Kinetics of Ligand Exchange in Iron(II) Complexes of 2,3,9,10-Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene

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Variable-temperature ^{1}H n.m.r. lineshape analysis has been used to determine the kinetics of axial ligand exchange in some iron(II) complexes of 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene (L^1). Exchange rates on FeL^1 follow the order 2-methylimidazole $\gg$ 1-methylimidazole $\simeq$ imidazole. Rates of 1-methylimidazole exchange show *cis* effects of the order tetraphenylporphinate $\gg$ L^1 > tetrabenzo[*b,f,j,n*][1,5,9,13]tetra-azacyclohexadecine ~ bis[dimethylglyoximate(1−)] ~ phthalocyaninate(2−), which are interpreted in terms of σ and π bonding and the hole size of the macrocycle.

MANY earlier investigations have been reported [1-8] on substitution reactions in low-spin iron(II) macrocyclic derivatives. In such systems the microsymmetry of the iron atom is either D_{4h} or C_{4v}, with four nitrogen atoms in a square plane and part of a more or less rigid ring system {*e.g.* tetraphenylporphinate (tpp), bis[dimethylglyoximate(1−)] $(Hdmg)_2$, phthalocyaninate (pc), 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene (L^1), or tetrabenzo[*b,f,j,n*][1,5,9,13]-tetra-azacyclohexadecine (L^2)}. The axial sites are occupied by the ligands taking part in the observed rate processes. All of the systems studied so far undergo substitution reactions *via* a dissociative mechanism involving a five-co-ordinate intermediate. The rationale for studying a wide variety of macrocyclic systems is to shed light on the factors affecting axial ligation to metal complexes of this type. While the macrocycle L^1 bears no more than a superficial resemblance to the haem group, and in many instances shows major chemical differences, it is of interest because it does show some qualitative similarities to an iron porphyrin. For example, both systems give low-spin diamagnetic complexes by addition of axial ligands, both reversibly bind CO,[8] and both undergo photochemical dissociation of CO.[9] However, the rates and equilibrium constants involved [10] are considerably different, and it is therefore of interest to investigate how such differences can be related to structural and electronic features of the macrocycle.

The lability of an axial ligand in these systems can be related to a variety of factors, such as the iron–ligand bond strength, *trans* and *cis* effects, flexibility, strain, and the hole size of the macrocycle, conjugation, ligand-field strength, and net charge of the complex, steric interactions, and solvent effects. In this study we have used ^{1}H n.m.r. full lineshape analysis to study ligand-exchange reactions of $[FeL^1(imH)_2]^{2+}$, $[FeL^1(1Me\text{-}im)_2]^{2+}$, and $[FeL^1(NCMe)(2Me\text{-}im)]^{2+}$ (imH = imidazole, 1Me-im = 1-methylimidazole, and 2Me-im = 2-methylimidazole), and compared them with similar complexes of tpp, pc, L^2, and $Hdmg^-$. Metal imidazole complexes have been the subject of an earlier review,[11] which provides general background material to the present study.

TABLE 1

Hydrogen-1 n.m.r. spectra in CD_3CN solution at 28 °C

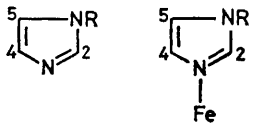
(*a*) Imidazole resonances in p.p.m. downfield from $SiMe_4$ [a]

	imH	$[FeL^1(imH)_2]^{2+}$	1Me-im	$[FeL^1(1Me\text{-}im)_2]^{2+}$	2Me-im	$[FeL^1(NCMe)(2Me\text{-}im)]^{2+}$
H^2	7.64	6.58	7.43	6.34		
H^4	7.08	5.87	7.00	5.76	6.89	5.57
H^5	7.08	6.90	6.93	6.77	6.89	6.71
Me			3.69	3.51		

(*b*) L^1 Resonances in p.p.m. downfield from $SiMe_4$

	$[FeL^1(NCMe)_2]^{2+}$	$[FeL^1(imH)_2]^{2+}$	$[FeL^1(1Me\text{-}im)_2]^{2+}$	$[FeL^1(NCMe)(2Me\text{-}im)]^{2+}$
Me	2.66	2.80	2.80	2.79
α-CH_2	*ca.* 4.00	3.94	3.92	*ca.* 4.00

[a] Numbering system for imidazole resonances:



RESULTS AND DISCUSSION

N.M.R. Spectra and Equilibrium Constants.—The ^{1}H resonances of the free imidazoles and the iron(II) L^1 complexes at 28 °C in CD_3CN solution are shown in Table 1. For the free ligands our assignments agree well with those quoted by Grimmett.[12] For the complexes it is necessary to decide which species are actually present in solution before attempting the assignment of specific imidazole resonances. The spectrum of $[FeL^1(NCMe)_2]^{2+}$ obtained by dissolving $[FeL^1(NCMe)_2][PF_6]_2$ in CD_3CN is unambiguous and the assignments of the L^1 α-CH_2 and CH_3 resonances agree with those of Baldwin *et al.*[8]

