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Trans Effect on the Rates of Rotation of the Axially Coordinated Imidazoles in Low Spin Iron(III) Porphyrin Complexes

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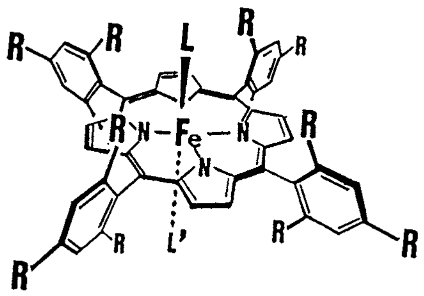
Rates of rotation of 2-methylimidazole, as studied by DNMR method, showed a drastic increase when the 6th ligand L' in the porphyrin complex $[(R\text{-}TPP)Fe(2\text{-}MeIm)(L')]^+Cl^-$was replaced by the less hindered ligands. The result was ascribed to the steric interactions between the 6th ligand and the ferric porphyrin part.

Recently, we reported the first example1) of the hindered rotation of coordinated 2-methylimidazole(2-MeIm) in low spin tetramesitylporphyrinatoiron(III) complex, $[(R\text{-}TPP)Fe(L)_2]^+$ where L= 2-MeIm and R= Me. After this finding, we have been interested in how the ligand trans to 2-MeIm affects the rate of rotation. This kind of kinetic data must help us understand both the steric and electronic interactions between two axial ligands via the ferric porphyrin ring.2) In this paper, we wish to report a very large increase in the rate of rotation of 2-MeIm on replacing one of the 2-MeIm ligands in $[(Me\text{-}TPP)Fe(2\text{-}MeIm)_2]^+Cl^-$(**1**) by the less hindered one.

By the addition of both 1-MeIm (6.0 equiv.) and 2-MeIm (3.0 equiv.) into a CD_2Cl_2 solution of $[(Me\text{-}TPP)Fe]^+Cl^-$(1.0 equiv.), mixed imidazole complex $[(Me\text{-}TPP)Fe(2\text{-}MeIm)(1\text{-}MeIm)]^+Cl^-$(**2**) was obtained together with **1** and $[(Me\text{-}TPP)Fe(1\text{-}MeIm)_2]^+Cl^-$(**3**). The ^1H NMR spectra of the pyrrole region at various temperatures were shown in Fig. 1. Although the pyrrole signal of **1** disappeared at -15 °C and reappeared as four signals below -25 °C due to a slow rotation of 2-MeIm ligands,1) that of **2** remained as a relatively sharp singlet even at -46 °C. This signal, however, broadened at lower temperature and almost disappeared at -88 °C. Thus, there is about 70 °C difference in temperature between the two complexes to exhibit a similar shape of the pyrrole signal. Similarly, the p-Me signal of **1** split into two signals below -22 °C, while that of **2** remained as singlet even at -88 °C. If



$[(\text{R-TPP})\text{Fe}(\text{L})(\text{L}')]^+$

1: R=Me, L=2-MeIm, L'=2-MeIm
2: R=Me, L=2-MeIm, L'=1-MeIm
3: R=Me, L=1-MeIm, L'=1-MeIm
4: R=Me, L=2-MeIm, L'=CN^-

we assume that the coalescence temperature of **2** is -88 °C and that the difference in chemical shifts of the p-Me protons in frozen conformation is 120 Hz as in the case of 1, the activation free energy($\Delta G_c^{\neq}$) is calculated to be 8.8 kcal mol^{-1}. Since the p-Me signal appeared as a sharp singlet at -88 °C, the $\Delta G_c^{\neq}$ must be far below this value.

