High-spin [Fe(TTP)(THF)$_2$]

Chuan-Jiang Hu, **Bruce C. Noll**, and **W. Robert. Scheidt**[*]
Department of Chemistry and Biochemistry, 251 Nieuwland Science Hall, University of Notre Dame, Notre Dame, IN 46556-5670, USA

Key indicators

Single-crystal X-ray study; T = 100 K; Mean σ(C–C) = 0.002 Å; R factor = 0.038; wR factor = 0.102; Data-to-parameter ratio = 25.4

The title compound, bis(tetrahydrofuran)(5,10,15,20-tetra-*p*-tolylporphyrinato) iron(II), [Fe($C_{48}H_{36}N_4$)(C_4H_8O)$_2$] or [Fe(TTP)(THF)$_2$] (TTP = dianion of *meso*-tetratolylporphyrin), is a six-coordinate high-spin iron(II) tetratolylporphyrin with two tetrahydrofuran molecules as axial ligands. The Fe^{II} atom is at an inversion center. The average Fe—N distance is 2.067 (7) Å and the Fe—O distance is 2.3208 (8) Å.

Comment

Reed *et al.* 1980 reported the structure of the first six-coordinate high-spin iron(II) porphyrinate, [Fe(TPP)(THF)$_2$]. Subsequently, Lecomte *et al.* 1986 performed an electron-density study of the compound. In this paper, we report the molecular structure of another six-coordinate high-spin iron(II) porphyrinate, the title compound, (I), [Fe(TTP)(THF)$_2$].

(I)
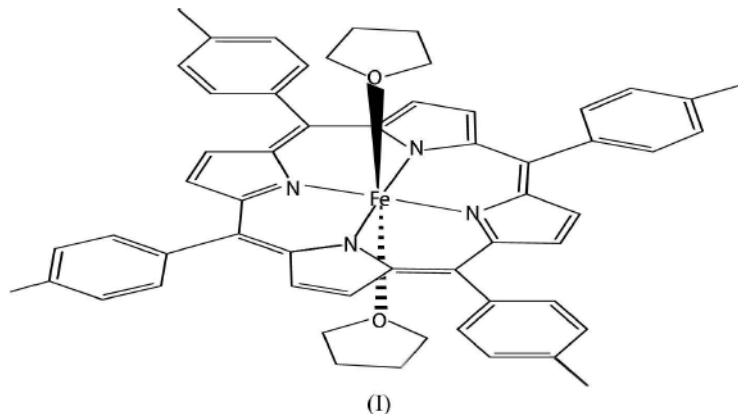
The molecular structure of (I), with the atom-numbering scheme, is shown in Fig. 1. The Fe^{II} atom is located at a crystallographic inversion center. As a result, the Fe^{II} atom is centered in the porphyrin plane. The independent Fe—N bond distances are 2.0619 (9) and 2.0713 (9) Å, which are similar to those in [Fe(TPP)(THF)$_2$] (2.054 and 2.060 Å; Reed *et al.*, 1980). These values are substantially longer than the value of 1.996 (6) Å in the low-

Correspondence e-mail: scheidt.1@nd.edu.

spin six-coordinate iron(II) porphyrinate [Fe(TPP)(THT)$_2$] (THT is tetrahydrothiophene; Mashiko *et al.*, 1979).

The axial Fe—O bond distance [2.3208 (8) Å] is similar to the value of 2.351 (3) Å in [Fe(TPP)(THF)$_2$] (Reed *et al.*, 1980). This bond distance indicates that the THF ligand is a weak-field ligand. The Fe—O vector is tipped by 1.3 (1)° from the normal to the mean plane through the plane of the four N atoms. This is smaller than the 4.3° tip seen in [Fe(TPP) (THF)$_2$] (Reed *et al.*, 1980). This deviation also breaks the D_{4h} symmetry of the FeN$_4$O$_2$ coordination. The THF ligand has an envelope configuration with approximate C_s symmetry. The O atom is displaced from the mean plane of the four C atoms by 0.56 (3) Å.

Experimental

All experimental manipulations were performed under a purified nitrogen atmosphere using standard Schlenk techniques. [Fe(TTP)]$_2$O (35 mg) was reduced in tetrahydrofuran (10 ml) in the presence of excess EtSH overnight. The solution was transfered into glass tubes and layered with hexane. A week later, high-quality red crystals of (I) formed.

