talysis are the acceleration of ligand dissociation from the metal ion and deformation of the porphyrin. The former would appear to be easier to accomplish.

It should be noted that these conclusions relate to reactions of 2+ metal ions of the first transition series under mildly acidic (Hambright and Chock's study[5]) or neutral conditions (this work and Longo's study[6]). Other mechanisms may pertain under strongly basic conditions or with more highly charged metal ions and almost certainly pertain to metalation reactions involving oxidative addition.[53-56]

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Registry No. H-*N*-CH_3TPP, 51552-53-5; Cu(II), 15158-11-9; Zn(II), 23713-49-7; Co(II), 22541-53-3; Mn(II), 16397-91-4; Ni(II), 14701-22-5.

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Axial Labilization by Macrocyclic Ligands. 1. Kinetics of Replacement of Axial Acetonitrile by Imidazole and *N*-Methylimidazole in Iron(II) Complexes of 2,3,9,10-Tetramethyl- and 2,3,9,10-Tetraphenyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraenes

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The results of a study of the kinetics of substitution of axial acetonitrile by imidazole and *N*-methylimidazole in two complexes of the type $FeL(An)_2^{2+}$, where L represents a 14-membered, tetraaza macrocyclic ligand, in acetonitrile and acetone solvents are presented. The axial substitution kinetics are consistent with a dissociative (D) mechanism, with dissociation of the first acetonitrile molecule as the rate-determining step. The dissociative rate constant changes substantially when peripheral substituents on the macrocycle, L, are changed from methyl to phenyl groups, the difference stemming primarily from a higher activation enthalpy in the latter case. The difference in activation parameters is discussed in terms of the structures of the macrocycles. The results are compared with those from similar studies.

Introduction

Transition-metal complexes containing macrocyclic ligands have been studied in recent years as models for biological molecules which contain porphyrin-bound metal ions. One particular area of interest in these model studies has been the labilization of metal–axial donor bonds by macrocyclic ligands

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disposed in planar fashion about the metal ion. This phenomenon is thought to be at least part of the reason for the rapidity of action of proteins and enzymes containing a metal porphyrin moiety at the active site. Consequently, an understanding of macrocycle-promoted labilization is mandatory if the related biological systems are to be fully comprehended.

Stynes, James, and co-workers have performed several kinetics studies of axial substitution in iron porphyrin[1,2] and phthalocyanine complexes,[3-6] one study of bis(dimethylglyoximate) complexes of iron(II),[7] one study of an iron(II) complex containing the synthetic macrocyclic ligand TAAB,[8] and, most recently, a study of axial ligand exchange in several iron complexes containing the macrocyclic ligand L_1 (vide infra), shown in eq 1.[9] Several other groups have also been active in this area.[10-20] With the exception of the studies reported in ref 8 and 9, however, very little attention has been paid to the use of synthetic macrocyclic ligands in studies of the axial labilization phenomenon. Since new classes of such ligands allow for extensive and systematic structural variation of several types (namely, the degree and location of unsaturation, ring size, the extent of substitution on the ring, charge, and type(s) of donor atom(s)), we feel that study of their metal complexes should allow for a systematic examination of the structural basis for axial labilization.

We present here the results of a study of the substitution kinetics of axial acetonitrile (An) by imidazole (Im) and *N*-methylimidazole (MeIm) in complexes of the type $FeL(An)_2^{2+}$, where L represents a 14-membered, tetraaza macrocyclic ligand, in acetonitrile and acetone solvents. The reactions and ligands, L, are shown in eq 1. According to our

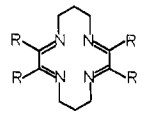
$$FeL(An)_2^{2+} + 2X \overset{S}{\rightleftharpoons} FeL(X)_2^{2+} + 2An \qquad (1)$$

L = L_1, X = MeIm, S = acetonitrile, acetone;
X = Im, S = acetonitrile

L = L_2, X = MeIm, S = acetonitrile, acetone;
X = Im, S = acetonitrile, acetone

L_1 = Me_4[14]tetraeneN$_4$ (R = Me)[21]

L_2 = Ph_4[14]tetraeneN$_4$ (R = Ph)



results, axial substitution in reaction 1 proceeds by a dissociative (D) mechanism, with dissociation of the first acetonitrile molecule as the rate-determining step. The dissociative rate constant is substantially larger when L = L_1 than when L = L_2, the difference stemming primarily from a higher activation enthalpy in the latter case. The difference in activation parameters is discussed in terms of the structures of the macrocycles. Finally, the results are compared with those from the similar studies reported in ref 8 and 9.

