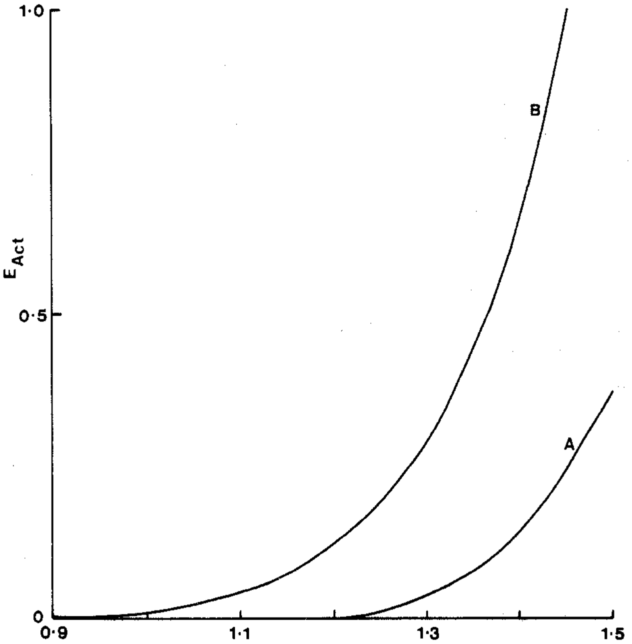

Figure 6. Activation energy for racemization of M(bidentate)$_3$-(unidentate) by a double-opposed-initiated twist mechanism (curve A), $R = 1.00$, and of M(bidentate)$_3$ by a Bailar twist mechanism (curve B), $n = 6$.

it may be noted that the minimum due to stereochemistry C_1 moves to higher ϕ_D until it corresponds to a capped trigonal prism rather than to a stereochemistry intermediate between a capped trigonal prism and a pentagonal bipyramid.[2] The important feature is that the progressive stabilization of the capped trigonal antiprism as the unidentate ligand is withdrawn is relatively small. In all cases the minimum activation energy for racemization is simply the energy required to climb out of the well of stereochemistry A. Even at $R =$ 1.4, which must be considered to be a fairly weak metal–unidentate ligand interaction, the activation energy for this "double-opposed-initiated" twisting is less than half that for the Bailar twist mechanism.

The detailed relation between the value of R and the activation energy for these racemization reactions is shown in Figure 5, which shows that the solvent-assisted double-opposed-initiated twist mechanism is more probable than the solvent-hindered triple-twist mechanism as long as $R < 2.0$. When $R = \infty$, the activated complex of stereochemistry B_2 for this double-opposed-initiated twist becomes identical with the activated complex for the Ray and Dutt twist, or twisting around an imaginary C_3 axis (operation A_8 of ref 1). Similarly the activated complex of stereochemistry C_1 becomes identical with the activated complex of the Bailar twist.

The effect of changing the normalized bite b of the bidentate ligand on the activation energies for the solvent-free Bailar twist and the solvent-assisted double-opposed-initiated twist for $R = 1$ is shown in Figure 6. The activation energies for both processes decrease as expected as b is decreased, but for the latter to a greater extent.

These general conclusions are not altered by using values of $n = 1$ or 12 in the assumed repulsive law.

In summary, it is concluded that the mechanism of racemization may change from a triple-twist process to a double-opposed-initiated twist process as the coordinating ability of the solvent increases. These two processes are experimentally distinguishable if asymmetric chelating agents are used.[1]

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Characterization of Heptacyanovanadate(III)

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The structure of the heptacyanovanadate(III) ion, $V(CN)_7^{4-}$, has been shown to be a pentagonal bipyramid from a single-crystal X-ray crystallographic study of $K_4V(CN)_7 \cdot 2H_2O$.[1,2] Although this anion had been prepared in a number of studies,[3-11] its structure, frequently presumed to be octahedral, had never been explicitly determined. The possibility of seven-coordination, however, had indeed been recognized by several groups of workers.[6-11] Since this same material was most likely prepared by Alexander and Gray[7] (although they formulated it as a hexacyanide, their analytical results are essentially perfect for $K_4V(CN)_7 \cdot 2H_2O$) and since they reported difficulty in repeating the synthesis, a separate and detailed elaboration of the synthesis and properties of $K_4V(CN)_7 \cdot 2H_2O$ appears warranted. Further impetus stems from reports that anhydrous[10] and monohydrated[9] forms of the same material have been prepared. The $V(CN)_7^{4-}$ anion need not necessarily have the same structure in these several compounds in view of the work on the analogous $Mo(CN)_7^{4-}$ complex which indicates that, while in the anhydrous potassium salt and in an aqueous solution the seven-coordinate anion has a pentagonal-bipyramidal structure, monocapped trigonal-prismatic coordination obtains in the dihydrate.[12]

