Bull. Chem. Soc. Jpn., ***68***, *197—203(1995)*

Effects of *ortho*-Methyl Substituents on the Rate of Dissociation of Imidazole Ligands in Tetraarylporphyrinatocobalt(III) Complexes

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(Received July 22, 1994)

Dissociation rates of the imidazoles in $[Co(tpp)(L)_2]^+$ and $[Co(tmp)(L)_2]^+$, where L is an unhindered imidazole such as 1-methylimidazole or a hindered imidazole such as 2-alkylimidazole, have been determined in chloroform-*d* solution by the ^{1}H NMR saturation transfer method. The rate constants in the tmp complexes were smaller than those of the corresponding tpp complexes in every imidazole ligand examined. The largest difference between these two systems was observed in bis(1,2-dimethylimidazole) complexes and the ratio of the rate constants, k(tpp)/k(tmp), reached as much as 2500 at 90 °C. While the rate constants greatly increased in the tpp system on going from the unhindered imidazole to the hindered one, the increase was rather small in the tmp system. These results were interpreted in tems of the deformation of the porphyrinatocobalt core: Since the two hidered ligands in the tmp complexes are fixed perpendicularly in the cavities created by the deformed porphyrin ring, the distance between the 2-alkyl and the deformed porphyrinatocobalt core would increase, which results in weakening the steric repulsion and slowing down the dissociation rate. The attractive interaction between the *ortho*-methyls and the imidazole π system would also contribute to the stability of the tmp complexes.

Studies on the dissociation process and the rate of dissociation of axially coordinated imidazole ligands in iron(III) porphyrin complexes are quite important to understand the properties of heme proteins, since most of the heme proteins have at least one histidine imidazole ligand at the axial position.[1] In bis(imidazole)tetraphenylporphyrinatoiron(III) complexes $[Fe(tpp)(L)_2]^+$, ligand exchange is known to proceed by a dissociative mechanism (1) in the presence of excess ligand and the mono-ligated species $[Fe(tpp)(L)]^+$ is assumed to be a transition state or an unstable intermediate in the reaction.[2]

$$
\begin{aligned}
[Fe(tpp)(L)(L)]^+ + L^* &\rightleftarrows [Fe(tpp)(L)]^+ + L + L^* \\
&\rightleftarrows [Fe(tpp)(L)(L^*)]^+ + L \quad (1)
\end{aligned}
$$

Recently, we have reported that the *ortho*-methyl subsituents in bis(imidazole)tetramesitylporphyrinatoiron(III)$[Fe(tmp)(L)_2]^+$ complexes rather stabilize the axial imidazole ligands both kinetically and thermodynamically in spite of their apparent steric hindrance to the ligands; the dissociation rates of imidazole ligands in tmp complexes are much smaller than those of the corresponding tpp complexes.[3] Furthermore, the sterically hindered imidazoles such as 2-methylimidazole (2-MeIm) are more effectively stabilized by the *o*-methyls as compared to the sterically unhindered imidazoles such as 1-methylimidazole (1-MeIm); the dissociation rate of 1-MeIm decreased by 1/17 at 25 °C on going from tpp to tmp, while that of 2-Melm decreased by 1/640 for the same change.[3] In order to obtain further information on the *ortho*-methyl effects in metalloporphyrin chemistry, the dissociation rates of imidazole ligands in the corresponding cobalt(III) systems, $[Co^{III}(tpp)(L)_2]^+$ and $[Co^{III}(tmp)(L)_2]^+$, have been examined. Since binding energies of cobalt(III) toward various ligands are in general much larger than those of the corresponding iron(III)-ligand bonds,[4] *ortho*-methyls may affect the dissociation rates in a different manner. In this paper we would like to report the dissociation rates of the imidazole ligands in $[Co^{III}(tpp)(L)_2]^+$ and $[Co^{III}(tmp)(L)_2]^+$ together with the interpretation on the results.

Abbreviations: Abbreviations used in this paper are as follows. H_2tpp and H_2tmp, *meso*-tetraphenylporphyrin and *meso*-tetramesitylporphyrin, respectively; $[Co^{III}(tpp)]Cl$ and $[Co^{III}(tmp)]Cl$, *meso*-tetraphenylporphyrinatocobalt(III) chloride and *meso*-tetramesitylporphyrinatocobalt(III) chloride, respectively; $[Co(tpp)(L)_2]^+$ and $[Co(tmp)(L)_2]^+$, bis(imidazole)tetraphenylporphyrinatocobalt(III) ion and bis(imidazole)tetramesitylporphyrinatocobalt(III) ion where L is imidazole (H-Im), 1-methylimidazole (1-MeIm), 2-methylimidzole (2-MeIm), 2-ethylimidazole (2-EtIm), 2-isopropylimidazole (2-^{i}PrIm), or 1,2-dimethylimidazole (1,2-Me_2Im). In Fig. 1 are given

