long NITPHEN–NITPHEN interactions, which open interesting new possibilities to obtain magnetic materials. We are currently attempting to isolate other similar compounds.

Registry No. $CuCl_2(NIPHEN)_2$, 103816-75-7.

Supplementary Material Available: Tables of magnetic data and anisotropic thermal parameters for the non-hydrogen atoms for $CuCl_2(NITPHEN)_2$ (3 pages); tables of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

Molecular Environment Effects on the Reactivity of Porphyrins. Influence of Basket-Handle Superstructures on the Formation of Five-Coordinated Complexes of Iron(II) with Neutral Nitrogen Bases

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Abstract: The association constants of two nitrogen bases, 1,2-dimethylimidazole and 2-methylpyridine, giving rise to five-coordinated iron(II) complexes, have been determined in a series of six iron porphyrins, involving besides tetraphenylporphyrin and orthotetraanisylporphyrin, two ether-linked $(C12)_2$ basket-handle porphyrins, protected on one face and on both faces, respectively, and the corresponding two $(C12)_2$ secondary amide linked basket-handle porphyrins. Comparison between the unprotected and superstructured complexes shows that the presence of the chains has two effects. One derives from the steric hindrance to axial ligation in porphyrins that are protected on both faces. The other and more remarkable effect is the significant enhancement of the affinity of iron(II) toward the nitrogen base resulting from the presence of the secondary amide groups borne by the chains.

It has been shown recently that the grafting of protecting basket-handle carbon chains[2] onto the ortho position of the phenyl rings of tetraphenylporphyrin complexes produces remarkable microenvironment effects on the reactivity of the central metal complex,[3] in a manner reminiscent of the functions of the protein chains toward the reactivity of the prosthetic groups in metallo proteins. Of particular relevance to the following discussion is the observation that the presence of ether-linked and secondary amide-linked basket-handle superstructures strongly influences the reactivity of iron porphyrins in reactions that involve the creation of a negative charge on the porphyrin complex.[3a,c,e,f]

Three main effects were identified and estimated.[4] Steric protection by the chains of the negatively charged complexes from external solvation renders the reaction more difficult in the ether-linked series. Steric protection against solvation also exists in the amide-linked series. It is however largely overcompensated by a "local solvation" effect resulting from the interaction of the negative charge with the CONH dipoles which, on the overall, facilitates the reaction. These effects have been demonstrated to significantly influence the thermodynamics of several reactions: $(Fe^{I})^- + e^- \rightleftarrows Fe(\text{“0”})^{2-}$, $(S)Fe^{II} + e^- \rightleftarrows (Fe^{I})^- + S$, (where S is a coordinating solvent molecule), $(S)Fe^{II} + Cl^- \rightleftarrows Fe^{II}Cl^- + (S)$,[3a,f] $(S)Fe^{II} + OH^- \rightleftarrows Fe(OH)^- + (S)$,[3c] $Fe^{III}Cl + e^- \rightleftarrows Fe^{II}Cl^-$,[3f] $Fe^{III}R + e^- \rightleftarrows Fe^{II}R^-$, $Fe^{II}R^- + e^- \rightleftarrows Fe^{I}R^{2-}$ (where R is an alkyl group).[3e] In those of these reactions which involve the cleavage of an axial ligand or the exchange between two axial ligands, steric hindrance of ligation by the chains has also been shown to influence the thermodynamics of the reaction leading to ligand discrimination effects in the latter case.[3a,f] The kinetics of the $(S)Fe^{II} + Cl^- \rightleftarrows Fe^{II}Cl^- + S$ reaction has also been shown to be similarly influenced by the presence of the chains.[3f] This is also the case for the nucleophilic reactivity of the $(Fe^{I})^-$ and $Fe(\text{“0”})^{2-}$ complexes toward alkyl halides.[3e]

Another point of interest, along the same lines, is the question of the possible influence of basket-handle chains upon the coordination of iron(II) porphyrins by *neutral ligands*. There is, a priori, little doublt that the chains should influence these reactions by steric hindrance to axial coordination. The actually interesting question is whether dipolar interactions with the CONH groups contained in the amide-linked basket-handle chains are able to significantly influence not only the coordination of negatively charged ligands as already demonstrated but also the axial coordination of neutral ligands. Answering this question was the aim of the work described hereafter.[5] In this purpose, we investigated the coordination of iron(II) with 1,2-dimethylimidazole ($1,2\text{-}Me_2Im$) and 2-methylpyridine (2-MePy) in the series of

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[2] (a) Basket-handle protected porphyrins are a particular case in a vast series of superstructured porphyrins that have been synthesized during the past decade in the aim of mimicking particular functions of the surrounding protein chains in several metallo proteins. For leading references in this area, see ref 2b–i. (b) Collman, J. P. *Acc. Chem. Res.* **1977**, *10*, 265. (c) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139. (d) Smith, P. D.; James, B. R.; Dolphin, D. H. *Coord. Chem. Rev.* **1981**, *39*, 31. (e) Traylor, T. G. *Acc. Chem. Res.* **1981**, *14*, 102. (f) Bogatskii, A. V.; Zhilina, Z. I. *Russ. Chem. Rev.* **1982**, *51*, 592. (g) Collman, J. P.; Halpert, T. R.; Suslick, K. S. *Metal Ion Activation of Dioxygen*; Spiro, T. G., Ed.; Wiley: New York, 1980; pp 1–72. (h) Baldwin, J. E.; Perlmutter, P. *Top. Curr. Chem.* **1984**, *121*, 181. (i) Dolphin, D. H. *Struct. Bonding*, in preparation.

