

Low Spin Nitric Oxide Complexes of Manganese Tetraphenylporphyrin

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As part of a systematic examination of the occurrence and properties of diatomic molecule complexes of metalloporphyrins,¹⁻⁴ we have investigated the interaction of tetraphenylporphyrin manganese(II), $\text{Mn}^{\text{II}}\text{TPP}$, and $\text{Mn}^{\text{III}}\text{TPP}(\text{X})$ ($\text{X} = \text{Cl}^-$, CH_3CO_2^- (Ac^-), CN^-), with nitric oxide. The low spin nature of the resulting complexes is unique to nitrosyl ligands in manganese porphyrin chemistry.^{5,6}

Tetraphenylporphyrin manganese(III) chloride and acetate (Ac) were prepared by reported procedures.⁵ Distillation of ethanol into a degassed toluene solution of $\text{Mn}^{\text{III}}\text{TPP}\text{Cl}$ in contact with solid NaBH_4 resulted in reduction to a $\text{Mn}^{\text{II}}\text{TPP}$ complex. Epr spectra for the $\text{Mn}^{\text{II}}\text{TPP}$ species consist of g_{\perp} (5.9) and g_{\parallel} (2.0) transitions with ^{55}Mn hyperfine in both regions characteristic of a high spin ($S = 5/2$) complex.^{5,7} This $\text{Mn}^{\text{II}}\text{TPP}$ complex reacts with nitric oxide to give an isolable red solid with a single $\nu\text{N}-\text{O}$ band at 1760 cm^{-1} . The absence of coordinated solvent absorption in the IR spectrum and elemental analysis establish this complex as $\text{MnTPP}(\text{NO})$. Scheidt, Piciulo and Rupprecht have prepared the 3-methylpyridine adduct of $\text{MnTPP}(\text{NO})$ and X-ray structure determination demonstrates a near linear $\text{Mn}-\text{NO}$ unit.⁶ The observed $\text{N}-\text{O}$ stretching frequency of 1760 cm^{-1} in $\text{MnTPP}(\text{NO})$ is similar to that reported in $[\text{Mn}(\text{CN})_5\text{NO}]^{-3}$ ($\nu\text{NO} = 1725\text{ cm}^{-1}$).⁸ Effective back π bonding associated with a linear $\text{Mn}^{\text{I}}-\text{NO}^+$ unit is responsible for the relatively low position for νNO . The reactivity of $\text{Mn}^{\text{II}}\text{TPP}$ with nitric oxide parallels that of Mn^{II} hemoproteins. Solid $\text{Mn}^{\text{II}}\text{TPP}$ species are also found to absorb nitric oxide producing the same complex ($\nu\text{NO} = 1760\text{ cm}^{-1}$).

Mixing an aqueous solution of KCN with $\text{Mn}^{\text{III}}\text{TPP}(\text{Ac})$ dissolved in ethanol leads to the precipitation of a cyanide complex which is subsequently extracted into toluene and crystallized

($\nu\text{CN} = 2130\text{ cm}^{-1}$). Addition of nitric oxide (500 torr) to a degassed toluene solution of $\text{MnTPP}(\text{CN})$ and freezing to -150°C resulted in appearance of an epr spectrum characteristic for a $S = 1/2$ species. The toluene solution and glass epr spectra for $\text{MnTPP}(\text{CN})$ in the presence of nitric oxide are shown in Fig. 1.

