Inorg. Chem. **1993,** *32,* 941–947

Reactions of Fe^{III}(*meso*-$\alpha,\alpha,\alpha,\alpha$-tetrakis[*o*-(*N*-methylisonicotinamido)phenyl]porphyrin)$^{5+}$ and Fe^{III}(*meso*-tetrakis[*N*-methylpyridinium-4-yl]porphyrin)$^{5+}$ with CN$^-$, CO$_2^-$, and O$_2^-$

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Received September 4, 1992

The picket fence porphyrin, Fe^{III}(*meso*-$\alpha,\alpha,\alpha,\alpha$-tetrakis[*o*-(*N*-methylisonicotinamido)phenyl]porphyrin), α^4-Fe^{III}(TMINP)$^{5+}$, shows two proton ionization steps in the pH regions commonly observed for water soluble Fe^{III} porphyrins: pK_{1a} = 6.1; pK_{2a} = 10.0. α^4-Fe^{III}(TMINP)(OH)$^{4+}$ is found to have a considerably lower tendency to dimerize than the previously reported isomeric Fe^{III}(OH)(*meso*-$\alpha,\alpha,\alpha,\alpha$-tetrakis[*o*-(*N*-methylnicotinamido)phenyl]porphyrin)$^{4+}$, α^4-Fe^{III}(TMNP)(OH)$^{4+}$.[10] The difference in dimer stabilities is attributed to the higher concentration of positive charge around Fe^{III} in the *iso*nicotinamido isomer. Fe^{III}(*meso*-tetrakis[*N*-methylpyridinium-4-yl]porphyrin)$^{5+}$, Fe^{III}(TMPyP)$^{5+}$, and α^4-Fe^{III}(TMINP)$^{5+}$ form very stable Fe^{III}(porph)(CN)$_2^{3+}$ complexes that in alkaline solutions are fully formed at millimolar excesses of CN$^-$. The stability constant for the latter dicyanoporphyrin complex is higher than that for the former, again a manifestation of the higher positive charge near the metal ion of the picket fence porphyrin. Fe^{III}(TMPyP)(CN)$_2^{3+}$ has a sufficiently positive reduction potential that it is easily, but slowly, reduced to Fe^{II}(TMPyP)(CN)$_2^{2+}$ by slight excesses of CN$^-$. α^4-Fe^{III}(TMINP)(CN)$_2^{3+}$ is not reduced by CN$^-$. The carbon dioxide radical anion, CO$_2^-$, reduces Fe^{III}(TMPyP)$^{5+}$ and α^4-Fe^{III}(TMINP)$^{5+}$ at diffusion-controlled rates with a steric factor contributing to a slightly smaller rate constant in the case of the picket fence porphyrin. Rates of reduction by the superoxide radical, O$_2^-$, are less than diffusion controlled with rate constants for the reactions of Fe^{III}(TMPyP)$^{5+}$, $\alpha^3\beta$-Fe^{III}(TMINP)$^{5+}$ and Fe^{III}(TPPS$_4$)$^{3-}$ (tetra(4-sulfonatophenyl)porphyrin) following their E$_{1/2}$ values in accordance with the Marcus equation. A high rate constant for α^4-Fe^{III}(TMINP)$^{5+}$ reduction implicates a different reaction mechanism that is postulated to involve the prebinding of O$_2^-$ within the pocket formed by the porphin ring substituents.

Interest exists in the properties of the iron porphyrins with respect to their ability to serve as catalysts for superoxide dismutation:

$$\mathrm{Fe^{III}(porph) + O_2^- \rightarrow Fe^{II}(porph) + O_2}$$

$$\mathrm{Fe^{II}(porph) + O_2^- + H^+ \rightarrow Fe^{III}(porph) + HO_2^-}$$

Fe^{III}(*meso*-tetrakis(*N*-methylpyridinium-4-yl)porphyrin), Fe^{III}(TMPyP)$^{5+}$, has been found to be an excellent catalyst for the disproportionation of O$_2^-$.[1-5] It was also reported that binding CN$^-$ to the porphyrin induces a substantial decrease in its activity toward O$_2^-$, although rates with other radicals were unaffected.[4] However, disagreement regarding the nature of the interactions between the porphyrin and CN$^-$ interferes with an understanding of the cause of this inhibition. It was concluded from spectrophotometric titrations with CN$^-$ in alkaline media that Fe^{III}TMPyP^{5+} has a high affinity for CN$^-$ and forms Fe^{III}TMPyP(CN)$_2^{3+}$ quantitatively at approximately millimolar excess concentrations of CN$^-$.[6] No evidence was obtained for the formation of observable quantities of an intermediate 1:1 porphyrin/CN$^-$ complex. In contrast to these observations, Arifuku and co-workers[7] reported that the absorption spectra show two distinct phases as CN$^-$ is added to Fe^{III}TMPyP^{5+} in alkaline solutions. The first of these phases, complete at millimolar concentrations of CN$^-$, was attributed to the formation of a 1:1 CN$^-$/porphyrin complex, and the second phase, observed at much higher CN$^-$ concentrations, to the formation of a 2:1 complex.

In this investigation of the relative reactivities of α^4-tetrakis[*o*-(*N*-methylisonicotinamido)phenyl]Fe^{III} porphyrin, α^4-Fe^{III}(TMINP)$^{5+}$, and Fe^{III}(TMPyP)$^{5+}$ toward O$_2^-$ and CO$_2^-$ radicals, the occasion arose to examine CN$^-$ binding to both porphyrins. It was found that in alkaline media formation of the dicyano complexes is complete at millimolar, or lower, concentrations of CN$^-$, but the second reaction observed with α^4-Fe^{III}(TMPyP)$^{5+}$ results from the reduction of the Fe^{III} porphyrin by excess CN$^-$, a reaction that is not observed with α^4-Fe^{III}(TMINP)$^{5+}$. O$_2^-$ reacts faster with α^4-Fe^{III}(TMINP^5)$^+$ than with Fe^{III}(TMPyP)$^{5+}$ but the opposite is the case with respect to the rates of reaction with CO$_2^-$.

Experimental Section

Fe^{III}(TMPyP)Cl$_5$ was kindly donated by Dr. T. Kuwana, Fe^{III}(TMINP)Cl$_5$ was obtained from MidCentury Chemicals, Posen, IL. Solid porphyrins were stored below 0 °C. Solutions of the porphyrins were prepared by first dissolving the weighed solids in distilled water and then adding buffers and sufficient NaNO$_3$ to bring the final ionic strength to 0.10 M, prior to adjusting the solution to the desired pH. This procedure was found to be necessary in preparing solutions of Fe^{III}(TMPyP)$^{5+}$ in alkaline buffers because of the aggregation behavior of the porphyrin when dissolved directly in these buffers. Polymeric species are formed that very slowly dissociate to monomer. Freshly prepared porphyrin solutions were stored at 4 °C and brought to 25 °C in a waterbath prior to use. Photodecomposition was minimized by wrapping all glassware containing porphyrin solutions with foil.

Porphyrin solutions used for pH-absorbance and CN$^-$ ligation studies contained 3 mM buffer (either phosphate for pH's below 8, or carbonate for the higher pH solutions) and 0.1 M NaNO$_3$. In experiments involving

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[†] The Ohio State University.

