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Hydrogen Bonding in Metalloporphyrin Reactions. Reaction of (Tetraphenylporphinato)iron(III) Chloride and Imidazole

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A detailed kinetic study is reported for the reaction Fe(TPP)Cl + 2HIm → Fe(TPP)(HIm)$_2$$^+Cl^-$. In acetone the rapid reversible formation of the mono(imidazole) intermediate Fe(TPP)(HIm)Cl is followed by rate-determining chloride ionization and further HIm addition to give the low-spin bis(imidazole) product. Hydrogen bonding from free imidazole to the chloride in the intermediate greatly accelerates the ionization and causes the rate law for the overall reaction to be second order in imidazole. This behavior contrasts with the analogous reaction with *N*-methylimidazole, for which the chloride ionization is unassisted and the rate law first order in *N*-MeIm at low concentrations of *N*-MeIm. The relationship between these results and hydrogen bonding from a distal histidine to a coordinated anion (e.g., superoxide) in hemoproteins is discussed. The intermediate Fe(TPP)(HIm)Cl was prepared in solution at −78 °C and characterized by electronic spectral and conductivity measurements. It is a rare example of a six-coordinate high-spin iron(III) porphyrin with nonidentical axial ligands.

Introduction

Iron porphyrins function as prosthetic groups in a variety of proteins, including hemoglobin, myoglobin, catalases, peroxidases, and cytochromes. In these hemoproteins the heme iron is coordinated to one or two axial ligands. The most common axial ligand is an imidazole imine nitrogen from a histidine residue. Hydrogen bonding from the pyrrole N–H of the coordinated (or proximal) imidazole to a basic site (usually carbonyl) on the polypeptide backbone is believed to influence protein structure and reactivity.[2]

A second type of hydrogen bonding involves an external (or distal) hydrogen donor and an axially coordinated substrate molecule such as dioxygen or a peroxide.[3] There has been speculation for two decades[4] that one function of the E7 distal histidine in myoglobin and hemoglobin may be to stabilize the polar iron–dioxygen moiety, usually formulated as coordinated superoxide, Fe^{III}–O_2^-. It was suggested that the distal imidazole forms a hydrogen bond to the superoxide that is strong enough to provide stabilization but not so strong as to lead to proton transfer and irreversible oxidation to Fe(III) and HO_2. Over the years evidence supporting this hypothesis has accumulated from (1) studies of proton-dependent autoxidation and superoxide formation with MbO_2, HbO_2, and oxy-P450,[5-11] (2) properties of mutant hemoglobins,[12,13] and (3) Raman and ESR studies.[14-16] Very recently, neutron diffraction has confirmed[17] hydrogen bonding from the E7 histidine to dioxygen in MbO_2 while X-ray diffraction studies of HbO_2 suggest[18] quite strong hydrogen bonds in the α subunits and weaker ones in the β subunits.

Studies of protein-free iron(II) and cobalt(II) porphyrin complexes show that hydrogen bonding to coordinated dioxygen may have important consequences. Autoxidation rates of iron(II) deuteroporphyrins in 50% pyridine/50% solvent correlate with the solvent protic character and not polarity.[19] The rate of oxidation of oxy cobalt(II) porphyrins to cobalt(III) species correlates with the proton acidity of the solvent[20] or nucleophile.[21] The dioxygen affinity of cobalt(II) macrocycles is increased in the presence of strong hydrogen bond donors such as trifluoroethanol.[22] The variation of dioxygen binding to synthetic iron(II) and cobalt(II) porphyrins is a complicated function of steric, solvation, polarity, and hydrogen-bonding effects.[22-26] However, it is clear that generally the O_2 affinity increases as groups on the distal side become more polar and/or possess the ability to hydrogen bond to the coordinated superoxide.

Although there is now considerable qualitative evidence that distal type hydrogen bonding is important in some reactions of metalloporphyrins and hemoproteins, a quantitative assessment of the effect on reaction rates and thermodynamics is not available. In a recent report,[27] we demonstrated that hydrogen bonding from the solvent or other external reagent has a large effect on the kinetics of reaction 1. TPP is the

$$\text{Fe(TPP)Cl} + 2N\text{-MeIm} \rightarrow \text{Fe(TPP)}(N\text{-MeIm})_2^+\text{Cl}^- \quad (1)$$

dianion of tetraphenylporphyrin, and *N*-MeIm is *N*-methylimidazole. In this reaction the high-spin Fe(TPP)Cl reacts very rapidly to form high-spin six-coordinate Fe(TPP)(*N*-MeIm)Cl, which undergoes rate-determining chloride ionization and then rapid conversion to product. The chloride ionization is greatly accelerated by hydrogen bond donors. In a preliminary communication in 1979[28] we noted that the biologically more relevant ligand imidazole (HIm) follows a greatly different rate and rate law compared to those of the

