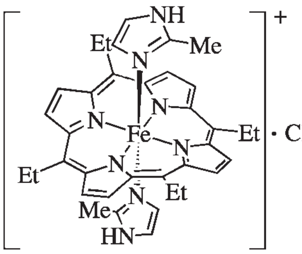
Structure Analysis of Highly S_4-Ruffled Bis(2-methylimidazole)(*meso*-tetraethylporphyrinato)iron(III) Chloride

Yoshiki Ohgo,[†] Takahisa Ikeue,[†] Takashi Saitoh,[††] and Mikio Nakamura*[†,††]
[†]*Department of Chemistry, Toho University School of Medicine, Ota-ku, Tokyo 143-8540*
[††]*Divison of Biomolecular Science, Graduate School of Science, Toho University, Funabashi, 274-8510*

(Received December 17, 2001; CL-011264)

The X-ray crystallographic analysis of low spin bis(2-methylimidazole)(*meso*-tetraethylporphyrinato)iron(III) has revealed that the porphyrin ring is highly S_4-ruffled and that the maximum deviation of the *meso*-carbon from the least-squares plane of the $[Fe(C_{20}N_4)]$ core reaches as much as 0.73(1) Å.

Much attention has been paid to deformed porphyrins and their metal complexes since they are widely found in naturally occurring hemoproteins such as cytochromes c and peroxidases.[1] Elucidation of the physicochemical properties caused by the ring deformation is, therefore, quite important not only to understand the role and functions of these hemoproteins but also to develop new functional materials.[2,3] In the previous papers, we have reported that the $(d_{xz}, d_{yz})^4(d_{xy})^1$ state is stabilized in a series of low spin six-coordinated (*meso*-tetraalkylporphyrinato)iron(III) complexes when axially coordinated HIm is replaced by much bulkier 2-MeIm or 2-^{i}PrIm.[4–6] We have ascribed the result to the strongly S_4 ruffled deformation of the porphyrin core caused by the severe steric interaction with the bulky ligands. Although ample examples have been reported on the molecular structures of low spin iron(III) porphyrins, the porphyrins examined are in most cases confined to octaethylporphyrin, *meso*-tetraphenylporphyrin, and *meso*-tetraarylporphyrins.[7] In this paper, we report the molecular structure of $[Fe(TEtP)(2\text{-}MeIm)_2]^+$ which is the first example of low spin iron(III) complex of *meso*-tetraalkylpoprhyrin.



meso-Tetraethylporphyrin was prepared according to the literature method.[8] Insertion of iron followed by the addition of excess 2-MeIm yielded the purple solid. The solid was then recrystallized from chloroform-heptane solution by slow evaporation of the solvents. The molecular structure of $[Fe(TEtP)(2\text{-}MeIm)_2]^+$ is shown in Figure 1.[9] As expected, the porphyrin ring is highly deformed. The axially coordinated 2-MeIm ligands are placed perpendicularly along the diagonal C_{meso}-Fe-C_{meso} axes. The dihedral angle between the two 2-MeIm ligands is 87(2) °. The average Fe-N_p (N_p; Nitrogen atoms of porphyrin) bond length is fairly short, 1.932(14) Å. The perpendicular displacements of the peripheral carbon atoms from the least-squares plane of the $[Fe(C_{20}N_4)]$ core are shown in Figure 2. While the four nitrogen atoms are located almost on the least-squares plane, i.e. 0.01(1), −0.02(1), −0.05(1), and −0.08(1) Å, the four *meso* carbons are deviated alternately up and down from this plane by 0.69(1), −0.73(1), 0.71(2), and −0.70(2) Å. Thus, the porphyrin core is highly S_4 ruffled as expected from the NMR results reported previously.[2,10] The ruffling dihedral angles between two pairs of diagonal pyrroles reach as much as 45.0(5) ° and 47.9(5) °. The highly ruffled conformation creates the mutually perpendicular clefts along the C_{meso}-Fe-C_{meso} axes above and below the porphyrin ring. The planar axial ligands coordinate to the iron(III) along these clefts to minimize the steric repulsion with the porphyrin core. These structural features explain why the $(d_{xz}, d_{yz})^4(d_{xy})^1$ state is stabilized in $[Fe(TEtP)(2\text{-}MeIm)_2]^+$ as compared with $[Fe(TEtP)(HIm)_2]^+$. As reported, the interaction between the iron d_{xy} and porphyrin a_{2u} orbitals is strengthened in highly S_4 ruffled complex; this interaction must be very weak in the planar complex due to the orthogonality of these orbitals.[11] In contrast, the interaction between the iron d_π(d_{xz} and d_{yz}) and porphyrin $3e_g$ orbitals is weakened due to the less effective overlaps between these orbitals.[2,10] The increase in the d_{xy}-a_{2u} interaction destabilizes the d_{xy} orbital while the decrease in the d_π-$3e_g$ interaction stabilizes the d_π orbitals, leading to the stabilization of the $(d_{xz}, d_{yz})^4(d_{xy})^1$ state.

