necessary to obtain such spectra due to the sensitivity of dilute solutions of this compound to light and to trace impurities in the solvent. The lack of hyperfine in the EPR spectra is consistent with that expected for an a_{1u} porphyrin radical with meso substituents.[11,12]

The factors controlling the intradimer electron-transfer rate might include (1) anion coordination, (2) intermolecular interactions, or (3) lattice-induced site asymmetry. The first of these is unlikely, since the infrared spectrum of **4** as a Nujol mull does not show the resonances associated with triflate coordination in $Fe(TPP)CF_3SO_3$[13] and since it is doubtful that hexachloroantimonate is coordinated in **3**. The second factor is probably unimportant in these compounds since the EPR spectrum in frozen dilute glass is similar to **4** in the solid. X-ray powder diffraction patterns for **3** and **4** are qualitatively different. This suggests that differences in lattice asymmetry due to the different counterions may be influencing the electronic structure.

An interesting comparison may be made between **3** and **4** and analogous μ-oxo systems. $(FeTPP)_2O^+$ also has one unpaired electron in its π-system.[8,14] The Mössbauer spectrum of $[(FeTPP)_2O](ClO_4)$ consists of one doublet at 77 K.[14] We have obtained a Mössbauer spectrum of $[(FeTPP)_2O](SbCl_6)$ at 77 K, and it also consists of one doublet. Thus, the μ-oxo species do not exhibit the same sensitivity to counterion as the μ-nitrido complexes.

In conclusion, $(FeTPP)_2N^{2+}$ is an iron(IV) porphyrin π-cation-radical species. This is the only such synthetic complex to date that is stable indefinitely at room temperature. The counterion has a profound effect on the inter-porphyrin electron-transfer rate. The sensitivity of the electronic structure to such subtle changes illustrates the major influences that minor perturbations may have in related biological systems.

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School of Chemical Sciences
University of Illinois at
Urbana-Champaign
Urbana, Illinois 61801

Daniel R. English
David N. Hendrickson*
Kenneth S. Suslick*

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Articles

Contribution from the Laboratoire d'Electrochimie de l'Université de Paris 7, 75251 Paris Cédex 05, France, and Institut Curie, Section de Biologie, Unité INSERM 219, Centre Universitaire, 91405 Orsay, France

Redox Properties and Stability of Hydroxy Complexes of Protected Iron(III) and Iron(II) Porphyrins

DORIS LEXA,[1a] MICHEL MOMENTEAU,[1b] JEAN-MICHEL SAVEANT,*[1a] and FENG XU[1a]

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Efficient protection from μ-oxo dimer formation in hydroxy complexes of iron(III) tetraphenylporphyrin is provided by 12-carbon aliphatic hydrocarbon ("basket-handle") chains anchored through amide or ether linking in the ortho position of the phenyl groups in a cross-trans arrangement. Electrochemical reduction of the iron(III) hydroxo complexes in benzonitrile yields reversibly the corresponding stable iron(II) hydroxo complexes. The redox characteristics of the $Fe^{III}OH/Fe^{II}OH^-$ couple and the stability constants of both its members have been derived from cyclic voltammetry and thin-layer electrochemistry. They appear to be sensitive to variation of the molecular environment as offered by the presence of either amide or ether groups in the vicinity of the heme ring. The discussion of the data involves comparison with the corresponding chloro complexes, the characteristics of which have been determined in the same fashion.

Introduction

The description and rationalization of the physicochemical characteristics of the complexes of iron porphyrins with dioxygen and the various species resulting from its reduction are of essential importance for the understanding of the transport and activation properties of hemoproteins.[2] Regarding the hydroxyl ion, detailed studies have long been hampered by the conversion of the hydroxoiron(III) complexes into the corresponding μ-oxo dimer.[3] Previous investigation of the electrochemical reduction of the Fe^{III}–O–Fe^{III} complex in dimethylformamide indicated that it undergoes a $2e^- + H^+$ reduction cleavage, leading to $Fe^{II}OH$ and Fe^{II}.[4] μ-oxo dimerization thus appears to take place only at the Fe^{III} oxidation level. Recently however, a few examples of true iron(III) OH^- porphyrin complexes have been reported in the tetraphenylporphyrin series, μ-oxo dimerization being prevented, at least partially, by protecting structures anchored at various positions of the phenyl ring.[5] There are however no data so far

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(1) (a) Université de Paris. (b) Institut Curie.

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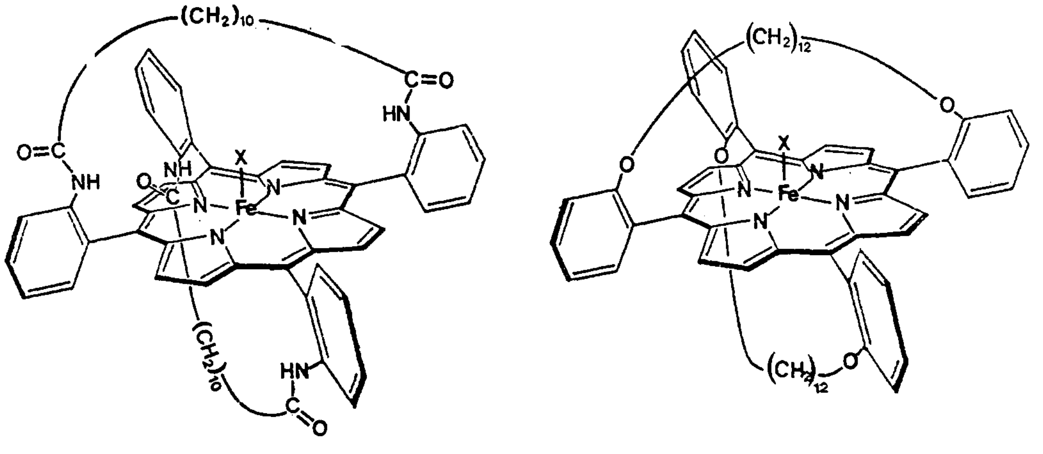
Chart I



a(C$_{12}$)$_2$-CT

e(C$_{12}$)$_2$-CT

X=OH$^-$,Cl$^-$

concerning the stability of the Fe–OH bond at both the Fe^{III} and Fe^{II} oxidation states. According to a quite recent investigation of the electrochemistry of iron tetraphenylporphyrin (TPP) in dimethyl sulfoxide,[6] it appears that μ-oxo dimer formation is not an important pathway in this solvent, thus allowing the Fe^{III}OH and Fe^{II}OH complexes to be characterized by their UV–vis spectra.