When 2-methylimidazole is added to $[FeL^1(NCMe)_2][PF_6]_2$ in ligand : complex ratios varying from 1.4 : 1.0 to 13.2 : 1.0 the n.m.r. spectrum shows a mixture of unchanged $[FeL^1(NCMe)_2]^{2+}$ (L^1 CH_3 resonance at 2.66 p.p.m.) and a single new complex, with an L^1 CH_3 resonance at 2.79 p.p.m. The ratio of the areas under the two L^1 CH_3 peaks is a linear function of the concentration of free 2-methylimidazole (Table 3). The new complex is thus a mono- and not a bis-(imidazole) species. Although Collman and Reed [13] reported that the mono(2-methylimidazole) complex of tetraphenylporphinatoiron(II) was five-co-ordinate and paramagnetic, the corresponding L^1 complex is almost certainly six-co-ordinate since its n.m.r. spectrum shows it is definitely diamagnetic. It is accordingly formulated as the mono(solvent) complex $[FeL^1(NCMe)(2Me\text{-}im)]^{2+}$. The equilibrium constant at 28 °C for reaction (1) was

$$[FeL^1(NCMe)_2]^{2+} + 2Me\text{-}im \overset{k_1}{\rightleftharpoons} [FeL^1(NCMe)(2Me\text{-}im)]^{2+} + MeCN \quad (1)$$

determined by recording the ^1H n.m.r. spectrum of a CD_3CN solution of $[FeL^1(NCMe)_2]^{2+}$ after successive additions of known amounts of 2-methylimidazole. The relative concentrations of $[FeL^1(NCMe)_2]^{2+}$ and $[FeL^1(NCMe)(2Me\text{-}im)]^{2+}$ were measured from the areas under the peaks of their respective L^1 CH_3 resonances. The absolute concentration of $[FeL^1(NCMe)(2Me\text{-}im)]^{2+}$ was obtained by comparing one twelfth of the area under its L^1 CH_3 peak with one half the area under the ring-proton peak of 2-methylimidazole. A value of $K_1 = 7.5 \pm 0.3$ dm^3 mol^{-1} was obtained by an unweighted least-squares analysis of the linear dependence of the ratio $[FeL^1(NCMe)(2Me\text{-}im)^{2+}] : [FeL^1(NCMe)_2{}^{2+}]$ on the concentration of free 2-methylimidazole.

When a 5 : 1 excess of imidazole is added to $[FeL^1(NCMe)_2]^{2+}$ the L^1 CH_3 peak of the substrate disappears completely and a single new peak appears at 2.80 p.p.m. This agrees with Rose's value for the chemical shift of $[FeL^1(imH)_2]^{2+}$; there is no sign of the presence of any $[FeL^1(NCMe)(imH)]^{2+}$ (L^1 CH_3 resonance at [8] 2.73 p.p.m.). In the 1-methylimidazole system the spectrum of a CD_3CN solution of $[FeL^1(1Me\text{-}im)_2][PF_6]_2$ shows no sign of free 1-methylimidazole, or of any $[FeL^1(NCMe)_2]^{2+}$, and the complex resonances are invariant on adding free 1-methylimidazole. The observed spectrum was therefore assigned to $[FeL^1(1Me\text{-}im)_2]^{2+}$. Assuming that the lowest concentration of the mono(imidazole) complexes which could be detected was 10% of the total complex concentration, the known total concentrations of the complexes and the free ligands give the lower limits of the equilibrium constants of reactions (2) and (3) as >200 and >70 dm^3 mol^{-1} respectively. Baldwin *et al.*[8]

$$[FeL^1(NCMe)(imH)]^{2+} + imH \overset{K_2}{\rightleftharpoons} [FeL^1(imH)_2]^{2+} + MeCN \quad (2)$$

$$[FeL^1(NCMe)(1Me\text{-}im)]^{2+} + 1Me\text{-}im \overset{K_3}{\rightleftharpoons} [FeL^1(1Me\text{-}im)_2]^{2+} + MeCN \quad (3)$$

estimated that the equilibrium constant for reaction (2) is only one seventh of that for (4). This gives the value

$$[FeL^1(NCMe)_2]^{2+} + imH \overset{K_4}{\rightleftharpoons} [FeL^1(NCMe)(imH)]^{2+} + MeCN \quad (4)$$

of K_4 as >1 400 dm^3 mol^{-1}; if the same ratio is assumed for K_3/K_5 as for K_2/K_4, the value of K_5 is >490 dm^3 mol^{-1}.

