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## Electrochemistry of Hanging-Base Basket-Handle Iron Porphyrins. Coordination of Iron(II) by the Base and Dioxygen

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The reductive electrochemistry of a series of iron(III) porphyrins bearing two cross-trans basket-handle chains, one of which includes a pyridine or an imidazole pendant ligand, is investigated in benzonitrile by means of cyclic voltammetry and spectroelectrochemical techniques. Comparison of the standard potentials of parent basket-handle porphyrins not involving a hanging base allows the determination of the association constants of iron(III) and iron(II) with the base. Their variations are discussed in terms of the nature of the base, and length of the attaching strap, and the presence or absence of secondary amide groups in the handle. The equilibrium and rate constants of the association of the iron(II)-base complex with dioxygen have also been determined from cyclic voltammetric data. It appears that the oxygen affinity is an increasing function of the iron(II)-base association. The same correlation also exists concerning the carbon monoxide activity. These results are used to further unravel the factors that govern the binding of O<sub>2</sub> and CO to iron(II) porphyrins.

The electrochemistry of superstructured iron porphyrins has received recent attention as a means of demonstrating supramolecular effects, namely the possibility of modifying the reactivity of a central reactant by a built-in micro environment that influences the reactivity without participating directly in the reaction.<sup>2</sup> With "basket-handle" chains attached at the ortho positions of the phenyl rings of tetraphenylporphyrin by ether or secondary amide linkages, quite large effects have been found on redox and coordination reactions that involve the creation of a negative charge.<sup>2</sup> Three types of effects have been thus identified: protection against solvation by steric hindrance to the approach of the solvent molecules; "local solvation" resulting from the interaction of secondary amide groups included in the chains with negatively charged porphyrins; steric discrimination between axial ligands.<sup>2,3</sup>

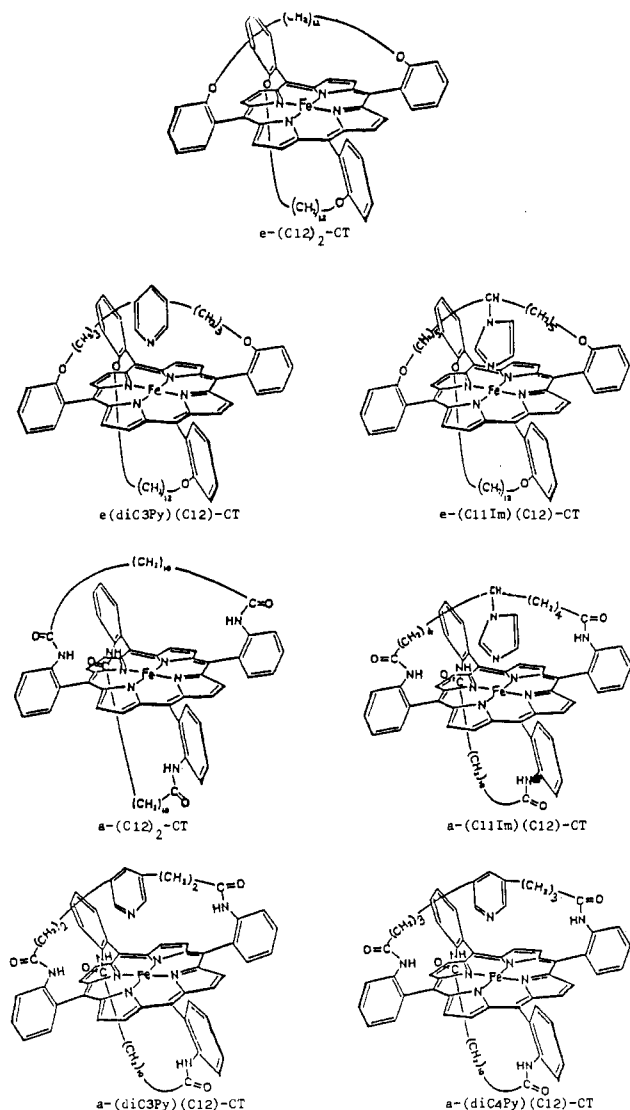
More closely relevant to the present discussion is the observation that the polar interactions with the secondary amide groups included in the chains stabilizes not only the negatively charged iron porphyrin complexes but also the complexes of iron(II) with neutral nitrogen bases as shown in the case of 1,2-dimethylimidazole and 2-methylpyridine.<sup>4</sup>

We describe hereafter the electrochemical behavior of a series of hanging-base basket-handle iron porphyrins, which derive from tetraphenylporphyrin by grafting two basket-handle chains at the ortho positions of the phenyl rings through ether or amide linkages, with, on one side, a nitrogen base, imidazole or pyridine, hung in the chain so as to provide a possible axial coordination to the central iron(II) complex (Figure 1). From the standard potentials of the Fe(II)/Fe(I) and Fe(III)/Fe(II) redox couples obtained

in this series and those obtained without hanging base, we will derive the association constant of the hanging base with the iron porphyrins. The stability of the hanging-base-iron(II) complex will be discussed as a function of the presence or absence of dipolar secondary amide groups in the chains, the length of the chain bearing the base, and the nature of the base, imidazole or pyridine. The addition of dioxygen on the resulting iron(II) complex has also been derived from electrochemical measurements. This will allow us to parallel the stability of the iron(II)-dioxygen adduct with the strength of the iron(II)-hanging-base bond.

This factor has not been systematically investigated in the abundant work devoted to the analysis of the various factors (steric hindrance, cis and trans electronic effects, local polarity, solvation) that may govern the stability of dioxygen-iron(II) porphyrin complexes.<sup>6</sup> These studies have involved a large variety of syn-

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 (3) (a) Effects of a different nature were observed in an electrochemical investigation of superstructured porphyrins involving short straps containing only carbon atoms attached to the pyrroles of etioporphyrin I. The changes induced in the electrochemical properties of the free base and the zinc and magnesium complexes 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.; Wijesekera, T. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *164*, 335.  
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 (5) Abbreviations: TPP = 5,10,15,20-tetraphenylporphyrin. In Figure 1, c and a stand for ether-linked and amide-linked chains, respectively, and CT stands for a cross-trans arrangement of the chains. 1-MeIm, 2-MeIm, 1,2-Me<sub>2</sub>Im, and DClm are 1-methyl-, 2-methyl-, 1,2-dimethyl-, and 1,5-dicyclohexylimidazole, respectively. PhCN, PhCH<sub>3</sub>, and PhH are benzonitrile, toluene, and benzene respectively. BHP = basket-handle porphyrin; HBBHP = hanging-base basket-handle porphyrin.  
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**Figure 1.** Investigated basket-handle and hanging-base basket-handle porphyrins.<sup>5</sup>

thetic superstructured porphyrin models aiming at a better understanding of the factors controlling the dioxygen affinity and the dioxygen/carbon monoxide discrimination in hemoglobins and myoglobins.<sup>6</sup>

## Results

With all porphyrins shown in Figure 1, the cyclic voltammetry investigation started with the hydroxy-iron(III) complex. Figure 2 shows typical cyclic voltammograms obtained with the a-(diC<sub>3</sub>py)(C12)-CT and e-(diC<sub>3</sub>py)(C12)-CT porphyrins as compared to the two corresponding basket-handle porphyrins, a-(C12)<sub>2</sub>-CT and e-(C12)<sub>2</sub>-CT, which do not bear a pendant base.<sup>15a</sup> Dashed lines represent the voltammograms obtained upon neutralization of the iron(III)-hydroxy complexes by an equimolar solution of perchloric acid in benzonitrile, which thus show the characteristics of the reduction of the [Fe<sup>III</sup>]<sup>+</sup>ClO<sub>4</sub><sup>-</sup> complexes.

In the presence of an equimolar amount of OH<sup>-</sup> ions, a single Fe(III)/Fe(II) wave, largely displaced toward negative potentials, is observed with the two hanging-base porphyrins as in the case of the two corresponding basket-handle porphyrins. This indicates

that in the hanging-base porphyrins, iron(III) is complexed by OH<sup>-</sup> rather than by the base.

A different situation arises for the reduction of iron(II). In the case of the a-(C12)<sub>2</sub>-CT porphyrin, a single quasi-reversible wave is observed, close to the Fe(I)/Fe("O") wave.<sup>16,17</sup> Upon neutralization the wave becomes reversible and is shifted toward much less negative potentials. This picture results from the strong complexation of iron(II) by the OH<sup>-</sup> ions favored, as discussed earlier,<sup>2b,d</sup> by the presence of the secondary amide groups attaching the chains to the phenyl ring. After neutralization, the reversible wave features the reaction Fe<sup>II</sup>(PhCN) + e<sup>-</sup> ⇌ [Fe<sup>I</sup>] + PhCN. With the corresponding hanging-base porphyrin, a-(diC<sub>3</sub>py)-(C12)-CT, two cathodic waves are observed for the reduction of iron(II), the second of which occurs at about the same potential as the preceding [Fe<sup>II</sup>OH]<sup>-</sup> wave. Upon neutralization, a single reversible wave is observed at the potential of the first of the two former waves. It is noticed that this reversible wave arises at a potential that is significantly negative to that of the reversible wave obtained upon neutralization with the a-(C12)<sub>2</sub>-CT porphyrin.