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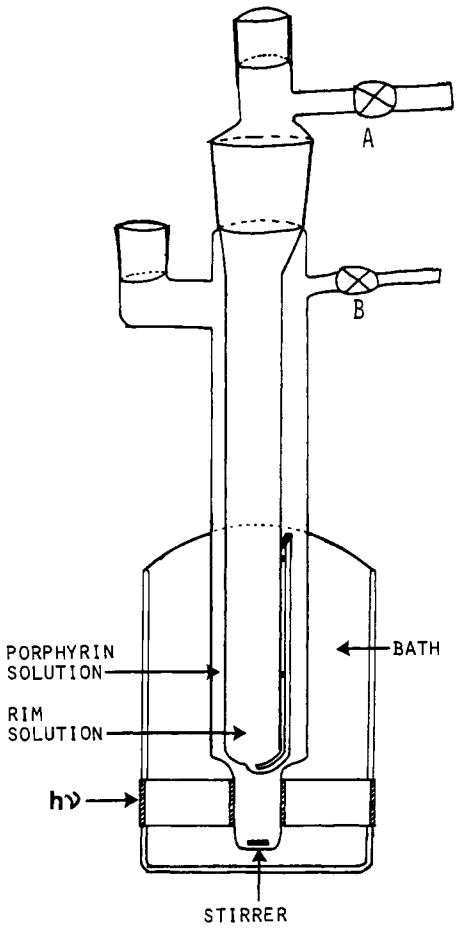

Figure 1. Optical cell for mixing solutions and recording visible spectra at low temperatures.

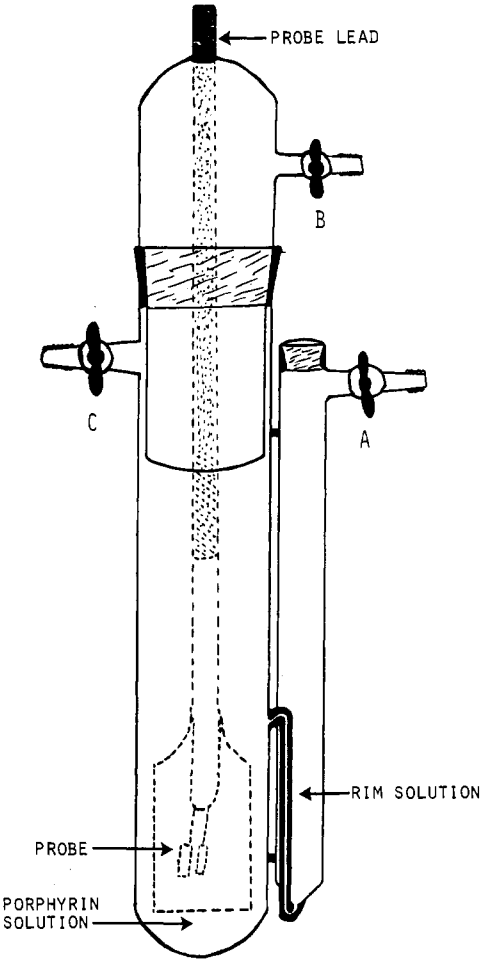

Figure 2. Apparatus for mixing solutions and recording conductivities at low temperatures.

N-alkylated imidazoles, although both HIm and *N*-MeIm give low-spin bisadducts, $Fe(TPP)(RIm)_2^+Cl^-$. In this paper we present results of a detailed investigation of reaction 2 and

$$Fe(TPP)Cl + 2HIm \rightarrow Fe(TPP)(HIm)_2^+Cl^- \quad (2)$$

demonstrate that hydrogen bonding from HIm to chloride in Fe(TPP)(HIm)Cl accounts for the differing behavior of HIm and *N*-MeIm. Thus, hydrogen bonding of an external or distal imidazole to an anionic ligand in an iron(III) porphyrin is shown to cause a rate acceleration by a factor of ca. 100. This result suggests that distal histidine hydrogen bonding to superoxide in HbO_2 and MbO_2 can reasonably be expected to significantly influence the kinetics and thermodynamics of oxygenation.

Experimental Section

Solvents were purified as previously described.[27] Infrared spectra were recorded on a Perkin-Elmer 681 instrument and ESR spectra on a Bruker ER-420 spectrometer. Visible spectra were recorded at room temperature on Gilford 250 and Perkin-Elmer 552 spectrometers. Optical spectra at low temperature were recorded on a Perkin-Elmer 552 instrument by using a special quartz cell designed by us and built by W. A. Sales, Ltd., Wheeling, Il. The cell, illustrated in Figure 1, was designed so that two separated reactant solutions can be precooled under dry nitrogen. In a typical experiment 50 mL of metalloporphyrin solution was placed in the outer chamber. The imidazole solution (1 mL) was placed in the inner chamber, which is connected to the outer one via capillary tubing. The solutions were cooled in the Dewar with dry ice/acetone. Mixing was effected by applying dry nitrogen in valve A with valve B open. A magnetic stirring bar located just below the light path was used to mix the solution.

