Dynamics and Thermodynamics of Axial Ligation in Metalloporphyrins. 6. Axial Lability of Nitrogenous Bases in Low-Spin Ferric Complexes and the Role of Five-Coordinate Transient Species

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Abstract: Proton NMR line width analysis has been used to characterize the axial lability of nitrogenous bases in bis-ligated, low-spin ferric complexes of synthetic porphyrins. In the presence of excess ligand, ligand exchange proceeds by a dissociative mechanism, with a five-coordinate transition state. The axial lability of imidazoles is increased by electron-donating substituents on the porphyrin, electron-withdrawing substituents on the imidazole, or steric interference of ligand substituents. Pyridines are much more labile than imidazoles. At higher temperatures and small excesses of free ligand, dynamic line broadening of the pyrrole proton in the low-spin complex as well as excess broadening of the axial ligand signals indicate that the five-coordinate species has been stabilized sufficiently that it must be considered as an intermediate in the ligand exchange process.

The role of iron porphyrin in binding various substrates in hemoproteins[2-5] is not a static but a dynamic one, where the proper biological function of the protein requires delicate control of the axial ligand labilities. These iron–ligand bond-making and bond-breaking processes are important not only for the substrates in proteins such as myoglobins,[2] hemoglobin,[2] peroxidase,[3] catalase,[3] etc., but have also been postulated[4,7] to involve the amino acid side chains which provide a ligating function in the resting enzyme.

In some hemoproteins the substrate lability can be controlled by allosteric effects such as the Bohr proton or organic phosphates,[2] which operate at some protein site removed from the heme. In order to understand the possible mechanisms by which such remote protein perturbations[2,6] can be transmitted to the iron by cis and/or trans effects,[7] the factors which influence the ligand lability in model heme compounds must first be characterized. Although a number of substitution reactions of model compounds have been reported, virtually all of the work has involved the diamagnetic ferrous compounds.[8] The labilities of some solvents[9] and halide ions[10] coordinated to high-spin ferric porphyrins have also been reported; the coordination geometries of the solvent species are not known.[9] The axial ligand labilities in some Ru(II) porphyrins have also been characterized.[11,12] Since the substrate labilities in ferric hemoproteins[3-5] are also of considerable interest, we have pursued a proton NMR study of the low-spin, bis-ligated ferric complexes of synthetic porphyrins in order to elucidate the factors which may influence the ligand lability. Preliminary data on the mechanism of the ligand exchange[13] as well as some rate data[13-15] have already appeared.

The possibility for such a dynamic study became evident during a proton NMR investigation[13,16] of the thermodynamics of axial ligation of substituted imidazoles and pyridines, where we observed that, although separate resonances were observed for free and coordinated ligands, the peaks were broadened by ligand exchange. Analysis of such lifetime broadening by standard techniques[17] will provide the desired ligand labilities.

Although there are two steps in the formation of bis complexes,[16,18,19] i.e.,

$$\mathrm{PFeX} + \mathrm{L} \overset{K_1}{\rightleftharpoons} \mathrm{PFeL^+X^-} \qquad (1)$$

and

$$\mathrm{PFeL^+X^-} + \mathrm{L} \overset{K_2}{\rightleftharpoons} \mathrm{PFeL_2^+X^-} \qquad (2)$$

the only observed[16] reaction in our thermodynamic study was the overall reaction, (i.e., $K_2 \gg K_1$), i.e.,

$$\mathrm{PFeX} + 2\mathrm{L} \overset{\beta_2}{\rightleftharpoons} \mathrm{PFeL_2^+X^-} \qquad (3)$$

where $\beta_2 = K_1K_2$. No direct evidence for the existence of the five-coordinated species, $\mathrm{PFeL^+X^-}$, was obtainable.[16]

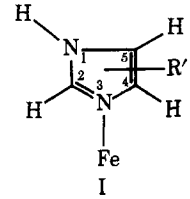
Our preliminary NMR line broadening studies of ligand exchange indicated[13] that it was a dissociative process, as described by

$$\mathrm{PFeL_2^+X^-} + \mathrm{L^*} \rightleftarrows [\mathrm{PFeL^+X^-} + \mathrm{L}] + \mathrm{L^*} \rightleftarrows \mathrm{PFeLL^{*+}X^-} + \mathrm{L} \qquad (4)$$

where the elusive monoligated species is the activated complex. If $\mathrm{PFeL^+X^-}$ is indeed only very short-lived, then exchange line broadening[17] should arise only for the free, L_f, and coordinated, L_c, ligand.

If, on the other hand, $\mathrm{PFeL^+X^-}$ is long-lived and exists in significant amounts in solution, it must be considered an intermediate. In this case, not only will ligand exchange kinetics be more complex,[17] but the porphyrin resonances will also exhibit dynamic line broadening due to the interconversion of the porphyrin between the mono and di adducts. Thus a detailed line width analysis will determine if $\mathrm{PFeL^+X^-}$ is a transition state or an intermediate.

