Nitric Oxide Complexes of Manganese and Chromium Tetraphenylporphyrin

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Abstract: Nitric oxide forms 1:1 low spin complexes with $Cr^{II}TPP$, $Cr^{III}TPP(X)$, $Mn^{II}TPP$, and $Mn^{III}TPP(X)$ species. MnTPP(X)(NO) ($X^- = Cl^-, CH_3CO_2^-, CN^-$) and CrTPP(NO) complexes have the $S = \frac{1}{2}$ ground state and EPR spectra diagnostic for the odd electron occupying a molecular orbital of predominantly metal d_{xy} character. MnTPP(X)(NO) complexes and the isoelectronic CrTPP(NO) species are assigned the $(d_{xz,yz})^4\ (d_{xy})^1$ ground configuration. Narrow lines in the isotropic EPR spectrum of CrTPP(NO) permit resolution of nitrogen-14 hyperfine from both nitric oxide (6.5 G) and the porphyrin pyrrole nitrogens (3.15 G). The metal nuclear hyperfine coupling constants in these complexes $\langle A\ ^{55}Mn\rangle = 88.3$ G and $\langle A\ ^{53}Cr\rangle = 21.2$ G are indicative of the odd electron being relatively localized on the metal. All of these nitric oxide complexes are formulated as $M{-}NO^+$ species, although $d\pi \rightarrow \pi^*$ bonding substantially reduces this charge separation. Within isoelectronic sets such as (d^5) MnTPP(Cl)(NO) ($\nu_{NO} = 1830\ cm^{-1}$), CrTPP(NO) ($\nu_{NO} = 1700\ cm^{-1}$), or (d^6) FeTPP(Cl)(NO) ($\nu_{NO} = 1880\ cm^{-1}$), MnTPP(NO) ($\nu_{NO} = 1760\ cm^{-1}$), the nitric oxide stretching frequencies are substantially smaller for the complex where the metal has the lower formal oxidation state. Electronic spectra for the chromium porphyrin species are typical for metalloporphyrins, while spectra for MnTPP(X) and MnTPP(X)(NO) complexes are highly irregular. VOTPP fails to form a nitric oxide complex even in the low temperature glass media.

The coordination chemistry of diatomic molecules with metalloporphyrins is in a period of rapid development. A wide array of diatomic molecule complexes of metalloporphyrins has recently been reported.[1-11] The focus of attention on these materials has been promoted by interest in heme protein model systems and in evaluating these systems for coordination-modified small molecule reactivity. Our efforts in this area have been largely directed at the systematic examination of the occurrence and properties of this class of diatomic molecule complexes.[1-3] As part of this systematic study, we have examined the interaction of tetraphenylporphyrin complexes of Mn(II), (III) and Cr(II), (III) with nitric oxide.

Experimental Section

$MnTPP(CH_3CO_2)$, [MnTPP(Ac)], was prepared by refluxing manganous acetate and tetraphenylporphyrin in acetic acid.[12-14] Chromatography of the crude product on alumina with $CHCl_3$ produced the hydroxide complex.[14] Reconversion to the acetate complex was accomplished by dissolving the hydroxide in refluxing acetic acid and reducing the volume until crystallization occurred upon cooling. The chloride complex was obtained similarly from an acetic acid solution saturated with NaCl. The acetate and chloride complexes were recrystallized from toluene.

MnTPP(CN) was prepared by dropwise addition of a saturated aqueous solution of KCN to a methanolic solution of MnTPP(OH) until precipitation occurred. The cyanide complex was then extracted into toluene and crystallized ($\nu_{CN} = 2130\ cm^{-1}$).

The methanol adduct of $Cr^{III}TPP(OCH_3)$ was prepared by the method of Fleischer and Srivastava[15] and purified by alumina chromatography. The hydrate of $Cr^{II}TPP$ was prepared and purified by the method of Gogan and Siddiqui.[16] $Cr^{II}TPP$ and $Mn^{II}TPP$ species were also prepared by the $NaBH_4$ reduction of the respective metal(III) complexes in a mixed ethanol–chloroform solvent system.

Nitric oxide complexes were formed by exposing a toluene solution or the pure solid metalloporphyrin complexes to 500–700 mm of nitric oxide.

C.P. grade nitric oxide was purchased from Matheson Gas Products and was passed through a column of KOH pellets to free it of higher nitrogen oxides. Toluene was dried over P_2O_5 and vacuum distilled. Other reagents were used as supplied.