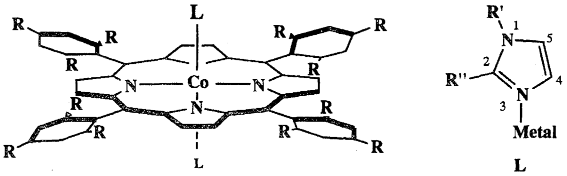

Fig. 1. $[Co(tpp)(L)_2]^+$ (R=H) and $[Co(tmp)(L)_2]^+$ (R=CH_3) studied in this paper. L's are 1-MeIm, 2-MeIm, 2-EtIm, 2-^{i}PrIm, and 1,2-Me_2Im.

$[Co(tpp)(L)_2]^+$ and $[Co(tmp)(L)_2]^+$ together with the numbering of the imidazole ligands.

Experimental

Sunthesis: Tetraphenylporphyrinatocobalt(II), $[Co^{II}(tpp)]$, was prepared according to the literature.[5] The chloroform solution of the cobalt(II) complex was stirred overnight with excess imidazole (L) under air to form bis(imidazole) complex, $[Co^{III}(tpp)(L)_2]^+$.[6] Elution with dichloromethane–methanol (99 : 1) in the chlomatography on neutral alumina yielded a pure bis(imidazole) complex. Similar reactions were carried out to prepare $[Co^{III}(tmp)(L)_2]^+$.

^{1}H NMR Measurement: Chloroform-*d* solutions were prepared under argon. ^{1}H NMR spectra were recorded on a JEOL FX90Q spectrometer operating at 89.55 MHz. In each measurement, sample concentration was kept in the range of 0.007 to 0.010 mol dm^{-3}. Chemical shifts were read based on the internal TMS or solvent peak. For the saturation transfer measurement, argon was introduced into the chloroform-*d* solution consisting of bis(imidazole) complex and ca. 2 equiv of free imidazole through a glass capillary tube in order to remove the oxygen dissolved in the solution. The sample tubes were then sealed and the ^{1}H NMR spectra were measured in the temperature range 16 to 90 °C. The concentration ratios of free and coordinated imidazole ligands, which are necessary to determine the dissociation rates, were accurately measured by the integration of the methyl signals. The spectrometer temperature was calibrated by the method described by Van Geet.[7]

Results and Discussion

Kinetic Measurements: Exchange rates of the coordinated imidazoles were determined in chloroform-*d* solution by the saturation transfer method.[3,8,9] The effective spin-lattice relaxation time of free imidazole methyl protons, $T_{1(\mathrm{f})}^{\mathrm{eff}}$, was experimentally determined using the conventional inversion-recovery method under the saturation of a coordinated imidazole methyl signal. The effective spin-lattice relaxation rate, $1/T_{1(\mathrm{f})}^{\mathrm{eff}}$, in a ligand exchange system is given by Eq. 2, where $T_{1(\mathrm{f})}$ is the spin-lattice relaxation time of the free methyl protons in the absence of exchange and $k_{(\mathrm{f})}$ is the exchange rate constant of the free imidazole. Eq. 2 indicates that a plot of $1/T_{1(\mathrm{f})}^{\mathrm{eff}}$ against inverse temperature gives a curvature in the exchange system because $1/T_{1(\mathrm{f})}$ usually decreases at higher temperature in contrast with the rate constant $k_{(\mathrm{f})}$.

$$1/T_{1(\mathrm{f})}^{\mathrm{eff}} = 1/T_{1(\mathrm{f})} + k_{(\mathrm{f})} \qquad (2)$$

$$M(0)/M(\infty) = k_{\mathrm{f}}T_{1(\mathrm{f})} + 1 \qquad (3)$$

In this situation, the integral intensity of the free methyl signal decreases according to Eq. 3, where $M(\infty)$ and $M(0)$ denote the magnetization of the free methyl signal observed with and without irradiation of the coordinated methyl signal, respectively. In Fig. 2 are given

