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Axial Labilization by Macrocyclic Ligands. 2. Further Kinetics Studies of Axial Substitution in Iron(II) Complexes of Tetrasubstituted Bis(α-diimine) Macrocyclic Ligands

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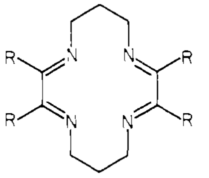
The results of a study of the kinetics of substitution of axial acetonitrile by *N*-methylimidazole in the complexes $FeL_3(An)_2^{2+}$ and $FeL_4(An)_2^{2+}$ (L_3 and L_4 are macrocyclic ligands with structures as defined below) in acetone solvent are presented. As for the analogous systems containing the macrocyclic ligands L_1 and L_2 (also defined below), the axial substitution reactions proceed by a D mechanism, with replacement of the first acetonitrile molecule occurring more rapidly than replacement of the second. The dissociative rate constants and activation parameters ($\Delta H^\ddagger$ and $\Delta S^\ddagger$) for replacement of the second acetonitrile molecule have been measured and have been found to correlate well with the structure of the macrocyclic ligand. Specifically, as the donor ability of the macrocyclic ligand decreases in the order $L_1 > L_4 > L_3 > L_2$, the dissociative rate constant steadily decreases and the enthalpy of activation correspondingly increases.

Axial labilization by macrocyclic ligands is a phenomenon of much current research interest.[1-5] In a previous paper, we reported the results of a study of the axial ligand substitution kinetics of the low-spin iron(II) complexes of the synthetic macrocyclic ligands, $Me_4[14]tetraeneN_4$ (L_1) and $Ph_4[14]$-$tetraeneN_4$ (L_2).[1] Herein we report the results of further studies of this type, involving the systems indicated in reaction 1. As in the previous two systems (L = L_1, L_2), reaction 1 proceeds by a dissociative (D) mechanism. Dissociative rate constants and activation enthalpies reflect the electronic effects arising from the phenyl substituents, which appear to have a direct effect on the donor ability of the macrocycle.

$$FeL(An)_2^{2+} + 2X \rightleftarrows FeLX_2^{2+} + 2An \qquad (1)$$



L

L = L_3, X = *N*-methylimidazole (MeIm),
 solvent = acetonitrile (An), acetone
L = L_4, X = MeIm, solvent = acetone
 L_3 = $(p\text{-MePh})_4[14]tetraeneN_4$ (R = *p*-methylphenyl)
 L_4 = $(p\text{-MeOPh})_4[14]tetraeneN_4$ (R = *p*-methoxyphenyl)

Experimental Section

Reagents. Reagent grace acetonitrile was refluxed over P_2O_5 and then distilled from P_2O_5 under nitrogen atmosphere. Reagent grade acetone, imidazole, and *N*-methylimidazole were dried and/or purified as previously described.[1] All other materials were reagent grade and were used without further purification.

Synthesis. $FeL_3(An)_2(PF_6)_2$ and $FeL_4(An)_2(PF_6)_2$ were both synthesized by the following method, which is a modification of previously developed procedures.[6,7] All operations were carried out under a nitrogen atmosphere unless otherwise noted. 1,3-Diaminopropane (0.012 mol) was dissolved in 50 mL of methanol, and 0.012 mol of glacial acetic acid was added, with stirring. The appropriate para-substituted benzil (0.012 mol) (Aldrich) was then added and the solution stirred at reflux for about 1 h. During this time the benzil dissolved to give a green-yellow solution.

