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Weak Attractive Interaction between Axially Coordinated Imidazoles and meso-Substituents in Low Spin Tetraarylporphyrinato-iron(III) Complexes

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Thermodynamics for the formation of low spin tetrakis(2,4,6-trialkylphenyl)porphyrinato-iron(III) was studied. In sharp contrast to the case of phenyl porphyrin, triisopropylphenyl analogue showed a larger negative enthalpy of formation with 1,2-dimethylimidazole than with 1-methylimidazole. The finding is clear evidence for the attractive interaction between the ortho-alkyl groups and the imidazole moiety.

Much attention has been paid recently to the weak attractive interaction between nonpolar groups, since such interaction sometimes plays an important role in determining conformational equilibria[1-5] and complexation reactions.[6-8] In previous papers,[9] we reported that the axial imidazoles bind more strongly and dissociate more slowly from low spin tetrakis(2,4,6-trimethylphenyl)porphyrinato-iron(III) as compared with the sterically less hindered tetraphenylporphyrinato-iron(III), and explained these unusual results by assuming the weak attractive interaction between imidazoles and meso-substituents. In order to confirm this assumption, we have prepared some porphyrins carrying bulky alkyl groups at 2, 4, and 6 positions of the meso-phenyl groups and measured the thermodynamic parameters for the formation of low spin complexes. In this paper, we wish to report our observation showing that the attractive interaction does exist between nonpolar groups of some low spin porphyrinato-iron(III) complexes and determine their stability and lability.

Tetraarylporphyrins (PH_2) carrying alkyl groups at 2, 4, and 6 positions of the meso-phenyl groups were synthesized similarly as their methyl analogue.[10] Insertino of iron using $FeCl_2$, followed by the addition of 10% HCl, yielded high spin complex (PFe^+Cl^-) which was then converted to the low spin complex ($PFeL_2^+Cl^-$) by the addition of imidazole base (L) as shown in Eq. 1. Since imidazoles with N-H bond stabilize low spin complexes through N-H•••N hydrogen bond between the free and coordinated imidazoles,[11,12] 1-methylimidazole (1-MeIm) and 1,2-dimethyl-

$$PFe^+Cl^- + 2L \rightleftharpoons [PFeL_2]^+Cl^- \qquad (1)$$

imidazole (1,2-Me_2Im) were used as the axial ligands. The low spin complexes examined in this study are listed in Fig. 1 together with their abbreviations.

Complexes	R	L	Abbreviation
1a	H	1-MeIm	$[(H-P)Fe(1-MeIm)_2]^+$
1b	H	1,2-Me_2Im	$[(H-P)Fe(1,2-Me_2Im)_2]^+$
2a	Me	1-MeIm	$[(Me-P)Fe(1-MeIm)_2]^+$
2b	Me	1,2-Me_2Im	$[(Me-P)Fe(1,2-Me_2Im)_2]^+$
3a	Et	1-MeIm	$[(Et-P)Fe(1-MeIm)_2]^+$
3b	Et	1,2-Me_2Im	$[(Et-P)Fe(1,2-Me_2Im)_2]^+$
4a	^{i}Pr	1-MeIm	$[(^{i}Pr-P)Fe(1-MeIm)_2]^+$
4b	^{i}Pr	1,2-Me_2Im	$[(^{i}Pr-P)Fe(1,2-Me_2Im)_2]^+$

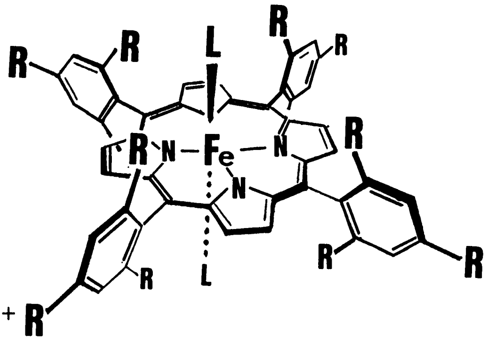

Fig. 1. Low spin iron(III) porphyrins.

Thermodynamic parameters for the formation of low spin complexes were determined by the ^1H NMR integration method[13)] and they are listed in Table 1 together with the temperature range where the spectra were analyzed.

