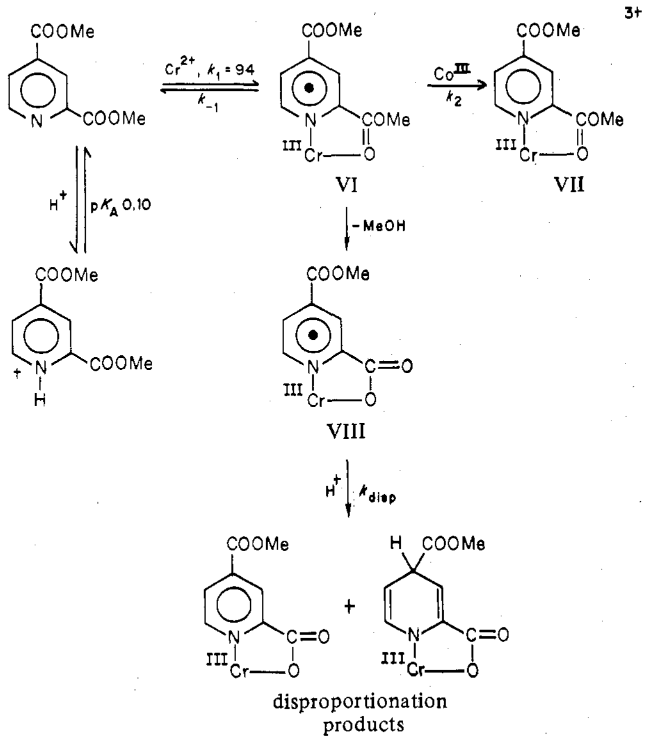
Scheme II



which should undergo rapid disproportionation in the same manner.[22-24]

Registry No. $Co(NH_3)_5py^{3+}$, 31011-67-3; $Co(NH_3)_5(pyrazole)^{3+}$, 38671-07-7; $Co(en)_3^{3+}$, 14878-41-2; N-CH_3-2,4-$(COOCH_3)_2(NC_5H_3)$, 65878-79-7; 2,4-$(COOCH_3)_2(NC_5H_3)$, 25658-36-0; 2,4-$(COOH)_2(NC_5H_3)$, 499-80-9; N-CH_3-2,4-$(COOH)_2(NC_5H_3)$, 62778-02-3; 2,5-$(COOH)_2(NC_5H_3)$, 100-26-5; 2,5-$(COOCH_3)_2(NC_5H_3)$, 881-86-7; 2,6-$(COOH)_2(NC_5H_3)$, 499-83-2; 3,4-$(COOH)_2(NC_5H_3)$, 490-11-9; 2,3-$(COOH)_2(NC_5H_3)$, 89-00-9; 4-$COOOH(NC_5H_4)$, 55-22-1; 3,5-$(COOH)_2(NC_5H_3)$, 499-81-0; 2-COOH-4-$CONH_2(NC_5H_3)$, 24195-08-2; Cr^{2+}, 22541-79-3; Eu^{2+}, 16910-54-6.

References and Notes

(1) Sponsorship of this work by the National Science Foundation (Grant CHE74-03876 AO1) is gratefully acknowledged.
(2) (a) J. R. Barber, Jr., and E. S. Gould, *J. Am. Chem. Soc.*, **93**, 4045 (1971); (b) C. Norris and F. Nordmeyer, *ibid.*, **93**, 4044 (1971); (c) Y.-T. Fanchiang, R. R. Carlson, P. K. Thamburaj, and E. S. Gould, *ibid.*, **99**, 1073 (1977).
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(14) The intercept of such a plot is $1/k_{lim}$, whereas the slope is $1/K_A k_{lim}$.
(15) R. W. Green and H. K. Tong, *J. Am. Chem. Soc.*, **78**, 4896 (1956), report that incorporation of a 2-COOMe group on the pyridine ring decreases pK_A of the parent heterocycle (pK_A 5.17) by 3 units, whereas incorporation of 4-COOMe decreases pK_A by 2 units. The pK_A 0.10, obtained here for the 2,4-diester, suggests that these substituent effects are additive.
(16) Note that as a consequence of the low k_2 value for $Co(en)_3^{3+}$, reductions of this complex, as accelerated by the diester, are first order in Co(III), whereas with the pyridine- and pyrazole-bound oxidants (see, for example, Table II), Co(III) dependency is less steep than that corresponding to a first-order relationship.
(17) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964).
(18) F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, **13**, 2647 (1974).
(19) This change almost certainly does not occur by substitution at the Cr(III) center, which is slow, but rather through redissociation of II to Cr^{2+} and the parent 2,4-diacid. The implication here is that the steady state involving the more stable radical II is more slowly established than that involving radical cation III.
(20) See, for example, E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964).
(21) See, for example, E. S. Gould, *J. Am. Chem. Soc.*, **90**, 1740 (1968).
(22) The proposed sequence for the formation of the blue product(s) from the diester in the absence of Co(III)

$$Cr^{2+} + Est \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} VI\cdot \xrightarrow{k_2} VIII\cdot$$

$$2VIII\cdot \xrightarrow{k_3} \text{products}$$

leads, assuming the steady-state approximation to be applicable to VI· and VIII·, to the rate law

$$\text{rate} = \frac{k_1 k_2 [Cr^{2+}][Est]}{k_2 + k_{-1}}$$

(23) Powerful catalysis of the hydrolysis of ester groups by coordinated metal ions has long been known.[24] Why such hydrolysis should occur in radical ion VI, but not in chelate VII, remains a puzzling point.
(24) See, for example: (a) H. Kroll, *J. Am. Chem. Soc.*, **74**, 2036 (1952); (b) M. L. Bender and B. W. Turnquest, *ibid.*, **79**, 1889 (1957).