$$[FeL^1(NCMe)_2]^{2+} + 1Me\text{-}im \overset{K_5}{\rightleftharpoons} [FeL^1(NCMe)(1Me\text{-}im)]^{2+} + MeCN \quad (5)$$

The equilibrium constant for reaction (1) is much less than the lower limits calculated for (4) and (5). This can be ascribed to steric hindrance between the CH_3 group α to the donor nitrogen atom in 2-methylimidazole and the L^1 methylene protons. Such strain could be relieved to some extent by the iron atom moving out of the plane of the macrocyclic ligand towards the 2-methylimidazole, but the 2Me-im complex would probably still be less stable than the corresponding complexes of imidazole and 1-methylimidazole. The failure to detect a bis(2-methylimidazole) complex may be due to the fact that this type of distortion to relieve steric strain is precluded by the higher symmetry of a bis complex.

In assigning the imidazole-ring resonances, the simplest case is that of 2-methylimidazole. The free ligand shows only one ring resonance (at 6.89 p.p.m.), rapid tautomerism of the amine proton between the two nitrogen atoms making positions 4 and 5 equivalent. Complexation removes this tautomerism and two different resonances are observed. It was assumed that H^4, being closer to the metal ion, would be affected most by co-ordination, so the peak at 5.57 p.p.m. was assigned to H^4 and that at 6.71 p.p.m. to H^5. Similar shifts in the H^4 and H^5 resonances on complexation were assumed for the imidazole and 1-methylimidazole complexes, giving the assignments shown in Table 1. The H^2 resonances were then assigned by elimination. Added evidence in favour of the assignments is that the changes in the presumed H^2 resonances on complexation are very similar in the imidazole and 1-methylimidazole systems.

Kinetics.—The rates of the exchange reactions (6)—(8) were obtained by complete lineshape analysis of the

$$[FeL^1(imH)_2]^{2+} + imH \rightleftharpoons [FeL^1(imH)_2]^{2+} + imH \quad (6)$$

$$[FeL^1(1Me\text{-}im)_2]^{2+} + 1Me\text{-}im \rightleftharpoons [FeL^1(1Me\text{-}im)_2]^{2+} + 1Me\text{-}im \quad (7)$$

$$[FeL^1(NCMe)(2Me\text{-}im)]^{2+} + 2Me\text{-}im \rightleftharpoons [FeL^1(NCMe)(2Me\text{-}im)]^{2+} + 2Me\text{-}im \quad (8)$$

observed imidazole resonances of a solution containing the complex and a known excess of the exchanging ligand. The resonances of the imidazole-ring protons were used for reactions (6) and (8); the imidazole methyl resonances were also used for reaction (7). This gave a three-site exchange for reaction (8), combined two- and

three-site exchanges occurring with a common rate constant for (6), and four sets of two-site exchanges occurring with a common rate constant for (7). Because of the gradual accumulation of paramagnetic products of decomposition caused by the high temperatures necessary to effect exchange, systematic corrections (based on the temperature and time of exposure) to the values of chemical shifts and linewidths characteristic of the non-exchanging systems had to be made for the imidazole and 1-methylimidazole systems. Such corrections were unnecessary in the 2-methylimidazole system where much lower temperatures were used.

given by the inverse of the lifetime of the exchanging ligand in the complex is equal to k_1, the rate constant for dissociative loss of X from $[FeL^1(L)X]^{2+}$.

$$[FeL^1(L)X]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [FeL^1(L)]^{2+} + X \qquad (9)$$

$$[FeL^1(L)]^{2+} + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [FeL^1(L)S]^{2+}$$

From the data given in Table 2 for reactions (6) and (7), rate constants for these reactions at 0 °C can be calculated. For $[FeL^1(imH)_2]^{2+}$ our data predict $k_1 = (7.5 \pm 1.4) \times 10^{-3}$ s^{-1}; using conventional visible