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(1) Pasternack, R. F.; Halliwell, B. *J. Am. Chem. Soc.* **1979**, *101*, 1026.

(2) Pasternack, R. F.; Skowrenck, W. R., Jr. *J. Inorg. Biochem.* **1979**, *11*, 261.

(3) Ilan, Y.; Rabani, J.; Fridovich, I.; Pasternack, R. F. *Inorg. Nucl. Chem. Lett.* **1981**, *93*, 17.

(4) Solomon, D.; Peretz, P.; Faraggi, M. *J. Phys. Chem.* **1982**, *86*, 1842–1849.

(5) Faraggi, M.; Peretz, P.; Weinraub, D. *Int. J. Radiat. Biol.* **1986**, *49*, 951–958.

(6) Weinraub, D.; Peretz, P.; Faraggi, M. *J. Phys. Chem.* **1982**, *86*, 1839–1842.

(7) Arifuku, F.; Ujimoto, K.; Kurihara, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 149.

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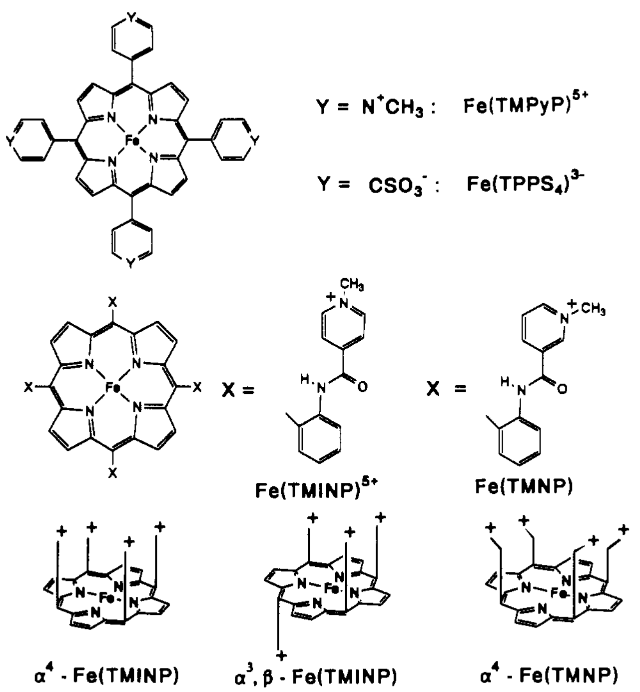

$Fe^{III}TMPyP^{5+}$ final porphyrin concentrations were in the range of (1–2) $\times 10^{-5}$ M. Titrations in which the total CN^- concentration was <0.004 M were performed continuously because equilibration is relatively fast and the spectra are stable for several hours. At higher CN^- concentrations, slow spectral changes were observed after the rapid development of the color of the cyano complex that is formed at lower CN^- concentrations. Titrations in this range were performed batchwise, and mixed solutions were brought to a steady state by allowing them to stand for 24 h before spectral measurements were made. Because of the scarcity of the starting material spectrophotometric studies on the picket fence porphyrin were performed using concentrations of 3.8×10^{-6} M porphyrin. Reactions with CN^- were rapid. Dithionite reduction to the Fe^{II} porphyrins was accomplished by mixing dearaeted porphyrin stock solutions with 3×10^{-4} M sodium dithionite, at pH 8, in a 2:1 ratio.

Radical anions were generated using a Varian V-7715A linear accelerator operated in the 3–4 MeV energy range with a pulse width of 200 ns. Pulses routinely yielded about a 1 μM radical concentration. Beam intensities were adjusted using thin metal absorbers between the beam source and the cell. This method of decreasing the dose provided better reproducibility than reducing the pulse width. Over a four hour period the relative variability of the dose from pulse to pulse was generally less than ±10%. Dosimetry was performed using 10 mM KSCN.[8a]

The pulse radiolysis studies on the porphyrins were performed using 5 mM aqueous phosphate buffer at a pH of 5.6. Distilled water which had been passed through a Millipore Corp. ultrapurification apparatus was employed throughout. Porphyrin concentrations were varied in the range 5×10^{-6} to 5×10^{-5} M in 0.1 M formate. The Hart technique[8b] was used to saturate solutions prior to use with the appropriate gas, either nitrous oxide to give CO_2^- as the secondary radical, or oxygen(or air) to give O_2^-. Trace oxygen was removed from nitrous oxide using a series of five wash bottles, three containing lightly amalgamated zinc and 0.1 M vanadyl sulfate and the last two containing distilled water. Oxygen was washed twice with pure water before being used to saturate the reaction solution. Reactions were monitored at wavelengths where the absorption of Fe^{II} porphyrins is dominant, 445 nm for $Fe^{II}(TMPyP)^{5+}$ and 435 nm for $Fe^{II}(TMINP)^{5+}$.

All rates were determined under pseudo-first-order conditions, with porphyrin in large excess over radical, so that pseudo-first-order rate constants could be calculated from the changes in optical densities of the absorbing species as a function of time. By varying the total porphyrin concentrations it was possible to obtain the second order rate constants from the slopes of plots of the first-order rate constants vs porphyrin concentration.

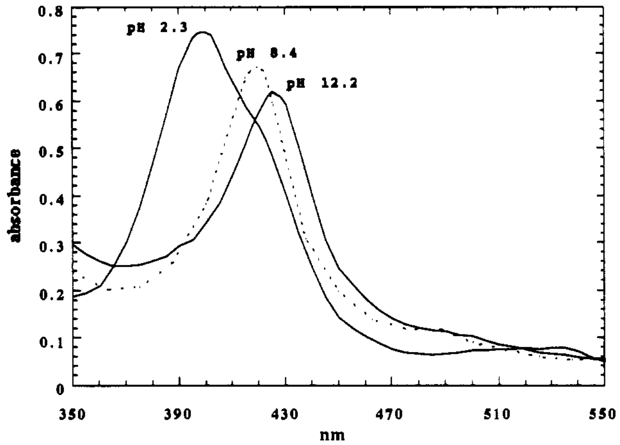

Figure 1. Absorption spectra of α^4-$Fe^{III}(TMINP)^{5+}$ as a function of pH.

Problems were encountered in the study of the reduction of $Fe^{III}(TMINP)^{5+}$ by superoxide when the solutions had been saturated with pure O_2 prior to irradiation. Multiphasic rate behavior arose from the oxidation of the Fe^{II} form, presumably by reaction with O_2^-. Substituting air for pure O_2 lessened this source of interference and provided satisfactory rate curves.

The computer program MINUIT[9] was used to perform nonlinear curve fitting to the spectrophotometric titration curves. This program was used first in the SIMPLEX fitting mode to obtain preliminary values of the parameters being fit; then, in the polynomial fitting mode to refine the values.

Results

Ionization and dimerization reactions established[10–12] for Fe^{III} porphyrins and pertinent to the present investigation are summarized in Scheme I. Spectra of α^4-$Fe^{III}TMINP^{5+}$ solutions are presented in Figure 1 at pH values where the aqua, monohydroxy, and dihydroxy forms dominate. Plots of the absorbancies at 426, 418 and 398 nm vs pH, Figure 2, reveal the first proton ionization occurs in the region of pH 6.0 and the second in the region of pH 10.0.