Experimental Section

Reagents. Reagent grade acetonitrile (J. T. Baker) was refluxed over calcium hydride for 4–6 h under dry air, distilled under dry air, and collected over Linde 4A molecular sieves which had been activated at 320 °C for 8 h. Reagent grade acetone was stored several days over calcium chloride, refluxed over calcium chloride in a nitrogen atmosphere for 2 h, distilled under nitrogen, and collected over activated Linde 4A molecular sieves. Imidazole (Eastman) was purified by sublimation in vacuo at 70 °C; *N*-methylimidazole (Aldrich) was distilled from KOH under reduced pressure and collected over activated 4A molecular sieves. All other materials were reagent grade and were used without further purification.

Syntheses. $FeL_1(An)_2(PF_6)_2$ and $FeL_1(Im)_2(PF_6)_2$ were synthesized by published procedures[22,23] and were characterized by IR and UV–visible spectroscopy.

$FeL_2(An)_2(PF_6)_2$ was synthesized by a modification of the procedure developed by Welsh et al. for the synthesis of $[CoL_2Br_2]Br$.[24] All operations were carried out under a nitrogen atmosphere unless otherwise noted. 1,3-Diaminopropane (0.03 mol) was dissolved in 50 mL of methanol, and 0.03 mol of glacial acetic acid was added, with stirring. The resulting solution was refluxed 0.5 h to remove dissolved oxygen. Benzil (0.03 mol) was then added and the solution was stirred at reflux for 20 min. During this time the solution turned from yellow to green.

Simultaneously with the procedure above, 0.03 mol of $FeCl_2 \cdot 4H_2O$ and 0.0015 mol of $SnCl_2 \cdot 2H_2O$ were slurried with 50 mL of MeOH. After complete dissolution of $FeCl_2 \cdot 4H_2O$, the solution was filtered to remove undissolved Fe_2O_3 and the pale yellow-green filtrate was added dropwise to the ligand solution from above. An intense cyan color resulted, which rapidly turned to a deep blue. The solution was refluxed for 24 h. At the end of this time, 0.1 mol of glacial acetic acid and 0.2 mol of acetonitrile were added, and the solution was filtered in air to remove a dark green solid. (No precautions were taken to exclude air after this point.) The intensely blue filtrate was reduced in volume by a factor of 2 by using a rotary evaporator and was then treated with 10 mL of an aqueous solution containing 0.15 mol of NH_4PF_6. This caused an immediate color change to purple. The solution was again rotary evaporated until solid began to form. Refrigeration, followed by filtration, yielded dark purple crystals of product. These were washed with a small quantity of cold methanol and then with ether and dried in vacuo. Anal. Calcd for $C_{38}H_{38}N_6P_2F_{12}Fe$: C, 49.37; H, 4.14; N, 9.09. Found: C, 49.66; H, 4.31; N, 8.84. IR (KBr pellet): 3020–3065 (m), 2950 (m), 2300 (w, CH_3CN), 1770–1980 (w), 1600–1630 (w, br), 1580 (w, sp), 1495 (w), 1315–1330 (s, overlapping bands), 1270 (s), 1000–1120 (m, 4 bands), 960 (w), 850 (vs, PF_6^-), 710 (vs, sp), 590 (vs, sp). Visible electronic spectrum (CH_3CN solution): λ_{max} (ϵ) 594 (13.3×10^3 M^{-1} cm^{-1}), 552 nm (sh).

Physical Methods. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. IR spectra were obtained from Nujol mulls and/or KBr pellets by using a Perkin-Elmer Model 457 grating infrared spectrometer. Visible electronic spectra were measured with a Perkin-Elmer Model 323 UV–vis–near-IR spectrophotometer, and NMR spectra were obtained by using a Hitachi Perkin-Elmer Model R-24B 60 MHz NMR spectrometer. Ligand-substitution kinetics were studied with a Nortech SF-3A Canterbury stopped-flow spectrophotometer, equipped with a constant-temperature bath and coupled with a Tektronix RM 504 oscilloscope and Tektronix C-12 oscilloscope camera. The stopped-flow apparatus was tested by using the iron(III) thiocyanate reaction.[25] Reactions (1) were studied under conditions for pseudo-order kinetics in iron reactant. In both cases, L = L_1 and L_2, disappearance of reactant was monitored (556 nm for $FeL_1(An)_2^{2+}$ and 594 nm for $FeL_2(An)_2^{2+}$).

Results and Discussion

Reaction 1 (L_1, X = MeIm, S = Acetonitrile). Solutions of $FeL_1(An)_2^{2+}$ in acetonitrile react rapidly with added *N*-methylimidazole to produce blue-green solutions having visible absorption maxima at 672 and 622 nm (sh). These absorptions correspond closely with those of the complex $FeL_1(Im)_2^{2+}$, synthesized and characterized independently, indicating that the product is $FeL_1(MeIm)_2^{2+}$. The reaction is first order in iron, as shown by the strict linearity, over several half-lives, of plots of ln $(A - A_\infty)$ vs. t. Here A is the absorbance at time t, and A_∞ is the absorbance at equilibrium, measured at 556 nm. The slopes of such plots yield pseudo-first-order rate constants, k_{obsd} which increase linearly with the concentration of incoming ligand, MeIm, over a tenfold range of concentration. A plot of k_{obsd} at 30 °C vs. MeIm concentration is shown in Figure 1a.