Conductivity measurements at variable temperatures were made with a Beckman RC-16B2 conductivity bridge and a Beckman dipping conductivity cell enclosed in a special apparatus of our design (see Figure 2). To make a measurement, 50 mL of metalloporphyrin solution was placed in the main chamber containing the probe. The imidazole solution (1 mL) was placed in the side arm, which is connected to the main chamber by a capillary tube. The apparatus was then cooled in a dry ice/acetone slush bath while dry nitrogen gas flowed slowly in valve C and out the hole at the top through which the cell cable exits. To mix the solutions, valve B was opened and nitrogen gas applied through valve A, forcing the imidazole solution into the main chamber. The solutions were mixed by moving the probe head up and down.

Kinetic studies at and below room temperature were performed as previously described.[27]

Results and Discussion

Aggregation of Imidazole. Imidazoles not substituted at the pyrrole nitrogen are known to associate via intermolecular hydrogen bonding.[29-35] In acetone the aggregation can be satisfactorily described by a simple monomer (M)–dimer (D) equilibrium.[29] By measuring the relative intensities of the monomer and dimer N–H stretching bands in the IR region as a function of imidazole concentration (0.005–2.00 M), we estimated the $2M \rightleftharpoons D$ equilibrium constant to be approximately 0.6 M^{-1} at 25 °C, a value close to that previously reported.[29] This means that imidazole is significantly di-

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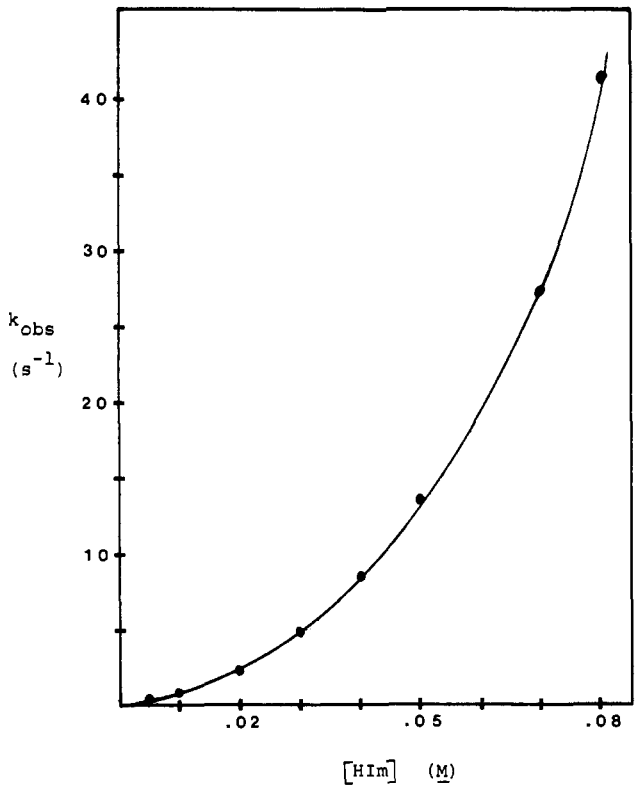

Figure 3. Rate constants for Fe(TPP)Cl + 2HIm → Fe(TPP)-$(HIm)_2^+Cl^-$ in acetone at 25 °C.

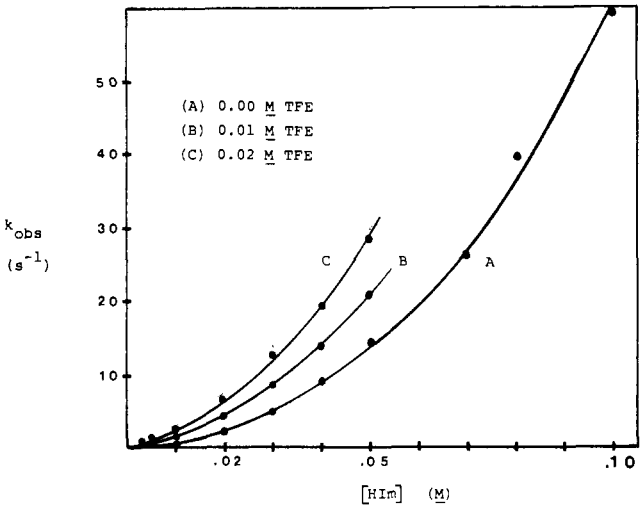

Figure 4. Effect of trifluoroethanol (TFE) on the rate constants for Fe(TPP)Cl + 2HIm → Fe(TPP)$(HIm)_2^+Cl^-$ in acetone at 25 °C.

merized (greater than 10%) above 0.15 M in acetone. As shown below, imidazole association can greatly affect the kinetic behavior of reaction 2. The effect on the equilibrium constant of reaction 2 has been discussed by Walker et al.[36]

