Steric Effects in the Reactions of Zinc(II) and Iron(III) 'Capped' Porphyrins

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Equilibrium constants were measured for the reactions of a capped zinc porphyrin with 1-methylimidazole (mim) and of metal imidazolate complexes of Cu^{II} and Ni^{II} and for zinc 5,10,15,20-tetra(*o*-methoxyphenyl)porphyrinole with mim in toluene at 20, 25, 30, and 35 °C. Enthalpy and entropy values obtained from a least-squares fit of a plot of $\ln K$ *vs.* $1/T$ indicate that the effect of the capping benzene on the thermodynamics of the axial ligation reaction is entropic rather than enthalpic. Monoadducts of iron(III) porphyrins can be prepared using the sterically hindered 'capped' porphyrin. The axial adduct with the copper(II) imidazolate complex has the same binuclear core, $Fe^{III}Cu^{II}$, as the resting form of the mammalian enzyme cytochrome c oxidase.

Metalloporphyrins have been used in studies of Lewis acid–base interactions, axial ligation, electrochemistry of the metal and the porphyrin ligand, and reversible oxygen binding. Their widespread use stems from the stability of the porphyrin chelate and their obvious relevance as models of the active site structures of several enzyme systems in which a metalloporphyrin core plays a key role in substrate binding and/or electron transfer. Crucial to their use as active site models is the ability to control reactions which occur at the central metal ion or on ligands co-ordinated to the central metal ion. Numerous studies have shown that the axial ligation of metalloporphyrins is subject to solvent, electronic, thermodynamic, and steric control. This last effect may be the most important for controlling the outcome of reactions of metalloporphyrins and is the subject of this investigation as a means of regulating the number of axial ligands which can bind to a metalloporphyrin. Control of the stoicheiometry of axial ligation is essential for the modelling of enzymes thought to contain a five-co-ordinate iron porphyrin since, in the presence of axial bases, bis adducts of iron(II) and iron(III) porphyrins are generally favoured over monoadducts. The pursuit of sterically hindered porphyrins for the problem of modelling the reversible oxygen binding by haemoglobin has resulted in some of the most elegant work in biological modelling studies and has provided a starting point for a study of this sort. Thus iron(II) complexes of 'picket-fence',[1] 'strapped',[2] and 'capped'[3] porphyrins contain a group which prevents the approach of a second porphyrin molecule within the distance required for oxidation and dimerization while allowing the binding of oxygen within the cavity formed by the blocking group. In particular the metal complexes of the capped porphyrin H_2cap† can bind larger bases, such as imidazole, to the central metal on the unprotected side of the porphyrin only.

The purpose of the present work is to explore the thermodynamic effect of capping benzene on axial ligation reactions of H_2cap metal complexes and to determine the effect of this blocking group on the stoicheiometry of the reaction of the iron(III) complex with imidazole donors. In general the reaction of unhindered iron(III) porphyrins with nitrogenous bases produces bis adducts because the six-co-ordinate product is stabilized by the change from high spin to low spin.[4] Several iron(II) 'capped' porphyrins, however, have been shown to form a monoadduct with unhindered ligands, such as mim, by preventing approach of an axial ligand on one face.[5] Prior to this report, this strategy has not been exploited for controlling the stoicheiometry of adducts of iron(III) porphyrins. In this work, the reaction of $[Fe(cap)]^+$ with an imidazole donor is shown to give the monoadduct, $[Fe(cap)L]^+$. Synthesis of models of cytochrome c oxidase (cco), which, in its resting state, is thought to contain a five-co-ordinate porphyrin iron(III) coupled through a bridging ligand (*e.g.* thiolate or imidazolate) to a copper(II) centre,[6] is likewise possible using $[Fe(cap)]^+$ and a suitable copper chelate, [CuL′]. Preliminary results of this project are reported here. Although the steric effect on stoicheiometry is easily rationalized, sufficient data are not available to understand the influence of the capping benzene on the energy changes occurring during axial ligation which will affect the position of equilibrium for adduct formation. The effects of the 'cap' on the thermodynamics of axial ligation were studied using zinc(II) as the central metal ion instead of iron(III) for the following reasons: (1) zinc porphyrins are electronically and spectrally simpler than their iron counterparts, (2) the reaction may be studied without the complication of a spin-state change, which is probable in the case of iron(III) (admixed $S = \frac{3}{2}, \frac{5}{2}$ for complexes of weak-field anions to $S = \frac{5}{2}$ for nitrogen donors), and (3) the effect of the blocking group on stoicheiometry may be ignored because monoligation occurs even with the unhindered [Zn(tpp)], allowing a direct comparison between the hindered and unhindered cases.