Table 1. Thermodynamic Parameters for the Formation of Low Spin Complexes

Complexes		ΔH kcal mol^{-1} a)	ΔS e. u. b)	ΔG(-35°C) kcal mol^{-1}	Temp °C
$[(H-P)Fe(1-MeIm)_2]^+$	(1a)	-26.5 ± 0.7	-75 ± 3	-8.7	-10 ∿ 27
$[(H-P)Fe(1,2-Me_2Im)_2]^+$	(1b)	-20.6 ± 0.6	-73 ± 3	-3.2	-61 ∿ -30
$[(Me-P)Fe(1-MeIm)_2]^+$	(2a)	-28.0 ± 0.5	-76 ± 2	$-9.9^{d)}$	6 ∿ 42
$[(Me-P)Fe(1,2-Me_2Im)_2]^+$	(2b)	-27.8 ± 1.1	-86 ± 4	$-7.3^{d)}$	-20 ∿ 6
$[(Et-P)Fe(1-MeIm)_2]^+$	(3a)	-27.2 ± 1.0	-69 ± 4	-10.8	6 ∿ 37
$[(Et-P)Fe(1,2-Me_2Im)_2]^+$	(3b)	-28.2 ± 1.1	-87 ± 4	-7.5	-20 ∿ 6
$[(^{i}Pr-P)Fe(1-MeIm)_2]^+$	(4a)	-27.2 ± 1.3	-73 ± 6	-9.8	-8 ∿ 22
$[(^{i}Pr-P)Fe(1,2-Me_2Im)_2]^+$	(4b)	-29.1 ± 1.5	-91 ± 6	-7.4	-20 ∿ -1

a) 1 kcal = 4.18 kJ. b) 1 e. u. = 4.18 J mol^{-1} K^{-1}. c) Enthalpy and entropy of formation were reported to be -26.1 ± 1.2 kcal mol^{-1} and -73 ± 6 e. u., respectively.[12)] d) The ΔΔG(2) obtained by this method gave a little smaller value than the one reported previously.[9)]

The data in Table 1 show that the free energy of formation increases in each porphyrin as the axial ligand changes from 1-MeIm to 1,2-Me_2Im. The result is ascribed to the steric repulsion between the porphyrin ring and the 2-methyl group of the imidazole moiety. Close examination of the data, however, reveals that the increase in free energy differs to a great extent depending upon the porphyrin; while the free energy increases by 5.5 kcal mol^{-1} on going from $[(H-P)Fe(1-MeIm)_2]^+$ (1a) to $[(H-P)Fe(1,2-Me_2Im)_2]^+$ (1b), the increase is only 2.4

kcal mol^{-1} for the corresponding change in $[(^{i}Pr\text{-}P)FeL_2]^+$ (4). Since the free energy of formtaion consists of the enthalpy and entropy of formation, examination of those parameters should give much information on the stability of the complexes. As for the differences in enthalpy of formation between 1-MeIm and 1,2-Me_2Im complexes, $\Delta\Delta H = \Delta H(1\text{-MeIm}) - \Delta H(1,2\text{-}Me_2Im)$, they increase from -5.9 kcal mol^{-1} in $[(H\text{-}P)FeL_2]^+$ (1) to +1.9 kcal mol^{-1} in $[(^{i}Pr\text{-}P)FeL_2]^+$ (4). Correspondingly, the differences in entropy of formation, $\Delta\Delta S = \Delta S(1\text{-MeIm}) - \Delta S(1,2\text{-}Me_2Im)$, increase from -2 e. u. in $[(H\text{-}P)FeL_2]^+$ (1) to +18 e. u. in $[(Et\text{-}P)FeL_2]^+$ (3) and $[(^{i}Pr\text{-}P)FeL_2]^+$ (4).

Before discussing the meaning of these results, we have to consider the accuracy of the thermodynamic parameters. The values for enthalpy and entropy of formation obtained by the ^{1}H NMR integration method are supposed to contain 5 to 10 % error due to a rather limited temperature range where correct ratios of integration can be measured.[12)] Thus, the difference in enthalpy of formation between $[(^{i}Pr\text{-}P)Fe(1\text{-MeIm})_2]^+$ (4a) and $[(^{i}Pr\text{-}P)Fe(1,2\text{-}Me_2Im)_2]^+$ (4b), +1.9 kcal mol^{-1}, could be reversed. In order to find out if this is the case, a $CDCl_3$ solution containing both 1-MeIm (2.0 equiv.) and 1,2-Me_2Im (10.0 equiv.) was added to $(^{i}Pr\text{-}P)FeCl$ (1.0 equiv.) placed in an NMR sample tube and the integration ratios between 4a and 4b were measured over a wide range of temperature. The ratios of formation constants, $\beta_2(4a)/\beta_2(4b)$, changed from 44 at 27 °C to 14 at -51 °C. The plot of $\ln[\beta_2(4a)/\beta_2(4b)]$ vs. inverse temperature (T^{-1}) gave a linear line as shown in Fig. 2. Based on these results, $\Delta\Delta H(4)$ and $\Delta\Delta S(4)$ were calculated to be +1.9 kcal mol^{-1} and +14 e. u., respectively. These values are consistent with the data in Table 1. Similar experiments were carried out for $[(Me\text{-}P)FeL_2]^+$ (2) and $[(Et\text{-}P)FeL_2]^+$ (3). The plot also gave linear lines as Fig. 2 shows. The $\Delta\Delta H$ and $\Delta\Delta S$ were determined to be -0.2 kcal mol^{-1} and +10 e. u. for 2 and +0.7 kcal mol^{-1} and +12 e. u. for 3.