Kinetic Studies. Rate measurements of reaction 2 were made in acetone. Figure 3 illustrates the rate dependence on the HIm concentration at 25 °C. A plot of k_{obsd} vs. $[HIm]^2$ is linear with a correlation coefficient of 0.99, slope of 5900 ± 200 M^{-2} s^{-1}, and intercept of zero within error. The addition of small amounts of trifluoroethanol, a good hydrogen bonder, caused the reaction to speed up noticeably as shown in Figure 4. Reaction 2 was found to be second order in HIm over the temperature range +25 to −12 °C; an Eyring plot of the

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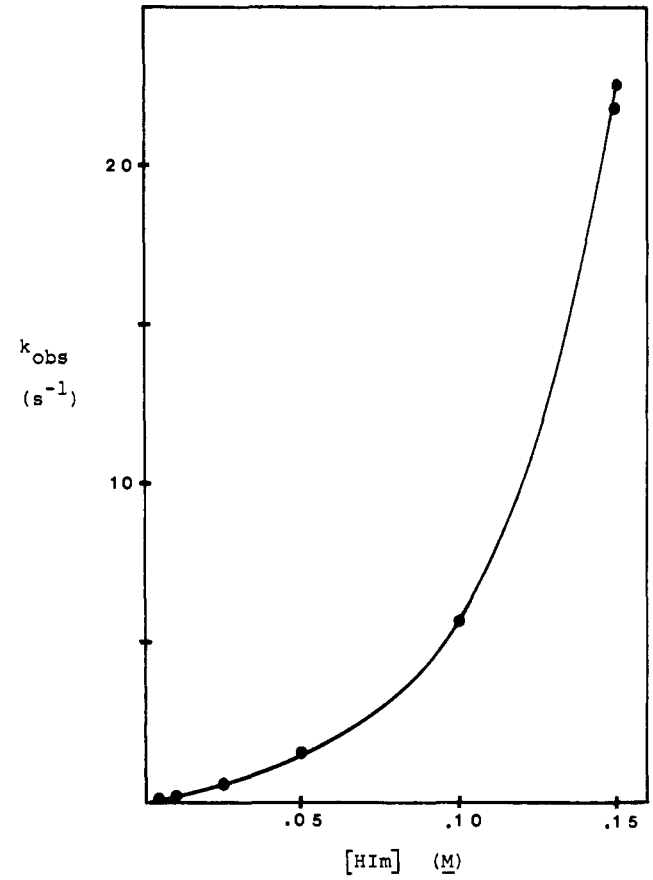


Figure 5. Rate constants for Fe(TPP)Cl + 2HIm → Fe(TPP)-$(HIm)_2^+Cl^-$ in acetone at −25 °C.

third-order rate constants for four temperatures within this range gave $\Delta H^\ddagger$ = 5.4 ± 0.2 kcal/mol and $\Delta S^\ddagger$ = −23 ± 2 cal/(deg mol). At −25 °C the rate data, shown in Figure 5, were greater than second order for [HIm] > 0.05 M. As discussed below, this is probably due to dimerization of the imidazole nucleophile. Similarly, rate accelerations and orders greater than second were observed when chloroform and benzene were used as solvents.

In our previous study[27] of the reaction of Fe(TPP)Cl and *N*-MeIm we proposed the mechanism given in eq 3–5 to ex-

$$\text{Fe(TPP)Cl} + \textit{N}\text{-MeIm} \underset{}{\overset{K_1}{\rightleftharpoons}} \text{Fe(TPP)}(\textit{N}\text{-MeIm})\text{Cl} \quad (3)$$

$$\text{Fe(TPP)}(\textit{N}\text{-MeIm})\text{Cl} \xrightarrow{k_1} \text{Fe(TPP)}(\textit{N}\text{-MeIm})^+\text{Cl}^- \quad (4)$$

$$\text{Fe(TPP)}(\textit{N}\text{-MeIm})^+\text{Cl}^- + \textit{N}\text{-MeIm} \xrightarrow{\text{fast}} \text{Fe(TPP)}(\textit{N}\text{-MeIm})_2^+\text{Cl}^- \quad (5)$$

$$k_{obsd} = \frac{k_1 K_1 [\textit{N}\text{-MeIm}]}{1 + K_1 [\textit{N}\text{-MeIm}]} \quad (6)$$

plain the observed rate law, eq 6. K_1 represents a rapid reversible preequilibrium followed by rate-determining chloride ionization from the (high-spin) mono(imidazole) intermediate. HIm reacts with Fe(TPP)Cl much more rapidly than *N*-MeIm and also follows a different rate law. We propose the mechanism shown in eq 7–9. Again K_1 represents a rapid pree-