Instrumentation and procedures for obtaining EPR, electronic, and infrared spectra have been described previously.[2]

Results

Manganese(III) tetraphenylporphyrin complexes are high spin d^4 systems and no EPR spectra were observed in either toluene solution (295 K) or glass media (100 K). Exposure of degassed toluene solutions of MnTPP(CN) to 500 Torr of nitric oxide at 295 K produces a new species with a six-line isotropic EPR spectrum characteristic for low spin d^5 ($S = \frac{1}{2}$) species with ^{55}Mn ($I = \frac{5}{2}$) hyperfine splitting (Figure 1). Freezing to 100 K resulted in anisotropic EPR spectra shown in Figure 1. EPR parameters observed for frozen toluene solutions of MnTPP(X)(NO) ($X^- = Cl^-, Ac^-$) were indistinguishable from the cyanide complex. Electronic spectral changes accompany formation of the nitric oxide complex as illustrated for the cyanide complex in Figure 2. Thorough degassing of solutions containing MnTPP(X)(NO) complexes resulted in loss of the EPR signal and the reappearance of the electronic spectra for MnTPP(X) ($X^- = Cl^-, CH_3CO_2^-, CN^-$). Infrared spectra from Nujol mulls of MnTPP(Ac) exposed to nitric oxide (500 Torr) reveal the presence of a new band at 1830 cm^{-1}. Exhaustive evacuation of the nitric oxide results in the disappearance of the 1830 cm^{-1} ir band. These spectroscopic changes are attributed to the reversible formation of the low spin ($S = \frac{1}{2}$) complexes MnTPP(X)(NO) ($X^- = Cl^-, CN^-, Ac^-$).

Distillation of ethanol into a degassed toluene solution of $Mn^{III}TPP(X)$ ($X^- = Cl^-, CN^-, Ac^-$) in contact with sodium borohydride resulted in a reduction to a $Mn^{II}TPP$ complex. Reduction is characterized by a color change from green to violet. EPR spectra for the $Mn^{II}TPP$ species in frozen toluene glass (130 K) consist of $g_\perp$ (5.9) and $g_\parallel$ (2.0) transitions with ^{55}Mn hyperfine in both regions characteristic of a high spin ($S = \frac{5}{2}$) complex[14,17] (Figure 3). Electronic spectra for the $Mn^{II}TPP$ species at 77 K in toluene glass media are found in Figure 4.

The $Mn^{II}TPP$ complex in solution or the solid state interacts with oxygen, ultimately resulting in oxidation to a Mn(III) species. Addition of carbon monoxide (1 atm) to a toluene solution of the $Mn^{II}TPP$ complex had no discernible effect on the EPR or electronic spectra. There is no evidence for carbon monoxide coordinating $Mn^{II}TPP$.

Addition of nitric oxide to either a toluene solution of $Mn^{II}TPP$ or the solid complex resulted in an immediate

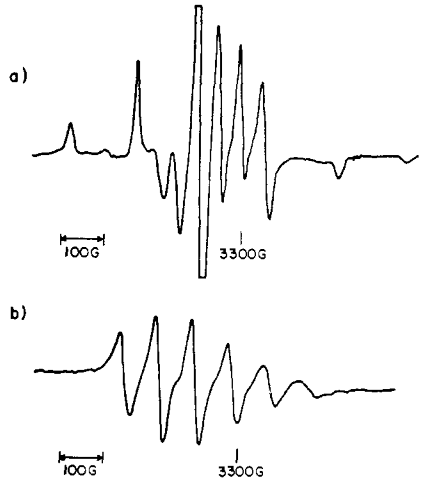

Figure 1. EPR spectra for MnTPP(CN)(NO) (ν = 9.139 GHz): (a) toluene glass (130 K) $g_{\parallel} = 1.98$, $g_{\perp} = 2.019$, $A_{\perp}\ {}^{55}\text{Mn} = -52.2$ G, $A_{\parallel}\ {}^{55}\text{Mn} = -161.5$ G; (b) toluene solution (295 K) $\langle g \rangle = 2.010$, $\langle A\ {}^{55}\text{Mn} \rangle = -88.2$ G (corrected to second order).