[3] (a) Lexa, D.; Momenteau, M.; Rentien, P.; Rytz, G.; Savéant, J. M.; Xu, F. *J. Am. Chem. Soc.* **1984**, *106*, 4755. (b) Lexa, D.; Maillard, P.; Momenteau, M.; Savéant, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 6321. (c) Lexa, D.; Momenteau, M.; Savéant, J. M.; Xu, F. *Inorg. Chem.* **1985**, *24*, 122. (d) Croisy, A.; Lexa, D.; Momenteau, M.; Savéant, J. M. *Organometallics* **1985**, *4*, 1574. (e) Lexa, D.; Savéant, J. M., Wang, D. L. *Organometallics* **1986**, *5*, 1428. (f) Gueutin, C.; Lexa, D.; Momenteau, M.; Savéant, J. M.; Xu, F. *Inorg. Chem.*, in press.

[4] (a) Effects of different nature were observed in an electrochemical investigation of superstructured porphyrins involving short straps containing only carbon atoms.[4b] The changes induced in the electrochemical properties there appear to result from the distortion of the porphyrin ring caused by the shortness of the straps. (b) Becker, J. Y.; Dolphin, D.; Paine, J. B.; Wijesehera, T. *J. Electroanal. Chem.* **1984**, *164*, 335.

[5] Indirect evidence that such an effect could exist has been obtained[3f] in the investigation of the $SFe^{II} + e^- \rightleftarrows (Fe^{I})^- + S$ reaction (where S is a coordinating solvent molecule) as a function of the nature of the solvent and of the porphyrin superstructure in the same ether-linked and amide-linked basket-handle series as investigated here.

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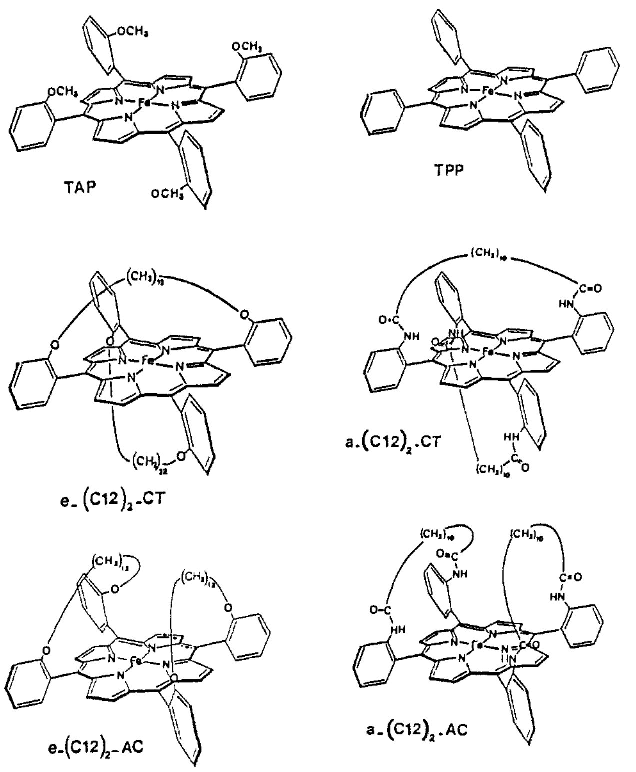

Figure 1. Tetraphenylporphyrin (TPP), tetraorthoanisylporphyrin (TAP), ether-linked (e-) and amide-linked (a-) basket-handle porphyrins investigated in this work. AC (adjacent-cis) and CT (cross-trans) describe the spatial arrangement of the chains.

porphyrins shown in Figure 1, which contains besides the two unprotected porphyrins, TAP and TPP, two ether-linked basket-handle porphyrins protected on one face (e-(C12)$_2$-AC) and on both faces (e-(C12)$_2$-CT), and the corresponding amide-linked basket-handle porphyrins (a-(C12)$_2$-AC, a-(C12)$_2$-CT). The choice of the solvent, 1,2-dichloroethane (DCE) was dictated by its noncoordinating character, thus avoiding the complication of a competitive axial coordination of iron(II) by the solvent and the nitrogen base. Sterically encumbered nitrogen bases were used in order to obtain five-coordinated complexes.[6a]

The equilibrium constants for the binding of one 1,2-Me$_2$Im molecule with iron(II) has been previously determined in toluene, for several simple and superstructured porphyrins, TPP,[6b] T(*p*-OCH$_3$)PP,[6c] picket fence,[6d] pocket,[6e] and capped porphyrins.[6c] A significant decrease in the association constant was observed when passing from simple porphyrins to the capped porphyrins in which the superstructure is bound to the phenyl rings of TPP by an ether linkage.[6c] This was attributed to steric restraints in the five-coordinated complex due to the attached cap.[6c]