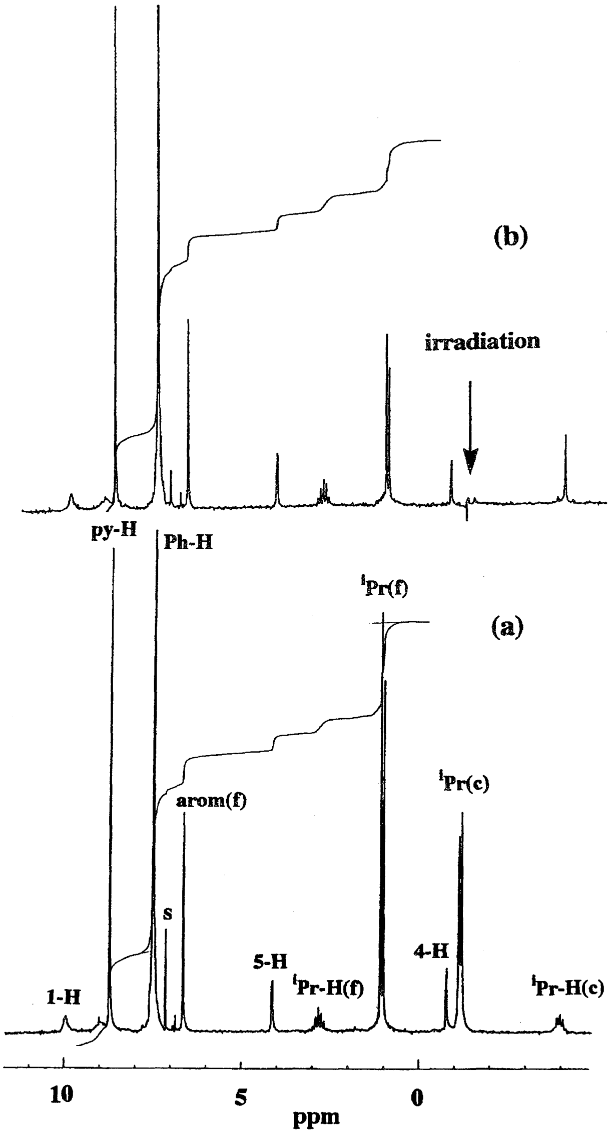

Fig. 2. (a) ^{1}H NMR spectrum of $[Co(tpp)(2\text{-}^i PrIm)_2]^+$ taken at 68 °C. Signal assignment: Ph-H; *meso*-phenyl protons. Py-H; pyrrole protons. 1-H, 4-H, and 5-H; ring protons of the coordinated imidazole. ^{i}Pr(c) and ^{i}Pr-H(c); isopropyl methyl and methine protons of coordinated imidazole. ^{i}Pr(f) and ^{i}Pr-H(f); isopropyl methyl and methine protons of free imidazole. arom(f); aromatic protons of free imidazole. s; chloroform. (b) ^{1}H NMR spectrum of $[Co(tpp)(2\text{-}^i PrIm)_2]^+$ taken at 68 °C with irradiation of the methyl signal of the coordinated 2-^{i}PrIm ligand ^{i}Pr(c). The ratio of magnetizations of the methyl signals, $M(0)/M(\infty)$, was determined to be 2.51 by the integration of these signals.

the ^{1}H NMR spectra of $[\mathrm{Co(tpp)(2\text{-}^{\mathit{i}}PrIm)_2}]^+$ taken at 68 °C with and without irradiation of the methyl signal of coordinated 2-^{i}PrIm. It is clearly shown that the intensity of the free methyl signal decreased to a great extent when the coordinated methyl signal was saturated by irradiation. The ratio $M(0)/M(\infty)$ in Eq. 3 is experimentally obtained by the integration of these signals. Thus, we can determine both $T_{1(\mathrm{f})}$ and k_f by solving simultaneous Eqs. 2 and 3. The saturation transfer method can be applied to exchange systems where every chemical component is at equilibrium. In the present case, $k_\mathrm{f}[\mathrm{L_f}]=k_\mathrm{c}[\mathrm{L_c}]$ where $[\mathrm{L_f}]$ and $[\mathrm{L_c}]$ are the concentrations of free and coordinated ligands, respectively, and k_c is the rate constant of the coordinated ligand in the ligand exchange reaction. As described in the next section, the rate constant k_c is equal to the rate constant for ligand dissociation k_diss and is expressed by Eq. 4.

$$k_\mathrm{diss} = k_\mathrm{c} = 1/T_{1(\mathrm{f})}^{\mathrm{eff}}\{1 - M(\infty)/M(0)\}([\mathrm{L_f}]/[\mathrm{L_c}]) \qquad (4)$$