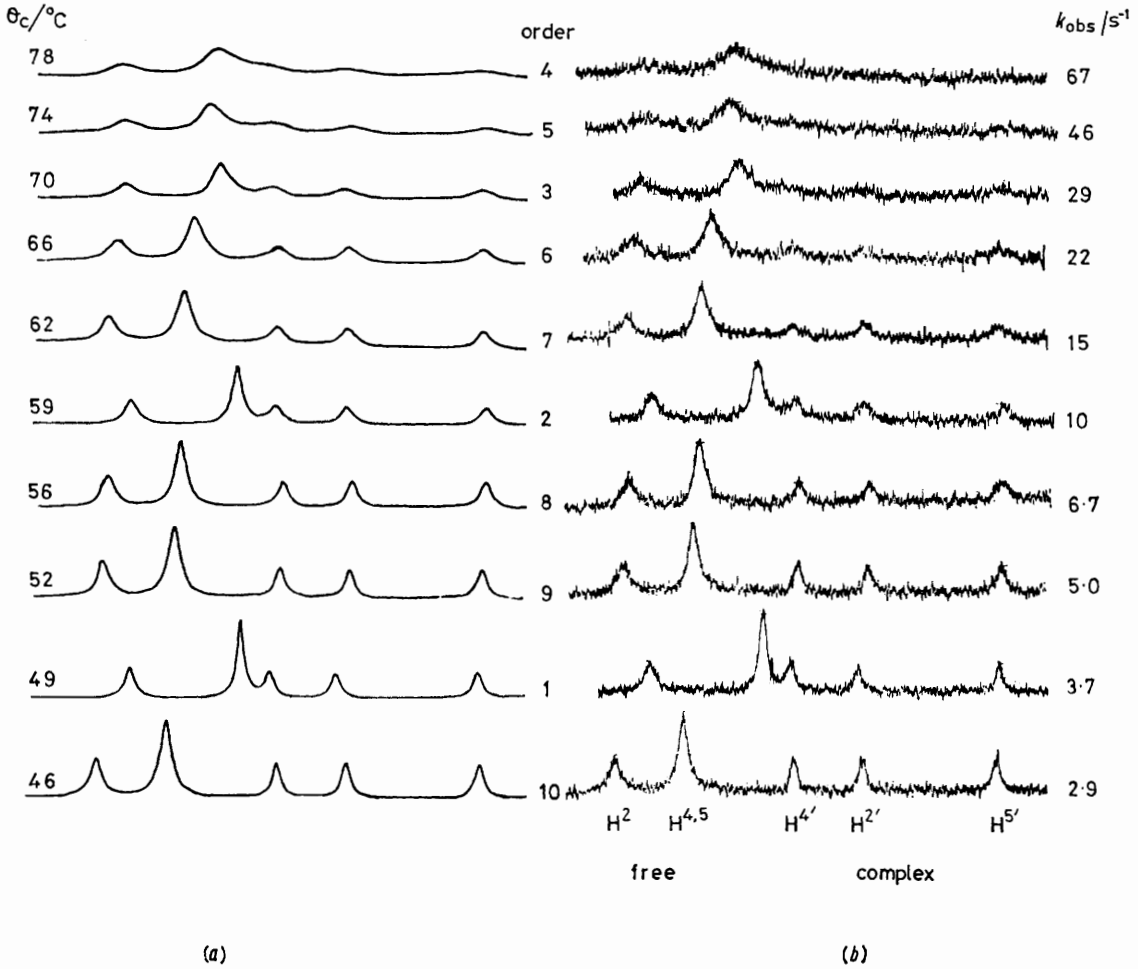


FIGURE 1 Calculated (*a*) and experimental n.m.r. spectra (*b*) obtained for exchange of $[FeL^1(imH)_2]^{2+}$ with free imidazole. Total imidazole concentration = 0.1 mol dm^{-3}, ratio of free : complexed = 1.5 : 1

The observed and calculated spectra and rate constants are shown in Figures 1, 2, and 3 for reactions (6), (7), and (8) respectively. The derived activation parameters and the percentage errors in $k_{obs.}$ (given by a least-squares fit to the Eyring equation) are given in Table 2.

Much evidence has been gathered for the assignment of an S_N1(lim) mechanism to the substitution reactions of iron(II) complexes of macrocyclic ligands.[1-7] Interpreting our data in terms of such a mechanism we obtain the reaction sequence (9). Since the system is at equilibrium it can be shown that the rate constant $k_{obs.}$

spectroscopy at 0 °C to follow the reaction of $[FeL^1(imH)_2]^{2+}$ with $PhCH_2NC$, a value of $k_{obs.}$ (presumed equal to k_1) of 1.25×10^{-2} s^{-1} is found.[10] Considering the long extrapolation (46 °C) and two orders of magnitude in $k_{obs.}$ involved in applying our data there is fairly good agreement between the two values. Since the n.m.r. study was carried out at 10^{-2} mol dm^{-3} complex while the visible-spectroscopic studies were made at *ca.* 10^{-4} mol dm^{-3}, ionic-strength differences could also account for the discrepancy. For $[FeL^1(1Me\text{-}im)_2]^{2+}$ the agreement is not as good; our data predict $k_1 = (2.6 \pm$

0.6) $\times$ 10^{-2} s^{-1} and the value measured by Singh and Stynes [10] is 7.3 $\times$ 10^{-3} s^{-1}. If the latter value is included in our Eyring plot, $\Delta H^{\ddagger}$ for reaction (7) becomes 21.0 $\pm$ 0.8 kcal mol^{-1},* $\Delta S^{\ddagger} = 9 \pm 3$ cal K^{-1} mol^{-1}, and the uncertainty in $k_{obs.}$ is 32%, with the n.m.r. results deviating systematically from the new least-squares line. Again there is a long extrapolation involved in our calculations, and ionic-strength differences between the two experiments, but in addition the lineshape analysis is more complicated and decomposition to paramagnetic