Results

The complexation of the various iron(II) porphyrins with 1,2-Me$_2$Im and 2-MePy was investigated at 20 °C both by thin-layer spectroelectrochemistry and cyclic voltammetry starting from the Fe^{III}Cl complex and reducing it at an appropriate potential. The spectroelectrochemical method appeared simpler and more accurate than cyclic voltammetry for the following reasons. The equilibrium constant can be derived from the peak shift of the Fe(II)/Fe(I) cyclic voltammetric wave upon addition of the base. However, the wave is not completely reversible with all porphyrins in the series. This is the case when the association constant for the complexation of Fe(II) with Cl$^-$ is large (a-(C12)$_2$-AC and a-(C12)$_2$-CT).[3f] The starting wave is then split into two waves with the first having a kinetic character. This corresponds to the occurrence of a CE mechanism in which the reduction at the first wave corresponds to the reduction of the four-coordinated complex continuously regenerated from the decomposition of the chloro complex. In the case of the two ether-linked basket-handle compounds, the Fe(II)/Fe(I) wave exhibits a slight catalytic character.[3f] As discussed before this is likely to result from the reaction of the nucleophilic iron(I) complex with DCE as in the case of alkyl monohalides.[3e,f,7] The fact that this problem is encountered with the two ether-linked basket-handle porphyrins and not with the other four porphyrins derives from the same microenvironment effects as discussed in the introduction.[3d] In all cases it was however possible to use the cyclic voltammetry method along procedures that have been already described in the case of complexation of iron(II) by chloride ions.[3f] The results thus obtained were consistent with the spectroelectrochemical results.

Three procedures were used in thin layer spectroelectrochemistry according to the values of the association constant of chloride ions and that of the neutral base with iron(II). The simplest case is that of the two ether-linked basket-handle porphyrins where the association constant of the Cl$^-$ ions is small enough (200 and 45 for the AC and CT isomers, respectively[3f]) for the dissociation of the Fe^{II}Cl$^-$ complex to be practically complete in the concentration range employed (10^{-6}–10^{-5} M). A typical example of the titration procedure (*procedure A*) then used is shown in Figure 2 (e-(C12)$_2$-AC and 1,2-Me$_2$-Im). In the Soret region, we start from a two-band spectrum characteristic of a four-coordinated complex[8] and go, upon addition of the base, to a single Soret band (Figure 2a). To obtain the equilibrium constant, the data were treated by using the following equation, a simple extension of the usual spectrometric titration procedure for taking into account that the ligand may not be in excess over the porphyrin

$$\frac{1}{D-D_0}=\frac{1}{D_\infty-D_0}\left[1+\frac{1}{K_A^B\left([B]-[P]\dfrac{D-D_0}{D_\infty-D_0}\right)}\right]$$

where [B] and [P] are the concentrations of the ligand and the porphyrin, respectively, K_A^B the association constant, D the observed absorbance, D_0 the absorbance of the starting four-coordinated porphyrins, and D_∞ that of the complex ligated with one molecule of B. Once, $D_\infty - D_0$ has been determined from extrapolation at infinite [B], the determination of K_A^B is as shown on Figure 2b. This procedure was applied for the two ether-linked basket-handle porphyrins with both 1,2-Me$_2$Im and 2-MePy.

With the four other porphyrins the association constant of iron(II) with Cl$^-$ ions is too large for the concentration of the Fe(II)Cl$^-$ complex to be neglected in the porphyrin concentration range employed. Under these conditions, two procedures were used according to the relative magnitudes of the association constants with Cl$^-$ and the base. In the case of TPP and TAP with both bases and in that of a-(C12)$_2$-AC and a-(C12)$_2$-CT with 1,2-Me$_2$Im, it is possible to introduce Cl$^-$ ions in excess over the porphyrin and still obtain a significant conversion of the chloro complex into the base complex for reasonable values of the base concentration. The procedure then used (*procedure B*) simply consists in the application of the standard $1/(D - D_0)$ vs. $1/[B]$ plotting technique which leads to the ratio $K_A^B/K_A^{Cl^-}$ of the two association constants. Knowing $K_A^{Cl^-}$ from previous measurements[3f] then allows the determination of K_A^B. This procedure is illustrated in Figure 3 with the example of the complexation of (TPP)Fe^{II} by 2-MePy.

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(6) (a) TPP and T(*p*-OCH$_3$)PP iron(II) can be coordinated by two molecules of 1,2-Me$_2$Im, but the second association constant is much lower than the first.[6b] (b) Hashimoto, T.; Dyer, R. L.; Crossler, M. J.; Baldwin, J. E.; Basolo, F. *J. Am. Chem. Soc.* **1982**, *104*, 2101. (c) Ellis, P. E.; Linard, J. E.; Szymanski, T.; Jones, R. D.; Budge, J. R.; Basolo, F. *J. Am. Chem. Soc.* **1980**, *102*, 1889. (d) Collman, J. P.; Brauman, J. I.; Doxsee, K. M.; Halbert, T. R.; Suslick, K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 564. (e) Collman, J. P.; Brauman, J. I.; Collins, T. J.; Iverson, B.; Sessler, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 2450.

