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The Axial-Ligand Replacement of the [Tetrakis(1-methyl-4-pyridinio)porphine]iron(III) Ion by the Cyanide Ion in a Highly Alkaline Aqueous Solution

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The axial-ligand replacement of the [Tetrakis(1-methyl-4-pyridinio)porphine]iron(III) ion by the cyanide ion was investigated in a highly alkaline aqueous solution by means of the spectrophotometric method at 25 °C. In the course of the replacement, a protolytic equilibrium between monocyanomonoaqua- and monocyanomonohydroxo complex ions was observed; the $p(K_a/\mathrm{mol\,dm^{-3}})$ value of the monocyanomonoaqua complex ion was found to be 12.2 ± 1.1. In the formation of the dicyano complex ion, the rate-determining step was the second replacement of axial ligands, i.e., from the monocyano complex ion to the dicyano-complex ion; according as the pH is 11 or 13, the equilibrium constant was found to be 38.0 $\mathrm{mol^{-1}\,dm^3}$ or 11.0, while the rate constant was 1.07×10^{-3} or 4.23×10^{-3} $\mathrm{mol^{-3}\,dm^3\,s^{-1}}$.

Iron porphyrin complexes are regarded as model compounds for studying the redox properties in the respiratory-electron-transport chain, which contains such elements as cytochromes.[1,2] In order to clarify the basic properties of iron porphyrins, we have been investigating the equilibrium situation and properties of the [Tetrakis(1-methyl-4-pyridinio)porphine]iron(III) ion (abbreviated as Fe(III)–TMPyP) in aqueous solutions.[3] As a result of the investigation, it has been found that monomeric Fe(III)–TMPyP$(H_2O)_2$, Fe(III)–TMPyP$(OH)(H_2O)$, and Fe(III)–TMPyP$(OH)_2$ are, in turn, the predominant species in the solutions with pH values of pH<5.5, 5.5<pH<12 and pH>12 respectively; it has also been found that monomeric Fe(II)–TMPyP$(H_2O)_2$ and Fe(II)–TMPyP$(OH)(H_2O)$ are predominant in the ranges of pH<11.5 and pH>11.5 respectively.

As subsequent experiments, we intended to investigate the effects of axial ligands on the redox potential. The cyanide ion was chosen as an axial ligand to investigate at first, because the preliminary experiments on the axial-ligand replacement of aqua- or hydroxo-Fe(III)–TMPyP ion by various ligands showed that only the addition of the cyanide ion induced shifts both in the position of the Soret band and in the redox potential of the central metal (Fe(III)/Fe(II)).

The substitution equilibria for various axial ligands of Fe(III)–TMPyP ions have previously been reported by Fleischer et al.,[4,5] Pasternack et al.,[6,7] Goff and Morgan,[8,9] and Weinraup et al.[10] However, for a monocyano Fe(III)–TMPyP ion in an aqueous solution, the kind of axial ligand at the trans position to CN^- can not be inferred from the descriptions in those papers or also in the paper relating to the axial-ligand replacement of Cr(III)–TMPyP by CN^-.[11]

The main purpose of the present paper is to infer the axial ligand at the trans position to the cyano group in the monocyano Fe(III)–TMPyP ion in an aqueous solution and to determine the equilibrium constant in the protolytic equilibrium between different monocyano ions and kinetic parameters for the axial replacement of the Fe(III)–TMPyP ion by the cyanide ion.

Experimental

Fe(III)–TMPyP perchlorate was prepared by metal insertion into TMPyP tetra(*p*-toluenesulfonate) (Dojindo Laboratories) with Mohr's salt according to the method of Hambright and Fleischer,[12] with a slight modification, and was stored in an about 3.5×10^{-4} $\mathrm{mol\,dm^{-3}}$ aqueous solution. All the other chemicals were of a guaranteed reagent grade (Wako Pure Chemical Industries) and were used without further purification.