The first-order dependence of the rate on incoming ligand concentration implies that the first substitution step is rate determining. The resulting mixed complex apparently then reacts very rapidly to form the $(MeIm)_2$ product. Similar behavior is observed for all the reactions (1) and is consistent with the known trans-labilizing influence of imidazoles.[10,11] Least-squares analysis of the plot in Figure 1a yields a slope of 29.4 ± 1.8 M^{-1} s^{-1} and an intercept of 0.20 ± 0.25 s^{-1}. (The errors quoted here and subsequently represent 99% confidence

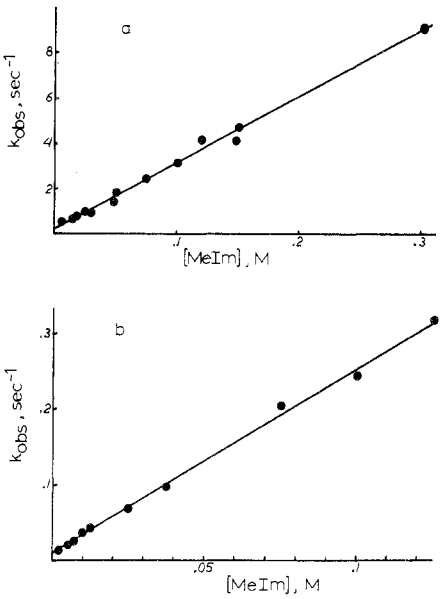


Figure 1. (a) Plot of k_{obsd} vs. [MeIm], L = L_1, CH_3CN solvent, T = 30 °C. (b) Plot of k_{obsd} vs. [MeIm], L = L_2, CH_3CN solvent, T = 40 °C.

limits. Since the error in the intercept exceeds the magnitude of the intercept, we consider the latter to be zero within experimental error. The same consideration holds for subsequent least-squares treatments.)

The plot in Figure 1a implies a rate law of the general form rate = k[MeIm][$FeL_1(An)_2$], which is consistent with a large number of mechanistic schemes. Unfortunately, since the solvent and the leaving ligand are the same, no data regarding the dependence of the rate on the leaving ligand concentration may be obtained, and no definitive demonstration of mechanism is possible in acetonitrile solvent. We therefore undertook a study of the same reaction in acetone solvent in order to clarify the mechanistic picture.

Reaction 1 (L_1, X = MeIm, S = Acetone). Acetone was chosen as solvent both because it readily dissolves all participant species and because it competes poorly with both acetonitrile and *N*-methylimidazole as a ligand. We established this for the case of acetonitrile by recording the visible electronic spectrum of $\sim 5 \times 10^{-4}$ M solutions of $FeL_1(An)_2^{2+}$ in acetone in the presence of varying concentrations of acetonitrile. The spectrum of the bis(acetonitrile) species is invariant down to acetonitrile concentrations of (at least) 0.05 M. As *N*-methylimidazole is superior to acetonitrile as a ligand toward Fe(II), acetone is expected to compete with it even less effectively than with acetonitrile.

Kinetics studies were performed in acetone at 30 °C, as a function of the concentrations of both entering (MeIm) and leaving (An) ligands. Plots of k_{obsd} vs. [MeIm] and $[An]^{-1}$ were linear over very substantial concentration ranges, no deviation from linearity being observed up to the maximum rates measurable with our stopped-flow apparatus. In an effort to detect such deviations, we performed similar studies at 14 °C, with the results shown in Figure 2a. At acetonitrile and *N*-methylimidazole concentrations of 0.1 M, the rate becomes independent of the concentration of incoming ligand, the limiting rate constant having the value 41.3 ± 6.1 s^{-1} at 14 °C (determined as the average value of k_{obsd} for [MeIm] ≥ 0.1 M).