This work determines the thermodynamic effect of the capping benzene on axial ligation reactions, illustrates a generally applicable approach to stoicheiometric control of the axial ligation reactions of iron(III) porphyrins, and provides a route to an imidazolate-bridged iron–copper binuclear complex as a model for cco.

Experimental

Toluene and tetrahydrofuran (thf) were distilled from sodium metal and benzophenone before use. Dimethyl sulphoxide (dmso) was used as received. 1-Methylimidazole was vacuum distilled from CaH_2 and stored over molecular sieves prior to use.

Metal Imidazolate Complexes.—The copper(II) and nickel(II) imidazolate complexes, [ML′], were prepared by the literature method and recrystallized from ethanol before use.[7]

Porphyrins and Metalloporphyrins.—The porphyrins H_2tpp, H_2tomp,[8] and H_2tpmp and their zinc complexes were

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† The abbreviations used are as follows: tpp is the dianion of 5,10,15,20-tetraphenylporphyrin, tomp and tpmp are corresponding *ortho*- and *para*-methoxy-substituted tetraphenylporphyrins, H_2cap is the capped porphyrin shown in Figure 2, mim is 1-methylimidazole, and [ML′] is the copper or nickel imidazolate complex shown in Figure 2.

Table. Thermodynamic values for reaction of zinc porphyrins with axial bases in toluene: ΔH/kJ mol^{-1}, ΔS/J K^{-1} mol^{-1}, K_{298} dm^3 mol^{-1}.

	Base		
Porphyrin	mim	[CuL′]	[NiL′]
[Zn(tpp)][a]	−42.9	−41.9	−43.3
	−53.1	−41.0	−49.0
	5.41×10^4	1.52×10^5	1.10×10^5
[Zn(tomp)][b]	−41.2	—	—
	−63.4	—	—
	8.28×10^3	—	—
[Zn(cap)][b]	−42.3	−42.7	−40.8
	−75.8	−65.3	−61.8
	2.85×10^3	1.18×10^4	8.39×10^3
[Zn(tpmp)][b]	−52.0	—	—
	−85.6	—	—
	4.48×10^4	—	—

[a] Ref. 13. [b] This work.

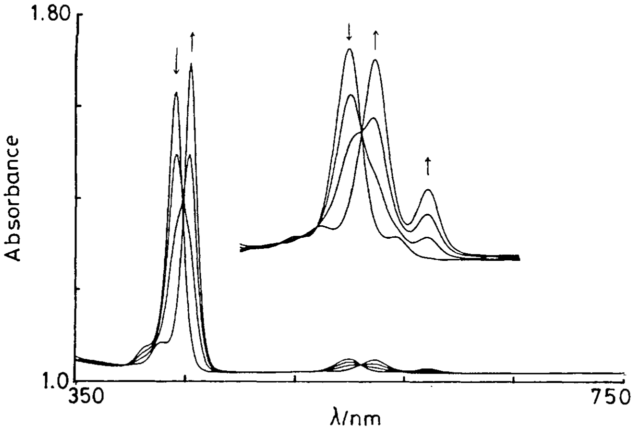

Figure 1. Spectral changes on reaction of [Zn(cap)] with 1-methylimidazole in toluene. $\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1}): [Zn(cap)], 423, (417 000), 548 (20 800), and 582 (2 480); [Zn(cap)(mim)], 434 (458 000), 567 (18 700), and 605 (6 450)