Since the structure of $K_4V(CN)_7 \cdot 2H_2O$ is now firmly established, we herein report a vibrational study in the cyanide stretching region (infrared and Raman in both the solid state and aqueous cyanide) and an electron spin resonance study of the species present in solution. An emission observed while examining the Raman spectrum is interpreted in terms of a ligand field study which has already been presented;[13] a molecular orbital treatment of this fundamentally interesting species has also been given.[14]

Experimental Section

All preparative work was carried out in a nitrogen-purged glove bag. Oxygen-free water was prepared by refluxing for 1.5 hr while purging with nitrogen. All other solvents were purged with nitrogen for 1 hr prior to use. Infrared spectra were obtained on a Beckman IR-12 spectrophotometer. CaF_2 cells were used for solution infrared spectra. Raman spectra were obtained on a Cary Model 82 Raman spectrophotometer using a Coherent Radiation Model 52B krypton ion

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laser. Solution spectra were obtained with the standard liquid multipass cell available from Cary using a defocused laser beam; a stream of nitrogen directed at a solid sample was sufficient to prevent air oxidation of the $K_4V(CN)_7 \cdot 2H_2O$. The esr spectra were recorded with a Varian Model E6-A spectrometer; a standard flat cell was used for solutions at room temperature. Spectra at 77°K were recorded by immersion of samples in standard quartz esr tubes into a dewar.

$K_4V(CN)_7 \cdot 2H_2O$ was prepared by the following modification of the method of Locke and Edwards.[3] VCl_3 from Alfa Inorganics (2.48 g) was dissolved in 6 ml of water at 0°. Deoxygenated 6 *M* HCl was added dropwise with stirring until the solution turned green (~4–5 drops). This solution was added dropwise with stirring to a solution of 9.4 g KCN in 13 ml of water that was also at 0°. An intensely colored violet precipitate formed which dissolved almost completely upon stirring at 0° for 10 min and then at room temperature for 0.5 hr. The small amount of violet precipitate remaining after this period was separated by filtration, and 25 drops of ethanol were slowly added. After 24 hr at 0° deep red crystals had formed which were washed with 1 ml of 0° water and then 5–10 ml of ethanol; the crystals were dried at room temperature on a vacuum line for 4 hr. A second crop of crystals may be obtained by adding 25 drops of ethanol to the mother liquor and following the above procedure. The compound was stored under nitrogen in a Schlenk tube in the freezer (*ca.* −5°). Attempts to isolate sodium and tetrabutylammonium salts were unsuccessful. *Anal.*[15] Calcd for $K_4V(CN)_7 \cdot 2H_2O$: C, 19.76; H, 0.95; N, 23.04. Found: C, 19.23; H, 0.91; N, 23.55.

An attempt to prepare a methyl isocyanide analog by dropwise addition of VCl_3 in ethanol to an excess of CH_3NC[16] produced a purple solution from which no well-defined compound could be isolated. Extensive efforts in this direction were not continued.

Results and Discussion

Synthetic Studies. The procedure outlined is quite reproducible and leads to the compound $K_4V(CN)_7 \cdot 2H_2O$ as established by crystallographic studies.[1,2] Since a material formulated as $K_4V(CN)_7$ by Nast and Rehder[10] was prepared in nonaqueous media and since a compound of composition $K_4V(CN)_7 \cdot H_2O$,[9] although prepared similarly to the method given above, was washed in a different manner (methanol and ether followed by drying *in vacuo* for an unspecified length of time), the existence of potassium salts of the $V(CN)_7^{4-}$ anion as a dihydrate, a monohydrate, and an anhydrous material may in fact be real. The infrared spectra in the cyanide stretching region of the three compounds are sufficiently similar, however, to suggest that the geometry of the anions in all cases is the same. $K_4V(CN)_7 \cdot 2H_2O$ survives brief handling in air but decomposes to a greenish powder upon prolonged exposure. Aqueous deoxygenated solutions turn green unless a large excess of cyanide is present. The solution behavior is more fully discussed in the discussion of the electron spin resonance spectra (*vide infra*). It is unfortunate that other salts of $V(CN)_7^{4-}$ could not be isolated in view of the dependence of structure on cation found for $Mo(CN)_7^{4-}$.[12]