Reaction 1 (L_1, X = Im, S = Acetonitrile). The final spectrum obtained by reacting $FeL_1(An)_2^{2+}$ with a large excess of imidazole in acetonitrile is identical with the spectrum of an acetonitrile solution of $FeL_1(Im)_2(PF_6)_2$ containing a slight excess of Im, confirming that the product of the reaction is

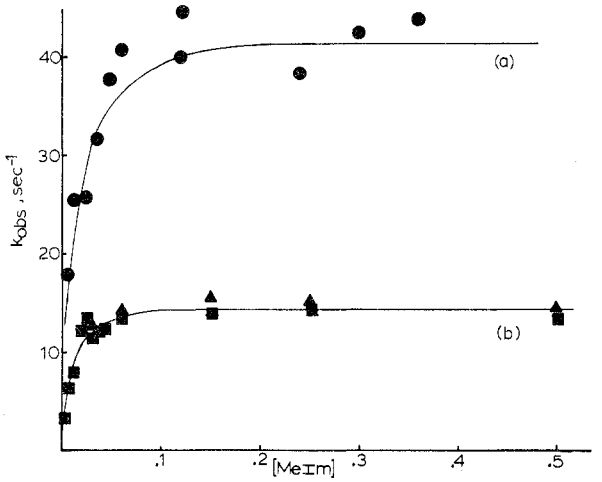


Figure 2. (a) Plot of k_{obsd} vs. [MeIm], L = L_1, acetone solvent, T = 14 °C, [An] = 0.096 M. (b) Plot of k_{obsd} vs. [MeIm], [Im], L = L_2, acetone solvent, T = 40 °C, [An] = 0.096 M: ■, MeIm; ▲, Im.

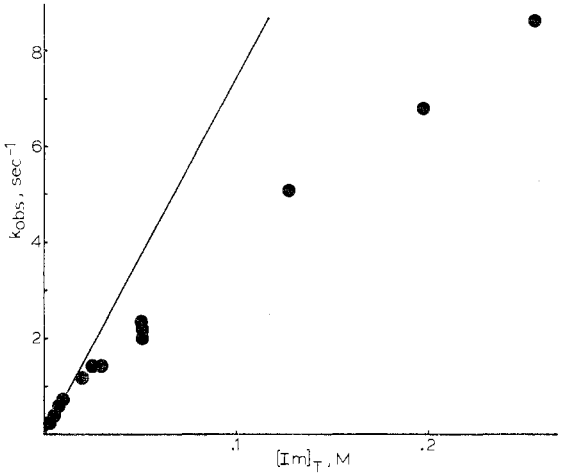


Figure 3. Plot of k_{obsd} vs. [Im], L = L_1, CH_3CN solvent, T = 30 °C.

$FeL_1(Im)_2^{2+}$. A plot of the observed pseudo-first-order rate constant for the substitution reaction against the concentration of imidazole is shown in Figure 3. The plot differs from the corresponding plot for MeIm in that it exhibits a pronounced bend at [Im] ≃ 0.02 M. This behavior may be rationalized in terms of the known tendency[26] for imidazole to hydrogen bond strongly with itself in most solvents. If it is assumed that this self-association leads to dimer formation (the situation may be more complex), it is possible to estimate the value of the equilibrium constant, K, for dimer formation from observed rate constants taken from the curved portion of the graph. We have done this for several such points and have obtained reasonably consistent values for K.[27]

Experimental support for self-association in this system is obtained from the NMR spectra of acetonitrile solutions containing varying concentrations of imidazole, which reveal a downfield shift of the imidazole N–H resonance with increasing concentration. A total shift of 1.45 ppm over the concentration range between 0.13 and 1.0 M is observed. These shifts are very similar to those observed by Balch and Doonan[26] in dichloromethane solutions of imidazole. Although it is difficult to assess the magnitude of the self-association constant from NMR data, since interaction with solvent will also cause a downfield shift, the data are certainly consistent with substantial hydrogen bonding.

Several previous studies of the kinetics of reaction of imidazole with complexes of iron[10-12,28] have failed to show the curvature which we observe. In most such cases,[10,11,28] the

Table I. Rate Data for the Reaction[a]

$$FeLY_2 + mX \xrightarrow{S} FeLY_nX_m + (2-n)Y \quad (n+m=2)$$

L	Y	X	m	S	T, °C	$k'_X k_{-Y}/k_Y$	k_{-Y}, s^{-1}	k'_X/k_Y[b]	$\Delta H^{\ddagger}$,[c] kcal/mol	$\Delta S^{\ddagger}$,[c] eu	ref
L_1	An	MeIm	2	acetone	14		41.3		16.2	5.3	this work
					30	710	195[d]	3.6			this work
				acetonitrile	30	560	195[e]	2.9			this work
		Im		acetonitrile	30	1430	195[e]	7.3			this work
	MeIm	MeIm	1	acetonitrile	30		0.76[f]		17.9	0	9
		BzlNC					0.0073				
	Im	Im	1	acetonitrile	30		0.42[f]		21.5	11	9
		BzlNC					0.0125				
L_2	An	MeIm	2	acetone	40		13.7		21.7	16.0	this work
					30		4.4[d]				this work
				acetonitrile	40	46.5	13.7[e]	3.39			this work
		Im		acetone	40		15.1				this work
		Im		acetonitrile	40	44.8	15.1[e]	2.97			this work
TAAB	MeIm	BzlNC	1	acetonitrile	30		0.0146[g]		26.2	19.5	8
				butanone	30		0.0064				8
	py	BzlNC	1	acetonitrile	30		0.111[h]		27.1	26.5	8

