

Methoxy[*meso*-5,10,15,20-tetrakis-(2,6-difluorophenyl)porphyrinato]-iron(III), [Fe(TDFPP)(OCH₃)]

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Received 10 January 2001

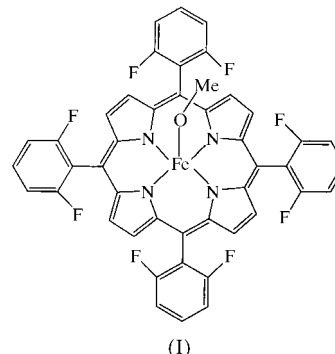
Accepted 13 February 2001

The crystal structure of the title compound, [Fe(C₄₄H₂₀F₈N₄)(CH₃O)], has been determined. The Fe atom lies 0.485 (1) Å out of the plane of the four N atoms to which it is coordinated and from the inversion centre at the origin of the unit cell. The methoxy group is axially coordinated to the Fe atom with O—Fe—N angles of 106.3 (2) and 102.4 (2)°, a C—O—Fe angle of 128.3 (5)° and an Fe—O distance of 1.788 (5) Å. Difluorophenyl rings are tilted from the porphyrin (por) plane with torsion angles of −68.1 (6) and 77.7 (5)° across the two C_{por}—C—C—C_{ar} systems.

Comment

The active site of heme-dependent enzymes is composed of an Fe^{III} ion coordinated in the equatorial plane to the four N atoms of protoporphyrin IX and two possible coordination sites of the metal ion in axial positions. The axial sites of electron-transfer enzymes are occupied by two amino acid residues, while only one amino acid is coordinated to the metal for peroxidase, catalase and P-450 monooxygenase. The latter enzymes can have one labile position for coordination of substrates or oxidants (Andersson & Dawson, 1991). The most important difference among the various heme-dependent enzymes is the nature of their axial ligands. The coordinated atom in peroxidase, catalase and P-450 is the N of histidine (Chung & Van Wart, 1992), O[−] of tyrosine (Chung & Van Wart, 1992; Benecky *et al.*, 1993) and S[−] of cysteine (Egawa *et al.*, 1994), respectively. The specific chemical properties of each enzyme may be due to its axial ligand. We have elucidated that the cysteinyl ligand of P-450 plays an important role in the catalytic cycle of P-450. Also, we recently observed that the reactive oxygenating intermediates of iron(III) porphyrin complexes as model compounds of P-450 are altered by anionic axial ligands (Nam, Lim, Oh *et al.*, 2000;

Nam, Lim & Oh, 2000; Nam, Lim, Moon & Kim, 2000). During the study of the anionic acid ligand effect, we obtained the crystal of an iron(III) porphyrin complex with a methoxy ligand in the axial position. We now report the structure of an electron-deficient iron porphyrin complex, [Fe(TDFPP)(OCH₃)] [TDFPP is the *meso*-tetrakis(2,6-difluorophenyl)-porphyrinate dianion], (I).



In space group $P2_1/n$ with $Z = 2$, the molecules lie on inversion centres, as might be expected for some symmetrically substituted square-planar molecules. In the case of (I), the basic geometry of the molecule is square-pyramidal and the Fe atom lies 0.485 (1) Å out of the plane of the four N atoms to which it is coordinated and from the inversion centre at the origin of the unit cell. The Fe atom (and the coordinated methoxy ligand) is thus disordered over two sites (50:50) by the inversion symmetry. There is additional conformational

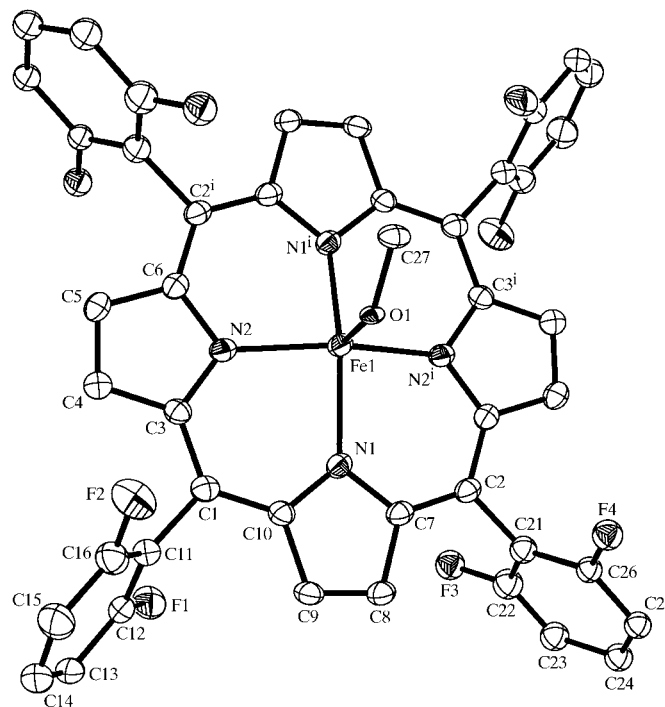


Figure 1

View of the title molecule showing the labelling scheme. Ellipsoids are drawn at the 30% probability level. All H atoms have been omitted for clarity and only one component of disorder is shown. (The symmetry code is as in Table 1.)