In principle, rate constants for dissociation can be directly obtained by observing the change in intensity of the *coordinated* methyl signal with and without irradiation of the *free* methyl signal. In the present case, however, it was difficult to obtain the rate constants by this procedure because of a very short spin-lattice relaxation time of the coordinated methyl protons $T_{1(\mathrm{c})}$; exchange rate does not contribute to the effective spin-lattice relaxation rate in Eq. 2. In other words, $1/T_{1(\mathrm{c})}^{\mathrm{eff}}$ was nearly the same as $1/T_{1(\mathrm{c})}$ and increased linearly with inverse temperature, making it difficult to obtain reliable rate constants in the temperature range examined. In Fig. 3 is shown the temperature dependence of the effective spin-lattice relaxation rates of the free (Fig. 3a) and the coordinated (Fig. 3b) imidazole methyl signals of $[\mathrm{Co^{III}(tmp)(2\text{-}EtIm)_2}]\mathrm{Cl}$ and $[\mathrm{Co^{III}(tmp)(1,2\text{-}Me_2Im)_2}]\mathrm{Cl}$ as typical examples. Thus, we determined the rate constant for ligand dissociation by irradiating the *coordinated* imidazole methyl signal and observing the concomitant change in signal intensities of the *free* imidazole methyl signal. As described later, dissociation rates of the tmp complexes are very slow at ambient temperature and they were measurable only at 80 to 90 °C; the ratios $M(0)/M(\infty)$ were nearly 1.0 at lower temperature. Thus, rate constants for dissociation of the tmp complexes were compared at 90 °C as listed in Table 1. In contrast with the tmp complexes, the dissociation rates of the tpp complexes were too fast to determine above 70 °C except for bis(1-MeIm) complex; irradiation of the coordinated methyl signal at 90 °C resulted in the extraordinary decrease of the free methyl signals and made the $M(0)/M(\infty)$ value very unreliable. Thus, rate constants were extrapolated to 90 °C from the low temperature.

Mechanism of Ligand Exchange: As described above, rates for ligand exchange were measured only at 80 to 90 °C in the tmp complexes; measurement at higher termperature was impossible because of the solvent used. Thus, we could not obtain the activation parameters for the ligand exchange reaction. In the tpp complexes, rate constants were obtained at several different temperatures. Eyring's plots of these data yielded the activation enthalpies and entropies. Values for $\Delta H^{\neq}$ and $\Delta S^{\neq}$ in $[\mathrm{Co^{III}(tpp)(L)_2}]\mathrm{Cl}$, in which L is 2-MeIm, 2-EtIm, 2-^{i}PrIm, or 1,2-Me$_2$Im, are 96 kJ mol^{-1} and +36 J mol^{-1} K^{-1}, 100 and +47, 95 and +29, and 97 and +67, respectively. Since these data were obtained from four to five rate data, we have to use them with reservation. However, the large positive values for $\Delta S^{\neq}$ must be the indication that the ligand exchange proceeds by a dissociative mechanism as in

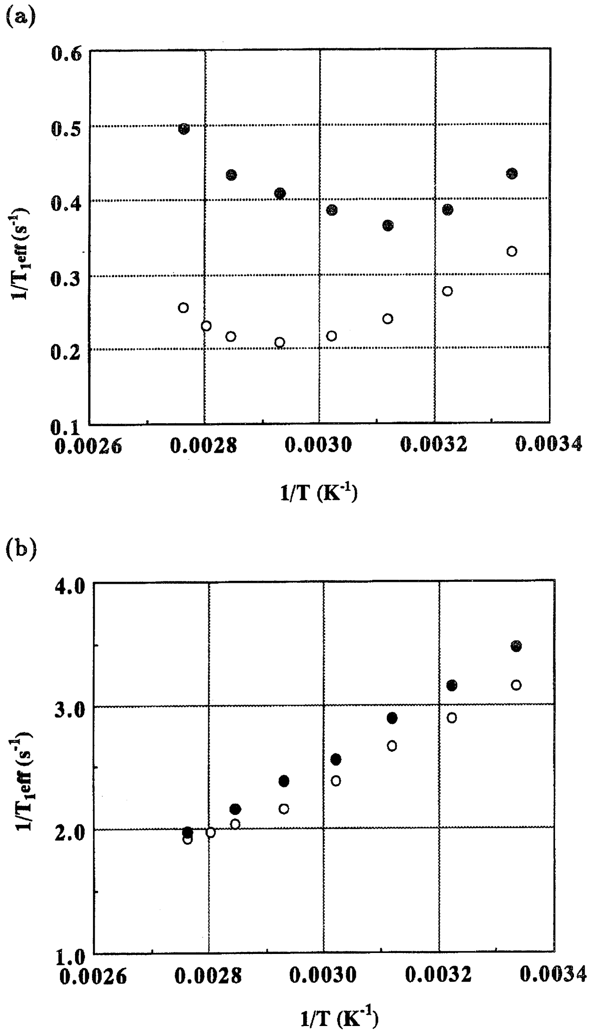

Fig. 3. (a) Temperature dependence of the effective spin-lattice relaxation rates of the free 2-EtIm (○) and 1,2-Me$_2$Im (●) under the irradiation of the corresponding methyl signals in $[\mathrm{Co(tmp)(2\text{-}EtIm)_2}]^+$ and $[\mathrm{Co(tmp)(1,2\text{-}Me_2Im)_2}]^+$, respectively. (b) Temperature dependence of the effective spin-lattice relaxation rates of the methyl protons of the coordinated 2-EtIm (○) and 1,2-Me$_2$Im (●) under the irradiation of the corresponding signals of the free ligands.

