Spectroscopic Studies and Bonding Model for Nitric Oxide Complexes of Iron Porphyrins

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Abstract: Fe^{III}TPPCl reacts reversibly with nitric oxide to form FeTPP(Cl)(NO) which is spectroscopically studied in toluene solution, glass media, and Nujol mulls. This diamagnetic nitric oxide complex is formulated as Fe^{II}TPP(Cl$^-$)(NO$^+$). In the presence of methanol, Fe^{III}TPPCl reacts with excess nitric oxide to produce Fe^{II}TPP(NO). This reaction is thought to proceed *via* the methanolysis of coordinated NO$^+$ in the intermediate Fe^{II}TPP(Cl$^-$)(NO$^+$) complex. Fe^{II}TPP(NO) has a doublet ground state with the odd electron in a molecular orbital with Fe (d$_{z^2}$) and NO (σ_N) character. Fe^{II}TPP(NO) adds nitrogen donors in the sixth coordination position which have epr spectra showing ^{14}N hyperfine from both nitrogen bonded ligands. A second nitric oxide is reversibly coordinated by Fe^{II}TPP(NO) to form FeTPP(NO)$_2$, which on the basis of magnetic and spectroscopic properties is formulated as Fe^{II}TPP(NO$^-$)(NO$^+$). Two N–O stretching frequencies are observed consistent with linear Fe^{II}-NO$^+$ and bent Fe^{II}NO$^-$ units. Bonding models are presented for the nitric oxide complexes and generalized for related complexes of diatomic molecules.

Complexes of diatomic molecules with metalloporphyrins and their relationship to hemoprotein complexes have been a focal point for model systems studies.[1-10] Hemoprotein reactions with nitric oxide have been extensively examined. Both the Fe(II) and Fe(III) forms of myoglobin and hemoglobin react with nitric oxide to form Fe^{II}NO derivatives.[11,12] Ferric cytochrome peroxidase and horseradish peroxidase, however, are not reduced by nitric oxide, but form low spin adducts.[13,14] Examination of the interaction of nitric oxide with Fe(II) and Fe(III) porphyrin complexes under defined conditions can provide insight into the nature of the hemoprotein–nitric oxide complexes and the reductive nitrosylation reaction. In this paper we report on the observation and spectroscopic studies of NO complexes of Fe^{II}TPP and Fe^{III}TPPCl along with a general bonding model for complexes of this type.

Experimental Section

Materials. Tetraphenylporphyriniron(III) chloride (FeTPPCl) was prepared by literature methods.[15,16] Purification was effected

by chromatography on aluminum oxide (Woelm neutral, activity grade 1). This procedure resulted in formation of some (FeTPP)$_2$O dimer which was converted to the chloride by shaking with HCl.[17]

Fe^{II}TPP(NO) was prepared by dissolving Fe^{III}TPPCl in degassed toluene on a vacuum line, followed by addition of nitric oxide and methanol. The solution was then pumped to dryness and the solid was isolated in air.

C.P. 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$_2$O$_5$ and vacuum distilled. Methanol was freshly distilled from Mg(OCH$_3$)$_2$ and then vacuum distilled. Piperidine was dried over KOH and distilled from P$_2$O$_5$. Pyridine was dried over molecular sieves and vacuum distilled.

Procedure. Samples for epr and electronic spectra were prepared on a high vacuum line by placing the solid iron porphyrin in a 4-mm quartz tube fitted with a vacuum stopcock and evacuating. Solvents were degassed and introduced by vacuum distillation.

Solution magnetic susceptibilities were measured by the nmr method.[18] Solutions were prepared with a deuterated toluene-cyclohexane solvent and susceptibility measurements were made from the cyclohexane shifts. Measurements of iron complexes in the presence of nitric oxide were corrected by independent studies of the solvent with nitric oxide at the same pressure and temperature condition.