The concentration of the Fe(III)–TMPyP stok solution was accurately determined spectrophotometrically by the use of a molar-absorption coefficient at 403 nm: 1.02×10^5 $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$ at pH 2 and an ionic strength of 0.1 $\mathrm{mol\,dm^{-3}}$.[6] Sample solutions were prepared by diluting the stock solution with deionized distilled water. The pH of the sample solution was then adjusted with a sodium hydroxide solution. The ionic strength was adjusted to 0.1 $\mathrm{mol\,dm^{-3}}$ with a sodium sulfate solution except when the pH was above 13.

A Hitachi 228 spectrophotometer was used for the spectrophotometric investigation. Measurements of the pH were made on a TOA HM-5B pH meter. The concentrations of the cyanide ion are expressed by the values calculated from the weight of the potassium cyanide dissolved.

The equilibrium constant and the number of protons transferred between the different monocyano complexes were obtained by spectrophotometric pH titration at a constant pCN; on the contrary, the formation constant and the number of cyanide ions transferred between monocyano and dicyano complexes were obtained by pCN titration at a constant pH.

The rate of cyano substitution was measured as follows. A small volume of a 1.00 $\mathrm{mol\,dm^{-3}}$ KCN aqueous solution, adjusted to the appropriate pH, was added quickly to a dilute Fe(III)–TMPyP aqueous solution adjusted to the same pH as the KCN solution. The resulting mixed solution, which included a large excess of cyanide ions to Fe(III)-TMPyP, was stirred vigorously. Then, the time-course of the absorbance at the Soret peak of the dicyano complex in the mixed solution was followed on the spectrophotometer.

All the measurements were performed at 25 °C.

Results and Discussion

Time-Course of Absorption Spectra after the Addition of CN$^-$. Fe(III)-TMPyP species in aqueous solutions are predominantly present as a monoaquamonohydroxo complex at pH 11 and as a dihydroxo complex at pH 13.[3] A solution of potassium cyanide was added to a Fe(III)-TMPyP solution of pH 11 or 13. Figure 1 shows the time-course of the visible spectra of the Fe(III)-TMPyP solutions after the addition of KCN. The dotted lines represent the spectra of CN$^-$-free solutions; the other lines are the spectra of the mixed solutions containing Fe(III)-TMPyP and KCN at concentrations of 1.00×10^{-5} mol dm^{-3} and 5.00×10^{-2} mol dm^{-3} respectively. At both pH 11 and 13, the Soret band shows the characteristic maximum absorption peaks for the species formed by the 1st or 2nd substitution by CN$^-$. On the other hand, the Q (0—0 and 0—1) band shows the blue shift by ca. 20 nm due to the 1st substitution by CN$^-$, while, because of the 2nd substitution by CN$^-$, no shift, but an increase in the Q band, was observed. These spectral changes may be attributable to the following step-by-step substitution reactions, Eq. 1 or 2, at pH 11 or 13:

$$\underset{\text{(I)}}{\text{Fe(III)-TMPyP(H}_2\text{O)(OH)}} \rightleftharpoons \text{(II)} \rightleftharpoons \underset{\text{(III)}}{\text{Fe(III)-TMPyP(CN)}_2}, \qquad (1)$$

$$\underset{\text{(I}'\text{)}}{\text{Fe(III)-TMPyP(OH)}_2} \rightleftharpoons \underset{\text{(II}'\text{)}}{\text{Fe(III)-TMPyP(OH)(CN)}} \rightleftharpoons \underset{\text{(III)}}{\text{Fe(III)-TMPyP(CN)}_2}. \qquad (2)$$