Scheme I

$$Fe^{III}(porph)(H_2O)_2 \overset{K_{1a}}{\rightleftharpoons} Fe^{III}(porph)(H_2O)(OH) + H^+$$

$$Fe^{III}(porph)(H_2O)(OH) \overset{K_{2a}}{\rightleftharpoons} Fe^{III}(porph)(OH)_2 + H^+$$

$$2Fe^{III}(porph)(H_2O)(OH) \overset{K_d}{\rightleftharpoons} (porph)Fe^{III}OFe^{III}(porph) + H_2O$$

Reported log K_d values indicate a wide range of dimer stabilities for open face porphyrins. $Fe^{III}TMPyP(OH)^{4-}$ forms a dimer having a relatively low stability, log K_d is about 3.8[10,11], while tetrakis(*N*-methylnicotinamido)porphyrin, $Fe^{III}(TMNP)(OH)^{3+}$, which is isomeric to the picket fence porphyrin studied here, has a very high stability, log K_d = 7.3.[10] Because of the low picket fence porphyrin concentration employed in this investigation it was not possible to directly resolve a dimerization constant from the absorbance–pH data. To circumvent this difficulty best least squares values of pK_{a1} and pK_{a2} were obtained by fitting absorbance–pH curves to two limiting models in which K_d was held invariant. These models corresponded to the formation of a highly stable dimer (for which log K_d was assumed to be equal

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[8] (a) Fielden, E. M. *The study of fast processes and transient species by electron pulse radiolysis*; Baxendale, J. H., Busi, F., Eds.; Reidel: Dordrecht, 1982; pp 49–63. (b) Thomas, J.; Gordon, S.; Hart, E. *J. Phys. Chem.* **1964**, *68*, 1524.

[9] James, F.; Roos, M. *Comput. Phys. Commun.* **1975**, *10*, 343–367.

[10] Miskelly, G. M.; Webley, W. S.; Clark, C. R.; Buckingham, D. A. *Inorg. Chem.* **1988**, *27*, 3773–3781.

[11] Tondreau, G. A.; Wilkins, R. G. *Inorg. Chem.* **1986**, *25*, 2745–2750.

[12] Forshey, P. A.; Kuwana, T. *Inorg. Chem.* **1981**, *20*, 693–700.

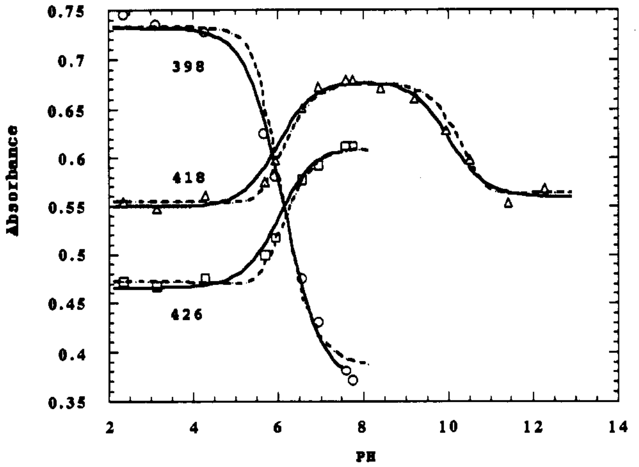

Figure 2. Analysis of the pH-dependent changes in the absorbancies of α^4-Fe^{III}(TMINP)$^{5+}$: (—) best fit for no dimer model; (- -) best fit for strong dimer model.

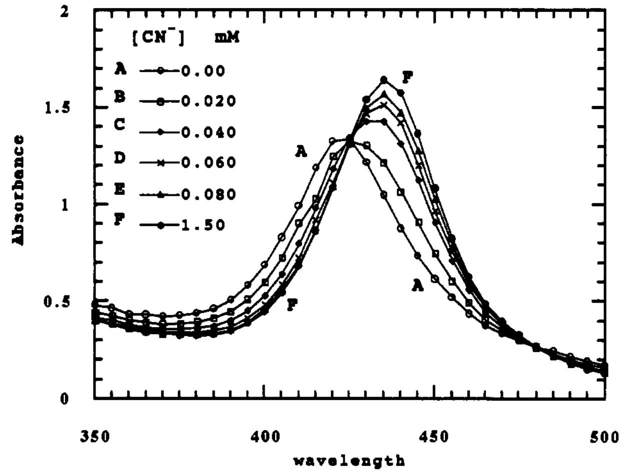

Figure 3. Spectral changes occuring during the titration of Fe^{III}-(TMPyP)(OH)$^{4+}$ with CN$^-$ at low concentrations.

to 7.3, and, hereafter, referred to as the **SD** model) and no dimer (the **ND** model).

A best least squares value of pK_{a1} was obtained by fitting calculated absorbance-pH curves to the data in the pH range 2.5–8.5 simultaneously for three wavelengths shown in Figure 2. Both dimer models were found capable of giving excellent agreement between calculated curves and the observed data points, as can be by the excellent fit of the theoretical curves. The **ND** model (solid line) yielded a slightly better fit ($\chi^2_{red} = 2.0$) than the **SD** model (dotted line, $\chi^2_{red} = 2.6$). Absorbance changes at 398 and 426 nm in the higher pH region had too small amplitudes to be useful for evaluating pK_{a2}, but the changes at 418 nm were satisfactory for this purpose. Here again, the **ND** model gave a slightly better fit to the observed data points. The **ND** model yielded best values of pK_{1a} and pK_{2a} equal to 6.07 and 10.1. The **SD** model yielded corresponding values of 7.0 and 9.2.

Spectral changes for the two stages observed in the titration of Fe^{III}(TMPyP)(OH)4$^+$ with CN$^-$ in solutions at pH 8.8 are shown in Figure 3 for 0–5 mM total CN$^-$ and in Figure 4 for the steady-state spectra at 4–75 mM CN$^-$ concentrations. The isosbestic point near 425 nm indicates that only two absorbing components are present in the porphyrin–CN$^-$ solutions having low ligand concentrations. This conclusion is confirmed by the results of factor analysis[13,14] performed on absorbancies at seven wavelengths for 14 experiments over which the CN$^-$ concentration was varied. Calculated eigenvalues as a function of the number of assumed components are presented in Table I for data obtained at pH 8.8 and 10.4. At the former pH the eigenvalues for one and two components are clearly larger than those calculated assuming more components. The eigenvalues for three, or more, components lie close to the noise limited value. Furthermore, the Malinkowski IND function[14] passes through a minimum at two components. Thus, the presence of only two components which contribute to the absorbance at these wavelengths is clearly indicated.

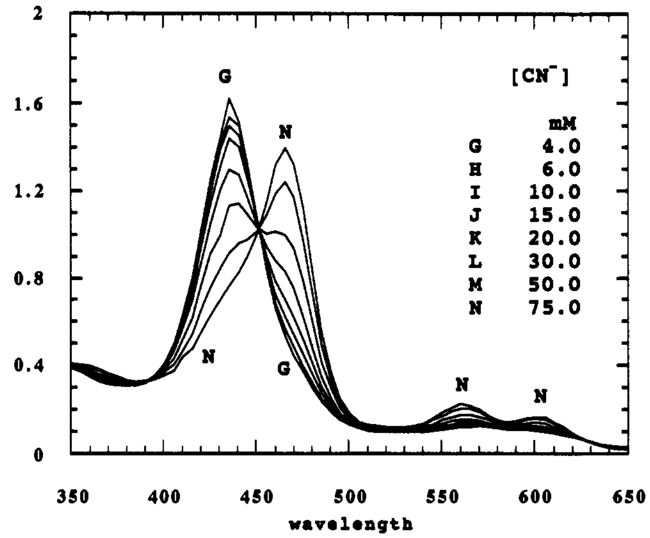

Figure 4. Spectral Changes occuring during the second stage of the titration of Fe^{III}(TMPyP)(OH)$^{4+}$ with CN$^-$.

