Rotationally Fixed 2-Methylbenzimidazole Ligand in Nonplanar Cobalt(III)-Porphyrin Complexes

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Dynamic ^1H and ^{13}C NMR studies have revealed that the 2-methylbenzimidazole ligand in bis(2-methylbenzimidazole)tetraphenylporphyrinatocobalt(III), [Co(tpp)(2-MeBzIm)$_2$]Cl, is fixed relative to the porphyrin ring. Fixation of the ligand was ascribed to the nonplanar nature of the porphyrin ring caused by the severe steric repulsion between the ligand and meso-substituents.

The nonplanar porphyrin rings have attracted much attention because various biological systems containing porphyrins and related tetrapyrroles are found to have distorted rings which could not only modulate their redox properties[1] but control the dynamic behavior of coordinated ligands. One method to obtain nonplanar porphyrins is a dodeca-substitution to the porphyrin periphery; steric repulsion among peripheral substituents distorts the porphyrin either to saddle or to ruffled forms.[2] In a previous paper, we have reported that the low spin [Fe(tmp)(2-MeBzIm)$_2$]Cl showed various unusual spectroscopic properties.[3,4] For example, ^1H NMR pyrrole shifts were ca. 0 ppm at -60 °C, which are quite different from those of the typical low spin bis-imidazole complexes, -15 to -30 ppm.[5] The reduced isotropic shifts of the pyrrole protons suggest the existence of a distorted ring, since the ring distortion would decrease the p_π (porphyrin)-d_π(iron) interactions. Thus, the coordination of sterically hindered ligands to metalloporphyrin could be another method to obtain nonplanar porphyrin rings. In Fe(III) system, however, bis(2-MeBzIm) complexes are unstable and they are formed only at a very low temperature.[4] Thus, much stabler Co(III) complexes have been chosen for the study of nonplanar porphyrin rings. In this paper, we would like to report that the Co(III)-porphyrin complexes with sterically hindered imidazoles are highly distorted and that the distortion of the ring freezes the ligand rotation.

Diamagnetic [Co(tpp)(2-MeBzIm)$_2$]Cl was obtained by the addition of 3.0 equiv of 2-MeBzIm into a $CDCl_3$ solution of [Co(tpp)]Cl. The ^1H NMR spectrum showed an AB quartet (δ = 8.64, 8.88 ppm, J = 5.2 Hz) and two singlets (δ = 8.69, 8.82 ppm) for the pyrrole protons at 0 °C. The ^{13}C NMR spectrum of the meso-^{13}C enriched [Co(tpp)(2-MeBzIm)$_2$]Cl showed two singlets with equal intensity at δ 119.24 and 119.67 ppm. Both the ^1H and ^{13}C signals coalesced at higher temperature as shown in Fig. 1. The splitting patterns of these signals suggest that the two bulky 2-MeBzIm ligands are fixed either perpendicularly over the diagonal Cmeso-Co-Cmeso axes or over the diagonal N-Co-N axes in a parallel fashion as shown in Fig. 2. The perpendicular alignment must be the case since the analogous [Co(tmp)(2-MeBzIm)$_2$]Cl showed two meso-^{13}C and *four* o-methyl ^1H signals. We and others have reported some examples on the hindered imidazole rotation in tetraarylporphyrin complexes.[5-7] The meso-aryl groups in those complexes have bulky substituents at the ortho positions. Thus, this is the first example on the fixation of imidazole ligands in the parent tpp system. It should be noted that the fixation was possible only in the 2-MeBzIm complex; other complexes with bulky ligands such as 2-RIm or BzIm gave single pyrrole-^1H and meso-^{13}C signals even at -78 °C in $CDCl_3$-CD_2Cl_2 solution.

In the tmp system, signal splitting was observed even in the complexes with 2-RIm. No splitting was observed, however, in bis(1-MeIm) complex. The activation free energies were determined at coalescence temperatures of the meso-^{13}C signals and they were listed in Table 1. These values correspond to the ligand rotation, not to the ligand dissociation, since no saturation transfer was observed between free and coordinated ligands at the temperature range where signal broadening was observed.[8] The data indicate that the barriers to rotation increase as the 2-substituent of imidazole changes from H, Me, Et, and then to ^{i}Pr groups. The barrier to rotation of the bulkiest 2-MeBzIm ligand was, however, less than that of 2-^{i}PrIm, which was ascribed to the destabilization of the ground state of rotation due to the severe steric repulsion between 2-MeBzIm and porphyrin core.