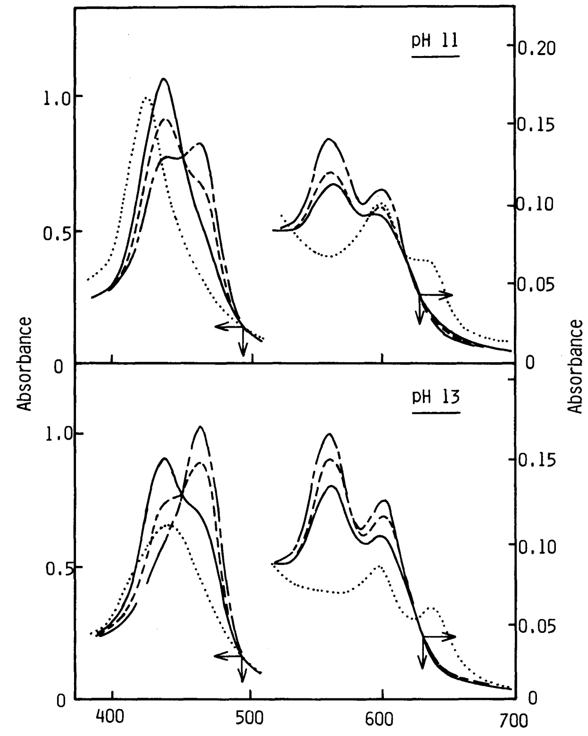


Fig. 1. The time-course of absorption spectra of Fe(III)-TMPyP aqueous solutions after addition of cyanide ion.
……: No addition, ——: 2 min, — —: 30 min, ––––: 4 h 10 min (pH 11) or 2 h (pH 13).
Fe(III)-TMPyP: 1.00×10^{-5} mol dm^{-3}, KCN: 5.00×10^{-2} mol dm^{-3}.

As may be seen in Fig. 1, the monocyano complexes, II and II′, both have Soret bands with the same maximum absorption wavelength, 437 nm, and their Q band spectra are similar in shape.

The 2nd substitution is much slower than the 1st substitution. An electron-withdrawing property of CN$^-$, caused by back-donation to its empty antibonding π-orbital, probably makes the 2nd substitution slow down compared to the 1st step. Within two minutes after the addition of CN$^-$, the 1st step of substitution is almost complete, while the 2nd step seems to have proceeded slightly, as is shown in Fig. 1.

At pH 13, the absorption band of 437 nm (the Soret band of II′) was scarcely observed after two hours, while at pH 11 the peak of 437 nm remained distinctly even after four hours. Such observation indicates that the 2nd step of substitution at pH 13 is faster than that at pH 11, even though the concentration of hydroxide ions in the pH 13 solution is about 100 times that in the pH 11 solution. If the II species is the same as II′, the rate of the 2nd substitution step at pH 11 should be faster than that at pH 13. Therefore, in spite of the similarity in shape of the two absorption spectra, the II species differs from the II′ species; they are identified as Fe(III)-TMPyP(H_2O)(CN) and Fe(III)-TMPyP(OH)(CN) respectively.

Acid-Dissociation Equilibrium of Fe(III)-TMPyP-(H_2O)(CN). Figure 2 shows the spectrophotometric pCN titration curves of Fe(III)-TMPyP obtained at the Soret-band maximum of the III species, 465 nm. A change in absorption attributable to an equilibrium between monocyano and dicyano complexes is observed in the pCN range from 1 to 3, and in the pCN range above 4 the absorption is gradually reduced with an increase in the value of pCN because of a dissociation equilibrium of

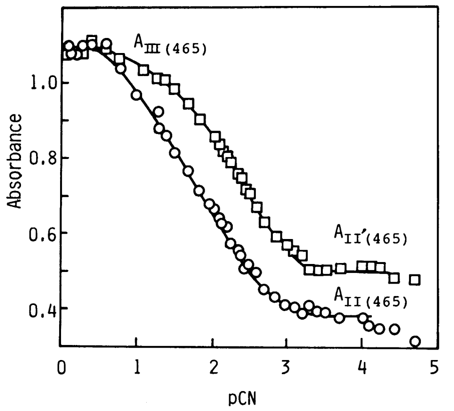


Fig. 2. Spectrophotometric pCN titration curves for Fe(III)-TMPyP in aqueous solutions at pH 11 (○) and 13 (□).
$A_{II(465)}$: Absorbance of monocyano complex at pH 11.
$A_{II'(465)}$: Absorbance of monocyano complex at pH 13.
$A_{III(465)}$: Absorbance of dicyano complex.
Fe(III)-TMPyP: 1.00×10^{-5} mol dm^{-3}.

