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[5,10,15,20-Tetrakis(pentafluorophenyl)porphyrinato]iron(II) benzene disolvate

Yunghee Oh,[a] Byoung-Chul Shin,[b] Dale Swenson,[c] Harold M. Goff[c] and Sung Kwon Kang[d]*

[a]Department of Chemistry, Dong-eui University, Busan 614-714, South Korea, [b]Department of Advanced Materials Engineering, Dong-eui University, Busan 614-714, South Korea, [c]Department of Chemistry, University of Iowa, Iowa City, IA 52242, USA, and [d]Department of Chemistry, Chungnam National University, Daejeon 305-764, South Korea
Correspondence e-mail: skkang@cnu.ac.kr

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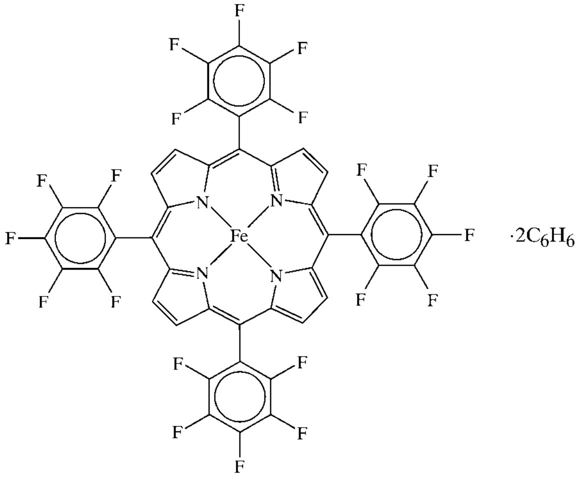
The title compound, $[Fe(C_{44}H_8F_{20}N_4)]\cdot 2C_6H_6$, contains a four-coordinated Fe^{II} atom, which lies on a center of symmetry. The porphyrin macrocycle is planar, and the Fe—N bond distances are in the range 1.9891 (13)–1.9982 (13) Å. The spin state of the Fe^{II} atom is intermediate ($S = 1$), as confirmed by NMR spectroscopy. The asymmetric unit contains two half benzene molecules, each lying about an independent inversion centre; one of the benzene rings is located just below (and by inversion symmetry, another is just above) the Fe atom, where it interacts weakly with the porphyrin ring.

Comment

As iron(II) porphyrin is an active site in heme proteins in biological systems, its structural features attract chemists and biologists. However, structural research on Fe^{II} porphyrins has progressed slowly because of their instability under aerobic conditions. Collman *et al.* (1975) prepared (5,10,15,20-tetraphenylporphinato)iron(II), $(TPP)Fe^{II}$, from the reduction of (TPP)FeCl by $Cr(acac)_2$ (acac is acetylacetonate) in benzene solution and recrystallization from a benzene/ethanol solution. This four-coordinated complex has Fe^{II} in an unusual intermediate spin state. A few years later, iron(II) porphyrin in a high spin state was reported in a biaxially tetrahydrofuran-coordinated iron(II) complex (Reed *et al.*, 1980). We have prepared the title compound, $(F_{20}TPP)Fe\cdot 2C_6H_6$, (I), from the reduction of $(F_{20}TPP)FeCl$ by mercury-activated zinc powder in benzene (Landrum *et al.*, 1980), and its crystal structure is reported here.

The porphyrin ring in (I) is essentially planar and the Fe atom is located on a center of symmetry (Fig. 1). The four pentafluorophenyl rings make dihedral angles of 73.0 (1) and 75.8 (1)° with the porphyrin plane (Fig. 2). The Fe—N bond distances depend on the amount by which the core is ruffled, and the geometry and iron spin state of the porphyrin ring. The mean Fe—N distance [1.994 (1) Å; Table 1] in (I) is longer than that in (TPP)Fe [1.972 (4) Å; Collman *et al.*, 1975], in which the core is slightly ruffled. Similar results were reported for Co^{II} complexes, with a mean Co—N distance of 1.976 (5) Å for $(F_{20}TPP)Co$ and 1.949 (5) Å for the more ruffled (TPP)Co (Kadish *et al.*, 1990). In the β-pyrrole-brominated six-coordinated iron(II) complex, $(F_{20}TPPBr_8)Fe(py)_2$ (py is pyridine), the Fe—N distance is 1.963 (7) Å as a result of steric hindrance between the Br and phenyl-substituted F atoms (Grinstaff *et al.*, 1995). The average Fe—N distance in the intermediate or low spin state is shorter than that in high-spin six-coordinated complexes such as $(TPP)Fe^{II}(THF)_2$ [2.057 (2) Å; Reed *et al.*, 1980]. This differ-



