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Fixation of One of Imidazole Ligands in Low Spin Bis-imidazole Ferric Porphyrin Complexes

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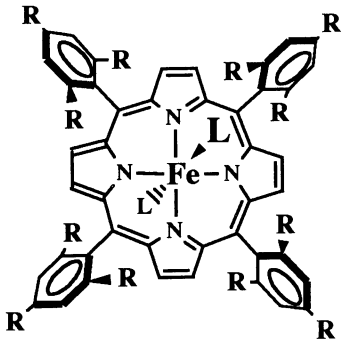
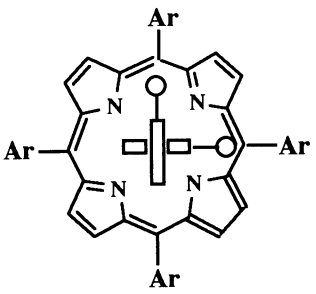
Low spin ferric porphyrin complexes carrying rapidly rotating 1-methylimidazole and rotationally fixed 2-isopropylimidazole have been prepared. Chemical shift range of the pyrrole protons at -56 °C was nearly twice as much as that of the bis(hindered imidazole) complex. Orientation of the fixed ligand relative to the porphyrin plane was determined based on the splitting pattern of the *meso*-^{13}C signals.

Spectral properties such as NMR[1] and ESR[2] of naturally occurring heme proteins are controlled by various factors. In the case of heme proteins carrying at least one histidine group as axial ligand, orientation of the ligand relative to the heme plane is considered to be one of the factors.[3] This is because p(π) orbitals of histidine(L) can interact with degenerated d(π) orbitals of iron(M) in L to M π-donation mode and raise the energy levels of the two orbitals to a different extent.[4] As a result, an unpaired electron of iron is dispersed unequally to the four pyrroles of the porphyrin ring. This will cause a large difference in chemical shifts of the peripheral methyl protons. It is difficult, however, to extract the orientation effect of the ligands in heme proteins. Thus, in order to elucidate the orientation effect of the axial ligands, suitable iron complexes of synthetic porphyrins are necessary in which rotation of the ligands is hindered.

We have succeeded in obtaining the first examples of the low spin complexes where the rotation of axial ligands slowed down on the NMR time scale.[5] One of such examples is bis(2-methylimidazole)tetramesitylporphinatoiron(III) chloride, (Me-TPP)Fe(2-MeIm)$_2$ Cl, where two ligands are perpendicularly fixed as shown in (**1**).[6] In contrast, synthesis of the complexes with parallelly fixed imidazole ligands has been hampered. This is because introduction of hindered ligands to slow down their rotation necessarily causes the deformation of the porphinato core. In fact, recent X-ray results of (H-TPP)Fe(2-MeIm)$_2$ClO$_4$ and analogous complexes have revealed that the porphinato cores have S_4 ruffled structure and that the axial ligands are placed perpendicularly in



(R-TPP)Fe(L)$_2$Cl



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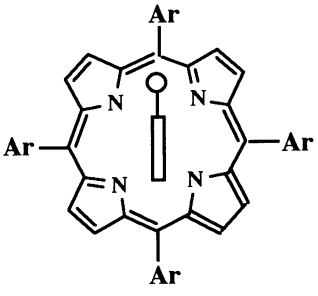

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the cavities created along diagonal *meso* C-C axes.[7,8] Thus, we designed a complex in which one of the axial ligands is fixed and the other is rapidly rotating. Since the orientation effect of the rapidly rotating ligand is canceled out, the complex corresponds to the one with two parallelly aligned ligands. In this paper, we would like to report the preparation and spectral properties of such complexes.

