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SUBSTITUTION OF THE AXIAL LIGAND IN BIS(3,4-DIMETHYLPYRIDINE)BIS(2,2'-DIFURYLGLYOXIMATO)IRON(II) BY CYANIDE IN CHLOROFORM

Yoshihiro SASAKI
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

The reaction of bis(3,4-dimethylpyridine)bis(2,2'-difurylglyoximato)iron(II), [Fe(Hfr)$_2$(3,4-me$_2$py)$_2$], with ⓀCN is studied spectrophotometrically in chloroform, where ⓀCN represents KCN with 18-crown-6. The nitrogen base molecules in the complex are substituted stepwisely by cyanide. The mechanisms of the two reaction steps are discussed on the basis of the measurements of the pseudo-first-order rate constants.

Many investigations have been reported on axial ligand substitution reactions in six-coordinated iron(II) complexes with planar macrocyclic ligands.$^{1-4)}$ In the systems studied so far nitrogen bases, oxygen, carbon monoxide, etc. have been used as axial ligand in order to simulate biological functions of hemoproteins. The substitution reactions and those of metalloporphyrins with oxygen proceed substantially through a dissociative mechanism.$^{5)}$ Isolations and identifications of some five-coordinated metalloporphyrins make sure of the mechanism. It was reported that bis(α-diketone dioximato)iron(II) complexes react with cyanide to form anionic complexes of dicyanobis(α-diketone dioximato)iron(II).$^{6)}$ Such a reaction system seems to be one of few objects for understanding of ligand substitution reactions of electrically neutral or negatively charged complexes with anionic ligand in organic solvent. In this work, the author studied the reaction of bis(3,4-dimethylpyridine)bis(2,2'-difurylglyoximato)iron(II), [Fe(Hfr)$_2$(3,4-me$_2$py)$_2$], with potassium cyanide, KCN, in chloroform containing 18-crown-6, 18C6, in order to reveal reaction mechanism of the axial ligand substitution by cyanide in the inert solvent.

3,4-Dimethylpyridine, 3,4-me$_2$py, was distilled from KOH solution prior to use. KCN, 18C6 and chloroform of guaranteed grade were used without further purification. KCN was dissolved in chloroform containing 18C6. [Fe(Hfr)$_2$(3,4-me$_2$py)$_2$] was prepared according to the method reported previously.$^{3)}$ Visible spectra were measured with a Hitachi 323 automatic recording spectrophotometer, equipped with a thermostated cell-holder. Kinetic measurements were made under the conditions giving rise to pseudo-first-order rate constants. The ln(A-A$_\infty$) vs. time plots were linear for at least 3-half-lives.

The spectral change of [Fe(Hfr)$_2$(3,4-me$_2$py)$_2$]-ⓀCN (KCN with 18C6) system with time is shown in Fig. 1. The spectrum of the complex (1 in Fig. 1, λ_{max}=578 nm, ε= 23800 M^{-1} cm^{-1} (1 M = 1 mol dm^{-3})) changed into the spectrum 2 (λ_{max}=561 nm, ε= 22800 M^{-1} cm^{-1}) after 30 min, exhibiting an isosbestic point at 567 nm. The

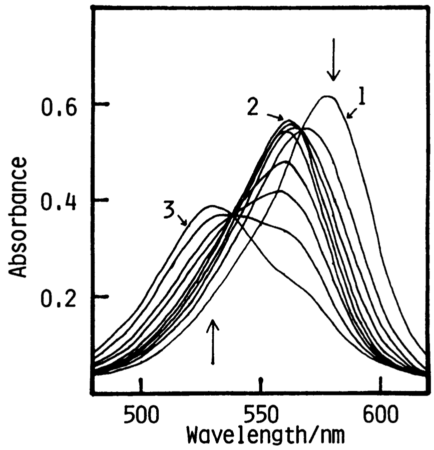

Fig. 1. Time dependence of spectrum of $[\mathrm{Fe(Hfr)_2(3,4\text{-}me_2py)_2}]$-ⓀCN system in chloroform at 25 °C. $[\mathrm{Fe(Hfr)_2(3,4\text{-}me_2py)_2}]=2.58\times10^{-5}$ M, $[\mathrm{3,4\text{-}me_2py}]=2.61\times10^{-4}$ M, $[\text{Ⓚ}\mathrm{CN}]=5.35\times10^{-3}$ M and $[\mathrm{18C6}]=1.65\times10^{-2}$ M (1 M = 1 mol $\mathrm{dm^{-3}}$).

