

Spectroelectrochemical Characterization of Solvent-Related Changes in Axial Ligation of Manganese(II) and -(III) Tetraphenylporphyrins

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Introduction

Manganese porphyrins continue to be of interest as catalysts for the epoxidation of olefins,¹ models for the behavior of cytochrome P-450,² and DNA binding and cleavage reagents.³ Axial ligation coupled with redox chemistry is important in many of these applications. Recently, we investigated the influence of methanol bonding on the electron transfer reactivity of chloro(tetraphenylporphyrinato)manganese(III), Mn(TPP)Cl,⁴ and the kinetics of electrochemical Mn(TPP)Cl reduction in a series of aprotic solvents.⁵ The Mn^{III/II} heterogeneous electron transfer rate was found to be limited, in part, by the inner-shell barrier associated with movement of the Mn atom with respect to the porphyrin plane.⁶ Thus, it became important to establish that the axial Cl⁻ ligand was retained in both oxidation states. In addition, review of the recent literature^{7–12} reveals that many issues regarding axial ligation in Mn porphyrin chemistry remain unresolved.

Many techniques have been used to investigate axial ligation in metalloporphyrins. However, conventional UV/visible absorption spectroscopy remains useful for study of Mn porphyrins because the electronic spectra of these species are intense, unique and quite sensitive to the coordination environment of the metal. Thin-layer spectroelectrochemistry provides a means of obtaining accurate values of molar absorptivity ratios for adjacent oxidation states of these systems. This paper presents the results of a visible wavelength spectroelectrochemical investigation of Mn(TPP)Cl reduction in several non-aqueous solvents. The objectives of the study are to identify the conditions and spectroscopic features associated with solvent related changes in axial ligation in the Mn^{II} and Mn^{III} oxidation states.

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Experimental Section

Reagents. Mn(TPP)Cl was purchased from Aldrich Chemical and used as received. Tetra-*n*-butylammonium tetrafluoroborate (Bu₄NBF₄) was purchased from Southwestern Analytical Chemicals and vacuum desiccated before use. Solvents were purchased commercially in the purest form available and treated further by the following procedures. Methylene chloride, 1,2-dichloroethane, and acetonitrile were distilled over P₂O₅. Nitromethane, benzonitrile, acetone, propylene carbonate (PC), tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were dried over activated molecular sieves. Further purification of acetone was attempted by distillation from molecular sieves and by distillation from molecular sieves and potassium permanganate.

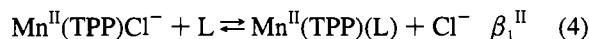
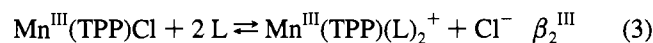
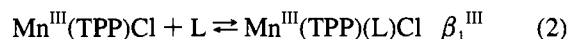
Equipment and Procedures. Spectroelectrochemical experiments were carried out in an optically transparent thin-layer cell having a Pt mesh working electrode and an optical path length of 0.2 mm. The cell design has been described.¹³ The reference electrode was an aqueous Ag/AgCl (3 M KCl) half-cell immersed in a salt bridge containing the solvent of interest and supporting electrolyte. Spectrophotometric measurements were made with a Hewlett-Packard 8450A diode array spectrophotometer. The working electrode potential was controlled with an IBM EC-225 potentiostat. Mn(TPP)Cl concentrations were on the order of 2–3 × 10⁻⁵ M.

Results and Discussion

Mn(TPP)Cl undergoes quasi-reversible one-electron reduction at ca. -0.25 V versus Ag/AgCl. In non-coordinating solvents such as methylene chloride and 1,2-dichloroethane the axial Cl⁻ ligand is bound to the metal in both oxidation states, and the electrode reaction is described by eq 1.⁴ In coordinating solvents



or when potential ligands are present, the stoichiometry of reaction 1 may change owing to formation of the six-coordinate Mn^{III} forms, Mn(TPP)(L)Cl and Mn(TPP)(L)₂⁺, and/or the five-coordinate Mn^{II} form, Mn(TPP)(L). Equilibrium reactions for formation of these species are given by eqs 2–4. In general,



$\beta_2^{\text{III}}[\text{L}]/[\text{Cl}^-] > \beta_1^{\text{III}}$; thus, Mn^{III}(TPP)Cl and Mn^{III}(TPP)(L)₂⁺ are the principal Mn(III) species in solution. These forms can be distinguished by the energy and intensity of their Soret bands and the relative intensities of the α and β components of their Q absorption bands. Likewise, distinction between Mn^{II}(TPP)Cl⁻ and Mn^{II}(TPP)(L) can be made by examination of these spectroscopic features.

