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Electron-Transfer and Ligand-Addition Reactions of (*meso*-Tetraphenylporphinato)manganese(II) and -manganese(III) Chloride

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The electron-transfer and ligand-addition reactions of (*meso*-tetraphenylporphinato)manganese(II) and -manganese(III) chloride were investigated by polarography and cyclic voltammetry in dichloromethane. A mechanism of electron transfer was proposed in both the presence and absence of nitrogenous base. Formation constants for binding of six different substituted pyridines by Mn(II) and Mn(III) were calculated. Under the experimental conditions only five-coordinate complexes existed in solution. Binding of the substituted pyridine to (TPP)MnCl produced the complex $[(TPP)MnL]^+$ rather than (TPP)Mn(L)(Cl). In all cases K_1 for (TPP)MnL formation was greater than that for $[(TPP)MnL]^+$. A linear correlation between the log of the formation constant of the pentacoordinate complex and the pK_a of the added ligand was found.

During recent years the electron-transfer properties of synthetic porphyrins have been extensively reported in the literature.[1] The thermodynamic half-wave potentials, electrochemical reversibility of these electron-transfer reactions, and the overall electrode mechanism are dependent on a number of factors: the type of electrode reaction, i.e., π radical or metal centered; the solvent composition; the degree of axial ligation; the overall porphyrin basicity. Electrode reactions of over 30 different metalloporphyrins have been characterized with the most extensive characterization being reactions of iron, cobalt, and manganese complexes.

Recently several papers have been published which suggest a relationship between potentials for metalloporphyrin oxidation and dioxygen binding ability of the five- or six-coordinate transition-metal complex.[2,3] For porphyrin complexes containing Fe, Cr, or Co the electrochemical ease of oxidation, metal(II) $\rightleftharpoons$ metal(III), varies in the order Cr(II) > Fe(II) > Co(II)[4] which is the order of O_2 binding by the metal ion. Mn(II) has an oxidation potential between Fe(II) and Cr(II) but yields a log K_{O_2} several orders of magnitude less than that predicted from the half-wave potentials.[3] From the literature we know that half-wave potentials for the Co(III)/Co(II) or the Fe(III)/Fe(II) couple as well as the degree of dioxygen binding vary directly with the strength of the nitrogenous base and/or stability constants for formation of the five- or six-coordinate complexes.[5-8] In this context, it is of some interest to understand the relationships between redox potentials and stability constants for axial ligand addition.

In earlier papers, we reported the effect of axial ligand binding on half-wave potentials and electron-transfer kinetics for oxidation of Fe(II),[6,7,10] Co(II),[6,8] and Mn(II)[11] metalloporphyrins. This latter study involved the reactions of chloro[tetrakis(*p*-chlorophenyl)porphinato]manganese(III), ((*p*-Cl)TPP)MnCl, in Me_2SO–imidazole mixtures. In this mixed solvent system the electron-transfer rate constant significantly decreases with increasing imidazole concentration (presumably due to axial complexation). In the presence of 1 M imidazole the rate constant is almost 3 orders of magnitude slower than the corresponding standard rate constant in neat Me_2SO. Unfortunately, due to the extremely irreversible electron transfer, no information on stoichiometry or complex stability could be obtained from this initial study.

In the nonbonding solvent dichloromethane a similar decrease in rate constant for the Mn(III)/Mn(II) reduction is observed upon pyridine complexation. However, the decrease in $k°$ does not occur until much higher ligand concentrations and clear-cut information can be obtained regarding the stoichiometry of the reacting complexes at low ligand concentrations.[12] In this paper, we describe electrode reactions where either the reactant, the product, or both reactant and product involve five-coordinate manganese porphyrins. The reversible electrode reactions which are described can be written as follows:

$$L + (TPP)MnCl \overset{e^-}{\rightleftharpoons} (TPP)MnL + Cl^- \tag{1}$$

$$(TPP)MnL^+ \overset{e^-}{\rightleftharpoons} (TPP)MnL \tag{2}$$

where TPP^{2-} represents the unsubstituted tetraphenylporphyrin and L is pyridine or substituted pyridine. We have limited our discussion to reactions involving only the Mn(III) $\rightleftharpoons$ Mn(II) electrode reactions.