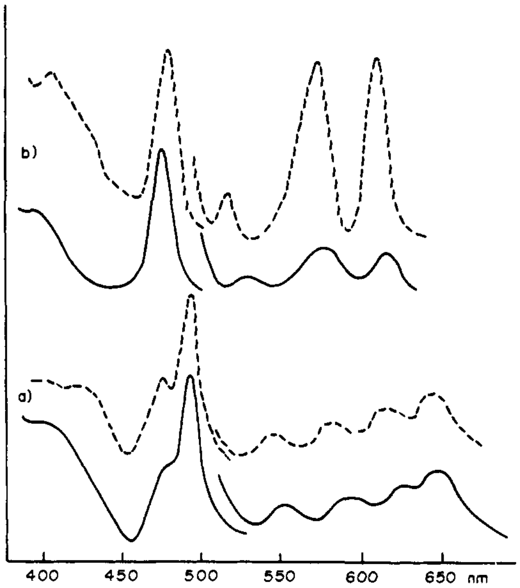

Figure 2. Electronic spectra for manganese porphyrin complexes in toluene solution and glass media: (—) 295 K, (- - -) 77 K; (a) MnTPP(CN) species, (b) MnTPP(CN)(NO).

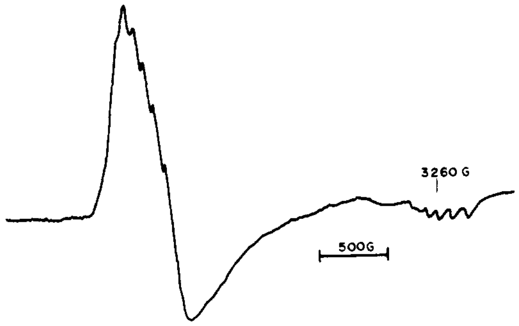

Figure 3. EPR spectrum for Mn$^{\text{II}}$TPP species in toluene glass (130 K): $g_{\parallel} = 2.0$, $g_{\perp} = 5.9$, $A_{\parallel}\ {}^{55}\text{Mn} = -81$ G, $A_{\perp}\ {}^{55}\text{Mn} = -72$ G.

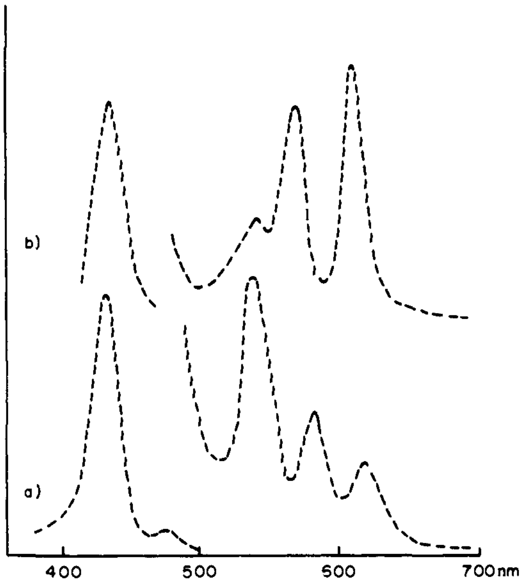

Figure 4. Electronic spectra in toluene glass (77 K): (a) Mn$^{\text{II}}$TPP species, (b) MnTPP(NO).

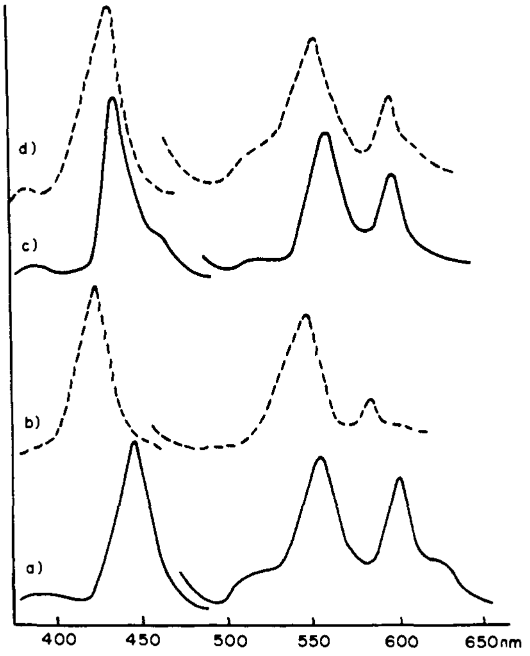

Figure 5. Electronic spectra for chromium tetraphenylporphyrin complexes in toluene solution (295 K): (a) Cr$^{\text{III}}$TPP(OCH$_3$) species, (b) CrTPP(OCH$_3$) + 400 Torr of NO, (c) Cr$^{\text{II}}$TPP species, (d) CrTPP(NO).

color change to a bright reddish orange. The complex that was isolated upon removal of the solvent was moderately air stable, but toluene solutions were rapidly oxidized by air. A single $\nu_{\text{N-O}}$ band at 1760 cm^{-1}, absence of coordinated solvent bands in the ir, and chemical analysis established this complex as MnTPP(NO). Solution magnetic susceptibility studies by the NMR method demonstrate that MnTPP(NO) is diamagnetic. Electronic spectra for MnTPP(NO) in toluene glass at 77 K appear in Figure 4.