Figure 1A illustrates the spectroelectrochemical reduction of Mn(TPP)Cl in propylene carbonate containing 0.1 M Bu₄NBF₄. The spectrum of the Mn(III) complex, observed with the working electrode potentiostated at 0 V, exhibits a Soret band maximum at 476 nm and Q _{α} and Q _{β} band maxima at 582 and 620 nm. In accordance with the terminology of Boucher,¹⁴ these bands are numbered V, IV, and III, respectively. The molar absorptivity ratios of bands III and IV and of bands IV and V are used to infer the identity of the axial ligand(s) of Mn(III). In propylene carbonate the ratios are $\epsilon_{\text{III}}/\epsilon_{\text{IV}} = 1.10$ and $\epsilon_{\text{IV}}/\epsilon_{\text{V}} = 0.104$. Similar values are found in all solvents in Table 1

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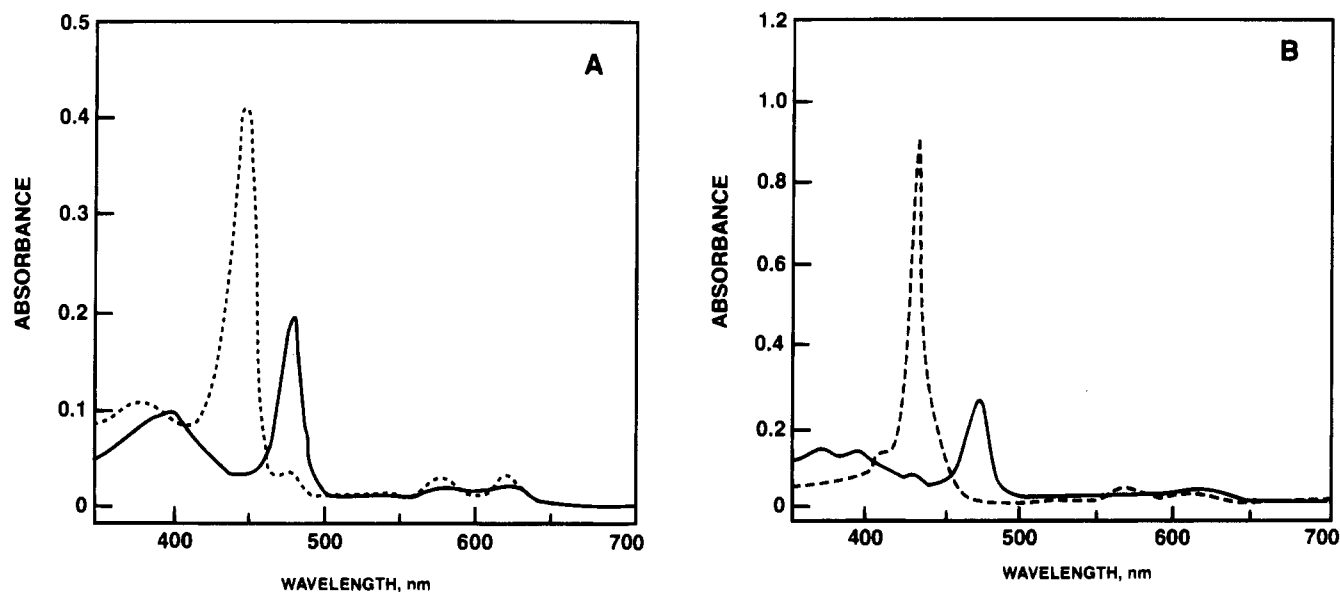


Figure 1. Spectroelectrochemical reduction of Mn(TPP)Cl in (A) propylene carbonate and (B) tetrahydrofuran containing 0.1 M Bu₄NBF₄. Working electrode potential: 0.0 V (—); -0.5 V (---).