We show hereafter that the protection of the iron porphyrin complex by aliphatic hydrocarbon chains in a cross-trans configuration (Chart I) efficiently prevents the formation of the μ-oxo dimer and thus allows the electrochemical and spectroelectrochemical investigation of the hydroxoiron(III) complex. In solvents where unprotected complexes would dimerize into the μ-oxo complex, the hydroxoiron(II) complex can be formed reversibly in this way and the stability constants determined for each oxidation state.

Two kinds of protecting structures were used consisting of two 12-carbon atom chains anchored in the ortho position of the phenyl ring so as to provide a cross-trans arrangement, the anchoring group being either an amide or an ether function (Chart I).[7,8] Previous investigations have shown that the presence of the chains and the nature of the anchoring groups exert a strong influence on the redox and coordination properties of porphyrin complexes.[9] Several examples of these molecular environment effects have been given: destabilization of the negatively charged complexes by the steric hindrance to solvation caused by the presence of the chains;[9a] stabilization of the same complexes by dipolar interactions with the amide groups linking the chains to the phenyl rings;[9a] improvement of the fixation of carbon monoxide on iron(I) porphyrins caused by the presence of the amide groups;[9b] two-electron reversible oxidation of Zn and Cu porphyrins induced by the presence of the same functionalities.[9c]

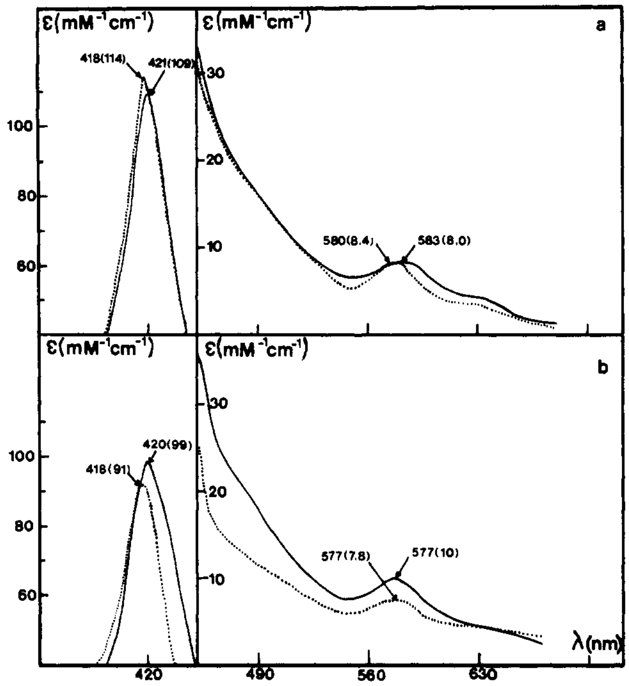


Figure 1. UV–vis spectra of the Fe^{III}OH complexes in PhCN (—) and toluene (---): (a) e-(C12)$_2$-CT; (b) a-(C12)$_2$-CT. Units: λ_{max} in nm; ϵ in mM^{-1} cm^{-1}.

It will be seen that, in the present case also, the nature of the chain-linking functionalities significantly influences the stability of the hydroxoiron complexes both at the III and II oxidation levels. The discussion of these effects will involve the comparison with the corresponding chloro complexes in the same reaction medium, which were investigated by using the same methods.

Results

Preparation and Characterization of the Hydroxoiron(III) a-(C12)$_2$-CT and e-(C12)$_2$-CT Complexes. Treatment of toluene solutions of e-(C12)$_2$-CT–Fe^{III}Cl and a-(C12)$_2$-CT–Fe^{III}Cl with a concentrated aqueous potassium carbonate solution gave new green derivatives. Their optical spectra exhibit one broad absorption band in the visible region (~580 nm) with a shoulder at 630 nm and one other in the Soret region at 418 nm (Figure 1). These spectra are not readily distinguished from that of

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(6) (a) Jones, S. E.; Srivastava, G. S.; Sawyer, D. T.; Traylor, T. G.; Mincey, T. C. *Inorg. Chem.* **1983**, *22*, 3903. (b) *N*-Methylacetamide appears to have similar properties as Me$_2$SO in this respect: Fe^{II}OH is not converted into the μ-oxo dimer, and the latter tends to decompose, leading back Fe^{III}OH.[6c] (c) Lexa, D.; Guentin, C.; Savéant, J. M., unpublished results.

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(8) Abbreviations: TPP, tetraphenylporphyrin dianion; a-(C12)$_2$-CT and e-(C12)$_2$-CT, protected tetraphenylporphyrin dianion as shown in Scheme I.