These observations indicate that, after neutralization, the "base-on" form of the iron(II) complex predominates over the "base-off" form. In the presence of an equimolar amount of OH<sup>-</sup> ions, a mixture of the "base-on" complex and the hydroxy complex is obtained containing a negligible amount of the "base-off" form. The two cathodic waves thus feature the reduction of the first and the second of these complexes respectively in the context of a "CE" (chemical-electrochemical) mechanism,<sup>18</sup> the chemical reaction being the conversion of the "base-on" complex into the hydroxy complex. Since, at the first of these waves, depletion of the "base-on" form at the electrode surface tends to be compensated by the conversion of the hydroxy complex, it follows that the latter predominates over the former at equilibrium.

In the ether-linked series, there is a small wave corresponding to the reaction [Fe<sup>II</sup>(PhCN)] + e<sup>-</sup> ⇌ [Fe<sup>I</sup>] + PhCN in the case of the e-(C12)<sub>2</sub>-CT porphyrin (Figure 2d),<sup>15b</sup> which indicates that the hydroxy complex does not completely predominate over the PhCN complex in contrast with the case of the corresponding amide-linked compound. This is in keeping with previous findings showing that the presence of the amide groups in the chains stabilizes the negatively charged complexes.<sup>2a,b,d</sup> The same type of voltammogram is also obtained with the corresponding hanging-base porphyrin, e-(diC<sub>3</sub>py)(C12)-CT. However, the reversible Fe(II)/Fe(I) wave (Figure 2b) is significantly shifted toward negative potential as compared with that of the e-(C12)<sub>2</sub>-CT porphyrin. It can thus be concluded that iron(II) then essentially exists as a mixture of the "base-on" form and the hydroxy complex. The latter still predominates over the former but less than with the corresponding amide-linked compound as expected from the strong stabilization of the negatively charged complexes by the secondary amide groups.<sup>2a,b,d</sup>

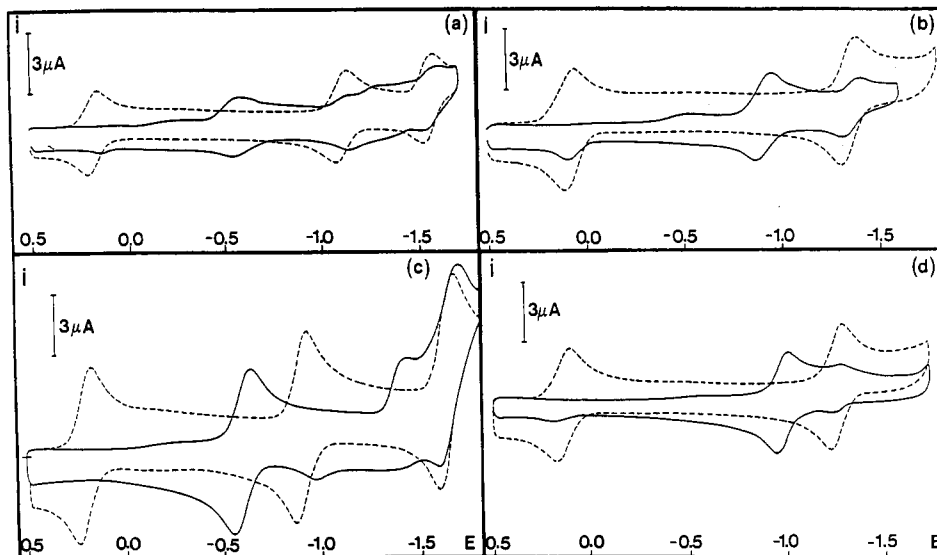
The same type of behavior is observed with the other hanging-base basket-handle porphyrins in the two series and therefore the conclusions as to the relative stability of the "base-off", "base-on", and hydroxy complexes remain qualitatively the same

(15) (a) The cyclic voltammetry of the two latter porphyrins has been described previously.<sup>2</sup> (b) The waves corresponding to the reactions [Fe<sup>II</sup>OH]<sup>-</sup> + e<sup>-</sup> ⇌ [Fe<sup>I</sup>] + OH<sup>-</sup> and [Fe<sup>I</sup>] + e<sup>-</sup> ⇌ Fe("O"), not represented on the figure, appear at more negative potentials, overlapped with the discharge of the supporting electrolyte.

(16) (a) There is good spectroscopic<sup>16b-h</sup> and chemical<sup>16i</sup> evidence that the dominant resonance form is a Fe(I) complex rather than a Fe(II) porphyrin anion radical and that it does not bear an axial ligand, at least at room temperature. (b) Cohen, I. A.; Ostfeld, D.; Lichtenstein, B. *J. Am. Chem. Soc.* **1972**, *74*, 4522. (c) Lexa, D.; Momenteau, M.; Mispelter, M. *Biochim. Biophys. Acta* **1974**, *338*, 151. (d) Kadish, K. M.; Larson, G.; Lexa, D.; Momenteau, M. *J. Am. Chem. Soc.* **1975**, *97*, 282. (e) Reed, C. A. *Adv. Chem. Ser.* **1982**, No. 201, 333. (f) Mashiko, T.; Reed, C. A.; Haller, K. J.; Scheidt, W. R. *Inorg. Chem.* **1984**, *23*, 3192. (g) Srivatsa, G. S.; Sawyer, D. T.; Boldt, N. J.; Bocian, D. F. *Inorg. Chem.* **1985**, *24*, 2123. (h) Hickman, D. L.; Shirazi, A.; Goff, H. M. *Inorg. Chem.* **1985**, *24*, 563. (i) Lexa, D.; Mispelter, J.; Savéant, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 6806.

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**Figure 2.** Cyclic voltammograms of the a-(diC3py)(C12)-CT (a, 0.2 mM), e-(diC3py)(C12)-CT (b, 0.5 mM), a-(C12)<sub>2</sub>-CT (c, 0.5 mM), and e-(C12)<sub>2</sub>-CT (d, 0.36 mM) hydroxyiron(III) porphyrin complexes in PhCN. Solid lines represent plots for hydroxy complexes; dotted lines represent plots after neutralization of the complex by an equimolar concentration of perchloric acid. Conditions: PhCN + 0.1 M NBu<sub>4</sub>ClO<sub>4</sub> at 20 °C; E, potential in V vs NaCl SCE; sweep rate, 0.1 V.s<sup>-1</sup>.

**Table I.** Standard Potentials and Association Constants of the Hanging-Base Basket-Handle Porphyrins<sup>a</sup>

porphyrin	$E^{\circ}_{\text{Fe(II)/Fe(I)}},^b$ V	$K^{\text{II}}_{\text{B}}{}^c$	$E^{\circ}_{\text{Fe(III)/Fe(II)}},^b$ V	$K^{\text{III}}_{\text{B}}{}^d$
e-(C12) <sub>2</sub> -CT	-1.239		0.200	
e-(C11Im)(C12)-CT	-1.415	$7.2 \times 10^2$	-0.031	$7.4 \times 10^6$
e-(diC3py)(C12)-CT	-1.329	$3.4 \times 10^1$	0.075	$4.8 \times 10^3$
a-(C12) <sub>2</sub> -CT	-0.895		0.212	
a-(C11Im)(C12)-CT	-1.180	$8.0 \times 10^4$	0.218	$6.3 \times 10^4$
a-(diC3py)(C12)-CT	-1.104	$3.9 \times 10^3{}^e$	0.176	$1.6 \times 10^4$
a-(diC4py)(C12)-CT	-1.030	$2.1 \times 10^2{}^e$	0.252	$4.3 \times 10^1$

<sup>a</sup> In PhCN + 0.1 M NBu<sub>4</sub>ClO<sub>4</sub> at 20 °C. <sup>b</sup> Vs. NaCl SCE. <sup>c</sup> From  $(RT/F)[\ln(1 + K^{\text{II}}_{\text{B}})] = E^{\circ}_{\text{Fe(II)/Fe(I)}_{\text{BHP}} - E^{\circ}_{\text{Fe(II)/Fe(I)}_{\text{HBBHP}}$  unless otherwise stated. <sup>d</sup> From  $(RT/F)[\ln(K^{\text{III}}_{\text{B}}/K^{\text{II}}_{\text{B}})] = E^{\circ}_{\text{Fe(III)/Fe(II)}_{\text{BHP}} - E^{\circ}_{\text{Fe(III)/Fe(II)}_{\text{HBBHP}}$ . <sup>e</sup> Value confirmed by the spectroelectrochemical method described in the text.

in the whole series of compounds.

Upon neutralization, all waves become reversible. The midpoint between the cathodic and anodic peak potentials then provides a measure of the standard potentials of the Fe(III)/Fe(II) and Fe(II)/Fe(I) couples in the whole series of porphyrins (Table I). Neutralization introduces in the solution an amount of water equal to the concentration of porphyrin i.e., 0.1–1 mM. The concentration of residual water in the solvent was larger,  $\approx 10$ –50 mM. Introduction of additional water to the solution in comparable concentrations did not affect the cyclic voltammograms noticeably.

The Fe(II)/Fe(I) wave then corresponds to the reduction of "base-on" iron(II) into "base-off" iron(I).<sup>16a,g,19</sup> The shift in standard potential when passing from the basket-handle porphyrin to the corresponding hanging-base basket-handle porphyrin then provides information about the association equilibrium constant,  $K^{\text{II}}_{\text{B}}$ , of the pendant base with iron(II).

$$\frac{RT}{F} \ln(1 + K^{\text{II}}_{\text{B}}) = E^{\circ}_{\text{B-off}} - E^{\circ}_{\text{B-on}}$$

Approximating  $E^{\circ}_{\text{B-off}}$  by the standard potential of the (C12)<sub>2</sub>-CT porphyrin, one obtains the  $K^{\text{II}}_{\text{B}}$  values listed in Table I.<sup>20</sup> Although

benzonitrile is not a strong ligand of iron(II),<sup>2d</sup> the association constant actually represents the replacement of a benzonitrile molecule by the pendant base as an axial ligand of iron(II).