[a] The substitution is presumed to proceed by the following mechanism (only the first two steps apply when $m = 1$): $FeLY_2 \rightleftarrows FeLY + Y$ k_{-Y}, k_Y; $FeLY + X \rightleftarrows FeLYX$ k'_X, k'_{-X}; $FeLYX \rightleftarrows FeLX + Y$ k'_{-Y}, k'_Y; $FeLX + X \rightarrow FeLX_2$ k_X. [b] Calculated from k_{-Y} and $k_{-Y}k'_X/k_Y$. [c] Corresponding to k_{-Y}. [d] Calculated from Eyring data. [e] Obtained from studies of reaction with MeIm in acetone solvent. The dissociative rate constant is assumed to have the same value in both solvents. [f] Calculated from the data in ref 9. The first value is based on NMR data; the second, on visible spectroscopic data. The visible spectroscopic values were measured at 0 °C. [g] Calculated from the data in ref 8. [h] See footnote 32.

maximum [Im] examined was ≤0.03 M, which should fall below the bend point. In a study[12] of replacement of axial Me_2SO by imidazole at iron(II) phthalocyanine, however, imidazole concentrations up to 1.5 M were examined, with no evidence of curvature in the plot of k_{obsd} vs. imidazole concentration. Significantly, this study was performed in Me_2SO solvent, a strong donor which should decrease the tendency for imidazole to dimerize. NMR measurements in our laboratories in fact reveal that, even at imidazole concentrations as high as 1.0 M, dimerization is minimal. It therefore has no effect on the rate constants measured in the earlier study.

At low concentrations of imidazole, where most of the imidazole should be in the monomer form, Figure 3 indicates that a linear relationship exists between k_{obsd} and the total imidazole concentration. The reaction is therefore first order in incoming ligand in acetonitrile solvent. Least-squares analysis of the data yields a slope of 74 ± 12 M^{-1} s^{-1} and an intercept of −0.01 ± 0.08 s^{-1}.

Due to the complication introduced by H bonding when imidazole is the incoming ligand, we did not extend the study of reaction 1, L = L_1, X = Im, to acetone medium.

Reaction 1 (L_2, X = MeIm, S = Acetonitrile). Results for this system are qualitatively similar to those obtained when L = L_1, with the exception that the reaction is approximately 2 orders of magnitude slower. In order to achieve rates convenient for measurement by stopped-flow methods, we studied the reaction at 40 °C. Pseudo-first-order rate constants, obtained from the slopes of plots of ln $(A - A_\infty)$ (at 594 nm) vs. t, are plotted vs. incoming ligand concentration in Figure 1b. Least-squares analysis of the data yields a slope of 2.43 ± 0.14 M^{-1} s^{-1} and an intercept of 0.0092 ± 0.0083 s^{-1}.

Reaction 1 (L_2, X = MeIm, S = Acetone). The behavior of this system was similar to the analogous system wherein L = L_1. Acetone competes poorly with acetonitrile for the axial coordination sites of the FeL_2^{2+} core, as indicated by the invariance of the characteristic $FeL_2(An)_2^{2+}$ visible electronic spectrum for all acetonitrile concentrations ≥0.05 M. It was therefore possible to determine the dependence of k_{obsd} on the leaving ligand concentration. At low incoming ligand concentrations, k_{obsd} varies directly with [MeIm] and inversely with [An]. At higher incoming-to-leaving-ligand-concentration ratios, however, k_{obsd} becomes independent of [MeIm], as shown in Figure 2b. The value of the limiting rate constant at 40 °C, determined as the average value of k_{obsd} for [MeIm] >0.06 M, is 13.7 ± 1.2 s^{-1}.

Reaction 1 (L_2, X = Im, S = Acetonitrile). This system is completely analogous to that for which L = L_1. A plot of k_{obsd} vs. [Im] is curved, presumably due to self-association. Least-squares treatment of the initial linear portion of the curve yields a slope of 2.3 ± 1.7 M^{-1} s^{-1} and an intercept of 0.02 ± 0.03 s^{-1}.

Reaction 1 (L_2, X = Im, S = Acetone). This system was investigated only at high concentrations of imidazole. Under these conditions, k_{obsd} was independent of this concentration, having the value 15.1 ± 1.4 s^{-1} at 40 °C. Within experimental error, this is the same limiting rate constant obtained when *N*-methylimidazole is the incoming ligand. The data points are included in Figure 2b.