Exposure of toluene or chloroform solutions of CrTPP(OMe) to nitric oxide (500 Torr) resulted in the spectroscopic changes indicative of nitric oxide complex formation (Figure 5). Degassing this solution resulted in reappearance of the CrTPP(OMe) electronic spectra, demonstrating facile reversibility of nitric oxide coordination.

Addition of nitric oxide to Cr$^{\text{II}}$TPP produces CrTPP(NO). The EPR spectrum for this new species appears in Figure 6. Nitrogen-14 hyperfine splitting from both nitric oxide and porphyrin pyrrole nitrogens is observed in the solution spectrum. The isotropic $\langle g \rangle$ and hyperfine coupling constants for ^{53}Cr, ^{14}N(NO), and ^{14}N (porphyrin) are given in Figure 6. Frozen toluene solutions of this substance resulted in the EPR spectra shown in Fig-

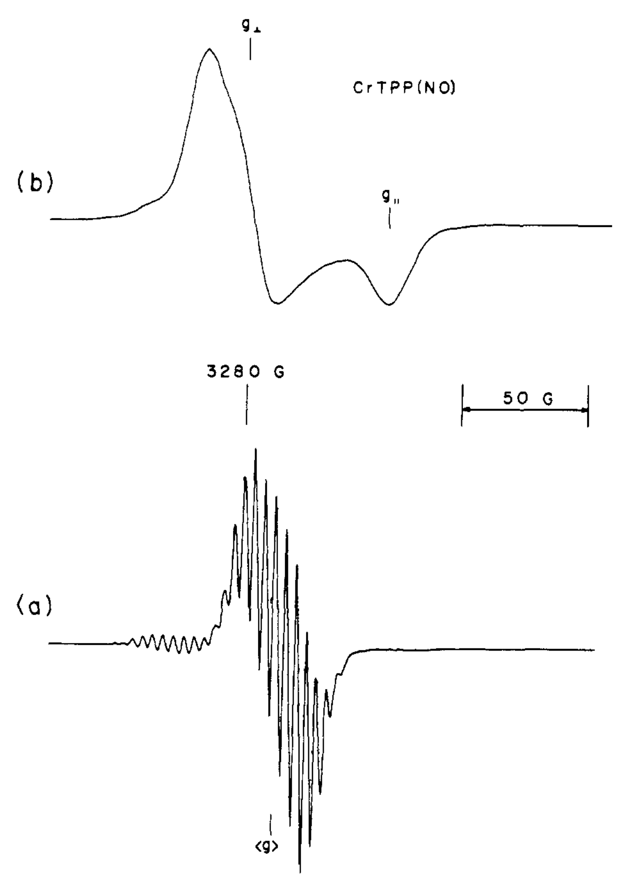

Figure 6. EPR spectra for CrTPP(NO) (ν = 9.140 GHz): (a) toluene solution (295 K) $\langle g \rangle$ = 1.993, $\langle A\ ^{53}Cr \rangle$ = 21.2 G, $\langle a\ ^{14}N \rangle$ (NO) = 6.5 G, $\langle a\ ^{14}N \rangle$ (porphyrin) = 3.15 G; (b) toluene glass (130 K) $g_{\parallel}$ = 1.97, $g_{\perp}$ = 2.00

ure 6b. The relatively broad nature of these spectra prohibited resolution of the ^{14}N hyperfine coupling apparent in the solution spectra. The anisotropic g values obtained from these spectra are consistent with the directly observed isotropic value from solution spectra. Electronic spectra for CrTPP(NO) in toluene solution and low temperature glass are shown in Figure 5. CrTPP(NO) can be isolated as a red solid with a ν_{NO} at 1700 cm^{-1}.

Treatment of a mixed chloroform-methanol solution of CrTPP(OMe) with nitric oxide results in an isotropic EPR spectrum identical with that shown in Figure 6a. Cr^{III}TPP(OMe) is reduced by nitric oxide in the presence of methanol to produce CrTPP(NO).