Since synthetic porphyrins yield much simpler proton NMR spectra[20,21] due to their high symmetry and permit the introduction of a controlled series of electronic perturbation, the ferric halide complexes of *meso*-tetraarylporphyrins,[22] RTPPFeX, octaethylporphyrin,[23] OEPFeX, and *meso*-tetra-*n*-propylporphyrin,[24] TPrPFeCl, were employed for the initial study. The axial ligands selected are the various substituted imidazoles,[16,21] R′Im, for which the numbering system of the coordinated ligand will be used, I, as well as 1-methylbenzimidazole, 1-CH_3Bzim, and 4-methylpyridine, 4-CH_3py.



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The bis complexes of all of these complexes have all been characterized and their proton NMR spectra assigned.[16,20] In

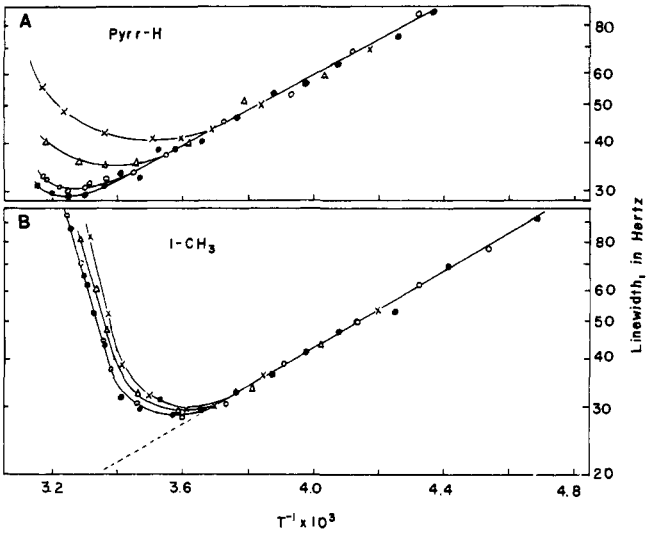

Figure 1. Plot of log line width for the pyrrole-H (A) and 1-CH_3 (B) vs. T^{-1} for TPPFe(1-CH_3Im)$_2^+Cl^-$ in $CDCl_3$: [TPPFe(1-CH_3Im)$_2^+Cl^-$] = 0.020 M, [1-CH_3Im]$_{free}$ = 0.010 M, -X-; 0.040 M, -Δ-; 0.080 M, -O-; and 0.160 M, -●-.

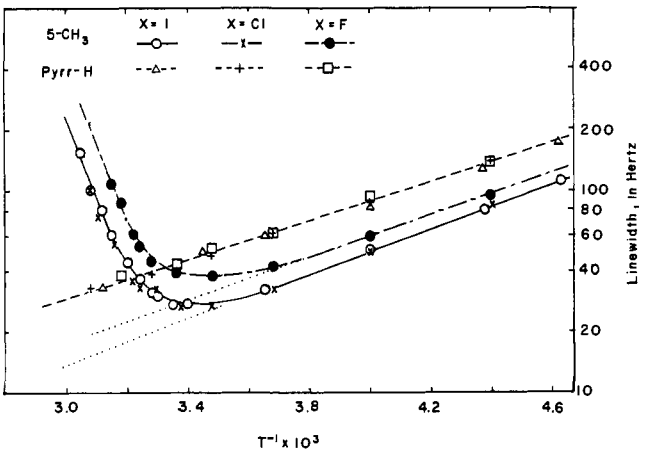

Figure 2. Plot of log line width for pyrrole-H and 5-CH_3 vs. T^{-1} for TPPFe(5-CH_3Im)$_2^+X^-$ in $CDCl_3$ for X = Cl, Br, and F. In all cases [TPPFe(5-CH_3Im)$_2^+X^-$] = 0.20 M, [5-CH_3Im]$_{free}$ = 0.160 M.

each case analysis of ligand exchange is facilitated by the presence of a methyl group on the ligand, which usually led to a well-resolved coordinated-ligand methyl peak amenable to line width analysis.[16]

Experimental Section

Sample Preparation. All porphyrin complexes and axial ligands have been prepared and characterized previously.[16,20] The desired bis complexes, $PFeL_2^+X^-$, were prepared in situ by weighing out accurately the desired amount of PFeX and L and adding 0.5 ml of $CDCl_3$. Except for the studies of the effect of $[PFeX]_0$ on line width, where it ranged from 0.005 to 0.070 M, $[PFeX]_0$ was maintained at 0.020 M. $[L]_0$ ranged from 0.050 to 0.350 M, and was maintained at 0.20 M for the determination of ligand labilities (vide infra).

NMR Spectra. Proton NMR spectra were recorded with a JEOL PS-100 FTNMR spectrometer equipped with an EC-100 data system, and operating at 99.5 MHz. Between 200 and 5000 transients were accumulated using a ~20-μs 90° pulse, and bandwidth between 4000 and 6250 Hz. All temperatures were measured to an accuracy of ±1 °C using a thermocouple in an NMR tube both prior to and after data accumulation.