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Electrochemistry of Iron Phthalocyanine Complexes in Nonaqueous Solvents and the Identification of Five-Coordinate Iron(I) Phthalocyanine Derivatives

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An electrochemical study (cyclic voltammetry, dc polarography, and differential-pulse polarography) of iron(II) phthalocyanine was carried out in pyridine, dimethyl sulfoxide, and dimethylacetamide with various supporting electrolytes. Oxidation to iron(III) and reduction to an iron(I) complex and an iron(I) phthalocyanine radical anion species were observed. Analysis of the cyclic voltammetry provided evidence for several following chemical reactions. The iron(I) complexes were shown to be five-coordinate and were characterized by electron spin resonance. A considerable dependence of the various redox couples upon the nature of the solvent and upon the supporting electrolyte was noted and explained. In this fashion back-donation was shown to be an important factor in the stabilization of the iron(II) species. The iron(I) phthalocyanines are low-spin d^7 complexes with a $d_{z^2}{}^1$ ground state. Superhyperfine coupling to axially coordinated pyridine, imidazole, and triphenylphosphine was observed.

It is now well established[1] that redox processes of iron-containing moieties play an indispensable role in biological electron-transfer processes. Intimately involved with this role is the ability of molecules such as hemoglobin and myoglobin

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Table I. Voltammetric Data[a] for Phthalocyanatoiron(II)

Solvent	Supporting electrolyte	Fe^{III}/Fe^{II}		Fe^{II}/Fe^{I}		$Fe^{I}Pc/Fe^{I}Pc(-3)$	
		E_{mp}, V	Δ_p,[b] mV	E_{mp} or $E_{1/2}$,[c] V	Δ_p,[b] mV	E_{mp} or $E_{1/2}$,[c] V	Δ_p, mV
py	TEAP	0.661	108 (0.99)	−1.069	53	−1.316	67
				−1.073 (58)[d]		−1.324 (57)[d]	
	TEABr	*e*		−1.053	66	−1.283	72
	LiCl	*e*		−1.084	77	*e*	
Me_2SO	TEAP	0.457	71	−0.711	68 (1.1)	−1.151	
				−0.869 (78)[d,f]		−1.169 (59)[d]	
	TEABr	0.394	84	−0.774	81	−1.165	68
	LiCl	0.352	72	−0.689	64	−1.109	70
DMA	TEAP	0.377	83	−0.549		−1.169	
				−0.912 (67)[d,f]		−1.143 (58)[d]	
	TEABr	0.168	68	−0.858	72	−1.194	65
	LiCl	−0.153	71	−0.641	70 (1.0)	−1.129	63

[a] For data collection information, see text. Data without a superscript were obtained at a platinum electrode. [b] Cathodic–anodic peak separation at 0.01 V/s scan rate—coulometry *n* value in parentheses. [c] $E_{1/2}$ values at DME; E_{mp} values for Pt (see footnote 8). [d] Data at a dropping-mercury electrode—slope of plot of log $[i/(i_d - i)]$ vs. E in parentheses. [e] No reproducible peaks observed. [f] Severe adsorption observed. To assess the possible variation in liquid-junction potentials, the half-wave potential for the ferrocene/ferrocenium couple was investigated in some of the above systems: py/TEAP, 0.5 V; py/LiCl, 0.68 V; Me_2SO/TEAP, 0.47 V; Me_2SO/LiCl, 0.51 V; Me_2SO/TEABr, 0.50 V. Dropping-mercury experiment utilized tetrabutylammonium perchlorate.

to transport molecular oxygen through the formation of molecular-oxygen adducts. Despite considerable effort,[2] the electronic and structural features which confer upon a molecule the ability to reversibly bind molecular oxygen are still poorly understood. However, it seems clear that the Fe^{II}/Fe^{III} redox couple must lie within a fairly narrow range near 0.0 V vs. SCE to possess this reversible binding capability in solution. Innumerable studies have appeared dealing with the redox electrochemistry of iron porphyrins.[3] It is evident that included among the factors which determine the potential of the Fe^{II}/Fe^{III} couple are the nature of the porphyrin and its side chains, the axial ligands if present, and any counterions present and also ion pairing, solvent, and oligomerization of the metalloporphyrin itself. Preliminary studies[4] with iron phthalocyanine,[5] a structural and electronic analogue of the iron porphyrins, led to the conclusion that this species might be generally more sensitive to some of these factors than the porphyrins themselves and therefore provide a more useful probe to investigate the influence of such factors. The detailed results of such a study are presented here. They include the behavior not only of the $Fe^{III}Pc(-2)/Fe^{II}Pc(-2)$ couple[6] but also of the $Fe^{II}Pc(-2)/Fe^{I}Pc(-2)$ and $Fe^{I}Pc(-2)/Fe^{I}Pc(-3)$ couples as a function of axial ligand (solvent) and counterion (supplied by the supporting electrolyte).

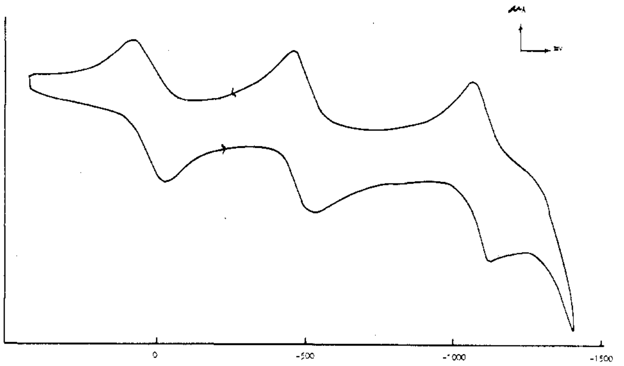

Figure 1. Equilibrium voltammogram for the system $Fe^{II}Pc$/DMA/LiCl (ca. 5 × 10^{-4} M). The lower half of the voltammogram involves reduction and the upper half oxidation.