Addition of 2-^{i}PrIm(3.0 equiv.) to a $CDCl_3$ solution of (Me-TPP)FeCl yielded low spin (Me-TPP)Fe(2-^{i}PrIm)$_2$Cl. Figure 1 shows the ^{1}H NMR spectrum of this complex taken at -15 °C. Assignment of the signals in Fig. 1 was carried out as reported previously.[5] The splitting pattern of the signals clearly indicates that the conformation of this complex is also given by (**1**). Signals at 0.2 and -7.1 ppm were assigned to the diastereotopic isopropyl methyls of the coordinated 2-^{i}PrIm based on the saturation transfer experiment. The large difference in chemical shifts is a direct evidence that the porphinato core is deviated from planarity even in solution.[9] To this solution, 1-MeIm was added gradually and subsequent reactions were monitored by ^{1}H NMR spectroscopy at -56 °C. Figure 2 shows the pyrrole region of the spectra obtained after the addition of 0.72, 1.4, and 4.3 equiv. of 1-MeIm, respectively. Signals A and C are assigned to the pyrrole protons of bis(2-^{i}PrIm) and bis(1-MeIm) complexes, respectively, by the comparison with authentic spectra. Thus, the other four peaks marked by B are assigned to those of mixed ligand complex, (Me-TPP)Fe(2-^{i}PrIm)(1-MeIm)Cl. As the complex gave four pyrrole signals, rotation of only one of the axial ligands, 2-^{i}PrIm, is supposed to be frozen; hindered rotation of both of the ligands should give eight pyrrole signals. In contrast to the case of (Me-TPP)Fe(2-^{i}PrIm)$_2$Cl, isopropyl methyl protons of the coordinated 2-^{i}PrIm showed only one signal

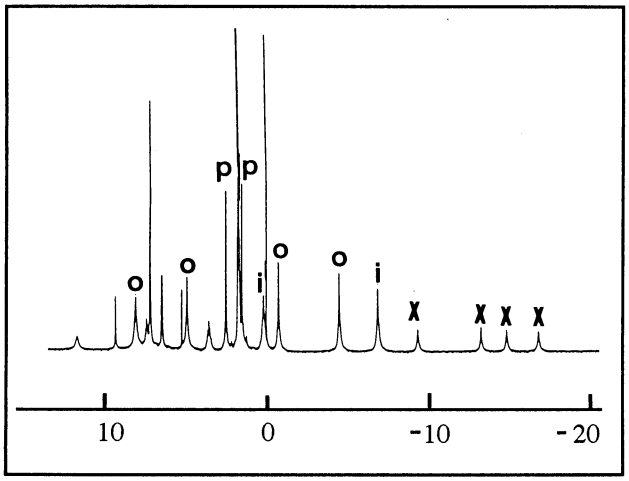

Fig. 1. ^{1}H NMR spectrum of (Me-TPP)Fe(2-^{i}PrIm)$_2$Cl in $CDCl_3$ at -15 °C. Assignment of the signals: o, o-methyl; p, p-methyl; x, pyrrole-H; i, isopropyl methyls of the coordinated 2-^{i}PrIm.

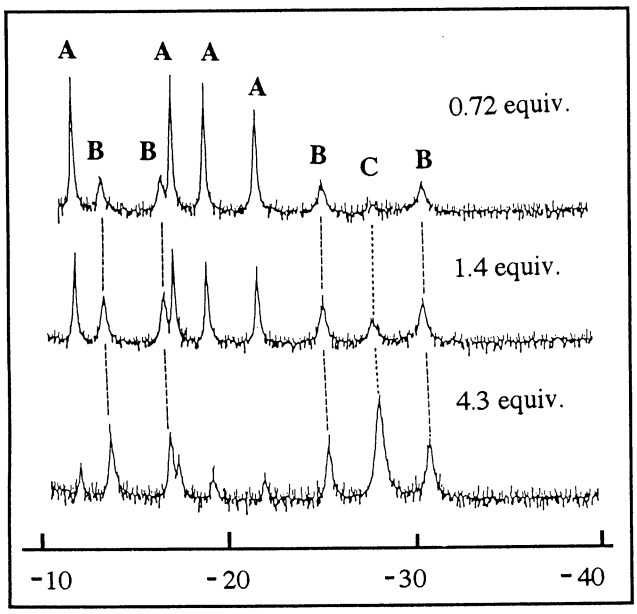

Fig. 2. Pyrrole region of the ^{1}H NMR spectra of (Me-TPP)Fe(2-^{i}PrIm)$_2$Cl at -56 °C in $CDCl_3$ after the addition of 0.72, 1.4, and 4.3 equiv. of 1-MeIm. Signals A, B, and C indicate the pyrrole protons of (Me-TPP)Fe(2-^{i}PrIm)$_2$Cl, (Me-TPP)Fe(2-^{i}PrIm)(1-MeIm)Cl, and (Me-TPP)Fe(1-MeIm)$_2$Cl, respectively.

corresponding to 6H at -2.8 ppm. This also supports the contrasting features on the rate of rotation of two different ligands; slow rotation of 1-MeIm makes two isopropyl methyl groups non-equivalent, giving two signals as in the case of (Me-TPP)Fe(2-^{i}PrIm)$_2$Cl. In Table 1 are given the chemical shifts of the pyrrole protons of some complexes at -56 °C. It is noteworthy that the spread of the pyrrole shifts of the mixed ligand complexes is much larger than that of the bis(hindered imidazole) complexes.