Table I. Results of Factor Analysis on Fe(TMPyP)$^{5+}$–CN$^-$ Spectral Changes

no. of components	eigenvalue	real error	IND
	pH 8.8 (14 experiments, 6 wavelengths)		
1	95.4	0.119	0.00476
2	0.99	0.005	0.00032
3	0.0006	0.004	0.00047
4	0.0005	0.003	0.00073
5	0.0002	0.0012	0.0012
	pH 10.4 (24 experiments, 5 wavelengths)		
1	87.2	0.100	0.0063
2	0.96	0.0050	0.00056
3	0.0015	0.0026	0.00064
4	0.0003	0.0012	0.0012

The results of factor analysis are somewhat less clear for data obtained at pH 10.4. The eigenvalue for a third component is substantially larger than the noise limited value, although it is still smaller than those for one and two components. The IND function also has a broader minimum. The intrusion of a minor third component is suggested.

The demonstration that only two principal absorbing components are present at pH 8.8, and to a major extent at pH 10.4, indicates a single ligation for which the principal equilibrium is of the type

$$[\mathrm{Fe^{III}(TMPyP)(OH)}]^{4+} + i\mathrm{CN^-} \overset{K_i}{=} [\mathrm{Fe^{III}(TMPyP)(OH)_{1-j}(CN)_i}]^{(5-i)+} + j\mathrm{OH^-} \quad (1)$$

$$i = 1, 2; j = 0, 1$$

To decide which value of i best describes the results requires recourse to the mass action law. In this analysis proton ionization and dimerization equilibrium constants reported by Miskelly et al.[10] were used because the conditions of ionic strength were identical to those employed here. The values pertinent to this

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(13) Hugus, Z Z.; El-Awady, A. A. *J. Phys. Chem.* **1971**, *75*, 2954.
(14) Malinkowski, E. R. *Anal. Chem.* **1977**, *49*, 612–617.
(15) Hambright, P.; Turner, A. Cohen, J. S.; Lyon, R. C.; Katz, A. *Inorg. Chim. Acta* **1987**, *128*, L11–L14.

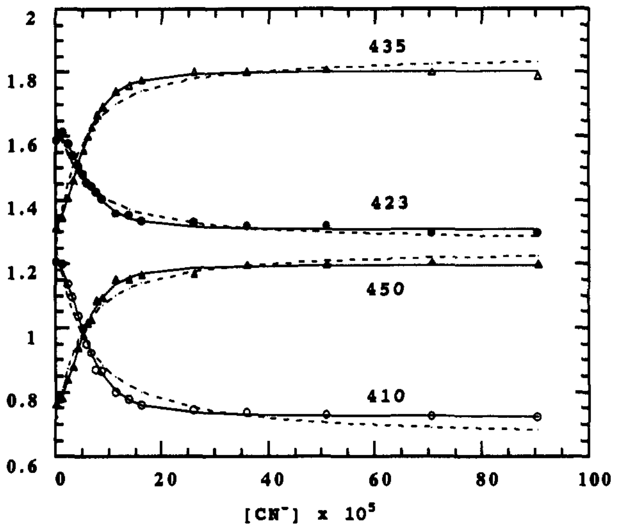

Figure 5. Analysis of the CN$^-$-dependent changes in the absorbancies of α^4-Fe^{III}(TMNIP)(OH)$^{4+}$ at low CN$^-$ concentrations (pH 9.57): (- -) best fit assuming $i = 1$; (—) best fit assuming $i = 2$.

investigation are pK_{a1} = 5.79, pK_{a2} = 11.71, and log K_d = 3.87. Calculations show that at a total Fe^{III}(TMPyP)(OH)$^{4+}$ concentration of 1.0 × 10^{-5} M, the dimer comprises less than 10% of the total porphyrin, so that the cyanation reactions are essentially monomeric in character.

Best values of K_i were obtained by fitting calculated curves to the observed curves for $i = 1$ and 2. Because of the high affinity of the porphyrin for CN$^-$, the equilibrium concentrations of the ligand at the initial points in the the spectrophotometric titrations are lower than their total concentrations, necessitating an iterative method to fit the data. Assuming a value for K_i for a given i and knowing the equilibrium constants for the formation of other adducts in the system (HCN, pK_a = 9.16, and dimer), it is possible using the Newton–Raphson method to solve the mass balance equations on total porphyrin and CN$^-$ for the equilibrium concentrations of the components. The sum-square difference between theoretical and observed absorbance–[CN$^-$] curves yields a value of the reduced chisquare, χ^2_{red}. Nonlinear curve fitting was employed to obtain the K_i which results in the minimum χ^2_{red}.

The results of these analyses for CN$^-$ titrations of solutions containing [Fe^{III}(TMPyP)(OH)]$^{4+}$ at pH 8.8, monitored at four wavelengths, are portrayed in Figure 5 for $i = 1$ (dashed lines) and for $i = 2$ (solid lines). At 410 and 423 nm the absorbance of the reactant species, [Fe^{III}TMPyP(OH)$^{4+}$], is dominant while the product species, [Fe^{III}(TMPyP)(OH)$_j$(CN)$_i$]$^{3+}$, contributes primarily to the absorbancies at 435 and 450 nm. The lines represent the theoretical values calculated using the best K_i which was found for each value of i. χ^2_{red} for the fit taking $i = 1$ is a rather mediocre 35. At [CN$^-$] concentrations >10 × 10^{-5} M the theoretical curves are seen to "average" the data, lying significantly below the observed data points at the lower [CN$^-$] values and significantly above at higher concentrations. The theoretical curves do not attain limiting A_∞ values even at 90 × 10^{-5} M CN$^-$.

In contrast, the fit shown for $i = 2$ is excellent with a χ^2_{red} of 2.9. The theoretical curves closely follow the trends in the data. The difference between the quality of the fit of the two models provides convincing evidence that in alkaline media, the principal equilibrium involves the addition of two CN$^-$ to the porphyrin in essentially a single step.

Log β_2 values (Fe^{III}(porph)$^{5+}$ + 2CN$^-$ = Fe^{III}(porph)(CN)$_2$$^{5+}$) calculated from the best K_i obtained at each investigated pH are presented in Table II. The values show very little dependence on pH, with those obtained at pH 8.81 and 9.23 being identical within the experimental errors. This independence on pH confirms that $j = 1$ in eq 1. The small trend toward increasing log β_2 with further increases in pH is additional evidence for the presence of minor concentrations of a third absorbing component at higher pH. The perturbation introduced by this third species is particularly strong at pH 10.4, where the observed data points at 435 nm were found to show increasingly small positive deviations from the theoretical plateau value as the CN$^-$ concentration was increased. This deviation is ascribed to the formation of the Fe^{II} porphyrin that is discussed in the following section.