Crystal data	
[Fe(C$_{48}$H$_{36}$N$_4$)(C$_4$H$_8$O)$_2$]	D_x = 1.312 Mg m^{-3}
M_r = 868.87	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 7064 reflections
a = 13.6820 (2) Å	
b = 9.7320 (1) Å	θ = 2.5–31.5°
c = 17.1014 (2) Å	μ = 0.39 mm^{-1}
β = 104.964 (1)°	T = 100 (2) K
V = 2199.89 (5) Å^3	Needle, red
Z = 2	0.49 × 0.15 × 0.09 mm
Data collection	
Bruker SMARTAPEX2 CCD area-detector diffractometer	7311 independent reflections 6283 reflections with $I > 2\sigma(I)$
ϕ and ω scans	R_{int} = 0.028
Absorption correction: multi-scan	θ_{max} = 31.5°
(*SADABS*; Sheldrick, 2004)	h = −20 → 17
T_{min} = 0.83, T_{max} = 0.97	k = −11 → 14
31 446 measured reflections	l = −22 → 25
Refinement	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 1.0408P]$
$R[F^2 > 2\sigma(F^2)]$ = 0.038	
$wR(F^2)$ = 0.102	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.04	$(\Delta/\sigma)_{max}$ = 0.001
7311 reflections	$\Delta\rho_{max}$ = 0.53 e Å^{-3}
288 parameters	$\Delta\rho_{min}$ = −0.31 e Å^{-3}
H-atom parameters constrained	

H atoms were positioned geometrically and treated as riding, with C—H distances in the range 0.95–0.99 Å and with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *APEX2* (Bruker Nonius, 2004); cell refinement: *APEX2* and *SAINT* (Bruker Nonius, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

Acknowledgments

References

Bruker Nonius (2004). *APEX2* and *SAINT* Bruker Nonius AXS, Madison, Wisconsin, USA.

Lecomte C, Blessing RH, Coppens P, Tabard A. J Am Chem Soc. 1986; 108:6942–6950.

Mashiko T, Marchon JC, Musser DT, Reed CA, Kastner ME, Scheidt WR. J Am Chem Soc. 1979; 101:3653–3655.

Reed CA, Mashiko T, Scheidt WR, Spartalian K, Lang G. J Am Chem Soc. 1980; 102:2302–2306.

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

Sheldrick, G. M. (2004). *SADABS* Version 2.10. University of Göttingen, Germany.

Spek AL. J Appl Cryst. 2003; 36:7–13.
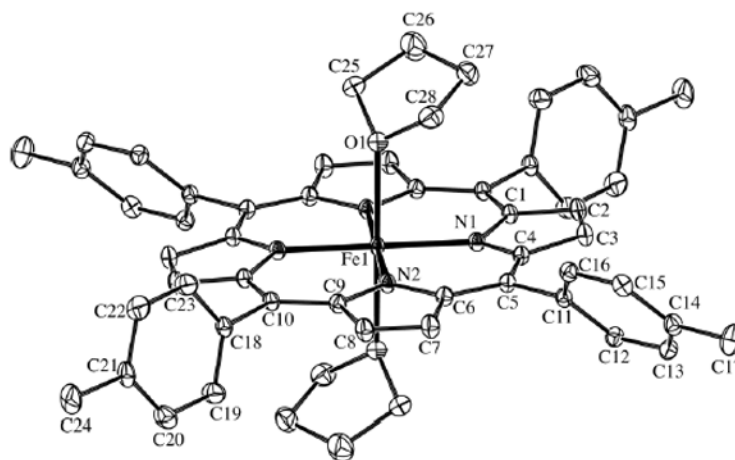
Figure 1.
The molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted. Unlabeled atoms are related by the symmetry operation $-x$, $1 - y$, $-z$.

Table 1

Selected geometric parameters (Å, °).

Fe1—N1	2.0619 (9)	Fe1—O1	2.3208 (8)
Fe1—N2	2.0713 (9)		
N1—Fe1—N2	89.57 (4)	N2—Fe1—O1	88.96 (3)
N1—Fe1—O1	89.34 (3)		