A similar approach was followed for determining the association constant of the pendant base with iron(III),  $K^{\text{III}}_{\text{B}}$ .

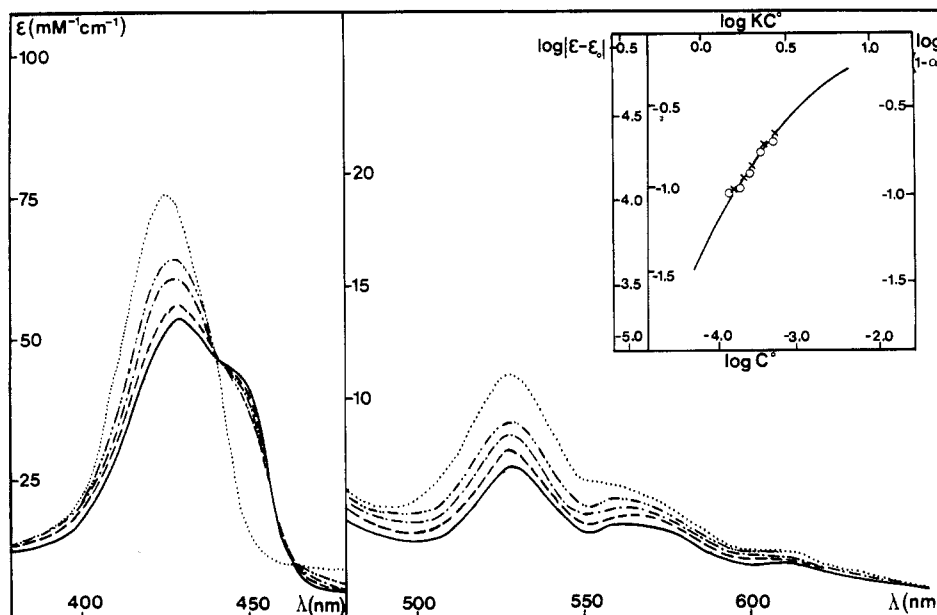
$$\frac{RT}{F} \ln \frac{K^{\text{III}}_{\text{B}}}{K^{\text{II}}_{\text{B}}} = E^{\circ}_{\text{B-off}} - E^{\circ}_{\text{B-on}}$$

$E^{\circ}_{\text{B-off}}$  was again approximated by the corresponding standard potential of the (C12)<sub>2</sub>-CT porphyrin in the same series. Knowing  $K^{\text{II}}_{\text{B}}$  as described above, one then obtains  $K^{\text{III}}_{\text{B}}$ . The ensuing  $K^{\text{III}}_{\text{B}}$  values are listed in Table I.

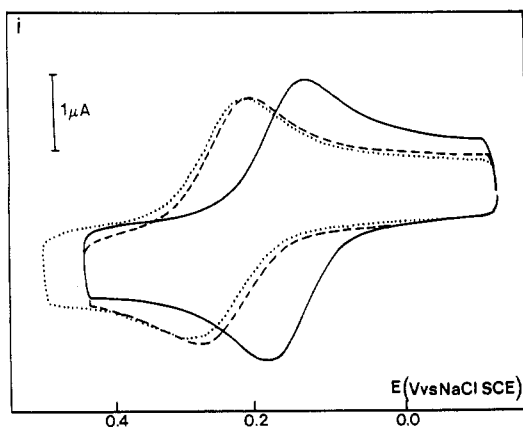
The values of  $K^{\text{III}}_{\text{B}}$  obtained by the above method have been checked, in two cases (a-(diC3py)(C12)-CT and a-(diC4py)<sub>2</sub>-CT)

(19) (a) The situation there is reminiscent of the case of the reduction of cobalt(II) vitamin B12 into cobalt(I) vitamin B12 as investigated earlier<sup>19b-g</sup> where it has been shown that the stronger the axial ligation the more irreversible the reduction process.<sup>19f,g</sup> (b) Lexa, D.; Savéant, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 2652. (c) Lexa, D.; Savéant, J. M.; Zickler, J. *J. Am. Chem. Soc.* **1977**, *99*, 2786. (d) Savéant, J. M.; Tacconi, M.; Lexa, D.; Zickler, J. In *Vitamin B12*; Zagalak, B.; Friedrich, W., Eds.; de Gruyter: Berlin, 1979; pp 203–212. (e) Faure, D.; Lexa, D.; Savéant, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *140*, 269. (f) *Ibid.* **1982**, *140*, 285. (g) Lexa, D.; Savéant, J. M. *Acc. Chem. Res.* **1983**, *16*, 235.

(20) (a) There are two possible sources of inaccuracy in this approximation. One derives from the possible involvement of iron(II) complexes coordinated by two molecules of PhCN. For steric reasons this would be destabilized in the base-off form as compared to the (C12)<sub>2</sub>-CT porphyrin. Thus  $E^{\circ}_{\text{B-off}} > E^{\circ}_{\text{BHP}}$ , which would lead to an underestimation of  $K^{\text{II}}_{\text{B}}$ . The other pertains to the stability of the iron(I) species. As discussed earlier,<sup>2d</sup> there is a possibility that the interaction of the [Fe]<sup>I</sup> species with PhCN (as an acceptor molecule) may be slightly smaller with the base-off complex than with the (C12)<sub>2</sub>-CT complex. Thus  $E^{\circ}_{\text{B-off}} < E^{\circ}_{\text{BHP}}$ , which would lead to an overestimation of  $K^{\text{II}}_{\text{B}}$  tending to cancel out with the first source of inaccuracy. (b) A different, although conceptually related, method has been used previously to measure the association constant of a base attached to the complex in the case of vitamin B12<sup>19b,19c-d</sup> and in that of "tailed" iron porphyrins.<sup>21</sup> It is based upon the shift in pK<sub>a</sub> of the base when passing from the base-off to the base-on form of the complex. The approximation in this case is that the base has the same pK<sub>a</sub> when it is in the base-off form and when it is detached from the complex. (21) Geibel, J.; Cannon, J.; Campbell, D.; Traylor, T. G. *J. Am. Chem. Soc.* **1978**, *100*, 3575.



**Figure 3.** UV-vis spectra of the [(a-(diC3py)(C12)-CT)Fe<sup>II</sup>(OH)]<sup>-</sup> porphyrin complex (obtained by in situ reduction of the [Fe<sup>III</sup>(OH)]<sup>-</sup> complex at -0.9 V vs. NaCl SCE at a platinum grid contained in a thin-layer cell) as a function of concentration in PhCN + 0.1 M NBu<sub>4</sub>ClO<sub>4</sub> at *T* = 20 °C. Porphyrin concentrations (mM): 0.5 (—), 0.36 (---), 0.27 (-·-·), 0.20 (- - -), 0.12 + 0.12 mM HClO<sub>4</sub> (···). Inset: determination of  $K_{\text{B}}^{\text{II}}$ .  $\epsilon$  and  $\epsilon_0$  are the observed and [Fe<sup>II</sup>B] (from the last experiment) molar absorption coefficients, respectively.  $\alpha$  is the dissociation coefficient of the [Fe<sup>II</sup>(OH)] complex.  $\times$  and  $\circ$  are experimental points ( $\log |\epsilon - \epsilon_0|$  vs.  $\log C_{\text{porph}}$ ) at  $\lambda = 530$  and  $426$  nm respectively. Solid line represents the theoretical dilution curve.<sup>2c</sup>



**Figure 4.** Cyclic voltammetry of the [(a-(diC3py)(C12)-CT)Fe<sup>III</sup>ClO<sub>4</sub>] porphyrin complex (0.2 mM) in PhCN + 0.1 M NBu<sub>4</sub>ClO<sub>4</sub> as a function of the oxygen partial pressure.  $P_{\text{O}_2}$  (atm): 0 (—), 0.67 (---), 1 (···). Conditions: sweep rate, 0.1 V s<sup>-1</sup>; *T*, 20 °C.

by a spectroelectrochemical method based on a different approximation than that used in the cyclic voltammetry method. Figure 3 shows the variations of the UV-vis spectrum of the [(a-(diC3py)(C12)-CT)Fe<sup>II</sup>(OH)]<sup>-</sup> porphyrins upon dilution. Since the “base-off” form concentration is negligible, the variations of the spectrum feature the dissociation of the hydroxy complex into the “base-on” complex. The association constant of the pendant base can be derived from these variations according to an already described procedure,<sup>2b</sup> provided the association constant of OH<sup>-</sup> with the “base-off” form of the iron(II) complex is known. The approximation was used in this connection is that the latter constant is the same as the corresponding constant for the a-(C12)<sub>2</sub>-CT basket-handle porphyrin.