(7) Lexa, D.; Mispelter, J.; Savéant, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 6806.

(8) (a) Brault, D.; Rougee, M. *Biochemistry* **1974**, *13*, 4598. (b) Momenteau, M.; Loock, B. *J. Mol. Catal.* **1980**, *7*, 315. (c) Kadish, K. M.; Rhodes, R. K. *Inorg. Chem.* **1983**, *22*, 1090.

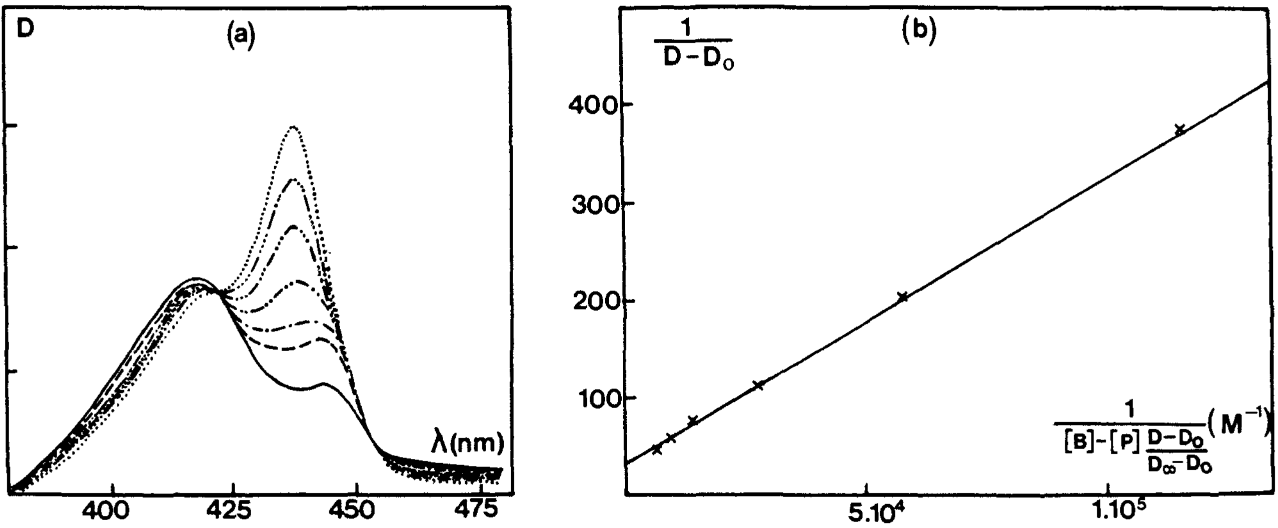

Figure 2. Determination of the association equilibrium constant of (e-$(C12)_2$-CT)Fe^{II} with 1,2-Me_2Im. Thin-layer spectroelectrochemistry of (e-$(C12)_2$-CT)$Fe^{III}Cl$ (3.6×10^{-6} M) in DCE + 0.1 M *n*-Bu_4NClO_4 at 20 °C. Electrolysis potential, −0.9 V vs. NaCl SCE: (a) Soret bands as a function of 1,2-Me_2Im concentration (M) 0 (—), 9.10^{-6} (- - -), 1.8×10^{-5} (-·····-), 3.6×10^{-5} (-····-), 7.1×10^{-5} (-··-), 1.1×10^{-4} (-·-), 1.4×10^{-4} (····) and (b) treatment of the data at λ = 438 nm according to procedure A (see text).