Orientation of the fixed ligand relative to the porphyrin plane was determined by ^{13}C NMR spectroscopy. A $CDCl_3$ solution of (Me-TPP)-Fe(2-^{i}PrIm)$_2$Cl with 99% *meso*^{13}C was titrated by 1-MeIm. As Fig. 3a shows, two signals of bis(2-^{i}PrIm) complex marked by A appeared at 81 and 163 ppm with equal intensity in the absence of 1-MeIm. When 1-MeIm was added, the intensities of these signals weakened while those of B and C increased. On further addition of 1-MeIm, signals B decreased relative to signal C. Since the signal C is assigned to the *meso* carbons of bis(1-MeIm) complex, signals B with 1:2:1 intensity ratio are those of mixed ligand complex. These results clearly suggest that the conformation of 2-^{i}PrIm is given by **2** where 2-^{i}PrIm ligand is placed over diagonal *meso* C-C axis.

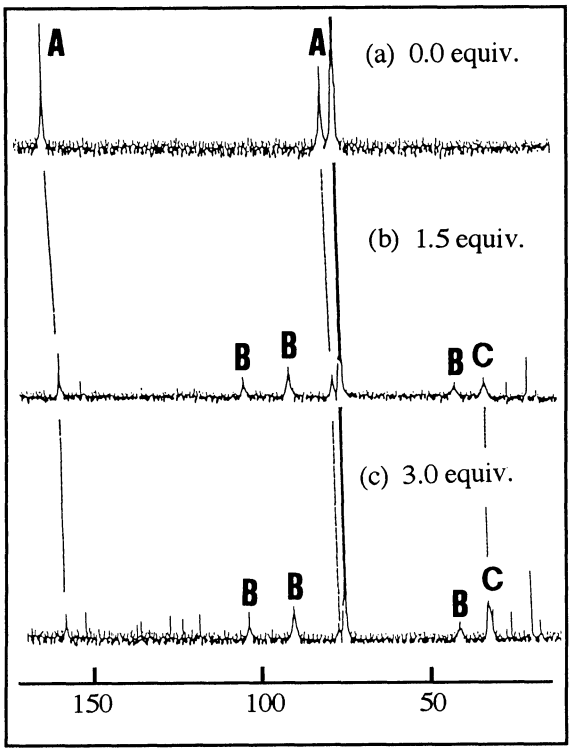

Fig. 3. ^{13}C NMR spectra of *meso*^{13}C enriched (Me-TPP)Fe(2-^{i}PrIm)$_2$Cl (a) in the absence of 1-MeIm, (b) after the addition of 1.5 equiv. of 1-MeIm, and (c) 3.0 equiv. of 1-MeIm at -56 °C. Signals A, B, and C are the meso carbons of (Me-TPP)Fe(2-^{i}PrIm)$_2$Cl, (Me-TPP)Fe(2-^{i}PrIm)(1-MeIm)Cl, and (Me-TPP)Fe(1-MeIm)$_2$Cl, respectively.

The X-ray crystallographic studies have revealed that, in the low spin complexes with sterically unhindered ligands, ligands tend to take mutually parallel alignment.[2] Thus, in the case of mixed ligand complex with both hindered and unhindered ligands, population of the parallel conformation might not be small. This must be the reason why the spread of the pyrrole protons is nearly twice as much as that for the bis(hindered imidazle) complexes. Quite recently, Walker et al. reported that a bulky carboxamide group at the ortho position of tetraphenyl porphinatoiron(III) complex prevents rotation of one of the axial 1-MeIm ligands.[10] In these systems, however, concomitant occurrence of the hindered rotation of the ortho-amide group makes the interpretation of the spectra rather complicated. Thus, the complexes presented here are the first unambiguous examples of the low spin bis(imidazole) complexes in which one of the ligands is fixed while the other is rotating rapidly.

