boring ethyl groups would very much increase if Ni(OEPMe₂) were dehydrogenated to α,γ-dimethyloctaethylporphinatonickel(II), Ni(ODM). Therefore, Ni(OEPMe₂) is air-stable. Ni(ODM) may be obtained, however, by metal insertion into the parent porphine.[19] In Ni(ODM), the methyl···methylene carbon contacts are expected to be substantially smaller than the $\geqslant 3.9$ Å contacts found for Ni(OEPMe₂). Indeed, if Ni(ODM) has the same highly ruffled core of Ni(OEP),[31b] the nonbonded contacts can be calculated to be an unreasonably tight 2.8 Å. Hence, Ni(ODM) must represent a metalloporphyrin with a severely distorted core.

Spectroscopic Studies for Tetraphenylporphyrincobalt(II) Complexes of CO, NO, O₂, RNC, and (RO)₃P, and a Bonding Model for Complexes of CO, NO, and O₂ with Cobalt(II) and Iron(II) Porphyrins

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Abstract: Epr and electronic spectra are reported for tetraphenylporphyrincobalt(II) [Co^{II}TPP] complexes of CO, NO, O₂, (CH₃O)₃P, and nitrogen donors. Epr spectra show that each Co^{II}TPP complex with a closed shell ligand has a $(d_{zz,yz}, d_{xy})^6(d_z^2)^1$ ground configuration. Ligand hyperfine coupling constants (^{13}C and ^{31}P) are reported for the CO, (CH₃O)₃P, and (Bu)₃P complexes and are used in examining the nature of the ligand σ-donor orbitals. The carbon monoxide donor orbital is found to be essentially a sp hybrid, while the phosphorus donor orbital character is very sensitive to substituents. Toluene glass electronic spectra for Co^{II}TPP complexes of CO, NO, and O₂ are reported. Two bands are observed in the Soret region of the CO and NO complexes. Co^{II}TPP complexes of CO, CH₃NC, and R₃P form dioxygen complexes with epr spectra consistent with the odd electron occupying a highly localized oxygen based π^* level. A molecular orbital model is proposed for correlating the structure and bonding in adducts of diatomic molecules with low spin cobalt(II) and iron(II) complexes. This model is found to be compatible with all available data on CO, NO, and O₂ complexes of cobalt(II) and iron(II) porphyrins and is used as a basis for a myoglobin–O₂ model.

Cobalt(II) porphyrins and related low spin cobalt(II) complexes have recently received considerable attention because of their unusual ability to form dioxygen complexes reversibly.[1-12] Nitrogen donor

adducts and their dioxygen complexes have been thoroughly studied, but little is yet known about the corresponding complexes with potential π-acceptor ligands such as CO, CH₃NC, and R₃P.

This paper in part reports on epr and electronic spectral studies for Co^{II}TPP complexes of CO, NO, O₂, CH₃NC, and (CH₃O)₃P. A molecular orbital bonding model is used in discussing and correlating the general electronic, magnetic, and molecular structures for complexes of diatomic molecules with Co^{II}TPP. This model is extended to the CO, NO, and O₂ complexes of iron(II) porphyrins including hemeproteins.

Experimental Section

Materials. Tetraphenylporphyrincobalt(II) [Co^{II}TPP] was prepared according to the procedure of Rothemund and Menotti.[13]

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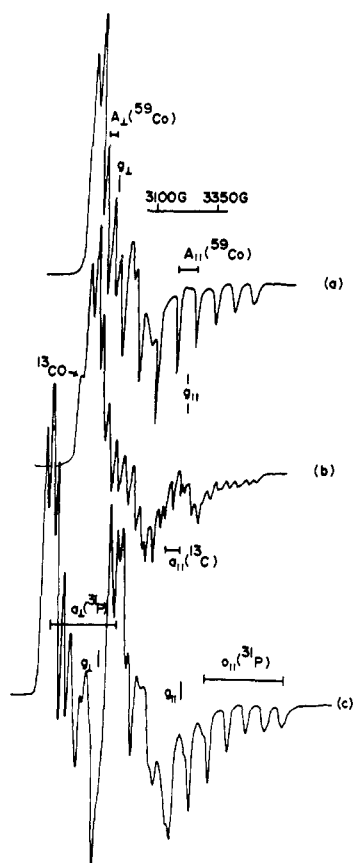
Figure 1. Epr spectra for $Co^{II}TPP$ with carbon monoxide and trimethyl phosphite in toluene glass $(-150°)$: (a) $Co^{II}TPP \cdot {}^{12}CO$, (b) 55% ${}^{13}CO$, 45% ${}^{12}CO$, (c) $Co^{II}TPP \cdot P(OCH_3)_3$.