Simultaneously with the procedure above, 0.053 mol of iron powder and 0.053 mol of $FeCl_3$ were placed in 125 mL of methanol, and the slurry was brought to boiling, with stirring. Stannous chloride dihydrate (0.0044 mol) was then added. The slurry was cooled to room temperature and filtered through Celite to remove unreacted iron. The appropriate fraction (14 mL) of the pale green filtrate was added dropwise to the ligand solution from above, followed by the addition of 0.012 mol of anhydrous sodium acetate. An intense cyan color resulted, which rapidly turned a deep blue. The solution was refluxed for 48 h. At the end of this time, 15 mL of acetonitrile were added to the purple solution, resulting in a color change to deep blue. The solution was filtered in air, the filtrate was reduced in volume by one-third and refiltered, and a solution of 5 g of NH_4PF_6 in 10 mL of H_2O was added. In the case L = L_4, 10 mL of ethanol was added at this point to promote crystallization. Refrigeration, followed by filtration, yielded dark purple crystals of $FeL(An)_2(PF_6)_2$. These were washed with cold methanol, then ether, and recrystallized from acetonitrile/ethanol. The complexes were characterized by IR and UV-visible spectroscopy.[8]

Physical Methods. IR spectra were obtained from Nujol mulls and/or KBr pellets by using a Perkin-Elmer Model 397 grating infrared spectrometer. Visible electronic spectra and ligand substitution kinetics data for reactions in acetonitrile solvent were obtained with a Perkin-Elmer Model 323 spectrophotometer. Ligand substitution kinetics in acetone solvent were studied with a Nortech SF-3A Canterbury stopped-flow system which has been previously described.[1] Reactions of eq 1 were studied under conditions for pseudoorder kinetics in iron reactant. Disappearance of iron reactant (at 592 nm for L = L_3, 582 nm for L = L_4; both MLCT bands) and appearance and subsequent disappearance of the mixed complex $FeL(An)X^{2+}$ (at 655 nm) were monitored.

Special Precautions. We have observed that $FeL_3(An)_2^{2+}$ and $FeL_4(An)_2^{2+}$ have a much greater tendency to undergo replacement of axial acetonitrile by water than do the corresponding complexes in which L = L_1 and L_2.[1] This was particularly noticeable in acetone solvent. So that interference by water could be avoided, solvents were rigorously dried as described above and solutions of the iron complexes were prepared in a N_2-filled glovebag. When these precautions were taken, no noticeable replacement of acetonitrile by water was observed.

Results and Discussion

Reaction 1 (Acetonitrile Solvent). This reaction was examined only for the case L = L_3. Solutions of $FeL_3(An)_2^{2+}$ in acetonitrile react fairly rapidly with added *N*-methylimidazole to produce solutions having visible absorption spectra corresponding to those of the species $FeL_3(MeIm)_2^{2+}$. The

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Table I. k_{obsd} as a Function of [MeIm] for Reaction 1, $L = L_3$ (Acetonitrile Solvent, $T = 20$ °C, $[\mathrm{Fe}] = 4.79 \times 10^{-5}$ M)

[MeIm], M	k_{obsd}, s^{-1} [a]	[MeIm], M	k_{obsd}, s^{-1} [a]
0.008	0.0069	0.100	0.0352
0.016	0.0073	0.130	0.0432
0.029	0.0141	0.150	0.0485
0.057	0.0227	0.172	0.0529
0.086	0.0287		

[a] Each value represents the mean of at least three separate experiments.

reaction is first order in iron, as shown by 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 $\lambda_{\max}$ for $\mathrm{FeL_3(An)_2}^{2+}$. The slopes of such plots yield pseudo-first-order rate constants, k_{obsd}, which increase linearly with the concentration of incoming ligand, MeIm, over at least a 20-fold range of concentration. Values of k_{obsd} at 20 °C as a function of MeIm concentration for $L = L_3$ are shown in Table I.

We have previously stated[1] that the first-order dependence of the rate on incoming ligand concentration implies that the first substitution step is rate determining. However, in a recent publication,[5] Sweigart and co-workers have shown that in reactions of the type

$$\mathrm{FePcY_2} + 2\mathrm{X} \rightleftarrows \mathrm{FePcX_2} + 2\mathrm{Y} \qquad (2)$$