Experimental Section

The iron(II) phthalocyanine was prepared according to standard procedures[5] and was purified by soxhlet extracting out the contaminants with methanol and then subliming the extract residue (400 × 10^{-6} mm). The product was sublimed a minimum of three times before use in electrochemistry. The solvents (pyridine (py), dimethyl sulfoxide (Me_2SO), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMA)) and supporting electrolytes (tetraethylammonium perchlorate (TEAP), tetraethylammonium bromide (TEABr), tetraethylammonium chloride (TEACl), and lithium chloride) were purified by standard techniques.[7] Ultrahigh-purity nitrogen (Linde) was used as the purging gas. Cyclic voltammetric data were obtained with a McKee-Pedersen (Danville, Calif.) modular electronic electrochemical system. A three-electrode configuration was employed, using platinum wires as working and auxiliary electrodes and a standard calomel electrode (SCE) as reference. The SCE was connected to the solution either by a double bridge containing saturated KCl solution adjacent to the SCE, and the solvent and supporting electrolyte adjacent to the solution, or by a porous Vycor rod, impregnated with solvent and supporting electrolyte. The reported midpoint potentials (E_{mp})[8] (i.e., average of anodic and cathodic peaks for each couple) are averages obtained over a series of scan rates from 0.005 to 50 V/s and over several different runs. The data were obtained from the first-scan cyclic voltammogram initiated, where possible, at the rest potential (zero current) and scanning each couple independently. Differential-pulse polarography and conventional dc polarography were obtained with a Princeton Applied Research Model 174A polarograph.

Controlled-potential coulometric experiments were performed with a variable constant-potential power supply and current integrator, built at York University and based on conventional circuits. The cell used for the coulometric experiments was a 100-mL beaker fitted with a tight-fitting Teflon cap, through which the nitrogen bubbler and outlet, the SCE reference electrode, and the connection to the working electrode were inserted. A side arm with a 7-mm O-ring joint was connected to the beaker to house the auxiliary electrode. The auxiliary electrode could then be separated from solution by placing a Kel-F cation- or anion-exchange membrane between the halves of the joint and then clamping the joint together with a spring clamp. The working electrode for controlled-potential oxidations was a platinum mesh cylinder, 3.5 cm in diameter by 5.0 cm in height. A mercury pool (5.0-cm diameter) was the working electrode for controlled-potential reductions. A platinum plate (2.0 × 4.0 cm) was used as the auxiliary electrode. For certain reductions, a combined electrochemical, visible, and ESR spectroscopic cell (Ace Glass) was used. The species produced were studied with a 12-in. magnet Varian E-line EPR spectrometer and a Varian Cary 14 spectrophotometer.

Results and Discussion

A typical cyclic voltammogram is shown in Figure 1. The important experimental parameters obtained for various solvents and supporting electrolytes are summarized in Table I. Over the scan width of the voltammograms, there are typically three pairs of peaks. Through consideration of the polarographic data we conclude that the most positive anodic wave corresponds to oxidation of the bulk solution and the two more negative cathodic waves to net reduction. The slopes of plots of log $[i/(i_d - i)]$ vs. E at a dropping-mercury electrode as well as controlled-potential coulometry indicated that each redox step involved a one-electron transfer.[9] Electronic spectra and electron spin resonance (ESR) spectra were employed to identify the species involved in each couple.

The bulk solution contained iron(II) phthalocyanine ($Fe^{II}Pc(-2)$) with coordinated solvent[5] and existed, therefore, as the six-coordinate, low-spin, diamagnetic $(solvent)_2Fe^{II}Pc(-2)$. With pyridine as solvent, this diamagnetic species may be isolated;[5] the other solvents bind more weakly and a six-coordinate species cannot be isolated in the solid state. We believe nevertheless that the species in DMA, Me_2SO, and DMF are six-coordinate because of the similarity of their electronic spectra with the spectrum obtained in the pyridine solution and because of the lack of similarity with the spectrum of $Fe^{II}Pc(-2)$ dissolved in chlorobenzene,[10] in which it must necessarily be square planar and four-coordinate.

(i) Most Positive Couple (within the Range −0.2 to +0.8 V). The anodic wave describes a net one-electron oxidation and is clearly attributable to $Fe^{III}Pc(-2)/Fe^{II}Pc(-2)$. The potential is certainly not sufficiently positive to arise from oxidation of the ring.[11]

Ferric phthalocyanines have not previously been unequivocally identified. The complex previously regarded to be $ClFe^{III}Pc(-2)$, prepared from ferrous phthalocyanine and hot hydrochloric acid, is now considered to be better defined[6] as $Fe^{II}Pc(-2)\cdot HCl$. Thus, electrochemical oxidation provides a convenient route to this series of compounds. However, the potential for this oxidation varies over a considerable voltage range (Table I) and is critically dependent upon both solvent and supporting electrolyte. Pyridine solutions provide the most positive potentials (+0.701 V) and it is clear that the iron(III) state in this solvent is unstable with respect to iron(II). Indeed, at slow scan rates there is a marked loss of current for the cathodic return wave. This is attributed to chemical reduction following electrochemical oxidation; i.e., some of the electrochemically generated ferric phthalocyanine is chemically returned to ferrous phthalocyanine before the return scan causes electrochemical reduction. When the system is cooled to ice temperature, the reduction to iron(II) is markedly slowed and, as a consequence, relatively larger cathodic currents are observed. The Fe(III) probably oxidizes pyridine to 2,2′-bipyridyl which is electrochemically inactive over the potential range studied. However, we did not pursue this avenue.

At the other extreme the potential for oxidation of iron(II) phthalocyanine in DMA containing chloride ion as a supporting electrolyte is negative (−0.132 V). Far from being unstable in this medium, the ferric state is so stable that solutions of ferrous phthalocyanine in DMA/Cl^- are air (oxygen) sensitive. Such a system provides the route of choice for entry into ferric phthalocyanine chemistry.[12] The ferric state is confirmed by its electronic spectrum, which differs from that of ferrous phthalocyanine (Figure 2) and is inconsistent with the cation radical,[6] and by its ESR spectrum, which is characteristic of six-coordinate low-spin iron(III) complexes.[13] The spectrum exhibits three resonances near $g = 2$ (in DMA/Cl $g_1 = 2.05$, $g_2 = 2.29$, and $g_3 = 2.68$). An ESR study of an electrochemically oxidized $Fe^{II}Pc$/py solution, in contrast to the DMA system mentioned above, shows only a weak free-radical $g = 2.003$ signal. This is attributed to some trace of oxidized organic species obtained through reaction of the highly oxidizing transient species $(py)_2Fe^{III}Pc(-2)$.