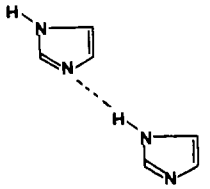
$$\text{Fe(TPP)Cl} + \text{HIm} \underset{}{\overset{K_1}{\rightleftharpoons}} \text{Fe(TPP)(HIm)Cl} \quad (7)$$

$$\text{Fe(TPP)(HIm)Cl} + \text{HIm} \xrightarrow{k_1} \text{Fe(TPP)(HIm)}_2^+\text{Cl}^- \quad (8)$$

$$k_{obsd} = \frac{k_1 K_1 [\text{HIm}]^2}{1 + K_1 [\text{HIm}]} \quad (9)$$

quilibrium and k_1 the rate-determining step in which the chloride ionization is assisted via hydrogen bonding to imidazole. The reaction given in eq 8 may consist of several elementary steps; e.g., the entering HIm need not be the one assisting the chloride ionization. Nevertheless, the essential features are given by eq 7 and 8. Our previous demonstration that hydrogen bonding to the chloride from trifluoroethanol or solvent (e.g., $CHCl_3$) greatly accelerates reaction 4 strongly supports the mechanism for HIm. The limiting zero-order behavior required by eq 6 at high *N*-MeIm concentrations was readily observed, but analogous limiting first-order kinetics at high HIm concentrations (eq 9) was not observed because the chloride ionization is so fast with HIm (eq 8) that HIm concentrations large enough to saturate the denominator in eq 9 gave rates too large to observe at 25 °C. Working at low temperatures cannot solve this dilemma due to imidazole aggregation. The detection and characterization of the mono(imidazole) intermediate, Fe(TPP)(HIm)Cl, discussed in the following section provides additional support for the proposed mechanism.

Imidazole aggregation induced by lowering the temperature in acetone or by using more nonpolar solvents ($CHCl_3$, C_6H_6) caused a rate acceleration and rate order greater than 2 in total imidazole concentration. This implies that imidazole aggregates are more reactive than the monomeric species. This can reasonably be ascribed to an increase in k_1 and/or K_1. Hydrogen bonding as shown by



should increase the basicity of the imine nitrogen and thereby increase K_1; it should also increase the ability of the (free) N–H to hydrogen bond to the coordinated chloride and increase k_1.

The mechanistic interpretation of the results in Figure 4 is that trifluoroethanol can compete with imidazole at hydrogen bonding to the chloride in Fe(TPP)(HIm)Cl.

A reasonable mechanistic alternative to eq 7 and 8 is a conjugate base one, in which free imidazole deprotonates the coordinated imidazole in Fe(TPP)(HIm)Cl and thereby accelerates chloride ionization. Such a mechanism would predict second-order kinetics in HIm, as observed. However, this mechanism seems unlikely because 1,10-phenanthroline (0.005 M) was found to have no effect on the rate constant ([HIm] = 0.05 M). Experiments with Proton Sponge (Aldrich) gave similar results. These experiments are persuasive but not definitive because interactions between free imidazole and the added base must occur and possibly affect the rates.

Characterization of Fe(TPP)(HIm)Cl. We previously reported[27] direct spectroscopic evidence for the Fe(TPP)(*N*-MeIm)Cl intermediate in eq 3. Similar evidence is now presented for Fe(TPP)(HIm)Cl. At a wavelength of 530 nm the calculated and observed absorbance changes ($A_\infty - A_0$ and ΔA_{obsd}, respectively) for reaction 2 did not agree. Moreover, the discrepancy was a function of the HIm concentration. This is clear evidence for the reversible formation of an intermediate. Assuming the reaction is given by eq 7, a plot of eq 10

$$A_\infty - \Delta A_{obsd} = \frac{-1}{K_1}\frac{A_\infty - A_0 - \Delta A_{obsd}}{[\mathrm{HIm}]} + A_1 \qquad (10)$$

should be linear, where A_1 is the absorbance of the intermediate. The plot is shown in Figure 6 and gives a value of 13 ± 2 M^{-1} for K_1 in acetone at 25 °C. With *N*-MeIm K_1 has a value[27] of 3.5 M^{-1}. In principle the optical spectrum of the