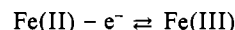
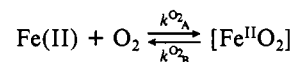
The thermodynamic and kinetic characteristics of the addition of dioxygen to the “base-on” iron(II) porphyrins in benzonitrile were determined in the following way. We start from the anodic wave corresponding to the oxidation of Fe(II) into Fe(III), which is reversible in the absence of oxygen, and observe its variations upon introduction of oxygen into the solution. Figure 4 shows a typical example of these variations in the case of the a-(diC3py)(C12)-CT porphyrin. Introduction of oxygen leads to a decrease of the peak height of the anodic wave and a positive

**Table II.** Oxygenation Equilibrium<sup>25</sup> and Rate Constants of the “Base-On” Hanging-Base Basket-Handle Porphyrins<sup>a,b</sup>

porphyrin	$K_{\text{O}_2}^{\text{II}}$ , M <sup>-1</sup>	$k_{\text{O}_2\text{A}}$ , M <sup>-1</sup> s <sup>-1</sup>	$k_{\text{O}_2\text{D}}$ , s <sup>-1</sup>
e-(C11Im)(C12)-CT	$1.2 \times 10^4$	$2.3 \times 10^6$	$2.0 \times 10^2$
e-(diC3py)(C12)-CT	$7.4 \times 10^2$	$3.0 \times 10^5$	$4.1 \times 10^2$
a-(C11Im)(C12)-CT	$4.0 \times 10^4$	$6.3 \times 10^6$	$1.6 \times 10^2$
a-(diC3py)(C12)-CT	$6.0 \times 10^3$	$1.6 \times 10^6$	$2.7 \times 10^2$
a-(diC4py)(C12)-CT <sup>c</sup>	$7.0 \times 10^2$	$2.3 \times 10^5$	$3.3 \times 10^2$

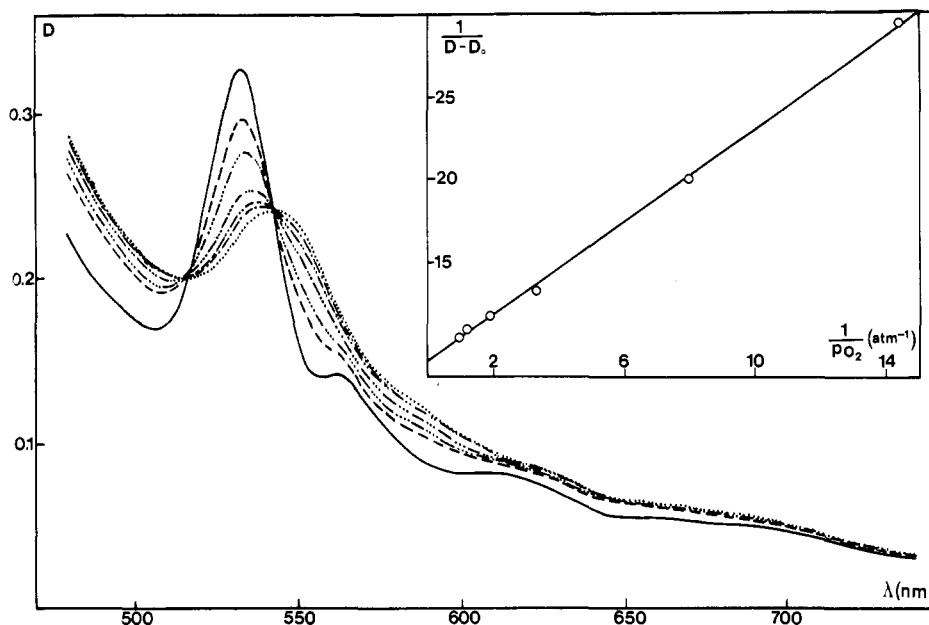
<sup>a</sup> In PhCN + 0.1 M NBu<sub>4</sub>ClO<sub>4</sub> at 20 °C. <sup>b</sup> Determined by the cyclic voltammetry method (see text). <sup>c</sup> Constants determined in addition by the spectroelectrochemical method (see text).

shift of its peak potential as expected to result from the formation of the dioxygen adduct in the context of a “CE” mechanism:



in which the electron-transfer step is preceded by the dissociation of the [Fe<sup>II</sup>O<sub>2</sub>] adduct. From the two available observables, the peak height and the shift of the half-peak potential, we can derive the equilibrium and rate constants according to procedures that have been previously developed.<sup>2a,4,18</sup> In this context, the procedure is greatly simplified if we can assume that pseudo-first-order conditions prevail for the formation of the dioxygen adduct. That these conditions can be achieved results from the following considerations. The solubility and diffusion coefficient of dioxygen in dimethylformamide (DMF) have been determined as 4.1 mM atm<sup>-1</sup> and  $1.1 \times 10^{-4}$  cm<sup>2</sup> s<sup>-1</sup>,<sup>22</sup> respectively. On the other hand, the reversible wave of dioxygen in PhCN is 1.2 times higher than that in DMF. Assuming that the diffusion coefficients are inversely proportional to the viscosity of the solvent,<sup>23</sup> according to the Stokes-Einstein law, it follows that the solubility and

- (22) (a) James, H. T.; Braman, R. F. *Anal. Chim. Acta* **1959**, *48*, 411. (b) Sawyer, D. T.; Chiericato, G., Jr.; Angelis, C. T.; Nanni, E. J., Jr.; Tsuchiya, T. *Anal. Chem.* **1982**, *54*, 1720.  
 (23) (a) The viscosities are 1.24 and 0.845 for PhCN<sup>23b</sup> and DMF<sup>23c</sup> respectively. (b) *Handbook of Chemistry and Physics*, 60th ed.; CRC: Boca Raton, FL, 1979; p F52. (c) Janz, G. J.; Tomkins, R. P. T. *Non Aqueous Electrolytes Handbook*; Academic: New York, 1972.



**Figure 5.** UV-vis spectra of the [(a-(diC4py)(C12)-CT)Fe<sup>II</sup>] porphyrin complex (from the reduction of 0.35 mM of the [Fe<sup>III</sup>]<sup>+</sup>, ClO<sub>4</sub><sup>-</sup> complex at -0.3 V vs. NaCl SCE in PhCN + 0.1 M NBu<sub>4</sub>ClO<sub>4</sub>, t = 20 °C) as a function of the dioxygen partial pressure. *p*O<sub>2</sub> (atm): 0 (—) 0.07 (---), 0.15 (- · - ·), 0.3 (····), 0.52 (- - - -), 0.79 (- · - ·), 1.00 (· · · ·). Insert: Hill plot at λ = 533 nm (*D* = observed absorbance; *D*<sub>0</sub> = absorbance at *p*O<sub>2</sub> = 0).

diffusion coefficient of dioxygen are 5.3 mM atm<sup>-1</sup> and 8 × 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>, respectively.<sup>24</sup> With 1 atm of oxygen and a millimolar concentration of porphyrin, the ratio of the corresponding fluxes (*D*<sup>1/2</sup>*C*) is larger than 10, showing that the pseudo-first-order conditions are indeed achieved. Lower pressures of dioxygen can also be used, provided the concentration of porphyrin is decreased accordingly. Such conditions have been maintained throughout our determinations of the oxygenation constants. The results thus obtained are listed in Table II (the O<sub>2</sub> solubility in PhCN thus estimated has been used to obtain the association equilibrium constant). Another method was used to check the values of *K*<sup>II</sup><sub>O<sub>2</sub></sub> obtained by the above cyclic voltammetry method in the case of the a-(diC4py)(C12)-CT porphyrin. It consists in generating the Fe(II) complex electrochemically in a thin-layer cell and observing the variations in the UV-vis spectrum as a function of the partial pressure of dioxygen. These are shown in Figure 5 together with the Hill plot allowing the determination of the association equilibrium constant. The latter was found to be 8.0 × 10<sup>2</sup> M<sup>-1</sup>, in excellent agreement with the value obtained from the cyclic voltammetry method.

## Discussion

Perusal of Table I indicates a first remarkable effect: for the same superstructure of the values of the association constant of iron(II) with the pendant base are systematically lower, by a factor

about 100, in the ether-linked series than in the amide-linked series, both with imidazole and pyridine as pendant base. This is similar to what we have recently observed in the complexation of iron(II) by free 1,2-dimethylimidazole and 2-methylpyridine in ether-linked and amide-linked basket-handle porphyrins.<sup>4</sup> The explanation of this phenomenon is thus the same in both cases, namely, that the stabilization of the "base-on" form by the secondary amide groups included in chains is mainly the result of dipole-dipole interactions between the amide groups and the Fe(II)-base dipole. The latter appears to have mostly an induced rather than a permanent character as was concluded from the fact that protection against external solvation by the chains appears almost negligible.<sup>4</sup> On the other hand, part of the effect may come from the unfavorable inductive electron-donating effect of the ether group on complexation. This was however shown to be small, of the order of 1.5, from the comparison of the complexation of TPP and TAP iron(II) with 1,2-dimethylimidazole and 2-methylpyridine.<sup>4</sup> We can thus estimate that the stabilizing effect of the secondary amide groups is by a factor of the order of 70, i.e., ~ 100 meV in terms of free energy. As noted earlier, the coordination of the pendant base actually involves the displacement of a weakly bound benzonitrile molecule. The effect of the CONH groups should thus tend to be larger in a noncoordinating solvent.