Initial voltammograms with varying scan sweep rate were analyzed using the treatment of Nicholson and Shain[14] (N-S). Nicholson and Shain[14] discussed various electrochemical mechanisms including, for example, reversible electron transfer and reversible electron transfer associated with a preceding or following reversible or irreversible chemical equilibrium. They showed that these and other mechanisms may be identified by cyclic voltammetry by analyzing the change in peak potentials and peak currents as a function of scan rate. Qualitative analyses of these variations provide a means of identifying the mechanism, while a more quantitative analysis can yield kinetic parameters. We have used these techniques in a qualitative fashion in this work to determine, primarily, when a solvent molecule is lost from the coordination sphere during an electrochemical process. The reader is referred to the original literature for details of these procedures[14] which will be referred to here as a "Nicholson–Shain analysis" (N-S). In our studies we considered the variation in current ratio i_a/i_c (Figure 3), anodic–cathodic peak separation, and cathodic peak potential as a function of scan rate. The oxidation wave is characterized through "Nicholson–Shain analysis" as a fast reversible electron transfer followed by a

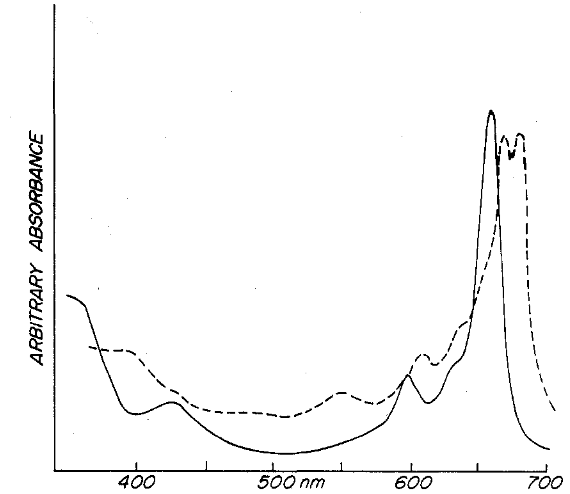

Figure 2. Electronic spectrum of iron phthalocyanine dissolved in DMA/LiCl before, —, (ferrous phthalocyanine) and after, - - -, addition of oxygen gas (ferric phthalocyanine).

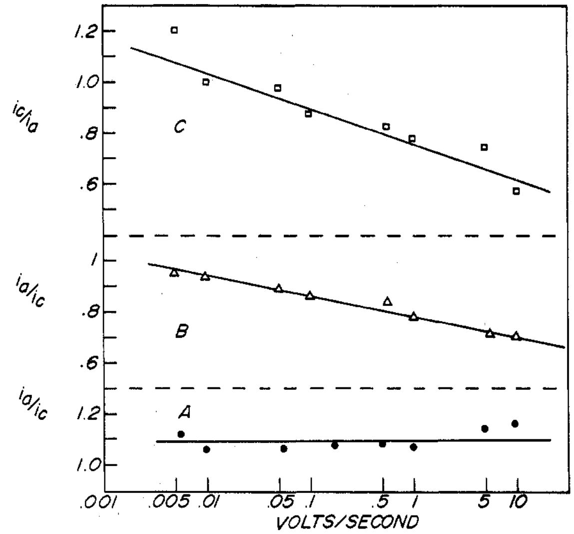

Figure 3. Nicholson–Shain plots for iron phthalocyanine in DMA/TEAP: A, $Fe^{I}Pc(-2)/Fe^{I}Pc(-3)$; B, $Fe^{II}Pc(-2)/Fe^{I}Pc(-2)$; C, $Fe^{III}Pc(-2)/Fe^{II}Pc(-2)$. A plot of the anodic:cathodic peak current ratio (i_a/i_c) vs. V/s. For the oxidation couple (Fe^{III}/Fe^{II}), the inverse ratio is plotted. These data were obtained from the first voltammetric cycle with the initial and turnover potentials adjusted to study each couple separately from the other two.

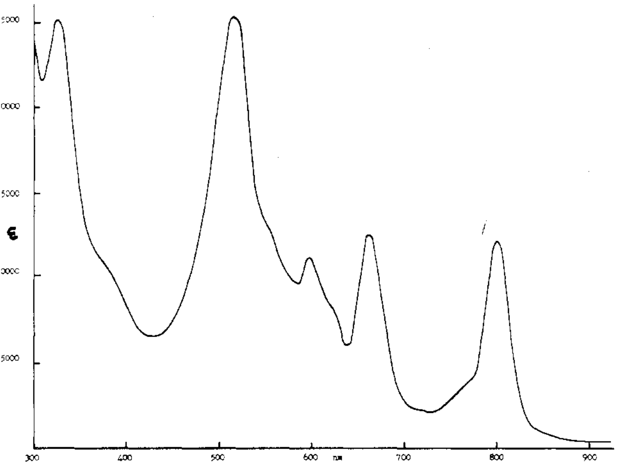

Figure 4. Electronic spectrum of (py)$Fe^{I}Pc(-2)$ in py/LiCl. The major peak and shoulder positions (cm^{-1}) (molar extinction coefficients in parentheses) are 30 615 (24 975), 26 572 sh, 19 405 (24 975), 16 800 (11 000), 16 250 sh, 15 130 (24 570), 13 890 sh, and 12 480 (11 880).

reversible chemical reaction. Thus, from these data and the ESR data we conclude that the following reactions occur

$$(\text{solvent})_2Fe^{II}Pc(-2) \rightleftharpoons [(\text{solvent})_2Fe^{III}Pc(-2)]^+ + e^- \qquad (1)$$

$$[(\text{solvent})_2Fe^{III}Pc(-2)]^+ + X^- \rightleftharpoons (\text{solvent})(X^-)Fe^{III}Pc(-2) + \text{solvent} \qquad (2)$$

This reaction pathway is further supported by the observation, discussed in detail below, that the potential of the couple is critically dependent upon the nature of X^-. Note that simple ion pairing would not show up in the N–S treatment as a following chemical reaction, since it is an extremely fast process (diffusion limited). Electrophoresis of the ferric phthalocyanine solution implies that the species is nonionic, though we doubt that equilibrium 2 will always lie fully to the right.