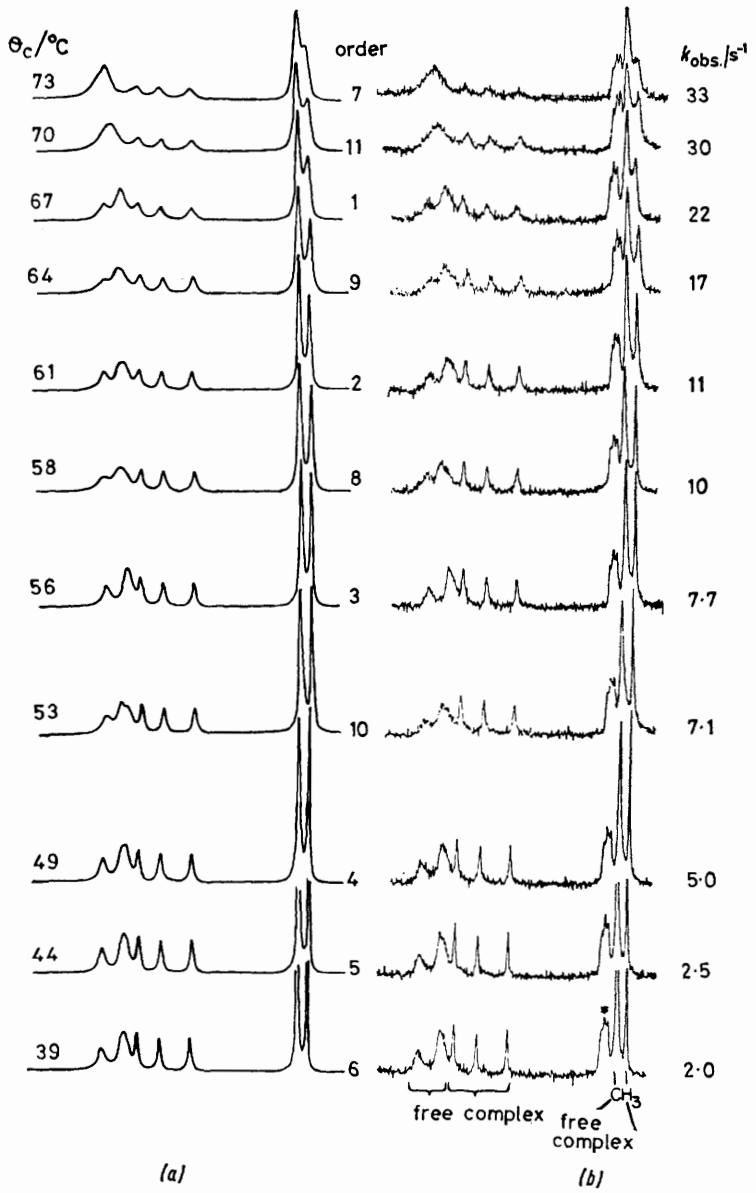


FIGURE 2 Calculated (*a*) and experimental n.m.r. spectra (*b*) obtained for exchange of $[FeL^1(1Me\text{-}im)_2]^{2+}$ with 1-methylimidazole. Total 1-methylimidazole concentration = 0.2 mol dm^{-3}, ratio of free : complexed = 1.7 : 1. The asterisk indicates α-CH_2 of L^1

TABLE 2

Imidazole exchange in iron(II) L^1 complexes

Complex	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	Percentage error in $k_{obs.}$
$[FeL^1(imH)_2]^{2+}$	21.5 $\pm$ 0.5	11 $\pm$ 2	8
$FeL^1(1Me\text{-}im)_2]^{2+}$	17.9 $\pm$ 0.7	0 $\pm$ 2	11
$[FeL^1(NCMe)(2Me\text{-}im)]^{2+}$	17.1 $\pm$ 1.1	11 $\pm$ 4	21

* Throughout this paper: 1 cal = 4.184 J.

TABLE 3

Determination of the equilibrium constant for formation of $[FeL^1(NCMe)(2Me\text{-}im)]^{2+}$

$[FeL^1(L)S^{2+}] : [FeL^1S_2^{2+}]$	$[L_{free}]$/mol dm^{-3}
0.55	0.035
0.63	0.082
1.36	0.17
1.53	0.19
2.30	0.33
3.08	0.41

L = 2Me-im, S = MeCN; an unweighted least-squares analysis gives $K_1 = 7.5 \pm 0.3$ dm^3 mol^{-1}.

products more marked for $[FeL^1(1Me\text{-}im)_2]^{2+}$ than the other complexes. Thus, the agreement between the results from n.m.r. and visible spectroscopy is probably as good as can be expected in this case; however, the n.m.r. activation parameters for $[FeL^1(1Me\text{-}im)_2]^{2+}$ should perhaps be regarded with some caution.