The electronic and EPR spectra for VOTPP are unaffected by the presence of nitric oxide in toluene solution or glass media. VOTPP fails to form a nitric oxide complex even in low temperature glass media.

Discussion

The similar EPR and electronic spectra for MnTPP(X)(NO) (X^- = Cl^-, Ac^-, CN^-) complexes imply closely related electronic structures. The EPR g values, ($g_{\perp} > g_{\parallel}$), ^{55}Mn hyperfine coupling constants and absence of large ^{14}N hyperfine splitting place the odd electron in a d_{xy} MO for these complexes.[18] Very similar EPR spectra are obtained for $[Mn(CN)_5(NO)]^{2-}$ and for vanadyl porphyrins which have a single unpaired electron in the metal d_{xy} orbital.[18,19] Comparison of $\langle A\ (^{55}Mn) \rangle$ for MnTPP(CN)(NO) (88.2 G) with the isotropic ^{55}Mn coupling constant in $[Mn(CN)_5(NO)]^{2-}$ (77.4 G)[20] and [MnTPP] (81 G) (Figure 7) illustrates the similarity with other manganese(II) complexes. MnTPP(CN)(NO) has an axially symmetric g tensor, consistent with a near linear Mn-NO unit. The reactivity of Mn^{III}TPP(X) complexes with nitric oxide contrasts with Mn^{III} substituted heme proteins where no nitric oxide complexes have been observed.[17]

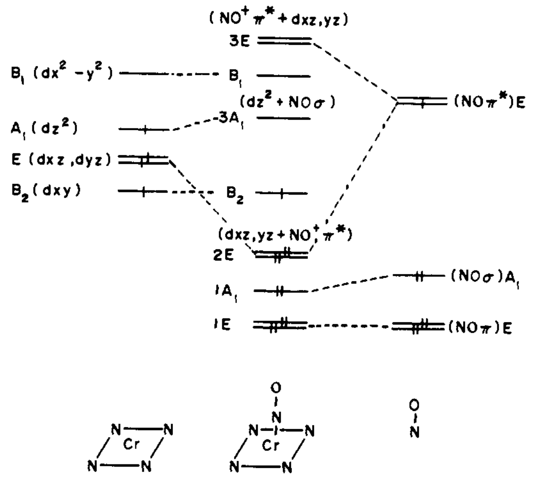

Figure 7. Schematic molecular orbital diagram for CrTPP(NO).

Cr^{III}TPP(OMe) reacts with nitric oxide in the presence of methanol to form CrTPP(NO). This reductive nitrosylation probably proceeds by the following sequence of reactions previously proposed for iron porphyrins:[2,21]

$$CrTPP(OMe) + NO \rightleftarrows CrTPP(OMe)(NO)$$

$$CrTPP(OMe)(NO) + CH_3OH \rightarrow Cr^{II}TPP + CH_3ONO + CH_3OH$$

$$Cr^{II}TPP + NO \rightarrow CrTPP(NO)$$

This process can be considered to result from nucleophilic attack of CH_3OH on coordinated NO^+.

CrTPP(NO) behaves as a low spin d^5 (S = ½) species and the EPR g values ($g_{\perp} > g_{\parallel}$) place the odd electron in the d_{xy} MO in analogy with the isovalence electron complex MnTPP(X)(NO). The isotropic EPR spectrum for CrTPP(NO) is complicated by the appearance of ^{14}N hyperfine splitting from four equivalent porphyrin pyrrole nitrogens $\langle a\ ^{14}N \rangle$ = 3.15 G and one nitric oxide $\langle a\ ^{14}N \rangle$ = 6.5 G. The isotropic coupling constants $\langle a\ ^{14}N \rangle$ (NO) = 6.5 G and $\langle A\ ^{53}Cr \rangle$ = 21.2 G are comparable to the values reported for the electronically related complexes $[Cr(CN)_5NO]^{3-}$ [20] (($\langle a\ ^{14}N \rangle$ (NO) = 5.7 G; $\langle A\ ^{53}Cr \rangle$ = 19.1 G) and $[Cr(NH_3)_5NO]^{2+}$ [22] (($\langle a\ ^{14}N \rangle$ (NO) = 6.98 G; $\langle A\ ^{53}Cr \rangle$ = 25 G). The mechanism for the ^{14}N coupling probably has its origin in an indirect configuration interaction or spin polarization effect, as previously suggested for $[Mn(CN)_5NO]^{2-}$ and $[Cr(CN)_5NO]^{3-}$ [20] and $[Cr(NH_3)_5NO]^{2+}$.[22] A small deviation of the Cr-N-O angle from 180° could also account for the observed ^{14}N hyperfine interaction, since any nonlinearity of the CrNO group will produce a finite overlap between the d_{xy} orbital of chromium and the π orbitals of nitric oxide.[23]

