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Spin State and Rotational Orientation of Iron Porphyrin Complexes with Hindered 2-Methylbenzimidazole as Axial Ligands

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Sterically very hindered 2-methylbenzimidazole can bind high spin *meso*-tetraarylporphinatoiron(III) chloride to form a bis-ligated complex if the *meso*-aryl groups carry alkyl groups at 2,6-positions. The spin state and ligand orientation of this complex are discussed based on the NMR and EPR spectra.

Rotational orientation of axial imidazoles (L) is considered to affect various properties of heme proteins.[1)] However, hemes are placed in a highly unsymmetrical environment, making it difficult to estimate its contribution to the observed properties. The X-ray crystal studies of the model complexes have revealed that, while unhindered ligands tend to take mutually parallel alignment, hindered ligands such as 2-methylimidazole (2-MeIm) prefer perpendicular orientation.[2)] In contrast, solution studies have been hampered because of the difficulty of ligand fixation.[3,4)]

We have reported that the rotation of coordinated 2-MeIm is hindered in bis-ligated meso-tetrakis(2,4,6-trialkylphenyl)porphinatoiron(III) chloride [(R-TPP)Fe(L)$_2$]Cl, in which R is methyl (Me), ethyl (Et), or isopropyl (iPr), to form a perpendicular conformation.[5,6)] Here, we wish to report the formation of sterically very hindered 2-methylbenzimidazole (2-MeBzIm) complexes and to discuss the spin state, ligand orientation, and the peculiar NMR and EPR behaviors.

Addition of 2-MeBzIm (6.0 equiv.) to a CD_2Cl_2 solution of (Me-TPP)FeCl gave no change in the ^{1}H NMR spectrum at 25 °C. However, a drastic change was observed at lower temperatures as shown in Fig. 1, indicating the formation of a new species. Thus, o-Me and m-H split into four and p-Me into two signals as in the case of [(Me-TPP)Fe(2-MeIm)$_2$]Cl. Pyrrole protons also gave four signals which moved to lower magnetic field at lower temperatures with a shift range less than 1 ppm at -58 °C.[7)] These signals were assigned based on the integral intensities, partially relaxed NMR, and spectra of perdeuterated pyrrole derivatives. Signals at δ -2.2 and 5.3 ppm in Fig.1C were assigned to the aromatic protons of 2-MeBzIm, since both of them correspond to 2H. These two peaks assure the formation of the bis(2-MeBzIm) complex. The splitting pattern at -58 °C clearly supports the perpendicular alignment of the ligands.[5)]