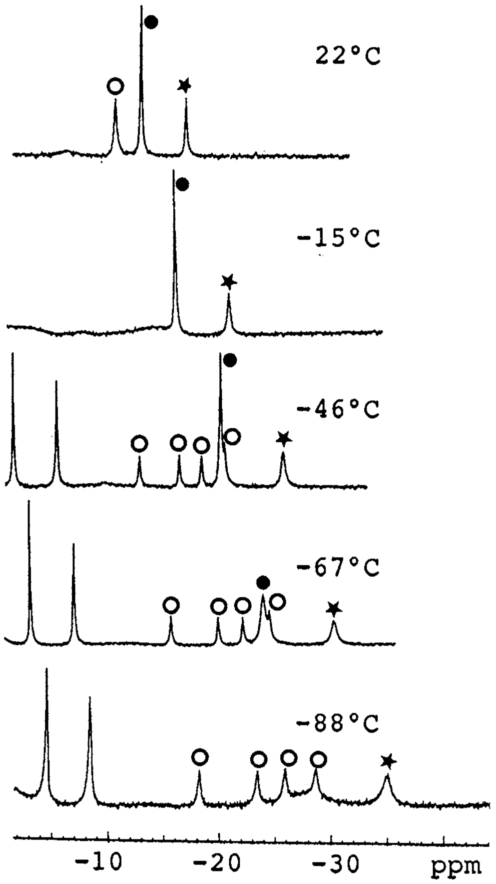


Fig. 1. Temperature dependent ^{1}H NMR of pyrrole region. (1)...○; (2)...●;(3)...★

Another ligand of interest is cyanide (CN^-) because of its strong σ donating and π accepting ability. The mixed ligand complex, [(Me-TPP)Fe(2-MeIm)(CN)] was prepared as a single product by the addition of 5.0 equiv. of 2-MeIm and 1.3 equiv. of KCN into a CD_2Cl_2 solution of the high spin complex. The ^{1}H-NMR spectrum at 20 °C showed o-Me at 1.51(12H) and 1.75 (12H), m-H at 8.21(4H) and 8.29(4H), p-Me at 2.39(12H), and pyrrole-H at -5.4 (8H) ppm. At -88 °C, the pyrrole and o-Me signals disappeared, while the p-Me remained as a singlet. Thus, the $\Delta G_c^{\neq}$ of this complex is estimated to be less than 8.8 kcal mol^{-1}. These results clearly demonstrate that the rate of rotation of 2-MeIm ligand in $[(\text{Me-TPP})\text{Fe}(\text{2-MeIm})_2]^+Cl^-$ is greatly enhanced when the 6th ligand L' is replaced by 1-MeIm or CN^-.

Before discussing the reasons for this anormaly, the conformation of these complexes must be considered. For this purpose, the activation free energies for rotation of 2-MeIm and 1,2-Me_2Im in a series of low spin complexes were determined from the coalescence temperatures (T_c) of the p-

Table 1. Activation Free Energies for Rotation of 2-MeIm and 1,2-Me_2Im in [(R-TPP)Fe(L)(L')]

R	L	L'	Tc °C	$\Delta G_c^{\neq}$ kcal[a] mol^{-1}
H	2-MeIm	2-MeIm	< -88	< 8.8
	1,2-Me_2Im	1,2-Me_2Im	< -88	< 8.8
Me	2-MeIm	2-MeIm	-22.0	12.0
	1,2-Me_2Im	1,2-Me_2Im	-34.4	11.3
	2-MeIm	1-MeIm	< -88	< 8.8
	2-MeIm	CN^-	< -88	< 8.8
Et	2-MeIm	2-MeIm	-10.6	12.7
	1,2-Me_2Im	1,2-Me_2Im	-25.1	11.9
^{i}Pr	2-MeIm	2-MeIm	-4.4	12.9
	1,2-Me_2Im	1,2-Me_2Im	-19.9	12.4

a) 1 cal = 4.184 J.

alkyl signals as listed in Table 1. These data indicate that the activation free energy increases as the alkyl group becomes bulky. The gradual increase in barrier suggests that the conformation at the transition state for rotation is the one where imidazole ring eclipses C(meso)-Fe-C(meso) axis. This, in turn, supports our proposal that the two imidazole ligands are oriented perpendicularly along N-Fe-N axis in the ground state.[1)]