(ii) Reduction Couples (within the Range −0.5 to −1.4 V). Previous workers[15–17] have considered the reduction of iron phthalocyanine without arriving at a clear conclusion about the nature of the reduction products. The first reduction might reasonably lead to $Fe^{I}Pc(-2)$ or $Fe^{II}Pc(-3)$ (neglecting axial ligands). The reduction product once formed may be unstable with respect to disproportionation, though such an event should be detectable through product analysis. With "nonreducible" metals such as Zn, Clack and co-workers observed two reduction waves between 0 and −1.4 V attributed to the first- and second-ring reductions with electrons entering the lowest empty e_g orbital on the phthalocyanine ring.[5] Curiously, they were unable to observe[15] any redox waves in this region with iron(II) phthalocyanine,[18] the first wave appearing at −1.56 V (DMF/ClO_4). We had no difficulty in observing two reduction waves prior to the −1.56-V wave, which we also detected but did not investigate further. Clack and Yandle[16] prepared the first two reduction products by chemical reduction of iron(II) phthalocyanine with a sodium film. The electronic spectra they reported for these species are closely similar to those spectra we recorded for the first two electrochemically generated species. Taube[17] isolated these two products as their lithium salts, with tetrahydrofuran of crystallization, and reported their magnetic moments. He did not report electronic spectra but did comment on the colors of the solutions and solids, which were invariably different from one another. The solid-state magnetic data will not necessarily agree with the magnetic properties predicted for these species, once identified. The electronic structure in the solid state, influenced by lattice energy, may not be the same as the electronic structure in solution. Taube's solution colors do agree with those observed here and by Clack and Yandle.[16]

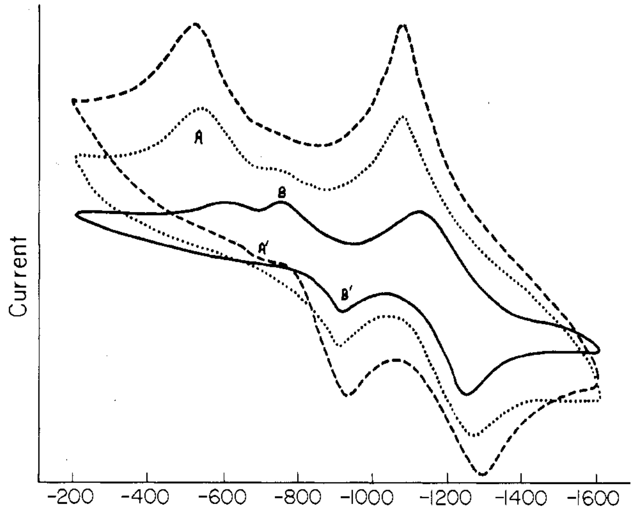

Figure 5. Variable-scan-rate data for the system $Fe^{II}Pc/DMA/TEABr$, illustrating the effect of scan rate upon the first and second reduction couples. Scan rates from lower to upper curves are 0.1, 10, and 50 V/s, respectively. Wave A does not appear in a voltammogram scanned at 0.01 V/s. The lower half of each curve involves reduction.

These two species have colors dominated by intense absorption near 19 000 cm^{-1} (Figure 4). While such bands are characteristic of phthalocyanine anion radicals,[19] one may also expect perturbation of the conventional phthalocyanine spectrum by low-valency metal ions to induce similar shifts.

(a) First Reduction Product. This is characterized by its electron spin resonance spectrum (see below for full details) as a five-coordinate complex of low-spin d^7 iron(I), namely, (solvent)$Fe^{I}Pc(-2)$.

The alternative, that the first reduced species is (solvent)$_2Fe^{II}Pc(-3)$, an anion radical, is excluded since this species, having a diamagnetic iron center, would exhibit an isotropic free-spin ESR signal. At low scan rates this couple generates a pair of waves. N–S analysis infers a reversible electron transfer followed by a reversible chemical reaction. This is in agreement with the postulate of reduction of the six-coordinate iron(II) complex to a six-coordinate iron(I) species which then loses a ligand to form the final five-coordinate product. However, at higher scan rates, a second pair of waves appears (Figure 5). The relative peak heights of the two pairs of waves are dependent upon scan rate (Figure 5). Allowing for the formation of a five-coordinate iron(I) species allows us to invoke the equilibria

$$(\text{solvent})_2Fe^{II}Pc(-2) + e^- \rightleftharpoons (\text{solvent})_2Fe^{I}Pc(-2) \qquad (3)$$

$$(\text{solvent})_2Fe^{I}Pc(-2) \rightleftharpoons (\text{solvent})Fe^{I}Pc(-2) + \text{solvent} \qquad (4)$$

$$(\text{solvent})Fe^{I}Pc(-2) \rightleftharpoons (\text{solvent})Fe^{II}Pc(-2) + e^- \qquad (5)$$

$$(\text{solvent})Fe^{II}Pc(-2) + \text{solvent} \rightleftharpoons (\text{solvent})_2Fe^{II}Pc(-2) \qquad (6)$$

The ease of oxidation of a low-spin d^7 complex depends to a substantial degree upon how destabilized is the d_{z^2} orbital containing the odd electron. On this basis, couple 3, having six-coordinate iron, will undoubtedly lie at more negative potentials than couple 5 (also see solvent dependence discussion below). We therefore associate equilibrium 3 with couple B, B′ and equilibrium 5 with couple A, A′ in Figure 5.

Reduction of the six-coordinate iron(II) species (eq 3) leads to rapid loss of a ligand (eq 4). At slow scans, on the reverse sweep, there is time for reaction 4 to proceed to a large degree to the left; hence wave B is more prominent than wave A. At high scan rates, there is insufficient time for reaction 4 to proceed to the left, allowing reaction 5 to dominate; hence wave

A is more intense than wave B. The existence of wave A′ as a weak feature at high scan rates implies that equilibrium 6 does not proceed so rapidly to the right. There is some five-coordinate iron(II) species left at the electrode, at high sweep rates, to be reduced.