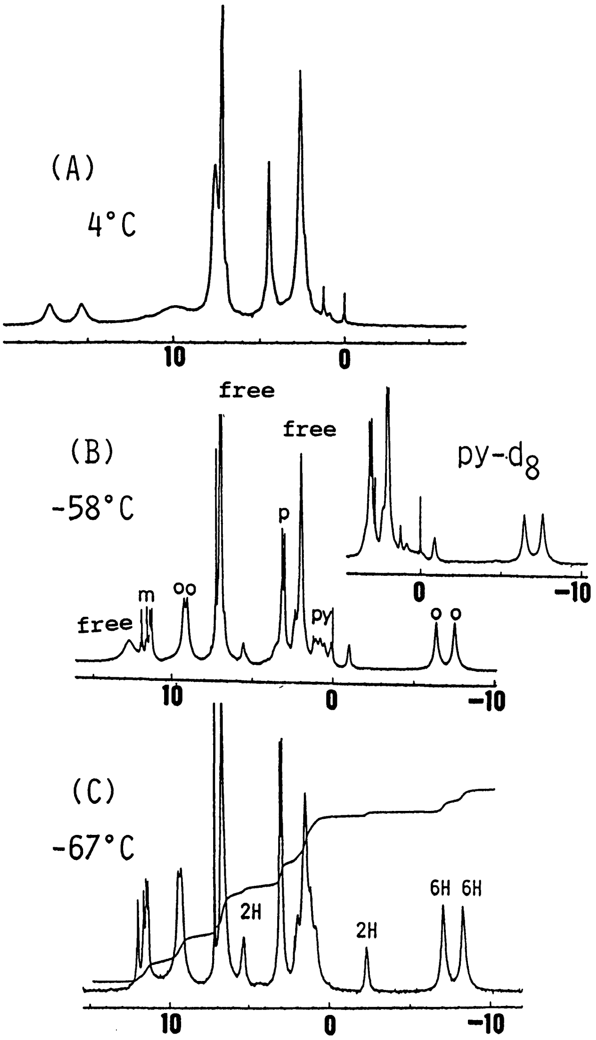

Fig. 1. ^{1}H NMR spectra of (Me-TPP)FeCl in the presence of 6.0 equiv. of 2-MeBzIm. (A) 4 °C; (B) -58 °C; (C) -67 °C. Spectrum of pyrrole deuterated complex at -58 °C was inserted in Fig. 1B.

As described above, shift range of the pyrrole protons of the 2-MeBzIm complex is extremely small compared with those of the other low spin complexes with hindered imidazole rotation.[5)] These results suggest that the pyrrole β carbons have nearly the same spin densities even in the fixed conformation. The ^{13}C NMR spectra of the *meso*-^{13}C enriched complexes were also measured to know the spin densities of the *meso* carbons. While the 2-MeIm complex gave two *meso* signals at δ 72 and 152 ppm at -67 °C, the 2-MeBzIm complex showed only one signal at δ 380 ppm even at -88 °C. The ^{1}H and ^{13}C NMR results thus indicate that an unpaired electron of iron is dispersed isotropically to the four pyrrole rings of the 2-MeBzIm complex. Curie plots of the *meso* carbons of some complexes are given in Fig. 2. It is noteworthy that the signal moves to lower field when the steric hindrance of the axial ligand increases; *meso* carbon shifts are 40, 80 and 150, and 321 ppm at -52 °C for the 1-MeIm, 2-MeIm, and 2-MeBzIm complexes, respectively.

We suggested in our previous paper that the hindered ligands such as 2-MeIm takes a mutually perpendicular alignment over N-Fe-N axis based on ^{1}H NMR data.[5)] However, low temperature ^{13}C NMR spectra showed two signals for the *meso* carbons rather than three expected from the proposed orientation. Since an accidental coincidence of the two signals seems to be improbable in the case of *meso* carbons which are located close to the paramagnetic center, the ligand orientation suggested in the previous paper might be corrected from "perpendicular orientation over N-Fe-N axis" to "perpendicular orientation over the diagonal *meso*-carbons".

As mentioned, NMR spectral properties of [(Me-TPP)Fe(2-MeBzIm)$_2$]Cl, especially of pyrrole protons, are quite different from those of other low spin complexes in the following aspects; 1) curvature in Curie plot, 2) reversed temperature dependence, and 3) low field shifts. The single peak of the *meso* carbons at rather low field is also different from other low spin complexes with hindered imidazole ligands. Thus, the solution magnetic moments of [(R-TPP)Fe]Cl were measured by Evans method in the presence of 8.0 equiv. of 2-MeBzIm. The results in Fig. 3 indicate that, although the magnetic moment of [(H-TPP)Fe]Cl was kept at 5.8 to 5.6 B.M.,$^{8)}$ those of the ortho-substituted complexes decreased when the temperature was lowered. At the lowest temperature attained, the magnetic moment of [Me-TPP)Fe(2-MeBzIm)$_2$]Cl reached as small as 2.6 B.M. The value is still higher than the spin only value expected for S = 1/2 complex. These magnetic data together with the peculiar behavior of the pyrrole signals suggest that the complex either is in a fast equilibrium between S = 1/2 and 3/2 states or has a spin admixed nature, though S = 1/2 character is considered to be dominant at lower temperature.$^{9)}$