Comparison of the *K*<sup>II</sup><sub>B</sub> values in the last two entries of Table I shows the effect of the length of the chains bearing the pyridine ligand. Passing from a diC3 to a diC4 chain, there is a decrease of the association constant by more than a factor of 10. It is visible on molecular models that the diC4 chain has to fold back for the nitrogen atom to be located at a bonding distance from the iron atom whereas this is not the case for the diC3 chain. Note in this connection, that with a different porphyrin, 8,18-bis(2-(carbo-benzyloxy)ethyl)-2,7,12,17-tetramethylporphyrin, with a strap attached at the 3,13-pyrrole carbons containing a pyridine with five atoms on each side, the base is not coordinated to iron(II), due, at least in part, to the same type of steric constraints.<sup>9b</sup>

Another effect is that of the nature of the pendant base. It is seen (Table I) that in both the ether-linked and the amide-linked series a decrease of about 20 in *K*<sup>II</sup><sub>B</sub> is observed when going from imidazole to pyridine. This is in keeping with previous observations showing that 1-methylimidazole is a better ligand for Fe<sup>II</sup>TPP than pyridine.<sup>26</sup> The fact that the decrease is of the same order

(24) (a) The solubility in PhCN is close to that in toluene (5.35 mM atm<sup>-1</sup>). (b) Linke, W.; Seidell, A. *Solubilities of Inorganic and Metalorganic Compounds*; Van Nostrand: Princeton, NJ, 1958.

(25) (a) O<sub>2</sub> and CO binding constants are often<sup>7</sup> expressed in terms of *p*<sub>1/2</sub> (value of the partial pressure of the gaseous ligand corresponding to equimolar amount of the starting complex and the O<sub>2</sub> or CO adduct) even for comparison of affinities in different solvents.<sup>7b</sup> This has been justified in a recent publication (see footnote 20 in ref 12b) by stating that "the activity of the dissolved CO in different solvents is constant at constant ambient CO partial pressure" (implicitly the same would be true for dioxygen or any other gas). This statement is conceptually incorrect:<sup>25b</sup> the standard chemical potential (at infinite dilution, i.e. in the Henry's region) has no reason to remain the same when changing solvent (the change in standard potential is actually a measure of the change in solvation). It follows that the proportionality coefficient between activity and partial pressure changes from one solvent to another. A correct approach,<sup>28b</sup> although approximate, is to compare the equilibrium constants in terms of M<sup>-1</sup>, assuming the activity coefficient of the gas to be unity, which seems a good approximation in view of the fact that they are uncharged species and that the solutions are very dilute. (b) Denbigh, K. *The Principles of Chemical Equilibrium*, 2nd ed.; University Press: Cambridge, England, 1966; pp 249-252, 281, 282.

(26) (a) By a factor of about 30 in benzene at 20 °C.<sup>26b</sup> (b) Momenteau, M.; Loock, B.; Bisagni, E.; Rougee, M. *Can. J. Chem.* 1979, 57, 1804.

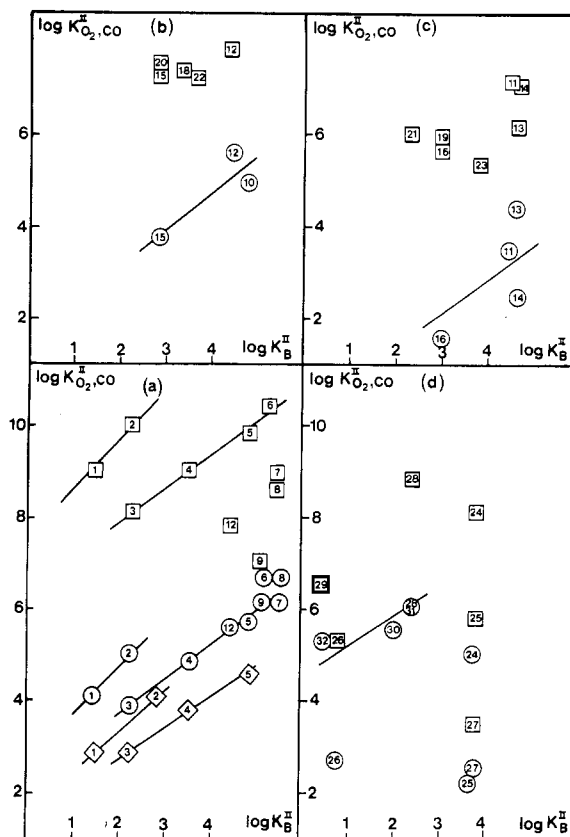
of magnitude in our case and in the case of TPP with free bases confirms that the steric constraints to the binding of the base are not very strong in the diC3py structure.

Also in the case of the complexation of iron(III) by the pendant base, the diC4py structure is less efficient than the diC3py structure (Table I). On the other hand, whereas the  $K_{\text{B}}^{\text{III}}$  values are systematically larger in the amide-linked series than those in the ether-linked series this is no longer the case for the  $K_{\text{B}}^{\text{III}}$ . In other words, whereas the  $K_{\text{B}}^{\text{III}}$  values are much larger than the  $K_{\text{B}}^{\text{II}}$  values in the ether series, they are much closer one to the other in the amide series. This might be related to a turning inside out of one or several NHCO groups in the "base-off" form, stabilizing the corresponding iron(III) complex by interaction of the positive charge with the inverted dipole. There is precedence of such turning inside out of the NHCO dipoles upon modifying the state of the iron atom in picket-fence porphyrins.<sup>27</sup> An indication in the same direction is that quick and approximate determinations of the enthalpies and entropies of hanging-base association with iron(III) showed that these are negative, as expected, in the ether series but are positive in the amide series. Clearly, however, this interpretation is rather uncertain, calling for the gathering of additional evidence.

As regards the association constants of the "base-on" iron(II) complex with dioxygen (Table II), a first observation is that they are systematically smaller in PhCN than in toluene<sup>14d</sup> by a factor that is close to 10 in the whole series. Part of this difference may come from uncertainties in the determination of the solubility of dioxygen in PhCN (see above) and in toluene.<sup>7b</sup> This would however not involve a factor of 10. The most likely reason of this lowering of the association constant from toluene to benzonitrile is a weak binding of a PhCN molecule as sixth ligand, which has to be displaced by dioxygen, whereas in toluene the sixth coordination site is vacant.

As we have seen above, the strength of the association of iron(II) with the pendant base is a function of the nature of the base, the length of the connecting strap, and the presence of secondary amide groups in the chains. The question arises whether the association with dioxygen follows the same trends. The result is shown in Figure 6a, which represents an attempt to correlate the free energy of dioxygen association with the free energy of the iron(II)-pendant-base bond in benzonitrile. Assuming that the latter quantity does not vary considerably when going to PhCN to toluene, we have also represented correlations between the association of dioxygen and carbon monoxide in toluene<sup>14d</sup> (Table III) and the iron(II)-pendant-base coordination in benzonitrile. There is a general correlation in the series between the two free energies: the stronger the iron(II)-base bond, the stronger the association with dioxygen whatever the particular reason that makes the iron(II)-base coordination vary. We however note that the correlation line in the amide-linked series is slightly below that in the ether-linked series. It is also remarkable that, in the amide-linked series, the strength of the association with CO also increases with that of the iron(II)-base bond at the same rate as for the association with dioxygen.

The identification of the various factors influencing the association of iron(II) with dioxygen and carbon monoxide, by use of various superstructured porphyrins modeling hemoglobin and myoglobin, has been the object of active investigation. To help the discussion of the various effects that are involved,<sup>7-14,28-30</sup> we



**Figure 6.** Variations of the association constants of dioxygen and carbon monoxide with iron(II),  $K_{\text{O}_2}^{\text{II}}$  and  $K_{\text{CO}}^{\text{II}}$ , with the association constant of the fifth ligand,  $K_{\text{B}}^{\text{II}}$  (see Table III): ( $\diamond$ )  $K_{\text{O}_2}^{\text{II}}$  in PhCN, ( $\circ$ )  $K_{\text{O}_2}^{\text{II}}$  in PhCH<sub>3</sub>, ( $\square$ )  $K_{\text{CO}}^{\text{II}}$  in PhCH<sub>3</sub>. For the grouping of the porphyrins in four categories, a-d, see text.

have represented the variations of  $K_{\text{O}_2}^{\text{II}}$  and  $K_{\text{CO}}^{\text{II}}$  with  $K_{\text{B}}^{\text{II}}$  in Figure 6 from previous studies in the cases where  $K_{\text{B}}^{\text{II}}$  was available (data summarized in Table III). Besides, qualitative studies have also been carried out, helping to uncover some of these effects.

**Cis Electronic Effects.** Electron-donating substitution of the porphyrin ring increases O<sub>2</sub> affinity without changing CO affinity significantly.<sup>30b,c</sup>

**Trans Electronic (Proximal-Base) Effects.** The observation that imidazole is a better ligand of iron(II) than pyridine<sup>26</sup> has been used to investigate trans electronic effects on the binding of O<sub>2</sub> and CO.<sup>8a,21,30d,f</sup> For O<sub>2</sub>, there is a significant increase of the affinity when passing from pyridine to imidazole. A similar observation can be made on the data displayed in Figure 6: there is a general trend of increasing  $K_{\text{O}_2}^{\text{II}}$  upon increasing  $K_{\text{B}}^{\text{II}}$  at least for systems not involving too severe distal-side steric hindrance (which is the case for the 24-27 systems). This, together with the above mentioned cis electronic effect, led to the suggestion that separation of charge in the  $[\text{Fe}^{\text{II}}]^{\delta+}-\text{O}-\text{O}^{\delta-}$  adduct has a stabilizing effect on its formation.<sup>7c-e,31</sup> The situation concerning CO binding is more ambiguous. With chelated mesoheme porphyrins in suspension in an aqueous solution of cetyltrimethylammonium bromide, the variation of CO affinity when passing

(27) (a) Jameson, G. B.; Robinson, W. T.; Collman, J. P.; Sorrell, T. N. *Inorg. Chem.* **1978**, *17*, 858. (b) Walker, F. A. *J. Am. Chem. Soc.* **1980**, *102*, 3254.