Unexpected ligand fixation in [Co(tpp)(2-MeBzIm)$_2$]Cl could be ascribed to the flexibility of the porphyrin ring; the large steric repulsion between the coordinated 2-MeBzIm and meso-

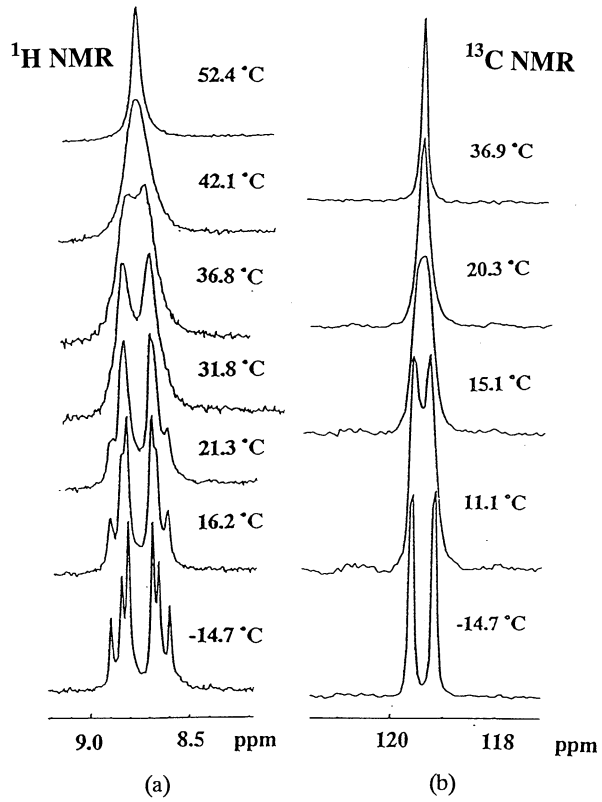

Figure 1. Temperature dependent NMR spectra of [Co(tpp)(2-MeBzIm)$_2$]Cl. (a) pyrrole ^1H and (b) *meso*-^{13}C signals.

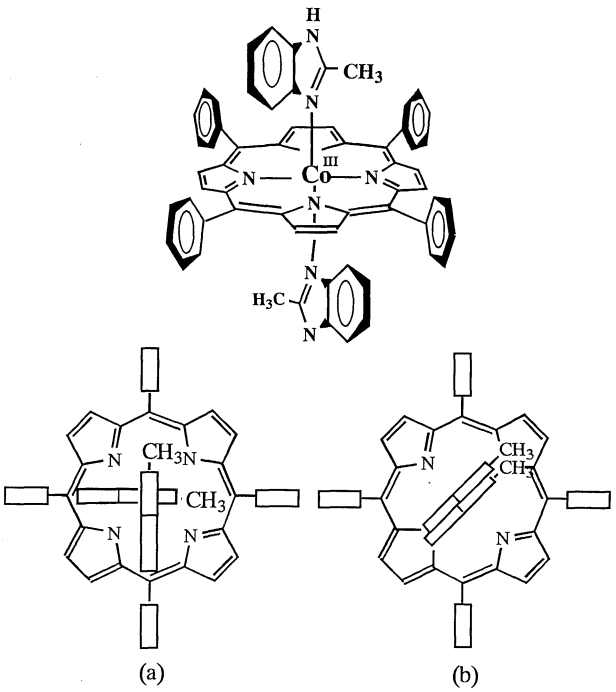

Figure 2. Possible conformations of $[Co(tpp)(2\text{-}MeBzIm)_2]Cl$. Perpendicular alignment (a) and parallel alignment(b).