T_1 measurements were performed using the conventional 180°-t-90° pulse sequence,[25] where t is the delay between the two pulses. The accurately determined 90° pulse was 19.2 μs. The T_1's were determined from the usual plot[25] of $A_t - A_\infty$ vs. t, where A_t and A_∞ are the intensities of the line after a delay of t s (A_t) and $\geq 6T_1$ s (A_∞).

Line Width Analysis. Since NMR data were obtainable only in the slow exchange region (vide infra), the preexchange lifetime, τ_i, in the site corresponding to the signal being observed, is given[17,26] by

$$\pi\delta_{i,obsd} = T'^{-1}_{2i} = T_{2i}^{-1} + \tau_i^{-1} \quad (5)$$

where δ_i is the line width at half height, T'_{2i} the effective spin-spin relaxation time, and T_{2i} the spin-spin relaxation time in the absence of exchange. For data analysis, eq 5 can be rearranged to:

$$\delta_{i,obsd} - \delta_i = 1/\pi\tau_i \quad (6)$$

where δ_i is now the line width in the absence of exchange. δ_i can be obtained experimentally by determining δ_i over a wide temperature range in the region of no exchange and extrapolating into the exchange region.[26] In the absence of exchange effects, we expect a linear plot of log δ_i vs. T^{-1}, with δ_i increasing with decreasing T.[26] Furthermore, the slope of δ_i vs. T^{-1} will be the same for nonequivalent protons in the complex (i.e., pyrrole-H), such that if the nonexchange region is not attainable over a wide enough temperature to accurately establish the slope, the δ_i in the exchange region can be obtained by setting the slope of the plot to that observed for a nonexchanging proton.[26] Hence δ_i could be determined to an accuracy of 5% in all cases. The observed line width, $\delta_{i,obsd}$, could be determined to an accuracy of 3-8% depending on the width. Thus the resulting exchange rates, τ_i^{-1}, were obtainable with uncertainties of 5-10%.

The activation parameters for ligand lability were obtained from the computer least-squares analysis of the temperature dependence of τ_i^{-1}; $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were derived from the slope and intercept of an Eyring plot (τ_i^{-1}/k vs. T^{-1}). The sizable uncertainties in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ reflect the uncertainty in the individually determined τ_i^{-1}'s as well as the rather restricted temperature range over which kinetic data was obtainable (vide infra).

Results

The influence of temperature on the line widths of the 1-CH_3 and pyrrole-H peak in TPPFe(1-CH_3Im)$_2^+Cl^-$ in $CDCl_3$ as a function of the $[1\text{-}CH_3Im]_0/[TPPFeX]_0$ ratio is depicted in Figure 1. The effect of halide ion (X) on the coordinated 5-CH_3 peak line width in TPPFe(5-CH_3Im)$_2^+X^-$ as a function of a temperature is illustrated in Figure 2. The preexchange lifetime of the coordinated ligands, obtained from the coordinated ligand methyl line width by standard analysis,[17,26] are listed in Table I for a variety of ligands and porphyrins. These data in Table I were obtained in the presence of a large excess (10:1) of ligand (vide infra). The effect of temperature on the preexchange lifetimes of a select number of systems is illustrated in Figure 3 in the form of an Eyring plot. The resulting activation parameters are included in Table I.

A plot of $\ln(A_\infty - A_t)$ vs. t from a 180°-t-90° T_1 determination[25] of the pyrrole peak in TPPFe(1-CH_3Im)$_2^+Cl^-$ is illustrated in Figure 4; $[1\text{-}CH_3Im]_0/[TPPFeCl]_0 = 8$ for this solution. The pyrrole-H T_1's and T_2's as well as the T_1/T_2 ratio in this solution as a function of temperature are listed in Table II.

Discussion

The line width data for the coordinated 1-CH_3 peak in TPPFe(1-CH_3-Im)$_2^+Cl^-$ in B of Figure 1 clearly reveal chemical exchange effects[17,26] for $T > 270$ K. The free 1-CH_3Im methyl peak displayed a similar increase in line width, but this peak overlapped with both porphyrin phenyl resonances as well as a persistent impurity peak, making accurate line width analysis difficult. Furthermore, it has been indicated[14] that the noncoordinated ligand also interacts with the paramagnetic porphyrin in some specific way (in addition to coordination). The latter effect makes it more difficult to accurately determine the small exchange broadening.