Table 1. Rate Constants (s^{-1}) for the Dissociation of Imidazole Ligands in $[M(tpp)(L)_2]Cl$ and $[M(tmp)(L)_2]Cl$ ($M=Co^{III}$ or Fe^{III}) at 90 °C in $CDCl_3$ Solutions
Values in parentheses are $\Delta G^{\neq}$ ($kJ\,mol^{-1}$) at 90 °C.

L	$[Co(tpp)(L)_2]Cl^{a)}$		$[Co(tmp)(L)_2]Cl^{a)}$		$[Fe(tpp)(L)_2]Cl^{b)}$		$[Fe(tmp)(L)_2]Cl^{b)}$	
1-MeIm	2.0×10^{-1}	(94)	0.74×10^{-1}	(97)	6.8×10^{4}	(56)	0.71×10^{4}	(63)
2-MeIm	82×10^{-1}	(83)	3.8×10^{-1}	(92)	160×10^{4}	(46)	1.7×10^{4}	(60)
2-EtIm	60×10^{-1}	(84)	0.96×10^{-1}	(97)	1600×10^{4}	(39)	4.4×10^{4}	(57)
2-^{i}PrIm	48×10^{-1}	(85)	3.4×10^{-1}	(93)	$270\times10^{4a)}$	(45)	$14\times10^{4a)}$	(54)
1,2-Me_2Im	2800×10^{-1}	(73)	1.1×10^{-1}	(96)	1200×10^{4}	(40)	5.2×10^{4}	(57)

a) This work. b) Calculated from Ref. 3 except for $[Fe(tpp)(2\text{-}^iPrIm)_2]Cl$ and $[Fe(tmp)(2\text{-}^iPrIm)_2]Cl$.

Table 2. Chemical Shifts (ppm) of a) $[Co(tpp)(L)_2]Cl$ and b) $[Co(tmp)(L)_2]Cl$ in $CDCl_3$ at 27 °C
Numbers in parentheses indicate the chemical shifts of the alkyl protons.

a) $[Co(tpp)(L)_2]Cl$

				Imidazole protons			
L	Aromatic protons		Py-H	1	2	4	5
1-MeIm	7.6—7.8 7.9—8.1	(12H) (8H)	8.98	(2.04)	0.59	0.10	4.74
2-MeIm	7.4—7.7	(20H)	8.80	13.8	(−2.29)	−0.44	4.14
2-EtIm	7.6—7.7	(20H)	8.78	9.8	(−2.64) (−1.03)	−0.63	4.17
2-^{i}PrIm	7.5—7.6	(20H)	8.84	10.2	(−3.97) (−1.13)	−0.72	4.19
1,2-Me_2Im	7.7—7.8	(20H)	8.92	(2.0)	(−2.29)	−0.35	4.58

b) $[Co(tmp)(L)_2]Cl$

					Imidazole protons			
L	*o*-Me	*m*-H	*p*-Me	Py-H	1	2	4	5
1-MeIm	1.51	7.18	2.53	8.76	(2.08)	0.88	0.47	4.87
2-MeIm	−0.40 −0.09 2.50 2.74	6.61 6.72 7.32 7.40	2.50	8.63	9.8	(−2.20)	−0.26	4.15
2-EtIm	−0.17 0.15 2.75 2.80	6.72 6.82 7.37	2.45	8.56	10.1	(−2.35) (−0.69)	−0.17	4.48
2-^{i}PrIm	−0.31 0.11 2.65 2.79	6.63 6.76 7.35	2.45 2.49	8.52 8.55 8.67 8.72	10.6	(−3.68) (−1.06) (−0.99)	−0.43	4.29
1,2-Me_2Im	−0.18 0.08 2.77	6.75 6.83 7.39	2.47	8.74	(2.00)	(−2.07)	−0.14	4.75

the case of tetraphenylporphyrinatoiron(III) complexes shown in Eq. 1.[2)] Thus, a mono-ligated species would be a transition state or an unstable intermediate. Since we observed no line broadening of the porphyrin signals in bis-ligated complex due to the exchange with the mono-ligated complex which might exist in solution, the concentration of the latter species must be negligibly small if any.