Experimental Section

Cyclic voltammograms and polarograms were obtained on a EG&G Princeton Applied Research Model 174 polarographic analyzer in conjunction with a Houston Instruments Model 2000 X-Y recorder. A three-electrode system was used, consisting of a platinum working electrode for cyclic voltammetry or a dropping mercury electrode (DME) for polarography, a platinum counterelectrode, and a commercial saturated calomel electrode containing aqueous lithium chloride fill solution (Radiometer Type K 901) (SLCE). The SLCE was separated from the bulk of the solution by a bridge filled with solvent and supporting electrolyte. Solutions in the bridge were changed periodically to avoid aqueous contamination from entering the cell via the SCE. Spectroscopic measurements were taken on either a Cary 14 or a Beckman Model 26 spectrophotometer using cells of 1.0 and 0.5 mm thickness. All spectrophotometric measurements were made on solutions containing 0.1 M TBAP. Stability constants were determined from the shifts of half-wave potentials as a function of ligand concentration. The method of calculation has been described in previous publications.[6,13]

Tetrabutylammonium perchlorate, TBAP, and tetraethylammonium chloride, (TEA)Cl (Eastman Chemical Co.), were dried at 40 °C under vacuum. 4-Cyanopyridine was recrystallized from benzene or benzene–heptane mixtures. Pyridine, 3-chloropyridine, and 3-bromopyridine were distilled over KOH. Dichloromethane, CH_2Cl_2, and all other substituted pyridines were used without further purification. (Tetraphenylporphinato)manganese(III) chloride, (TPP)MnCl, was synthesized by the method of Adler et al.[14] Solutions were purged of oxygen by passing purified nitrogen through them prior to running cyclic voltammograms and polarograms. After degassing of the solution, a blanket of nitrogen was kept over the solution. All experiments were carried out in a controlled temperature room of 22 ± 1 °C and potentials are reported with respect to the lithium chloride saturated calomel electrode (SLCE).

Results and Discussion

Reduction of (TPP)MnCl in CH_2Cl_2 yielded a well-defined polarographic wave at $E_{1/2} = -0.33$ V (Figure 1a). No other oxidation or reduction was observed between +1.2 and −1.4 V. As reported for other solvents,[15] diagnostic plots of the polarographic maximum current vs. $h^{1/2}$ were linear, indicating diffusion control.[16] However, the wave shape was broader than predicted for a reversible one-electron transfer and gave a quasi-reversible separation of $E_{3/4} - E_{1/4} = 105 \pm 10$ mV.[16] Cyclic voltammograms of (TPP)MnCl were recorded at

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Table I. Formation Constant for Complexation of (TPP)MnCl and (TPP)Mn with Substituted Pyridines

no.	ligand	pK_a	σ[a]	log (formation constant)	
				(TPP)MnL[b]	$(TPP)MnL^+$[c]
1	4-cyanopyridine	1.86[d]	0.66	1.14	0.43
2	3-bromopyridine	2.84[d]	0.391	1.85	0.43
3	pyridine	5.27[e]	0.00	2.70	1.10
4	3-picoline	5.63[f]	−0.069	3.36	1.68
5	4-picoline	6.03[f]	−0.170	3.24	1.97
6	3,4-lutidine	6.46[e]	−0.239	2.99	1.72

[a] John A. Dean, "Lange's Handbook of Chemistry", 79th ed, McGraw-Hill, New York, 1973. [b] Reaction: $(TPP)MnCl + L \rightleftarrows (TPP)MnL^+ + Cl^-$. [c] Reaction: $[(TPP)MnCl]^- + L \rightleftarrows (TPP)MnL + Cl^-$. [d] K. Schofield, "Hetero-Aromatic Nitrogen Compounds", Plenum Press, New York, 1967, p 146. [e] A. Albert, *Phys. Methods Heterocycl. Chem.*, 1, 1 (1963). [f] Z. Rappoport, "Handbook of Tables for Organic Compound Identification", 3rd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967.