If the temperature is raised sufficiently, it should be possible to collapse the free and coordinated ligand peaks.[17,26] Analysis of the averaged line width will similarly yield kinetic data

Table I. Axial Ligand Exchange Rate Data for Low-Spin $PFeL_2^+X^-$ Complexes

P	X	L	τ_M^{-1}(298 K)[a]	$\Delta H^{\ddagger}$ [b]	$\Delta S^{\ddagger}/R$ [c]
p-CH_3OTPP	Cl	1-CH_3Im	102 ± 8	20.3 ± 1.8	9.3 ± 3.0
p-CH_3TPP	Cl		81 ± 6		
p-CH_3TPP	I		88 ± 6		
TPP	Cl		66 ± 5	20.1 ± 2.0	8.7 ± 3.4
p-ClTPP	Cl		35 ± 3		
OEP	Cl		950 ± 80[d]	17.2 ± 1.8	8.3 ± 3.0
OEP	I		980 ± 80[d]		
TPrP	Cl		73 ± 7		
TPP	Cl	5-CH_3Im	14 ± 2	21.1 ± 1.9	8.6 ± 3.2
	Br		14 ± 2		
	I		15 ± 2		
	F		28 ± 3		
	Cl	1-CH_3-5-ClIm	950 ± 100[d]		
	Cl	1-CH_3Bzim	230 ± 70[e]		
	Cl	1-CH_3Im	0.006[e]		
	I	4-CH_3py	1900 ± 200[d]	17.4 ± 2.0	7.5 ± 3.8

[a] In s^{-1}, in $CDCl_3$ at 298 K, unless noted otherwise. [b] $\Delta H^{\ddagger}$ in kcal/mol. [c] $\Delta S^{\ddagger}/R$ in entropy units. [d] Rate extrapolated to 298 K. [e] τ_M^{-1}(235 K) (obtained for 1-CH_3Im using $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$).

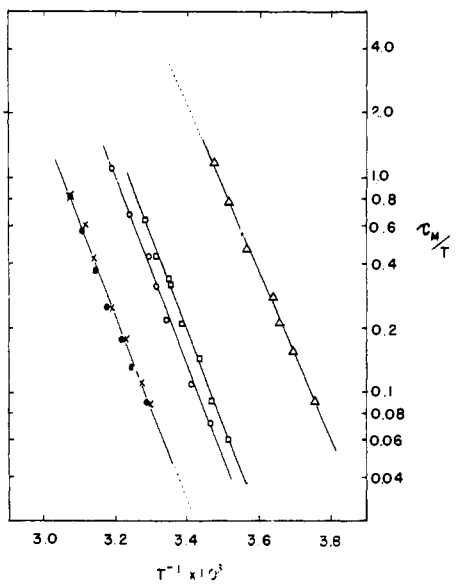

Figure 3. Plot of log τ_M^{-1}/T vs. T^{-1} for $PFeL_2^+X^-$ in $CDCl_3$; $[PFeL_2^+X^-] = 0.020$ M, $[L]_{free} = 0.160$ M in all cases. *p*-CH_3OTPP(1-CH_3Im)$_2^+Cl^-$ -□-; TPPFe(1-CH_3Im)$_2^+Cl^-$, -○-; OEPFe(1-CH_3-Im)$_2^+Cl^-$, -△-; TPPFe(5-CH_3Im)$_2^+$Cl, -●-; TPPFe(5-CH_3Im)$_2^+I^-$, -×-.

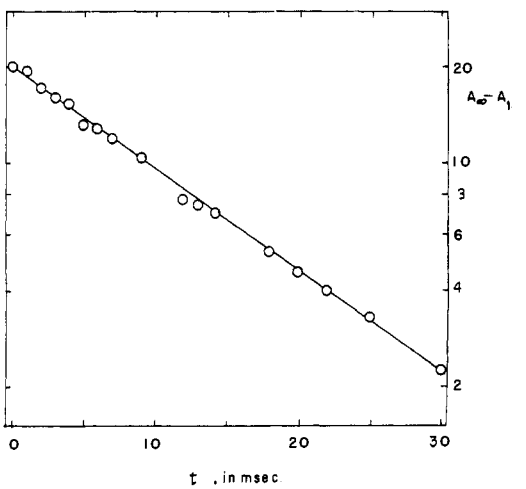

Figure 4. Plot of log $(A_\infty - A_t)$ vs. t for pyrrole-H in TPPFe(1-CH_3-Im)$_2^+Cl^-$ in $CDCl_3$; $[TPPFe(1\text{-}CH_3Im)_2^+Cl^-] = 0.020$ M, $[1\text{-}CH_3Im]_{free} = 0.160$ M; $T = 35$ °C.

which would extend the temperature region needed to obtain accurate kinetic parameters from an Eyring plot. However, such a collapse of the two signals was not attainable in our systems due to the inability in keeping the complex in the bis low-spin form for $T > 320$ K. Our previous NMR analysis of the thermodynamics of axial ligation is consistent with this observation.[16] Moreover, it can be shown that the dynamic line broadening at such temperatures reflects a much more complex kinetic process than simple ligand exchange from the low-spin complex (vide infra). Hence, for experimental reasons, we will restrict ourselves to analyzing the region of slow chemical exchange, for which the line broadening of the coordinated ligand peaks will yield[17,26] directly τ_M, the coordinated axial ligand preexchange lifetime in the bis complex.