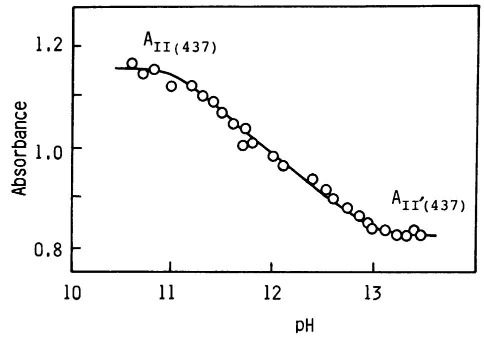


Fig. 3. Spectrophotometric pH titration curve at 437 nm for Fe(III)-TMPyP aqueous solutions containing cyanide ion.
Fe(III)-TMPyP: 1.00×10^{-5} mol dm^{-3}.
KCN: 3.00×10^{-4} mol dm^{-3}.

the two monocyano complexes. In this figure, $A_{III(465)}$ represents the absorbance at a high concentration of CN⁻, while $A_{II(465)}$ and $A_{II'(465)}$ represent the absorbances at pH 11 and 13 respectively at a low concentration of CN⁻, i.e., 3<pCN<4. Although the average values of $A_{III(465)}$ obtained separately at pH 11 and 13 virtually agreed with each other, the values of $A_{II(465)}$ and $A_{II'(465)}$ differ from one another, suggesting a change in the monocyano complex species with the pH.

Therefore, a spectrophotometric pH titration of complex solutions of pCN 3.52 was carried out over the pH range from 10.5 to 13.5 at 437 nm, which was the Soret maximum wavelength of the II and II′ species. The monocyano complexes are the predominant species in solutions with this pCN value, as is shown in Fig. 2. Figure 3 shows the titration curve thus obtained, indicating the existence of the following equilibrium between the II and II′ species:

$$\underset{\text{(II)}}{\text{Fe(III)-TMPyP(H}_2\text{O)(CN)}} \xrightleftharpoons{K_a} \underset{\text{(II}')}{\text{Fe(III)-TMPyP(OH)(CN)}} + n\text{H}^+ \tag{3}$$

$$K_a = \frac{[\text{II}'][\text{H}^+]^n}{[\text{II}]} \tag{4}$$

The value of pK_a was obtained from the data in Fig. 3 using Eq. 5:

$$\log \frac{|A_{II(437)} - A_{(437)}|}{|A_{(437)} - A_{II'(437)}|} = n\cdot\text{pH} - \text{p}K_a \tag{5}$$

A plot of the left-hand side of Eq. 5 vs. pH gives a straight line, as is shown in Fig. 4. The values of p(K_a/mol dm^{-3})[†] and n were estimated to be 12.2±1.1 and 1.02±0.09 from the slope and the intercept respectively of this straight line. Since the n value is close to unity, the equilibrium between Fe(III)-TMPyP(H_2O)(CN) and Fe(III)-TMPyP(OH)(CN) consists of one proton-transfer step. The molar absorption coefficients of the II, II′, and III species at 437 and 465 nm were also obtained from the data in Figs. 2 and 3; they are listed in Table 1.

Formation Constant of Fe(III)-TMPyP(CN)$_2$. Figure 1 indicates that the first step of CN⁻ substitution is rapid enough and that the second step is the rate-determining step in the presence of a large excess of CN⁻ to the complex. Therefore, the concentrations of the I and I′ species can be ignored except for an extremely early stage of substitution. Then, the reactions observed at pH 11 and 13 are approximately represented by:

$$\text{II} + \text{CN}^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \text{III} \tag{6}$$

and:

$$\text{II}' + \text{CN}^- \underset{k_b'}{\overset{k_f'}{\rightleftharpoons}} \text{III} + \text{OH}^- \tag{7}$$

Table 1. Molar-Absorption Coefficients at 437 and 465 nm of Monocyano and Dicyano Complexes at pH 11 and 13

Wavelength	437 nm	465 nm
pH 11		
ε_{II}/mol^{-1} dm^3 cm^{-1}	1.15×10^5	3.87×10^4
ε_{III}/mol^{-1} dm^3 cm^{-1}	—	1.10×10^5
pH 13		
$\varepsilon_{II'}$/mol^{-1} dm^3 cm^{-1}	8.30×10^4	5.06×10^4
ε_{III}/mol^{-1} dm^3 cm^{-1}	—	1.09×10^5

[†] K_a is the equilibrium constant in terms of concentration.

