

μ -Oxo-bis[(2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrinato)-iron(III)] bis(dichloromethane) solvate

Ming Li, Maoyu Shang, Hugues F. Duval and W. Robert Scheidt*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA

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

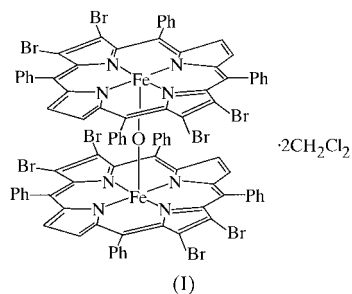
Received 21 February 2000

Accepted 24 July 2000

The precise structure of the title compound, $[\text{Fe}_2\text{O}(\text{C}_{44}\text{H}_{24}\text{Br}_4\text{N}_4)_2] \cdot 2\text{CH}_2\text{Cl}_2$, is reported. The Fe—N distances are non-equivalent in pairs because of the asymmetric peripheral substitution; the values are 2.098 Å to the brominated rings and 2.041 Å to the other two rings. The Fe—O bond distance is 1.7583 (4) Å. The molecule has required twofold symmetry so that there is one unique porphyrin macrocycle and one Fe—O bond length in contrast to a previous report on the same species.

Comment

Kadish *et al.* (1997) previously described the molecular structure of the title compound, (I), in which there are highly disordered alcohol molecules of solvation. In this paper, we report the precise structure of the species. There is an obvious difference between the current and previous crystal structures. Owing to the different solvents used for crystallization, two different space groups are found for the same species, *i.e.* $P2_1/n$ and $C2/c$. Consequently, there are two non-equivalent porphyrin macrocycles and Fe—O distances [1.775 (8) and 1.741 (8) Å] in the previous structure. The present molecule, however, has a twofold axis which passes through the bridging



O atom and is perpendicular to a line joining the two Fe atoms, leading to the rigorous requirement that the two porphyrin macrocycles be equivalent. Fig. 1 shows a top view of the title compound. The two Fe—O bond lengths are the same at

1.7583 (4) Å, a distance which is comparable with those found in the analogous non-brominated compounds $[\text{Fe}(\text{TPP})]_2\text{O}$ [1.763 (1) Å; Hoffmann *et al.*, 1972] and $[\text{Fe}(\text{TPFP})]_2\text{O}$ [1.775 (1) Å; Gold *et al.*, 1988]. However, the conformation of the porphyrin cores and the Fe—N distances in the two crystalline species are not significantly different.

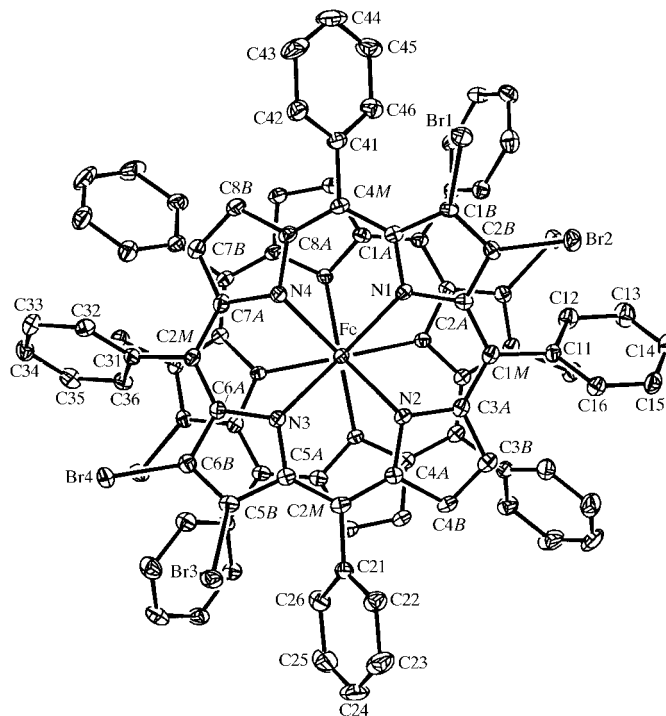


Figure 1

Top view of $[\text{Fe}(\text{TPPBr}_4)]_2\text{O}$. Displacement ellipsoids are drawn at the 50% probability level. Porphyrin H atoms have been omitted for clarity.

As pointed out by Scheidt (2000), the introduction of Br atoms on opposite pyrrole rings contributes to an interaction between the *meso*- and β -substituents, resulting in an increase in the N···N distance for the two β -substituted pyrrole rings, unequal angles subtended at the methine C atom for the *exo* substituent and non-planar cores. The transannular N···N distance of 4.062 Å between the two brominated pyrrole rings is longer than the distance of 3.970 Å in the other direction. Also, the Fe—N bond lengths to the brominated pyrrole N atoms are longer than the bond lengths to the unsubstituted pyrrole rings (2.098 *versus* 2.041 Å; Table 1). However, the average Fe—N distance of 2.07 (3) Å in the present structure is shorter than the average Fe—N distances of 2.087 (5) Å in $[\text{Fe}(\text{TPP})]_2\text{O}$ and 2.088 (11) Å in $[\text{Fe}(\text{TPFP})]_2\text{O}$, owing to the saddled and ruffled porphyrin cores in the title compound. On the other hand, the same peripheral substituent effect induces two distinct saddled core conformations to minimize unfavorable contact between the Br atoms and the phenyl rings in $[\text{Fe}(\text{TPPBr}_4)(\text{NO})]$ (Scheidt *et al.*, 2000), while $[\text{Zn}(\text{TPPBr}_4)]$ (Zou *et al.*, 1997) is planar and $[\text{Ni}(\text{TPPBr}_4)]$ (Zou *et al.*, 1994) is ruffled. In all cases, the M—N bonds to the brominated pyrrole ring are longer.