(b) The Second Reduction Product. We entertain the possibilities $Fe^{II}Pc(-4)$, $Fe^{I}Pc(-3)$ and, possibly, $Fe^{0}Pc(-2)$. Necessarily all these species possess an even number of electrons and are expected to be ESR quiet at least down to liquid-nitrogen temperature.

The voltage separation between the first and second reduced species varies from about 0.2 V in pyridine to about 0.6 V in DMA. The voltage separation between the second and third reduced species,[15] the last believed to be the dianion, is about 0.4 V. The voltage separation between phthalocyanine mono- and dianions has been observed[15] to be about 0.4 V. This separation is unlikely to be solvent dependent. These data lead to the conclusion that the second reduced species is $Fe^{I}Pc(-3)$. While these specific data do not entirely rule out $Fe^{II}Pc(-4)$, such a species does seem excluded by a detailed study of the nature of the second reduction wave. A Nicholson–Shain analysis reveals this wave, for most of the solvent/supporting electrolyte systems, to be a reversible charge transfer with little evidence for a subsequent chemical reaction.

The anodic:cathodic peak current ratio is essentially unity over several decades of scan rate (Figure 3A). For most systems the anodic–cathodic peak separation is close to 60 mV and is essentially independent of scan rate. In a few cases the change in cathodic peak potential with change in scan rate is not zero, as would be expected for a simple reversible charge transfer,[14] but does show a little dependence upon scan rate. We conclude that although there may, in some cases, be some subtle secondary process occurring, the most important component of the reaction is reversible electron transfer without a coupled chemical reaction. This is consistent with the process

$$\text{(solvent)}Fe^{I}Pc(-2) + e^- \rightleftharpoons \text{(solvent)}Fe^{I}Pc(-3) \qquad (7)$$

in which no change of axial ligands is involved. If an iron(II) complex were to be formed, it would surely possess two axial ligands, viz.

$$\text{(solvent)}Fe^{I}Pc(-2) + e^- \rightleftharpoons \text{(solvent)}Fe^{II}Pc(-4) \qquad (8)$$

$$\text{(solvent)}Fe^{II}Pc(-4) + \text{solvent} \rightleftharpoons \text{(solvent)}_2Fe^{II}Pc(-4) \qquad (9)$$

and this solvent binding would show up in the voltammogram as a following chemical reaction.

(c) Reduction at a Dropping-Mercury Electrode. For comparative purposes, data are also included in Table I for some systems using a dropping-mercury electrode and conventional dc polarography. A plot of log $[i/(i_d - i)]$ vs. E gave, in most cases, a slope near 59 mV indicative of the expected one-electron reduction. The $E_{1/2}$ values were obtained from such plots and also by differential-pulse polarography at the DME. In all but two cases, these agreed reasonably well with the values obtained at a platinum electrode. The exceptions were the potentials of the first reduction wave in Me_2SO and in DMA. However, both of these waves showed severe adsorption problems which undoubtedly account for the discrepancies. No adsorption was observed for the other waves.

Solvent and Supporting Electrolyte Dependence. The redox waves reflect, in various degrees, the following principles. Where trivalent or higher species are formed, the supporting electrolyte becomes the counterion for the higher oxidation state species and a dependence of half-wave potential upon supporting electrolyte is observed. This is clear, for example, with the $Fe^{III}Pc(-2)/Fe^{II}Pc(-2)$ couple. The potential of this couple shifts negatively in the sequence

$$ClO_4^- < Br^- < Cl^- \qquad (10)$$

due to reaction 2. The sequence (10) reflects increasing electronegativity of the ion favoring the higher oxidation state. The other couples do not have an appreciable dependence upon supporting electrolyte.

The solvent dependence is explainable in terms of the π-acceptor capability of the phthalocyanine ring.[4] Strongly donating solvents, acting as axial ligands, enhance the capability of the metal to back-donate to the phthalocyanine ring. Donation by these ligands increases in the order[20]

$$\text{DMA} = \text{DMF} < Me_2SO < \text{py} \qquad (11)$$

The ferrous state is stabilized in this sequence as the iron atom back-donates more charge to the ring, and hence the potential of the Fe^{III}/Fe^{II} couple becomes more positive. Presumably, back-bonding is not very important with the more positively charged iron(III). Had a σ mechanism been important, the reverse effect would have been expected, with the ferric state being favored by the best donor ligand. Thus, the observed data unequivocally indicate that the π mechanism is dominant with iron. We note that equilibrium 2 will shift to the left with the more strongly donating ligands, facilitating the shift to more positive potentials.

The $Fe^{II}Pc(-2)/Fe^{I}Pc(-2)$ couple is also highly solvent dependent, but now the pyridine provides the most negative potential; i.e., the sequence is the inverse of the oxidation wave. The solvent dependence reflects the destabilization of the d_{z^2} electron as the donicity of the ligand increases. This is a σ mechanism, which, however, is synergistically enhanced by the resulting high stabilization of the iron(II) state in most donor solvents. The two effects act in concert and provide the considerable solvent dependence observed. It is clear from the above discussion that iron redox couples may be "tuned" over a considerable potential range by changes of environment. Similar, though noticeably less pronounced, trends have been observed with iron porphyrins.[3a,21] There is a putative biological role for such tuning in that conformational changes in the protein component of a cytochrome may alter the environment of the iron atom sufficiently to significantly alter the potential of the Fe^{II}/Fe^{III} couple.

Iron(I) Phthalocyanines. Controlled-potential reduction in any one of the above systems at a voltage about 200 mV more negative than the first reduction wave generates a purple reduction product. These species possess an ESR spectrum characteristic of a low-spin d^7 ion and must, therefore, be regarded as derivatives of iron(I) phthalocyanine(−2).

