-Tetraethylporphyrinato)bis(tetrahydrofuran)iron(III) perchlorate

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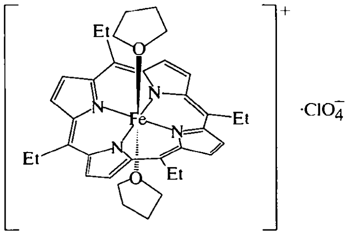
Abstract

In the title compound, (5,10,15,20-tetraethylporphyrinato-κ^4N)bis(tetrahydrofuran-O)iron(III) perchlorate, $[Fe(C_{28}H_{28}N_4)(C_4H_8O)_2]ClO_4$, the Fe^{III} atom has a slightly distorted octahedral coordination. The porphyrin ring of the complex cation, which has twofold symmetry, has an S_4-ruffled structure and the maximum deviation of the *meso*-carbon from the least-squares plane of the $FeC_{20}N_4$ core is 0.274 (3) Å. The average Fe—N bond distance is 2.006 (3) Å.

Comment

meso-Tetraalkylporphyrin–iron(III) complexes have attracted much attention because of the difference in their physicochemical properties compared with those of tetraarylporphyrin complexes (Veyrat *et al.*, 1995; Nakamura *et al.*, 1996, 1998; Saitoh *et al.* 1997; Wolowiec *et al.*, 1998; Ikeue *et al.*, 1999); one of the reasons for the difference is the deformed porphyrin core in the former complexes. We reported that the ground-state electron configuration of low-spin ferric porphyrin complexes changes from the common $(d_{xy})^2(d_{xz},d_{yz})^3$ to the rare $(d_{xz},d_{yz})^4(d_{xy})^1$ as the S_4-ruffling of the porphyrin ring increases (Nakamura *et al.*, 1997). It is not clear, however, how the spin state of ferric ions is affected by the nonplanarity of the porphyrin ring. Thus, a series of (*meso*-tetraalkylporphyrinato)iron(III) complexes, [Fe(TRP)]*X* (*R* = H, Me, Et or ^{i}Pr; *X* = Cl^- or ClO_4^-), have been prepared and their spin states examined. In the course of this study, we succeeded in obtaining crystals of good enough quality for single-crystal X-ray analysis. To the best of our knowledge, this is the first X-ray structure determination of (*meso*-tetraalkylporphyrinato)bis(tetrahydrofuran-*O*)iron(III) perchlorate, (I).



(I)

The molecular structure of (I) is shown in Fig. 1. The N2—Fe1—N3 bond axes lie on a twofold axis. The porphyrin ring shows an S_4-ruffled structure where the shifts of the *meso*-C atoms C5 and C10 from the least-squares plane of the $FeC_{20}N_4$ porphyrinato core are 0.274 (3) and −0.214 (3) Å, respectively. The tetrahydrofuran (thf) ring lies along the diagonal $C_{meso}\cdots Fe\cdots C_{meso}$ axis. Although the Fe—N bond distances [average 2.006 (3) Å] are significantly shorter than those of high-spin complexes such as [Fe(TPP)]Cl (average 2.070 Å; Scheidt & Lee, 1987; Scheidt & Finnegan, 1989), they are comparable to the corresponding bond lengths of [Fe(OEP)(thf)$_2$]ClO$_4$ (1.999 Å); the latter complex is known as an intermediate spin state (Masuda *et al.*, 1982; Cheng *et al.*, 1994; TPP is *meso*-tetraphenylporphyrin and OEP is octaethylporphyrin). A recent report on the structure of the analogous [Fe(TPP)(thf)$_2$]ClO$_4$ complex (Chen *et al.*, 1998) revealed Fe—N distances (average 2.016 Å) longer than those of (I). Correspondingly, the magnetic moment of [Fe(TPP)(thf)$_2$]ClO$_4$ determined by the Evans method is 5.4 BM (or μ_B) at 298 K *versus* 4.5 BM for (I) at the same temperature. Taken together, (I) is best presented as the spin admixed *S* = 5/2, 3/2 complex, with a major contribution of the *S* = 3/2 state.

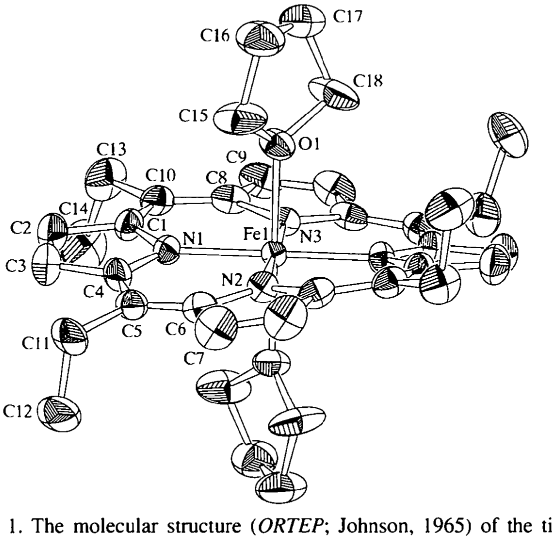


Fig. 1. The molecular structure (*ORTEP*; Johnson, 1965) of the title compound with the atomic numbering. Displacement ellipsoids are shown at the 50% probability level and H atoms have been omitted for clarity.