An additional complication in the analysis of the coordinated 1-CH_3 line width data is evident in part A of Figure 1, where we observe that, under some conditions, even the pyrrole-H of the complex is exhibiting lifetime broadening. This broadening of the pyrrole-H at higher temperatures can be suppressed simply by the addition of more ligand. Thus for $[L]_0/[PFeX]_0 \geq 6$, there is no detectable pyrrole-H broadening in the region where 1-CH_3 line widths are obtainable. Hence the only dynamic line broadening arises for the free and coordinated ligand consistent with the process depicted in eq 4 with τ_M and τ_f, the preexchange lifetimes for the ligand in the bis complex and free in solution,[17,26] respectively, with

$$\tau_f = (p_f/p_M)\tau_M \qquad (7)$$

where p_f and p_M are the mole fraction in these two sites. All subsequent discussion of ligand labilities and kinetic parameters will be based on ligand line width data obtained under the

Table II. Temperature Dependence of Pyrrole-H T_1 and T_2 in TPPFe(1-MeIm)$_2^+$ Cl^-[a]

Temp, °C	T_1,[b] ms	T_2,[b] ms	T_1/T_2
25	13.3	12.6	1.06 ± 0.15
35	13.4	10.5	1.28 ± 0.16
45	12.9	8.7	1.48 ± 0.20
55	13.3	7.5	1.77 ± 0.23

[a] In $CDCl_3$; $[TPPFeCl]_0 = 0.010$ M, $[1\text{-}CH_3Im]_0 = 0.080$ M. [b] Estimated uncertainty ±1 ms.

condition where the pyrrole-H exhibits no lifetime broadening, and for which eq 5 is thus valid. The analysis of line width data under conditions where pyrrole-H is also exchange broadened will be treated separately in the last section.

Mechanism of Ligand Exchange. As shown in Figure 1, for $[L]_0/[TPPFeCl]_0 \geq 6$ where only the methyl peak is exchange broadened, the 1-CH_3 line width is independent of $[L]_0$. Similarly, increasing the porphyrin concentration left the 1-CH_3 line width unaltered, indicating that τ_M is independent of $[L]_0$. The free ligand preexchange lifetime, τ_f, of course depends on $[L]_0$ via eq 7. This lack of dependence of τ_M on free ligand for all of our ligands dictates that the mechanism of ligand exchange for the bis complex is dissociative,[14] with bond rupture as the rate-limiting step, as depicted in eq 4. Under the limited conditions where line broadening can also be measured for the free ligand, eq 7 is satisfied,[17] so that $PFeL^+X^-$ must be very short-lived. Hence at high $[L]_0/[PFeX]_0$ ratios and low temperatures, $PFeL^+X^-$ is a *transition* state for the ligand exchange from this bis complex.

The rate data,[17,26] τ_M^{-1} (298 K), obtained in the slow-exchange region are tabulated in Table I. The temperature dependence of τ_M^{-1}, determined for a number of cases for which the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are given in Table I, turned out to be very similar in spite of a range of τ_M^{-1}'s at 298 K. Only for $OEPFe(1\text{-}CH_3Im)_2^+Cl^-$ did the increased rate reflect itself in a significant decrease in $\Delta H^{\ddagger}$. The $\Delta H^{\ddagger}$'s are very similar to values reported[12] earlier for ligand exchange of various nitrogenous bases in Ru(II) porphyrins. The sizable uncertainties in our $\Delta H^{\ddagger}$ values arise because of the relatively narrow temperature range over which rate data could be obtained in the slow-exchange region. Although the temperature dependence of the τ_M^{-1}'s for a number of other complexes were measured, even more restricted temperature ranges yielded similar kinetic parameters as in Table I, but with much larger uncertainties. For some systems, the small β_2's precluded[16] any high-temperature work.

The $\Delta S^{\ddagger}/R$ values for all systems were found to be positive, in the range 7–10 eu, which is consistent with the dissociative mechanism depicted in eq 4.

Effect of Porphyrin. The effect of porphyrin basicity is most clearly seen in the series p-$RTPPFe(1\text{-}CH_3Im)_2^+Cl^-$, (Table I). The rates increase in the order of increased electron-donating strength of p-R, Cl < H < CH_3 < CH_3O. The plot of τ_M^{-1} for these four complexes vs. the Taft σ_p parameters[28] gave a straight line with a negative slope. The rate variations in these four systems were too small to clearly manifest themselves in different $\Delta H^{\ddagger}$'s. In the case of the most basic porphyrin,[23] $OEPFe(1\text{-}CH_3Im)_2^+Cl$, the much larger lability is reflected in a sizable decrease in $\Delta H^{\ddagger}$.

This increased ligand lability with porphyrin basicity is consistent with the increased stabilization of the five-coordinate transition state, $PFeL^+X^-$. It may be noted that the ligand lability in the p-$RTPPFe(1\text{-}CH_3Im)_2^+Cl^-$ series varies in the same order as the ligand affinities[16,18] (β_2) as R is altered.