synthesized by the method of Adler *et al.*[9] The complexes [Zn(tpp)] and [Zn(tpmp)] were chromatographed on dry alumina in $CHCl_3$, stripped of solvent, dried at 120 °C, and stored at 0 °C. Chromatography alone was not sufficient for purification of [Zn(tomp)] as it contains significant chlorin impurity. Photo-oxidation[10] of a benzene solution of [Zn(tomp)] with a fluorescent light for 36 h followed by chromatography as described above and recrystallization from a dichloromethane–heptane mixture resulted in chlorin-free material.

The porphyrin H_2cap and the corresponding complexes [Zn(cap)] and [Fe(cap)Cl] were prepared and purified by the method of Baldwin and co-workers.[11]

[Fe(cap)]ClO_4. The preparation and all subsequent manipulations of this porphyrin were carried out in a Vacuum Atmospheres dry-box. The general procedure for this metathesis reaction is that employed for the preparation of [Fe(tpp)]ClO_4.[12] Reaction of $AgClO_4$ (0.036 g, 0.17 mmol) and [Fe(cap)Cl] (0.195 g, 0.174 mmol) in thf (20 cm^3) resulted in the precipitation of the product and AgCl. The precipitates were filtered off and the product separated by recrystallization from toluene and heptane. Yield 0.164 g (79%). U.v.–visible maximum in thf are at 406, 514, 635, and 650 nm.

Spectra.—U.v.–visible spectra were recorded on a Perkin-Elmer Lamda 4 or a PE model 576 spectrophotometer with sample cell temperatures regulated by a PE temperature controller. Absorbance data for the reactions of the zinc porphyrins were obtained as follows. A fixed aliquot of the metalloporphyrin and variable amounts of base in toluene were mixed and diluted to 2.5 cm^3 giving a series of solutions with constant metalloporphyrin concentration and varying base concentrations. The absorbances of the solutions at 550 nm were monitored as a function of base concentration. Spectra of [Fe(cap)]ClO_4 and its adducts were obtained from solutions prepared in the dry-box and sealed in cuvettes with rubber septa.

Calculations.—Equilibrium constants were determined from the data by the methods of Rose and Drago and of Miller and Dorough as described previously.[13] Raw absorbance data were corrected for the weak absorbance of [ML′] with the aid of a calibration curve. Enthalpies and entropies of reaction were determined from a least-squares fit of the temperature dependence of ln *K*.

Results and Discussion

Effect of the 'Cap' on Reactions of [Zn(cap)].—Equilibrium constants at 25 °C for the reactions of [Zn(tpp)], [Zn(tomp)], [Zn(tpmp)], and [Zn(cap)] with mim in toluene and the enthalpy and entropy terms for the reactions are given in the Table. Addition of mim to a toluene solution of any of the above zinc porphyrins shows essentially the same spectral changes, which are illustrated in Figure 1 for the reaction of [Zn(cap)]. The reactivity of the zinc porphyrins toward axial ligation decreases in the order [Zn(tpp)] > [Zn(tomp)] > [Zn(cap)]. It is immediately apparent from the data that the presence of the capping benzene in [Zn(cap)] has no significant effect on the enthalpy of reaction. The complex [Zn(tpp)] can be classified as an acid with a small *C*/*E* ratio (*C* represents the covalent contribution and *E* the electrostatic contribution to the enthalpy of acid–base reactions in poorly solvating media),[14] indicating that its interaction with the donor is largely electrostatic which may be a result of the zinc ion lying out of the plane of the porphyrin and the absence of low-energy *d* orbitals to participate in covalent bonding. Comparison of the reaction enthalpies indicates that no significant electronic differences in the porphyrins result from replacement of *o*-H in tpp with alkoxy groups in complexes of tomp and cap.