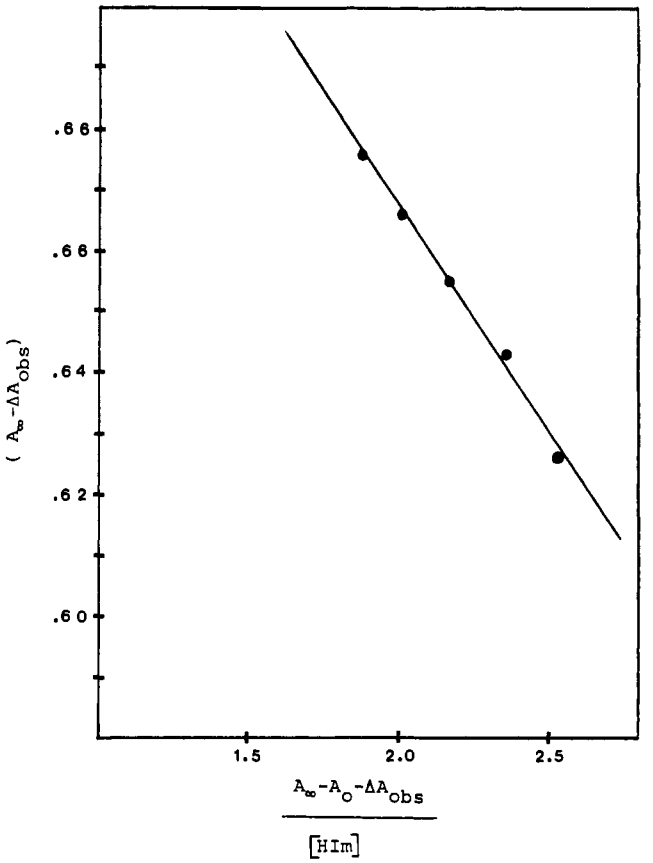


Figure 6. Plot of eq 10 in acetone at 25 °C and wavelength λ = 530 nm; [Fe(TPP)Cl] = 4.0 × 10^{-5} M, [HIm] = 0.040–0.080 M.

Fe(TPP)(HIm)Cl intermediate can be constructed from ΔA_{obsd} data, but in practice this is very difficult due to the speed of the reaction. However, at −78 °C the intermediate only slowly reacts to give the bis(imidazole) product. By use of the optical cell shown in Figure 1 an accurate spectrum of the intermediate was obtained (Figure 7). A virtually identical spectrum was obtained for Fe(TPP)(*N*-MeIm)Cl at −78 °C. With *N*-MeIm, reaction 1 is slow enough to permit the construction of the visible spectrum at 25 °C.[27] Most significantly, the spectra at 25 and −78 °C are identical and by inference this is also true of the intermediate with HIm. This proves that the kinetic intermediate and that trapped at low temperature are the same.

Using the apparatus shown in Figure 2, we made conductivity measurements at −78 °C. The solvent was a 1:5 (v/v) mixture of CH_2Cl_2 and acetone. The CH_2Cl_2 was added to enhance the solubility of Fe(TPP)Cl. The molar conductance of 1.0 × 10^{-3} M Fe(TPP)Cl was Λ = 0.97 Ω^{-1} cm^{-1} M^{-1} at −78 °C. Addition of HIm (1.0 × 10^{-3} M) to generate the intermediate caused a slight increase to Λ = 1.61 Ω^{-1} cm^{-1} M^{-1}. After this solution was warmed to room temperature and recooled, Λ was 2.67 Ω^{-1} cm^{-1} M^{-1}. Again warming, adding excess HIm (ca. 0.01 M) and recooling gave Λ = 13.3 Ω^{-1} cm^{-1} M^{-1}. As a reference, the salt $MePh_3P^+Br^-$ (1.0 × 10^{-3} M) gave Λ = 30.5 Ω^{-1} cm^{-1} M^{-1} at −78 °C.

The mono(imidazole) complex Fe(TPP)(*N*-MeIm)Cl was shown[27] by ESR spectroscopy to be high spin. The virtually identical optical spectrum for the HIm analogue as well as observations with iron protoporphyrin IX complexes[37] proves that Fe(TPP)(HIm)Cl is also high spin. Therefore, the spin changes in reactions 1 and 2 occur upon addition of the second imidazole, a fact that may account for the small values of K_1

(37) Meng, Q.; Tondreau, G. A.; Sweigart, D. A., to be submitted for publication.

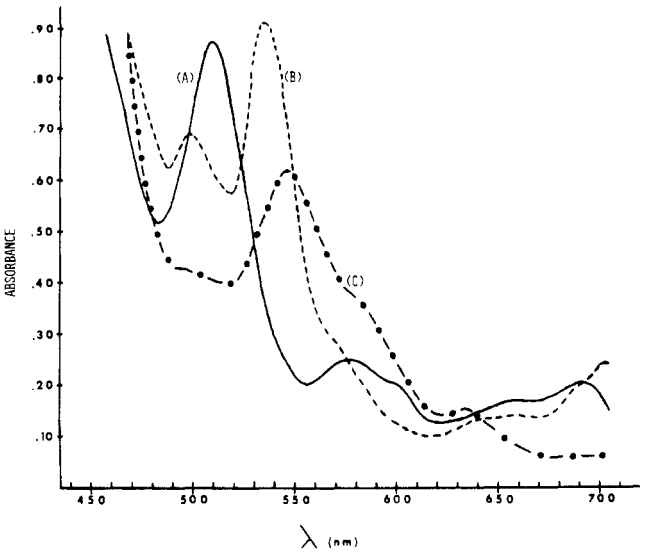


Figure 7. Spectra in acetone at −78 °C: (A) Fe(TPP)Cl; (B) Fe(TPP)Cl plus HIm to give the intermediate Fe(TPP)(HIm)Cl; (C) solution B warmed to room temperature and recooled to give Fe(TPP)$(HIm)_2^+Cl^-$.