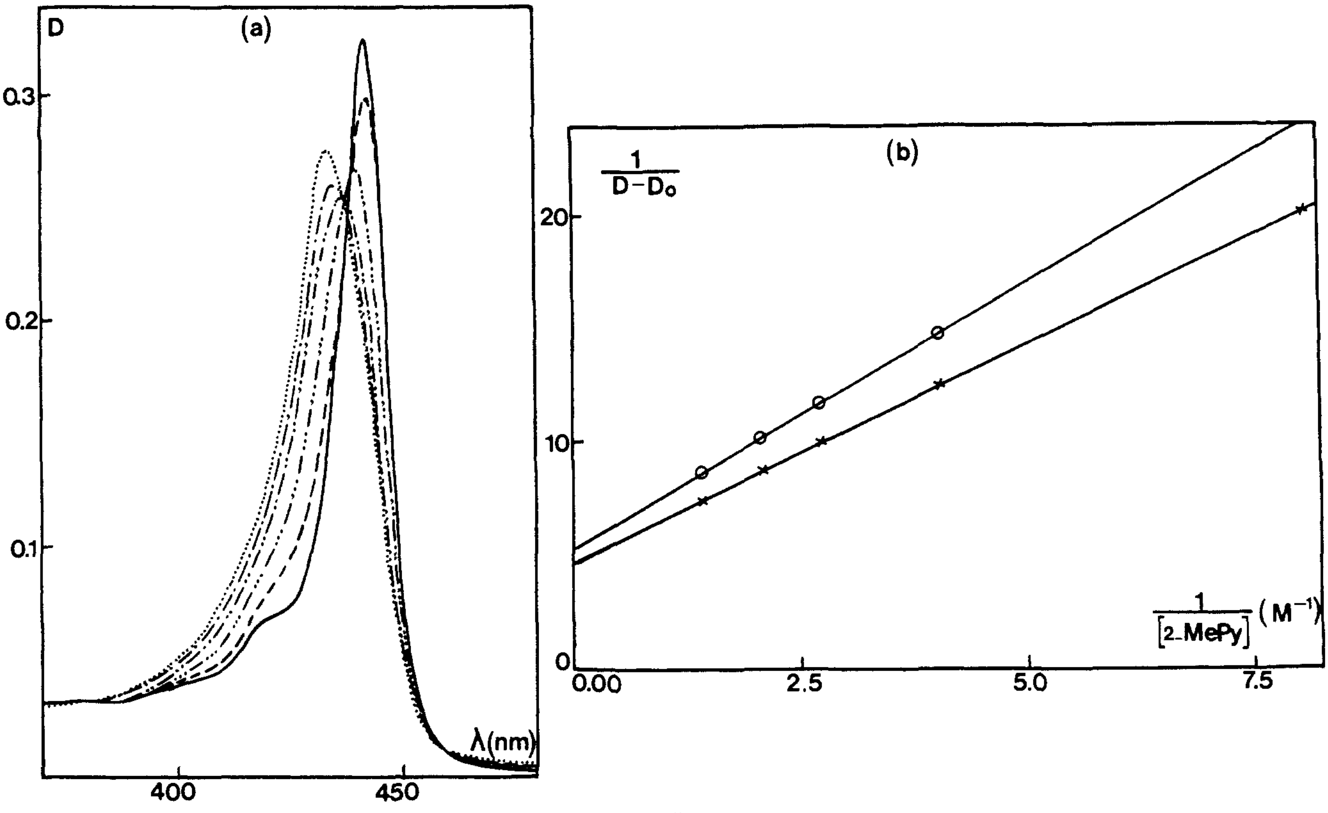

Figure 3. Determination of the association equilibrium constant of (TPP)Fe^{II} with 2-MePy. Thin-layer spectroelectrochemistry of (TPP) $Fe^{III}Cl$ (1.4×10^{-5} M) in DCE + 0.1 M *n*-Bu_4NClO_4 at 20 °C. Electrolysis potential, −0.9 V vs. NaCl SCE, Cl^- concentrated, 6.10^{-3} M: (a) UV–vis spectrum as a function 2-MePy concentration (M) 0 (—), 0.125 (- - -), 0.247 (-····-), 0.367 (-··-), 0.483 (-·-), 0.707 (····) and (b) treatment of the data at λ = 434 (×), 441 (○) nm according to procedure B (see text).

The association of 2-MePy with the two amide-linked basket-handle iron(II) porphyrins is too weak as compared to that of Cl^- ions for procedure B to be applied. No Cl^- ions were thus added to the solution over the stoichiometric amount contained in the starting $Fe^{III}Cl$ complex. The procedure we used (*procedure C*) was then as follows. Let α be the fraction of the starting $Fe^{II}Cl^-$ complex converted into the complex with the added base. α is given by

$$\alpha = \frac{(1+4K[P]/[B])^{1/2} - 1}{2K[P]/[B]} \qquad (1)$$

where $K = K_A^{Cl^-}/K_A^B$, is the ratio of the association constants with Cl^- and the base, respectively. On the other hand, $D - D_0 = (D_\infty - D_0)\alpha$ and thus $\log [D - D_0] = \log \alpha + \log [D_\infty - D_0]$. K (and thus K_A^B using the previously determined values of $K_A^{Cl^-}$[3f]) can then be obtained from the fitting of the experimental $\log [D - D_0]$ vs. $\log ([P]/[B])$ curves with the $\log \alpha$ vs. $\log (K[P]/[B])$ working curve obtained from the equation. An example of the treatment of the data along this procedure is given in Figure 4.

The association equilibrium constants obtained with the six porphyrins and the two bases are listed in Table I.

Discussion

The value of the association constant obtained here with TPP and 1,2-Me_2Im (4.1×10^4 M^{-1}) in DCE at 20 °C is very close