From the discussion described above, we can conclude that the enthalpy and entropy of formation of $[(Et\text{-}P)Fe(1,2\text{-}Me_2Im)_2]^+$ (3b) and $[(^{i}Pr\text{-}P)Fe(1,2\text{-}Me_2Im)_2]^+$ (4b) are, contrary to the case of $[(H\text{-}P)Fe(1,2\text{-}Me_2Im)_2]^+$ (1b), smaller than those

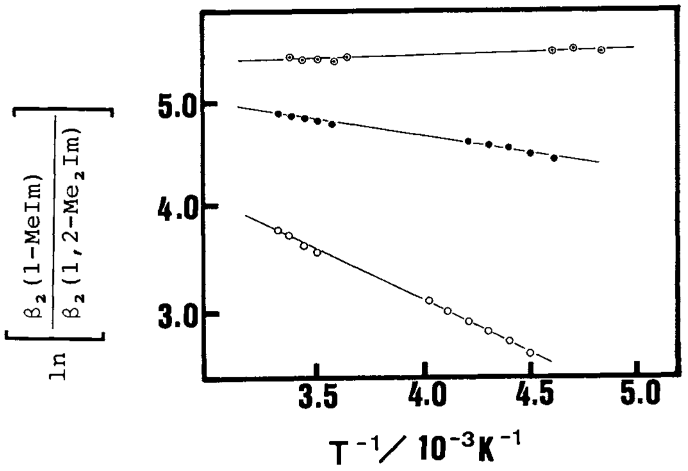

Fig. 2. Plot of $\ln[\beta_2(2a)/\beta_2(2b)]$ (⊙), $\ln[\beta_2(3a)/\beta_2(3b)]$ (●), and $\ln[\beta_2(4a)/\beta_2(4b)]$ (○) against T^{-1}.

of the corresponding 1-MeIm complexes. In other words, a large repulsive interaction between the 2-methyl group of the imidazole moiety and the porphyrin ring in $[(Et\text{-}P)Fe(1,2\text{-}Me_2Im)_2]^+$ (3b) and $[(^iPr\text{-}P)Fe(1,2\text{-}Me_2Im)_2]^+$ (4b) is canceled out by some attractive interactions. It is most reasonable to consider that the bulky alkyl substituents at the ortho positions of the phenyl groups attractively interact with the 2-methyl group and/or pi system of the imidazole. If we assume that the $\Delta\Delta H$(1) corresponds to the repulsive energy between the 2-methyl group and the porphyrin ring, the attractive energy in 4b is calculated to be 7.8 kcal mol^{-1}. The value seems to be too large for such interaction and some other kinds of interactions might be involved. It is, however, quite clear that the attractive interaction does exist between nonpolar groups of these complexes, controlling their stability and lability. Thus, the system is quite suitable to study the nature of weak attractive interaction involving alkyl groups.

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13) The accurately weighed high spin complex was placed in an NMR sample tube under nitrogen atmosphere, to which imidazole base (2.0 equiv.) was added as a $CDCl_3$ solution by means of a micro-syringe. The concentration of the high spin complex was regulated in the range of 0.015 to 0.020 mol dm^{-3} in each experiment. The ^1H NMR spectra were obtained using a JEOL FX90Q spectrometer operating at 89.55 MHz. Equilibrium constants corresponding to Eq. 1 were determined by integration of the m-H of the high spin complex and the methyl signal of the coordinated 1-MeIm or $1,2\text{-}Me_2Im$ at 7 to 9 different temperatures. Thermodynamic parameters were determined from the plot of $\ln(\beta_2)$ vs. T^{-1}.

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