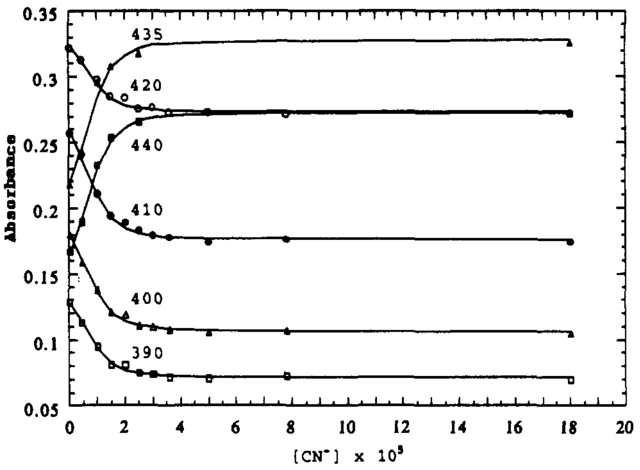

Figure 6. Analysis of the CN$^-$-dependent changes in the absorbancies of α^4-Fe^{III}(TMPyP)(OH)$^{4+}$ at low concentrations (pH 10.4): (—) calculated fit, $i = 2$.

Table II. Values of Stability Constants for Fe(III)(porph)$^{5+}$ + 2CN$^-$ = Fe(III)(porph)(CN)$_2$$^{3+}$

pH	log β_2 (M^{-2})	pH	log β_2 (M^{-2})
	porph = TMPyP		
8.81	13.00	10.03	13.31
9.28	13.03	10.4	13.56
	porph = α^4-TMINP		
9.6	14.6	10.2	14.7

After mixing solutions having still higher CN$^-$ concentrations, absorbance changes arising from the rapid formation of [Fe^{III}(TMPyP)(CN)$_2$]$^{3+}$ are observed to be followed by slow spectral changes. These changes are observed at all pHs investigated in the range 8.8–10.4. The steady-state spectra shown as a function of [CN$^-$] in Figure 4 are characterized by three isosbestic points at 385, 450 and 628 nm. This observation, together with factor analysis, indicates that [Fe^{III}(TMPyP)(CN)$_2$]$^{3+}$ reacts with CN$^-$ to produce one other species that has a different absorption spectrum. At 0.10 M CN$^-$ product formation is complete. The product absorption spectrum is characterized by an intense band at 464 nm and two less intense bands at 560 and 601 nm. This spectrum is identical to the spectrum of Fe^{II}(TMPyP)(CN)$_2$$^{2+}$ generated via the dithionite reduction of Fe^{III}(TMPyP)(CN)$_2$$^{3+}$. Exposure of a solution of either the product of the CN$^-$ reaction or the dithionite reduction to air results in 90% regeneration of the spectrum of the Fe^{III} porphyrin within $^1/_2$ h. Thus, the second stage reaction is the reduction of the Fe^{III} porphyrin to the Fe^{II} porphyrin by excess CN$^-$.

CN$^-$ ligation of α^4-Fe^{III}(TMINP)$^{5+}$ was examined in solutions buffered at pH 9.57 and 10.2. The picket fence porphyrin exhibits a high affinity for CN$^-$: an excess of only 5 × 10-5 M CN$^-$ is sufficient to fully ligate the porphyrin at pH 10.2. The spectrum of the product closely resembles that of Fe^{III}(TMPyP)(CN)$_2$$^{+3}$, but with the absorption maxima shifted to shorter wavelengths. The intense Soret band lies at 431 nm and two weaker bands at 566 and 600 nm. Spectral changes occuring during the titration at six wavelengths are presented in Figure 6. Curve-fitting of the absorbance–CN$^-$ curves simultaneously at these wavelengths was performed for both SD and ND models assuming $i = 1$ and 2.

The best fit for the pH 9.57 data was obtained with the **ND** model for $i = 2$ ($\chi^2_{red} = 2.5$). The calculated curves obtained using the best parameters are shown as the solid lines. The **SD** model for $i = 2$ yielded a poorer fit ($\chi^2_{red} = 4.6$). The **ND** model with i equals 1, gave an even poorer fit, $\chi^2_{red} = 10.8$. The data obtained at pH 10.2 also gave the best fit using the **ND** model with $i = 2$. Thus, a one-step ligation by two CN$^-$ is indicated. Values of β_2 for both pHs, given in Table II, are seen to be independent of pH within the uncertainty of the calculations.

α^4-Fe^{III}(TMINP)(CN)$_2^{3+}$ is not reduced by excess CN$^-$. The absorption spectrum of α^4-Fe^{III}(TMINP)(CN)$_2^{3+}$ in 0.015 M CN$^-$, pH 10.2, is stable and shows no evidence of the slow formation of a Fe^{II} form, even after solid KCN had been added in large excess to force the reduction. Reduction by dithionite yields α^4-Fe^{II}(TMINP)(CN)$_2^{2+}$ which has a spectrum resembling that of Fe^{II}(TMPyP)(CN)$_2^{2+}$, but the band maxima of the picket fence porphyrin lie at slightly shorter wavelengths: 438, 553, and 589 nm.

Reactions of CO$_2^-$ and O$_2^-$ radicals with excess Fe^{III}(TMPyP)$^{5+}$ and α^4-Fe^{III}(TMINP)$^{5+}$ gave excellent pseudo-first-order decay curves of the ferric porphyrins. Plots of the pseudo first order rate constants vs porphyrin concentration showed excellent linearity. The slopes provided the second-order rate constants presented in Table III.

Discussion

In general, the ionization behavior of α^4-Fe^{III}(TMINP)$^{5+}$ is consistent with earlier observations, summarized in Scheme I, of positively charged, water soluble (diaqua)Fe^{III} porphyrins.[10-12] Unfortunately, the question of the stability of the dimer form of the picket fence porphyrin is not directly resolved in this work because of the low porphyrin concentrations which had to be employed. If log K_d had a value characteristic of a moderately strong dimer, e.g. 5.0, only 34% of the porphyrin would be dimerized in an alkaline solution having a total porphyrin concentration of 3.8×10^{-6} M. The similarities in the absorption spectra of the monomer and dimer would make it difficult to obtain an accurate value of K_d unless an exhaustive series of experiments were performed. However, if log K_d were 7.3, which was found[10] for α^4-Fe^{III}(TMNP)(OH)$^{4+}$, then 92% of the porphyrin would be dimerized at this same total porphyrin concentration and a satisfactory value of K_d would be readily forthcoming.

In curve fitting to both the absorbance–pH and absorbance–[CN$^-$] data χ^2_{red} values were somewhat lower for ND models than for **SD** models in all cases. More conclusive evidence favoring the **ND** model is given by the values of pK_{a1} and pK_{a2}. With the **ND** model, p*K*a values of 6.1 and 10.0, respectively, were obtained, while values of 7.0 and 9.2 resulted with the **SD** model. The former pair of results lies in the range of pK_a's reported by Miskelly[10] for Fe^{III}(TMPyP)$^{5+}$, Fe^{III}(α^4-TMNP)$^{5+}$ and Fe^{III}($\alpha,\beta,\alpha,\beta$-TMNP)$^{5+}$ and are in very good agreement with those determined by Hambright[15] for Fe^{III}(α^3,β-TMINP)$^{5+}$. The values obtained with the **SD** model show an unusually high pK_{1a} and an unusually low pK_{2a}. This is contrary to expectations because changes in the chemical environment would affect both constants in similar ways. Thus, the preponderance of the evidence suggests that $^{4+}$(α^4-TMINP)Fe^{III}OFe^{III}(α^4-TMINP)$^{4+}$ is substantially less stable than isomeric $^{4+}$(α^4-TMNP)Fe^{III}OFe^{III}(α^4-TMNP)$^{4+}$. It must be emphasized that a dimer having intermediate stability can not be ruled out.