Infrared spectra were recorded as Nujol mulls. The spectra for nitric oxide adducts of FeTPPCl and FeTPP(NO) were obtained by employing a cell generously loaned to us by Professor D. Schmulbach. The mull was placed on the inner face of a window and the 5-mm path length between the two windows was evacuated. Nitric oxide could then be introduced and allowed to diffuse into the mull. Vibrational bands obscured by the spectrum of free nitric oxide were measured by evacuating the cell and recording the spectrum while the adduct was trapped in the mull. Infrared spectra were recorded with KRS-5 windows and electronic spectra with quartz windows.

Instrumentation. Epr spectra were recorded on a Varian Model V-4502 X-band spectrometer equipped with a Field Dial Mark I, Hewlett-Packard Model 7001 AM x-y recorder, and a Hewlett-Packard frequency meter, Model X-532B. Cooling was provided by a cold nitrogen gas stream using a Varian U-4557 variable temperature accessory to control the temperature to ±2°. Field calibrations were made with DPPH powder ($g = 2.0036$).

Electronic spectra were recorded on a Cary Model 14 recording spectrophotometer. Low temperature spectra were obtained by

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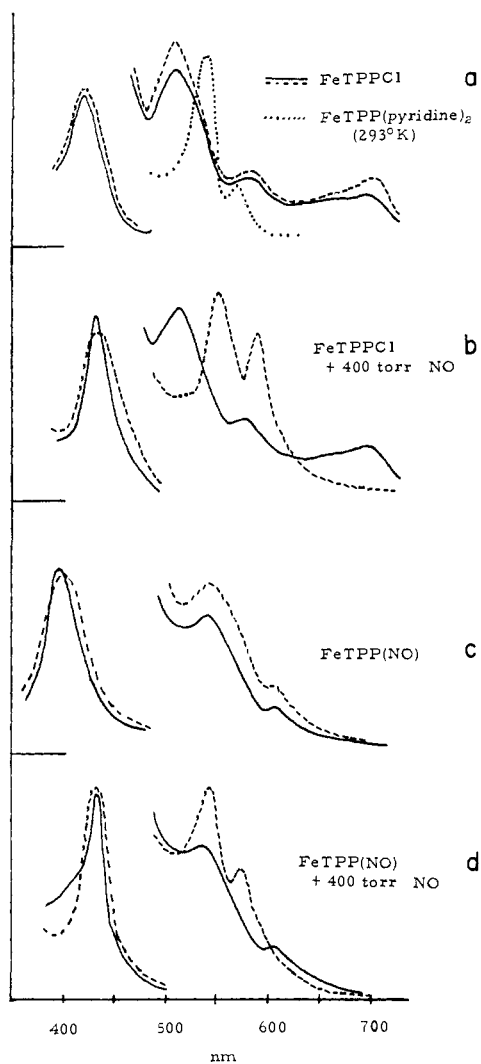
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Figure 1. Electronic spectra for tetraphenylporphyrin iron complexes (———, 293°K; ----, 77°K).

placing a 4-mm epr tube in a dewar with fused quartz optical windows. Infrared spectra were measured on a Perkin-Elmer 421 grating spectrophotometer. A 60 and HA 100 spectrometers with provision for temperature control were used in nmr measurements.

Results

FeTPP(Cl)(NO). FeTPPCl is a high spin Fe(III) complex with an $S = {}^5/_2$ ground state.[17] Electronic spectra for toluene solutions (293°K) of $Fe^{III}TPPCl$ as shown in Figure 1a are virtually unchanged by freezing to 77°K. Exposure of this solution to nitric oxide results in the reversible appearance of a new electronic spectrum which increases in intensity as the pressure of NO is increased or the temperature is lowered. The electronic spectrum that is observed on freezing to 77°K appears in Figure 1b. Spectral bands at 6905, 6565, and 5080 Å characteristic of high spin $Fe^{III}TPPCl$ disappear and new bands centered at 5770 and 5430 Å appear in toluene glass media. The new electronic spectrum is characteristic of a low spin complex and is closely related to $Fe^{II}TPP(C_5H_5N)_2$[19] (Figure 1a). Examination of H_2TPP under the same conditions eliminates the interaction of NO with the porphyrin ligand as the source of these spectral changes. Nujol