We note the similarity of the colors upon initial reaction for both the cyanide (aqueous) and isocyanide (nonaqueous) preparations and that the violet intermediate in the cyanide reaction has been suggested to be a dimeric hydroxy-bridged complex containing both V(III) and V(IV).[9] Interestingly, an intense blue-violet compound formulated as $Na_3V(CN)_6$ has been reported but remains incompletely characterized.[10] Also, a blue vanadium(III) complex presumably results from the oxidation of $K_4V(CN)_6 \cdot 3H_2O$.[17]

Vibrational Studies. The infrared spectrum of $K_4V(CN)_7 \cdot 2H_2O$ shows two bands in the cyano stretching region in a Nujol null (2100(s) and 2070 (m) cm^{-1}) and in 6.0 *M* aqueous KCN (2104 (s) and 2072 (m) cm^{-1}); in the latter spectrum a weak peak at 2080 cm^{-1} is attributed to free cyanide ion incompletely compensated for by the solution in the reference beam. Thus, the solution and solid-state infrared spectra are the same, implying that the species in solution is the $V(CN)_7^{4-}$ ion with pentagonal-bipyramidal geometry. In D_{5h} symmetry the fundamental cyano stretching modes a_2'' and e_1' are infrared active while there are three Raman-active modes, 2 a_1' and e_2'. The bands at ~2100 and ~2070 cm^{-1} are tentatively assigned as the e_1' and a_2'' modes, respectively, on the basis of their relative intensities. The solid-state Raman spectrum (568.2-nm excitation) shows bands at 2110 (m), 2104 (s), 2100 (s), and 2094 (sh, vw) cm^{-1}; a spectral band width of 2 cm^{-1} was required to resolve all bands and there may be some question as to the genuineness of the low-energy shoulder. The three prominent peaks in the solid-state spectrum are indeed consistent with pentagonal-bipyramidal symmetry; however, the less-than-perfect D_{5h} geometry seen in the crystal[1,2] may be responsible for the number of bands observed. Considerable difficulty was encountered in obtaining a solution spectrum, and only an unresolved and polarized line at *ca.* 2103 cm^{-1} has been observed; this is most likely one (or both, if they are accidentally degenerate) of the a_1' modes. The above data are consistent with a study of the $Mo(CN)_7^{4-}$ ion in aqueous solution (in which it presumably has symmetry D_{5h})[12] wherein two infrared bands were observed; also, only two of the predicted three Raman bands were seen, presumably due to either low intensity of the third band or accidental degeneracy. Thus, there is no evidence to indicate that $V(CN)_7^{4-}$ adopts the capped trigonal-prismatic structure or any other of the possible seven-coordinate structures[18] different from the pentagonal bipyramid either in solution or in the solid state; this conclusion also applies to the anhydrous[10] and monohydrated[9] forms of the complex.

Seven-coordinate complexes are generally considered to be stereochemically nonrigid.[19-21] There seems to be no doubt from the vibrational data that the pentagonal bipyramid is the ground-state geometry in solution for $V(CN)_7^{4-}$. More complex spectra would have been observed had any of the other seven-coordinate polyhedra (all of lower symmetry than D_{5h}) been present[12] (interpretative difficulties of the type encountered for the $Mo(CN)_8^{4-}$ ion,[22] wherein there were several structural possibilities, are not a problem here). This is not to say that $V(CN)_7^{4-}$ is a rigid structure, since the time scale for an infrared or Raman experiment is likely to be very short relative to the rate of any anticipated rate of interchange of the two nonequivalent sites (two axial and five equatorial ligands).[22] It is unfortunate that the paramagnetism of $V(CN)_7^{4-}$ will probably preclude the nmr studies which would be needed to obtain reliable information with respect to possible fluxional behavior.