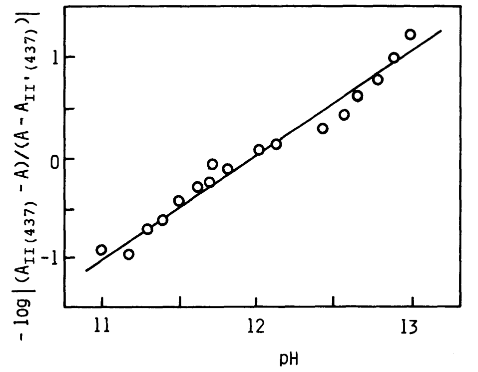


Fig. 4. Plot of left-hand side of Eq. 5 vs. pH.

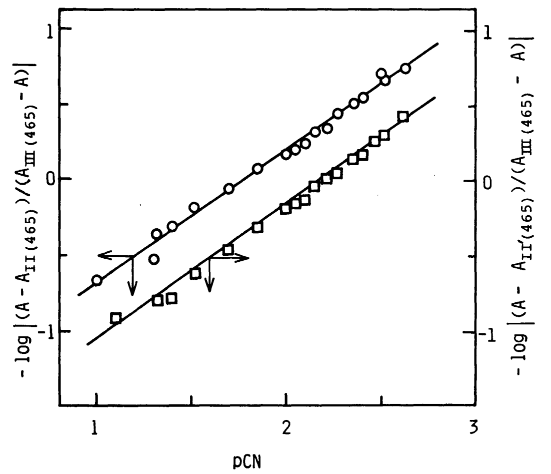


Fig. 5. Plots of left-hand sides of Eqs. 10 (○) and (11) (□) vs. pCN.

respectively, where k_f and k_f' are the formation rate constants of the III species and where k_b and k_b' are the rate constants of the reverse reactions. The values of the 2nd step-by-step formation constants of the III species at pH 11 and 13, as expressed by Eqs. 8 and 9, can be determined from the data in Fig. 2 and the molar absorption coefficient of the II and II′ species, by the use of Eqs. 10 and 11:

$$K = \frac{[\mathrm{III}]}{[\mathrm{II}][\mathrm{CN^-}]} = \frac{k_f}{k_b}, \tag{8}$$

$$K' = \frac{[\mathrm{III}][\mathrm{OH^-}]}{[\mathrm{II'}][\mathrm{CN^-}]} = \frac{k_f'}{k_b'}, \tag{9}$$

$$-\log\frac{|A_{(465)} - A_{\mathrm{II}(465)}|}{|A_{\mathrm{III}(465)} - A_{(465)}|} = \mathrm{p}K + \mathrm{pCN}, \tag{10}$$

$$-\log\frac{|A_{(465)} - A_{\mathrm{II'}(465)}|}{|A_{\mathrm{III}(465)} - A_{(465)}|} = \mathrm{p}K' + \log[\mathrm{OH^-}] + \mathrm{pCN}. \tag{11}$$

Figure 5 shows the linear relationship between the left-hand side of Eq. 10 or 11 and pCN. The transfer number of CN⁻ and the values of pK and pK' were obtained from the slope and the intercept at pCN=0 of these lines; they are listed in Table 2. The number of transferred CN⁻ at pH 11 is considerably smaller than unity.