(28) (a) 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. (b) Collman, J. P.; Brauman, J. I.; Doxsee, K. M. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 6035. (c) Collman, J. P.; Brauman, J. I.; Collins, T. J.; Iverson, B.; Sessler, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 2450.

(29) (a) Ellis, P. E.; Linard, J. E.; Szymanski, T.; Jones, R. D.; Budge, J. R.; Basolo, F. J. *Am. Chem. Soc.* **1980**, *102*, 1889. (b) Linard, J. E.; Ellis, P. E.; Budge, J. R.; Jones, R. D.; Basolo, F. J. *Am. Chem. Soc.* **1980**, *102*, 1896. (c) Hashimoto, T.; Dyer, R. L.; Crossley, M. J.; Baldwin, J. E.; Basolo, F. J. *Am. Chem. Soc.* **1982**, *104*, 2101.

(30) (a) Traylor, T. G.; Mitchell, M. J.; Tsuchiya, S.; Campbell, D. H.; Stynes, D. V.; Koga, N. *J. Am. Chem. Soc.* **1981**, *103*, 5234. (b) Traylor, T. G.; White, D. K.; Campbell, D. H.; Berzins, A. P. *J. Am. Chem. Soc.* **1981**, *103*, 4932. (c) Chang, C. K.; Traylor, T. G. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 1166. (d) Traylor, T. G.; Campbell, D. H.; Sharma, V.; Geibel, J. J. *Am. Chem. Soc.* **1979**, *101*, 5376. (e) Traylor, T. G.; Chang, C. K.; Geibel, J.; Berzins, A.; Mincey, T.; Cannon, J. J. *Am. Chem. Soc.* **1979**, *101*, 6716. (f) White, D. K.; Cannon, J. B.; Traylor, T. G. *J. Am. Chem. Soc.* **1979**, *101*, 2434.

(31) (a) That charge transfer exists in the  $\text{Fe}^{\text{II}}\text{O}_2$  complex is also supported by IR data.<sup>31b</sup> (b) Collman, J. P.; Brauman, J. I.; Halbert, T. R.; Suslick, K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 3333.

Table III. Constants of Association of Iron(II) with Axial Bases, Dioxygen, and Carbon Monoxide in Superstructured Porphyrins<sup>a,b,25</sup>

Porphyrin	Base	$K_B^{II}$ c	$K_{O_2}^{II}$ c	$K_{CO}^{II}$ c	Solvent	Reference	Conventional Number in fig. 6
Superstructured Tetraphenylporphyrins (Basket-Handle, Handle-Picket, Picket, Pocket, Capped)							
e-(diC3Py)(C12)-CT	Hanging Py	$3.4 \cdot 10^{-1}$ d —	$7.4 \cdot 10^2$ $7.5 \cdot 10^3$	— $9.9 \cdot 10^8$	PhCN PhCH <sub>3</sub>	This work 11d	1
e-(C11Im)(C12)-CT	Hanging Im	$7.2 \cdot 10^2$ d —	$1.2 \cdot 10^4$ $1.2 \cdot 10^5$	— $9.5 \cdot 10^9$ e	PhCN PhCH <sub>3</sub>	This work This work	2
a-(diC4Py)(C12)-CT	Hanging Py	$2.1 \cdot 10^2$ d —	$7.0 \cdot 10^2$ $6.4 \cdot 10^3$	— $1.2 \cdot 10^8$	PhCN PhCH <sub>3</sub>	This work 11d	3
a-(diC3Py)(C12)-CT	Hanging Py	$3.9 \cdot 10^3$ d —	$6.0 \cdot 10^3$ $7.0 \cdot 10^4$	— $1.2 \cdot 10^9$	PhCN PhCH <sub>3</sub>	This work 11d	4
a-(C11Im)(C12)-CT	Hanging Im	$8.0 \cdot 10^4$ d —	$4.0 \cdot 10^4$ $5.0 \cdot 10^5$	— $6.0 \cdot 10^9$	PhCN PhCH <sub>3</sub>	This work 11d	5
a-(C12)(Piv) <sub>2</sub>	1-MeIm	$1.9 \cdot 10^5$	$4.8 \cdot 10^6$	$2.4 \cdot 10^{10}$	PhCH <sub>3</sub>	11e	6
a-(C10)(Piv) <sub>2</sub>	"	$4.0 \cdot 10^5$	$1.1 \cdot 10^6$	$8.8 \cdot 10^8$	"	"	7
a-(C9)(Piv) <sub>2</sub>	"	$3.0 \cdot 10^5$	$4.3 \cdot 10^6$	$3.8 \cdot 10^8$	"	"	8
a-(C8)(Piv) <sub>2</sub>	"	$1.5 \cdot 10^5$	$1.4 \cdot 10^6$	$1.0 \cdot 10^7$	"	"	9
TPivPP	1-MeIm	$5.9 \cdot 10^4$	$8.7 \cdot 10^4$	—	1-1 EtOH-PhCH <sub>3</sub> PhCH <sub>3</sub>	14 28 a,b	10
	1,2-Me <sub>2</sub> Im	$3.7 \cdot 10^4$	$3.8 \cdot 10^3$	$1.2 \cdot 10^7$			11
PocPivPP	1-MeIm	$3.1 \cdot 10^4$	$4.0 \cdot 10^5$	$7.0 \cdot 10^7$	"	28c	12
	1,2-Me <sub>2</sub> Im	$5.0 \cdot 10^4$	$1.1 \cdot 10^4$	$1.6 \cdot 10^6$			13
BisPoc-PP	1,2-Me <sub>2</sub> Im	$5.0 \cdot 10^4$	$2.8 \cdot 10^2$	$1.2 \cdot 10^7$	"	12	14
T(C2cap)PP	1-MeIm	$7.9 \cdot 10^2$	$6.2 \cdot 10^2$	$2.0 \cdot 10^7$	"	29	15
	1,2-Me <sub>2</sub> Im	$1.1 \cdot 10^3$	$3.6 \cdot 10^1$	$5.3 \cdot 10^5$			16
	Py	$8.0 \cdot 10^1$	$1.0 \cdot 10^3$	"			17
T(C3Cap)PP	1,5-DCIm	$2.0 \cdot 10^3$	—	$2.5 \cdot 10^7$	"	"	18
	1,2-Me <sub>2</sub> Im	$1.0 \cdot 10^3$	—	$7.5 \cdot 10^5$			19
T(NapC2Cap)PP	1-MeIm	$7.4 \cdot 10^2$	—	$3.6 \cdot 10^7$	"	"	20
	1,2-Me <sub>2</sub> Im	$2.1 \cdot 10^2$	—	$1.1 \cdot 10^6$			21
T(C2CapNO <sub>2</sub> )PP	1-MeIm	$4.8 \cdot 10^3$	—	$1.5 \cdot 10^7$	"	"	22
	1,2-Me <sub>2</sub> Im	$7.8 \cdot 10^3$	—	$2.1 \cdot 10^7$			23
Superstructured Mesohemes (Cyclophane, Tailed)							
7,7 anthracene cyclophane	1,5 DCIm	$6.6 \cdot 10^3$	$1.0 \cdot 10^5$	$1.2 \cdot 10^8$	PhH	9b,30a	24
6,6 anthracene cyclophane	"	$6.0 \cdot 10^3$	$1.5 \cdot 10^2$	$6.2 \cdot 10^5$	"	"	25
6,6 adamantane cyclophane	"	6.0	$4.8 \cdot 10^2$	$1.9 \cdot 10^5$	PhCH <sub>3</sub>	9a,30a	26
5,5 pyridine cyclophane	"	$6.2 \cdot 10^3$	$2.6 \cdot 10^2$	$2.9 \cdot 10^3$	"	9b	27
Tailed (CH <sub>2</sub> ) <sub>2</sub> CONH,1-(CH <sub>2</sub> ) <sub>3</sub> Im	"	$2.5 \cdot 10^2$	$1.0 \cdot 10^6$	$6.0 \cdot 10^8$	water+ Cet-NMe <sub>3</sub> Br	21	28
Tailed 3,1-(CH <sub>2</sub> ) <sub>3</sub> ,2-MeIm	"	3.0	—	$3.1 \cdot 10^6$	"	"	29
Tailed 1-OCH <sub>2</sub> CH <sub>2</sub> Im	"	$1.2 \cdot 10^2$	$3.0 \cdot 10^5$	—	"	"	30
Tailed 1-NH(CH <sub>2</sub> ) <sub>4</sub> Im	"	$2.3 \cdot 10^2$	$1.2 \cdot 10^6$	—	"	"	31
Tailed N(1-(CH <sub>2</sub> ) <sub>3</sub> Im)	"	$\sim 1.0 \cdot 10^1$	$3.4 \cdot 10^5$	—	"	"	32

a : from  $P_{1/2}^{O_2}$  and  $P_{1/2}^{CO}$  taking as solubility of O<sub>2</sub> in PhCN (see text) and PhCH<sub>3</sub><sup>25</sup>,  $5.32 \text{ mM} \cdot \text{atm}^{-1}$ , of CO in PhCH<sub>3</sub>:  $7.2 \cdot 10^{-3} \text{ mM} \cdot \text{atm}^{-1}$  25. b : temperature ranging between 20 and 27°C. c : in M<sup>-1</sup> unless otherwise stated. d : dimensionless constant. e : determined by the method described in ref. 11d.

from pyridine to imidazole is very small,<sup>21,30d,e</sup> whereas a significant variation is observed with picket-fence porphyrins in toluene.<sup>28d</sup> Other systems, as represented in parts b and c of Figure 6, show a slight tendency of an increase of  $K^{II}_{CO}$  with  $K^{II}_B$  but to a less definite extent than for  $K^{II}_{O_2}$ . This is in keeping with the concept that charge separation is less important in the  $[Fe^{II}CO]$  complex than in the  $[Fe^{II}O_2]$  complex.<sup>7f,h</sup>

**Solvation Effects.** Comparison of  $O_2$  affinities in various solvents have shown that they increase with the polarity of the solvent,<sup>7</sup> providing further support for the separation of charge in the dioxygen adduct. In the case of CO, there does not seem to be any definite trend: the affinity is reported to sometimes decrease<sup>12b,30a,b,d</sup> and sometimes increase<sup>8c,29c</sup> with solvent polarity. This difference between the behaviors of the  $O_2$  and CO adducts is also visible in Figure 6b,c.