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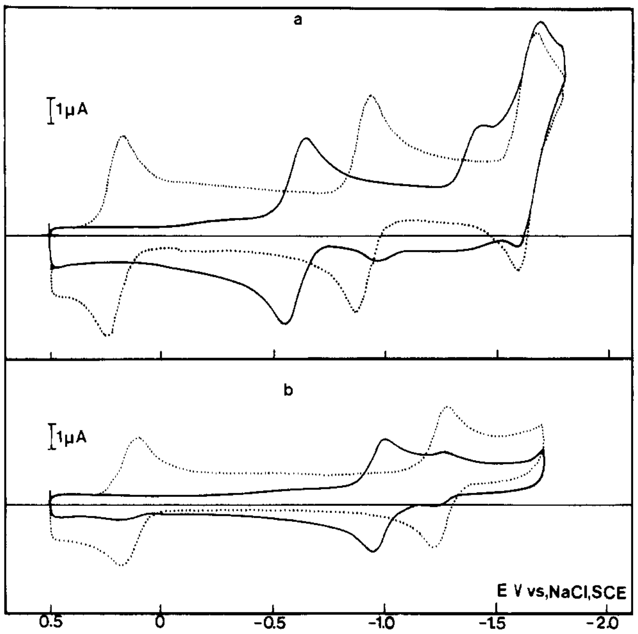

Figure 2. Cyclic voltammetry of the hydroxy complexes (—) and of the neutralized complexes (- - -) in PhCN/0.1 M NBu_4ClO_4 (sweep rate 0.1 V/s): (a) a-(C12)$_2$-CT-Fe^{III}OH (0.5 mM); (b) e-(C12)$_2$-CT-Fe^{III}OH (0.36 mM).

(μ-oxo)bis(tetraphenylporphyrin)iron(III) [λ_{max} 412 nm (ϵ 107.000), 574 (9200), 610 (4600)], except for a bathochromic shift of the absorption maxima.

Their ESR spectra in toluene at 77 K show a strong anisotropic g tensor with $g_\perp = 5.93$ and $g_\parallel = 1.98$. Such spectra are characteristic of high-spin ferric complexes ($S = {}^5/_2$) and are consistent with the monomeric nature of the hematine derivatives (P–Fe^{III}OH). Indeed, the μ-oxo dimers of unhindered porphyrins, prepared following the same procedure, do not show ESR spectra due to the associated antiferromagnetic exchange coupling between the hemin moieties.

The existence of hydroxy species is further supported by infrared spectroscopy. The IR spectra, taken in Nujol, show a broad absorption band at 3250 cm^{-1} due to the OH stretching vibration, which is not visible in those of chloride derivatives and μ-oxo dimeric compounds. On the other hand, the antisymmetric Fe–O–Fe stretching vibration is not found at 850 cm^{-1}, indicating the absence of μ-oxo dimers.[10]

Thus, the ESR and IR spectra allow secure identification of the hydroxy anion as an axial ligand in the two mononuclear ferric complexes studied here.

Cyclic Voltammetry of the Hydroxy Complexes in Benzonitrile. The voltammograms obtained for the reduction of the a-(C12)$_2$-CT-Fe^{III}OH and e-(C12)$_2$-CT-Fe^{III}OH complexes in benzonitrile with 0.1 M ClO_4NBu_4 as supporting electrolyte are shown in Figure 2. PhCN was selected as a solvent rather than the classical dimethylformamide (DMF) because it is expected to coordinate very weakly with the iron center due to its small donor number (11.9 instead of 26.6 for DMF)[11] and its rather large molecular size, which further disfavors coordination through steric hindrance by the C12, cross-trans chains. It also provides a better electroactivity window in the negative potential range than other poorly coordinating solvents such as methylene chloride. The electrophilic character of the latter solvent also makes it react on the iron(I) anion radical, which complicates the electrochemistry of the investigated porphyrin complexes, whereas no such reactions are observed with PhCN. In Figure 2 are also represented the voltammograms obtained upon neutralization of the hydroxy complexes by perchloric acid, i.e., the [Fe^{III}]$^+$ complexes with ClO_4^- as counteranion.[12] The latter exhibit two main one-electron reversible waves featuring the successive reductions of the [Fe^{III}]$^+$ into the [Fe^{II}] and [Fe^{I}] complexes.[13] A third reversible wave corresponding to the [Fe^{I}]$^-$/[Fe^{I}·]$^{2-}$ couple is observed with the amide-linked complex while it is too negative to be conveniently observed in PhCN with the ether-linked complex.[14]

Table I. Standard Potentials[a] and Association Constants[b] in Benzonitrile

	e-(C12)$_2$-CT	a-(C12)$_2$-CT	TPP
$E°$([Fe^{III}]$^+$/[Fe^{II}])	+0.193	+0.212	+0.200[c]
$E°$([Fe^{II}]/[Fe^{I}]$^-$)	−1.237	−0.895	−1.060[c]
$E°$([Fe^{I}]$^-$/[Fe·]$^{2-}$)		−1.630	−1.690[d]
$E°$([Fe^{III}OH]/[Fe^{II}OH]$^-$)	−0.958	−0.600	
$E°$([Fe^{III}Cl]/[Fe^{II}Cl]$^-$)	−0.558	−0.230	
$K^{II}_{OH^-}$	1.6×10^3	2.3×10^6	
$K^{III}_{OH^-}$	1.0×10^{23}	2.4×10^{20}	
$K^{II}_{Cl^-}$	2.2	2.5×10^5	
$K^{III}_{Cl^-}$	1.8×10^{13}	9.0×10^{12}	

[a] In V vs. NaCl SCE. [b] In M^{-1}. [c] From ref 13b. [d] From ref 9a.

In the presence of a stoichiometric amount of OH$^-$ ions, the Fe^{III}/Fe^{II} wave remains reversible but undergoes a dramatic negative shift in potential: 0.812 and 1.151 V for the amide- and ether-linked complexes, respectively. With a-(C12)$_2$-CT-Fe^{III}OH, no trace of reduction of uncomplexed Fe^{II} appears on the cathodic scan beyond the Fe^{III}OH/Fe^{II}OH wave and likewise no trace of oxidation of Fe^{II} appears on the reverse scan in the region where it is observed with the neutralized solution. This shows that the [Fe^{II}OH]$^-$ complex is very stable, exhibiting no tendency to dissociate even though the concentration of OH$^-$ is low (0.5 mM). Small waves corresponding to the reduction and oxidation of uncomplexed Fe^{II} appear on the cathodic and anodic traces, respectively, with the e-(C12)$_2$-CT-Fe^{III}OH complex showing that, although the Fe^{II}OH complex exists, its stability is less than in the case of the amide-linked complex. When the porphyrin concentration is decreased, the (reversible) reduction and (irreversible) oxidation waves further increase as expected from the dissociation of Fe^{II}OH.