Table 2. Equilibrium Constants and Number of Transfered Cyanide Ions between Monocyano and Dicyano Complexes at pH 11 and 13

	K/mol^{-1} dm^3	K'	n
pH 11	38.0	—	0.884
pH 13	—	11.0	0.919

Formation Rate Constant of the Dicyano Complex. Assuming Eq. 6 or 7 for the observed substitution, the formation rate or the III species is represented by:

$$\frac{d[\mathrm{III}]}{dt} = k_f[\mathrm{P}][\mathrm{CN^-}] - k_f\left([\mathrm{CN^-}] + \frac{1}{K}\right)[\mathrm{III}] \tag{12}$$

or:

$$\frac{d[\mathrm{III}]}{dt} = k_f'[\mathrm{P}][\mathrm{CN^-}] - k_f'\left([\mathrm{CN^-}] + \frac{[\mathrm{OH^-}]}{K'}\right)[\mathrm{III}], \tag{13}$$

where [P] is the total concentration of the complex species. In the presence of a large excess of CN⁻ to the complex species, therefore, the rate equation for substitution is expressed by Eq. 14 or 15 according as the pH value is 11 or 13:

$$\ln\left(\alpha - \frac{[\mathrm{III}]}{[\mathrm{P}]}\right) = \ln\alpha - k_f\beta t, \tag{14}$$

$$\ln\left(\alpha' - \frac{[\mathrm{III}]}{[\mathrm{P}]}\right) = \ln\alpha' - k_f'\beta' t, \tag{15}$$

where $\alpha=1/(1+1/K[\mathrm{CN^-}])$, $\alpha'=1/(1+[\mathrm{OH^-}]/K'[\mathrm{CN^-}])$, $\beta=1/K+[\mathrm{CN^-}]$ and $\beta'=[\mathrm{OH^-}]/K'+[\mathrm{CN^-}]$.

If the formation constant of the III species and the molar-absorption coefficient of the monocyano and dicyano complexes are known, the concentration of the III species can be obtained from the observed absorbance at an appropriate wavelength using Eq. 16 or 17 according as the pH value is 11 or 13:

$$[\mathrm{III}] = \frac{\mathrm{Abs}}{\varepsilon_{\mathrm{II}}/K[\mathrm{CN^-}] + \varepsilon_{\mathrm{III}}} \tag{16}$$

or:

$$[\mathrm{III}] = \frac{\mathrm{Abs}}{\varepsilon_{\mathrm{II'}}[\mathrm{OH^-}]/K'[\mathrm{CN^-}] + \varepsilon_{\mathrm{III}}}, \tag{17}$$

where Abs is the absorbance at a certain wavelength and where $\varepsilon_{\mathrm{II}}$, $\varepsilon_{\mathrm{II'}}$, and $\varepsilon_{\mathrm{III}}$ are the respective molar-absorption coefficients of the II, II′ and III species at the same wavelength. Consequently, the rate constants, k_f and k_f' can be obtained by the use of Eqs.

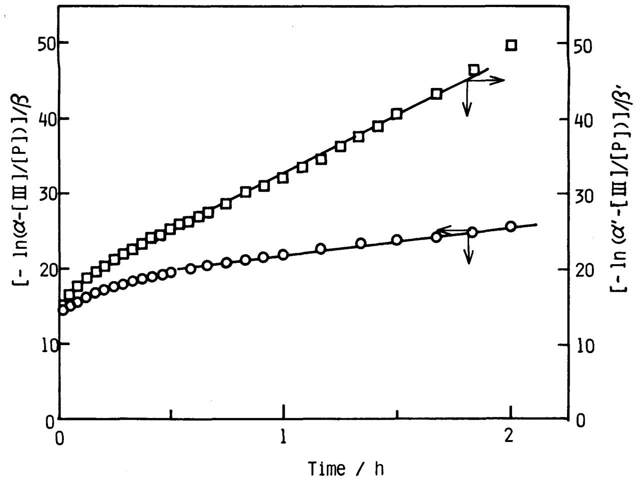
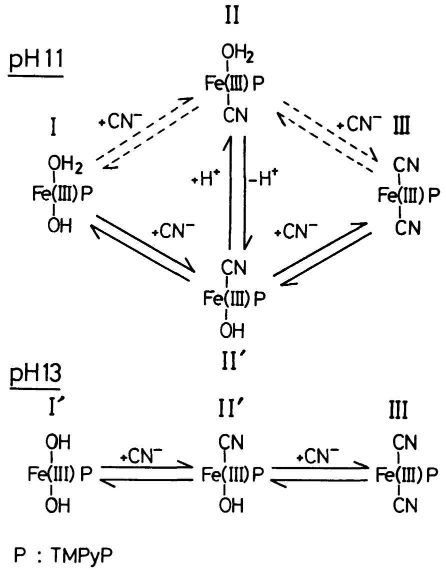


Fig. 6. Plots of $[-\ln(\alpha-[\mathrm{III}]/[\mathrm{P}])]/\beta$ vs. time (○ at pH 11) and $[-\ln(\alpha'-[\mathrm{III}]/[\mathrm{P}])]/\beta'$ vs. time (□ at pH 13).