where Pc = Phthalocyanine, either the first or the second substitution step may be rate determining, depending upon the natures of Y and X. For the particular case in which $\mathrm{Y} = \mathrm{P(OBu)_3}$ and X = Im, the rate of the first substitution is 5×10^5 times faster than that of the second, whereas when Y = pyridine and X = tri-*n*-butylphosphine, the first step is substantially slower than the second. In order to determine which situation prevails in the $\mathrm{FeL(An)_2}^{2+}$ complexes, we monitored the reaction at $\lambda_{\max}$ for the mixed complex, $\mathrm{FeL(An)(MeIm)}^{2+}$. In both cases, $L = L_3$ and $L = L_4$, we observed a very rapid absorbance increase, followed by a slower absorbance decrease at this wavelength. Further, the rate constant extracted from the absorbance decrease was the same as that obtained by monitoring disappearance of $\mathrm{FeL(An)_2}^{2+}$. The latter rate constant therefore corresponds to the second substitution step. We conclude that replacement of the second acetonitrile molecule is rate determining and consequently that our k_{obsd} values correspond to reaction 3. (Charges have been

$$\mathrm{FeL(An)(MeIm)} + \mathrm{MeIm} \rightarrow \mathrm{FeL(MeIm)_2} + \mathrm{An} \quad (3)$$

omitted here and from now on for clarity.) This conclusion applies not only to the studies in acetonitrile solvent but also to those performed in acetone solvent (vide infra).

Least-squares analysis of the data in Table I yields a slope of $0.29 \pm 0.03\ \mathrm{M^{-1}\,s^{-1}}$ and an intercept of $0.005 \pm 0.003\ \mathrm{s^{-1}}$. (The errors quoted here and subsequently represent 99% confidence limits. Since the error in the intercept is of the same magnitude as the intercept, we consider the latter to be zero within experimental error.)

The data in Table I imply a rate law of the general form rate = $k[\mathrm{MeIm}][\mathrm{FeL_3(An)_2}]$, which is consistent with many mechanistic schemes. Since the studies in acetonitrile solvent did not allow diagnosis of mechanism, we undertook studies of the ligand substitution reactions in acetone solvent for both $L = L_3$ and L_4.

Reaction 1 (Acetone Solvent). In order to demonstrate that acetone competes poorly with acetonitrile as a ligand toward the iron complexes under study, we recorded visible electronic absorption spectra of solutions containing $\sim 5 \times 10^{-5}$ M $\mathrm{FeL(An)_2(PF_6)_2}$ and varying acetonitrile concentrations in acetone solvent. The spectra of the bis(acetonitrile) species were invariant down to acetonitrile concentrations of ~ 0.05 M, indicating the weak axial ligating ability of acetone. (Note the special precautions taken to avoid interference by water coordination—see the Experimental Section.)

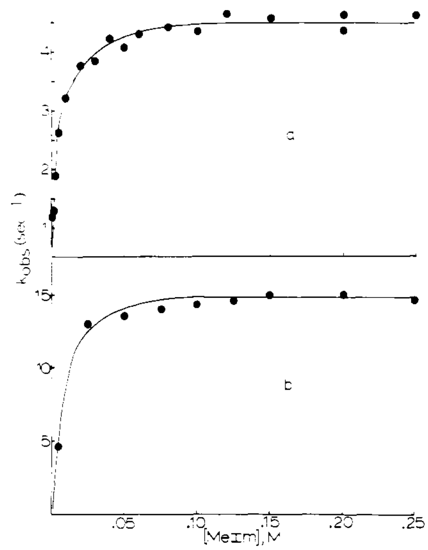

Figure 1. (a) Plot of k_{obsd} vs. [MeIm]: $L = L_3$, acetone solvent, $T = 25$ °C, [An] = 0.096 M. (b) Plot of k_{obsd} vs. [MeIm]: $L = L_4$, acetone solvent, $T = 30$ °C, [An] = 0.19 M.