mull electronic spectra of FeTPPCl in contact with 1 atm of nitric oxide are identical with those obtained in frozen toluene glasses demonstrating that this reaction also occurs in the solid state. Evacuation of the excess nitric oxide regenerates (∼1 hr) the FeTPPCl spectrum. Infrared spectra of similar mulls reveal the presence of a new band at 1880 cm⁻¹ which decreases in intensity and disappears when excess nitric oxide is removed. Appearance of the new electronic spectrum is accompanied by disappearance of the characteristic epr spectrum for $Fe^{III}TPPCl$,[20] and no new transitions are observed in the glass (77°K). These epr observations are consistent with formation of an even-electron species. Solution susceptibility measurements were made by the nmr method. In the presence of nitric oxide the average solution susceptibility associated with the iron porphyrin species decreases as the temperature is lowered or the pressure of nitric oxide increased. No difference in susceptibility between the sample and reference was detected for a 7×10^{-3} M solution of FeTPPCl at 1 atm of nitric oxide and 213°K. In contrast, Curie behavior is observed for FeTPPCl in the absence of nitric oxide. These spectral and magnetic observations on toluene solutions, glass media, and Nujol mulls are associated with nitric oxide binding the iron site to form the diamagnetic complex FeTPP(Cl)(NO).

A recent report of FeTPP(Cl)(NO) claims that this complex is high spin ($\mu = 4.5$ BM) with an electronic spectrum identical with that of FeTPPCl.[21] Although we observe a similar N-O stretching frequency (1880 cm⁻¹), we find that FeTPP(Cl)(NO) is diamagnetic and has an electronic spectrum characteristic of a low spin Fe(II) porphyrin.

FeTPP(NO). Toluene solutions of $Fe^{III}TPPCl$ in the presence of excess nitric oxide react with methanol to produce $Fe^{II}TPP(NO)$. FeTPP(NO) can be isolated in air and characterized by analytical and spectroscopic methods. Electronic spectra of FeTPP(NO) in toluene solution (293°K) are virtually unaffected by freezing to 77°K (Figure 1c). Infrared spectra for Nujol mulls of FeTPP(NO) have a strong band at 1700 cm⁻¹ associated with ν_{NO}. Spin susceptibility measurements (270-330°K) demonstrate a doublet ground state ($S = {}^1/_2$) and Curie behavior for FeTPP(NO). Toluene glass epr spectra show three g values with nitric oxide ¹⁴N hyperfine splitting in each region (Figure 2a).

FeTPP(NO) can form 1:1 adducts with donors such as pyridine and piperidine but no adducts of phosphorus donors (PF_3, $P(Bu)_3$, $P(BuO)_3$) were observed. The donors are only weakly bound and can be removed under vacuum. Epr spectra for FeTPP(NO)(B) (B = C_5H_5N, $C_5H_{11}N$) in toluene glass (130°K) show a rhombic g tensor, with ¹⁴N hyperfine splitting from both nitric oxide and the ring nitrogen donor in the g_z region (Figures 2b and 2c). These spectra are closely related to those for the NO complexes of Fe(II) myoglobin[11] and hemoglobin[22,23] where iron is axially coordinated by histidine.

FeTPP(NO)₂. Epr spectra for FeTPP(NO) in toluene solution are found in Figure 3. In the presence of nitric oxide the epr spectrum for FeTPP(NO) de-