Electron Spin Resonance Studies. Since esr spectra of d^2 ions are generally not observed because of zero-field splitting effects,[23] it was hoped that $V(CN)_7^{4-}$ would exhibit a well-defined esr spectrum. However, the spectrum at room temperature in aqueous cyanide (Figure 1) is a superposition of

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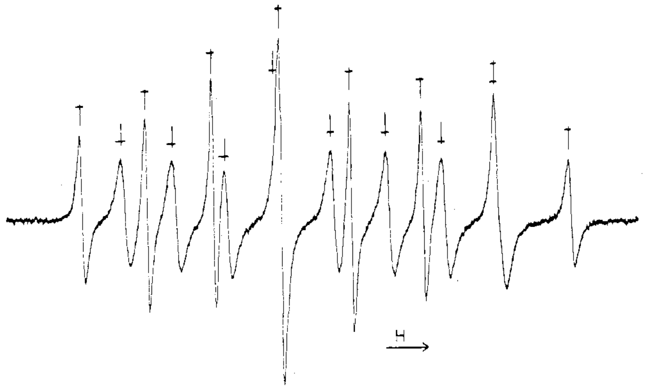

Figure 1. The esr spectrum of $K_4V(CN)_7 \cdot 2H_2O$ in 2.0 *M* aqueous cyanide: † represents resonances of $VO(CN)_5^{3-}$; ⸸ represents those of $V(CN)_6^{4-}$.

the spectra of $V(CN)_6^{4-}$ and $VO(CN)_5^{3-}$ as judged by comparison with literature data[24,25] and with genuine solutions of these ions. A frozen-glass spectrum at 77°K also shows resonances attributable only to the V(II) and V(IV) species. Solid-state spectra at room and liquid nitrogen temperature reveal only a broad absorption at high microwave power which can be attributed to $VO(CN)_5^{3-}$ impurities. Thus, while $V(CN)_7^{4-}$ gives no esr spectrum under our experimental conditions, it clearly disproportionates to $V(CN)_6^{4-}$ and $VO(CN)_5^{3-}$ in solution.

A disproportionation of V(III) in aqueous cyanide was suggested by Bennett and Nicholls[9] in their study of complex cyanides of vanadium. However, their evidence, based on absorption spectra, was not entirely conclusive because of the similarity of the visible spectra of the $V(CN)_6^{4-}$ and $V(CN)_7^{4-}$ ions. Also, we have never obtained a solid sample absolutely free of $VO(CN)_5^{3-}$ impurity (as judged by esr) and thus an electronic spectral band of the V(IV) species could be attributed to the impurities. Indeed, oxidation of $V(CN)_7^{4-}$ should produce $VO(CN)_5^{3-}$.

Upon dissolving $K_4V(CN)_7 \cdot 2H_2O$ in aqueous cyanide, the intense purple solution was obtained. The fate of the purple material was found to depend upon the cyanide concentration. For high $[CN^-]$ (*ca.* 1.0 *M* or greater) the solution became orange-red. For dilute concentrations (*ca.* 0.3 *M*) of cyanide, a greenish tinge to the solution appeared as the purple coloration faded; a precipitate also formed. By measuring the $VO(CN)_5^{3-}$ concentration using either the lowest or highest field resonance[26] (which are attributable solely to $VO(CN)_5^{3-}$; see Figure 1), a 2.0 *M* NaCN solution formally 0.050 *M* in $K_4V(CN)_7 \cdot 2H_2O$ was found to have a $VO(CN)_5^{3-}$ concentration of 4.7×10^{-3} *M*. (Because of experimental difficulties, the $VO(CN)_5^{3-}$ concentrations are accurate only to within ±10%; this uncertainty also reflects any $VO(CN)_5^{3-}$ impurity which may have been present in the $K_4V(CN)_7 \cdot 2H_2O$.) Immediate (*i.e.*, after the purple color had faded) dilution of this solution to a total vanadium concentration of 0.020 *M* in both 2.0 and 6.0 *M* NaCN gave solutions in which the concentration of $VO(CN)_5^{3-}$ was 1.2×10^{-3} *M* in *both* cases. A 0.3 *M* NaCN solution formally 0.050 *M* in $V(CN)_7^{4-}$ was diluted (while still purple) to 0.020 *M* in 0.3 and 3.0 *M* NaCN. While the more dilute cyanide solution never attained the red-orange color typical of solutions containing $V(CN)_7^{4-}$ (as judged by the vibrational studies), the 3.0 *M* solution assumed the red-orange color after 15 min and had a $VO(CN)_5^{3-}$ concentration of 3.4×10^{-3} *M*. Finally, mixing equal volumes of $VO(CN)_5^{3-}$ and $V(CN)_6^{4-}$ which were both 6.72×10^{-3} *M* in 3.0 *M* NaCN produced a solution that was *ca.* 3.4×10^{-3} *M* in both species. (The concentration of $V(CN)_6^{4-}$ was judged using the next to the lowest field resonance.) Thus, while $V(CN)_7^{4-}$ will produce $VO(CN)_5^{3-}$ and $V(CN)_6^{4-}$, the reverse reaction does not occur (at least over a period of 12 hr). The following scheme is proposed

$$\begin{array}{c} V(CN)_7^{4-} \rightleftharpoons \text{purple material} + CN^- \\ \downarrow \\ VO(CN)_5^{3-} + V(CN)_6^{4-} + CN^- \end{array}$$

The purple material, of unknown composition, will react with cyanide to form $V(CN)_7^{4-}$ (this is part of the synthetic procedure) or will decompose to produce the established cyanide species of V(II) and V(IV). Clearly the system is quite complicated and there is no assurance that more species are present than have been accounted for here.