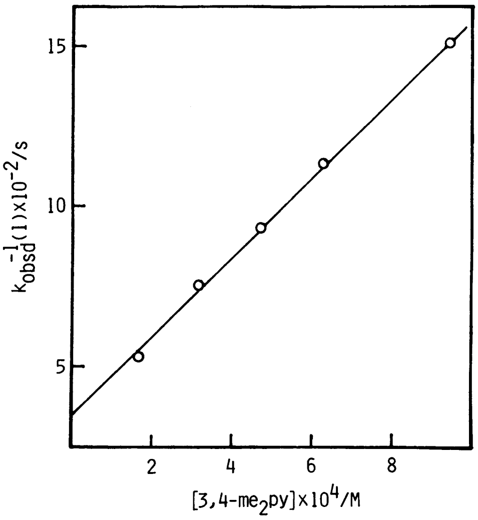

Fig. 2. Plots of $k_{obsd}^{-1}(1)$ vs. $[\mathrm{3,4\text{-}me_2py}]$. $[\text{Ⓚ}\mathrm{CN}]=4.71\times10^{-3}$ M (1 M = 1 mol $\mathrm{dm^{-3}}$).

spectrum 2 changed slowly into the spectrum 3 (λ_{max}=528 nm, ε=19200 $\mathrm{M^{-1}\ cm^{-1}}$) and isosbestic point was found at 538 nm. The latter spectral change was accelerated by photo-irradiation. $[\mathrm{Fe(Hfr)_2(pyridine)_2}]$- and $[\mathrm{Fe(Hfr)_2(butylamine)_2}]$-ⓀCN systems displayed similar spectral changes to that of $[\mathrm{Fe(Hfr)_2(3,4\text{-}me_2py)_2}]$-ⓀCN system and exhibited the spectrum 3 long time after. The results suggest that nitrogen base molecules in $[\mathrm{Fe(Hfr)_2(X)_2}]$ (X=base) are substituted stepwisely by cyanide:

$$[\mathrm{Fe(Hfr)_2(X)_2}] + \text{Ⓚ}\mathrm{CN} \xrightarrow[\text{fast}]{} \text{Ⓚ}[\mathrm{Fe(Hfr)_2(X)(CN)}] + \mathrm{X} \tag{1}$$

$$\text{Ⓚ}[\mathrm{Fe(Hfr)_2(X)(CN)}] + \text{Ⓚ}\mathrm{CN} \xrightarrow[\text{slow}]{} \text{Ⓚ}_2[\mathrm{Fe(Hfr)_2(CN)_2}] + \mathrm{X}. \tag{2}$$

For the reaction 1, a solution of $[\mathrm{Fe(Hfr)_2(3,4\text{-}me_2py)_2}]$ was mixed with a chloroform solution of ⓀCN and the absorbance change at 590 nm was monitored. For the reaction 2, the mixed solution was allowed to stand for 40 min and the absorbance at 561 nm was measured. Influences of the concentrations of 3,4-$\mathrm{me_2py}$ and ⓀCN on the pseudo-first-order rate constant of the reaction 1, $k_{obsd}(1)$, at 25 °C and that of the reaction 2, $k_{obsd}(2)$, at 30 °C are shown in Figs. 2-5. The plots of $k_{obsd}^{-1}(1)$ vs. $[\mathrm{3,4\text{-}me_2py}]$ and $k_{obsd}^{-1}(1)$ vs. $[\text{Ⓚ}\mathrm{CN}]^{-1/2}$ gave good straight lines and the values of the intercepts were equal. The plots of $k_{obsd}^{-1}(2)$ vs. $[\text{Ⓚ}\mathrm{CN}]^{-1}$ and $k_{obsd}^{-1}(2)$ vs. $[\mathrm{3,4\text{-}me_2py}]$ gave also good straight lines. However, the values of the intercepts were 19000 and 14100, respectively.

The mechanisms of the reactions 1 and 2 are expected to be of dissociative type, where the dissociation of base would be rate-determining. An extreme dissociative (D) mechanism is thought for the reaction 1, as reported in other systems.

$$[\mathrm{Fe(Hfr)_2(X)_2}] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Fe(Hfr)_2(X)}] + \mathrm{X} \tag{3}$$

$$[\mathrm{Fe(Hfr)_2(X)}] + \mathrm{CN^-} \xrightarrow{k_2} [\mathrm{Fe(Hfr)_2(X)(CN)}]^- \tag{4}$$

$$\text{Ⓚ}^+ + [\mathrm{Fe(Hfr)_2(X)(CN)}]^- \xrightarrow[\text{rapid}]{} \text{Ⓚ}[\mathrm{Fe(Hfr)_2(X)(CN)}] \tag{5}$$