A further cathodic irreversible wave is observed corresponding to the reduction of [Fe^{II}OH]$^-$ into [Fe^{I}]$^-$. As expected, it occurs at a much more negative potential than the reduction of the uncomplexed Fe^{II}, its irreversibility featuring the cleavage of the Fe–OH bond, which accompanies the Fe^{II} → Fe^{I} electron-transfer process.[15]

The difference between the standard potential of the [Fe^{III}OH]/[Fe^{II}OH]$^-$ and [Fe^{III}]$^+$/[Fe^{II}] couples is a measure of the ratio of the equilibrium constants of OH$^-$ ligation at the two oxidation states:

$$[\mathrm{Fe^{III}}]^+,\ \mathrm{ClO_4^-} + \mathrm{OH^-} \rightleftarrows [\mathrm{Fe^{III}OH}] + \mathrm{ClO_4^-} \qquad K^{III}_{OH^-}$$

$$[\mathrm{Fe^{II}}] + \mathrm{OH^-} \rightleftarrows [\mathrm{Fe^{II}OH}]^- \qquad K^{II}_{OH^-}$$

$$E^0([\mathrm{Fe^{III}}]^+/[\mathrm{Fe^{II}}]) - E^0([\mathrm{Fe^{III}OH}]/[\mathrm{Fe^{II}OH}]^-) = (RT/F)\ln (K^{III}_{OH^-}/K^{II}_{OH^-})$$

The large positive value of this standard potential difference indicates that Fe^{III} is much more strongly complexed by OH$^-$ than Fe^{II}. The determination of the standard potentials in the starting

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(10) Cohen, I. A. *J. Am. Chem. Soc.* **1969**, *91*, 1980.

(11) Gutman, V. "The Donor-Acceptor Approach to Molecular Interactions"; Plenum Press: New York, 1978; p 20.

(12) Addition of 2 equiv of OH$^-$ (NBu_4OH) to the neutralized solution regenerates the cyclic voltammetric patterns obtained directly with the starting hydroxy complexes.

(13) (a) For a general account of the electrochemistry of unprotected iron porphyrins in nonaqueous solvents, see ref 13b; for a description of the electrochemistry of protected iron porphyrins, see ref 9. (b) Kadish, K. M. In "Iron Porphyrins"; Lever, A. B. P., Gray, H. B., Eds.; Addison-Wesley: London, 1983; Part II, pp 161–249.

(14) The differences in the reductive behavior of the amide- and ether-linked chloro complexes in DMF have been already described and rationalized.[9a] The same general trends are likely to be followed in PhCN.

(15) The fact that the reoxidation wave of the Fe^{I} complex formed upon reduction of Fe^{II}OH is small (Figure 1) is presumably due to the large irreversibility of the Fe^{II}OH/Fe^{I} system: Fe^{I}, which is formed at very negative potential, partly diffuses into the solution before being reoxidized at a much more positive potential (the potential difference is ca. 500 mV).

Table II. UV-Visible Spectral Characteristics of the Fe^{III}- and $Fe^{II}Cl$ Complexes in Benzonitrile or Toluene

		λ_{max} $(\epsilon)^a$					
e-$(C_{12})_2$-CT	$Fe^{II\,b}$		430 (204)	530 (19)			
	$Fe^{II}Cl^{-\,b}$		447 (215)	530 (5.8)	570 (11)	614 (4.5)	
	$[Fe^{III}]^{+\,b}$		408 (124)	514 (13)		670 (2.3)	
	$Fe^{III}Cl^c$	362 (42)	422 (106)	508 (13)	577 (4.0)	655 (3.2)	685 (3.3)
	$Fe^{III}Cl^c$	382 (51)	423 (102)	511 (14)	580 (3.8)	660 (3.1)	687 (3.2)
a-$(C_{12})_2$-CT	$Fe^{II\,b}$		431 (149)	534 (12)			
	$Fe^{II}Cl^{-\,b}$		447 (152)	532 (6.1)	571 (14)	611 (6.3)	
	$[Fe^{III}]^{+\,b}$		408 (85)	514 (8.1)		640 (2.1)	
	$Fe^{III}Cl^c$	361.5 (41)	419 (104)	507.5 (12.6)	580 (3.9)	649.5 (3.2)	678 (3.0)
	$Fe^{III}Cl^b$	385 (42)	423 (83)	511 (12)	581 (4.1)	654 (3.5)	686 (3.1)

[a] λ_{max} in nm; ϵ in mM^{-1} cm^{-1}. [b] In benzonitrile. [c] In toluene.

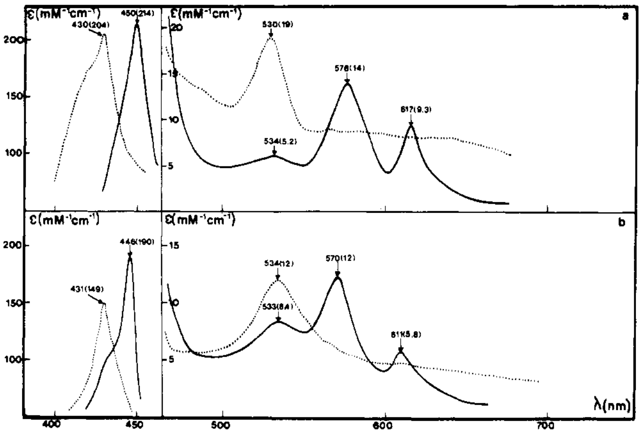

Figure 3. UV–vis spectra of $Fe^{II}OH$ (—) and Fe^{II} (---) complexes in PhCN: (a) e-$(C12)_2$-CT (0.099 mM) (spectrum of $Fe^{II}OH$ obtained in the presence of 10 mM NBu_4OH); (b) a-$(C12)_2$-CT (0.67 mM) (spectrum of $Fe^{II}OH$ obtained in the presence of stoichiometric amount of OH^-). Units: λ_{max} in nm; ϵ in mM^{-1} cm^{-1}.

and neutralized solutions (Table I) thus allows us to know the ratio of the association constants at the Fe^{III} and Fe^{II} oxidation levels.