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Table 1. Chemical shifts of the pyrrole protons of some (R-TPP)Fe(L)(L')Cl in $CDCl_3$ at -56 °C [a)]

R	L	L'	Chemical shifts ppm from TMS				Spread ppm
Me	1-MeIm	1-MeIm	-28.0				0.0
Me	2-MeIm	2-MeIm	-14.7	-19.0	-21.0	-23.3	8.6
Me	2-^{i}PrIm	2-^{i}PrIm	-12.9	-18.8	-20.6	-23.6	10.7
Me	2-^{i}PrIm	1-MeIm	-13.7	-17.0	-25.3	-30.8	17.1
Et	1-MeIm	1-MeIm	-28.5				0.0
Et	2-MeIm	2-MeIm	-15.1	-19.9	-21.7	-24.2	9.1
Et	2-^{i}PrIm	2-^{i}PrIm	-14.6	-20.4	-22.1	-25.7	11.1
Et	2-^{i}PrIm	1-MeIm	-13.8	-18.1	-27.9	-33.2	19.4
^{i}Pr	1-MeIm	1-MeIm	-27.3				0.0
^{i}Pr	2-MeIm	2-MeIm	-13.0	-17.6	-19.4	-21.5	8.5
^{i}Pr	2-^{i}PrIm	2-^{i}PrIm	-12.2	-17.6	-19.1	-22.3	10.1
^{i}Pr	2-^{i}PrIm	1-MeIm	-15.0	-16.5	-31.5	-33.0	18.0

a) Abbreviations: 1-MeIm, 1-Methylimidazole; 2-MeIm, 2-Methylimidazole; 2-^{i}PrIm, 2-Isopropylimidazole; (R-TPP)FeCl, Tetrakis(2,4,6-trialkylphenyl)porphinatoiron(III) chloride.

References

1) I. Bertini and C. Luchinat, "NMR of Paramagnetic Molecules in Biological Systems," ed by A. B. P. Lever and H. B. Gray, The Benjamin/Cummings, Menlo Park (1986), p. 165.

2) F. A. Walker, B. H. Huynh, W. R. Scheidt, and S. R. Osvath, *J. Am. Chem. Soc.*, **108**, 5288 (1986).

3) W. R. Scheidt and D. M. Chipman, *J. Am. Chem. Soc.*, **108**, 1163 (1986); Y. Yamamoto, N. Nanai, R. Chujo, and T. Suzuki, *FEBS Lett.*, **264**, 113 (1990).

4) T. G. Traylor and A. P. Berzinis, *J. Am. Chem. Soc.*, **102**, 2844 (1980); J. D. Satterlee, J. E. Erman, G. N. LaMar, K. M. Smith, and K. C. Langry, *ibid.*, **105**, 2099, (1983).

5) M. Nakamura and J. T. Groves, *Tetrahedron*, **44**, 3225 (1988); M. Nakamura and N. Nakamura, *Chem. Lett.*, **1991**, 627.

6) F. A. Walker and U. Simonis, *J. Am. Chem. Soc.*, **113**, 8652 (1991); M. Nakamura and N. Nakamura, *Chem. Lett.*, **1991**, 1885.

7) W. R. Scheidt, J. F. Kirner, J. L. Hoard, and C. A. Reed, *J. Am. Chem. Soc.*, **109**, 1963 (1987); M. K. Safo, G. P. Gupta, F. A. Walker, W. R. Scheidt, *ibid.*, **113**, 5497 (1991).

8) K. Hatano, M. K. Safo, F. A. Walker, and W. R. Scheidt, *Inorg. Chem.*, **30**, 1643 (1991).

9) K. M. Barkigia, M. D. Berber, J. Fajer, C. J. Medforth, M. W. Renner, and K. M. Smith, *J. Am. Chem. Soc.*, **112**, 8851 (1990).

10) H. Zhang, U. Simonis, and F. Ann Walker, *J. Am. Chem. Soc.*, **112**, 6124 (1990); F. A. Walker, U. Simonis, H. Zhang, J. M. Walker, T. M. Ruscitti, C. Kipp, M. A. Amputch, B. V. Castillo, III, S. H. Cody, D. L. Wilson, R. E. Graul, G. J. Yong, K. Tobin, J. T. West, and B. A. Barichievich, *New J. Chem.*, in press (1992).

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