Table 1. Spectroscopic Properties as a Function of Solvent for Manganese(III) and -(II) Tetrphenylporphyrin Complexes^a

solvent	DN ^b	dielec const ^c	Mn(III)			Mn(II)		
			λ_v , nm	$\epsilon_{III}/\epsilon_{IV}$	ϵ_{IV}/ϵ_V	λ_v , nm	$\epsilon_{III}/\epsilon_{IV}$	$\epsilon_V^{Mn(II)}/\epsilon_V^{Mn(III)}$
CH ₂ Cl ₂		8.9	476	1.18 ^d	0.082 ^d	444	1.04	2.17
ClCH ₂ CH ₂ Cl		10.4	476	1.17	0.088	444	0.99	1.91
CH ₃ NO ₂	2.7	35.9	476	1.15	0.081	441	1.15	2.28
C ₆ H ₅ CN	11.9	25.2	478	1.18	0.098	446	1.03	1.81
CH ₃ CN	14.1	35.9	474	1.17	0.107	440	1.07	1.91
PC	15.1	64.9	476	1.10	0.104	442	1.06	2.13
CH ₃ COCH ₃	17.0	20.6	474	1.12	0.123	442, 431	1.04	^e
THF	20.0	7.6	474	1.13	0.129	432	0.76	3.68
DMF	26.6	36.7	476	1.01	0.152	438	0.89	4.04
DMSO	29.8	46.4	478	0.99	0.157	436	0.85	3.51

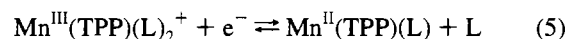
^a In solutions containing 0.1 M Bu₄NBF₄. ^b From ref 15. ^c From ref 16. ^d From ref 12. ^e Split band V, $\epsilon_V^{Mn(II)}/\epsilon_V^{Mn(III)}$ not reported.

that have a Gutmann donor number (DN)¹⁵ less than 17. The axial Cl⁻ ligand is considered to be retained under these conditions. A similar conclusion was reached in a conductimetric study by Kadish,⁷ who found Mn(TPP)Cl to be a nonelectrolyte in a similar range of solvents.

The spectrum of the Mn(II) complex in propylene carbonate is generated by holding the potential of the working electrode at -0.5 V. It reveals that the Soret band maximum shifts to 442 nm and intensifies relative to that of Mn(TPP)Cl giving $\epsilon_V^{Mn(II)}/\epsilon_V^{Mn(III)} = 2.13$. The Q bands also intensify and shift slightly in energy; however, the ratio $\epsilon_{III}/\epsilon_{IV}$ decreases by only a small amount upon reduction. Similar results are obtained for the first six solvents in Table 1 including CH₂Cl₂ and ClCH₂-CH₂Cl, for which it has been demonstrated⁴ that Cl⁻ is not lost following reduction to Mn(II) (eq 1). Therefore, the stoichiometries of the Mn^{III} and Mn^{II} species under these conditions are Mn(TPP)Cl and Mn(TPP)Cl⁻.

Figure 1B shows the results of the same experiment in 0.1 M Bu₄NBF₄/THF. In this solvent the oxidized complex exhibits a Soret band maximum at 474 nm and Q band intensity ratios of $\epsilon_{III}/\epsilon_{IV} = 1.13$ and $\epsilon_{IV}/\epsilon_V = 0.129$. In DMF and DMSO, which have larger donor numbers, the last two values are $\epsilon_{III}/\epsilon_{IV} \cong 1.0$ and $\epsilon_{IV}/\epsilon_V \cong 0.15$. Following reduction in these three