Stable Conformation of the $[Co(tmp)(L)_2]^+$: The ^1H NMR chemical shifts of the complexes examined in this study were summarized in Table 2. The data in Table 2 show that the *meso*-aryl protons of $[Co(tmp)(L)_2]^+$ with hindered imidazole ligands gave multiplets at 27 °C, indicating that these ligands stop rotating even at ambient temperature on the NMR time scale. The result is quite different from that of the corresponding iron complexes $[Fe(tmp)(L)_2]^+$ where signal splitting was observed only at low temperatures.[10,11)] Splitting pattern of the spectrum, four signals for the *o*- and *m*-protons in $[Co(tmp)(2\text{-}MeIm)_2]^+$, suggests that the ligands take a mutually perpendicular alignment above and below the porphyrin ring as in the case of the cor-

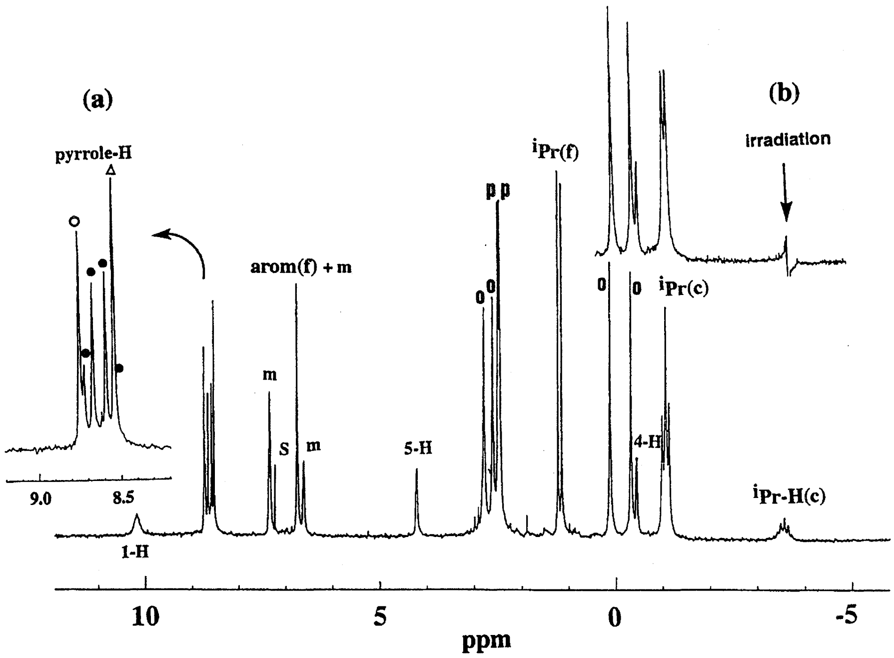

Fig. 4. ^{1}H NMR spectrum of $[Co(tmp)(2\text{-}^iPrIm)_2]^+$ in $CDCl_3$ taken at 28 °C. Signal assignment: *o*, *m*, and *p*; *ortho*-, *meta*-, and *para*-protons of the *meso*-mesityl groups. Other symbols are the same as those in Fig. 2. Inset: (a) Expansion of the pyrrole region, $\delta=8.5$—9.0. AB quartet are signified by ● and two singlets by ○ and △. (b) Irradiation of the signals at $\delta=-3.7$.

responding iron complexes $[Fe(tmp)(L)_2]^+$.[10,11] Other complexes showed smaller numbers of the signals for these protons; complexes with 2-EtIm, 2-^{i}PrIm, and 1,2-Me_2Im exhibited only three signals with 1 : 1 : 2 intensity ratios for the *m*-protons probably due to the accidental coincidence of one of the chemical shifts. Thus, we assume that they also take the same conformation. The ^{1}H NMR spectrum of the bis(2-^{i}PrIm) complex, $[Co(tmp)(2\text{-}^iPrIm)_2]^+$, is given in Fig. 4. The spectrum showed four chemical shifts for the pyrrole protons at quite close positions, $\delta=8.52$, 8.55, 8.67, and 8.72; two of them appeared as an AB quartet and the other two as two singlets as shown in Fig. 4a. The spectrum also exhibited two signals with equal intensity for the *p*-methyls. These results strongly suggest that the two 2-^{i}PrIm ligands are fixed perpendicularly along the diagonal C(*meso*)–Co–C(*meso*) axes as shown in Fig. 5a; fixation along the diagonal N–Co–N axes should give three signals for the *p*-methyl protons.[10—13] Pyrrole and *p*-methyl protons of the other complexes did not show clear splitting probably due to the closer chemical shifts. Imidazole protons of the positions 2 and 4 gave signals at very high fields as listed in Table 2 due to the ring current effect of the porphyrin moiety. Based on these results, stable conformation of the complexes carrying hindered axial imidazoles is concluded to be the one given in Fig. 5a. The fact that each imidazole proton gave one set of signals indicates that the conformation given in Fig. 5a is the only conformation in solution. It is noteworthy that the isopropyl methyl protons of $[Co(tmp)(2\text{-}^iPrIm)_2]^+$ showed two doublets, apparently a triplet, at around −1.0 ppm. This indicates that the two methyls are diastereotopic due to the perpendicular alignment of the fixed imidazole ligands. In fact, irradiation of the methine signals at $\delta=-3.68$ changed two doublets into two singlets at $\delta=-1.06$ and −0.99 as shown in Fig. 4b. On the contrary, isopropyl methyls in $[Co(tpp)(2\text{-}^iPrIm)_2]^+$ gave a doublet even at −60 °C, indicating that the rotation about Co–N(imidazole) bond is fast on the NMR time scale.