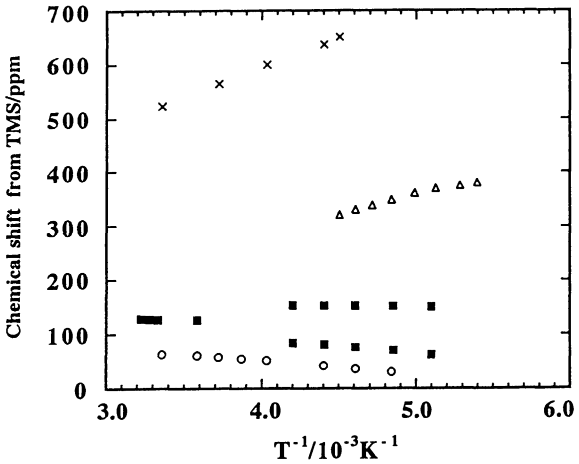

Fig. 2. Plots of meso-^{13}C shifts of [(R-TPP)Fe(L)$_2$]Cl against 1/T. high spin (X); 1-MeIm (o); 2-MeIm (■); 2-MeBzIm (Δ).

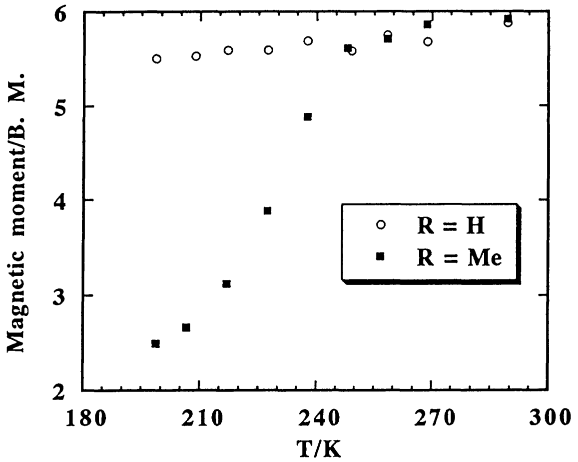

Fig. 3. Temperature dependence of magnetic moments of (R-TPP)-FeCl in the presence of 8 equ of 2-MeBzIm in CH$_2$Cl$_2$ solution.

The X-band EPR spectra of [(Me-TPP)Fe(L)$_2$]Cl were taken in CH_2Cl_2 glass at 5 K for L = 1-MeIm, 2-MeIm, and 2-MeBzIm complexes. The 1-MeIm complex gave commonly observed rhombic signals with g values equal to 2.9, 2.4, and 1.6.$^{10)}$ The 2-MeIm complex showed a so-called "strong g_{max} signal" at 3.2, which corresponds to 3.56 signal in [(H-TPP)Fe(2-MeIm)$_2$]Cl and is ascribed to the perpendicular orientation of the axial ligand.$^{11)}$ In contrast, the 2-MeBzIm complex exhibited signal at 2.6 which is in the low spin region.$^{12)}$ The g_{max} value is quite small in spite of the presence of sterically very hindered 2-MeBzIm ligands and their perpendicular alignment. In fact, it is smaller than those of most of the low spin bis(imidazole) complexes.$^{10)}$ Further study to elucidate the EPR properties of this unique complex is in progress.

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7) Pyrrole proton signals of [(Me-TPP)Fe(2-MeIm)]$_2$Cl spread over a range of 8.5 ppm at -58 °C.
8) Formation of [(H-TPP)Fe(2-MeBzIm)$_2$]Cl was reported based on the elctronic spectroscopy. In the present NMR study using 8 equiv. of 2-MeBzIm, no formation of the adduct was confirmed in the case of (H-TPP)FeCl. F. A. Walker, M-W Lo, and M. T. Ree, *J. Am. Chem. Soc*,**98**, 5552 (1976).
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