(I)

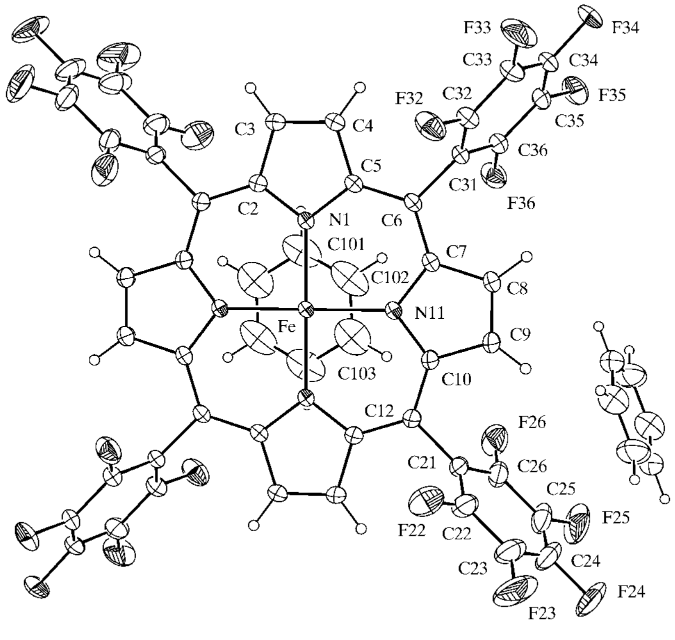


Figure 1
The molecular structure of (I), showing the atom-numbering scheme and 30% probability ellipsoids.

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ence is due to the empty $d_{x^2-y^2}$ orbital of the Fe^{II} atom in the intermediate spin state. The Fe—N distances for planar porphyrin complexes can give useful information about porphyrin skeleton contraction (Birnbaum *et al.*, 1995); the more contracted the skeleton, the shorter the metal–N distances and the smaller the C—N—C angles in the pyrrole ring. The average distances between the N atoms and the porphyrin center (or metal) are 2.052, 2.036, 1.996 and 1.994 Å for (F_{20}TPP)H_2, (F_{20}TPP)Zn, (F_{20}TPP)Cu and (F_{20}TPP)Fe, respectively (Birnbaum *et al.*, 1995), and the C—N—C angles are 107.4, 106.2, 105.2 and 105.3°, respectively.

As shown in Fig. 1, there is a benzene molecule below the porphyrin ring, and there are substantial interactions [3.062 (3)–3.416 (3) Å] between the Fe and the benzene C atoms, although the benzene ring is not directly coordinated to the Fe atom. It is well known that there are definite π–π interactions between metalloporphyrin molecules and aromatic solvents, with distances shorter than 3.3 Å being observed (Kadish *et al.*, 1990). In (I), the benzene ring lies sandwiched between two porphyrin rings (Fig. 3). In another sense, two benzene molecules are located at the top and bottom of the porphyrin ring. The spin state of the Fe^{II} atom in (I) is intermediate (S = 1), as confirmed by NMR studies. The pyrrole H-atom signal was reported at 5.1 p.p.m. in a benzene solution of (TPP)Fe^{II} (Goff *et al.*, 1977).

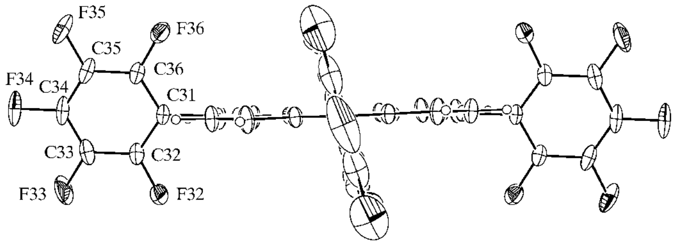

Figure 2
A side view of (I), showing the porphyrin planarity.