One could envisage using the location of the $[Fe^{II}OH]^-/[Fe^I]^-$ wave to gain information on $K^{II}_{OH^-}$. However, this wave is so irreversible, as described above, that it does not allow meaningful thermodynamic data to be obtained. We consequently used spectroelectrochemistry to determine $K^{II}_{OH^-}$ and also to obtain the UV–vis spectral characteristics of the $Fe^{II}OH$ complexes.

UV–Visible Spectroelectrochemistry of the Hydroxy Complexes. The spectra of the starting $Fe^{III}OH$ complexes in PhCN are shown in Figure 1 together with those obtained in toluene. The differences are small and compatible with solvent effects, indicating that the same complexes are obtained in both solvents.

Figure 3 shows the spectra of the $Fe^{II}OH$ (and Fe^{II}) complexes obtained by thin-layer electrochemistry of the corresponding Fe^{III} complexes.

The association constants were obtained using two procedures that led to the same results: the $Fe^{II}OH$ complex was either prepared in a coulometric cell and then transferred into a standard spectrophotometric cell or directly generated in a thin-layer cell (thickness 0.05 cm) containing a platinum grid as working electrode. The experiments were carried out at several concentrations of the $Fe^{II}OH$ complex without addition of OH^- so as to obtain the equilibrium constant $K^{II}_{OH^-}$ from the dissociation of the complex into Fe^{II} and OH^- upon dilution. The procedure used to derive $K^{II}_{OH^-}$ from these experiments (see Experimental Section) is illustrated in Figures 4 and 5 for the e-$(C12)_2$-CT and a-$(C12)_2$-CT complexes, respectively.

One $K^{II}_{OH^-}$ is known; $K^{III}_{OH^-}$ can be derived from the standard potential difference as described in the preceding section. The various thermodynamic data thus obtained are summarized in Table I.

Thermodynamic and Spectral Characteristics of the Chloro Complexes in Benzonitrile. The same procedures as described above were used in the case of the amide-linked basket-handle chloro complex that gives rise to a large Fe^{II}–Cl association constant. In the ether-linked case, the dissociation of the $Fe^{II}Cl$ complex is complete in the usable spectrophotometric concentration range. $K^{II}_{Cl^-}$ was then determined by thin-layer electrochemistry in the presence of large amounts of NBu_4Cl in the same way as already described in the case where DMF was used as solvent.[9a]

The resulting thermodynamic and spectral characteristics are summarized in Tables I and II, respectively.

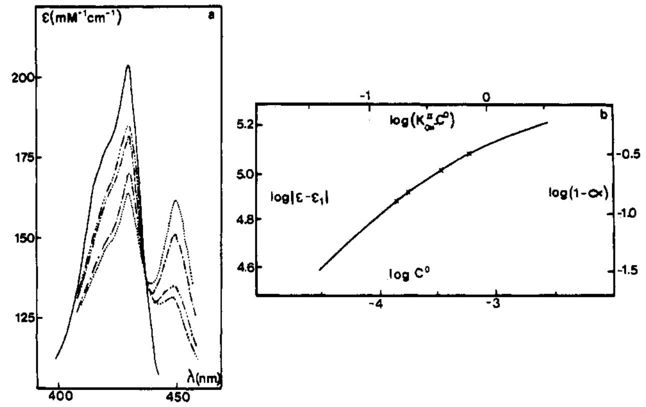

Figure 4. Spectrophotometric determination of the association constant of e-$(C12)_2$-CT-$Fe^{II}OH^-$ in benzonitrile + 0.1 M NBu_4ClO_4. $[Fe^{II}OH]^-$ concentration (mM): 0.078 (-···-), 0.099 (-··-), 0.19 (-·-), 0.30 (···), 0.11 + 0.14 mM $HClO_4$ (—). (a) Spectra in the Soret region. (b) Variation of log $|\epsilon - \epsilon_1|$ with concentration at λ = 450 nm (ϵ, observed extinction coefficient of Fe^{II} + $Fe^{II}OH^-$; ϵ_1, extinction coefficient of Fe^{II}) and fitting with the log $(1 - \alpha)$ vs. log $K^{II}{}_AC$ working curve (α, dissociation coefficient; see Experimental Section).

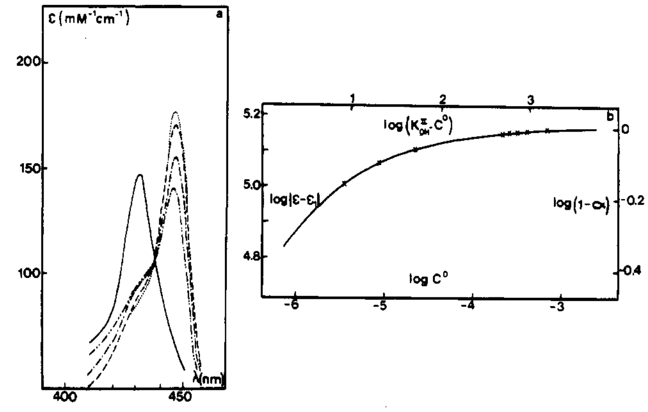

Figure 5. Spectrophotometric determination of the association constant of a-$(C12)_2$-CT-Fe^{II}–OH^- in benzonitrile + 0.1 M NBu_4ClO_4-$[Fe^{II}OH]^-$ concentration (mM): 0.69 (···), 0.022 (---), 0.0087 (-·-), 0.0035 (-··-), 0.24 + 0.24 $HClO_4$ (—). (a) Spectra in the Soret region. (b) Variation of log $|\epsilon - \epsilon_1|$ with concentration at λ = 448 nm and fitting with the log $(1 - \alpha)$ vs. log $K^{II}{}_AC$ working curve (ϵ, observed extinction coefficient of Fe^{II} + $Fe^{II}OH^-$; ϵ_1, extinction coefficient of Fe^{II}; α, dissociation coefficient; see Experimental Section).