compared to the overall stability constants.[36]

There has been some confusion concerning the structure of mono(imidazole) complexes. Attempts[36,38,39] to measure K_1 values for Fe(porphyrin)Cl and unhindered imidazoles (no substituent on C-2 carbon) via optical spectra give at best order of magnitude numbers because the addition of the second imidazole is easier than the first (i.e., $K_2 >> K_1$). This means that very little of the iron porphyrin exists as the mono-imidazole adduct at equilibrium. Electrochemical measurements by Walker[39] give a value of K_1 much larger than ours for the *N*-MeIm adduct. Noting the discrepancy between our results and hers, Walker made the suggestion that electrochemical and static spectral measurements refer to formation of the ionized adduct, Fe(TPP)$(RIm)^+Cl^-$, whereas our kinetic and low-temperature experiments refer to the six-coordinate un-ionized species. We regard this as a reasonable possibility.

The assertion that the Fe(TPP)(RIm)Cl species reported in this paper are six-coordinate is strongly supported by a number of observations, some of which are discussed elsewhere.[27] The kinetic data would be difficult to understand if the intermediate were a five-coordinate ion pair. The conductivity data show that the intermediate is nonconducting ($\Lambda = 1.61\ \Omega^{-1}\ cm^{-1}\ M^{-1}$) compared to the ion-paired bisadduct, Fe(TPP)$(HIm)_2^+Cl^-$ ($\Lambda = 13.3\ \Omega^{-1}\ cm^{-1}\ M^{-1}$). The somewhat low conductivity of Fe(TPP)$(HIm)_2^+Cl^-$ compared to that of $MePh_3P^+Br^-$ is probably due to hydrogen bonding from coordinated imidazole to the chloride.[40] The optical spectrum of Fe(TPP)(RIm)Cl also supports the six-coordinate formulation. With Fe(TPP)$^+SbF_6^-$[41,42] as the starting material, the five-coordinate Fe(TPP)(HIm)$^+SbF_6^-$ has been prepared;[42] its optical spectrum and that of Fe(TPP)(HIm)Cl are very different.

The Fe(TPP)(HIm)Cl complex is a very rare example of a six-coordinate high-spin iron(III) porphyrin containing a neutral and an anionic ligand. The only other example known to us is Fe(OEP)(py)(NCS)[43] (OEP is octaethylporphyrin).

The rate constant k_1 in eq 8 can be calculated from the values of k_1K_1 (5900 $M^{-2}\ s^{-1}$) and K_1 (13 M^{-1}), both determined in acetone at 25 °C. The result, $k_1 = 450 \pm 100\ M^{-1}\ s^{-1}$, is about 130 times greater than k_1 for unassisted chloride ionization (eq 4).[27] Thus "distal" type hydrogen bonding to an anion coordinated to an iron porphyrin can be very significant. Presumably hydrogen bonding to a ligand more basic than chloride, e.g., F^-, N_3^-, O_2^-, would be even more pronounced. Experiments designed to test this are in progress.

From the optical spectra recorded at −78 °C, a rough estimate of the formation constant for Fe(TPP)(RIm)Cl could be made: $K_1 \approx 2000\ M^{-1}$ (HIm); $K_1 \approx 850\ M^{-1}$ (*N*-MeIm). When these data and activation parameters presented above and previously reported[27] are combined, the following approximate results are obtained:

N-MeIm

$\Delta H^\circ_{K_1} \approx -6.0$ kcal/mol $\quad \Delta S^\circ_{K_1} \approx -17$ cal/(deg mol)

$\Delta H^\ddagger_{k_1} = 9.7$ kcal/mol $\quad \Delta S^\ddagger_{k_1} = -24$ cal/(deg mol)

HIm

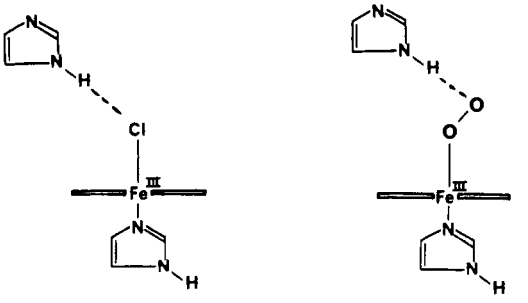
$\Delta H^\circ_{K_1} \approx -5.6$ kcal/mol $\quad \Delta S^\circ_{K_1} \approx -13$ cal/(deg mol)

$\Delta H^\ddagger_{k_1} \approx 11$ kcal/mol $\quad \Delta S^\ddagger_{k_1} \approx -10$ cal/(deg mol)

Although most of the data have large error limits, they do suggest that the rate acceleration due to hydrogen bonding from HIm is significantly, and perhaps largely, entropic in origin. This result is consistent with the usual trend seen for ionizations, in which easier ionization in a more polar environment is due to less negative entropy changes.[44] In our case the more polar environment is the hydrogen-bonded system Fe–Cl ··· HIm. A related way to rationalize the differences in $\Delta S^\ddagger$ is to note that hydrogen bonding of HIm to the developing chloride ion in the transition state liberates solvent molecules that otherwise would be involved in solvation of HIm and chloride.[45]

Conclusion. This work shows that Fe(TPP)Cl reacts rapidly with imidazole to form a high-spin six-coordinate intermediate, Fe(TPP)(HIm)Cl, that reacts further to give a low-spin bisadduct, Fe(TPP)$(HIm)_2^+Cl^-$. The rate-determining step in the overall reaction is chloride ionization from the intermediate, and this is greatly accelerated by hydrogen bonding from free imidazole.