Table 1. Activation free energies for ligand rotation obtained at the coalescence temperatures (Tc's) of the meso-^{13}C signals

L	$[Co(tpp)(L)_2]Cl$		$[Co(tmp)(L)_2]Cl$	
	$\Delta Gc^{\neq}$ / kJ mol^{-1}	(Tc) / °C	$\Delta Gc^{\neq}$ / kJ mol^{-1}	(Tc) / °C
1-MeIm	< 42	(< -72)	< 42	(< -72)
2-MeIm	< 42	(< -72)	60	(6.0)
2-EtIm	< 42	(< -72)	67	(30.8)
2-^{i}PrIm	< 42	(< -72)	> 85	(>100)
2-MeBzIm	63	(15.3)	75	(75.3)

phenyl groups can be weakened to a great extent in the S_4 ruffled conformation.[9] As a result, two ligand molecules are placed perpendicularly along the cavities created by the deformed porphyrin ring. As the rotation of each ligand proceeds, the steric energy increases by the repulsion between the ligand and the ruffled porphyrin core. Further rotation of the ligand causes ring inversion of the porphyrin to give another S_4 ruffled structure. In fact, recent X ray structure of $[Fe(tmp)(1,2\text{-}Me_2Im)_2]Cl$ has shown a large distortion of the porphyrin ring in the crystal state.[10] In the case of $[Co(tpp)(2\text{-}RIm)_2]Cl$, the cavities must be shallower due to weaker repulsion, resulting in the faster ligand rotation.

In order to elucidate the above hypothesis, UV-Vis spectra of a series of $[Co(tpp)(L)_2]Cl$ and $[Co(tmp)(L)_2]Cl$ were measured in CH_2Cl_2 solutions at 25 °C, where L's are HIm, 1-MeIm, 2-R-Im, 1-Me-2-RIm (R=Me, Et, ^{i}Pr), BzIm, 5,6-Me_2BzIm, and 1-R'-2-MeBzIm (R'=H, Me). Figure 3 shows the plots of absorption maxima of Soret bands against those of Q bands. Complexes with 1-R'-2-MeBzIm showed the longest wavelength and those with HIm and 1-MeIm showed the shortest. Recent experimental

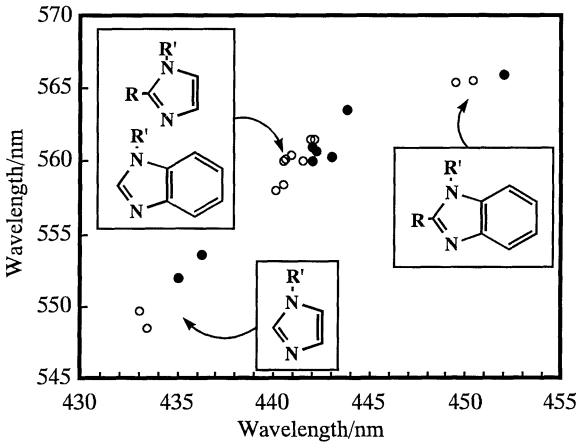

Figure 3. Plots of UV-Vis absorption maxima of Soret and Q bands of a series of $[Co(tpp)(L)_2]Cl$ (○) and $[Co(tmp)(L)_2]Cl$ (●) in CH_2Cl_2 solution at 25 °C.

and theoretical studies have revealed that the Soret and Q bands show red shifts on distortion of a porphyrin ring since the distortion mainly causes an increase in HOMO energy level relative to that of LUMO.[11] Thus, the large red shifts observed in bis(2-MeBzIm) complexes are ascribed to the nonplanar nature of the porphyrin rings.

In conclusion, we were able to show that the coordination of the hindered 2-MeBzIm and 2-RIm ligands distorts the porphyrin ring and that the distortion controls the ligand rotation.

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References and Notes

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3 Abbreviations. tpp and tmp, dianions of tetraphenyl- and tetramesitylporphyrin, respectively; HIm, imidazole; 2-RIm and 1-Me-2-RIm, 2-alkyl- and 2-alkyl-1-methyl-imidazoles, respectively, where R is methyl, ethyl or isopropyl; BzIm, benzimidazole; 2-MeBzIm, 2-methylbenzimidazole.
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8 Saturation transfer was indeed observed in [Co(tmp)(1,2-Me BzIm)$_2$] yielding the rate constant for ligand dissociation as 13 s^{-1} at 75 °C. The value is, however, too small compared with the one obtained from DNMR method.
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