Effect of Axial Base. For the sterically nonhindered imidazoles, the labilities in $TPPFeL_2^+Cl^-$ increase in the order 5-CH_3Im $\gtrsim$ 1-CH_3Im $\ll$ 1-CH_3-5-ClIm, which is the reverse order for the trend in β_2's.[18,20] Hence the stronger the L–Fe bond the less labile the ligand. Since the τ_M^{-1}'s are obtained with $[L]_0/[PFeX]_0 = 10$, the lability for 5-CH_3Im is that for coordinated ligand hydrogen bonded to a free ligand.[16] The single pyridine-type ligand was more labile than any imidazole; the weaker bond to the six-membered heterocycle was also noted in a smaller β_2.[16,20,28]

The role of steric effects is evident in the axial labilities of $TPPFeL_2^+Cl^-$ for L = 1-CH_3Im and 1-CH_3Bzim, (Table I), where the $\sim 4 \times 10^4$ increased lability (at 235 K) of the latter probably reflects primarily the steric interference of the ligand 4-H proton with the porphyrin.[30] A large decrease in β_2 was also observed[16] for the ligand, which was directly attributable to a large decrease in the enthalpy of bond formation.

Effect of Halide Ions. The ligand labilities of 1-CH_3Im was found to be unaffected by halide ions in $PFe(1\text{-}CH_3Im)_2^+X^-$ for P = TPP and OEP and X = Cl and I, as indicated by the data in Table I. The absence of any detectable influence on the kinetics is somewhat surprising, since these complexes have been shown[16,18,19] to exist as tight ion pairs in $CDCl_3$. However, this may be due largely to the absence of any specific site for halide interaction between X^- and the cationic complexes of 1-CH_3Im. Attempts to assess the effect of F^- on 1-CH_3Im exchange failed simply because no PFeF complex would form a bis, low-spin species with 1-CH_3Im.[16]

We had earlier suggested[16] hydrogen bonding of the polar[18] N–H of coordinated imidazoles to the halide ion in $PFe(Im)_2^+X^-$ as a source of the $\sim 10^3$ increase in β_2 over that of N-substituted imidazoles. It may therefore be expected that the lability of 5-CH_3Im be influenced by the nature of X. Indeed, 5-CH_3Im and Im, in contrast to 1-CH_3Im, readily yield the low-spin bis complexes with TPPFeF. The plots of coordinated 5-CH_3 and pyrrole-H line widths vs. temperature in $TPPFe(5\text{-}CH_3Im)_2^+X^-$ for X = Cl, I, and F are illustrated in Figure 2. The linearity of the line width plot for pyrrole-H indicates that only the bis complex lability is reflected in 5-CH_3 line width (vide infra).

Although exchange rates for X = Cl, Br, and I (Br data not included in Figure 2) are essentially identical, τ_M^{-1} for X = F is doubled over that of the other three halide ions (Table I). Since ion-pairing is complete for all X^-, as indicated by the validity of the determined β_2's,[16,18,19] it appears as if the strength of the N–H···X^- interaction is relatively weak for Cl^-, Br^-, and I^-, and does not permit a differentiation of labilities. For X = F, the strongest hydrogen bond acceptor, the lability is doubled due to the stabilization of the polar[18] N–H bond by F^-. This N–H···F^- interaction was proposed[31] earlier based on ESR spectra.

Addition of excess F^- in the form of n-$Bu_4N^+F^-$ to the $TPPFe(5\text{-}CH_3Im)_2^+F^-$ solution did not effect the 5-CH_3 line width, presumably because F^- ion paired more strongly to Bu_4N^+. This was verified by noting that addition of $Bu_4N^+Cl^-$ to the $TPPFe(5\text{-}CH_3Im)_2^+F^-$ solution decreased the 5-CH_3 line width to that characteristic of $TPPFe(5\text{-}CH_3Im)_2^+Cl^-$, while adding $Bu_4N^+F^-$ to a solution of $TPPPe(5\text{-}CH_3Im)_2^+Cl^-$ did not increase the 5-CH_3 line width to that found for the pure fluoride complex.

It should be noted that since only one coordinated 5-CH_3Im interacts with the F^-, (the two 5-CH_3 signals are equivalent on the NMR time scale due to rapid F^- exchange), the two ligands are nonequivalent. We do not know at this time whether 5-CH_3Im or 5-CH_3Im···F^- is the more labile ligand. Studies in progress on mixed ligand complexes may provide the answer to this. To what extent hydrogen bonding of one imidazole to F^- alters the lability of the trans ligand has important implications for the role of proximal imidazole hydrogen bonding in the labilization of substrate in hemoproteins.[2-7]

Five-Coordinated Transition State or Intermediate? The conditions for the NMR line-broadening description of a kinetic process involving only two sites (free L and L in the bis complex), and which must then obey eq 7, require[17] that any intermediate state for L between the two sites have a negligible lifetime; i.e., only a *transition state* exists between the two sites.

If the transition state gains a significant population, it must be considered an *intermediate* and several effects can be expected to arise in the dynamic NMR experiment. On the other hand, L now is averaged among three environments with nonzero populations, $PFeL_2^+X^-$, L, and $PFeL^+X^-$, such that dynamic line broadening may increase for the first two species

even if the third cannot be detected, and eq 5 would no longer be valid. Most importantly, since P now exists in two distinct environments, $PFeL_2^+X^-$ and $PFeL^+X^-$, porphyrin resonances can be also expected to exhibit dynamic line broadening.