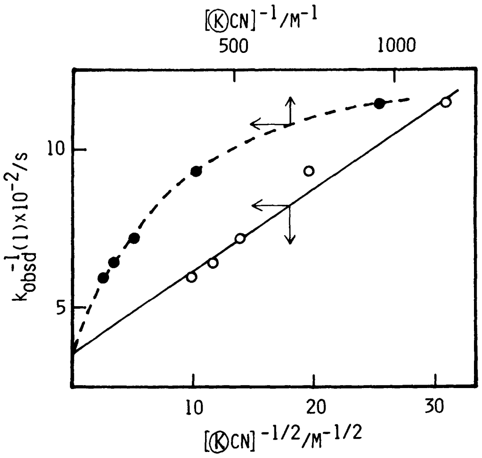

Fig. 3. Plots of $k_{obsd}^{-1}(1)$ vs. [ⓀCN]$^{-1/2}$. [3,4-me$_2$py]=4.70×10^{-4} M (1 M = 1 mol dm^{-3}).

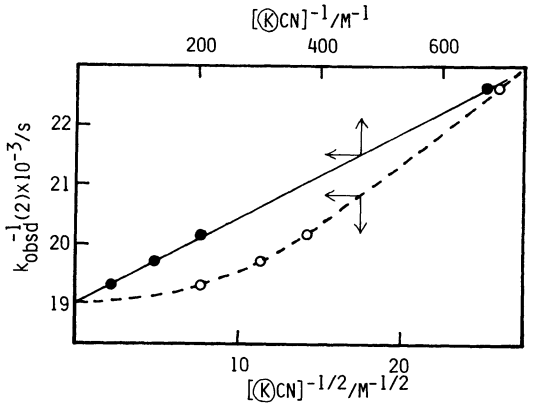

Fig. 4. Plots of $k_{obsd}^{-1}(2)$ vs. [ⓀCN]$^{-1}$. [3,4-me$_2$py]=6.22×10^{-4} M (1 M = 1 mol dm^{-3}).

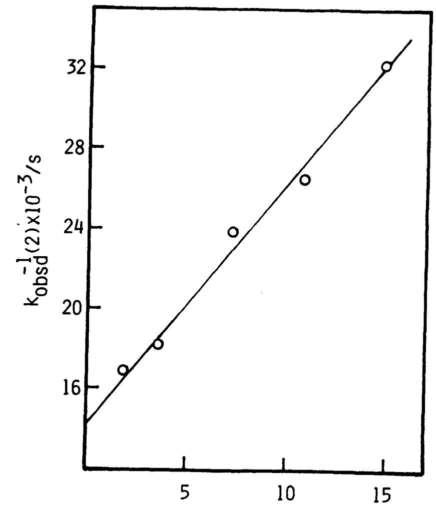

Fig. 5. Plots of $k_{obsd}^{-1}(2)$ vs. [3,4-me$_2$py]. [ⓀCN]=5.2×10^{-3} M (1 M = 1 mol dm^{-3}).

The value of the ion-pair dissociation constant of ⓀCN, K_D, in chloroform is anticipated to be very small. Therefore, the concentration of CN$^-$ can be represented by:

$$[\mathrm{CN}^-] = (K_D[\text{Ⓚ}\mathrm{CN}])^{1/2}. \qquad (6)$$

If we assume a steady-state concentration for the five-coordinated intermediate, $k_{obsd}(1)$ is given by:

$$1/k_{obsd}(1)=(1/k_1)(1+K_D^{-1/2}(k_{-1}/k_2)([\mathrm{X}]/[\text{Ⓚ}\mathrm{CN}]^{1/2})). \qquad (7)$$

Equation 7 fits in well with the reaction behavior shown in Figs. 2 and 3. For the reaction 2, we assume a dissociative interchange (I_d) mechanism where formation of the quadrupole, Ⓚ[Fe(Hfr)$_2$(X)(CN)]·ⓀCN, is taken into account.

$$\underset{(\mathrm{I})}{\text{Ⓚ}[\mathrm{Fe(Hfr)_2(X)(CN)}]} + \text{Ⓚ}\mathrm{CN} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{(\mathrm{II})}{\text{Ⓚ}[\mathrm{Fe(Hfr)_2(X)(CN)}]\cdot\text{Ⓚ}\mathrm{CN}} \qquad (8)$$

$$\text{Ⓚ}[\mathrm{Fe(Hfr)_2(X)(CN)}]\cdot\text{Ⓚ}\mathrm{CN} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \underset{(\mathrm{III})}{\text{Ⓚ}[\mathrm{Fe(Hfr)_2(CN)}]\cdot\text{Ⓚ}\mathrm{CN}} + \mathrm{X} \qquad (9)$$

$$\text{Ⓚ}[\mathrm{Fe(Hfr)_2(CN)}]\cdot\text{Ⓚ}\mathrm{CN} \xrightarrow{k_5} \underset{(\mathrm{IV})}{\text{Ⓚ}_2[\mathrm{Fe(Hfr)_2(CN)_2}]} \qquad (10)$$