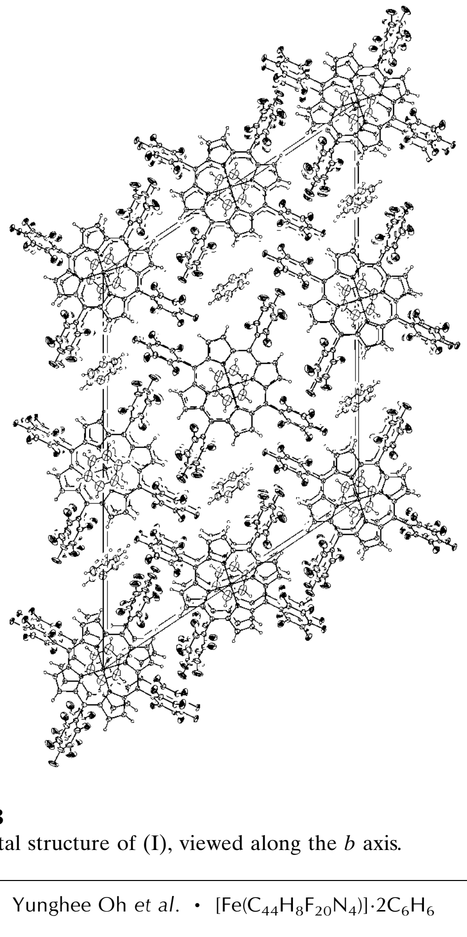

Figure 3
The crystal structure of (I), viewed along the *b* axis.

Experimental

All reactions were carried out in a dry-box filled with nitrogen. Solvents were purified and reagents were used without further purification. The title complex was synthesized by the reduction of (F_{20}TPP)FeCl (23.5 mmol, 0.025 g) with mercury-activated zinc powder in benzene (25 ml) at room temperature for 3 h (Landrum *et al.*, 1980). The resulting red solution was filtered to remove residual Zn(Hg) and $ZnCl_2$ and the filtrate was evaporated to one-third of its volume, at which point heptane (8 ml) was added and the precipitates were filtered off. Crystals of (I) suitable for X-ray analysis were obtained by slow evaporation of a solution of the precipitates in benzene. The complex was assigned by NMR in non-coordinating solvent [C_6D_6, δ_{pyrr} = 5.1 p.p.m. (Song & Goff, 1994)].

Crystal data

[Fe($C_{44}H_8F_{20}N_4$)]·2C_6H_6
M_r = 1184.61
Monoclinic, $C2/c$
a = 34.136 (7) Å
b = 6.4633 (13) Å
c = 26.356 (5) Å
β = 123.85 (3)°
V = 4829 (2) Å^3
Z = 4
D_x = 1.629 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10 744 reflections
θ = 2.9–27.5°
μ = 0.44 mm^{-1}
T = 190 (2) K
Block, dark purple
0.35 × 0.20 × 0.08 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
19 916 measured reflections
5520 independent reflections
4550 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 27.5°
$h = 0 \rightarrow 44$
$k = -8 \rightarrow 8$
$l = -34 \rightarrow 28$

Table 1
Selected geometric parameters (Å, °).

Fe—N11	1.9891 (13)	C5—C6	1.391 (2)
Fe—N1	1.9982 (13)	C6—C7	1.384 (2)
Fe—C102	3.062 (3)	C6—C31	1.496 (2)
Fe—C103	3.177 (3)	C7—N11	1.375 (2)
Fe—C101	3.416 (3)	C7—C8	1.435 (2)
N1—C5	1.373 (2)	C8—C9	1.344 (3)
N1—C2	1.374 (2)	C9—C10	1.435 (2)
C2—C3	1.435 (2)	C10—N11	1.374 (2)
C3—C4	1.349 (3)	C10—C12	1.387 (2)
C4—C5	1.434 (2)	C12—C2^i	1.387 (2)
N11—Fe—N1	89.92 (6)	C7—C6—C5	124.45 (14)
C5—N1—C2	105.30 (12)	N11—C7—C6	125.37 (14)
N1—C2—C12^i	125.04 (14)	N11—C7—C8	110.43 (14)
N1—C2—C3	110.47 (14)	C9—C8—C7	107.10 (15)
C4—C3—C2	106.80 (15)	C8—C9—C10	106.79 (16)
C3—C4—C5	107.03 (15)	N11—C10—C12	125.28 (14)
N1—C5—C6	125.25 (14)	N11—C10—C9	110.66 (14)

Symmetry code: (i) $-x, -y, -z$.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 3.8531P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R(F) = 0.037$	$(\Delta/\sigma)_{\max} < 0.001$
$wR(F^2) = 0.109$	$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$S = 1.03$	$\Delta\rho_{\min} = -0.41$ e Å^{-3}
5520 reflections	
366 parameters	
H-atom parameters constrained	

H atoms were positioned geometrically and constrained to ride on their attached atoms [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)]. The largest residuals in the final difference map were 0.81 Å from atom F22 ($\Delta\rho_{\max}$) and 0.57 Å from the Fe atom ($\Delta\rho_{\min}$).

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1150). Services for accessing these data are described at the back of the journal.

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