A possible explanation for the effect of the structural differences between the nicotinamide isomers on the dimer stabilities lies with the distribution of charge. A recent extensive study[36] on the 2-*N*-methylpyridyl isomer, Fe^{III}(2-TMPyP)$^{5+}$, has demonstrated that simple electrostatic effects arising from differences in the distance of the charged *N*-methylpyridyl groups from the porphine core account for substantial differences observed between Fe^{III}(2-TMPyP)$^{5+}$ and Fe^{III}(TMPyP)$^{5+}$, which is the 4-pyridyl isomer. The positively charged N-methylpyridyl groups of the *iso*nicotinamido picket fence porphyrin lie closer to the *z*-axis of the metal ion than those of its nicotinamdo isomer. The higher concentration of positive charge near the metal ion in the former would promote the binding of an anionic ligand within the enclosed pocket, which in the case of OH$^-$ binding would inhibit μ-oxo bridge formation. The higher concentration of positive charge would also destabilize the dimer electrostatically.

The metal ions in both α_4-Fe^{III}TMINP^{5+} and Fe^{III}TMPyP^{5+} have high affinities for CN$^-$ and acquire two ligands in apparent single-step reactions. We verify the conclusions drawn by Weinraub et al.[6] that only millimolar excess concentrations of CN$^-$ are necessary to bind two CN$^-$ to the axial Fe^{III} sites of Fe^{III}TMPyP^{5+}; however, β_2 for the formation of Fe^{III}(TMPyP)(CN)$_2^{3+}$ has been found here to be about a factor of 5 higher than a value calculated from the earlier study[6]. The lower formation constant is due, at least in part, to the employment of the Fleischer–Fine equation[16] without taking into consideration the difference between free CN$^-$ and total CN$^-$ concentrations in the initial stages of ligation. This difference can not be ignored and an iterative calculation is necessary to obtain an accurate value of the equilibrium constant.

The stability constant found for the formation of a α^4-Fe^{III}(TMINP)(CN)$_2^{3+}$ is higher than that determined for the TMPyP complex. This increase is attributed to the binding of one of the CN$^-$ ions within the positively charged pocket of the pocket fence porphyrin and to a greater d$_\pi$ electron density on the metal ion. In the TMPyP complex the dihedral angle between the *N*-methylpyridinium rings and the mean plane of the porphyrin core is about 60Å[17] which permits weak overlap between core and pyridinium ring π systems. Direct evidence for a more extensive π network in the TMPy porphyrin is obtained from a comparison of the absorption spectra of the two types of porphyrins. The spectra of the TMPy and TMIN porphyrins qualitatively resemble each other for a given type of complex, but the absorption bands of the TmPy porphyrin consistently lie at longer wavelengths than the corresponding bands of the picket fence porphyrin. Overlap of central metal ion d$_\pi$ orbitals with the π^* antibonding orbitals of this extended conjugated system drains electron density from the metal ion and weakens metal ion/CN$^-$ d$_{\pi-\pi^*}$ back bonding. The isonicotinamidyl π orbitals of the picket fence porphyrin are separated from those of the porphine core by –CH$_2$– groups which break the π network to the pyridyl rings. This difference in delocalization of the metal ion d electrons also has a major affect on the reduction potentials of the Fe^{III}/Fe^{II} couples in these porphyrins. Vide infra.

The apparent simultaneous binding of two CN$^-$ to the Fe^{III} porphyrins deserves comment. Apparent one-step multiligations can be observed in situations where the central metal ion undergoes an electron spin change as the degree of ligation increases,[18b] causing the stepwise constants for binding later ligands to be much higher than those for binding earlier. While this behavior could be the case here, CN$^-$ addition in other porphyrin systems is observed to procede in two distinct steps;[18-21] e.g., Goff and Morgan[19] report that in slightly acidic solutions two distinct steps are observed in the spectrophotometric titration of heme with

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(16) Fleischer, E. B.; Fine, D. A. *Inorg. Chim. Acta* **1978**, *29*, 267.
(17) Ivanca, M. A.; Lappin, A. G.; Scheidt, W. R. *Inorg. Chem.* **1991**, *30*, 711–718.
(18) (a) Wang, J.-T.; Yeh, H. J. C.; Johnson, D. F. *J. Am. Chem. Soc.* **1978**, *100*, 2400–2405. (b) Hambright, P.; Krishnamurthy, M. R.; Chock, P. B. J. Inorg. Nucl. Chem. **1975**, *37*, 557–561. (c) Morishima, I; Inubushi,T. *J. Am. Chem. Soc.* **1978**, *100*, 3568–3574.
(19) Goff, H.; Morgan, L. O. *Inorg. Chem.* **1976**, *15*, 2069.
(20) Kaziro, K.; Uchimura, F. Kikuchi, G. *J. Biochem.* **1956**, *43*, 539–552.
(21) Scheidt, W. R.; Haller, K. J.; Hatano, K. *J. Am. Chem. Soc.* **1980**, *102*, 3017.

$\mathrm{CN^-}$. The stepwise constant for binding the second $\mathrm{CN^-}$ to heme is found to be 58-fold smaller than the constant for binding the first.

Whether one step or two steps are observed in a titration involving very strongly bound ligands depends on reaction conditions. Single-step multiligation holds when only a very small excess of ligand is sufficient to convert a lower complex to a higher one. This situation could easily exist in the present reactions. As an illustration, if it is assumed that the step-wise constant for binding the first $\mathrm{CN^-}$ to a $\mathrm{Fe^{III}}$ porphyrin were 100 times greater than the stepwise constant for binding the second $\mathrm{CN^-}$, and $\log \beta_2$ is the same as that found here for forming $\mathrm{Fe^{III}(TMPyP(CN)_2{}^{3+}}$, then $\log K_1 = 8.25$ for

$$\mathrm{Fe^{III}(porphyrin) + CN^- = Fe^{III}(porphyrin)(CN)}$$

and $\log \mathrm{K}_2 = 6.25$ for

$$\mathrm{Fe^{III}(porphyrin)(CN) + CN^- = Fe^{III}(porphyrin)(CN)_2}$$

(charges omitted)

A distribution calculation shows that at pH 9.6 the maximum amount of porphyrin that can be present as $\mathrm{Fe^{III}(porphyrin)(CN)}$ is less than 8% of the total. In contrast, at pH 6.5, a maximum of about 72% of the porphyrin could be converted to the 1:1 cyano complex because proton competition drastically reduces the $\mathrm{CN^-}$ activity. A titration performed at the higher pH would show a curve consistent with the single step formation of the dicyano complex, while at the lower pH the titration curve would show two easily resolvable steps. Therefore, the present results do not necessarily imply that $K_2 > K_1$. Indeed, the opposite situation is likely to be the case with the α^4-picket fence porphyrin: the first $\mathrm{CN^-}$ is apt to be strongly bound within the pocket, while the second $\mathrm{CN^-}$ bound to the external site would have a more normal binding constant. Because β_2 is the product of the stepwise constants, this situation would give rise to a high value for β_2.