Discussion

It has previously been noticed[9a] that the association constant of Fe^{II} with Cl^- in DMF is much less in the ether-linked than in the amide-linked series. This was shown to be mainly due to stabilizing dipolar and/or H-bonding interaction of the amide groups with the negatively charged chloro complex and to a much lesser extent to the electron-donating properties of the ether groups.[9a] Inspection of the data listed in Table I shows that this is also true in PhCN, the difference being even larger in this solvent than in DMF (the ratio of this association constants is 10^5 in the first case and 2×10^3 in the second), which can be related to the fact that coordination with PhCN is weaker than with DMF (the donor numbers are 11.9 and 26.6, respectively[11,16]).

It appears that the same phenomenon occurs in the case of the $Fe^{II}OH$ complexes: $K^{II}_{OH^-}$ is 1000 times larger in the a-$(C12)_2$-CT than in the e-$(C12)_2$-CT complex (Table I). This confirms the importance of the dipolar interaction between the negatively charged porphyrin complexes and the amide present in their immediate vicinity as previously observed in the case of iron(II) chloro complexes, iron(I), iron(I) anion radicals,[9a] and iron(I) carbon monoxide complexes.[9b]

The variation between the e-$(C12)_2$-CT and a-$(C12)_2$-CT hydroxy complexes is however less than with the chloro complexes, a factor of 10^3 instead of 10^5. A possible explanation of this latter observation is the simultaneous or alternative occurrence of the following two effects of the chain-anchoring groups. H bonding between the oxygen atom in the ether groups and the hydrogen atom of the hydroxyl ligand may contribute to stabilize the hydroxy complex both by increasing the electron-donating character of OH^- and by decreasing electron donation from the ether moieties to the porphyrin ring. On the other hand, the stabilizing effect of the NHCO groups most likely depends upon the distribution of the negative change over the ligand, the iron atom, and the porphyrin ring.

Evidence of the existence of the latter effect has already been obtained in two instances. One concerns the fixation of carbon monoxide on iron(I) porphyrin complexes:[9b]

$$[Fe^I]^- + CO \rightleftharpoons [Fe^ICO]^- \leftrightarrow [Fe^{II}CO\cdot]^-$$

In the presence of a given axial ligand the stability of the Fe^ICO complex is greatly enhanced by the presence of amide-linked basket-handle chains, as compared to ether-linked chains and to those of standard TPP, in spite of the fact that both the starting Fe^I complex and the resulting Fe^ICO complex both bear a negative charge. This suggests that the transfer and concentration of the negative charge on the CO ligand render the dipolar stabilization more effective. H bonding between the amide group and the negatively charged oxygen of the CO ligand may also be, at least partially, responsible for the stabilization effect.

A second example is provided by the stabilization of the $Fe^{II}O_2$ adduct in amide-linked basket-handle porphyrins as compared to the ether-linked compounds,[17] despite the a priori favorable effect of electron donation to the porphyrin ring by the ether groups. Stabilization of the dioxygen adduct under the $^+Fe^{III}-O_2^-$ form is again likely to result from dipolar and/or H-bonding interaction.

In the present case, the stabilizing effect of negatively charged species by the NHCO groups may well be less with the OH^- than with the Cl^- ligand. It is indeed expected that the transfer of charge to the iron atom and the porphyrin ring be larger in the former case than in the latter. Alternatively or simultaneously, the Cl^- complex may be stabilized by H bonding between Cl and the NHCO groups where a similar interaction is not possible in the hydroxy complex.

Large association constants with OH^- are found at the Fe^{III} oxidation level (Table I). They are 7–10 orders of magnitude bigger than with Cl^-,[18] in agreement with the fact that OH^- is a stronger and harder base than Cl^-. Association of Fe^{III} with Cl^- is slightly bigger with e-$(C12)_2$-CT than with a-$(C12)_2$-CT, in spite of electron donation to the ring and the iron atom from the ether groups.[9a] It should be noted in this connection that the orientation of one or more NHCO may be different in neutral Fe^{II} and a fortiori in positively charged Fe^{III} complexes (the negative O end of the dipole pointing toward the porphyrin complex) from what they are in the negatively charged complexes (the positive H end of the dipoles pointing toward the porphyrin complex).[19] This effect would stabilize the $[Fe^{III}]^+$ form against the $[Fe^{III}Cl]$ form in the chloride coordination equilibrium, since coordination with NHCO is much more likely to occur in the first case than in the second and hence contributes to lower the association constant. The same would likewise be true for the association constant with OH^-.

We note, in addition, that the association constant of OH^- with Fe^{III} is significantly bigger with e-$(C12)_2$-CT than with a-$(C12)_2$-CT. The difference is much more than in the case of Cl^-, a factor of 10^3 instead of a factor of 2. The same two effects of the anchoring groups discussed in the case of Fe^{III} can again be invoked to explain this difference.

Conclusions

Several conclusions emerge from the preceding discussion: (i) The ether- and amide-linked cross-trans basket-handle structures offer an efficient protection of the $Fe^{III}OH$ complexes against formation of the μ-oxo dimer, allowing the electrochemistry and coordination chemistry of the hydroxoiron porphyrin complexes to be investigated at the Fe^{III} and Fe^{II} oxidation levels.

(ii) Coordination of iron(II) by OH^-, although considerably weaker than for iron(III), is however strong enough to make the $[Fe^{II}OH]^-$ stable in the millimolar concentration range.

