Fixation of the 2-Methylimidazole Ligand and Anomalous Pyrrole Chemical Shifts in Bis(2-methylimidazole)(*meso*-tetraalkylporphyrinato)iron(III) Chloride Caused by the Nonplanar Porphyrin Ring

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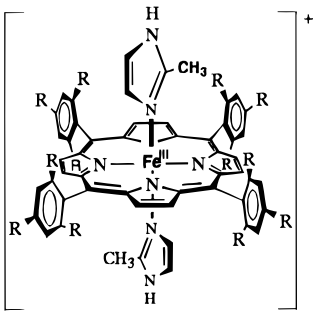
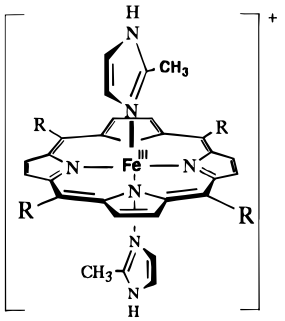
Variable temperature ^{1}H NMR measurement of a series of low spin bis(2-methylimidazole)(*meso*-tetraalkylporphyrinato)-iron(III) complexes, [Fe(TRP)(2-MeIm)$_2$]Cl (R = Me, Et, iPr), lead to an unambiguous conclusion on the fixation of the axially coordinated ligands. Furthermore, the pyrrole ^{1}H signals appeared in a so-called *diamagnetic region* (δ 0−10 ppm) in the isopropyl complex (R = iPr) in spite of the $S = {}^1/_2$ iron spin state. The anomaly was ascribed to the nonplanar nature of the porphyrin ring caused by the steric interaction between imidazole methyl and *meso*-alkyl substituents.

Extensive studies have been done on the synthesis and structure of nonplanar porphyrins due to their relevance to the biological functions of heme proteins and related tetrapyrroles.[1] We and others have reported that the coordination of sterically hindered imidazoles such as 2-methylimidazole (2-MeIm) into (tetramesitylporphyrinato)iron(III) induces the S_4 deformation of the porphyrin ring and restricts the imidazole rotation about N−Fe bonds on the NMR time scale in solution.[2] The deformation was ascribed to the severe steric repulsion between the *o*-methyls and axially coordinated 2-MeIm.[2b,3] In fact, recent crystallographic study of the analogous 1,2-dimethylimidazole (1,2-Me$_2$Im) complex, [Fe(Me-TPP)(1,2-Me$_2$Im)$_2$]ClO$_4$, has revealed that the porphyrin ring is highly ruffled in the solid and that the two axial ligands are placed along the cavities created by the deformed porphyrin ring.[4] These results indicate the importance of the direct interactions between 2-alkylimidazoles and bulky *meso*-aryl substituents for the hindered imidazole rotation. We are then interested in examining if less bulky alkyl groups in a series of (*meso*-tetraalkylporphyrinato)-iron(III) complexes, [Fe(TRP)(2-MeIm)$_2$]Cl (R = Me, Et, iPr),[5] can deform the porphyrin ring to such an extent as to hinder the rotation of the coordinated 2-MeIm ligands.



[Fe(*R*-TPP)(2-MeIm)$_2$]$^+$
R = H, Me, Et, iPr



[Fe(T*R*P)(2-MeIm)$_2$]$^+$
R = H, Me, Et, iPr

[Fe(TMeP)(2-MeIm)$_2$]Cl was obtained by the addition of 2-MeIm (7.0 equiv) to [Fe(TMeP)]Cl. Formation of the low spin bis-adduct was verified at −25 °C by the disappearance of the *meso*-methyl and pyrrole signals of the high spin complex at δ 153.0 and 102.9 ppm, respectively, and the concomitant appearance of the corresponding signals at δ 37.3 and δ −7.6 ppm. A singlet at −1.1 ppm at −72 °C, assigned to the methyl protons of the coordinated 2-MeIm based on the integral intensity (6H), further confirmed the formation of the bis-adduct. The methyl and pyrrole signals, quite unexpectedly, broadened and split into two and four peaks, respectively, on lowering the temperature as Figure 1 shows. The temperature dependent ^{1}H NMR spectra clearly indicate that the 2-MeIm ligands stop rotating even in the less bulky TMeP system. Medforth et al. reported the hindered rotation of the axially coordinated 3-chloropyridine and 3-phenylpyridine ligands in the (2,3,7,8,-12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrinato)co-balt(III) complex.[6] In this case, the porphyrin ring is nonplanar in itself regardless of the axial ligands due to the severe steric interactions among the peripheral substituents.[1] In our system, even the planar porphyrin ring, as revealed by the crystallographic studies on [Ni(TMeP)],[7] is deformed by the coordination of the hindered imidazole, resulting in the restricted imidazole rotation on the NMR time scale. Activation free energy was estimated at coalescence temperature (T_c = −51 °C) to be 40 kJ mol^{-1}. It should be noted that the activation free energy corresponds to the rate processes consisting of both the ligand rotation and the concomitant porphyrin ring inversion.[2b,8] Existence of the *meso*-methyl groups must be crucial to observe the ligand fixation by ^{1}H NMR since the unsubstituted (porphyrinato)iron(III) complex, [Fe(THP)(2-MeIm)$_2$]Cl, gave sharp singlets for the pyrrole (δ −29.8 ppm) and *meso* (δ −8.5 ppm) protons even at −67 °C.