Many four-, five-, and six-coordinate cobalt(II) porphyrins possess this low-spin d^7 configuration and their ESR spectra have been extensively studied.[22-25] Such complexes commonly have the odd electron in the axially directed d_{z^2} orbital. In such circumstances $g_\perp$ is invariably above 2.0 and depends upon the spin–orbit coupling coefficient λ (which is negative) and the energy separation between the d_{z^2} and d_{xz}, d_{yz} orbital (energy separation between $^2A_1$ and ^2E (ΔE)) according to

$$g_\perp = 2.002 - 6\lambda/\Delta E \qquad (12)$$

The magnitude of $g_\parallel$ is also dependent upon ground-state coupling to the ^2E state.[23] For large tetragonal distortion $g_\parallel$ is generally less than 2.0 whereas $g_\perp$ may be greater than 3.0. Both numbers approach 2.0 as the distortion decreases. Indeed $g_\parallel$ may increase above 2.0 but is always less than $g_\perp$ in a tetragonal complex.[22]

The alternative ground state $^2B_2$, with the odd electron in the d_{xy} orbital, has not been positively identified in this series of complexes. It is expected[23] to exhibit $g_\parallel$ below 2.0 and $g_\perp$ a little above 2.0. The magnitudes of the g factors themselves do not always allow a definitive distinction between the two possible ground states, at least in the absence of a detailed

Table II. Electron Spin Resonance Spectra of Iron(I) Phthalocyanine Derivatives $LFe^{I}Pc(-2)$

L[a]	Solvent/carrier[b]	$g_{\parallel}$	$g_{\perp}$	$\lvert A_L \rvert$,[c] cm^{-1}
Me_2SO	Me_2SO/TBAP	1.961	2.077	
Ph_3P	Me_2SO/TBAP	1.958	2.077	0.0122
py	py/LiCl	1.956	2.119	0.0012
DMA	DMA/LiCl	1.953	2.119	
im	DMA/LiCl	1.956	2.112	0.0012

[a] Triphenylphosphine (Ph_3P) and imidazole (im) were added to previously electrochemically prepared iron(I) phthalocyanine solutions to obtain these species. [b] Solvent/carrier system used to generate the iron(I) species (TBAP = tetrabutylammonium perchlorate). [c] A triplet signal was observed for pyridine and imidazole and a doublet for triphenylphosphine.

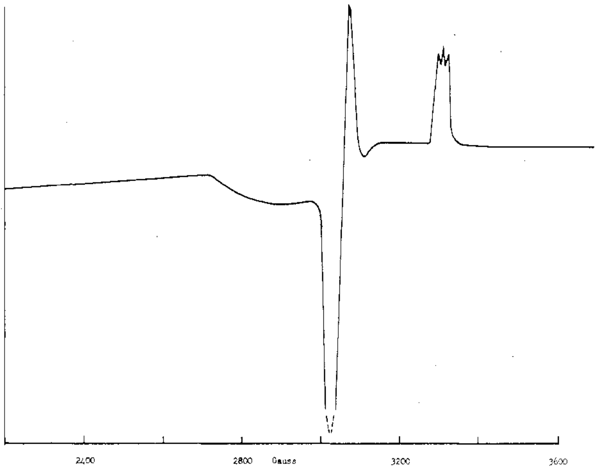

Figure 6. ESR spectrum of $(py)Fe^{I}Pc(-2)$ in pyridine/LiCl, at liquid-nitrogen temperature (receiver gain 1.6 × 10^4, modulation amplitude 10 G, frequency 9.070 GHz).

calculation. However, for five- or six-coordinate complexes when the axial ligand donor atom possesses a nonzero nuclear moment, this may couple to an odd electron in the d_{z^2} orbital but is not expected to couple to an odd electron in the d_{xy} orbital ($^2B_2$ ground term). Such coupling is frequently observed.[22,25]

The ESR spectra of the iron(I) species reported here (Table II) are consistent with a moderately distorted environment which by analogy with the cobalt(II) data alluded to above suggest four- or five-coordination. The observation of superhyperfine coupling to the nitrogen atoms of pyridine (Figure 6) and of imidazole (Table II) and specifically the observation of triplets rather than quintets confirm a five-coordinate system with a $^2A_1$ ground term. The magnitude of the superhyperfine coupling to the axial nitrogen ligands is typical of that observed with cobalt(II) porphyrins.[22,25]

In Me_2SO solution, but not in DMA or pyridine, we recorded an additional fairly strong signal at free spin $g = 2.002$. This must presumably arise from the presence of some electronically isomeric $(Me_2SO)_2Fe^{II}Pc(-3)$. Addition of triphenylphosphine to the Fe^{I}/Me_2SO system decreased the relative height of this free-spin absorption. In addition, the single line at $g_{\parallel} = 1.961$ (arising from $(Me_2SO)Fe^{I}Pc$) was replaced by an equal-intensity doublet centered at $g_{\parallel} = 1.940$, ascribed to $(Ph_3P)Fe^{I}Pc$. The superhyperfine coupling to phosphorus-31 (Table II) is appreciably less than that observed in tributylphosphine and trimethyl phosphite complexes of Co(TPP).[25] The existence of a doublet again infers a five-coordinate derivative. In contrast to the Co(TPP) system[25] there appears to be no phosphorus coupling to the perpendicular absorption.

The somewhat smaller spin–orbit coupling coefficient of iron(I) relative to cobalt(II) probably explains why $g_{\perp}$ is not as large as in comparable cobalt(II) complexes.

These solutions also exhibit additional, relatively weak, absorption at somewhat higher g (see Figure 6) which may be accompanied by additional weak absorption below $g = 2.0$ (especially in DMA without additional ligands). These signals are independent of the axial ligand and are tentatively attributed to four-coordinate planar iron(I) phthalocyanine which would be expected to exhibit such higher g absorption and which is presumably in equilibrium with the five-coordinate species. The signal is most clearly seen in Me_2SO solution and is evidently a multiplet.

It is curious that, despite the agreement in electronic spectra, Clack and Yandle in an earlier study[26] were unable to observe an ESR spectrum for singly reduced iron phthalocyanine. Shortly thereafter, Symons and co-workers[27] did indeed observe an ESR spectrum for iron phthalocyanine reduced by Na/THF, but it was a nine-line spectrum near free-spin g, very different from the spectrum we observe. We are at a loss to understand this observation unless Symons and co-workers inadvertently obtained more highly reduced anionic species.