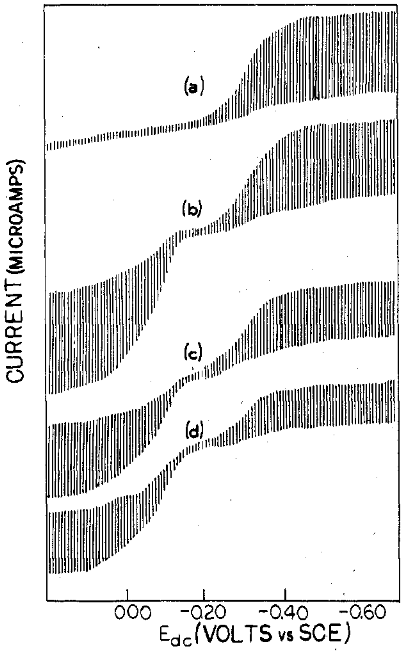


Figure 1. Polarograms of (a) 1.3×10^{-3} M (TPP)MnCl in CH_2Cl_2, (b) initial solution + 1.0×10^{-3} M (TEA)Cl, (c) 1.0×10^{-3} M (TPP)MnCl in Me_2SO, and (d) 0.73×10^{-3} M (TPP)MnCl in pyridine. All solutions contain 0.1 M TBAP as supporting electrolyte. Drop time = 1.0 s.

several scan rates and confirmed a quasi-reversible electron transfer. The reduction and reverse oxidation peaks were well defined, but separated by approximately 100–200 mV depending on scan rate. The ratio of $i_{p,a}/i_{p,c}$ was equal to unity indicating the absence of coupled chemical reactions.[17]

Similar reduction waves were obtained at a DME in Me_2SO (Figure 1c) and pyridine (Figure 1d). In these solutions, however, an oxidation wave was observed at about −0.05 V whose height was directly proportional to the concentration of (TPP)MnCl and which appeared to involve both the mercury electrode and the chloride ion from (TPP)MnCl. This was confirmed by addition of (TEA)Cl to solutions containing (TPP)MnCl. Addition of (TEA)Cl produced a mercury oxidation peak whose height was directly proportional to the concentration of added Cl^- (Figure 1b). Similar increases in the anodic polarographic current were also observed upon additions of (TEA)Cl to pyridine or Me_2SO solutions. However, as expected, no anodic oxidation process was obtained when a platinum electrode was used.

Effect of Solvent on Chloride Association. The X-ray structure of (TPP)Mn has been reported. The Mn(III) ion is five-coordinate with Mn removed from the porphyrin plane by about 0.23 Å toward the chloride.[18] Crystallographic data also show that a six-coordinate mixed-ligand complex may be formed on complexation with pyridine. The Mn(III) ion in this complex is displaced only 0.145 Å from the mean porphyrin plane toward the Cl and a pyridine molecule is bound trans to the Cl.[19] However, there is no evidence that mixed-ligand complexes of halides and pyridine are present in solution nor can we say much about metal–ligand distance in solution. Addition of (P)MnCl, where P = etioporphyrin, to a strongly bonding ligand or solvent molecule S, results in a displacement of the chloride ion according to eq 3,[20] where

$$(P)MnCl + xS \rightleftarrows (P)Mn(S)_x^+ + Cl^- \qquad (3)$$

x is either 1 or 2. Displacement of the halide by pyridine or Me_2SO has been postulated by Boucher,[20b] who showed that absorption spectra of PMnX were independent of the nature of X in bonding solvents. In this study displacement of chloride from (TPP)MnCl by Me_2SO or by pyridine as shown in eq 3 is confirmed by results of Figure 1c,d.[21] When the equilibrium for reaction 3 is shifted to the right, the liberated chloride ion becomes available to complex with the oxidation product of the DME and yield complexes of mercuric or mercurous ion.[22] This produces an anodic polarographic wave those height is proportional to the concentration of Cl^- in solution. In this investigation we obtained polarographic oxidation peaks for (TPP)MnCl in both Me_2SO and pyridine solutions, indicating free Cl^- in the bulk of solution. The oxidation current in either neat Me_2SO or pyridine was directly proportional to the concentration of (TPP)MnCl, indicating complete dissociation of the chloride ion from (TPP)MnCl.