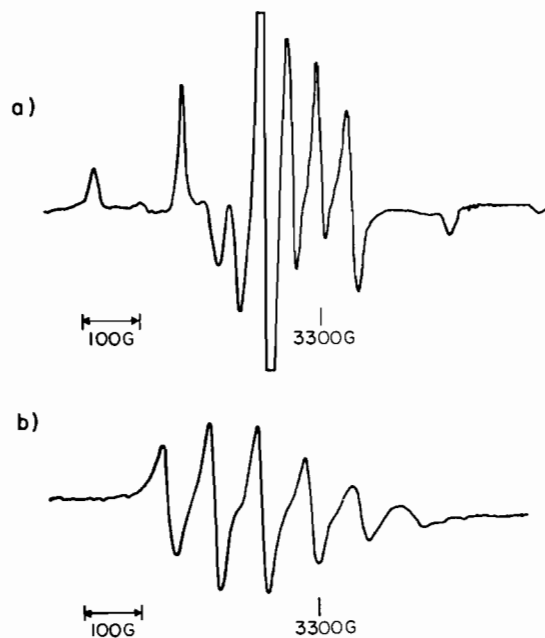


Fig. 1. Epr spectra for nitric oxide complexes of manganese porphyrins; a) $\text{MnTPP}(\text{CN})(\text{NO})$ in frozen toluene (130°K). $g_{\parallel} = 1.983$, $g_{\perp} = 2.019$, $A_{\parallel} (^{55}\text{Mn}) = -161.5\text{ G}$, $A_{\perp} (^{55}\text{Mn}) = -51.2\text{ G}$ (corrected to 2nd order); b) $\text{MnTPP}(\text{CN})(\text{NO})$ in toluene solution (295°K). $\langle g \rangle = 2.010$, $\langle A \rangle (^{55}\text{Mn}) = -88.2\text{ G}$ (corrected to 2nd order).

Closely related epr spectra are observed for the chloride and acetate complexes. Substantial electronic spectral changes accompany appearance of the new epr spectrum. Thorough degassing of these solutions results in loss of the epr signal and reappearance of the electronic spectra for $\text{MnTPP}(\text{X})$ ($\text{X} = \text{Cl}$, Ac , CN), demonstrating the facile reversibility of nitric oxide coordination. Similarly, solid $\text{MnTPP}(\text{Ac})$ in a vacuum fitted IR cell reversibly absorbs nitric oxide with appearance of a single νNO at 1830 cm^{-1} . These spectroscopic changes are associated with the reversible formation of low spin $\text{MnTPP}(\text{X})(\text{NO})$ complexes. The distribution of g values, ^{55}Mn hyperfine coupling constants and absence of ^{14}N hyperfine definitively place the odd electron in a d_{xy} m. o. for these

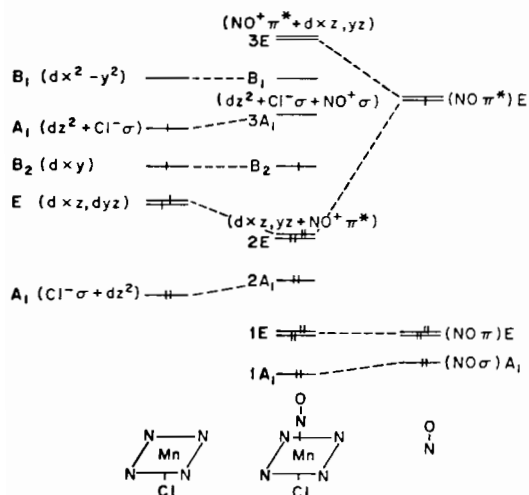


Fig. 2. Schematic molecular orbital diagram for $MnTPP(Cl)(NO)$.

complexes.⁹ $MnTPP(Cl)(NO)$ has an axially symmetric g tensor, consistent with a near linear Mn–NO unit. This reactivity of $Mn^{III}TPP(X)$ complexes with nitric oxide is in contrast with Mn^{III} hemoproteins where no nitric oxide complexes have been observed.⁷

A schematic m. o. diagram for $MnTPP(Cl)(NO)$ focusing on the metal d and nitric oxide π^* orbitals appears in Figure 2. Presence of the odd electron in the d_{xy} m.o. clearly demonstrates the complete transfer of the NO π^* electron to manganese resulting in effective reduction of Mn^{III} (d^4) to Mn^{II} (d^5). This complex can thus be formulated as $Mn^{II}TPP(Cl^-)(NO^+)$. The Mn^{II} – NO^+ unit is expected to be linear in order to maximize ($d_{xz, yz} \rightarrow \pi^*$) π bonding, which is consistent with the observed axially symmetric g tensor. The low spin nature of

$Mn^{II}TPP(Cl^-)(NO^+)$ is unique in manganese porphyrin complexes and preceded in manganese chemistry only by $[Mn(CN)_5NO]^{-3}$, which also has closely related epr parameters.^{9,10} Low spin ($S = \frac{1}{2}$, d^5) Fe^{III} porphyrin complexes such as cyanides have the odd electron in the d_{xz} (d_{yz}) rather than the d_{xy} as reported here for the low spin ($S = \frac{1}{2}$, d^5) $Mn^{II}(NO^+)$ species.¹¹ Strong π bonding in the $Mn^{II}(NO^+)$ unit is probably responsible for lowering the $d_{xz, yz}$ below the essentially non bonding d_{xy} .

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