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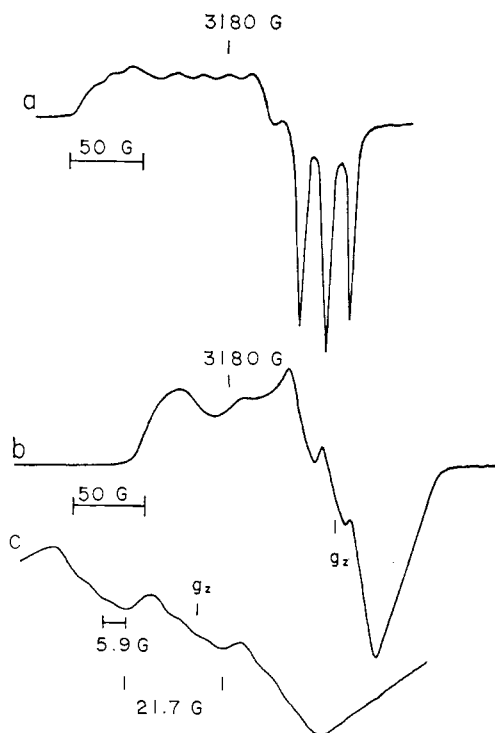(23) H. Kon, *J. Biol. Chem.*, **243**, 4350 (1968).

Figure 2. Epr spectra in toluene glass (120°K): (a) Fe^{II}TPP-(NO) (g_1 = 2.102, a_1(^{14}N) = 12.6 G; g_2 = 2.064, a_2(^{14}N) = 17.2 G; g_3 = 2.010, a_3(^{14}N) = 17.3 G), (b) Fe^{II}TPP(NO)(pip) (g_1 = 2.08; g_2 = 2.04; g_3 = 2.003, a_3(^{14}N) = 21.7 G), (c) g_z region of Fe^{II}-TPP(NO)(pip) showing nitrogen-14 splitting from nitric oxide (21.7 G) and piperidine (5.9 G).

creases in intensity as the pressure of NO is increased or the temperature is lowered. No epr transitions are detected in the glass media (77°K) which is consistent with the formation of an even-electron species. Disappearance of the FeTPP(NO) epr spectrum is accompanied by the appearance of a new electronic spectrum (Figure 1d) remarkably similar to FeTPP-(Cl)(NO) and low spin Fe^{II}TPP(C$_5$H$_5$N)$_2$. Identical electronic spectra are obtained from Nujol mulls of FeTPP(NO) in contact with 1 atm of nitric oxide. Removal of excess nitric oxide regenerates the FeTPP-(NO) spectrum after pumping for several hours. The infrared spectrum of the nitric oxide adduct of FeTPP-(NO) was measured by removing excess nitric oxide from the cell and recording the spectrum while the bis nitrosyl was trapped in the mull. Two N–O stretching frequencies were observed at 1870 and 1690 cm^{-1}. The 1870-cm^{-1} band decreased and disappeared upon evacuation of the cell. We associate these spectral changes with formation of FeTPP(NO)$_2$. Solution susceptibility measurements as a function of temperature indicate that FeTPP(NO)$_2$ is diamagnetic.

Discussion

FeTPP(NO) has a doublet (S = $^1/_2$) ground state and is conveniently studied by epr in both solution and glass media. Observation of ^{14}N hyperfine coupling from both nitric oxide and the ring nitrogen donor in FeTPP(NO)(B) (B = C$_5$H$_5$N, C$_5$H$_{11}$N) provides evidence for placing the odd electron in a molecular orbital with substantial iron d$_{z^2}$ character. The odd electron which originates on nitric oxide thus becomes highly delocalized to iron in the complex. The spin
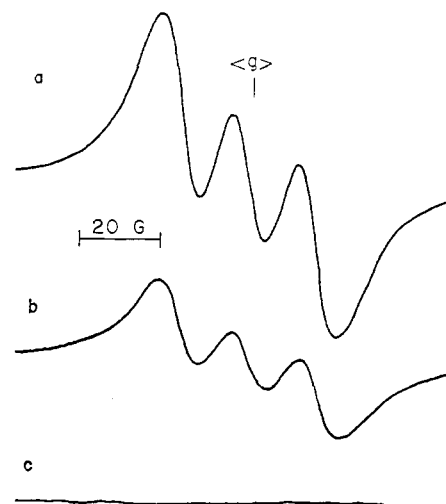