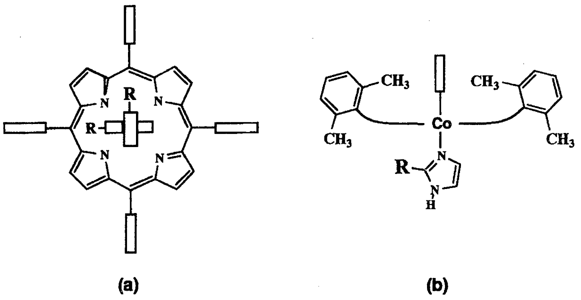

Fig. 5. (a) Stable conformation of $[Co(tmp)(L)_2]^+$ where L's are hindered imidazole ligands carrying 2-alkyl group. (b) Schematic representation of the deformed porphyrin ring.

Comparison between Cobalt(III) and Iron(III) Systems: In a previous paper, we have reported the activation parameters for ligand dissociation in iron(III) porphyrin complexes, $[Fe^{III}(tpp)(L)_2]^+$ and $[Fe^{III}(tmp)(L)_2]^+$, by using both DNMR and saturation transfer methods.[3] In the present study, however, the rates for dissociation were so slow that we could not obtain the rate constants in a wide range of temperature especially in the case of tmp system. Thus, the rate constants at 90 °C were compared between cobalt and iron systems. In order to do that, the rate constants of the iron complexes were extrapolated to 90 °C and they were also given in Table 1.

The data in Table 1 indicate that the rate constants for iron(III) complexes are larger than those of the corresponding cobalt(III) complexes by the factor of 10^5 at 90 °C. The activation free energies $\Delta G^{\neq}$ of the cobalt(III) complexes were calculated at 90 °C and listed in the parentheses of Table 1. The differences in $\Delta G^{\neq}$ between cobalt and the corresponding iron complexes were 32 to 45 $\mathrm{kJ\,mol^{-1}}$. Because of the stronger binding energies in cobalt(III) complexes, Co–N(imidazole) distances are expected to be shorter than the correspondign Fe–N(imidazole) distances. Although we have not yet succeeded in determining the crystal strucutures of $[\mathrm{Co(tmp)(L)_2}]^+$ and $[\mathrm{Fe(tmp)(L)_2}]^+$ with hindered imidazoles ligands (L), the Co–N(imidazole) bond distance of analogous $[\mathrm{Co(tpp)(H\text{-}Im)_2}]^+$ is 1.932 Å[14] and is shorter than those of $[\mathrm{Fe(tpp)(H\text{-}Im)_2}]^+$ and $[\mathrm{Fe(tpp)(1\text{-}MeIm)_2}]^+$ by ca. 0.04 Å.[15,16]

We have mentioned in the previous section that the barriers to rotation of coordinated imidazole ligands in cobalt(III) complexes are larger than those of the corresponding iron(III) complexes. The larger barriers in the cobalt complexes must be ascribed to the Co–N distances as compared with Fe–N; the short Co–N distance would cause a large steric repulsion between the 2-alkyl group of imidazole and the porphyrinatocobalt core at the transition state of rotation where the 2-alkyl group eclipses pyrrole nitrogen. Furthermore, it must be more difficult than the iron complexes to weaken the steric repulsion at the transition state of rotation by the expansion of the Co–N bond because of the strong Co–N bond; in some iron complexes, conversion from one conformation to another takes place by the dissociation and re-association of imidazole ligand which is prohibitted in the cobalt complexes because of the higher barriers to ligand dissociation.[12]