The data show that the differences in reactivity of the zinc porphyrins clearly arise from entropy effects. Specifically, the entropy of reaction becomes progressively more negative as the porphyrin becomes more sterically encumbered. The capping benzene in [Zn(cap)] does not prevent axial ligation since one side of the porphyrin is open to attack by base, but it clearly diminishes the reactivity of the porphyrin and lowers the entropy of reaction. At least two effects must be considered in discussing the observed entropies, phenyl group rotation and 'doming.' The four phenyl groups in tpp are nearly perpendicular to the porphyrin ring in the solid but are free to rotate in solution. The substitution of a methoxy group for an *ortho*-hydrogen on each phenyl ring is expected to hinder phenyl rotation to some extent and provide some steric restriction to axial ligation. Attachment of the cap to the *ortho* positions as in [Zn(cap)] eliminates phenyl group rotation and places even greater restrictions on an incoming ligand. A natural consequence of such a hindered binding site would be a loss of rotational freedom about the Zn–N_{base} bond due to steric interference between the phenyl rings and the base, resulting in a more negative entropy of reaction. The second effect must be discussed in terms of the possible structures of the ligated and unligated zinc porphyrin. Crystallographic investigation of the free base H_2cap[15] reveals a structure which is domed towards the capping benzene. Crystal structures of M^{2+} complexes of

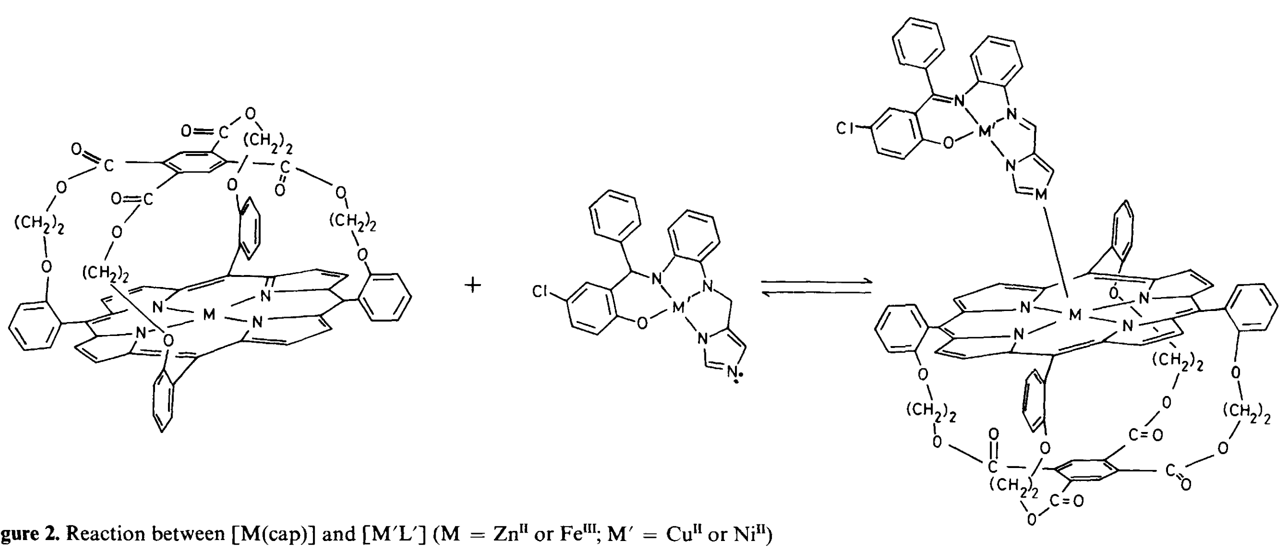

Figure 2. Reaction between [M(cap)] and [M′L′] (M = Zn^{II} or Fe^{III}; M′ = Cu^{II} or Ni^{II})