Experimental

Crystals of the title compound were obtained during an investigation of the oxidation reaction of $[\text{Fe}(\text{TPPBr}_4)(1\text{-MeIm})_2]$, where 1-MeIm is 1-methylimidazole.

Crystal data

$[\text{Fe}_2\text{O}(\text{C}_{44}\text{H}_{24}\text{Br}_4\text{N}_4)_2] \cdot 2\text{CH}_2\text{Cl}_2$	$D_x = 1.796 \text{ Mg m}^{-3}$
$M_r = 2154.18$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 250 reflections
$a = 35.161 (6) \text{ \AA}$	$\theta = -20.5\text{--}20.5^\circ$
$b = 13.763 (6) \text{ \AA}$	$\mu = 4.565 \text{ mm}^{-1}$
$c = 18.845 (3) \text{ \AA}$	$T = 130 (2) \text{ K}$
$\beta = 119.104 (12)^\circ$	Needle, red-brown
$V = 7968.4 \text{ \AA}^3$	$0.32 \times 0.12 \times 0.08 \text{ mm}$
$Z = 4$	

Data collection

Enraf-Nonius FAST area-detector diffractometer	7483 reflections with $I > 2\sigma(I)$
Ellipsoid-mask fitting scans	$R_{\text{int}} = 0.049$
Absorption correction: empirical (Blessing, 1997)	$\theta_{\text{max}} = 28.33^\circ$
$T_{\text{min}} = 0.492$, $T_{\text{max}} = 0.694$	$h = -35 \rightarrow 46$
25 463 measured reflections	$k = -12 \rightarrow 17$
9134 independent reflections	$l = -23 \rightarrow 22$
	Intensity decay: $< 1\%$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0581P)^2 + 11.1319P]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.099$	$(\Delta/\sigma)_{\text{max}} = 0.003$
$S = 1.041$	$\Delta\rho_{\text{max}} = 1.16 \text{ e \AA}^{-3}$
9134 reflections	$\Delta\rho_{\text{min}} = -0.63 \text{ e \AA}^{-3}$
511 parameters	Extinction correction: <i>SHELXL97</i>
H atoms idealized with riding models	Extinction coefficient: 0.00097 (5)

Data collection: *MADNES* (Pflugrath & Messerschmit, 1987); cell refinement: *MADNES*; data reduction: *MADNES*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Siemens, 1994).

We thank the National Institutes of Health for support of this research under grant GM-38401 to WRS. Funds for the purchase of the FAST area-detector diffractometer were provided through NIH grant RR-06709 to the University of Notre Dame.

Table 1

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

Fe—O1	1.7583 (4)	Fe—N1	2.097 (2)
Fe—N2	2.039 (2)	Fe—N3	2.100 (3)
Fe—N4	2.043 (2)		
O1—Fe—N2	104.12 (12)	Fe—O1—Fe ¹	178.7 (2)
O1—Fe—N4	102.91 (12)	C3A—C1M—C11	118.3 (3)
N2—Fe—N4	152.96 (11)	C2A—C1M—C11	118.7 (3)
O1—Fe—N1	106.26 (8)	C5A—C2M—C21	120.1 (3)
N2—Fe—N1	86.32 (10)	C4A—C2M—C21	115.6 (3)
N4—Fe—N1	86.82 (10)	C7A—C3M—C31	116.2 (3)
O1—Fe—N3	102.86 (8)	C6A—C3M—C31	120.0 (3)
N2—Fe—N3	87.21 (10)	C8A—C4M—C41	116.2 (3)
N4—Fe—N3	86.16 (10)	C1A—C4M—C41	119.7 (3)
N1—Fe—N3	150.88 (10)		

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1532). Services for accessing these data are described at the back of the journal.

References

- Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
- Farrugia, L. J. (1997). *ORTEP-3 for Windows*. Version 1.03. University of Glasgow, Scotland.
- Gold, A., Jayaraj, K., Doppelt, R., Fisher, J. & Weiss, R. (1988). *Inorg. Chim. Acta*, **150**, 177–180.
- Hoffmann, A. B., Collins, D. M., Day, V. W., Fleischer, E. B., Srivastava, T. S. & Hoard, J. L. (1972). *J. Am. Chem. Soc.* **94**, 3620–3626.
- Kadish, K. M., Autret, M., Ou, Z., Tagliatesta, P., Boschi, T. & Fares, V. (1997). *Inorg. Chem.* **36**, 204–207.
- Pflugrath, J. W. & Messerschmidt, A. (1987). *MADNES*. Enraf-Nonius, Delft, The Netherlands.
- Scheidt, W. R. (2000). *Systematics of the Stereochemistry of Porphyrins and Metalloporphyrins*. In *The Porphyrin Handbook*, Vol. 3, edited by K. M. Kadish, K. M. Smith & R. Guilard, ch. 16. San Diego, CA, and Burlington, MA: Academic Press.
- Scheidt, W. R., Duval, H. F., Neal, T. J. & Ellison, M. K. (2000). *J. Am. Chem. Soc.* **121**, 4651–4659.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Siemens (1994). *SHELXTL Reference Manual*. Version 5.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Zou, J., Li, M., Xu, Z. & You, X. (1994). *Acta Chim. Sin.* **52**, 683–692.
- Zou, J.-Z., Li, M., Xu, Z. & You, X.-Z. (1997). *Jiegou Huaxue (Chin. J. Struct. Chem.)*, **16**, 29–31.