We conclude that when $K_4V(CN)_7 \cdot 2H_2O$ is dissolved in concentrated cyanide, the primary species in solution is the $V(CN)_7^{4-}$ ion. For more dilute cyanide solutions, there is a greater amount of disproportionation products as well as an insoluble residue. The relationship of this work with the finding that the rate of exchange of free cyanide with the cyano complex of vanadium(III) is immeasurably rapid[7] is not immediately obvious. All evidence to date reaffirms the conclusion that the existence of a $V(CN)_6^{3-}$ complex in aqueous solution remains unsubstantiated.[6] Despite the work of Bennett and Nicholls, the purple material may contain the species $V(CN)_6^{3-}$; it is also possible that there are several different purple complexes in the vanadium–cyanide system under consideration.

Emission Studies. Use of 568.2-nm laser excitation in the solid-state Raman studies of the C–N stretching frequencies was necessitated by the observation of a very strong, intense, broad, and featureless emission centered *ca.* 12,900 cm^{-1}. The C–N modes were not observable against this background when 647.1-nm excitation was used, and thus the higher energy line was required. This emission, which occurs at the same absolute energy irrespective of the energy of the incident radiation, is to our knowledge the first one observed in a well-characterized seven-coordinate transition metal complex. Furthermore, the emission is observed only in the solid state; its nonexistence in aqueous media is likely caused by the various quenching mechanisms available in solution.[27] A crystal field treatment of $V(CN)_7^{4-}$ shows that within the manifold of the ground-state configuration $(d_{xz})^1(d_{yz})^1 = (e_1'')^2$ there are the two excited singlet states ${}^1E_2'$ and ${}^1A_1'$ which are above the ${}^3A_2'$ ground state by $6B + 2C$ and $12B + 4C$, respectively.[13] Using the derived value of B of 367 cm^{-1}, the most reasonable assignment for the 12,900-cm^{-1} emission is ${}^1A_1' \rightarrow {}^3A_2'$ which leads to a value for C of 2124 cm^{-1}. No other reasonable choice of B, in view of the findings that values of $B_{\text{complex}}/B_{\text{free ion}}$ for cyanide complexes are *ca.* 0.5,[7] would lead to the alternative assignment ${}^1E_2' \rightarrow {}^3A_2'$.

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Temperature-Jump Kinetic Study of a Ferric Porphyrin Monomer-Dimer Equilibrium in Aqueous Solution

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Stability constants have been measured for the monomer-dimer equilibrium of a number of different ferric porphyrins in aqueous solution. The actual species observed and their equilibrium behavior can be described as[2]

$$PFe(H_2O) = PFe(OH)^- + H^+ \tag{1}$$

$$PFe(OH)^- + OH^- = PFe(OH)_2{}^{2-} \tag{2}$$

$$2PFe(OH)_2{}^{2-} = [(PFe)_2(OH)_2O]^{4-} + H_2O \tag{3}$$

$$2PFe(OH)^- = [(PFe)_2O]^{2-} + H_2O \tag{4}$$

$$2FeP(H_2O) = [(PFe)_2O]^{2-} + 2H^+ + H_2O \tag{5}$$

With an ethylenediamine-substituted protoporphyrin (ENP),[3] reactions 1-3 occur. With a disulfonated deuterohemin (DPS_2),[4] reactions 1 and 4 are found while for the tetrasulfonated tetraphenylporphine ($TPPS_4$),[5] the evidence is only for process 5. The tetra-N-methylated tetrapyridylporphine (TMTPyP)[6] is reported to be similar to ENP, with several unusual features. A stopped-flow study of the kinetics of monomerization of the $FeTPPS_4$ dimer has been done.[5] Previous relaxation studies in this area[3,4,7,8] have involved porphyrins or metalloporphyrin dimers held together by moderate electrostatic polarization forces, in contrast to the oxy bridges found in iron porphyrin dimers. To gain a better understanding of the iron porphyrin monomer-dimer phenomena, we report a temperature-jump kinetic study on reaction 5 with $Fe^{III}TPPS_4$.