(1) Barkigia, K. M.; Berber, M. D.; Fajer, J.; Medforth, C. J.; Renner, M. W.; Smith, K. M. *J. Am. Chem. Soc*. **1990**, *112*, 8851.
(2) (a) Nakamura, M.; Groves, J. T. *Tetrahedron* **1988**, *44*, 3225. (b) Walker, F. A.; Simonis, U. *J. Am. Chem. Soc*. **1991**, *113*, 8652. (c) Nakamura, M.; Nakamura, N. *Chem. Lett*. **1991**, 1885. (d) Nakamura, M.; Tajima, K.; Tada, K.; Ishizu, K.; Nakamura, N. *Inorg. Chim. Acta* **1994**, *224*, 113.
(3) Nakamura, M. *Bull. Chem. Soc. Jpn*. **1995** , *68*, 197.
(4) Munro, O. Q.; Marques, H. M.; Debrunner, P. G.; Mohanrao, K.; Scheidt, W. R. *J. Am. Chem. Soc*. **1995**, *117*, 935.
(5) The synthesis and ^{1}H NMR chemical shifts of these complexes are given in the Supporting Information section.
(6) Medforth, C. J.; Muzzi, C. M.; Smith, K. M.; Abraham, R. J.; Hobbs, J. D.; Shelnutt, J. A. *J. Chem. Soc., Chem. Commun*. **1994** , 1843.
(7) Kutzler, F. W.; Swepston, P. N.; Berkovitch-Yellin, Z.; Ellis, D. E.; Ibers, J. A. *J. Am. Chem. Soc*. **1983** , *105*, 2996.
(8) Nakamura, M.; Ikezaki, A. *Chem. Lett*. **1995**, 733.

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Table 1. ^{1}H NMR Chemical Shifts of [Fe(TRP)(2-MeIm)$_2$]Cl in $CDCl_3/CD_2Cl_2$ at −35 °C

	H	Me	Et	iPr
py-H	−21.7 (−27.0)[a]	−8.2 (−6.3, −11.3, −14.4, −15.5)[b]	−9.4 (−8.2, −12.0, −14.7, −15.7)[b]	3.2, 4.3, 7.4, 7.8
meso-H	−3.6 (−6.2)[a]			
R (α-H)		38.7 (39.0, 49.6)[b]	16.9 (15.7, 16.5, 18.2)[b]	18.4, 21.6
R (*β*-H)			1.1 (0.3)[b]	3.4, 4.0, 6.1, 6.9
Im-CH_3	14.7 (16.6)[a]	1.4 (−1.6)[b]	2.8 (1.5)[b]	−4.2

[a] Values at −56 °C. [b] Values at −71 °C.

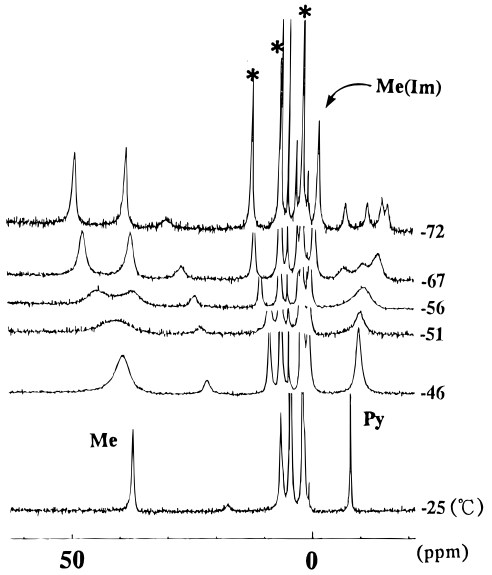

Figure 1. Temperature dependent ^{1}H NMR spectra (90 MHz) of [Fe(T*Me*P)(2-MeIm)$_2$]Cl (10 mM) in a $CD_2Cl_2/CDCl_3$ solution. Signal assignment: Me, *meso*-methyl; py, pyrrole *β*-H; Me(Im), methyl of the coordinated 2-MeIm. Signals for free 2-MeIm are denoted by asterisks.