A schematic MO diagram for CrTPP(NO) which is also appropriate for MnTPP(Cl)(NO) appears in Figure 7. This diagram focuses on the metal d and nitric oxide π^* levels which are the principal valence orbitals.[1,23] Formal one-electron reductions of Mn(III) and Cr(II) result from the transfer of the NO π^* electron to the metal site d_{xy} MO. In the formal sense these complexes may be described as Mn^{II}TPP(Cl^-)(NO^+) and Cr^{I}TPP(NO^+), although $d_{xz,yz} \rightarrow \pi^*$ back-bonding reduces or perhaps even reverses the M-NO charge separation. The Mn^{II}(NO^+) and Cr^{I}(NO^+) units are expected to be linear in order to maximize $d\pi \rightarrow \pi^*$ bonding, which is consistent with the observed axially symmetric g tensors for these species. Low spin ferric porphyrin species ($S = \frac{1}{2}$, d^5) such as the cyanide complexes have the odd electron in the $d_{xz \text{ or } yz}$,[24,25] rather than the d_{xy} observed for the $Mn^{II}NO^+$ species ($S = \frac{1}{2}$, d^5). Strong π bonding in the $Mn^{II}NO^+$ and $Cr^{I}NO^+$ units is probably responsible for lowering the $d_{xz,yz}$ below the essentially nonbonding d_{xy}.

The g and A value expressions for a singly occupied d_{xy} orbital are $g_{\parallel} = g_0(1 - [4\lambda\alpha^2\beta^2/\Delta E_{xy \rightarrow x^2-y^2}])$; $g_{\perp} = g_0(1 - [\lambda\delta^2\beta^2/\Delta E_{xz,yz \rightarrow xy}])$; $A_{\parallel} = P(-\frac{4}{7}\beta^2 - K + [g_{\parallel} - g_0] + \frac{3}{7}[g_{\perp} - g_0])$; $A_{\perp} = P(\frac{2}{7}\beta^2 - K + \frac{11}{14}[g_{\perp} - g_0])$ where α, β and δ are the fractional d populations in the molecular orbitals having d_{z^2}, d_{yz}, and d_{xz} population, respectively, and λ is the spin-orbit coupling constant for Mn(II) (λ_0 350 cm^{-1}).[26] A $g_{\perp}$ value close to 2.00 is indicative of the large combined effects of $d_{xz,yz}$–π^* mixing which both increases the $d_{xz,yz} \rightarrow d_{xy}$ energy separation and decreases the effective spin-orbit coupling constant. The electronically related pentacyanonitrosyl metal complexes have been treated in detail by Manoharan and Gray.[20]

The EPR spectrum reported here for $Mn^{II}TPP$ in a frozen toluene glass is unusual in having resolved ^{55}Mn hyperfine splitting, although similar EPR spectra were obtained for manganese(II) protoporphyrin IX embedded in Sephadex G-25 and in reconstituted apohemoproteins.[17,27] Interaction of high spin $Mn^{II}TPP$ (d^5, $S = \frac{5}{2}$) species with nitric oxide results in electron transfer to fill the Mn^{II} d_{xy} and produce a low spin Mn^{I}-NO^+ complex. The d^6 Mn^{I}-NO^+ unit is isoelectronic with Fe^{II}-CO species and the $Fe^{II}TPP(Cl^-)(NO^+)$ complex.[2] Linear metal-diatomic units which maximize $d_{xz,yz} \rightarrow \pi^*$ bonding are expected for these complexes. A near linear Mn-N-O angle of 176.2° has been observed in MnTPP(NO)(4-methylpiperidine).[4] $Mn^{II}TPP$ species mimic the high spin manganese(II) substituted heme proteins which add nitric oxide to form low spin nitric oxide complexes.[17]