Figure 3. Epr spectra for FeTPP(NO) in toluene. ⟨g⟩ = 2.054, ⟨a⟩(^{14}N) = 17.4 G: (a) 253°K, (b) 253°K, 400 Torr nitric oxide, (c) 203°K, 400 Torr nitric oxide.

density that reaches the donor atom for an axially coordinated ligand is dependent on the metal d$_{z^2}$ odd electron population. Comparison of the pyridine ^{14}N hyperfine splitting in the g_z region for CoTPP(py) (15.8 G)[24] where the odd electron is virtually localized in the d$_{z^2}$ with the corresponding value for FeTPP(NO)-(py) (5.9 G) is indicative of the substantial d$_{z^2}$ population in FeTPP(NO). Epr and Mössbauer studies have been used to demonstrate a similar electron distribution in the closely related Fe^{II}NO hemeproteins.[11,22,25]

The g value expressions for a (d$_{z^2}$)^1 configuration are[26]

$$g_{zz} = 2.002 \tag{1}$$

$$g_{xx} = 2.002 - 6\lambda\alpha^2\beta^2/\Delta E_{yz \to z^2} \tag{2}$$

$$g_{yy} = 2.002 - 6\lambda\alpha^2\beta^2/\Delta E_{xz \to z^2} \tag{3}$$

where λ is the spin–orbit coupling constant for Fe(II) ($\lambda_0 \sim 390$ cm^{-1})[27] and α, β, and γ are the fractional d populations in the molecular orbitals having d$_{z^2}$, d$_{yz}$, and d$_{xz}$ population, respectively. Coordination of FeTPP-(NO) by a donor molecule results in decreased g values (Figure 2b), due to the combined effects of the donor increasing ΔE values (elevation of the d$_{z^2}$) and decreasing α^2 (d$_{z^2}$ population) (eq 2 and 3). The decrease in d$_{z^2}$ odd electron population accompanying coordination of FeTPP(NO) by a donor is reflected in an increased ^{14}N coupling constant for nitric oxide as well as spin delocalization to the ring nitrogen donor (Figure 2).

Observation of three g values in FeTPP(NO) and the 1:1 nitrogen donor adducts indicates that the d$_{xz}$, d$_{yz}$ orbitals are nondegenerate (eq 2 and 3). Interaction of the filled metal dπ orbitals with the nitric oxide π^* provides an appropriate bonding mechanism for splitting of the d$_{xz}$, d$_{yz}$ when the iron–nitric oxide unit is bent and stationary on the epr time scale. Preliminary X-ray studies by Scheidt and Frisse demonstrate

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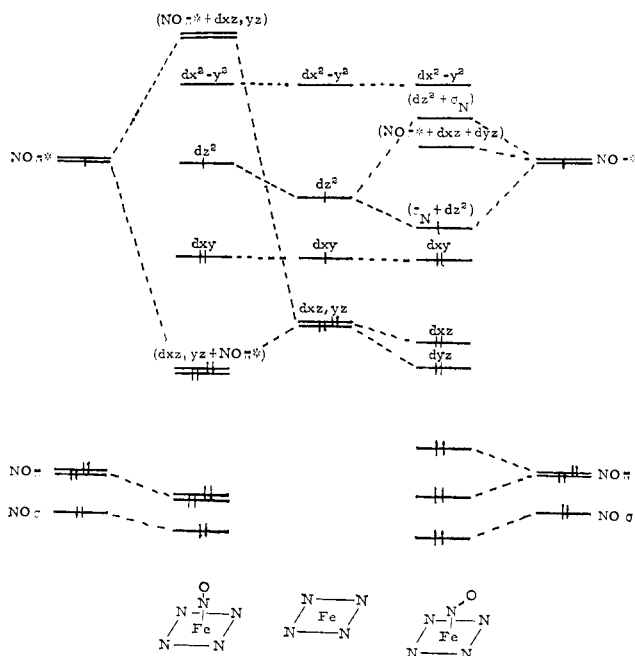
Figure 4. Schematic MO diagram for FeTPP(NO).