Kinetics studies were subsequently performed in acetone at 25 °C, as a function of the concentrations of both entering (MeIm) and leaving (An) ligands. This allowed us to determine the dependence of k_{obsd} on the leaving ligand concentration. At low incoming-to-leaving ligand concentration ratios, 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 1. (Figure 1a: $L = L_3$, 25 °C; Figure 1b: $L = L_4$, 30 °C.) The values of the limiting rate constants, determined as the average of k_{obsd} for [MeIm] > 0.07 M, are $4.5 \pm 0.2\ \mathrm{s^{-1}}$ at 25 °C and $14.8 \pm 0.4\ \mathrm{s^{-1}}$ at 30 °C for $\mathrm{FeL_3(An)_2}^{2+}$ and $\mathrm{FeL_4(An)_2}^{2+}$, respectively. We have previously shown that axial ligand substitution reactions of low-spin $\mathrm{FeL(An)_2}^{2+}$-type complexes proceed by a D mechanism. This is, in fact, generally the case for low-spin iron(II) complexes containing macrocyclic ligands. For the cases when $L = L_3$ and L_4, a D mechanism is indicated both by the attainment of a limiting rate at high concentration of incoming ligand and by rate retardation caused by an excess of leaving ligand, An. When the observation, cited earlier, that replacement of the second acetonitrile molecule is rate determining is taken into account, the D mechanism in eq 4–6

$$\mathrm{FeL(An)_2} + \mathrm{MeIm} \rightleftarrows \mathrm{FeL(An)(MeIm)} + \mathrm{An} \quad K, \text{ rapid} \qquad (4)$$

$$\mathrm{FeL(An)(MeIm)} \rightleftarrows \mathrm{FeL(MeIm)} + \mathrm{An} \quad k_{-\mathrm{An}}, k_{\mathrm{An}} \qquad (5)$$

$$\mathrm{FeL(MeIm)} + \mathrm{MeIm} \rightarrow \mathrm{FeL(MeIm)_2} \quad k_{\mathrm{MeIm}} \qquad (6)$$

applies to reaction 1. The rate law resulting from this mechanism, assuming a steady-state concentration for the five-coordinate intermediate, is given in eq 7 where $[\mathrm{Fe}]_{\mathrm{T}} = [\mathrm{FeL(An)_2}] + [\mathrm{FeL(An)(MeIm)}]$.

$$\text{rate} = k_{-\mathrm{An}} k_{\mathrm{MeIm}} K [\mathrm{Fe}]_{\mathrm{T}} [\mathrm{MeIm}]^2 / \{k_{\mathrm{An}}[\mathrm{An}]^2 + (k_{\mathrm{MeIm}} + k_{\mathrm{An}}K)[\mathrm{MeIm}][\mathrm{An}] + k_{\mathrm{MeIm}}K[\mathrm{MeIm}]^2\} \qquad (7)$$

Even in acetonitrile solvent, when [An] = 19.14 M, the first term in the denominator is too small to have an observable effect. The second term thus apparently dominates, leading to the rate law in eq 8.

Table II. Dissociative Rate and Activation Parameters for the $FeL(An)_2^{2+}$ Systems

	k_{-An}, s^{-1}	$\ln k_{-An}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	redox potential[a]
L_1 (R = Me)[b]	195	5.273	16.2	5.3	0.61
L_4 (R = *p*-MeOPh)	14.8	2.695	19.5	11.7	0.76
L_3 (R = *p*-MePh)	8.5	2.186	21.8	17.5	0.82
L_2 (R = Ph)[b]	4.4	1.482	21.7	16.0	0.86

[a] Reference 8. [b] Reference 1.

This is of the same form as the experimental rate law in acetonitrile solvent.

$$\text{rate} = \frac{k_{-An}k_{MeIm}K[Fe]_T[MeIm]}{(k_{MeIm} + k_{An}K)[An]} \tag{8}$$

Under conditions of relatively low acetonitrile concentration, such that the third term in the denominator dominates, eq 7 reduces to eq 9. Thus if a D mechanism is operative, the

$$\text{rate} = k_{-An}[Fe]_T \tag{9}$$

observed 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 5. This is observed experimentally. We therefore conclude that k_{-An}, the rate constant for dissociation of acetonitrile from $FeL(An)(MeIm)^{2+}$, has the value of 4.5 s^{-1} at 25 °C when L = L_3 and 14.9 s^{-1} at 30 °C when L = L_4.