**Proximal-Side Steric Effects.** It has been shown that iron(II) porphyrin complexes of 2-methyl or 1,2-dimethylimidazole bind  $O_2$  and CO significantly less than complexes of 1-methylimidazole,<sup>28a,29b,32</sup> which is attributed to the steric hindrance of the 2-methyl group that opposes the formation of the six-coordinated complex having the iron atom in the porphyrin plane.<sup>7</sup> This also appears in the comparison of the data in parts b and c of Figure 6.

**Distal-Side Steric Effects.** Cyclophane superstructures involving a bulky group (anthracene, adamantane, benzene) able to rotate in the attaching chain leads to a significant decrease of the  $O_2$  and CO affinities, which are of the same order of magnitude in both cases.<sup>9a,b,11d</sup> Capped structures or basket handles of decreasing lengths reduce the CO affinity but have little effect on  $O_2$  affinity.<sup>8c,11e,28d</sup> These results are in keeping with a steric differentiation of a linearly bound CO and an angularly bound  $O_2$ .

**Local Polarity (and/or Hydrogen-Bonding) Effects.** The introduction of polar groups, namely secondary amide functions, in the superstructure in the immediate vicinity of the porphyrin ring leads to an increase of the dioxygen affinity<sup>11</sup> as can be seen in Figure 6a. This has been related to strong polar interactions involving the formation of a hydrogen bond between the amide protons and the terminal oxygen of the complex.<sup>11b,d</sup> Evidence for polar interactions has also been gained in the case of picket-fence structures,<sup>13</sup> although not leading to the establishment of hydrogen bonds.<sup>11e</sup> The situation is more confused in the case of CO. On one hand differentiation between  $O_2$  and CO in a pyridine cyclophane porphyrin where the pyridine is bound to the chain through secondary amide linkages has been attributed to an H-bonding interaction between the amide proton and dioxygen.<sup>9b</sup> This would not exist with carbon monoxide in keeping with the concept that charge separation is smaller in the CO complex than in the  $O_2$  complex<sup>9b</sup> as discussed above. However, as visible in Figure 6a, the CO affinity increases with  $K^{II}_B$  approximately as much as does the  $O_2$  affinity in the amide-linked hanging-base basket-handle porphyrins investigated in this work.

The correlation between  $K^{II}_{O_2}$  and  $K^{II}_{CO}$  on one hand and  $K^{II}_B$  on the other that appears for the hanging-base basket-handle porphyrins also applies for other related porphyrins in which the superstructure is grafted at the ortho position of the phenyl rings by a secondary amide linkage. Porphyrins 6–9, which involve two picket-fence and one basket-handle of variable length on one side of the porphyrin, show, with 1-methylimidazole as the fifth ligand, dioxygen affinities that do not depend significantly upon the length of the basket-handle chain. The corresponding points are located very near to the correlation line of the hanging-base compounds investigated here. This is also the case for the Collman's pocket porphyrin (Figure 6a). There is thus, for this whole set of compounds, a striking parallelism between the variations of  $K^{II}_{O_2}$  and  $K^{II}_B$ .

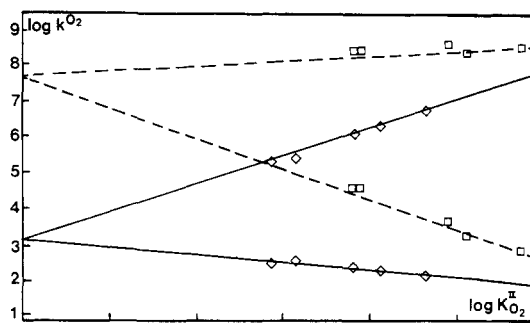


Figure 7. Variation of the dioxygen association (upper points,  $M^{-1} s^{-1}$ ) and dissociation (lower points,  $s^{-1}$ ) rate constants with the association constant  $K^{II}_{O_2}$  ( $M^{-1}$ ) in benzonitrile ( $\diamond$ ) and toluene ( $\square$ ).<sup>35</sup>

It is remarkable that the injection of more electron density from the coordinated base to iron(II) (when passing from pyridine to imidazole, or when the geometry of the chain is more favorable to the  $[Fe^{II}B]$  binding) as expressed by an increase in  $K^{II}_B$  results almost quantitatively into a stabilization of the dioxygen adduct as expressed by  $K^{II}_{O_2}$ . It is also noteworthy that the increase of  $K^{II}_{O_2}$  resulting from an increased local polarity due to the introduction of CONH groups in the chains parallels quantitatively the corresponding increase of  $K^{II}_B$ .

For the same  $K^{II}_B$ , the ether-linked structures give rise to a slightly larger  $K^{II}_{O_2}$  than the corresponding amide-linked structures. A plausible explanation is that the electron-donating inductive effect of the ether groups promotes a better separation of charges in the  $[Fe^{II}O_2]$  complex.

In the case of carbon monoxide, the point corresponding to the C12-handle bis(picket-fence)porphyrin (6) for which steric hindrance to CO binding is negligible, also falls on the same  $K^{II}_{CO}-K^{II}_B$  correlation line as the compounds investigated here. The other porphyrins of the same series as well as Collman's pocket porphyrin give points that fall below the line (Figure 6a) as expected from a large steric hindrance to CO binding. The significant increase (practically the same as for  $O_2$ ) of  $K^{II}_{CO}$  with  $K^{II}_B$  in this series points to the concept that the injection of charge from the coordinated base to the CO ligand through the iron atom is assisted by an electrostatic interaction with the polar environment offered by the CONH groups included in the chains. This is similar to the electron "push-pull" process previously invoked to explain similar effects observed in the stabilization of  $[Fe^I]-CO$  porphyrin complexes.<sup>34</sup> It is an example illustrating the possibility of two effects, here local polarity and trans electronic effects, acting synergistically rather than separately. These observations are not in contradiction with the lack of effect of solvent polarity on CO binding if one assumes that the separation of charges in the  $[Fe^{II}CO]$  adduct has an induced rather than a permanent character. Although involving only two data points, the results concerning the binding of CO with the two ether-linked basket-handle porphyrins (1, 2) are worth noting. They show that increasing the complexing power of the pendant base has a similar effect on CO binding as on  $O_2$  binding, pointing to the existence of charge separation in the former case as in the latter.

$O_2$  vs. CO differentiation thus appears to depend both on central steric effects<sup>11e,28d</sup> and local polarity effects.<sup>9b</sup> However, as regards the latter factor, the present study indicates that since in general local polarity can affect the CO affinity as well as the  $O_2$  affinity, differentiation hinges on a specific arrangement of the polar groups favoring the stabilization of the  $O_2$  adduct over that of the CO adduct.

Figure 7 shows how the association and dissociation rate constant  $k^{O_2}_A$  and  $k^{O_2}_D$  vary in benzonitrile with the association

(32) Rougée, M.; Brault, D. *Biochemistry* **1975**, *14*, 4100.

(33) (a) The inductive effect of the NHCO groups appears negligible, their Hammett  $\sigma$  constants being close to zero.<sup>33b</sup> (b) Zuman, P. *Substituent Effects in Organic Polarography*; Plenum: New York, 1967; p 46. (c) The inductive effect of the ether group on the stability of  $Fe(II)$ -neutral nitrogen base complexes is small.<sup>4</sup>

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(35) The values for the e-(C11Im)(C12)-CT porphyrin in toluene ( $K^{II}_{O_2} = 1.2 \times 10^5 M^{-1}$ ,  $k^{O_2}_A = 1.8 \times 10^8 M^{-1} s^{-1}$ ,  $k^{O_2}_D = 1.5 \times 10^3 s^{-1}$ ) were determined as previously described for the other porphyrins of the series.<sup>11d</sup>



equilibrium  $K^{\text{II}}_{\text{O}_2}$ . The correlation lines have slopes that are entirely different from that previously observed in toluene. This is to be related to the fact that in the first case we are dealing with the replacement of a PhCN molecule by dioxygen as discussed before rather than with an addition of dioxygen on a five-coordinated iron(II) complex as is the case in toluene.

### Experimental Section

The instrumentation and procedures for cyclic voltammetry and thin-layer spectroelectrochemistry were the same as already described. The oxygen partial pressure was adjusted to the desired value by means of a gas distributor containing ball-flow meters, one for oxygen and the other for argon.