cap are not available at present. However, an n.m.r. investigation of [Zn(cap] and of the free base porphyrin by Williams and co-workers[16] indicates that doming may be important in the zinc complex in solution. Only small differences in chemical shifts and a close similarity in coupling constants were observed for the ^1H resonances of [Zn(cap)] and cap. These observations indicate that on metallation little conformational change in the cap occurs, implying that the same degree of doming that occurs in the free base porphyrin also occurs in its Zn^{2+} complex. For this to be so, the zinc ion must be bound on the same side of the porphyrin as the cap since the zinc ion is expected to lie *ca.* 0.3 Å out of the porphyrin plane. If the zinc ion were bound on the opposite side of the porphyrin plane, doming in the opposite direction would be expected which would have resulted in significant changes in chemical shifts and coupling constants. Furthermore, in the case of [Zn(cap)], the authors determined that dimethyl sulphoxide (dmso) was bound underneath the cap, implying that the zinc atom also lies underneath the cap. If the zinc ion extends out of the plane on the side of the cap this becomes a factor which must be taken into account when interpreting the entropy changes involved on binding an axial base. Not only would the doming tend to tilt the phenyl groups more directly in the line of approach of an incoming base, but in order for a base the size of mim to bind the zinc atom would have to 'squeeze' through the hole of the porphyrin to get to the less hindered side. Inversion of a metal ion through the porphyrin hole has been observed for high-spin iron(III) in [tetra(*p*-tolyl)porphyrinato]iron chloride by n.m.r. spectroscopy.[17] However this squeeze is accomplished, considerable distortion of the porphyrin core must accompany axial ligation and would certainly contribute unfavourably to the entropy change. {This would not be significant for [Fe(cap)Cl][18] for which the crystal structure reveals that the iron lies above the unhindered porphyrin face displaced toward its axial chloride.}

The complex [Zn(cap)] was treated with a copper(II) or nickel(II) imidazolate complex, [ML′] to give the imidazolate-bridged binuclear system as shown in Figure 2 to demonstrate that binuclear systems could be formed with capped porphyrins and to provide another point of comparison of the entropy terms for the axial ligation of [Zn(tpp)] and [Zn(cap)]. Thermodynamic values for these reactions are given in the Table. As reported previously, ΔH for the reaction of [ML′] with [Zn(tpp)] in toluene is approximately the same as for the reaction with mim.[13] As in the reaction of zinc porphyrins with mim, no significant change in the enthalpy term is observed when [Zn(cap)] is substituted for [Zn(tpp)]. Large negative effects can be seen in the entropy terms, however, on changing to the sterically hindered porphyrin and are consistent with previous results for mim.

That the effect of the *o*-OMe and the capping benzene in the axial ligation reactions of [Zn(tomp)] and [Zn(cap)] is largely steric as opposed to electronic is emphasized by a comparison of the formation constants for the reactions of [Zn(tpp)], [Zn(tomp)], and [Zn(tpmp)] with mim. In the *para* position the methoxy group has no significant steric effect on the rotation of the phenyl rings but exhibits a large electronic effect on the ligation of mim. Donation of electron density onto the porphyrin periphery by resonance is reflected in a lowering of the formation constant for [Zn(tpmp)(mim)] by 17% compared with [Zn(tpp)(mim)]. In contrast the formation constant of [Zn(tomp)(mim)] is lowered by 85% of the value for [Zn(tpp)]. If the value of the formation constant is lowered by the *ortho*-methoxy group through an electronic effect similar to that of the *para*-methoxy group, similar values of *K* would be expected for the reaction of [Zn(tomp)] and [Zn(tpmp)] with mim. The large difference between these values points to the greater importance of the steric effect in reactions of [Zn(tomp)] than of [Zn(tpmp)]. In fact it is reasonable to assume that the greater the non-coplanarity of the phenyl rings the lower the electron-releasing effect of the methoxy group will be since a conjugative effect requires a planar pathway.