solvents, the Soret band shifts to 432–438 nm and intensifies and sharpens dramatically relative to its appearance in propylene carbonate. In addition, the relative intensities of the Q band absorptions invert. The observed values in THF, DMF, and DMSO are $\epsilon_V^{Mn(II)}/\epsilon_V^{Mn(III)} = 3.5$ –4.0 and $\epsilon_{III}/\epsilon_{IV}$ [for Mn(II)] = 0.76–0.89. The foregoing results are characteristic of the following chemical changes: (i) Mn(TPP)Cl is converted into a bis(solvated) Mn(TPP)(L)₂⁺ species in DMF and DMSO and (ii) a solvent molecule has replaced chloride ion as the axial ligand of Mn(II) in all three solvents. Conclusion (i) is supported by the spectral similarities between Mn(TPP)Cl in DMF and DMSO and the isolated complexes [Mn^{III}(TPP)(CH₃-OH)₂]ClO₄·CH₃OH¹⁷ and [Mn^{III}(TPP)(DMF)₂]ClO₄.¹⁸ Conclusion (ii) is supported by the spectral similarities between Mn(II)-tetrphenylporphyrin in THF, DMF, and DMSO and the product of Mn(TPP)Cl reduction in 1,2-dichloroethane containing large concentrations of methanol.⁴ Thus, in strong donor solvents (DMF and DMSO) reduction of Mn(III) proceeds according to:



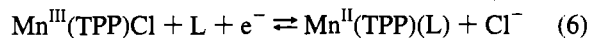
In solvents of intermediate donor strength reduction of Mn(III) proceeds by a combination of reactions 5 and 6 (THF) or a combination of reactions 1 and 6 (acetone, *vide infra*):

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These electrode reaction stoichiometries also are inferred from the $[\text{CH}_3\text{OH}]$ dependence of the potential for $\text{Mn}(\text{TPP})\text{Cl}$ reduction in 1,2-dichloroethane.⁴

The results in Table 1 provide a systematic basis for identifying solvent induced changes in axial ligation of $\text{Mn}(\text{II})$ and $\text{Mn}(\text{III})$ tetraphenylporphyrins. The axial chloride ligand of $\text{Mn}(\text{TPP})\text{Cl}$ is retained in solvents for which $\epsilon_{\text{III}}/\epsilon_{\text{IV}} = 1.14 \pm 0.04$ and $\epsilon_{\text{IV}}/\epsilon_{\text{V}} = 0.096 \pm 0.011$, whereas values of $\epsilon_{\text{III}}/\epsilon_{\text{IV}} \approx 1.0$ and $\epsilon_{\text{IV}}/\epsilon_{\text{V}} \approx 0.15$ indicate conversion to a bis(solvated) $\text{Mn}(\text{TPP})(\text{L})_2^+$ species. In the $\text{Mn}(\text{II})$ oxidation state replacement of chloride by a neutral axial ligand is characterized by a shift of the Soret band maximum from 443 ± 2 nm to 435 ± 3 nm, an increase in the value of $\epsilon_{\text{V}}^{\text{Mn}(\text{II})}/\epsilon_{\text{V}}^{\text{Mn}(\text{III})}$ from 2.0 ± 0.2 to 3.7 ± 0.3 and a decrease in $\epsilon_{\text{III}}/\epsilon_{\text{IV}}$ from 1.05 ± 0.05 to 0.83 ± 0.07 . These behaviors have been recognized in individual circumstances in manganese porphyrin spectroscopy,¹⁴ but have not been characterized systematically. Reasons for the changes are not well understood owing to the complex electronic structure of Mn porphyrins.¹⁹