The synthesis and characterization of the porphyrins investigated in this work have been described previously with the exception of the  $e\text{-(C11Im)(C12)-CT}$  compound:  $e\text{-(C12)}_2\text{-CT}$ ,<sup>11c</sup>  $a\text{-(C12)}_2\text{-CT}$ ,<sup>36b</sup>  $e\text{-(diC3py)(C12)-CT}$ ,<sup>36a</sup>  $a\text{-(diC3py)(C12)-CT}$ ,<sup>36b</sup>  $a\text{-(diC4py)(C12)-CT}$ ,<sup>36b</sup>  $a\text{-(C11Im)(C12)CT}$ .<sup>36b</sup> The  $e\text{-(C11Im)(C12)-CT}$  porphyrin was prepared along the lines of the same procedure as the  $e\text{-(diC3py)(C12)-CT}$  compound.<sup>36a</sup> Its characteristics are as follows. Anal. Calcd for  $\text{C}_{70}\text{H}_{73}\text{N}_6\text{O}_8$ : C, 79.14; H, 6.93; N, 7.91. Found: C, 78.94; H, 7.20; N,

8.00.  $^1\text{H NMR}$  (ppm): 8.78 (d,  $8 \times \text{H}_{\text{py}}$ ); 8.08 (d,  $4 \times \text{H}_6 \text{ Ph}$ ); 7.8-7.3 (m,  $12 \times \text{H Ph}$ ); 6.32, 5.91, 4.95 ( $3 \times \text{H Im}$ ); 3.9 (b,  $8 \times \text{OCH}_2$ ); 2.81 (b, CH); 1.32 to -1.72 ( $32 \times \text{methylene}$ ); -2.54 (s,  $2 \times \text{NH}$ ).

**Registry No.** ( $e\text{-(C12)}_2\text{-CT}$ ) $\text{Fe}^{\text{II}}$ , 105502-69-0; [( $e\text{-(C12)}_2\text{-CT}$ ) $\text{Fe}^{\text{I}}$ ] $^-$ , 79209-91-9; [( $e\text{-(C12)}_2\text{-CT}$ ) $\text{Fe}^{\text{III}}$ ] $^+$ , 93646-90-3; ( $e\text{-(C11Im)(C12)-CT}$ ) $\text{Fe}^{\text{II}}$ , 105502-70-3; [( $e\text{-(C11Im)(C12)-CT}$ ) $\text{Fe}^{\text{I}}$ ] $^-$ , 105502-71-4; [( $e\text{-(C11Im)(C12)-CT}$ ) $\text{Fe}^{\text{III}}$ ] $^+$ , 105502-75-8; ( $e\text{-(diC3py)(C12)-CT}$ ) $\text{Fe}^{\text{II}}$ , 82489-43-8; [( $e\text{-(diC3py)(C12)-CT}$ ) $\text{Fe}^{\text{I}}$ ] $^-$ , 105502-72-5; [( $e\text{-(diC3py)(C12)-CT}$ ) $\text{Fe}^{\text{III}}$ ] $^+$ , 105502-76-9; ( $a\text{-(C12)}_2\text{-CT}$ ) $\text{Fe}^{\text{II}}$ , 93646-94-7; [( $a\text{-(C12)}_2\text{-CT}$ ) $\text{Fe}^{\text{I}}$ ] $^-$ , 90838-20-3; [( $a\text{-(C12)}_2\text{-CT}$ ) $\text{Fe}^{\text{III}}$ ] $^+$ , 93646-93-6; ( $a\text{-(C11Im)(C12)-CT}$ ) $\text{Fe}^{\text{II}}$ , 88887-00-7; [( $a\text{-(C11Im)(C12)-CT}$ ) $\text{Fe}^{\text{I}}$ ] $^-$ , 105502-73-6; [( $a\text{-(C11Im)(C12)-CT}$ ) $\text{Fe}^{\text{III}}$ ] $^+$ , 105502-77-0; ( $a\text{-(diC3py)(C12)-CT}$ ) $\text{Fe}^{\text{II}}$ , 82568-76-1; [( $a\text{-(diC3py)(C12)-CT}$ ) $\text{Fe}^{\text{I}}$ ] $^-$ , 105502-74-7; [( $a\text{-(diC3py)(C12)-CT}$ ) $\text{Fe}^{\text{III}}$ ] $^+$ , 105502-78-1; ( $a\text{-(diC4py)(C12)-CT}$ ) $\text{Fe}^{\text{II}}$ , 98292-96-7; [( $a\text{-(diC4py)(C12)-CT}$ ) $\text{Fe}^{\text{I}}$ ] $^-$ , 105519-66-2; [( $a\text{-(diC4py)(C12)-CT}$ ) $\text{Fe}^{\text{III}}$ ] $^+$ , 105502-79-2; ( $a\text{-(diC3py)(C12)-CT}$ ) $\text{Fe}^{\text{III}}(\text{OH})$ , 105537-46-0; [( $a\text{-(diC3py)(C12)-CT}$ ) $\text{Fe}^{\text{II}}(\text{OH})$ ] $^-$ , 105502-80-5; ( $e\text{-(diC3py)(C12)-CT}$ ) $\text{Fe}^{\text{III}}(\text{OH})$ , 105519-67-3; ( $a\text{-(C12)}_2\text{-CT}$ ) $\text{Fe}^{\text{III}}(\text{OH})$ , 93646-95-8; ( $e\text{-(C12)}_2\text{-CT}$ ) $\text{Fe}^{\text{III}}(\text{OH})$ , 93646-91-4; ( $e\text{-(diC3py)(C12)-CT}$ ) $\text{Fe}^{\text{II}}(\text{O}_2)$ , 82498-70-2; ( $e\text{-(C11Im)(C12)-CT}$ ) $\text{Fe}^{\text{II}}(\text{O}_2)$ , 105519-68-4; ( $a\text{-(diC4py)(C12)-CT}$ ) $\text{Fe}^{\text{II}}(\text{O}_2)$ , 105519-69-5; ( $a\text{-(diC3py)(C12)-CT}$ ) $\text{Fe}^{\text{II}}(\text{O}_2)$ , 82498-69-9; ( $a\text{-(C11Im)(C12)-CT}$ ) $\text{Fe}^{\text{II}}(\text{O}_2)$ , 105519-70-8; ( $a\text{-(C11Im)(C12)-CT}$ ) $\text{Fe}^{\text{I}}(\text{CO})$ , 105502-81-6;  $\text{O}_2$ , 7782-44-7;  $\text{Bu}_4\text{NClO}_4$ , 1923-70-2;  $\text{CO}$ , 630-08-0.

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## Neutral Spin-Delocalized Mixed-Valence $\text{Mn}^{\text{I}}\text{Mn}^{\text{II}}$ Dimers Bridged by Alkoxide, Imidazolate, or Malonodinitrile Anions

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The complexes  $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_2\text{Mn}]_2(\mu\text{-L})$ ,  $\text{L} = t\text{-BuO}^-$ ,  $\text{AdO}^-$ , imidazolate,  $t\text{-BuC}(\text{CN})_2^-$ ,  $\text{HC}(\text{CN})_2^-$ , were produced from  $\text{Mn}^{\text{I}}$  precursor complexes by oxidation with  $\text{O}_2$  (air) or  $\text{PbO}_2$  in aprotic media and were characterized by EPR as spin-delocalized  $\text{Mn}^{\text{I}}\text{Mn}^{\text{II}}$  systems. Stability and extent of formation of these dimers depend on the  $\sigma$ -donor strength of the anionic bridging ligands and correlate with their basicity, the alkoxides being the strongest and the malonodinitrile anions the weakest bases. A comparison of the mixed-valence dimers with corresponding mononuclear low-spin  $\text{Mn}^{\text{II}}$  complexes  $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_2(\text{L})\text{Mn}$  reveals similar  $g$  values and halving of the  $^{55}\text{Mn}$  coupling constants, except for the alkoxide-bridged dimers, which exhibit some metal-metal interaction. Intervalence (IT) transitions of the imidazolate and malonodinitrile anion bridged  $\text{Mn}^{\text{I}}\text{Mn}^{\text{II}}$  dimers in toluene solution are remarkably similar to the IT features measured for corresponding  $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$  ammine complexes in aqueous solutions. The significance of the spectroscopic results with regard to photosynthetic  $\text{O}_2$ -evolving manganese centers is briefly discussed.

### Introduction

The vast majority of mixed-valence complexes with metal centers in  $d^5/d^6$  configurations involve the group 8 metals, especially ruthenium,<sup>1</sup> in their +II/+III oxidation states.<sup>2</sup> The paramount position of ruthenium ammine fragments in this chemistry is due to their kinetic stability in both oxidation states<sup>1,3</sup> and to the conveniently accessible redox potential range in which these complexes are available.<sup>1</sup> Considering these criteria, we have set out to search for organometallic systems with similar properties but which contain metals in lower oxidation states.<sup>4</sup> The kinetic stability and redox potential requirements for a ruthenium ammine related chemistry seem to be met by the  $(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Mn}(\text{L})$  complexes ( $\text{R} = \text{H, Me}$ ); ruthenium(II,III) systems are connected to manganese(I,II) by a diagonal relationship in the periodic table. Complexes with the substitutionally very inert<sup>5</sup> fragment  $(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Mn}$  undergo reversible one-electron oxidation over a potential range of more than 2 V;<sup>4b,6</sup> some stable oxidized species were characterized recently as low-spin manganese(II) complexes.<sup>4b</sup>

Mixed-valence complexes of manganese are currently attracting considerable attention<sup>7</sup> because such species were observed by EPR

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