Reduction of iron tetraphenylporphyrin[3c,28] leads to an iron(I) tetraphenylporphyrin derivative whose ESR spectrum is indicative of a low-spin d^7 ion. While $g_{\parallel}$ is slightly lower than for iron(I) phthalocyanine, $g_{\perp}$ is significantly larger (2.2–2.3). Moreover, no superhyperfine coupling could be observed to potentially axially coordinating ligands such as imidazole. It appears that the iron(I) tetraphenylporphyrin is indeed four-coordinate and presumably square planar.[3e] The existence of five-coordinate iron(I) phthalocyanines as opposed to four-coordinate iron(I) tetraphenylporphyrins may be explained in terms of the greater acceptor character of iron(I) when it is bound to the electron-withdrawing phthalocyanine unit vs. the more electron-donating porphyrin unit.[4] This view is further justified by the potentials of the Fe^{II}/Fe^{I} reduction couples themselves, the porphyrin being some 500 mV more negative than the phthalocyanine.[3e]

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Registry No. $(py)_2Fe^{II}Pc(2-)$, 20219-84-5; $(DMA)_2Fe^{II}Pc(2-)$, 65651-14-1; $(Me_2SO)_2Fe^{II}Pc(2-)$, 24804-11-3; $(DMF)_2Fe^{II}Pc(2-)$, 65651-15-2; $(Me_2SO)Fe^{I}Pc(2-)$, 65651-16-3; $(Ph_3P)Fe^{I}Pc(2-)$, 65651-17-4; $(py)Fe^{I}Pc(2-)$, 65651-18-5; $(DMA)Fe^{I}Pc(2-)$, 65651-19-6; $(im)Fe^{I}Pc(2-)$, 65651-20-9; $(py)(ClO_4)Fe^{III}Pc(2-)$, 65651-21-0; $(py)BrFe^{III}Pc(2-)$, 65651-22-1; $(py)ClFe^{III}Pc(2-)$, 65651-23-2; $(Me_2SO)(ClO_4)Fe^{III}Pc(2-)$, 65651-24-3; $(Me_2SO)BrFe^{III}Pc(2-)$, 65651-25-4; $(Me_2SO)ClFe^{III}Pc(2-)$, 65651-32-3; $(DMA)(ClO_4)Fe^{III}Pc(2-)$, 65651-29-8; $(DMA)BrFe^{III}Pc(2-)$, 65651-30-1; $(DMA)ClFe^{III}Pc(2-)$, 65651-31-2.

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Extrathermodynamic Relationships in Copper(II) Chelate Promoted Hydrolysis of Methyl Glycinate

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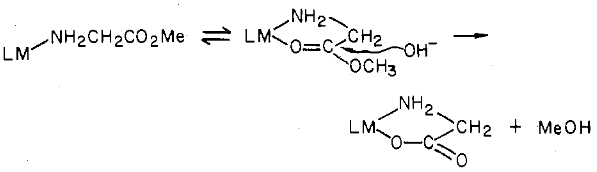
The second-order rate constants, rate = $k_{OH}[Cu(L)(MeGly)^{x+}][OH^-]$, for the hydrolysis of a series of methyl glycinate complexes of copper(II) chelates were determined as were their activation parameters. Tridentate and tetradentate copper(II) chelates fall on different isokinetic lines suggesting differing mechanisms or rate profiles. Both the strength of the donor atoms of the auxiliary ligands and the charge of the metal complex are shown to be important in determining the catalytic activity of the various copper(II) complexes.

Introduction

Metal-ion-promoted hydrolysis of amino acid esters has been studied by a number of research groups.[1-7] Three mechanisms have been proposed. One involves an initial rapidly established equilibrium in which ester group coordination occurs, followed by rate-determining OH^- attack (eq 1). The second involves rapid equilibrium formation of an M–OH complex, followed by intramolecular OH^- attack (eq 2). The third involves only OH^- attack on the coordinated ester (eq 3). In labile metal complex promoted reactions of amino acid esters, it has been very difficult to establish whether one or a combination of the above mechanisms is involved in the observed hydrolyses. It is for this reason that we have initiated a series of studies into extrathermodynamic relationships associated with metal chelate promoted hydrolysis of amino acid esters. Recently, we have determined[7,8] two isokinetic temperatures for three differing series of metal chelates. In this study a variety of tridentate and tetradentate Cu(II) chelates were studied in hopes of gaining some insight into the mechanism(s) involved and the auxiliary ligand features which possibly dictate the mechanism of hydrolysis.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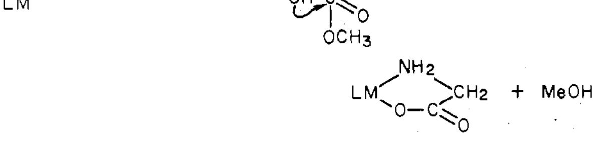
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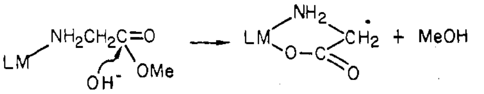
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Experimental Section

Reagents. Baker Analyzed reagent grade $Cu(NO_3)_2 \cdot 3H_2O$ was used for all metal solutions, which were standardized via standard ion-exchange techniques. Aliquots of the metal ion solution were passed through Dowex 50W-X8 strongly acidic cation-exchange resin, and the effluent solutions were titrated with standard NaOH solutions using phenolphthalein as an indicator.

The trihydrochloride salt of 2,2′,2″-triaminotriethylamine (tren·3HCl) was purchased from Strem Chemicals, Inc., and the hydrochloride salt of methyl glycinate (MeGly·HCl) and glycine (Gly) were obtained from Sigma Chemical Co. Nitrilotriacetic acid (NTA) was purchased from ICN Pharmaceuticals, and terpyridine (terpy) was purchased from K and K Laboratories. The above compounds were of the highest purity available and were used without further purification. Solutions of Cu^{II}terpy were prepared by addition of weighed amounts of ligand, that had been dried overnight in a desiccator (H_2SO_4) at 50 °C, to metal ion solutions.

The trihydrochloride salt of diethylenetriamine (dien·3HCl) was prepared by the addition of HCl to 50/50 C_2H_5OH/H_2O solutions of dien, which had been vacuum distilled according to Perrin.[9] Second

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