The relative reactivity of the three complexes is a function of the inherent lability of the leaving group, determined by iron–imidazole electronic interactions, above) may reflect differing solvation requirements of the two complexes. In $[FeL^1(imH)_2]^{2+}$ the leaving group contains an unco-ordinated secondary amine whose proton can hydrogen-bond to the solvent. The acidity of the proton will be greater in $[FeL^1(imH)_2]^{2+}$ than in the dissociative transition state, and it therefore participates less in hydrogen bonding as it proceeds along the reaction co-ordinate. This gives a positive $\Delta S^{\ddagger}$ and an unfavourable contribution to $\Delta H^{\ddagger}$. Such hydrogen

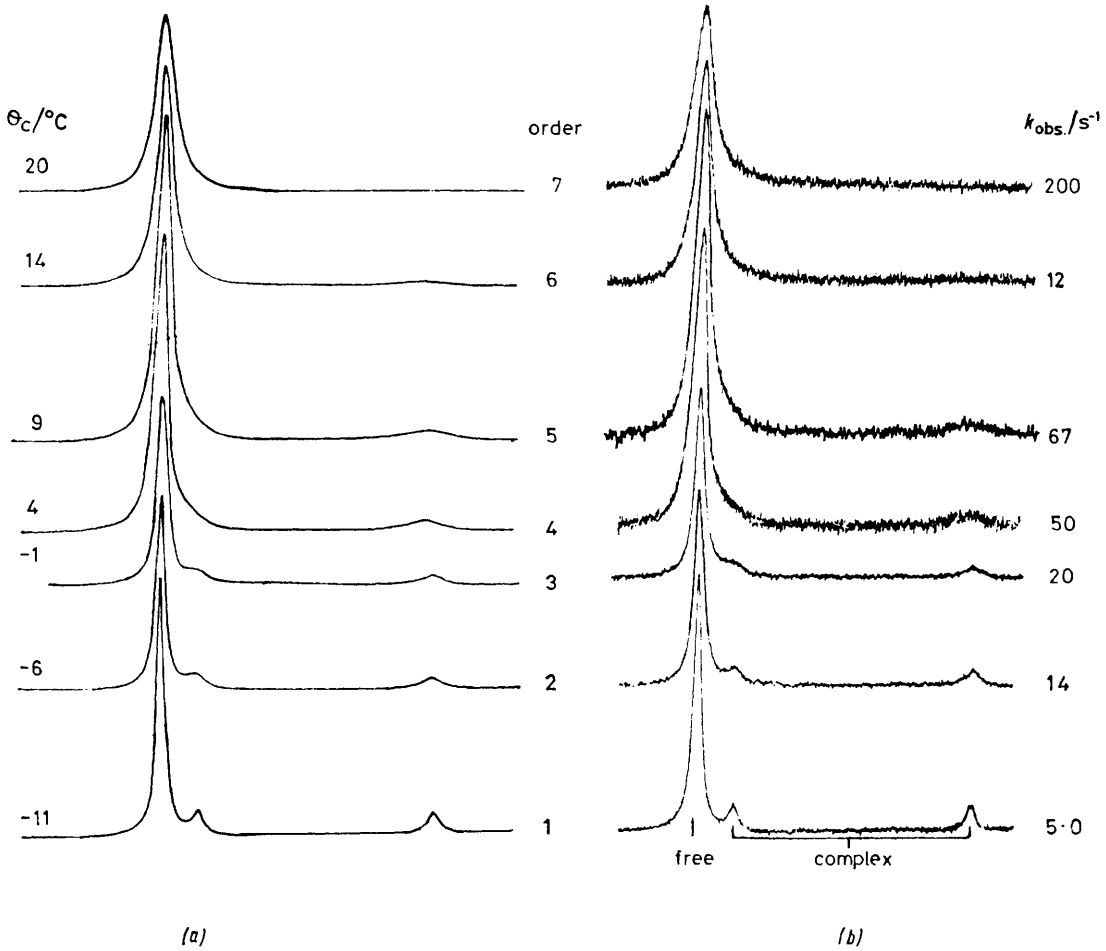


FIGURE 3 Calculated (*a*) and experimental n.m.r. spectra (*b*) obtained for exchange of $[FeL^1(NCMe)(2Me\text{-}im)]^{2+}$ with free 2-methylimidazole. Total 2-methylimidazole concentration = 0.09 mol dm^{-3}, ratio of free : complexed = 5.0 : 1