bent Fe–NO units in these complexes.[28] FeTPP(NO) is formally isoelectronic with other Fe(II) chelate species in which bent Fe–NO units have also been demonstrated.[29]

A molecular orbital scheme related to those previously suggested for nitric oxide complexes[24,30–32] is presented in Figure 4. Several of the principal features of the MO scheme are (1) linear diatomic–metal bonding maximizes $d\pi \rightarrow p\pi$ bonding, (2) bent diatomic–metal bonding removes the ligand π^* double degeneracy to produce one MO that is essentially a diatomic π^* and a second orbital appropriate for covalent σ bonding with the metal d_{z^2}, (3) bending of the diatomic–metal fragment is expected when either or both the metal d_{z^2} or the ligand π^* level are partially occupied, and (4) the degree of bending depends upon the relative importance of covalent σ bonding and π back-bonding.

The Nσ orbital generated by bending the Fe–N–O unit becomes singly occupied and the ligand based π^* orbital becomes empty in FeTPP(NO) (Figure 4). The odd electron occupies a molecular orbital of principally nitric oxide Nσ and Fe d_{z^2} character resulting in essentially a one-electron Fe–NO covalent σ bond. If an additional ligand were axially coordinated, then the donor MO for this ligand would also participate in the odd electron MO. Nitrogen-14 hyperfine splitting from both NO and the sixth nitrogen donor in FeTPP(NO)(B) (B = C_5H_5N, $C_5H_{11}N$) can only be explained in terms of an eigenvector of this type, demonstrating that this aspect of the MO model is correct.

In terms of a valence bonding model the Fe–NO σ

bonding would be a hybrid of one- and two-electron interactions (TPPFe · NO ↔ TPPFe:NO). Counting the metal d and ligand donor electrons, these resonance forms correspond to 15- or 16-electron cases. Additional coordination of a two-electron donor produces acceptable 17- or 18-electron cases. If the Fe–NO unit were linear, nitric oxide would function as a three-electron donor producing a 17-electron case. In this case occupation of the sixth-coordination site by a two-electron donor would produce an unfavorable 19-electron case.

The N–O stretching frequencies for FeTPP(NO) and FeTPP(NO)(pip) (pip = piperidine), 1700 and 1680 cm^{-1}, respectively, lie in the range frequently associated with NO$^-$. This has led to the assignment of FeTPP-(NO)(pip) as an Fe^{III}NO$^-$ species.[33] However, the empty Fe(II) d_{z^2} in these complexes functions as an acceptor orbital for the nitric oxide π^* electron resulting in partial reduction of iron(II). This charge redistribution in the σ system can be partially compensated by $d\pi \rightarrow p\pi$ back-bonding, but the net charge on nitric oxide should be either positive or close to zero. The origin of the relatively low ν_{NO} values stems from the bending of the Fe–NO unit irrespective of the charge distribution. The fully occupied π bonding orbitals of nitric oxide split upon bending to form one occupied π orbital (π bond) and an occupied σ orbital (oxygen "lone pair"), resulting in a reduced π bond order. Correlation of ν_{NO} with effective oxidation state is thus not valid for bent nitrosyl complexes.

FeTPP(Cl)(NO). Coordination of nitric oxide by FeTPPCl results in a low spin diamagnetic complex. The similarity in electronic spectra between FeTPP-(Cl)(NO) and diamagnetic Fe(II) porphyrin species suggests the formulation of this compound as a low spin Fe(II) complex, Fe^{II}TPP(Cl$^-$)(NO$^+$). The Fe^{II}NO$^+$ unit is thus formally isoelectronic with the better known Fe^{II}CO complexes.[9,34] Spectroscopic and magnetic properties for nitric oxide complexes of ferric peroxidases parallel those for FeTPP(Cl)(NO).[13,14]