Reactions of [Fe(cap)] *and* [Fe(cap)X].—Lowered formation constants of the five-co-ordinate monoadducts of both iron(II) and cobalt(II) complexes of cap with nitrogenous bases compared with similar values for 'flat' porphyrins have also been attributed to steric rather than electronic factors.[19] It is suggested that the presence of the *meso*-phenyl groups held rigidly in place in the metal 'capped' porphyrin may provide steric hindrance to the binding of an axial ligand and also restrict the movement of the metal out of the porphyrin plane toward the incoming base. The diminished reactivity of [Fe(cap)] is pronounced enough that its reaction with [ML′] results in no observation of five-co-ordinate product.

The axial ligation of iron(III) porphyrins is extremely sensitive to solvent, the presence of water, and the identity of the counter ion. No evidence of reaction is observed when [Fe(tpp)Cl] or [Fe(cap)]Cl is mixed with [CuL′] in toluene. This result is due to the diminished reactivity of [Fe(porphyrin)Cl] with axial bases in toluene and is attributed to strong association between the chloride ion and iron(III) in a non-co-ordinating solvent such as toluene. An increase in reactivity is expected on ionization of the counter ion through the use of a strongly co-ordinating solvent such as dmso or by the use of a weakly co-

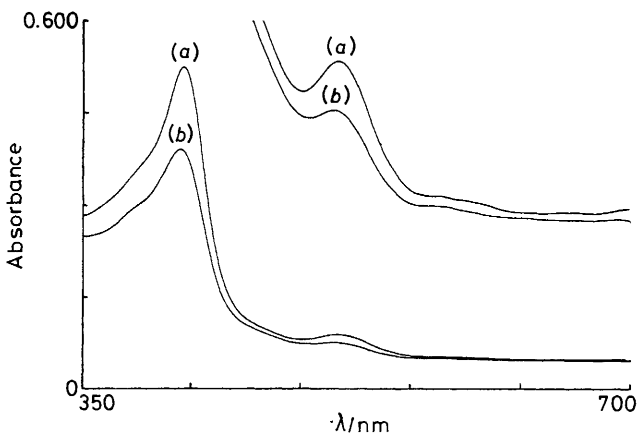

Figure 3. Spectrum of [CuL′–Fe(cap)]ClO$_4$. (*a*) $\lambda_{max.}$(toluene) 415 and 514 nm; (*b*) $\lambda_{max.}$(thf) 413 (ε 78 000) and 511 nm (8 500 dm^3 mol^{-1} cm^{-1})

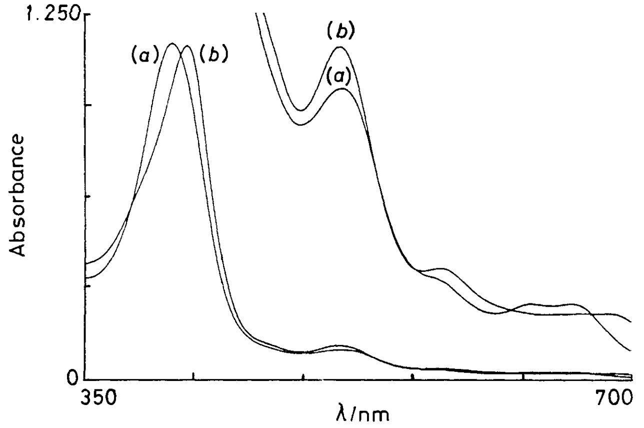

Figure 4. Spectra of (*a*) [Fe(cap)]ClO$_4$, $\lambda_{max.}$(thf) 404 (ε 79 000) and 516 nm (7 200 dm^3 mol^{-1} cm^{-1}) and (*b*) [Fe(cap)(dmim)]ClO$_4$ (dmim = 1,2-dimethylimidazole), $\lambda_{max.}$(thf) 416 (78 000) and 513 nm (7 800 dm^3 mol^{-1} cm^{-1})