Previous studies[1-9,15,16,18-20,29] have revealed that the axial ligand substitution reactions of low-spin iron(II) systems typically proceed by a D mechanism. However, the dissociative interchange (I_d) mechanism must also be considered since it is so commonly observed in substitutions at Co(III).[30] Both of these mechanisms predict that, at high concentration of incoming ligand, a limiting rate should be achieved. In acetone solvent, reaction 1 does indeed reach limiting rates, consistent with the predictions of either mechanism. However, the independence of the limiting rate on the nature of the incoming ligand is more consistent with the D than with the I_d mechanism, since in the latter case the entering ligand plays a role in the activation process. We therefore feel that our results are most consistent with a D pathway. A D mechanism applicable to reaction 1 is given in eq 2–5. Assuming, first, that

$$FeL(An)_2 \rightleftarrows FeLAn + An \quad k_{-An}, k_{An} \qquad (2)$$

$$FeLAn + X \rightleftarrows FeL(An)(X) \quad k'_X, k'_{-X} \qquad (3)$$

$$FeL(An)(X) \rightleftarrows FeLX + An \quad k'_{-An}, k'_{An} \qquad (4)$$

$$FeLX + X \rightleftarrows FeL(X)_2 \quad k_X, k_{-X} \qquad (5)$$

the steady-state assumption is valid for the two five-coordinate intermediates and the mixed complex, second, that $k'_{-An} > k'_{-X}$ (this assumption is necessary to rationalize first-order rather than second-order dependence on [X]), and, third, that k_{-X}

~ 0 (final spectra indicate that the reaction proceeds to completion), we obtain the pseudo-first-order rate law in eq 6.

$$\text{rate} = \left(\frac{k_{-An} k'_X[X]}{k_{An}[An] + k'_X[X]} \right) [FeL(An)_2] \qquad (6)$$

When reactions (1) are performed in acetonitrile solvent ([An] = 19.14 M), it is reasonable that $k_{An}[An] >> k'_X[X]$, leading to eq 7. This is of the same form as the experimental rate

$$\text{rate} = \left(\frac{k_{-An} k'_X[X]}{k_{An}[An]} \right) [FeL(An)_2] \qquad (7)$$

law in acetonitrile solvent, with $k = k_{-An} k'_X / k_{An}[An]$. Values of $k_{-An} k'_X / k_{An}$ obtained from the slopes of Figure 1 are presented in Table I (to read the table, replace An in the expressions in the text with Y).

Under conditions such that $k'_X[X] > k_{An}[An]$, eq 6 reduces to eq 8. Thus if a D mechanism is operative, the observed

$$\text{rate} = k_{-An}[FeL(An)_2] \qquad (8)$$

rate constant should become independent of incoming and leaving ligand concentrations when the leaving ligand can no longer effectively compete for the five-coordinate intermediate in eq 2. This is precisely what we observe experimentally. It is particularly significant that the limiting rate constant is independent of the *nature*, as well as the concentration, of incoming ligand in the FeL_2^{2+} system. This provides firm evidence for the D pathway. We therefore conclude that k_{-An}, the rate constant for dissociation of the first acetonitrile molecule from $FeL(An)_2^{2+}$, has the value of 41.3 s^{-1} at 14 °C when $L = L_1$ and 14.3 s^{-1} at 40 °C when $L = L_2$ (the latter value is the average for the MeIm and Im data).

The rate constant, k_{-An}, is extremely important to this study, in that it represents directly the rate at which the axial ligand dissociates from the iron center. k_{-An} should be a sensitive indicator of the effect of the in-plane macrocyclic ligand on the iron–axial ligand interaction. Implicit in k_{-An}, however, are the effects of both the activation enthalpy and entropy of bond dissociation, of which only $\Delta H^\ddagger$ is closely related to axial ligand bond strength. To determine $\Delta H^\ddagger$, we performed temperature studies of reaction 1, under limiting rate conditions, between 10 and 25 °C for $L = L_1$ and between 20 and 40 °C for $L = L_2$. MeIm was the incoming ligand in both cases. The activation parameters derived from the temperature studies are $\Delta H^\ddagger = 16.2 \pm 2.5$ kcal/mol and $\Delta S^\ddagger = 5.2 \pm 8.6$ eu for $L = L_1$ and $\Delta H^\ddagger = 21.7 \pm 2.1$ kcal/mol and $\Delta S^\ddagger = 16.0 \pm 7.0$ eu for $L = L_2$. These values are included in Table I. The relatively large, positive values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ support the dissociative nature of the mechanism. Values of k_{-An} at 30 °C, calculated from the temperature data, and the values of k'_X / k_{An}, calculated from the appropriate value of k_{-An} and the slopes of plots of k_{obsd} vs. [MeIm] at low concentrations of MeIm in acetone, are also included in Table I.