The N-O stretching frequency at 1760 cm^{-1} in MnTPP(NO) is similar to that in the electronically related $[Mn(CN)_5(NO)]^{3-}$ complex ($\nu_{NO} = 1725$ cm^{-1}).[28] Effective back π bonding associated with a linear $Mn^{I}NO^+$ unit is undoubtedly responsible for the position of ν_{NO}. Comparison of the ν_{NO} values in the isoelectronic (d^6) complexes MnTPP(NO), (Mn^{I}-NO^+), $\nu_{NO} = 1760$ cm^{-1}, and FeTPP(Cl)(NO), (Fe^{II}-NO^+)$\nu_{NO} = 1880$ cm^{-1}, illustrates the increased M-NO^+ back π bonding with decreased metal oxidation state. Similarly, the isoelectronic (d^5) pair CrTPP(NO), ($Cr^{I}NO^+$), and MnTPP(X)(NO), (Mn^{II}-NO^+) have ν_{NO} values of 1700 and 1830 cm^{-1}, respectively. The trend in ν_{NO} values in these nitrosyl complexes parallels those reported in the corresponding pentacyanonitrosyl metal complexes.[20]

Electronic spectra for metalloporphyrins are generally characterized by the uv (Soret) and visible absorption bands.[29] The Soret band is electronically allowed and is an order of magnitude more intense than the visible band which acquires intensity primarily from a vibronic mechanism.[30-33] Electronic spectra for all of the chromium tetraphenylporphyrin complexes are typical (Figure 5). High spin (d^4) manganese(III) porphyrin complexes have electronic spectra which dramatically deviate from the typical porphyrin spectra (Figure 4). Near degeneracy of the metal $d_{xz,yz}$ with the porphyrin π^* orbitals has been suggested by Boucher to result in extensive mixing of these orbitals.[13,14] Extra bands in the spectra are suspected to arise from charge transfer transitions. In particular the band near 4800 Å is characteristic of $Mn^{III}TPP(X)$ complexes and has been assigned to a porphyrin $\pi \rightarrow d_{xz,yz}$ transition.[13] Retention of a band in this region for the nitric oxide complexes of MnTPP(X) (Figure 5) is unexpected for this assignment. MnTPP(X)(NO) complexes are low spin d^5 cases with the configuration $(d_{xz,yz})^4$ $(d_{xy})^1$ and electronic transitions from the filled ligand π to the $d_{xz,yz}$ are thus not possible for these complexes.

Summary

A series of nitric oxide complexes of metal tetraphenylporphyrin complexes has been observed: CrTPP(X)(NO), CrTPP(NO), MnTPP(X)(NO), MnTPP(NO), FeTPP(X)(NO), FeTPP(NO), $FeTPP(NO)_2$, and CoTPP(NO).[1-5] All of these nitric oxide complexes have low spin ($S = 0$) or ($S = \frac{1}{2}$) ground states which maximize the opportunity for metal $d\pi$ donor and $d\sigma$ acceptor properties toward the nitric oxide ligand. The (d + π^*) seven and eight electron cases FeTPP(NO) and CoTPP(NO) have bent M-NO units and rely heavily on effective metal-nitric oxide σ covalent bonding for their stability. The Co-NO bond in CoTPP(NO) is formulated as a normal two-electron covalent bond in analogy with cobalt alkyl complexes. Complexes where the sum of metal d and nitric oxide π^* electrons is six or less are formulated as linear M-NO^+ ($d^n + \pi^{*0}$) species. All currently observed complexes of this type have a minimum of four (d + π^*) electrons which may be a requirement for nitric oxide complex formation. Four electrons are needed to fill the $d_{xz,yz}$ and provide the most effective back-bonding. In this regard the failure of the d^1 case VOTPP to bind nitric oxide is probably significant. The (d + π^*) five-electron complexes, CrTPP(NO) and Mn(TPP)(X)(NO), have the single odd electron in the d_{xy} orbital showing that the $d_{xz,yz}$ are at lower energy and filled which is consistent with the importance of the metal π donor properties.

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Energetics of Electrode Reactions. II.[1] The Relationship between Redox Potentials, Ionization Potentials, Electron Affinities, and Solvation Energies of Aromatic Hydrocarbons