The position of the N–O stretching vibration (1880 cm^{-1}) is only consistent with a linear Fe–NO fragment (vide ante) and is indicative of extensive π back-bonding. Similar values for ν_{NO} have been observed in formally isoelectric complexes with known linear metal–nitrosyl units: ν_{NO} = 1939 cm^{-1} for Fe(CN)$_5$(NO)$^{2-}$,[35,36] ν_{NO} = 1860 cm^{-1} for RuCl$_3$(NO)(PMePh$_2$)$_2$.[37,38]

A proposed schematic MO description for Fe^{II}TPP-(Cl$^-$)(NO$^+$) is given in Figure 5. The interaction of nitric oxide with the Fe(III) site results in an electron transfer from the NO π^* to the lower energy d orbitals. A linear Fe^{II}NO$^+$ fragment which maximizes $d\pi \rightarrow p\pi$ bonding is predicted because no extra stabilization is achieved upon bending when both the d_{z^2} and π^* orbitals are empty. The donor orbitals of Cl$^-$ and NO$^+$ form σ bonds with the empty Fe^{II} d_{z^2}, and the empty

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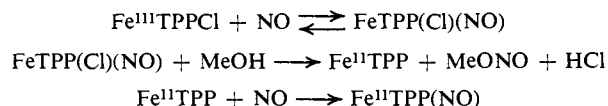
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NO^+ π^* functions as an acceptor toward the filled $d_{xz,yz}$. Spin pairing the d orbitals enhances both the $Fe^{II}-NO^+$ σ and π bonding by emptying the d_{z^2} and filling the $d_{xz,yz}$ and could be a requirement for nitric oxide complexes of this type. In valence bonding terms FeTPPCl is a 15-electron case and adds nitric oxide as a three-electron donor to form an 18-electron case $Fe^{II}TPP(Cl^-)(NO^+)$.

Reductive Nitrosylation. Addition of methanol and nitric oxide to a toluene solution of $Fe^{III}TPPCl$ results in reductive nitrosylation to form $Fe^{II}TPP(NO)$. The following reaction sequence in analogy with previous studies of reductive nitrosylation is proposed.[12,39]

$$Fe^{III}TPPCl + NO \rightleftarrows FeTPP(Cl)(NO)$$

$$FeTPP(Cl)(NO) + MeOH \longrightarrow Fe^{II}TPP + MeONO + HCl$$

$$Fe^{II}TPP + NO \longrightarrow Fe^{II}TPP(NO)$$

Direct observation of FeTPP(Cl)(NO) suggests this species as a probable intermediate. Formulation of this species as $Fe^{II}TPP(Cl^-)(NO^+)$ suggests that the role of the hydroxylic reagent is simply to react with coordinated NO^+. This reductive nitrosylation reaction must be closely related to the reactions of nitric oxide with aqueous solutions of hemin chloride[23] and ferric myoglobin[12] and hemoglobin[11] species.

Reactions of crystalline and freeze-dried metmyoglobin with nitric oxide have been examined in an attempt to trap a $MbFe^{III}NO$ complex. Solid metmyoglobin is found to react with nitric oxide to rapidly yield $MbFe^{II}NO$. Hydrolysis of the anticipated intermediate complex may well be effected by the water molecule in the heme sixth-coordinated position. We believe that reductive nitrosylation is a characteristic of an $Fe^{II}NO^+$ species when an appropriate reagent is available for reaction with coordinated NO^+. Failure of the ferric peroxidases to be reduced by nitric oxide provides an indication that the heme binding site is inaccessible to H_2O.

FeTPP(NO)(NO). FeTPP(NO) coordinates a second nitric oxide resulting in the diamagnetic complex $FeTPP(NO)_2$. Electronic spectra for this complex are closely related to those for FeTPP(Cl)(NO) and related low spin Fe(II) porphyrin complexes and suggest the formulation $Fe^{II}TPP(NO^-)(NO^+)$ in analogy with $Fe^{II}TPP(Cl^-)(NO^+)$.