We have previously discussed the importance of the dissociative rate constant, k_{-An}, and the associated activation parameters, ΔH^* and ΔS^*, in the context of our general program of study of axial labilization by macrocyclic ligands.[1] To determine the latter parameters, we performed temperature studies of reaction 1, under limiting rate conditions, for both macrocyclic ligand complexes. For L = L_3, studies were performed between 5 and 40 °C, and for L = L_4, between 15 and 40 °C. The activation parameters derived from the temperature studies are $\Delta H^* = 21.8 \pm 0.3$ kcal/mol and $\Delta S^* = 17.5 \pm 1.0$ eu for L = L_3 and $\Delta H^* = 19.5 \pm 3.8$ kcal/mol and $\Delta S^* = 11.7 \pm 6.4$ eu for L = L_4. These values, along with those for the closely related systems wherein L = L_1 and L_2,[1] are presented in Table II. The relatively large, positive values of ΔH^* and ΔS^* support the dissociative nature of the mechanism. Values of k_{-An} at 30 °C, calculated from the temperature data, are also presented in Table II along with k_{-An} values for the L_1 and L_2 systems.

The data in Table II suggest a definite correlation between k_{-An} (30 °C) and the electron-withdrawing or electron-donating characteristics of the substituents on the periphery of the macrocyclic ligand. As one proceeds from L_1, wherein R = CH_3, through L_4 and L_3 (R = *p*-CH_3OPh and *p*-MePh, respectively) to L_2, wherein R = Ph, there is a decrease in the electron-donating ability of the substituents. This is expected to cause a corresponding decrease in the macrocyclic donor ability, which should result in an increase in the iron–axial acetonitrile interaction, hence a decrease in rate of dissociation. This decrease is indeed observed. It has previously been shown that there is a direct correlation between the Hammett constants of the substituents and $E_{1/2}$ for the Fe^{II}–Fe^{III} couple in this series of complexes.[8] The $E_{1/2}$ values, included in Table II, therefore provide a reliable measure of the macrocyclic donor abilities. Figure 2a is a plot of $\ln k_{-An}$ (at 30 °C) against $E_{1/2}(Fe^{II}–Fe^{III})$. It can be seen that the correlation between the specific axial ligand dissociation rate and $E_{1/2}$ is quite good. A somewhat poorer, but still significant, correlation exists between $E_{1/2}$ and ΔH^*, the activation enthalpy for axial ligand dissociation. The appropriate plot is shown in Figure 2b. Significantly, this plot shows that ΔH^*, which is the best kinetically obtainable measure of the metal–axial ligand bond strength, can be used as an indicator of macrocycle donor ability, hence of macrocycle labilizing ability, within a series of closely related ligands. We are currently attempting to extend our investigation to include 14-membered tetraazamacrocycles which differ substantially from those discussed herein in order to determine the generality of the relationship between ΔH^* and macrocycle structure.

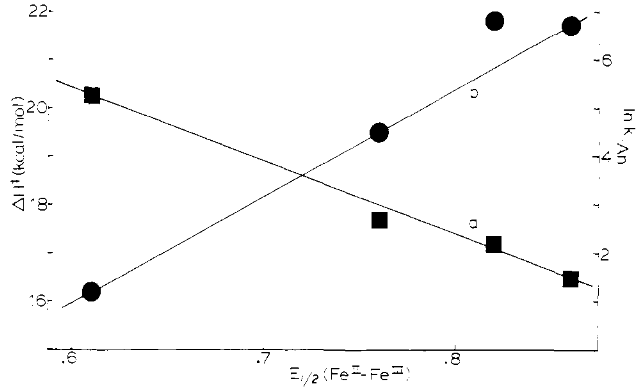

Figure 2. (a) Plot of $\ln k_{-An}$ vs. $E_{1/2}(Fe^{II}–Fe^{III})$ for the $FeL(An)_2^{2+}$ series. (b) Plot of ΔH^* vs. $E_{1/2}(Fe^{II}–Fe^{III})$ for the $FeL(An)_2^{2+}$ series.

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Registry No. $FeL_3(An)_2^{2+}$, 70368-94-4; $FeL_4(An)_2^{2+}$, 70368-96-6; MeIm, 616-47-7.