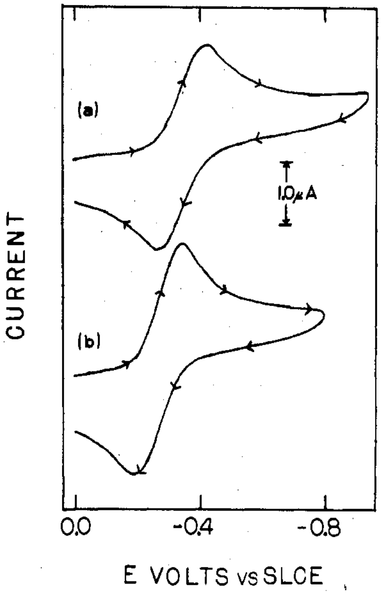


Figure 2. Cyclic voltammograms of 8.8×10^{-4} M (TPP)MnCl obtained at 0.50 V/s by using a platinum electrode in (a) CH_2Cl_2 and (b) CH_2Cl_2 containing 1.09 M pyridine. Solutions contain 0.1 M TBAP as supporting electrolyte.

Complexation of (TPP)MnCl and (TPP)Mn. Each of the ligands in Table I was titrated into CH_2Cl_2 solutions containing (TPP)MnCl, the cyclic voltammograms were recorded (see

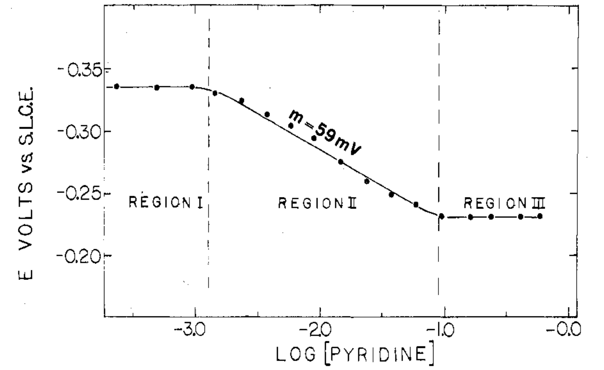


Figure 3. Plot of half-wave potential for the reduction of 1.0×10^{-3} M (TPP)MnCl vs. log (pyridine concentration). The regions I, II, and III correspond to the different electrode reactions which occur and are explained in text.

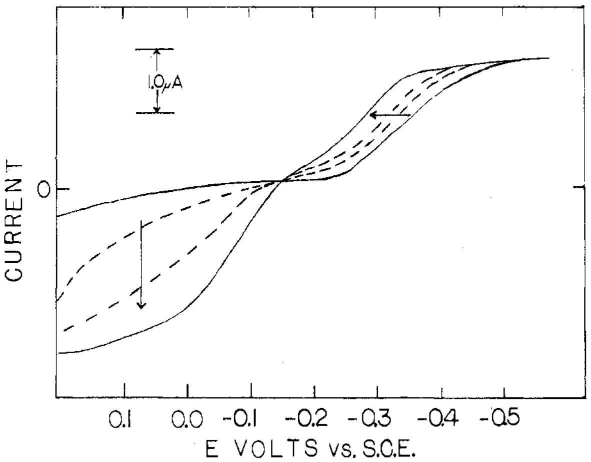


Figure 4. Polarograms obtained during the titration of 1.1×10^{-3} M (TPP)MnCl with the pyridine: (a) initial solution in CH_2Cl_2; (b) final solution in CH_2Cl_2, 1.0 M pyridine. The intermediate concentrations of pyridine are represented by the dashed lines.