Experimental evidence for formulating $FeTPP(NO)_2$ as containing two different types of coordinated nitrosyl ligands is obtained from the presence of two NO vibrations (1870 and 1690 cm^{-1}) in the mull spectrum of $FeTPP(NO)_2$. The band at 1870 cm^{-1} is in the range expected for a linear $Fe^{II}NO^+$ unit and the 1690-cm^{-1} band is consistent with a bent $Fe^{II}NO^-$ fragment. The similarity of ν_{NO} in $FeTPP(NO)_2$ (1870 cm^{-1}) and FeTPP(Cl)(NO) (1880 cm^{-1}) coupled with their nearly identical electronic spectra justifies the analogy in the formulation of their electronic structure. Support for this formulation comes from the molecular structure of the related complex $[RuCl(NO)_2(P(C_6H_5)_3)_2]$. This species contains linear (178°) and bent (138°) Ru–NO units and exhibits ν_{NO} bands at 1845 and 1687 cm^{-1}.[40]

Figure 5. Schematic MO diagram for FeTPP(Cl)(NO).

Two N–O stretching frequencies were also observed in a recently reported dinitrosyl complex of a Ru(II) porphyrin and originally attributed to solid state effects.[41] We believe this Ru(II) complex may be formulated as containing both coordinated NO^+ and NO^- in analogy with the isoelectronic $Fe^{II}TPP(NO)_2$ complex.

Inspection of the outline MO diagrams for FeTPP-(NO) and FeTPP(Cl)(NO) provides insight into why a species of this type may form. Interaction of nitric oxide with FeTPP(NO) results in transfer of the NO π^* electron to the singly occupied ($\sigma N + d_{z^2}$) MO in FeTPP(NO) (Figure 4) and coordination of nitric oxide as NO^+. Double occupation of the ($\sigma N + d_{z^2}$) orbital effectively produces a coordinated singlet NO^-. The principal features for an MO description for $FeTPP(NO^-)(NO^+)$ can be generated by substituting an NO^- σ donor orbital for the Cl^- donor orbital in Figure 5.

The reaction of FeTPP(NO) with nitric oxide to form $Fe^{II}TPP(NO^-)(NO^+)$ can be viewed as the conversion of a 15-electron to an 18-electron case. The $Fe^{II}NO^-$ unit is isoelectronic with the bent $Co^{III}NO^-$ unit in $CoTPP(NO)$[42] and with the $Fe^{II}O_2$ unit in oxyhemoglobin and the recently reported dioxygen complexes of Fe(II) porphyrins.[43]

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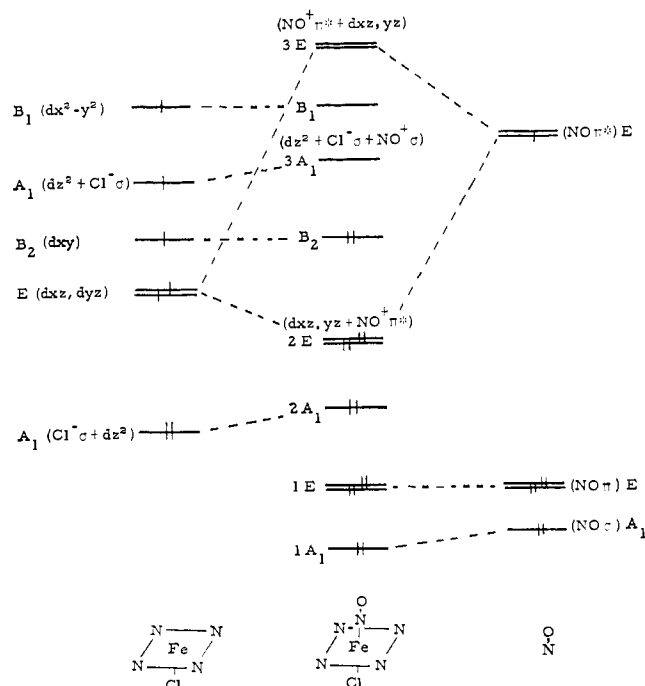
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