Experimental Section

$Fe^{III}TPPS_4$ was made by literature methods.[5] The equilibrium and kinetic studies were run at 20° with 0.05 *M* $NaNO_3$ and 0.02 *M* PIPES buffer. Equilibrium measurements were done with a Beckman Acta III recording spectrophotomer. The equilibrium constant for $FeTPPS_4$ dimerization (reaction 5) was determined in the same manner as described by other workers.[5] Our pK_D of 8.6 ± 0.2 is in good agreement with the value of 8.2 ± 0.3 at $\mu = 0.1$ (20°) reported earlier[5] while kinetic data were collected with a temperature-jump apparatus constructed in this laboratory.[9] The kinetics were followed at wavelengths between 390 and 430 nm, at pH values from 6.09 to 7.50, with total porphyrin concentrations 8.2×10^{-7}–1.7×10^{-5} *M*. The rate constants (±10%) were obtained from transmittance–time data using a nonlinear least-squares program.

Results and Discussion

A spectrophotometric titration of $Fe^{III}TPPS_4$ with base between pH 5 and 8 gave an excellent isosbestic point at 406 nm, and the absorption spectra were unchanged between pH 1 and 5 and from pH 8 to 12. This indicates that only the unhydrolyzed forms of the iron monomer and dimer are in significant concentration. No relaxations were found below pH 5 or above pH 8, where the monomer and dimer forms, respectively, predominate. Between pH 6 and 8 two absorbance changes were observed. The first, with a relaxation time of a few microseconds, was too fast to be resolved. The second, in the 100-msec range, was dependent on pH and total porphyrin concentration.

Assuming a mechanism of the form

$$PFe(H_2O) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PFe(OH)^- + H^+ \tag{6}$$

$$2PFe(OH)^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [(PFe)_2O]^{2-} + H_2O \tag{7}$$

with $PFe(OH)^-$ present as a low concentration intermediate, the reciprocal relaxation time for the slower process, τ^{-1}, is given by the expression

$$\tau^{-1}\left[1 + \frac{4k_1k_2(PFe(H_2O))}{k_{-1}{}^2(H^+)^2}\right] = \frac{4k_1{}^2k_2}{k_{-1}{}^2}\left[\frac{(PFe(H_2O))}{(H^+)^2}\right] + k_{-2} \tag{8}$$

The faster process has a more complicated concentration dependence and can be written down by standard methods.[10] Rearrangement of eq 8 yields an expression (Table I and Figure 1) whereby a plot of $(R + 1)/\tau^{-1}$ *vs.* R is linear with a slope of $1/k_1$ and an intercept of $1/k_{-2}$. Here, R is $4(PFe(H_2O))Q/(H^+)^2$ and Q is the equilibrium constant for eq 5; $Q = 2.5 \times 10^{-9}$ $M = k_1{}^2k_2/k_{-1}{}^2k_{-2}$. A least-squares analysis gives $k_1 = 3.37 \pm 0.17$ sec^{-1} and $k_{-2} = 0.90 \pm 0.05$ sec^{-1} at 20°, the "jump" temperature.

The low-concentration approximation on $PFe(OH)^-$ used in the kinetic derivation is in accord with the observed isosbestic point, which indicates a low concentration of $PFe(OH)^-$ with respect to both $PFe(H_2O)$ and the dimer. The assumption, for example, that eq 6 equilibrates rapidly relative to eq 7 is not consistent with the data.

Our results can be compared with those found for the monomerization of the $Fe^{III}TPPS_4$ dimer, measured by stopped-flow techniques.[5] The observed rate law was first order in dimer, with terms dependent ($k_{-3} = 840$ M^{-1} sec^{-1}) and independent ($k_{-2} = 41$ sec^{-1}) of (H^+). While K_D for this porphyrin depends strongly on ionic strength and temperature,[5] our k_{-2} value (0.9 sec^{-1}) is not in agreement with the stopped-flow results. The acid-dependent term k_{-3} is

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(1) (a) Howard University. (b) NIH.

(2) The total charges of the porphyrin species have been omitted for clarity. For example with $FeTPPS_4$, $(PFe)_2O$ has a net molecular formal charge of 8–, with two ionized tetrasulfonated ferric fragments assigned 3– each and the oxygen of the oxy bridge assigned 2–. (P) represents the porphyrin framework.

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