disorder in one of the substituted phenyl rings which is disordered over two sites with occupancies in the ratio 0.69:0.31. The difluorophenyl rings are tilted from the porphyrinate plane with torsion angles of -68.1 (6) and 77.7 (5) $^\circ$ for C10–C1–C11–C12 and C7–C2–C21–C22, respectively. The Fe–N bond lengths of 2.051 (4) and 2.104 (4) Å are longer than those of low-spin complexes (average 1.986 Å). The methoxy group is axially coordinated to the Fe atom, with angles of 106.3 (2) and 102.4 (2) $^\circ$ for O1–Fe1–N1 and O1–Fe1–N2, respectively. The Fe1–O1 distance is 1.788 (5) Å, which is a little shorter than that of the methoxyiron(III)–mesoporphyrin IX complex (Fe–O 1.842 Å; Hoard *et al.*, 1965).

Experimental

To a solution of Fe(TDFPP)Cl (4.0 mg, 0.0042 mmol) in CH₂Cl₂ (0.5 ml) was added sodium 2-methyl-2-propane thiolate (52 mg, 0.042 mmol) at room temperature. After the reaction mixture had been stirred for 3 h and then filtered through a 0.45 filter, methanol (3 ml) was added to the filtered solution. The filtrate was allowed to stand at room temperature for two weeks and crystals of compound (I) were then obtained.

Crystal data

[Fe(C ₄₄ H ₂₀ F ₈ N ₄)(CH ₃ O)]	$D_x = 1.542 \text{ Mg m}^{-3}$
$M_r = 843.3$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 11483 reflections
$a = 12.4526$ (4) Å	$\theta = 3.0\text{--}25.0^\circ$
$b = 12.6673$ (5) Å	$\mu = 0.50 \text{ mm}^{-1}$
$c = 12.6426$ (5) Å	$T = 150$ (1) K
$\beta = 114.39$ (3) $^\circ$	Plate, dark brown
$V = 1816.31$ (12) Å ³	$0.18 \times 0.18 \times 0.08 \text{ mm}$
$Z = 2$	

Data collection

KappaCCD diffractometer	3198 independent reflections
φ and ω scans with κ offsets	2188 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (DENZO-SMN; Otwinowski & Minor, 1997)	$R_{\text{int}} = 0.08$
$T_{\text{min}} = 0.915$, $T_{\text{max}} = 0.961$	$\theta_{\text{max}} = 25.0^\circ$
11483 measured reflections	$h = -14 \rightarrow 14$
	$k = -15 \rightarrow 15$
	$l = -15 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0657P)^2 + 4.6789P]$
$R[F^2 > 2\sigma(F^2)] = 0.079$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.207$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.44 \text{ e \AA}^{-3}$
3198 reflections	$\Delta\rho_{\text{min}} = -0.48 \text{ e \AA}^{-3}$
251 parameters	Extinction correction: SHELXTL/PC (Sheldrick, 1998)
H-atom parameters constrained	Extinction coefficient: 0.017 (3)

All H atoms, except water molecule H atoms, were inserted at calculated positions and treated as riding with isotropic displacement parameters. The C and F atoms of the disordered difluorophenyl ring were only allowed isotropic vibration parameters.

Table 1

Selected geometric parameters (Å, $^\circ$).

Fe1–O1	1.788 (5)	Fe1–N1	2.104 (4)
Fe1–N2	2.051 (4)	Fe1–N2 ⁱ	2.131 (4)
Fe1–N1 ⁱ	2.051 (4)	O1–C27	1.409 (10)
O1–Fe1–N2	102.4 (2)	O1–Fe1–N2 ⁱ	104.5 (2)
O1–Fe1–N1 ⁱ	100.8 (2)	N2–Fe1–N2 ⁱ	153.11 (8)
N2–Fe1–N1 ⁱ	89.02 (16)	N1 ⁱ –Fe1–N2 ⁱ	86.14 (16)
O1–Fe1–N1	106.3 (2)	N1–Fe1–N2 ⁱ	85.53 (16)
N2–Fe1–N1	86.86 (16)	C27–O1–Fe1	128.3 (5)
N1 ⁱ –Fe1–N1	152.88 (8)		
C10–C1–C11–C12	-68.1 (6)	C7–C2–C21–C22	77.7 (5)

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

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

Financial support from the Basic Research Program of the Korean Science & Engineering Foundation and the Women's University Research Fund is gratefully acknowledged. MHL and SWJ are the recipients of a Research Fellowship (Brain Korea 21 Program). Data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC (Canada).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1037). Services for accessing these data are described at the back of the journal.

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