Comparison of the Porphyrin: The data in Table 1 indicate that the dissociation rates of the tpp complexes are much larger than those of the tmp complexes. In the case of the bis(1-MeIm) complexes, rate constant increaed by 2.7 times on going from tmp to tpp. The increase became much larger, 14 to 63 times, in the hindered imidazole complexes. The results suggest that the *o*-methyl groups rather weaken the repulsion between the porphyrin core and the 2-alkyl group of imidazole ligand. The largest increase due to the lack of the *o*-methyl groups was observed in the bis(1,2-$\mathrm{Me_2Im}$) complexes. The increase in the rate constants reached as much as 2500 times; the lowest temperature to observe the decrease in intensity of the free methyl signal in the saturation transfer experiment was 20 °C in the tpp while it was 89 °C in the tmp complex. The crystallographic study of analogous $[\mathrm{Fe(tpp)(2\text{-}MeIm)_2}]^+$ has reveled that the porphyrinatoiron core has an S_4 ruffled structure and the two ligands are placed in the cavities created by the porphyrin core.[17] It is then assumed that the porphyrinatocobalt cores in $[\mathrm{Co(tpp)(L)_2}]^+$ and $[\mathrm{Co(tmp)(L)_2}]^+$ with hindered imidazole ligands also have S_4 ruffled structure in solution, though the interconversion from one ruffled structure to another is fast on the NMR time scale in the former complexes. Due to the deformation of the core, the repulsion between the 2-alkyl group of imidazole and the *o*-methyl groups of mesityl rings in $[\mathrm{Co(tmp)(L)_2}]^+$, which seems to be the major repulsive interaction if the porphyrin core is plannar, could be removed. Since two of the *o*-methyl signals corresponding to four methyls appeared at fairly high fields, $\delta=-0.4$ to 0.2, these methyls must be located close to the imidazole plane. Such a conformation is possible only when porphyrin ring is deformed as shown in Fig. 5b.[10—12] In fact, molecular mechanics study has revealed that the conversion of a planar porphyrin core into a ruffled one is not an energy consuming process.[18] Furthermore, the *o*-methyl groups possibly interact with the imidazole π system in an attractive fashion[19,20] as we have pointed out the possibility based on the thermodynamic study in the iron–porphyrin system.[3,21] The conformation shown in Fig. 5b is quite suitable for the *o*-methyls to interact attractively with the π electrons of the imidazole ring.

When one of the axial ligands starts to dissociate to form a mono-ligated intermediate, cobalt(III) ion concomitantly moves out of the porphyrin cavity as mono-ligated metalloporphyrin complexes generally exhibit. We speculate that the porphyrin structure would change during this process so that the steric repulsion between *o*-methyls and the other imidazole ring increases to make the dissociation rate slower than the corresponding tpp complexes. Thermodynamic data on the equilibrium between mono- and bis-ligated tpp and tmp complexes are necessary to prove this speculation, though they are not accessible at present.

Comparison of the Ligand: In both tpp and tmp systems, dissociation rate increased when unhindered 1-MeIm was replaced by the hindered 2-alkylimidazoles. The degree of increase, however, was greatly different in each system. The rate constants of the tpp system more sensitively changed depending on the axial ligands; the rate constant increased by 41 times on going from $[\mathrm{Co(tpp)(1\text{-}MeIm)_2}]^+$ to $[\mathrm{Co(tpp)(2\text{-}MeIm)_2}]^+$ while it was only 5.1 times in the tmp system. The increase in rate constants was more clearly observed in bis(1,2-$\mathrm{Me_2Im}$) complexes; the rate constant increased by ca. 1400 times in the tpp as compared to 1.5 times in the tmp complexes. We assume that the small dependence of the rate constants in tmp is ascribed to the deformed porphyrinatocobalt core. As mentioned, all of the hindered imidazole ligands are fixed along the diagonal C(*meso*)–Co–C(*meso*) axes in the deformed porphyrin core. The distance between 2-alkyl group and the porphyrinatocobalt core would increase by the deformation. As a result, the major steric repulsion, the repulsion between the 2-alkyl group and the porphyrinatocobalt core, would not increase too much enen if 2-H of imidazole is substituted by the bulkier methyl, ethyl, or isopropyl group. This must be one of the reasons why the dissociation rates in the tmp system are less sesitive to the axial ligands as compared to those in the tpp system. In addition, the attractive interaction between two of the *o*-methyls and imidazole π systems in both sides of the porphyrin ring, which is possible in the deformed porphyrinatocobalt core, might contribute to the small dependence of the rates on the axial ligands.

Another factor that might affect the lability of coordinated imidazole ligands is basicity. In the present system, however, basicity of the ligands showed little correlation with the dissociation rates; although 2-EtIm is stronger as a base ($\mathrm{p}K_\mathrm{b}=6.0$) than 1-MeIm ($\mathrm{p}K_\mathrm{b}=6.7$),[22)] dissociation rate of the former is faster than the latter as shown in Table 1. Thus, the rate for ligand dissociation in these systems is mainly controled by the steric effects between ligand and porphyrin.

This work was partly supported by a Grant in Aid for Scientific Research No. 05640617 from Ministry of Education, Science and Culture. The author also thanks Nishida Foundation for the Promotion of Basic Organic Chemistry for the financial support.

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