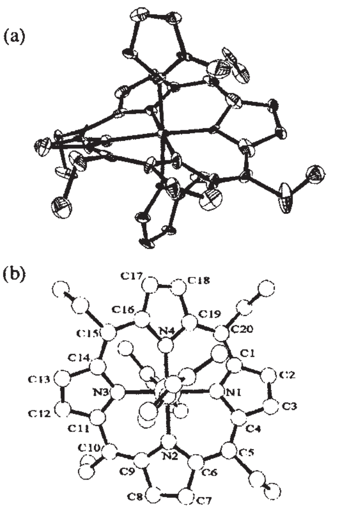


Figure 1. (a) ORTEP diagram of $[Fe(TEtP)(2\text{-}MeIm)_2]Cl$. The thermal ellipsoids enclose 30% probablilty. Hydrogen atoms are omitted for clarity. (b) Top view of $[Fe(TEtP)(2\text{-}MeIm)_2]Cl$ with atomic numbering.

Since $[Fe(TEtP)(2\text{-}MeIm)_2]^+$ is the first example of the structurally characterized low spin iron(III) complex of tetraalkylporphyrin, it is worthwhile to compare the structural data with those of analogous complexes. Table 1 lists the structural

Copyright © 2002 The Chemical Society of Japan

Table 1. Comparison of structural parameters for $[Fe(TEtP)(2\text{-}MeIm)_2]^+$ and related complexes

Complexes	Fe-N_p/Å$^{a)}$	Fe-N_{ax}/Å$^{b)}$	ϕ/deg$^{c)}$	$\Delta\phi$/deg$^{d)}$	ΔC_{meso}/Å$^{e)}$	ref
$[Fe(TPP)(1\text{-}MeIm)_2]^+$	1.982	1.974	32, 22	10	0.09	12
$[Fe(TMP)(1\text{-}MeIm)_2]^{+f)}$	1.986	1.965	42, 42	0	0	13
			23, 23	0	0	13
$[Fe(TPP)(2\text{-}MeIm)_2]^+$	1.971	2.013	32, 32	90	0.40	14
$[Fe(TMP)(1,2\text{-}Me_2Im)_2]^+$	1.937	2.004	45, 45	90	0.72	15
$[Fe(TEtP)(2\text{-}MeIm)_2]^+$	1.932(14)	2.017(12)	45(1), 41(1)	86.7(2)	0.71(2)	This work

a) The average bond length between the iron and the nitrogen atoms of porphyrin core.

b) The average bond length between the iron and the nitrogen atoms of axial imidazole ligand.

c) The dihedral angle between the coordinated imidazole and the N_p-Fe-N_{ax} plane.

d) The dihedral angle between the two axial ligands.

e) The perpendicular displacement of the four *meso* carbons from the least-squares plane of $[Fe(C_{20}N_4)]$ core.

f) The complex has two independent molecules in an asymmetric unit.

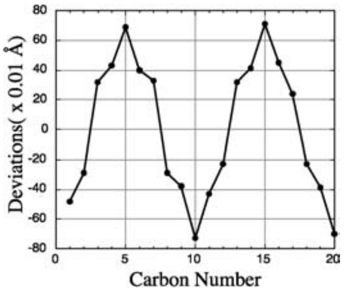


Figure 2. Displacements of the peripheral carbon atoms from the mean plane of the 24 atoms. Carbon numbers in abscissa are based on the IUPAC numbering system.

parameters for some low spin iron(III) complexes. The ruffling of the porphyrin core increases to a great extent on going from $[Fe(TPP)(1\text{-}MeIm)_2]^+$ to $[Fe(TPP)(2\text{-}MeIm)_2]^+$ as is revealed from the large increase in the ΔC_{meso} value. Thus, it is quite natural that the most ruffled porphyrin core in low spin iron(III) complexes is realized in $[Fe(TMP)(1,2\text{-}Me_2Im)_2]^+$ where fairly large steric repulsion is expected between the bulky mesityl groups at the *meso* positions and the bulky 1,2-Me_2Im ligands to deform the porphyrin core. As a result, $[Fe(TMP)(1,2\text{-}Me_2Im)_2]^+$ shows the shortest Fe-N_p bond, 1.937(12) Å. It is clear from the data in Table 1 that the porphyrin core of $[Fe(TEtP)(2\text{-}MeIm)_2]^+$ is deformed as much as that of $[Fe(TMP)(1,2\text{-}Me_2Im)_2]^+$; the average Fe-$N_p$ bond length is 1.932(14) Å and the average deviation of the *meso* carbons is 0.71(2) Å. Thus, $[Fe(TEtP)(2\text{-}MeIm)_2]^+$ is classified as one of the most ruffled low spin iron(III) porphyrins. It is surprising that ethyl and mesityl groups at the *meso* positions in each complex play a similar role in deforming the porphyrin ring in spite of the apparent difference in bulkiness between these groups. The results indicate that the *meso*-tetraalkylporphyrin ring is quite flexible and is easily deformed in the S_4-ruffled fashion to relieve the strain energy. Thus, the structural analyses of a series of bis(2-alkylimidzole)(*meso*-tetraalkylporphyrinato)iron(III) complexes could reveal the relationship between the degree and mode of porphyrin deformation and the physicochemical properties of the complexes quantitatively. Studies along these lines are now in progress in this group.