As indicated above, all complexes, under the conditions of low $[L]_0/[PFeX]_0$ ratios and/or high temperature, exhibited coordinated and free ligand line widths which were greater than predicted by the well-characterized exchange described by eq 4, and anomalous line broadening of the pyrrole-H in $PFeL_2^+X^-$. Both of these effects could be suppressed upon the addition of more ligand.

Two reasonable mechanisms can be envisaged to account for the above phenomena. Determination of both the T_1 and T_2 relaxation times[25,32] for the pyrrole-H will be shown to permit a clean differentiation between them.

On the one hand, it is known that certain bis-ligated ferric porphyrins (such as the dipyridinates of natural porphyrins[33]) undergo a very rapid spin equilibrium, $S = \frac{1}{2} \rightleftarrows S = \frac{5}{2}$. Since the spin conversion is very rapid,[23] only the completely averaged peak line widths or positions are observed.[32] The high-spin[34] state is known to have a much larger pyrrole-H line width than the low-spin state.[20] Since the $S = \frac{5}{2}$ state becomes populated only at higher temperatures,[33] it could cause the excess broadening observed.[35] Although such a spin equilibrium[33] is not expected to be suppressed by excess ligand, a simple solvent-composition effect on the position of equilibrium cannot be completely discounted. However, because spin conversion is so rapid, both line widths (T_2's) and T_1's would be completely averaged for the two spin states. Since $T_1 = T_2$ for each of the pure spin states,[32,34] the completely averaged peak must also have $T_1 = T_2$.

The more reasonable interpretation of the broadening of pyrrole-H and the excess broadening of the ligand peaks is that the process of ligand exchange is no longer describable by eq 4, since $PFeL^+X^-$ is no longer a transition state by NMR criteria,[17] but has a finite lifetime and solution population. As discussed above, the broadening of the pyrrole-H peak would arise from the onset of slow exchange of P between the $PFeL_2^+X^-$ and $PFeL^+X^-$ environments by the same dynamic process which averages L.

Clear evidence for the latter process is obtained by considering the effective T_1 and T_2 for the pyrrole-H peak in the presence and absence of the anomalous broadening. For the case of pyrrole-H exchange between two environments, one of which has a narrow line[20] (low-spin $PFeL_2^+X^-$ = site a), the other with a broad line[34] (high-spin $PFeL^+X^-$ = site b), and site a is much more populated than site b (as in the present case), the effective time constant for the recovery of the z magnetization in site a, T'_{1a}, has been derived,[32] and is given by:

$$T'_{1a}{}^{-1} = T_{1a}{}^{-1} + \frac{\tau_b}{\tau_a}\left(\frac{1}{T_{1b} + \tau_b}\right) \qquad (8)$$

where τ_a and τ_b are the preexchange lifetimes of the pyrrole-H in $PFeL_2^+X^-$ and $PFeL^+X^-$, respectively, and T_{1b} is the spin-lattice relaxation time in the latter site. Hence, the T'_{1a} will generally yield a multiple exponential.[15,32] Since site a is much more populated, we have not only $\tau_b \ll \tau_a$, but $T_{1b} < \tau_b$, so that eq 8 reduces[32] to

$$T'_{1a}{}^{-1} = T_{1a}{}^{-1} \qquad (9)$$

i.e., T_1 for the pyrrole-H in the low-spin complex is unaffected by exchange. The pyrrole-H signal for site b ($PFeL^+X^-$) is, of course, not observed due to its very low concentration and large line width.

T'_{2a} for pyrrole-H (in $PFeL_2^+X^-$) is given by the usual slow exchange limit form,[17,26] i.e.,

$$\pi\delta_p = T'_{2a}{}^{-1} = T_{2a}{}^{-1} + \tau_a{}^{-1} \qquad (10)$$

where δ_p is the observed pyrrole-H line width and $T_{2a}{}^{-1}$ charaterizes the line width in the absence of exchange. Since $T_{2a} = T_{1a}$, and $\tau_a{}^{-1}$ increases with temperature, we expect the T'_{1a}/T'_{2a} ratio to deviate appreciably from unity as we enter the region where the pyrrole-H is broadened.

Figure 4 illustrates the results of a T'_{1a} determination by a 180°-t-90° pulse sequence[25] of the pyrrole-H peak in $TPPFe(1\text{-}CH_3Im)_2^+Cl^-$ under conditions where the pyrrole-H experiences some anomalous broadening. It is clear that the $(A_\infty - A_t)$ vs. t plot[25] is described by a single exponential,[15,32] as in eq 9. In Table II we list the values of T'_{1a} (180°-t-90° pulse sequence) and T'_{2a} (line width) for low-spin pyrrole-H as a function of temperature. At 25 °C, pyrrole-H exhibits negligible exchange broadening and $T'_1 = T'_2$ as anticipated. As the temperature is increased and the pyrrole-H broadens, T'_1 remains essentially unaltered, but T'_2 decreases substantially. This increase in the T'_1/T'_2 ratio indicates that the pyrrole-H line width increase is due to the onset of a slow chemical exchange process.[17,32]