The value of the dissociative rate constant, k_{-An}, decreases dramatically, from 195 to 4.4 s^{-1} at 30 °C, when the methyl substituents of the macrocyclic ligand are replaced by phenyl groups. The data in Table I indicate that this is largely attributable to a 5 kcal/mol difference in the enthalpy of activation for the dissociative step. In attempting to rationalize this somewhat large difference in $\Delta H^\ddagger$ values, three factors must be considered:

1. Solvation. It is conceivable that the $\Delta H^\ddagger$ difference arises in part from different relative degrees of solvation of the ground and transition states in the two systems, $L = L_1$ and L_2. It is difficult to speculate on the expected magnitude of such solvation differences, but it seems unlikely that the full 5 kcal/mol discrepancy could result from replacing methyl with phenyl groups on the macrocycle.

2. Steric Strain. The possibility that steric factors lead to a larger rate when $L = L_1$ may be ruled out. It is almost certain that the phenyl substituents in L_2 lie perpendicular to the average plane of the macrocyclic ligand, thereby avoiding mutual steric interference. In this arrangement, however, the ortho hydrogens of the phenyl groups protrude into the regions occupied by the axial ligands. In L_1, on the other hand, the hydrogens of the methyl substituents point *away* from, and do not interfere at all with, the axial sites. Steric interaction should therefore be more severe in $FeL_2(An)_2^{2+}$ than in $FeL_1(An)_2^{2+}$, leading to a predicted ordering of $\Delta H^\ddagger$ values opposite to that observed. We conclude that, although steric factors may play a role in determining the relative rates, they are overshadowed by other effects.

3. Inherent Metal–Axial Ligand Bond Strength. To the extent that the preceding discussion is valid, we conclude that the 5 kcal/mol discrepancy in $\Delta H^\ddagger$ results primarily from a difference in the inherent strength of the iron–acetonitrile bond. This bond is thus stronger when $L = L_2$ than when $L = L_1$. It is tempting to attribute this to electron withdrawal by the phenyl substituents of the macrocycle, L_2. Such withdrawal should reduce the donor ability of the macrocyclic ligand, leading to an overall decrease in the d-orbital energies of iron and correspondingly increased overlap between the iron d_{z^2} orbital and the σ-donor orbitals of the axial ligands. The larger value of $\Delta S^\ddagger$ when $L = L_2$ is also consistent with a more ordered ground state—i.e., a stronger bond in $FeL_2(An)_2^{2+}$.

The rate constants for dissociation of pyridine from $Fe(DMGH)_2(py)_2$ (DMGH = the monoanion of dimethylglyoxime) and $Fe(DPGH)_2(py)_2$ (DPGH = the monoanion of diphenylglyoxime) are 7×10^{-3} [7] and 4.8×10^{-4} [18] s^{-1}, respectively, at 10 °C. This is the same relative order that we observe for methyl- and phenyl-substituted ligands and indicates that similar effects may be operative in the two systems. Some care must be taken in drawing this comparison, however, in that the two glyoxime systems were examined in different solvents.

Although much kinetic data for low-spin iron(II) complexes is available in the literature, much of it is not directly comparable with the data which we have presented here. The reason for this is twofold. First, the solvent medium in which the kinetics studies are performed may have a dramatic effect on the rate constants and activation parameters measured. Second, the charge on the complex may be quite important in influencing reaction rates, both from the standpoint of possible ion–dipole interactions between the complex and the incoming ligand and from the standpoint of the electron density at the iron center. It is therefore necessary that only species of the same charge, studied in the same or similar solvent media, be compared.

For these reasons, comparison of our data with existing data on iron(II) porphyrin, glyoxime, and phthalocyanine systems[1-7,10-20] is not justified. However, the studies of axial ligand substitution in complexes of the type $Fe(TAAB)Y_2^{2+}$,[8] where TAAB is a 16-membered, tetraaza, macrocyclic ligand resulting from the self-condensation of *o*-aminobenzaldehyde,[31] and of axial ligand exchange in complexes of the type $FeL_1(Y)_2^{2+}$ [9] are directly comparable with ours, from the standpoints of both overall charge and solvent. Some results from ref 8 and 9 are presented in Table I. The most significant numbers in the table are the enthalpies of activation for dissociation of Y from $FeL(Y)_2^{2+}$, since these most directly represent the strength of the iron–Y interaction. It is remarkable that $\Delta H^\ddagger$ is between 4.7 and 10.9 kcal/mol less for $FeL_1(Y)_2^{2+}$ than for $Fe(TAAB)Y_2^{2+}$, depending on the nature of the axial ligand. For a given axial ligand, MeIm, the difference is 8.3 kcal/mol. In addition, for L_1, as the donor ability of the axial ligand decreases, $\Delta H^\ddagger$ decreases, as expected (17.9 for MeIm

to 16.2 for An). When the macrocyclic ligand is L_2, the activation enthalpy increases over that for L_1, as discussed earlier, but is still substantially less than those observed for TAAB. Apparently, then, L_1, and to a lesser extent L_2, exerts a stronger labilizing influence on N-donor axial ligands than does TAAB.