steric effects, and solvation requirements, and of the *trans* effect of the other axial ligand. Considering relative rate constants and noting that in other iron(II) macrocyclic systems [5-7] methyl substitution of the *trans* amine ligand only changes its *trans* effect by a very small amount, we conclude that, in the iron(II) L^1 complexes, imidazole and 1-methylimidazole have the same inherent lability. The steric requirements of the two ligands are very similar, and provided that affinities for the proton parallel those for the FeL^1 moiety their electronic interactions with Fe^{II} are also comparable (pK_a 6.95 for imidazole, 7.33 for 1-methylimidazole [14]). However, the difference in the activation parameters of $[FeL^1(imH)_2]^{2+}$ and $[FeL^1(1Me\text{-}im)_2]^{2+}$, if genuine (see bonding cannot occur in $[FeL^1(1Me\text{-}im)_2]^{2+}$ and consequently $\Delta S^{\ddagger}$ is more negative and $\Delta H^{\ddagger}$ is lower for this complex.

Unfortunately, there is no definite evidence available, even in other iron(II) macrocyclic systems, about the *trans* effect of MeCN. However, the relatively weak bonding which can be inferred [8] from the fast rate of MeCN exchange in $[FeL^1(NCMe)_2]^{2+}$ makes it unlikely that the *trans* effect is large (at least when the leaving group is a predominantly σ donor like 2-methylimidazole). We therefore assign most of the reactivity of $[FeL^1(NCMe)(2Me\text{-}im)]^{2+}$ to a high inherent lability of 2-methylimidazole. The basicity of 2-methylimidazole (pK_a 7.86) [14] and presumably its electronic interaction

with FeL^1 are similar to those of the other imidazoles. Since co-ordinated 2-methylimidazole can hydrogen-bond to the solvent, solvation of $[FeL^1(NCMe)(2Me\text{-}im)]^{2+}$ is similar to that of $[FeL^1(imH)_2]^{2+}$. This is reflected in the similar values of $\Delta S^{\ddagger}$ for the two complexes. Most of the difference in reactivity of the complexes can be ascribed to the lower value of $\Delta H^{\ddagger}$ for $[FeL^1(NCMe)(2Me\text{-}im)]^{2+}$, which is due to steric hindrance between the methyl group α to the imidazole binding site and the methylene protons of the macrocyclic ligand. Such steric hindrance has already been invoked to explain the low equilibrium constant for reaction (1). Relief of steric strain by removal of the interfering 2-methylimidazole group from the region of the macrocycle assists in the reaction process. The high lability of co-ordinated 2-methylimidazole in $[Fe(pc)(2Me\text{-}im)_2]$ has been explained by similar steric interactions. Because steric hindrance can be reduced in $[FeL^1(NCMe)(2Me\text{-}im)]^{2+}$, but not in $[Fe(pc)(2Me\text{-}im)_2]$, by movement of the iron atom out of the plane of the macrocycle, we would expect the relative lability of 2-methylimidazole to be less in $[FeL^1(NCMe)(2Me\text{-}im)]^{2+}$ than in the bis complex. In practice $[FeL^1(NCMe)(2Me\text{-}im)]^{2+}$ is only *ca.* 10^3 times more labile than the unhindered $[FeL^1(1Me\text{-}im)_2]^{2+}$, whereas $[Fe(pc)(2Me\text{-}im)_2]$ is *ca.* 2×10^4 times more labile than $[Fe(pc)(1Me\text{-}im)_2]$.[5] If the overall steric requirements of the two macrocycles are similar, one associates a change of *ca.* 1.5 kcal mol^{-1} in $\Delta G^{\ddagger}$ with stabilisation of $[FeL^1(NCMe)(2Me\text{-}im)]^{2+}$ due to an out-of-plane displacement of the iron.

Table 4 gives values of the rate constants at 25 °C

TABLE 4

Rate constants at 25 °C for loss of 1Me-im from $[FeL(1Me\text{-}im)_2]$

	L				
	tpp [a]	L^1 [b]	L^2 [c]	$(Hdmg)_2$ [d]	pc [e]
$10^2k/s^{-1}$	330	45	0.69	0.16	0.13
	2.8×10^4			0.39	
	2.4×10^6			0.96	

[a] Calculated from data at −79 °C (ref. 1) assuming $\Delta H^{\ddagger}$ = 10, 20, and 30 kcal mol^{-1}, in CH_2Cl_2 solution. [b] This work, in CD_3CN solution. [c] Ref. 3, in MeCN solution. [d] Calculated from data at 10 °C (ref. 4) assuming $\Delta H^{\ddagger}$ = 10, 20, and 30 kcal mol^{-1}, in $CHCl_3$ solution. [e] At 23 °C (ref. 7), in toluene solution.

for the loss of 1-methylimidazole from $[FeL(1Me\text{-}im)_2]^{n+}$ (L = a macrocyclic ligand). Using these rate constants an order of decreasing *cis* effect of tpp $\gg L^1 > L^2 \sim (Hdmg)_2 \sim$ pc is obtained. Some caution must be exercised in comparing these values since the solvents used for the different studies ranged from acetonitrile to toluene, but it is clear that the charge on the complex is not dominant in determining reactivity.