Since the spin-equilibrium interpretation required that T_1 and T_2 remain equal, we attribute the anomalous line broadening of the coordinated low-spin complex peaks to slow exchange to the five-coordinate, monoadduct, $PFeL^+X^-$. Hence, $PFeL^+X^-$ has become a true intermediate in the exchange of axial ligands. The nonequivalence of T_1 and T_2 in the presence of the high-temperature pyrrole-H broadening rules out any fast exchange process, such as exchange with a six-coordinate high-spin PFeLX species. Although slow exchange to PFeLX is conceivable, it seems much less likely than to the five-coordinate $PFeL^+$, since the former process would involve two steps, the rupture of the Fe-L bond and the formation of the Fe-X bond.

Thus the present experiments yield line width data which reflect the situation where, by the criteria of dynamic NMR line broadening, it is possible to continuously vary the conditions from those where $PFeL^+X^-$ is a transition state ($[PFeL^+X^-] \simeq 0$, with only free and coordinated L exchange broadened), to those where $PFeL^+X^-$ is an intermediate in solution. The inability to further characterize this exchange phenomenon at this time precludes any detailed discussion of rates.

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Stereochemistry of Manganese Porphyrins. 2. The Toluene Solvate of $\alpha,\beta,\gamma,\delta$-Tetraphenylporphinatomanganese(II) at 20 and −175 °C[1]

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Abstract: The crystal and molecular structure of the toluene solvate of $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatomanganese(II) has been determined at 20 and −175 °C. This compound has been shown to bind oxygen reversibly at low temperatures. The compound crystallizes in the triclinic system, space group $P\bar{1}$. The unit cell has $a = 11.320$ (6), $b = 11.465$ (6), and $c = 10.487$ (6) Å, cos $\alpha = -0.3527$ (4), cos $\beta = -0.2307$ (4), and cos $\gamma = -0.3057$ (4), and $Z = 1$ at 20 °C and $a = 11.257$ (3), $b = 11.324$ (4), and $c = 10.367$ (4) Å, cos $\alpha = -0.3430$ (4), cos $\beta = -0.2227$ (3), and cos $\gamma = -0.3183$ (3), and $Z = 1$ at −175 °C. Measurement of diffracted intensities employed θ-2θ scans with graphite-monochromated Mo Kα radiation on a Syntex $P\bar{1}$ diffractometer. All independent reflections for $(\sin\theta)/\lambda \leq 0.742$ Å^{-1} (5640 unique observed data) were measured at 20 °C and for $(\sin\theta)/\lambda \leq 0.817$ Å^{-1} (6677 unique observed data) at −175 °C. These data were employed for the determination of structure using the heavy-atom method and full-matrix least-squares refinement. The final conventional and weighted discrepancy factors were 0.092 and 0.068 at 20 °C and 0.077 and 0.093 at −175 °C. The molecule has required C_i-$\bar{1}$ symmetry. The average Mn-N bond distance is in the range 2.082–2.092 Å, depending on the assumptions made in interpreting the least-squares refinements. The differences in the stereochemistry of the molecule at the two temperatures are minimal. The possible interaction of the toluene solvate molecules with the MnTPP molecule is discussed.

The determination of structure for high-spin four-coordinate $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatomanganese(II),[3a] to be written as MnTPP, was undertaken with several considerations in view.

A most obvious consideration was to extend our structural knowledge for divalent metalloporphyrins of the first row transition elements. Previous study has established structure for all members of the *meso*-tetraphenylporphyrin series from iron(II) to copper(II).[4-7] The structure of MnTPP thus allowed further study of the structural changes concomitant with the stepwise addition or subtraction of a d electron. It should be pointed out that such an analysis, in principle rather straightforward, is complicated by the appearance of low-, intermediate-, and high-spin spectroscopic states as the metal ion, and hence the d electron configuration, is changed.

A second consideration deals with an interesting problem of macrocyclic structure, namely, the structural accommodation to a "mismatch" in the size of the central metal ion and the central hole of the macrocycle. Two "mismatch" cases are apparent. If the metal ion is too small for the size of the central hole, complex formation must lead to metal-ligand bonds that are stretched. If the metal ion is too large, positioning of the metal ion in the center of the macrocyclic hole must lead to compressed metal-ligand bond lengths relative to the normal values for complexes with monodentate ligands. In the latter case, which is the one of immediate interest, it is clear that there must be some limit to bond compression. However, several alternatives to excessive bond compression are possible. For porphyrins or other planar, quasi-rigid macrocycles a limited radial expansion of the central hole can occur.[8] More flexible macrocyclic ligands coordinate to an overlarge metal ion with ligand folding and thereby achieve normal metal-ligand bond distances.[9] Another alternative is to change the effective size of the metal ion. For some transition metal ions, this is accomplished by changing the spin state of the ion.[10] Thus for several square-planar iron(II) complexes,[4,11-13]