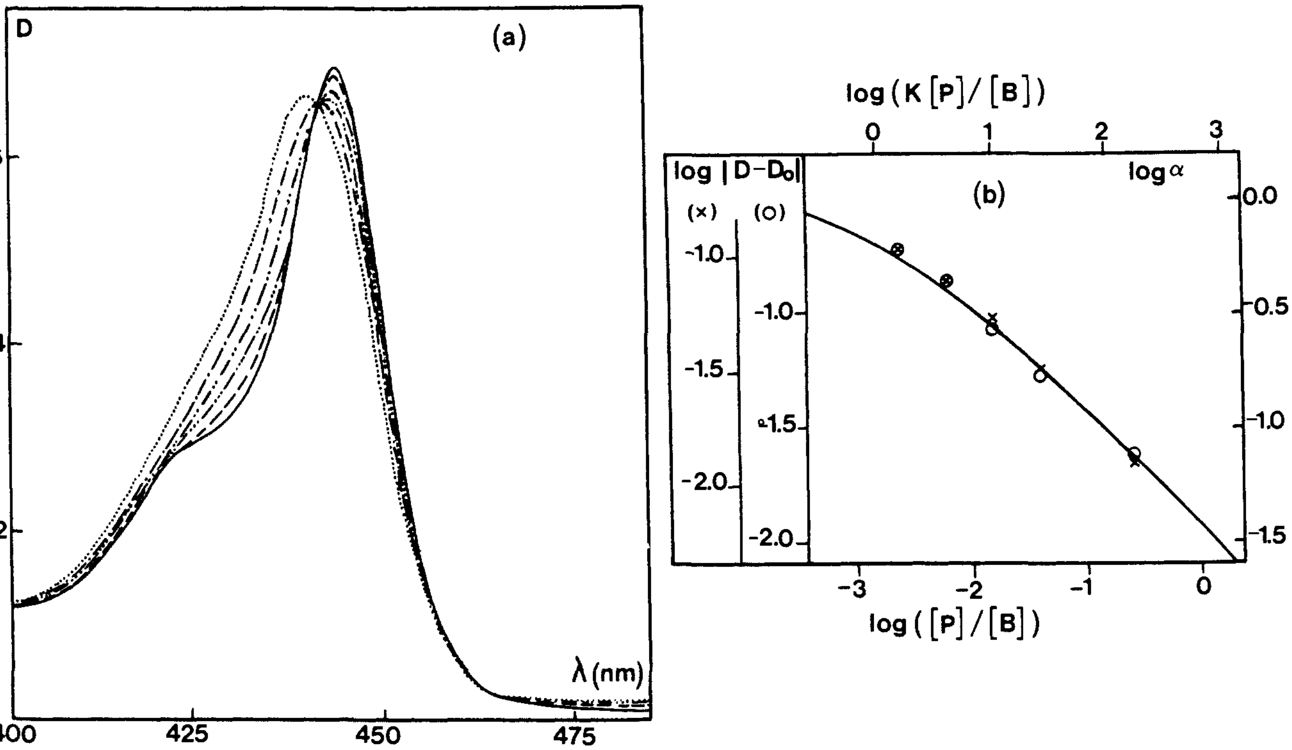

Figure 4. Determination of the association equilibrium constant of (a-$(C12)_2$-AC)Fe^{II} with 2-MePy. Thin-layer spectroelectrochemistry of a-$(C12)_2$-AC)$Fe^{III}Cl$ (6.5×10^{-5} M) in DCE + 0.1 M n-Bu_4NClO_4 at 20 °C. Electrolysis potential, −0.7 V vs. NaCl SCE (a) Soret band as a function of 2-MePy concentration (M) 0 (—), 2.5×10^{-4} (---), 1.8×10^{-3} (-····-), 4.3×10^{-3} (-··-), 9.3×10^{-3} (-·-), 2.5×10^{-2} (····) and (b) treatment of the data at 435 (O) and 445 (×) nm according to procedure C (see text).

Table I. Association Constants of 1,2-Dimethylimidazole and 2-methylpyridine with Iron(II) in Unprotected and Basket-Handle Porphyrins[a]

	1,2-Me_2Im		2-Me-Py	
porphyrin	K_A (M^{-1})[b]	K_A^{e-P}/K_A^{TAP} [c]	K_A (M^{-1})[b]	K_A^{e-P}/K_A^{TAP} [c]
TAP	$2{.}_6 \times 10^4$ (B)		$7{.}_2 10^1$ (B)	
e-$(C12)_2$-AC	$9{.}_5 \times 10^3$ (A)	0.37 (−25)	$4{.}_2$ 10^1 (A)	0.58 (−14)
e-C12$)_2$-CT	$1{.}_7 \times 10^3$ (A)	0.065 (−69)	$3{.}_9$ (A)	0.054 (−74)
		K_A^{a-P}/K_A^{TPP}		K_A^{a-P}/K_A^{TAP}
TPP	$4{.}_1 \times 10^4$ (B)		$1{.}_0 \times 10^2$ (B)	
a-$(C12)_2$-AC	$1{.}_1 \times 10^6$ (B)	27 (84)	$2{.}_0 \times 10^3$ (C)	20 (76)
a-$(C12)_2$-CT	$4{.}_9 \times 10^4$ (B)	1.2 (5)	$5{.}_0 \times 10^1$ (C)	0.5 (−18)

[a] At 20 °C in DCE + 0.1 M n-Bu_4NClO_4. [b] Association equilibrium constant. Between parentheses: designation of the experimental procedure (see the Results section). [c] Comparison between the unprotected and basket-handle prophyrins. Between parentheses: value of $(RT/F)\ln(K_A{}^{e-P}/K_A{}^{TAP})$ or $(RT/F)\ln(K_A{}^{a-P}/K_A{}^{TPP})$ in mV at 20 °C (e-P and a-P for ether-linked and amide-linked basket-handles, respectively).