ordinating counter ion such as perchlorate as described below for [Fe(cap)]$^+$. The use of dmso to enhance the reactivity of iron(III) porphyrin chlorides has serious disadvantages in that the presence of even small amounts of water is sufficient to form the hydroxy species under certain conditions as described below and the low volatility of dmso precludes the facile isolation of solids. In an earlier study, [Fe(tpp)Cl] was treated with [CuL′] in dmso to give the trinuclear system, [CuL′–Fe(tpp)–CuL′]Cl, as part of an effort to model the active site of cco.[20] Two shortcomings of this method for preparation of a cco model are that the stoicheiometry of the complex is 1:2 (FeCu$_2$) as opposed to the desired 1:1 and that it was not possible to isolate the product due to the low volatility of the solvent and the high solubility of the product in the solvent. It was thought that reaction of [Fe(cap)Cl] with [CuL′] in dmso would afford exclusively the monoadduct. However, the product of the reaction of [CuL′] or mim with [Fe(cap)Cl] was identified by visible bands at 577 and 619 nm as [Fe(cap)(OH)]. The reaction presumably occurs due to the presence of small amounts of water in the solvent [equation (1)]. That the desired compound

$$[\mathrm{Fe(cap)(H_2O)}]^+ + \mathrm{mim} \longrightarrow [\mathrm{Fe(cap)(OH)}] + \mathrm{Hmim}^+ \quad (1)$$

is not formed is a failure but it does point out the fact that the capping benzene does prevent bis adduct formation with amines of this size and that when this process is blocked the Bronsted–Lowry base characteristics of these species are manifested. Addition of small, flexible amines such as 1-aminopropane resulted in the reduction of the iron(III) porphyrin to [Fe(cap)(amine)$_2$] as determined by observation of bands at 532 and 562 nm which are in agreement with the values of Baldwin who prepared the compound by direct reaction of the [Fe(cap)] with amine in toluene. The achievement of six-co-ordinate complexes with 1-aminopropane is attributed to its unhindered nature and the ability of the capping benzene to twist enough to allow the amine to approach within bonding distance of the iron. The reduction of [Fe(cap)Cl] by primary aliphatic amines is expected in the light of the findings of Castro *et al.*[21] who report the reduction of [Fe(tpp)Cl] by several primary amines. This reduction has been found to proceed by initial formation of the bis(amine) adduct of Fe^{III}. Assuming the same mechanism is operative here, a bis-ligated iron(III) species is produced in this system despite the presence of a hindered face. Production of low-spin Fe^{III} on formation of the bisadduct and the accompanying crystal-field stabilization favours bis ligation whenever a sufficiently small amine is available for binding through the cap. This is then followed by reduction in the case of primary aliphatic amines. In the presence of an amine which is incapable of forming the bis adduct with the sterically hindered [Fe(cap)Cl], deprotonation of a water molecule (probably co-ordinated) and formation of the hydroxy complex is favoured.

The inability to produce a binuclear complex of [Fe(tpp)Cl] or [Fe(cap)Cl] with [CuL′] in toluene or dmso prompted investigation of the reactivity of the [Fe(cap)]ClO$_4$. Reaction of equimolar [CuL′] and [Fe(cap)]ClO$_4$ in dry toluene followed by addition of a small amount of heptane results in the precipitation of the monoadduct, [CuL′–Fe(cap)]ClO$_4$. Its spectra (Figure 3) in thf (413, 511 nm) and toluene (415, 514 nm) are very similar. The spectral changes observed on monoligation of [Fe(cap)]$^+$ by [CuL′] are nearly identical to those observed on reaction of 1,2-dimethylimidazole with [Fe(cap)]ClO$_4$ (see Figure 4) in thf and to those observed for the antiferromagnetically coupled [CuL′–Fe(cap)][B$_{11}$CH$_{12}$], which is produced in an analogous reaction of [Fe(cap)][B$_{11}$CH$_{12}$] with [CuL′].[22]

Acknowledgements

Acknowledgement is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Received 14*th March* 1989; *Paper* 9/01100E