Figure 2), and $E_{1/2}$ was plotted as a function of ligand concentration. This is illustrated in Figure 3 for the case of pyridine. Stepwise addition of pyridine produced an anodic potential shift of the Mn(III)/Mn(II) half-wave potential at intermediate ligand concentrations (region II) and no shift at either low concentrations of pyridine (region I) or high concentrations (region III). Similar behavior was observed for all of the ligands of Table I. The measured potential shifts by cyclic voltammetry at a platinum electrode were quantitatively similar to those observed at a DME. Plots of $i_p/v^{1/2}$ and $|E_{pa} - E_{pc}|$ were also constant, indicating diffusion control. The anodic shift of the Mn(III) $\rightleftarrows$ Mn(II) reaction and the magnitude of the initial slope (see Figure 3) indicate preferential stabilization of (TPP)Mn relative to (TPP)MnCl and can be accounted for by pyridine complexation with the product, (TPP)Mn, but not the reactant, (TPP)MnCl. With solutions containing less than 0.025 M pyridine only small changes were observed in the visible spectrum of (TPP)MnCl, thus confirming the initial lack of pyridine complexation to Mn(III). Assignment of a single ligand molecule to Mn(II) is derived from the initial 59-mV slope of $\Delta E_{1/2}/\log$ (L) in region II, Figure 3, and the preference of (TPP)Mn to form five-coordinate complexes. Bis(pyridine) complexes of manganese(II) porphyrins have been suggested in aqueous solutions,[20,23] but these have not been observed in nonaqueous media, where no concrete evidence exists for other than mono(ligand) adducts with manganese(II). Likewise, in the crystalline state, high-spin Mn(II) is invariably four- or five-coordinate.[18,24]

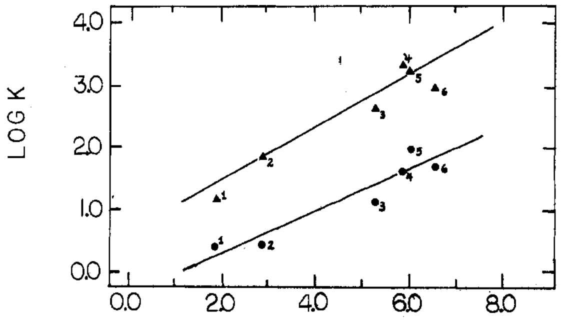
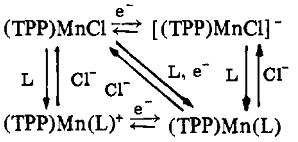


Figure 5. Plot of log K vs. pK_a of substituted pyridine: ▲, (TPP)MnL; ●, $[(TPP)MnL]^+$.

Scheme I



In CH_2Cl_2 containing 1 M pyridine, spectral data indicated the binding of pyridine by (TPP)MnCl. In order to determine whether, upon binding of Mn(III), a pyridine molecule displaced the chloride ion or was adding trans to the chloride to form (TPP)Mn(py)Cl, we monitored the appearance of the mercury oxidation wave at various points along the titration curve. The results of this are shown in Figure 4. No oxidation wave was initially observed at pyridine concentrations less than 10^{-2} M. Increasing the pyridine above this value caused a direct increase in the height of the oxidation peak until a maximum oxidation current was obtained. This maximum oxidation current was directly proportional to the concentration of (TPP)MnCl and, upon complete formation of $(TPP)Mn(py)^+$ (region III, Figure 3), was invariant with further additions of pyridine.

Electron-Transfer Mechanism. The shifts of potential as a function of ligand concentration were used to calculate stability constants for addition of each substituted pyridine to Mn(II) and Mn(III) in CH_2Cl_2. These values are listed in Table I. Figure 5 shows the plot of the log of the formation constant vs. the pK_a of the ligand. Although there is some scatter in the data, it is seen that the equilibrium constants of Mn(III) and Mn(II) generally increase as the pK_a of the substituted pyridine increases.