The differences among the three macrocyclic ligands may be discussed primarily in terms of ring size and inherent donor abilities of the imine nitrogens, since the degree of unsaturation in the inner ring is the same for all three ligands. For constant ring size, as we have seen above, changing the imine substituents from CH_3 to C_6H_5 has a marked effect, in the expected direction, on the iron(II)–axial ligand bond strength. This reflects a reduction in the inherent donor ability of the macrocyclic ligand. Similarly, when the size of the inner ring is increased by two, as in the TAAB ligand, the metal ion is not "squeezed" as tightly by the macrocycle; consequently, electron donation by the ring is lessened. This is manifested in an enhanced iron(II)–axial ligand interaction and hence an increased activation barrier for dissociation.

It is also notable that the ordering of $\Delta H^{\ddagger}$ values for L_1 and TAAB is consistent with the relative magnitudes of the in-plane ligand fields produced by these macrocycles. (Dq_{xy}(TAAB) = 1465 cm^{-1} and $Dq_{xy}(L_1)$ = 1767 cm^{-1}, measured from the electronic spectra of (dithiocyanato)nickel complexes of the macrocycles.[33]) Although Dq_{xy} for L_2 has not been determined, we predict on the basis of the data in Table I that it should lie between those for L_1 and TAAB.

In conclusion, we have shown that in complexes of the type $FeL(Y)_2^{2+}$, where L = L_1 and L_2 and Y = acetonitrile and *N*-methylimidazole, structural changes on the periphery of the macrocyclic ligand have a substantial effect on the ability of L to labilize the axial sites. We are in the process of extending our investigation to include several additional ligands of the type L = [X_4(14)tetraeneN_4], where X represents a variety of groups, to examine more fully the effects of peripheral substituents on the axial labilizing ability of the macrocycle.

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Note Added in Proof. Since this paper was accepted for publication, a report describing the synthesis of $FeL_2(An)_2(PF_6)_2$ has appeared.[34] Electronic spectral data are in reasonable agreement with ours.

Registry No. $FeL_1(An)_2^{2+}$, 49861-52-1; $FeL_2(An)_2(PF_6)_2$, 70369-09-4; MeIm, 616-47-7; Im, 288-32-4; 1,3-diaminopropane, 109-76-2; benzil, 134-81-6.

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Monomeric and Dimeric Pyrazole and Pyrazolyl Complexes of Ruthenium

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The first examples of well-characterized, monomeric ruthenium–pyrazole complexes have been obtained. The complexes include $[(bpy)_2Ru(pzH)_2]^{2+}$, $[(bpy)_2Ru(pz)(pzH)]^{+}$, and $(bpy)_2Ru(pz)_2\cdot H_2O$ (bpy = 2,2′-bipyridine, pzH = pyrazole, pz = pyrazolyl anion). From the results of cyclic voltammetry and electronic spectral measurements it is concluded that, in the complexes, the pzH ligand is a poorer π acceptor than pyridine while in its deprotonated form (pz), it is a better π donor than Cl^- ion. The pyrazole complexes can be deprotonated in solution giving the complex $(bpy)_2Ru(pz)_2$ which is itself capable of reacting as a chelating ligand. It undergoes a reaction with the labile solvent complex $[(bpy)_2Ru((CH_3)_2CO)_2]^{2+}$ giving the doubly bridged dimer $[(bpy)_2Ru^{II}(pz)_2Ru^{II}(bpy)_2]^{2+}$. The reactivity of the mixed-valence form of this ion, $[(bpy)_2Ru^{II}(pz)_2Ru^{III}(bpy)_2]^{3+}$, is similar to that reported for the previously characterized chloro-bridged dimers $[(bpy)_2RuCl_2Ru(bpy)_2]^{3+}$, in that it undergoes an asymmetrical cleavage reaction in CH_3CN solution.

Trofimenko has described syntheses and physical properties for the ions $HB(pz)_3^-$ and $B(pz)_4^-$ which can function as either η^2 or η^3 ligands when bound to metal ions.[1] Dimeric complexes such as $(CO)_2Rh(pz)_2Rh(CO)_2$[2] and $[(\eta^5\text{-}C_5H_5)Ti(pz)_2Ti(\eta^5\text{-}C_5H_5)]$[3] have also been prepared by using the pyrazolyl group (pz) as a bridging ligand. The preparations involve the direct

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