Experimental

meso-Tetraethylporphyrin was prepared according to the literature method of Neya & Funasaki (1997). Insertion of iron was carried out in refluxing methanol–chloroform (1:3) with FeCl$_2$·4H$_2$O, and the chloroiron(III) complex was converted into the iron(III) perchlorate complex by treatment with silver perchlorate in tetrahydrofuran solution. The solid thus obtained was recrystallized from tetrahydrofuran–heptane (3:1).

Crystal data

[Fe(C$_{28}$H$_{28}$N$_4$)(C$_4$H$_8$O)$_2$]-ClO$_4$
M_r = 720.05
Monoclinic
*C*2/*c*
a = 13.939 (5) Å
b = 16.806 (5) Å
c = 15.596 (4) Å
β = 107.11 (2)°
V = 3492.0 (19) Å^3
Z = 4
D_x = 1.370 Mg m^{-3}
D_m not measured

Mo *K*α radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 14.90–14.96°
μ = 0.559 mm^{-1}
T = 298 K
Prismatic
0.5 × 0.5 × 0.4 mm
Brown

Data collection

Rigaku AFC-5 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.736, T_{max} = 0.800
4171 measured reflections
4011 independent reflections

2440 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 27.50°
$h = 0 \rightarrow 18$
$k = -21 \rightarrow 0$
$l = -20 \rightarrow 19$
3 standard reflections every 100 reflections intensity decay: 22.58%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.157$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.689 e Å^{-3}
$\Delta\rho_{min}$ = −0.401 e Å^{-3}

$S = 1.050$
4011 reflections
245 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0799P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: *SHELXL*97
Extinction coefficient: 0.0033 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Fe1	1	0.18788 (3)	1/4	0.0308 (2)
Cl1	1	0.32889 (10)	3/4	0.0943 (7)
O1	0.84485 (15)	0.18926 (13)	0.16903 (15)	0.0465 (6)
O2†	0.9406 (18)	0.3715 (10)	0.7945 (12)	0.157 (9)
O3†	1.0973 (14)	0.3250 (15)	0.8106 (11)	0.281 (12)
O4†	0.9975 (17)	0.3675 (11)	0.6743 (8)	0.141 (10)
O5†	0.9591 (15)	0.2552 (4)	0.7274 (10)	0.167 (10)
N1	1.04664 (18)	0.18755 (15)	0.13964 (15)	0.0356 (6)
N2	1	0.0685 (2)	1/4	0.0351 (8)
N3	1	0.3067 (2)	1/4	0.0354 (8)
C1	1.0583 (2)	0.2537 (2)	0.0899 (2)	0.0409 (8)
C2	1.0948 (3)	0.2274 (3)	0.0176 (2)	0.0580 (10)
C3	1.1078 (3)	0.1485 (3)	0.0254 (2)	0.0586 (10)
C4	1.0780 (2)	0.1225 (2)	0.1013 (2)	0.0409 (8)
C5	1.0784 (2)	0.0434 (2)	0.1290 (2)	0.0426 (8)
C6	0.9619 (3)	0.01898 (18)	0.3035 (2)	0.0422 (8)
C7	0.9763 (3)	−0.0618 (2)	0.2812 (3)	0.0613 (11)
C8	1.0178 (2)	0.35624 (18)	0.1848 (2)	0.0411 (8)
C9	1.0107 (3)	0.43728 (19)	0.2113 (3)	0.0542 (10)
C10	1.0439 (2)	0.33208 (19)	0.1095 (2)	0.0430 (8)
C11	1.1283 (3)	−0.0183 (2)	0.0855 (3)	0.0593 (10)
C12	1.2383 (3)	−0.0251 (3)	0.1323 (3)	0.0843 (15)
C13	1.0672 (3)	0.3962 (2)	0.0492 (3)	0.0643 (11)
C14	1.1779 (4)	0.4198 (3)	0.0790 (3)	0.0901 (16)
C15	0.7988 (3)	0.1301 (3)	0.1058 (3)	0.0769 (14)
C16	0.6904 (3)	0.1532 (3)	0.0681 (3)	0.0819 (14)
C17	0.6817 (3)	0.2342 (3)	0.1053 (3)	0.0709 (12)
C18	0.7674 (3)	0.2365 (3)	0.1885 (3)	0.0734 (13)

† Site occupancy = 0.50.

Table 2. *Selected geometric parameters* (Å, °)

Fe1—N3	1.997 (4)	Fe1—N1	2.011 (2)
Fe1—N2	2.006 (3)	Fe1—O1	2.160 (2)
N3—Fe1—N2	180.0	N1—Fe1—O1	91.1 (1)
N3—Fe1—N1	90.16 (7)	C4—N1—Fe1	126.7 (2)
N2—Fe1—N1	89.84 (7)	C1—N1—Fe1	126.5 (2)
N3—Fe1—O1	89.38 (6)	C6—N2—Fe1	126.8 (2)
N2—Fe1—O1	90.62 (6)	C8—N3—Fe1	126.8 (2)

There is an orientational disorder of the perchlorate anion. The Cl1 atom lies on a twofold axis and the O2–O5 atoms were introduced with a site-occupation factor of 0.5. 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 values were constrained to 1.2 times the equivalent isotropic U value of their attached atoms (1.5 for methyl groups). A correction was applied for the deterioration of crystallinity.

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*92 (Altomare *et al.*, 1994). 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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1008). Services for accessing these data are described at the back of the journal.

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