Two solvents in Table 1 exhibit borderline behavior. In THF and acetone the $\text{Mn}(\text{III})$ $\epsilon_{\text{IV}}/\epsilon_{\text{V}}$ result lies between the approximate values of 0.1 and 0.15 that characterize $\text{Mn}^{\text{III}}(\text{TPP})\text{Cl}$ and $\text{Mn}^{\text{III}}(\text{TPP})(\text{L})_2^+$, respectively. Foran et al.⁹ recently investigated the influence of ionic strength on axial ligand dissociation of $\text{Mn}(\text{III})$ porphyrins in tetrahydrofuran. On the basis of their findings, a value of $\epsilon_{\text{IV}}/\epsilon_{\text{V}} \approx 0.125$ is consistent with a mixture of $\text{Mn}(\text{TPP})\text{Cl}$ and $\text{Mn}(\text{TPP})(\text{THF})_2^+$ or $\text{Mn}(\text{TPP})(\text{acetone})_2^+$ in our experiments. Following reduction in THF a single Soret band is present at 432 nm (Figure 1B), indicating that the electrode product is $\text{Mn}^{\text{II}}(\text{TPP})(\text{THF})$. In acetone, electrochemical reduction produces a spectrum with Soret bands at 431 and 442 nm (Figure 2). This is consistent with a mixture of Mn^{II} species bearing neutral and anionic axial ligands. The higher energy band is present in repeatedly purified solvent; thus, the axial ligand probably is acetone rather than H_2O present as an impurity in the solvent. However, as shown in Figure 2, addition of a small amount of water to an acetone solution of $\text{Mn}^{\text{III}}(\text{TPP})\text{Cl}$ in 0.1 M Bu_4NBF_4 prior to electrolysis results in an enhancement of the 431 nm peak after reduction. This indicates that H_2O (DN = 18)¹⁵ can replace acetone as the axial ligand. In any event, the experiment in Figure 2 supports the assignment of the higher energy absorption to a Mn^{II} porphyrin in which a neutral molecule has replaced Cl^- as the axial ligand.

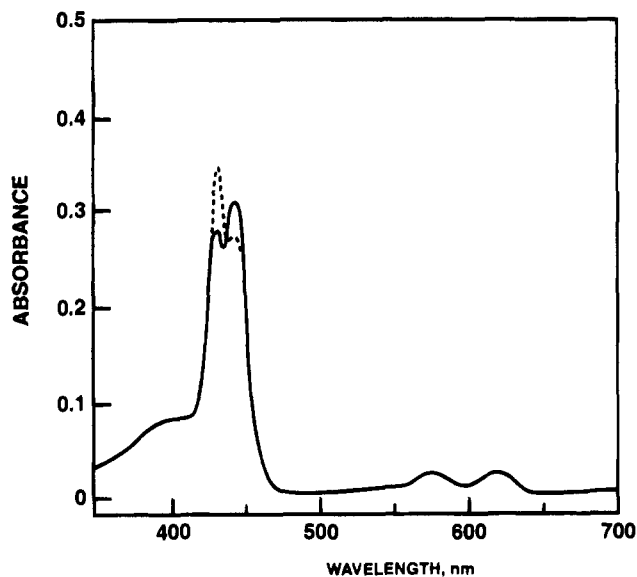


Figure 2. Spectroelectrochemical reduction of $\text{Mn}(\text{TPP})\text{Cl}$: (—) in acetone containing 0.1 M Bu_4NBF_4 and (---) after addition of 2.78 μmol of H_2O . Working electrode potential: -0.5 V.

The results in Table 1 demonstrate that donor number and not dielectric constant is the solvent property that controls axial ligand dissociation. Solvents with $\text{DN} \approx 17$ appear to be capable of promoting partial or complete dissociation of axial Cl^- , whereas those with a smaller donor number are ineffective in this regard. This conclusion may depend on substituent groups and other aspects of porphyrin structure. For example, Arasasingham and Bruce⁸ observed dissociation of Cl^- from $\text{Mn}^{\text{III}}(\text{TMP})\text{Cl}$ (TMP = tetramesitylporphyrin) following its reduction to Mn^{II} in CH_3CN , whereas this does not occur for $\text{Mn}^{\text{III}}(\text{TPP})\text{Cl}$. Also, Foran et al.⁹ found the ionic strength dependence of axial ligand dissociation from manganese(III) tetraarylporphyrin chlorides to be a function of the aromatic substituent groups. Finally, we note that the ease of chloride displacement is dependent on manganese oxidation state, but only to a small extent. In general, solvents with $\text{DN} \geq 17$ sustain at least some Cl^- dissociation in both oxidation states. Examination of $\epsilon_{\text{III}}/\epsilon_{\text{IV}}$ and $\epsilon_{\text{IV}}/\epsilon_{\text{V}}$ results for acetone and THF suggests that dissociation from $\text{Mn}(\text{II})$ is slightly easier than from $\text{Mn}(\text{III})$.

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