A possible mechanism for the rotation of 2-MeIm ligands in [(R-TPP)Fe-$(2\text{-MeIm})_2]^+Cl^-$ (1) is shown in Fig. 2. In this mechanism, rotation occurs in a stepwise fashion: rotation of one of the ligands by 90° converts perpendicular conformation(**A**) to parallel conformations (**B**) and (**C**). The predominance of **A** over **B** and **C** can be explained in terms of the relief of strain by the S_4 ruffling of the porphyrinato core:[3)] saddle shaped deformation[4)] of the porphyrin ring could weaken the repulsion between hindered ligands and porphyrin ring in **A**, while such a deformation must be smaller in **B** and **C**. As mentioned, the transition state for the imidazole rotation is given by **D** or **D'** where one of the ligands eclipses C(meso)-Fe-C(meso) axis. In contrast, the energy state of **E** where both of the axial ligands eclipse C(meso)-Fe-C(meso) axis is supposed to be higher than those of **D** and **D'**, since the repulsive interactions take place simultaneously between hindered ligands and o-alkyl groups.

If one of the ligands is replaced by the less hindered ligand as in the case of [(R-TPP)Fe(2-MeIm)(1-MeIm)]$^+Cl^-$ (2), the rotation via **E** would become possible as well as the rotation via **D** and **D'**: the repulsion between 2-MeIm and o-alkyl groups can be weakened by the S_4 ruffling of the porphyrinato core which is expected to be more effective in perpendicular conformation (**E**) than in any other conformations. In the case of the cyanide complex (**4**) , the 6th ligand has a cylindrical symmetry to affect no substantial steric effect on the 2-MeIm ligand, thus allowing its rapid rotation.

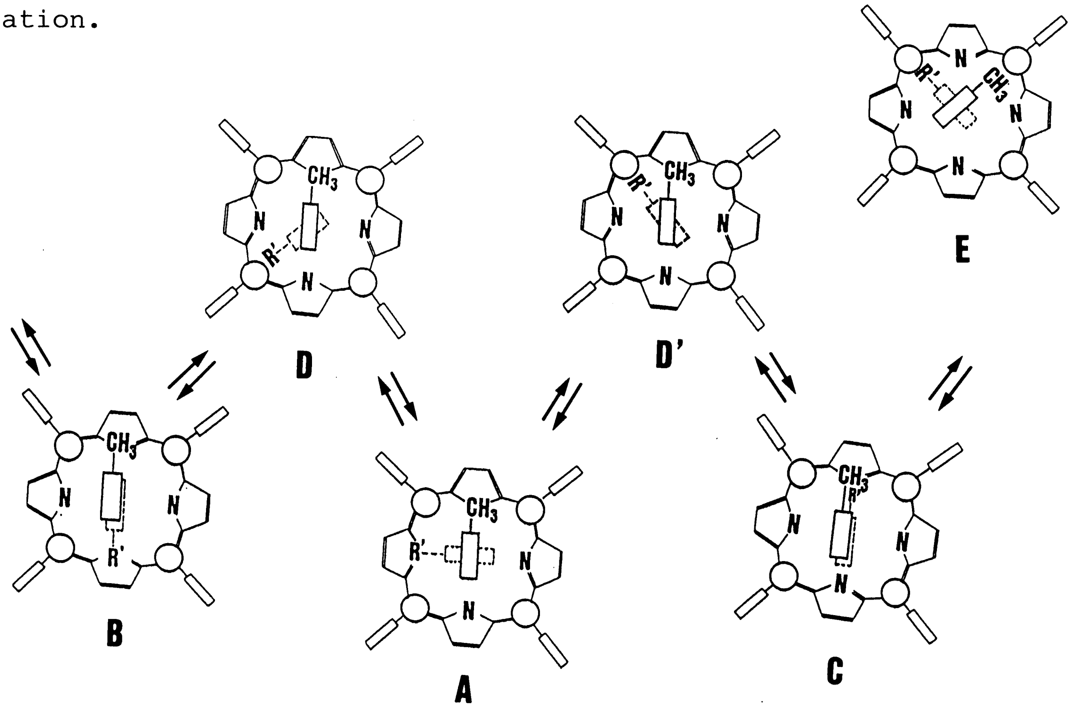


Fig. 2. Mechanism for imidazole rotation.

In summary, the anomalous increase in the rate of rotation, caused by the replacement of one of the axial ligands by the less hindered one, was ascribed to the relief of the strain at the transition state of rotation.

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