to that reported previously in toluene at 23 °C,[6b] showing that the influence of the solvent is small. The constant with 2-MePy is significantly smaller (by a factor of about 400) than with 1,2-Me_2Im which falls in line with previous observations showing that 1-MeIm is a much stronger ligand of TPP iron(II) than pyridine.[9]

The electron-donating effect of the four methoxy groups in the ortho position of the phenyl rings in TAP on the association constant is quite small (less than a factor of 2) with both bases.[10]

Concerning the effect of the basket-handle chains on the association constant, the most striking feature of the data listed in Table I is the quite significant increase, observed with both bases, when passing from TPP to a-$(C12)_2$-AC, i.e., when introducing four NHCO groups close to the porphyrin ring without increasing notably steric hindrance against ligation. Since the Hammett σ of an NHCO substituent is practically zero,[11] this cannot be attributed to an electron withdrawing effect through the phenyl rings but rather to a through-space effect of the NHCO dipoles (Figure 5). Another observation, congruent with the latter, is that the association constants are about the same, with both bases, for TPP and the a-$(C12)_2$-CT porphyrin where steric hindrance against axial ligation certainly exists (Figure 5); the destabilization resulting from seric hindrance thus appears to be compensated by an effect of the NHCO groups of the same kind as in the a-$(C12)_2$-AC isomer.

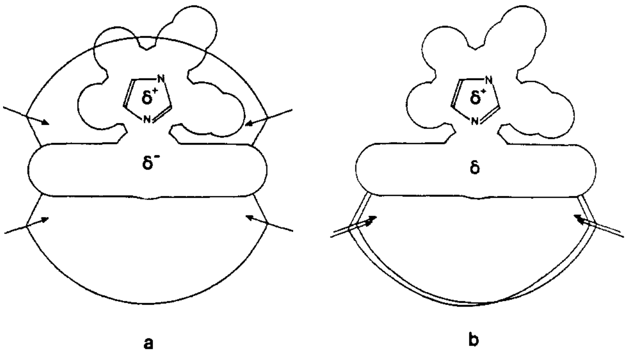

Figure 5. Schematic representation of the stabilization of the Fe^{II}–1,2-Me_2Im complex from the dipolar interactions with the NHCO groups in a a-$(C12)_2$-CT (a) and a-$(C12)_2$-AC (b) basket-handle structure. The iron atom is represented 0.4 Å out of the porphyrin plane.[12]

On the other hand, the effect of the ether-linked basket-handle structure on the binding of the two bases is best estimated by comparison of the two corresponding porphyrins with TAP since the electron-donating effect of the ether groups through the phenyl

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(9) (a) By a factor of about 30 in benzene at 20 °C.[9b] (b) Momenteau, M.; Loock, B.; Bisagni, E.; Rougee, M. *Can. J. Chem.* **1979**, *57*, 1804.

(10) This is also true with T(p-OCH_3)PPFe(II) and 1,2-Me_2Im as reported earlier.[6b]

(11) Zuman, P. *Substituent Effects in Organic Polarography*; Plenum Press: New York, 1967; p 46.

Table II. Specific Effect of the NHCO Groups on the Coordination of Iron(II) by Neutral Nitrogen Bases

basket-handle superstructure	1,2-Me_2Im[a]	2-MePy[a]
$(C12)_2$-AC	73 (109)	34 (89)
$(C12)_2$-CT	18 (73)	10 (56)

[a] $(K_A{}^{a\text{-}P}/K_A{}^{TPP})/(K_A{}^{e\text{-}P}/K_A{}^{TAP})$. Between parentheses, value of (RT/F) ln of the preceding expression in mV at 20 °C, representing the stabilizing effect of the NHCO groups in terms of free energy.

rings should be about the same in the series. It is seen (Table I) that the presence of the chains, in the AC configuration, has a quite small effect on the association constant, i.e., a slight decrease by a factor of 2–3. If we assume that the two chains on the same side of the porphyrin ring completely hinder the binding of the base, a decrease of the equilibrium constant by a factor of 2 would result since only one side of the porphyrin is accessible to the axial ligand. It can thus be concluded that protection against solvation has a small effect, if any, on the binding of a neutral axial ligand unlike what was observed with reactions that create a negative charge on the iron porphyrin complex.[3a,3f,13]

In the case of the e-$(C12)_2$-CT there is a definite decrease (by a factor of 15–20) of the association constant clearly resulting (Figure 5) from steric hindrance by the chain located on the same side as the neutral axial ligand.