Table 3. Rate Constants of the Axial Replacement of Monocyano and Dicyano Complexes

pH 11	
k_f/mol^{-1} dm^3 s^{-1}	1.07×10^{-3}
k_b/s^{-1}	2.82×10^{-5}
pH 13	
k'_f/mol^{-1} dm^3 s^{-1}	4.23×10^{-3}
k'_b/mol^{-1} dm^3 s^{-1}	3.83×10^{-4}



Scheme 1.

14 and 15.

Figure 6 shows the plots of $[-\ln(\alpha-[\mathrm{III}]/[\mathrm{P}])]/\beta$ at pH 11 and $[-\ln(\alpha'-[\mathrm{III}']/[\mathrm{P}])]/\beta'$ at pH 13 against the reaction time *t* calculated from the data of the time-course of absorbance at 465 nm, the Soret maximum of the III species, after the addition of CN⁻ to a Fe(III)-TMPyP solution, in which the concentrations of the complex species and CN⁻ were 1.00×10^{-5} and 5.00×10^{-3} mol dm^{-3} respectively in a mixed solution. These lines show a good linearity except for the initial stage of reactions. The rate constants of formation were obtained from the slopes of these straight lines, and the rate constants of the reverse reaction, k_b and k'_b were calculated by the use of Eqs. 8 and 9. The values of the constants are listed in Table 3. The value of k'_f is almost four times that of k_f. This apparently indicates that the CN⁻ ion replaces the axial hydroxo ligand more easily than the axial aqua ligand in an aqueous solution, though this seems unreasonable because of the repulsion between the negative-charged ions. This finding may be interpreted in terms of the difference in the spin state of monocyano-complexes, as will be described in the next section.

Mechanisms of Substitution. The mechanism of the substitution of CN⁻ for the axial ligand of the Fe(III)-TMPyP species in a highly alkaline aqueous solution is summarized in Scheme 1. The solid lines express the main routes of substitution, while the dashed lines express the alternative routes.

Since the II and II' species differ from one another, and since the pK_a value of the II species is 12.2 in the protolytic equilibrium between II and II', the predominant monocyano species in aqueous solutions have been regarded as Fe(III)-TMPyP(H_2O)(CN) at pH 11 and Fe(III)-TMPyP(OH)(CN) at pH 13. It is considered hardly possible, because of the negative charge of the cyanide ion and the stronger donation of the hydroxo ligand than that of the aqua ligand, that the cyanide ion prefers to replace the hydroxo ligand rather than the aqua ligand of the monoaquamonohydroxo complex (I).[13,14] Therefore, the monohydroxomonocyano complex (II') is probably formed first by the replacement of the species I; then the rapid protolysis[15] follows to give monoaquamonocyano complex (II) at pH 11.

In the 2nd substitution, the cyanide ion replaces the ligand at the trans position to the cyano-ligand of II' more easily than that of II, as may be seen in Fig. 1 and Table 3. This behavior is presumably attributable to the difference in the spin states of monocyano-complexes; that is, the spin state of the II' species, in comparison with that of II, is close to that of III.[16,17] Therefore, the 2nd substitution at pH 11 occurs via the II' species as an intermediate; this species exists in a smaller quantity relative to the II species. Therefore, the value of the apparent rate constant, k_f, at pH 11 is smaller (seemingly by about one fourth) than the k'_f at pH 13. Similarly, it is probably ascribable to the similarity in the spin state between I' and II' species that the 1st substitution at pH 13 is faster than that at pH 11, as may be seen in

Fig. 1.

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