The lability of 1-methylimidazole in the tpp, pc, and $(Hdmg)_2$ systems has been discussed previously.[4,5,7] The large ring size of tpp (*ca.* 2 Å) [15] gives a weak ligand field which puts its iron(II) complexes close to the spin-crossover point. The high lability of the axial ligands can then be interpreted in terms of a spin change occurring during the dissociation of the axial ligand.[5,7] The smaller ring sizes of pc [7,16] and $(Hdmg)_2$ [17] give stronger in-plane ligand fields, which result in weaker axial binding, but also preclude formation of high-spin transition states. The latter effect is most important, and the pc and $(Hdmg)_2$ complexes react much more slowly than the tpp complex. Like tpp, the undistorted L^2 has a hole size which is larger than the radius of low spin Fe^{2+} ion,[18] but unlike the heavily conjugated tpp the two imine functions in L^2 are isolated and the L^2 ring can pucker [3,18] to accommodate the Fe^{2+} ion. Ring puckering in the ground state gives an orientation of nitrogen lone pairs which is not ideally suited for overlap with metal *d* orbitals, and the strength of axial ligand binding is thus enhanced. In addition the ground-state distortion of L^2 does not lie along the reaction co-ordinate for formation of a high-spin five-co-ordinate transition state, where by analogy to high-spin iron porphyrins [19,20] the iron atom lies 0.5—0.8 Å above the plane of the macrocycle. Axial substitutions are therefore slow in L^2 complexes. The 14-membered L^1 ligand has a smaller hole size [21] than the 16-membered L^2 and the pairwise conjugation of the imine groups in L^1 keeps the ligand relatively flat.[21] Both these effects result in better overlap of the nitrogen lone pairs of L^1 with Fe^{2+} orbitals, giving stronger in-plane and weaker axial binding. Stronger in-plane binding also stabilises the dissociative transition state. As a result of both effects, $[FeL^1(1Me\text{-}im)_2]^{2+}$ loses 1-methylimidazole 60 times more rapidly than does $[FeL^2(1Me\text{-}im)_2]^{2+}$.

EXPERIMENTAL

The complexes $[FeL^1(NCMe)_2][PF_6]_2$ and $[FeL^1(1Me\text{-}im)_2][PF_6]_2$ were prepared by the method of Baldwin *et al.*[8]

N.M.R. Spectra.—Spectra of CD_3CN solutions were recorded on a Varian HA-100 spectrometer using internal $SiMe_4$ as the reference lock signal, or on a Varian CFT-20 spectrometer using the solvent ^1H resonance at 1.96 p.p.m. as the reference signal. Peak areas were measured by planimetry or integration. Because the complexes slowly decompose to paramagnetic species in the presence of excess of imidazole, samples were prepared and run as quickly as possible. For the kinetic measurements both spectrometers were equipped with Varian V-4341/V-6057 variable-temperature accessories. Temperatures above ambient were measured using the difference in chemical shifts of the ethylene glycol ^1H resonances.[22] Below room temperature the difference in chemical shifts of the methanol doublet and quartet were used.[22]

Kinetics.—Lineshape analysis was performed on a Hewlett-Packard 2100 minicomputer using a Fortran program based on the approach of Johnson and Moreland.[23,*]

* The equations quoted by these workers were first modified so that their equation (5) read $I(\nu) = -\mathrm{Im}\{i\omega_r M_0(P.A.^{-1}1)\}$ in the general case and

$$I(\nu) = -\omega_r M_0 \mathrm{Re}\left\{(P_A,P_B)\begin{pmatrix} -[\alpha_A + (1/\tau_A)] & 1/\tau_A \\ 1/\tau_B & -[\alpha_B + (1/\tau_B)] \end{pmatrix}^{-1}\begin{pmatrix} 1 \\ 1 \end{pmatrix}\right\}$$

for the specific case of two-site exchange. In addition, their definition of α_n (n = A, B, *etc.*) was modified to read $\alpha_n = i2\pi(\nu - \nu_n) + T_{2(n)}^{-1}$.

The program was used to give values of τ, the lifetime of the complexed imidazoles; values of $k_{obs.}$, the rate constants for reactions (6)—(8), were given by the reciprocal of τ. Activation parameters were obtained from an unweighted least-squares analysis of the dependence of $\log(k_{obs.}/T)$ on $1/T$. Such an analysis assumes a constant percentage error in $k_{obs.}$.

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