Reduction of $\mathrm{Fe^{III}}$ porphyrins by $\mathrm{CN^-}$ has been observed in nonaqueous systems,[22,23] but this reaction does not seem to have been reported for aqueous media prior to our preliminary report.[24] Cyclic voltammetry performed on $\mathrm{Fe^{III}(TMPyP)^{5+}}$ [25] and on the picket fence isomer α^3,β-$\mathrm{Fe^{III}(TMINP)^{5+}}$ [5] in the presence and absence of $\mathrm{CN^-}$ provides a clue to the origin of the difference in the redox behavior of the two types of porphyrins toward $\mathrm{CN^-}$. On cyanation in alkaline solutions the reduction potential of the $\mathrm{Fe^{III}/Fe^{II}}$ couple of TMPy porphyrine undergoes a substantial positive shift that is not duplicated in the $\mathrm{Fe^{III}}$ TMIN porphyrin.

In acidic solutions $\mathrm{Fe^{III}(TMPyP)^{5+}}$ and α^3,β-$\mathrm{Fe^{III}(TMINP)^{5+}}$ have close lying, slightly positive reduction potentials: $\mathrm{Fe^{III}(TMPyP)^{5+} + e^- = Fe^{II}(TMPyP)^{4+}}$, $\mathrm{E}_{1/2} = +0.13$ V vs NHE;[12,26] α^3,β-$\mathrm{Fe^{III}(TMINP)^{5+} + e^-} = \alpha^3,\beta$-$\mathrm{Fe^{II}(TMINP)^{4+}}$, $\mathrm{E}_{1/2} = +0.08$ V vs NHE.[5]

In alkaline media, these potentials are predicted to shift to more negative values because of the ionization and consequent stabilization of the $\mathrm{Fe^{III}}$ valence state. At pH 9.6 the reduction potentials of the $\mathrm{Fe^{III}/Fe^{II}}$ couples of the TMPy and TMIN porphyrins are estimated, respectively, to be about -0.10 V and -0.13 vs NHE. The constants pertaining to Scheme I reported by Miskelly, et al. were employed in the former estimation, and those reported by Hambright[15] were used in the second. In agreement with the first estimate, Airufuku et al.[25] report an $E_{1/2}$ of -0.08 volts vs NHE for the almost reversible reduction of 1×10^{-4} M $\mathrm{Fe^{III}(TMPyP)(OH)^{4+}}$ at pH 10.8. The addition of excess $\mathrm{CN^-}$ to the solution causes the potential of the $\mathrm{Fe^{III}/Fe^{II}}$ couple to become more positive: $\mathrm{Fe^{III}(TMPyP)(CN)_2{}^{3+} + e^- = Fe^{II}(TMPyP)(CN)_2{}^{2+}}$, $E_{1/2} = +0.24$ V vs NHE.[25]

It is this large positive shift of 0.3 V in the redox potential that initiates the oxidation of excess $\mathrm{CN^-}$ in alkaline solutions.

In contrast, cyanation of the picket fence porphyrin induces a smaller shift in potential, α^3,β-$\mathrm{Fe^{III}(TMINP)(CN)_2{}^{3+} + e^-} = \alpha^3,\beta$-$\mathrm{Fe^{II}(TMINP)(CN)_2{}^{2+}}$, $E_{1/2} = -0.02$ V vs NHE.[5]

The potential of the couple remains too negative to oxidize $\mathrm{CN^-}$. Because of the higher concentration of positive charge in the pocket formed by the ring substituents and the presumed tighter binding of $\mathrm{CN^-}$, α^4-$\mathrm{Fe^{III}(TMINP)(CN)_2{}^{3+}}$ should be an even poorer oxidant than its α^3,β-isomer.

An inner sphere reaction mechanism has been established for the oxidation of $\mathrm{CN^-}$ in nonaqueous media,[23] and a similar pathway seems reasonable here, at least for the first step. A secondary reaction of the $\mathrm{CNO^-}$ product with excess $\mathrm{CN^-}$ to generate $\mathrm{(CN)_2}$, should lead to slow irreversible formation of $\mathrm{HCO_2NH_2}$ in the reaction mixture[27]

$$\mathrm{Fe^{III}(TMPyP)(CN)_2{}^{3+} \rightleftharpoons Fe^{II}(TMPyP)(CN)^{3+} + CN^{\bullet}}$$

$$\mathrm{Fe^{II}(TMPyP)(CN)^{3+} + CN^- \rightleftharpoons Fe^{II}(TMPyP)(CN)_2{}^{2+}}$$

$$\mathrm{Fe^{III}(TMPyP)(CN)_2{}^{3+} + CN^{\bullet} + 2OH^- \rightleftharpoons Fe^{II}(TMPyP)(CN)_2{}^{2+} + CNO^-}$$

$$\mathrm{CNO^- + CN^- + H_2O \rightleftharpoons (CN)_2 + 2OH^-}$$

$$\mathrm{(CN)_2 + OH^- \rightarrow HOCO_2NH_2}$$

In addition to forming $\mathrm{HCO_2NH_2}$, $\mathrm{(CN)_2}$ is converted to polymeric materials in the presence of $\mathrm{CN^-}$.[28] The true distribution of products of the oxidation of $\mathrm{CN^-}$ under the present reaction conditions is not known.

The facile reoxidation of the reduced porphyrin by air implies that $\mathrm{Fe^{III}(TMPyP)(CN)_2{}^{3+}}$ is able to catalyze the oxidation of $\mathrm{CN^-}$ by $\mathrm{O_2}$

$$\mathrm{CN^- + {}^1/_2O_2 \xrightarrow{FeTMPyP} CNO^- \rightarrow \text{other products}}$$

Reaction Rates with the Radical Ions. Second-order rate constants for the reaction of the $\mathrm{Fe^{III}}$ porphyrins with $\mathrm{CO_2^-}$ and $\mathrm{O_2^-}$ under slightly acidic conditions are presented in Table III. The rate of $\mathrm{CO_2^-}$ reduction of $\mathrm{Fe^{III}(TMPyP)^{5+}}$ found here is in excellent agreement with the values determined by earlier workers[4,29] considering differences in reaction conditions. Our rate constant for $\mathrm{O_2^-}$ reduction of $\mathrm{Fe^{III}(TMPyP)^{5+}}$ is in excellent agreement with that reported Solomon, et al.[4]

Rate constants for reduction of porphyrins by $\mathrm{CO_2^-}$ lie in the diffusion-controlled range. α^4-$\mathrm{Fe^{III}(TMINP)^{5+}}$ reacts slightly more slowly than $\mathrm{Fe^{III}(TMPyP)^{5+}}$ with $\mathrm{CO_2^-}$, possibly reflecting steric interference between the bent formyl radical[34,35] and the