Introduction of much bulkier substituents would further increase the porphyrin nonplanarity and fix the conformation of the complex at higher temperature. The (*meso*-tetraisopropylporphyrinato)iron(III) complex, [Fe(TiPrP)(2-MeIm)$_2$]Cl, must be a good candidate since the corresponding nickel complex, [Ni(TiPrP], has a nonplanar porphyrin ring with the *meso*-carbon atoms displaced up to 0.74 A.[9] The ^{1}H NMR spectrum of [Fe(TiPrP)(2-MeIm)$_2$]Cl showed a broad signal (δ 16 ppm) for the isopropyl methine protons even at 25 °C. This signal split into two below 17 °C, yielding the activation free energy of 56 kJ mol^{-1} at this temperature. Since the methyl signal of the coordinated 2-MeIm exhibited line broadening in a similar temperature range as the isopropyl methine signals, the ligand rotation in this case must proceed through a dissociative mechanism.[2d] In fact, saturation transfer was observed at 0 °C between the methyl signals of the free and coordinated 2-MeIm ligands. The most remarkable point in the ^{1}H NMR spectra of this complex is the apparent absence of the pyrrole signals in the expected high field region at ambient temperature; ferric porphyrin complexes having two imidazole ligands conventionally give pyrrole signals at around −15 ppm at room temperature.[10] At lower temperature, we could observe four pyrrole signals each corresponding to 2H; the chemical shifts of these signals were determined to be δ 3.2, 4.3, 7.4, and 7.8 ppm at −35 °C based on the spectral comparison with the deuterated complex. Possibility of the reduction of ferric ($S = {}^1/_2$) to ferrous ($S = 0$) ion can be ruled out since the isopropyl methine protons appear at fairly low field, 18.0 and 21.3 ppm at −35 °C. No example has ever been reported to exhibit the pyrrole *β*-proton signals at such a low magnetic field. Thus, this is the first example of the low spin bis(imidazole)-ferric porphyrin complex showing a pyrrole signal in a so-called *diamagnetic region*.[11] The ^{1}H NMR spectrum also showed four methyl signals δ 3.4, 4.0, 6.1, and 6.9 ppm at −35 °C, indicating that the isopropyl methyls became diastereotopic in the fixed conformation. The splitting patterns of the pyrrole and *meso*-methyl signals clearly indicate that the stable conformation is the one where two imidazoles are aligned perpendicularly along the diagonal $C_{meso}-Fe-C_{meso}$ axis as in the case of [Fe(Me-TPP)(2-MeIm)$_2$]Cl.[2b,c]

We have reported, based on the ^{1}H NMR study of 32 low spin [Fe(R-TPP)(L)$_2$]Cl complexes, that the chemical shifts of the pyrrole protons vary depending on the steric interactions between the porphyrin core and imidazole ligands (L); pyrrole signals of the complexes carrying unhindered imidazoles appear at very high fields (−25 to −28 ppm at −56 °C), while those of the *ortho*-substituted complexes with hindered imidazoles appear at rather low fields (−14 to −19 ppm at −56 °C).[2d] The tendency was explained in terms of the nonplanarity of the porphyrin ring since the ring deformation would deteriorate the iron (d_π)−porphyrin (p_π) overlaps and decrease the spin densities on the pyrrole carbons. The anomalous pyrrole proton shifts in [Fe(TiPrP)(2-MeIm)$_2$]Cl would be explained similarly by the weak $d_\pi-p_\pi$ interaction in a strongly ruffled porphyrin ring. In Table 1 are listed the chemical shifts of some protons in a series of [Fe(TRP)(2-MeIm)$_2$]Cl complexes (R = H, Me, Et, iPr). The data clearly indicate that the pyrrole signals move to lower magnetic field on going from H to Me and Et and then to iPr complexes, which is in accordance with the expected nonplanarity of the porphyrin ring.

In summary, we showed the fixation of the 2-MeIm ligand in a simple low spin [Fe (TRP)(2-MeIm)$_2$]Cl system together with the anomalous chemical shifts of the pyrrole protons and ascribed them to the nonplanar porphyrin ring.

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Supporting Information Available: Figures showing temperature dependent ^{1}H NMR spectra (90 MHz) of [Fe(TEtP)(2-MeIm)$_2$]Cl, ^{1}H NMR spectra (400 MHz) of [Fe(TiPrP)(2-MeIm)$_2$]Cl (py-d_8) and [Fe(TiPrP)(2-MeIm)$_2$]Cl (py-h_8) taken at −35 °C, and Curie plots of isopropyl methine and imidazole methyl signals of [Fe(TiPrP)-(2-MeIm)$_2$]Cl and text giving the synthesis of free base porphyrins and their iron(III) complexes (4 pages). Ordering information is given on any current masthead page.

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(9) Ema, T.; Senge, M. O.; Nelson, N. Y.; Ogoshi, H.; Smith, K. M. *Angew. Chem.* **1994**, *106*, 1951; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1879.

(10) Bertini, I.; Luchinat, C. *NMR of Paramagnetic Molecules in Biological Systems*; Benjamin/Cummings: Menlo Park, CA, 1986; p 182.

(11) Some low spin ferric porphyrin complexes with low basicity axial ligands such as *tert*-butyl isocyanide, 4-cyanopyridine, and dimethyl phenylphosphonite show pyrrole protons at unusually low magnetic field. (a) Simonneaux, G.; Hindre, F.; Le Plouzennec, M. *Inorg. Chem.* **1989**, *28*, 823. (b) Safo, M. K.; Gupta, G. P.; Watson, C. T.; Simonis, U.; Walker, F. A.; Scheidt, W. R. *J. Am. Chem. Soc.* **1992**, *114*, 7066. (c) Guillemot, M.; Simonneaux, G. *J. Chem. Soc., Chem. Commun.* **1995**, 2093.