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Abstract: Reversible oxidation and reduction potentials for alternant aromatic hydrocarbons (AAH) correlate linearly with ionization potentials (IP) and electron affinities (EA), and the slopes of the correlation lines were found to be equal to unity indicating that the solvation energies of AAH ions do not vary throughout the series. Oxidation and reduction potentials for AAH were observed to be symmetrically disposed about a common potential M_{AAH} (−0.31 V vs. SCE). The solution redox potentials were found to be related to IP and EA in the gas phase by $E_{\mathrm{M}} = \mathrm{IP} - \phi + (\Delta G°_{\mathrm{solv}})^{\pm} = \phi - \mathrm{EA} + (\Delta G°_{\mathrm{solv}})^{\pm}$, where ϕ is equal to 4.4 eV, and $(\Delta G°_{\mathrm{solv}})^{\pm}$ is equal to one-half of the sum of the solvation energies of the positive and negative ions. Furthermore, it was concluded that the solvation energies of the positive and negative ions of AAH are the same and equal to −1.94 eV. The value of the solvation energies calculated as above was verified by identity with those obtained from $-(E_{\mathrm{O}} - E_{\mathrm{R}}) = \mathrm{EA} - \mathrm{IP} - 2(\Delta G°_{\mathrm{solv}})^{\pm}$, where the sums of the redox potentials are independent of a reference potential. Correlation of E_{sum} with IP and EA indicated that the quantity is zero for the hypothetical AAH having IP = 6.27 and EA = 2.35 eV, indicating that the compound should be 50% ionized in solution. AAH having EA values greater than 2.36 eV would be completely ionized in acetonitrile solution according to: $2\mathrm{AAH} \rightleftarrows \mathrm{AAH}^+ + \mathrm{AAH}^-$. The driving force for the ionization reaction is the solvation energies of the ions.

Numerous correlations of oxidation and reduction electrode potentials with ionization potentials and electron affinities have been reported[2] and discussed.[3,4] The comment has been made[5] that it is best to use reversible potentials in order to obtain meaningful correlations. However, it was implied that the use of reversible potentials is not completely necessary. The reported correlation lines invariably have slopes somewhat less than unity and this is generally attributed to changes in solvation energies in a series of compounds.[2] However, most correlations have involved the use of irreversible half-wave potentials and, since the ions of compounds exhibiting the highest ionization potentials and lowest electron affinities are also the most reactive, the deviations observed in slope could just as well arise from kinetic behavior.

In a preliminary report of this work, it was suggested that, since the chemical solvation energies of the positive and negative ions of alternant aromatic hydrocarbons (AAH) are expected to be equal, the oxidation and reduction potentials should also be symmetric about zero, and that the common midpoint potential for AAH should be considered the zero point against which to measure the energy change of an electrode reaction. Attempts to calculate "absolute" electrode potentials[6] have not been successful due to the lack of an exact value for a solvation energy, lack of knowledge of surface potentials of metals, and lack of an absolute value for the chemical potential of the electron.[7] Real solvation energies of AAH ions have been calculated from redox potentials referred to an "absolute" scale leading to the result that, in acetonitrile, the positive ions invariably have significantly higher real solvation energies.[8]

In this paper the recently developed techniques for measuring reversible oxidation[9] and reduction[10] potentials in aprotic solvents are employed to give reversible redox potentials for several AAH and the reversible potentials are correlated with the recently calculated IP and EA values.[2]

Correlation Method

The energetics of reduction in solution as compared with the gas phase electron affinity (EA) for aromatic hydrocarbons was first analyzed in detail by Hoijtink,[11] and essentially the same derivation has been used by more recent authors.[2,3] When an electron adds to a molecule in the gas phase, energy is liberated which is equal to −EA (eq 1). In solution, the free energy change reflected by the half-wave potential of a reversible one-electron reduction is given by (2) or (3). $(\Delta G°)_{\mathrm{solv}}$ is the difference in free energies of solvation of the hydrocarbon and its anion. Neglecting entropy effects, substitution of EA into (3) gives (4).

$$\mathrm{R} + \mathrm{e} \rightarrow \mathrm{R}^- \qquad \Delta H° = -\mathrm{EA} \tag{1}$$

$$\Delta G° = (G°_{\mathrm{R}})_{\mathrm{sol}} - (G°_{\mathrm{R^-}})_{\mathrm{sol}} + (G°_{\mathrm{electron}})_{\mathrm{Hg}} \tag{2}$$

$$\Delta G° = (G°_{\mathrm{R}})_{\mathrm{gas}} - (G°_{\mathrm{R^-}})_{\mathrm{gas}} + (G°_{\mathrm{electron}})_{\mathrm{Hg}} + (\Delta G°)_{\mathrm{solv}} \tag{3}$$

$$\Delta G° = \mathrm{EA} + (G°_{\mathrm{electron}})_{\mathrm{Hg}} + (\Delta G°)_{\mathrm{solv}} \tag{4}$$