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(22) LaMer, G. N.; DelGaudio, J. *Adv. Chem. Ser.* **1977**, *102*, 207–226.
(23) DelGaudio, J.; LaMer, G. N. *J. Am. Chem. Soc.* **1976**, *98*, 3014–3015.
(24) Barnitz, V.; Leussing, D. L. *J. Inorg. Biochem.* **1991**, *43*, 336.
(25) Arifuku, F.; Watanabe, O.; Ujimoto, K.; Kurihara, H. *Electrochim. Acta* **1988**, *33*, 933–937.
(26) Barley, M. H.; Rhodes, M. R.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 1746.
(27) Wang, Y. L.; Lee, H. D.; Beach, M. W.; Margerum, D. W. *Inorg. Chem.* **1987**, *26*, 2444–2449.
(28) Skarda, V.; Ivkovich, D.; Labes, M. M. *J. Polymer Sci.* **1985**, *23*, 107–117.
(29) Wilkins, P. C.; Wilkins, R. G. *Inorg. Chem.* **1986**, *25*, 1908–1910.
(30) Chevalet, J.; Rouelle, F.; Gierst, L.; Lambert, J. P. *J. Electroanal. Chem. Interfacial Electrochem.* **1972**, *39*, 201–216.
(31) Wilshire, J.; Sawyer, D. T. *Acc. Chem. Res.* **1979**, *12*, 105–110. Sawyer, D. T., Valentine, J. S. *Acc. Chem. Res.* **1982**, *15*, 200.
(32) Airey, P. L.; Sutton, H. C. *J. Chem. Soc., Faraday Trans. 1* **1976**, *1976*, 2441–2451.
(33) Koppenol, W. H.; Rush, J. D. *J. Phys. Chem.* **1987**, *91*, 4430-4431.
(34) Kafafi, Z. H.; Hauge, R. H.; Pillups, W. E.; Margrave, J. L. *Inorg. Chem.* **1984**, *23*, 177–183.
(35) Jordan, K. D. *J. Phys. Chem.* **1984**, *88*, 2459–2465.

Table III. Second-Order Rate Constants for the Reaction of Fe^{III} Porphyrins with O_2^- and CO_2^-

rate constant	ref
$Fe^{III}(TMPyP)^{5+} + CO_2^- = Fe^{II}(TMPyP)^{4+} + CO_2$	
1.4×10^{10}	this work[a]
7.5×10^9	4[b]
1.3×10^{10}	29[c]
$Fe^{III}(\alpha^4\text{-}TMINP)^{5+} + CO_2 = Fe^{II}(\alpha^4\text{-}TMINP)^{4+} + CO_2$	
6.1×10^9	this work[a]
$Fe^{III}(\alpha^3,\beta\text{-}TMINP)^{5+} + CO_2 = Fe^{II}(\alpha^3,\beta\text{-}TMINP)^{4+} + CO_2$	
5.9×10^9	5[d]
$Fe^{III}(TMPyP)^{5+} + O_2^- = Fe^{II}(TEMPyP)^{4+} + O_2$	
1.2×10^8	this work[a]
2.2×10^8	4[b]
$Fe^{III}(\alpha^4\text{-}TMINP)^{5+} + O_2^- = Fe^{II}(\alpha^4\text{-}TMINP)^{4+} + O_2$	
8.1×10^8	this work[a]
$Fe^{III}(\alpha^3,\beta\text{-}TMINP)^{5+} + O_2^- = Fe^{II}(\alpha^3,\beta\text{-}TMINP)^{4+} + O_2$	
7.6×10^7	5[d]
$Fe^{III}(TPPS)^{3-} + O_2^- = Fe^{II}(TPPS)^{4-} + O_2$	
8×10^6	38

[a] 0.10 M HCO_2^-; pH 5.6. [b] 0.10 M HCO_2^-; pH 5.6–8.3. [c] 0.050 M HCO_2^-; pH 8.0. [d] $I = 0.10$.

porphine ring substituents. Rate constants for the reduction of the isomers α^3,β-$Fe^{III}(TMINP)^{5+}$ and α^4-$Fe^{III}(TMINP)^{5+}$ are essentially identical, as is expected for diffusion-controlled processes.

Rate constants for O_2^- reduction are about 2 orders of magnitude slower. The slower rate is consistent with the much more positive reduction potential of O_2^-

$$O_2(aq) + e^- = O_2^- \qquad E° = -0.16 \text{ V vs NHE}^{30-32}$$

$$CO_2(aq) + e^- = CO_2^- \qquad E° = -1.8 \text{ V vs NHE}^{33}$$

α^4-$Fe(TMINP)^{5+}$ reacts significantly faster than $Fe^{III}(TMPyP)^{5+}$, α^3,β-$Fe^{III}(TMINP)^{5+}$, or $Fe^{III}(TPPS_4)^{3-}$ with O_2^-. The rate constants of these last three porphyrins to follow their reduction potential in accordance with the Marcus equation,[37] eq 2. From respective $E_{1/2}$ values of +0.13,[12,26] 0.077,[38] and 0.00[38] V vs NHE, the intrinsic barriers, ΔG_0^* for reaction with O_2^-, are calculated to be 9.8, 10.0 and 9.8 kcal mol^{-1}.

$$\Delta G^* = \Delta G_0^* + \Delta G°/2 + (\Delta G°)^2/16\Delta G_0^* \qquad (2)$$

Taking ΔG_0^* equal to 9.9 kcal mol^{-1}, the reverse calculation using the rate constant determined for the reaction of α^4-$Fe^{III}(TMINP)^{5+}$ with O_2^- indicates that $E°$ should lie in the vicinity of +0.3 V vs NHE for the reduction α^4-$Fe^{III}(TMINP)^{5+} + e^- = \alpha^4$-$Fe^{II}(TMINP)^{4+}$. However, such a high positive reduction potential is incompatible with the observed inertness of the porphyrin toward reduction by CN^-. The source of the high rate constant must then lie in a change in the reaction mechanism. It is reasonable to expect that the mechanism involves the rapid binding of O_2^- within the positively charged pocket of the picket fence porphyrin prior to electron transfer, which would then be facilitated. A tendency for preequilibrium binding of O_2^- would be decreased in the case of the $\alpha^3\beta$-isomer and be totally absent in $Fe^{III}(TMPyP)^{5+}$.

In view of the increase in $E_{1/2}$ on cyanation of $Fe^{III}(TMPyP)(OH)^{4+}$, it is expected that the rate constant for reduction by O_2^- would also show an increase, instead of the inhibition by CN^- that has been observed.[4] However, the presence of unknown and time dependent concentrations of $Fe^{II}(TMPyP)(CN)_2^{2+}$ and oxidation products of CN^- in the reaction mixture obscures an interpretation of the inhibiting effect of CN^-. A more thorough study of this system is necessary before the inhibition is understood.

$\alpha^3\beta$-$Fe(TMINP)^{5+}$ has been found to be an excellent catalyst for superoxide dismutation.[5] The high reaction rate of α^4-$Fe^{III}(TMINP)^{5+}$ with O_2^- and the sensitivity of the reduced form toward oxidants imply that this picket fence porphyrin would be even a better catalyst.

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(36) Rodgers, K. R.; Reed, R. A.; Su, O.; Spiro, T. *Inorg. Chem.* **1992**, *31*, 2688–2700.

(37) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155; *J. Phys. Chem.* **1968**, *72*, 891.

(38) Peretz, P.; Solomon, D.; Weinraub, D.; Faraggi, M. *Int. J. Radiat. Biol.* **1982**, *42*, 449–456.