(iii) The presence of the chains and the nature of the anchoring groups exert a strong influence on the coordination chemistry of the iron at both the Fe^{II} and Fe^{III} levels. Stabilization of the negatively charged species by the NHCO groups acting as a "built-in" acceptor solvent strongly contributes to the coordination of Fe^{II} by OH^-, similar to what was previously observed with Cl^-. Comparison between the coordination of OH^- and Cl^- shows that further effects of the chain-anchoring groups occur in both the Fe^{III} and Fe^{II} complexes.

Experimental Section

UV–Vis and ESR Spectroscopies. Optical spectra in the Soret and visible regions were recorded on a Varian DMS 100 or a Varian Cary 210 spectrophotometer. ESR spectra (concentration 10^{-3} M) were recorded on a Varian (V 4502) X-band spectrometer at 77 K. The magnetic field strength was calculated from the nuclear resonance frequency of a proton probe located close to the cavity. This frequency was determined with a Hewlett-Packard 5245L frequency counter. The microwave frequency was measured with a calibrated wavemeter. Infrared spectra were obtained from Nujol mulls of the solid complexes on a Nicolet 5MX FT/IR spectrophotometer.

Hydroxoiron(III) Basket-Handle Porphyrins. Ether and amide basket-handle porphyrins (cross-trans-linked isomer) e-$(C12)_2$-CT and a-$(C12)_2$-CT were synthesized according to previously described methods.[7] Anaerobic insertion of iron into these compounds was carried out with iron(II) chloride in dimethylformamide under reflux in the presence of 2,6-dimethylpyridine.[7] Chromatography on silica gel and usual treatment of the solutions gave chloroiron(III) derivatives. Pure $Fe^{III}OH$ complexes were obtained by shaking a toluene solution of chloroiron(III) porphyrins (0.1 mol) with a saturated aqueous potassium carbonate solution for 12

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(16) (a) Since the association constant with DMF is itself small, 2 in CH_2Cl_2[16b] and 6 in benzene,[16c] for $Fe^{II}TPP$, it follows that coordination by PhCN should be practically negligible. (b) Bottomley, L. A.; Kadish, K. M. *Inorg. Chem.* **1981**, *20*, 1348. (c) Brault, D.; Rougée, M. *Biochemistry* **1974**, *13*, 4591.

(17) (a) Momenteau, M.; Lavalette, D. *J. Chem. Soc., Chem. Commun.* **1982**, 341. (b) Mispelter, J.; Momenteau, M.; Lavalette, D.; Lhoste, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 5165.

(18) (a) The association constants of Fe^{III} with Cl^- are themselves quite large. $K^{III}_{Cl^-}$ is only 2.4×10^5 M^{-1} in DMF for TPP,[18b] which underscores the lesser donating power of PhCN as compared to DMF as already discussed in the case of the Fe^{II} complexes. (b) Lexa, D.; Rentien, P.; Savéant, J. M.; Xu, F., submitted for publication.

(19) (a) The X-ray structure of the aquoiron(II) tetrahydrothiophene tetrapivaloylporphyrin[19b] shows that the oxygen atom of one of the four NHCO groups is coordinated to the iron atom. (b) Jameson, G. B.; Robinson, W. T.; Collman, J. P.; Sorrell, T. N. *Inorg. Chem.* **1978**, *17*, 858.

h. The organic solution was separated from the mixture and dried (K_2CO_3). Evaporation of the solution gave desired complexes, which were precipitated from toluene–hexane as dark solids.

Other Chemicals. PhCN from commercial origin was refluxed on P_2O_5 for 24 h and distilled before use. NBu_4ClO_4 and NBu_4Cl (Fluka purum) were recrystallized twice from acetone–water mixtures and dried under reduced pressure at 50 °C. $HClO_4$ solutions in PhCN were prepared from 70% aqueous perchloric acid (Prolabo).

Cyclic Voltammetry and Spectroelectrochemistry. The instrumentation, cells, and electrodes for cyclic voltammetry and thin-layer spectroelectrochemistry were the same as previously described.[9a] In the spectrophotometric experiments, preelectrolyzed solutions of the Fe^{II} complexes were used the electrolysis was carried out in a coulometric cell with a graphite working electrode, a platinum-wire counterelectrode, and a NaCl SCE reference electrode.

The determination of $K^{II}{}_A$ for e-$(C12)_2$-CT–$Fe^{II}OH$, a-$(C12)_2$-CT–Fe^{II} OH and a-$(C12)_2$-CT–$Fe^{II}Cl$ derived from the variations of the UV–vis spectrum with concentration (C) according to the following procedure. Let α be the dissociation coefficient of the complex:

$$\alpha = [(1 + 4K^{II}{}_AC)^{1/2} - 1]/2K^{II}{}_AC$$

At a given C, the observed extinction coefficient, α, is given by

$$\epsilon - \epsilon_1 = (\epsilon_2 - \epsilon_1)(1 - \alpha)$$

where ϵ_1 and ϵ_2 are the extinction coefficients of the $[Fe^{II}]$ and $[Fe^{II}OH]^-$ complex at the same wavelength. ϵ_1 is known from the spectrum of the neutralized solution. As shown in Figures 4 and 5, the experimental log $|\epsilon - \epsilon_1|$ vs. log C plot is fitted with the log $(1 - \alpha)$ vs. log $(K^{II}{}_AC)$ working curve by sliding of both the horizontal and vertical axis. The coincidence of the experimental and theoretical horizontal scales gives the value of $K^{II}{}_A$, and the coincidence of the vertical scales gives ϵ_2. The range of concentration was selected so as to obtain a range of α values sufficiently different from 0 and 1.