The linear increase in K_1 with increase in pK_a of the added ligand is not novel and has been observed for five-coordinate complexes of (TPP)Zn, (TPP)Cd, and (TPP)Hg with substituted pyridines[25] and (TPP)CrCl with both pyridines and imidazoles.[26] Similar results have also been observed for bis(ligand) adducts of (TPP)Fe in CH_2Cl_2.[27] What is novel is the magnitude of the stability constants for (TPP)Mn. Recently, Basolo and co-workers[3] measured the formation constant in toluene for the reaction

$$\text{(TPP)Mn} + \text{4-CNpy} \rightleftarrows \text{(TPP)Mn(4-CNpy)} \qquad (4)$$

Their log K = 2.55 at 23 °C is significantly larger than our value of log K = 1.14 for the same ligand and can be accounted for by the presence of Cl^- bound to Mn(II) in our system. Thus our measurement for the binding of cyanopyridine by manganese(II) actually involves the displacement reaction

$$[\text{(TPP)MnCl}]^- + \text{4-CNpy} \rightleftarrows \text{(TPP)Mn(4-CNpy)} + Cl^- \qquad (5)$$

Electrochemical titrations of $(TPP)MnClO_4$ and (TPP)MnCl with Cl^-, as well as other anions, indicate that halides are strongly complexed by Mn(II)[28] and that, in the case of Cl^-, the dissociation constant for $[(TPP)MnCl]^-$ is approximately

10^{-2}. This accounts for a 100 mV shift in half-wave potentials for Mn(III) $\rightleftharpoons$ Mn(II), as well as a substantial decrease in the formation constants for five-coordinate complexes with substituted pyridines, when compared to the uncomplexed (TPP)Mn. Strong axial binding of a neutral metalloporphyrin by halides has been recently demonstrated by Valentine[29] for the reactions of (TPP)Zn.

Thus, on the basis of the data presented, the oxidation–reduction mechanism shown in Scheme I may be proposed in CH_2Cl_2–0.1 M TBAP. In CH_2Cl_2 without nitrogenous base, the reactant is (TPP)MnCl. Additions of the substituted pyridine shift the equilibrium toward (TPP)Mn(L)$^+$, producing free Cl^- which may react with the Hg of the DME. At high ligand concentrations, the Cl^- oxidation peak becomes constant and Mn(III) reduction potential stops shifting as a function of ligand concentration (region III, Figure 2) as predicted for an electrode reaction involving identical axial coordination by the oxidized and the reduced species. In this region the electronic absorption spectrum of Mn(III) is identical with that obtained in neat pyridine.

As we have already demonstrated,[11] large changes in electron-transfer reversibility are observed for manganese(III) porphyrins in mixed solvent systems where six-coordinate, mixed-ligand complexes *may* be formed. In this study only five-coordinate complexes were observed, and the electron-transfer reactions were much more reversible. Whether this change in the heterogeneous rate of electron transfer is a function of the ligand type (pyridine vs. imidazole), the presence of a second axial ligand, or a result of competition between ligands of different donor atoms (imidazole and Me_2SO) is presently unknown. Further studies to answer these questions are now in progress.

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Registry No. (TPP)MnCl, 32195-55-4; (TPP)Mn, 31004-82-7; (TPP)Mn(4-cyanopyridine), 67383-36-2; (TPP)Mn(3-bromopyridine), 71155-83-4; (TPP)Mn(pyridine), 57034-31-8; (TPP)Mn(3-picoline), 71155-84-5; (TPP)Mn(4-picoline), 71155-85-6; (TPP)Mn(3,4-lutidine), 67368-75-6; (TPP)Mn(4-cyanopyridine)$^+$, 71155-86-7; (TPP)Mn(3-bromopyridine)$^+$, 71155-83-4; (TPP)Mn(pyridine)$^+$, 71155-87-8; (TPP)Mn(3-picoline)$^+$, 71155-88-9; (TPP)Mn(4-picoline)$^+$, 71155-89-0; (TPP)Mn(3,4-lutidine)$^+$, 71155-90-3.

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