We thank Professors, Yuji Ohashi and Hidehiro Uekusa, Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, for the assistance during the X-ray measurements. This work was supported by the Grant in Aid for Scientific Research on Priority Areas (A)(No 12020257 to MN) from Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

1 J. D. Hobbs and J. A. Shelnutt, *J. Protein Chem.*, **14**, 19 (1995).

2 T. Ikeue, Y. Ohgo, T. Saitoh, T. Yamaguchi, and M. Nakamura, *Inorg. Chem.*, **40**, 3423 (2001).

3 T. Ikeue, Y. Ohgo, T. Yamaguchi, M. Takahashi, M. Takeda, and M. Nakamura, *Angew. Chem., Int. Ed. Engl.*, **40**, 2617 (2001).

4 M. Nakamura, T. Ikeue, S. Neya, N. Funasaki, and N. Nakamura, *Inorg. Chem.*, **35**, 3731 (1996).

5 M. Nakamura, T. Ikeue, H. Fujii, T. Yoshimura, and K. Tajima, *Inorg. Chem.* **37**, 2405 (1998).

6 Abbreviations: HIm, 2-MeIm, 2-^{i}PrIm: imidazole, 2-methylimidazole, and 2-isopropylimidazole, respectively. TEtP, TPP, TMP: dianions of *meso*-tetraethylporphyrin, *meso*-tetraphenylporphyrin, and *meso*-tetra-mesitylporphyrins, respectively.

7 W. R. Scheidt, "The Porphyrin Handbook," ed. by K. M. Kadish, K. M. Smith, and R. Guilard, Academic Press, San Diego (2000), Vol. 3, Chap. 16, pp 49–112.

8 S. Neya and N. Funasaki, *J. Heterocycl. Chem.*, **34**, 689 (1997).

9 Crystal data for $[Fe(TEtP)(2\text{-}MeIm)_2]Cl$: $[Fe(C_{28}H_{28}N_4)(C_4H_6N_2)_2]Cl\cdot H_2O$ (fw = 692.06), Crystal size: 0.20 × 0.20× 0.05 mm, Space group $P2_1/n$(#14), a = 13.627(5) Å, b = 15.461(5) Å, c = 19.211(11) Å, $\beta = 108.55(4)°$; V = 3837(3) Å^3. F(000) = 1452, Z = 4, Dc = 1.198 g/cm^3, graphite monocromated Mo Kα radiation ($\lambda = 0.71069$ Å), $2\theta_{max} = 55.0°$. Intensity data were collected on a Rigaku AFC5R (rotating anode) diffractometer. The final cycle of full matrix least-squares refinement was based on 1327 observed reflections ($I > 2\sigma(I)$ and 407 variable parameters, and converged R1 = 0.0974. S (goodness of fit) = 0.946. Maximum peak in final differential map is 0.73 eÅ^{-3}.

10 T. Ikeue, Y. Ohgo, T. Saitoh, M. Nakamura, H. Fujii, and M. Yokoyama, *J. Am. Chem. Soc.*, **122**, 4068 (2000).

11 F. A. Walker, "The Porphyrin Handbook," ed. by K. M. Kadish, K. M. Smith, and R. Guilard, Academic Press, San Diego (2000), Vol. 5, Chap. 36, pp 81–183.

12 T. B. Higgins, M. K. Safo, and W. R. Scheidt, *Inorg. Chim. Acta*, **178**, 261 (1990).

13 M. K. Safo, G. P. Gupta, F. A. Walker, and W. R. Schiedt, *J. Am. Chem. Soc.*, **113**, 5497 (1991).

14 W. R. Scheidt, J. F. Kirner, J. L. Hoard, and C. A. Reed, *J. Am. Chem. Soc.*, **109**, 1963 (1987).

15 O. Q. Munro, H. M. Marques, P. G. Debrunner, K. Mohanrao, and W. R. Scheidt, *J. Am. Chem. Soc.*, **117**, 935 (1995).