Registry No. [e-$(C12)_2$-CT–$Fe^{III}]^+$, 93646-90-3; e-$(C12)_2$-CT–Fe^{II}, 70196-65-5; [e-$(C12)_2$-CT–$Fe^{I}]^-$, 79209-91-9; e-$(C12)_2$-CT–$Fe^{III}OH$, 93646-91-4; [e-$(C12)_2$-CT–$Fe^{II}OH]^-$, 93646-92-5; e-$(C12)_2$-CT–$Fe^{III}Cl$, 79198-03-1; [e-$(C12)_2$-CT–$Fe^{II}Cl]^-$, 90837-98-2; [a-$(C12)_2$-CT–$Fe^{III}]^+$, 93646-93-6; a-$(C12)_2$-CT–Fe^{II}, 93646-94-7; [a-$(C12)_2$-CT–$Fe^{I}]^-$, 90838-20-3; [a-$(C12)_2$-CT–$Fe^{0}]^{2-}$, 90838-23-6; a-$(C12)_2$-CT–$Fe^{III}OH$, 93646-95-8; [a-$(C12)_2$-CT–$Fe^{II}OH]^-$, 93646-96-9; a-$(C12)_2$-CT–$Fe^{III}Cl$, 90838-12-3; [a-$(C12)_2$-CT–$Fe^{II}Cl]^-$, 90838-14-5; K_2CO_3, 584-08-7.

Contribution from the Departments of Chemistry, University of Wollongong, Wollongong, N.S.W., Australia 2500,
and University of Virginia, Charlottesville, Virginia 22901

Copper(II) and Nickel(II) Complexes of Unsymmetrical Tetradentate Schiff Base Ligands

ROSLYN ATKINS,[1a] GREG BREWER,[1b] ERNEST KOKOT,[1a] GARRY M. MOCKLER,[1a] and EKK SINN*[1b]

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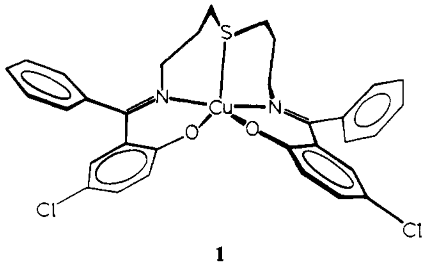
A systematic synthesis is described for new types of unsymmetrical tetradentate Schiff base ligands, from the condensation of different aldehydes and ketones with the two amino groups of 1,2-diaminobenzene. 5-Chloro-2-hydroxybenzophenone (HCBP), dissolved in methanol, reacts with one amino group of 1,2-diaminobenzene to form a tridentate Schiff base ligand (HCBP-PHEN). The free amino group of this ligand can then be reacted with a series of substituted salicylaldehydes (XSALH) to form unsymmetrical tetradentate Schiff base ligands (HCBP-PHEN-XSALH). These ligands react with copper(II) and nickel(II) acetates to form complexes of the type M(CBP-PHEN-XSAL). The physicochemical properties of a series of these complexes have been measured. The crystal structures of three of the copper complexes have been determined. Crystal data for [Cu(CBP-PHEN-SAL)]·CH_3OH: space group $P\bar{1}$, $Z = 2$, $a = 8.666$ (4) Å, $b = 10.061$ (4) Å, $c = 14.104$ (8) Å, $\alpha = 103.01$ (3)°, $\beta = 104.38$ (4)°, $\gamma = 93.07$ (2)°, $V = 1153$ Å^3, $R = 5.5\%$ for 2259 reflections. Crystal data for [Cu(CBP-PHEN-5-ClSAL)]·H_2O: space group $P2_1/c$, $Z = 4$, $a = 15.296$ (6) Å, $b = 7.166$ (2) Å, $c = 25.288$ (6) Å, $\beta = 107.68$ (3)°, $V = 2641$ Å^3, $R = 6.9\%$ for 1220 reflections. Crystal data for [Cu(CBP-PHEN-5-OCH_3SAL)]·CH_3OH: space group $P\bar{1}$, $Z = 2$, $a = 8.973$ (3) Å, $b = 10.148$ (9) Å, $c = 15.836$ (5) Å, $\alpha = 98.80$ (4)°, $\beta = 118.35$ (3)°, $\gamma = 95.18$ (5)°, $V = 1232$ Å^3, $R = 6.4\%$ for 1875 reflections. A 2-mol portion of 5-chloro-2-hydroxybenzophenone, in the absence of solvent, reacts, on refluxing, with 1 mol of 1,2-diaminobenzene to form the symmetrical tetradentate Schiff base ligand HCBP-PHEN-HCBP. The nickel(II) complex of this ligand has been prepared and its crystal structure determined. Crystal data for [Ni(CBP-PHEN-CBP)]: space group $P\bar{1}$, $Z = 2$, $a = 8.516$ (3) Å, $b = 10.783$ (3) Å, $c = 13.057$ (3) Å, $\alpha = 78.82$ (4)°, $\beta = 80.40$ (4)°, $\gamma = 86.28$ (2) °, $V = 1295$ Å^3, $R = 5.6\%$ for 2510 reflections. [Cu(CBP-PHEN-Im)] differs from its analogue in that it is hindered from forming the CuO_2Cu bridge with metal salts and hexafluoroacetylacetonate (hfa) complexes. However, it can still form adducts via imidazole bridging, and its adducts with $Cu(hfa)_2$ and $Co(hfa)_2$ were formed to demonstrate this.

Introduction

Transition metals occur in metalloenzymes[2-5] bound to a macrocycle such as a heme ring or to donor atoms of peptide chains usually in a distorted environment, as in hemerythrin[4] (Fe_2) or hemocyanin[5] (Cu_2). Symmetric tetradentate Schiff base (TSB) complexes of cobalt(II) have been used extensively as macrocycle models, while asymmetric complexes are required to model the irregular binding of peptides. Asymmetric complexes can be produced by distorting the planar geometry of M(TSB) complexes with the addition of a weak fifth donor atom such as S or O in **1**[6,7] or by incomplete Schiff base condensation as in **2**.[8] Alter-



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[1] (a) University of Wollongong. (b) University of Virginia.

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