Equation 8 represents association between the ion pair, ⓀCN and Ⓚ[Fe(Hfr)$_2$(X)(CN)], and the equilibrium reaction is thought to be rapid. The formation constant of the quadrupole, K_Q, (or the association constant) is expressed as follows:

$$K_Q = [\mathrm{II}]/([\mathrm{I}][\text{Ⓚ}\mathrm{CN}]). \qquad (11)$$

Therefore, if we assume a steady-state concentration for the five-coordinated intermediate, III, $k_{obsd}(2)$ is given by:

$$1/k_{obsd}(2) = (1/k_4)(1 + 1/(K_Q[\text{Ⓚ}CN]))(1 + (k_{-4}/k_5)[X]). \qquad (12)$$

Equation 12 can explain well the reaction behavior shown in Figs. 4 and 5.

Table 1. Rate parameters for $[Fe(Hfr)_2(3,4\text{-}me_2py)_2]$-ⓀCN system

$10^3 k_1$	$2.9\pm0.2\ s^{-1}$	25 °C
$(k_{-1}/k_2)(K_D^{-1/2})$	200	
$10^5 k_4$	$7.5\text{-}8.1\ s^{-1}$	30 °C
k_{-4}/k_5	670-860	
K_Q	$1400\text{-}3500\ M^{-1}$	

Solvent: Chloroform
$1\ M = 1\ mol\ dm^{-3}$.

The rate parameters for $[Fe(Hfr)_2(3,4\text{-}me_2py)_2]$-ⓀCN system, obtained by slope analysis, are tabulated in Table 1. The k_1 value estimated in this study was in agreement with that of $[Fe(Hfr)_2(3,4\text{-}me_2py)_2]$-CO system ($3.4\times10^{-3}\ s^{-1}$), supporting the D mechanism for the reaction 1.[3] Based on the K_D values of some potassium salts with crown ethers in organic solvents, the K_D of ⓀCN in chloroform (dielectric constant=4.7) is expected to be of the order of $\approx10^{-5}$ M.[7] Therefore, the value of k_{-1}/k_2 ratio is approximately equal to 1, which seems to be a conceivable value. For the reaction 2, some plausible mechanisms were examined, which were D and I_d mechanisms assuming to start with the dissociation of X in Ⓚ$[Fe(Hfr)_2(X)(CN)]$ and a I_d mechanism taking account of the triple ion, Ⓚ$[Fe(Hfr)_2(X)(CN)]\cdot CN^-$. These mechanisms were not consistent with the reaction behavior shown in Figs. 4 and 5. The K_Q value estimated, which seems to be considerably large, is in the same degree with those of the formation constants of ion-pair dimers for some tetrabutylammonium salts in benzene (dielectric constant=2.3).[8] The quadrupole, Ⓚ$[Fe(Hfr)_2(3,4\text{-}me_2py)(CN)]\cdot$ⓀCN, was not recognized in this study, based on measurements of visible spectra. Such a large K_Q value may be possible in the case that the ion pair, Ⓚ$[Fe(Hfr)_2(3,4\text{-}me_2py)(CN)]$, possesses a large dipole moment.

References

1) D. V. Stynes, Inorg. Chem., 16, 1170 (1977).
2) I. W. Pang and D. V. Stynes, Inorg. Chem., 16, 2192 (1977).
3) Y. Sasaki, Bull. Chem. Soc. Jpn., 56, 881 (1983) and the references cited therein.
4) N. K. Kildahl, K. J. Balkus, Jr., and M. J. Flynn, Inorg. Chem., 22, 589 (1983).
5) B. R. James, "The Porphyrins," ed by D. Dolphin, Academic Press, New York (1978), Vol. 5, p. 205.
6) B. W. Dale, R. J. P. Williams, P. R. Edwards, and C. E. Johnson, Trans. Faraday Soc., 64, 620 (1968).
7) A. I. Popov and Jean-Marie Lehn, "Coordination Chemistry of Macrocyclic Compounds," ed by G. A. Melson, Plenum Press, New York (1979), p. 537.
8) E. Grunwald, S. Highsmith, and Ting-Po I, "Ions and Ion pairs in Organic Reactions," ed by M. Szwarc, John Wiley and Sons, New York (1974), Vol. 2, p. 471.

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