These results show that distal type hydrogen bonding to anions coordinated to iron porphyrins



can significantly influence reaction kinetics and thermodynamics.

To further assess the importance of hydrogen bonding to substrates in hemoproteins containing an appropriate distal group, we are investigating the reactions of metal–proto-

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prophyrin IX systems containing axial ligands such as F^-, N_3^-, and O_2^-.

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Registry No. Fe(TPP)(HIm)Cl, 54453-30-4; Fe(TPP)Cl, 16456-81-8; TFE, 75-89-8; HIm, 288-32-4.

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Synthesis and Properties of Substituted (Phthalocyaninato)iron and -cobalt Compounds and Their Pyridine Adducts

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A direct route to peripherally substituted (phthalocyaninato)metal derivatives R_mPcM (R = *t*-Bu, *m* = 4, M = Fe, Co; R = CH_3O, *m* = 8, M = Fe, Co; R = NO_2, *m* = 4, M = Co; R = CH_3, *m* = 8, M = Fe; R = Cl, *m* = 16, M = Fe) is described. Their thermal stabilities, UV/vis and mass spectra, and solubilities are reported. The coordination behavior of these metallomacrocycles to base molecules has been investigated in a model reaction with pyridine. The synthesis of the pyridine adducts $R_mPcM(py)_2$ is presented. The new complexes have been characterized by thermal analyses (TG, DTA). The thermal properties of the pyridine adducts, and in the case of the cobalt complexes the coordination number of the central metal atom, are correlated with peripheral substituent effects.

Introduction

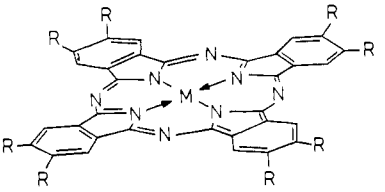
Our interest in the coordination chemistry of peripherally substituted metallophthalocyanines is based on a concept for the design of one-dimensional organic conductors.[1] The basic structural feature of these conducting materials is a linear arrangement of transition-metal atoms (e.g., Fe, Ru, Co), bridged by linear bidentate π-electron-containing ligands (e.g., pyrazine, 1,4-diisocyanobenzene, cyanide). This one-dimensional structure is stabilized by planar, tetradentate macrocyclic systems (e.g., phthalocyaninate, Pc^{2-}, tetraaza[18]annulenate, taa^{2-}) complexing each central metal atom in its equatorial plane.[2]

Detailed investigations of related macrocyclic systems show a correlation of the coordination behavior of the metal complex with its peripheral substituents.[3]

In our work the knowledge of a similar relationship would help in assessing the factors governing the stabilization of the required linear-chain compounds.

A wide variety of peripherally substituted phthalocyanines is described with the emphasis lying in the synthesis of these compounds.[4-8] In contrast, very little is known concerning the chemical behavior and physical properties of these complexes.[9-13] In order to study this effect, we worked out several routes to peripherally substituted phthalocyaninato systems.

Recently we reported the syntheses of 2,3,9,10,16,17,23,24-octasubstituted phthalocyanines **1** with R = CF_3 and $-(CH_2)_nOR'$.[14,15]



1

In this paper we present some of our new results on the synthesis and properties of substituted (phthalocyaninato)iron and -cobalt and the pyridine adducts of these metallophthalocyanines. The thermal stabilities, UV/vis spectra, and solubilities of the metal complexes are also discussed.

Results and Discussion

Synthesis of R_mPcM. Both the "nitrile" and "anhydride" methods[4,16,17] were used for the preparation of the substituted (phthalocyaninato)iron and -cobalt derivatives **4–11** (Table I).

In the anhydride method substituted phthalic anhydrides **2** were employed as starting materials; these are converted to metal-containing phthalocyanines in the presence of urea and metal halides when ammonium molybdate is used as a catalyst (method A, Table I). The nitrile method can be used in two ways: (1) by starting with substituted phthalonitriles **3**, which react with metal halides (method B), or (2) by using metal carbonyls (method C)[18] to produce the metallophthalocyanines. All of the conversions were carried out in high-boiling solvents. Substituted phthalonitriles **3** often must be prepared through the sequence dicarboxylic acid → anhydride → imide → amide

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