The steric hindrance factors are likely to be practically the same in the ether-linked and amide-linked basket-handle series for the same arrangement of the chains. The rigidity of the amide-linked chains is expected to be somewhat larger than that of the ether-linked chains at their extremity but not in the center where steric hindrance mostly takes place. A measure of the specific effect of the NHCO groups on the reactivity of iron(II) toward 1,2-Me_2Im and 2-MePy is therefore provided by

$$\frac{K_A{}^{a\text{-}P}}{K_A{}^{TPP}}:\frac{K_A{}^{e\text{-}P}}{K_A{}^{TAP}}$$

in terms of equilibrium constants and

$$\frac{RT}{F}\ln\left(\frac{K_A{}^{a\text{-}P}}{K_A{}^{TPP}}\cdot\frac{K_A{}^{TAP}}{K_A{}^{e\text{-}P}}\right)$$

in terms of free energy, where a-P and e-P designate the amide-linked and ether-linked basket-handle porphyrins, respectively. The values of these parameters are listed in Table II. It is seen that the presence of the NHCO groups induces a significant increase of the reactivity of iron(II) toward both 1,2-Me_2Im and 2-MePy. Note that if the amide-linked chains exert a (slightly) larger steric effect than the ether-linked chains this would lead to a (slight) underestimation of the specific effect of the NHCO groups. This increased reactivity can be explained in terms of stabilizing interactions between the NHCO dipoles and the dipole resulting from the donation of electron density from the nitrogen base to the iron atom and the porphyrin ring. This is similar to the previously evidenced effect of NHCO groups on the reactions which create a negative charge on the iron and the porphyrin ring.[3a,d,f] There are, however, two important differences between the two cases. One is that the effect is significantly smaller (100 meV at most instead of 300–400 meV) as expected from the fact that dipole–dipole interactions are weaker than dipole–charge interactions. The second derives from the different behaviors toward solvation. It appears that the reactivity of iron(II) toward the two neutral bases is rather insensitive to solvation unlike the case of the reactions creating a negative charge.[3a,d,f] This points to the concept that the Fe(II)–B dipole is mostly an induced dipole, as such giving rise to significant interactions with the almost fixed NHCO dipoles borne by the basket-handle chains and to weak interactions with the fluctuating solvent dipoles. In this connection, the term "local solvation" coined for naming the NHCO dipole–negative charge interactions deserves the quotation marks it was used with.[3f] On one hand, these interactions as well as the interactions with the solvent are of the same kind being both dipole–charge interactions. On the other however, they differ by the fact that the NHCO dipoles in the basket-handle structure are likely to fluctuate much less than the solvent dipoles.

Two additional facts are worth noting. The effect of the NHCO groups is somewhat stronger with 1,2-Me_2Im than with 2-MePy (by about the same amount with the AC and CT configurations). This falls in line with the former being a stronger ligand than the second, hence having a greater propensity to donate more electron density to the iron atom and the porphyrin ring. On the other hand, the effect of the NHCO groups is stronger in the AC configuration than in the CT configuration (by about the same amount for the two bases). This can be explained by a better geometrical location of the NHCO dipoles for interacting with the induced Fe(II)–B dipole in the former case than in the second as visible on the schematic representation given in Figure 5.

Experimental Section

The solvent (DCE) and supporting electrolyte (n-Bu_4NClO_4) were of the same origin as previously described.[3a] The cells, electrodes, and instrumentation used in the cyclic voltammetry and thin-layer spectroelectrochemistry experiments have already been described.[3a] TPP and TAP were prepared as previously described.[15,14a] The synthesis and characterization of the various basket-handle porphyrins have been previously described[14] with the exception of a-$(C12)_2$-AC. This was obtained in the same way as the CT isomer[14b] starting from the $\alpha\alpha\alpha\alpha$ atropo isomer of 5,10,15,20-tetrakis(o-amidophenyl)porphyrin [^1H NMR δ (ppm) ($CDCl_3$) 8.83 (D), 8 × (H_{pyr}), 8.85 (D), 2 × (H_6-Phe), 7.25–7.82 (m, 12 × H-Phe), 6.87 (s, 4 × NHCO), 1.42–0.50 (m, 20 × methylene), –2.74 (s, 2 × NH)]. 1,2-Me_2Im was used (Fluka AG) as received; 2-MePy (Aldrich) was distilled under reduced pressure before use.

Registry No. TAP 1,2-Me_2Im complex, 103852-13-7; TAP 2-Me-Py complex, 103852-14-8; e-$(C12)_2$-AC 1,2-Me_2Im complex, 103852-15-9; e-$(C12)_2$-AC 2-Me-Py complex, 103852-16-0; e-$(C12)_2$-CT 1,2-Me_2Im complex, 103852-17-1; e-$(C12)_2$-CT 2-Me-Py complex, 103852-18-2; TPP 1,2-Me_2Im complex, 72186-60-8; TPP 2-Me-Py complex, 64685-89-8; a-$(C12)_2$-AC 1,2-Me_2Im complex, 103852-19-3; a-$(C12)_2$-AC 2-Me-Py complex, 103852-20-6; a-$(C12)_2$-CT 1,2-Me_2Im complex, 103852-21-7; a-$(C12)_2$-CT 2-Me-Py complex, 103883-59-6.

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(13) The decrease in K_A^B is much less than in the case of ether-linked capped porphyrins[6c] pointing to the conclusion that the steric restraints invoked to explain the behavior of these compounds[6c] are much less important in the present case.

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