The impure product was then chromatographed on aluminum oxide (Woelm neutral, activity grade 1) purchased from Waters Associates Inc., Framingham, Mass., using benzene (thiophene free) from Fisher Scientific Co. as the eluent. The $Co^{II}TPP$ was stored under vacuum and used in subsequent studies.

Oxygen was obtained from Union Carbide Corp., Linde Division, while CP grade carbon monoxide was supplied by Matheson Gas Products. These gases were determined to be of adequate purity and used as supplied. CP grade nitric oxide was also a Matheson Gas Products material but was passed over KOH pellets to free it of higher nitrogen oxides.

Methylisonitrile was a gift from Dr. E. L. Muetterties at E. I. Dupont and Co. Trimethyl phosphite was obtained from Matheson Coleman and Bell and stored over P_2O_5. Toluene was purchased from Fisher Scientific Co. and stored over P_2O_5.

Procedure. Samples for epr and glass electronic spectral studies were prepared on a vacuum line in quartz epr tubes fitted with a ground-glass joint and high-vacuum stopcock.

The $Co^{II}TPP$ was introduced into the tube either as the solid or its toluene solution. The toluene solutions of $Co^{II}TPP$ were then degassed by the usual freeze–pump–thaw method. When working with solid $Co^{II}TPP$, the epr tube was evacuated, and degassed toluene was distilled from P_2O_5 into the tube.

Liquid ligands were degassed and then distilled into the tube containing $Co^{II}TPP$. Gaseous ligands were allowed to react with the $Co^{II}TPP$ solution by initially pressurizing the vacuum line with the ligand (usually one-half atmosphere pressure was quite sufficient) and then opening the stopcock to the $Co^{II}TPP$ solution. The system was then cooled and warmed several times to ensure adequate mixing.

$Co^{II}TPP \cdot NO$ was prepared according to the above procedure but on a much larger scale. Solid $Co^{II}TPP$ was placed in a suitable reaction vessel, mounted on a vacuum line fitted with Teflon stopcocks, and evacuated. Degassed toluene was distilled into the flask and the resulting solution subjected to one-half atmosphere of NO which had been scrubbed of higher nitrogen oxides. After mixing had been accomplished through frequent cooling and warming of the sample, the solution was pumped to dryness. The reac-
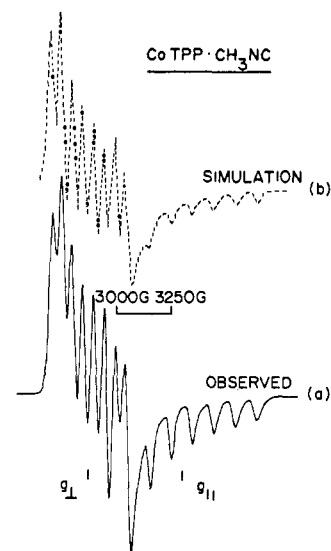

Figure 2. Epr spectra for $Co^{II}TPP \cdot CH_3NC$ in toluene glass $(-150°)$(a) and computer simulation (b).

tion vessel was then sealed and transferred to a Vacuum Atmosphere Corp. inert atmosphere box where the sample was mulled with Nujol for the purpose of recording its infrared spectrum. The sample prepared in this manner had a ν_{N-O} of 1700 cm^{-1} which compares favorably with similar compounds.[14]

Instrumentation. Spectra were taken on a Varian Model V-4502 X-band spectrometer at 100°K, equipped with a Field Dial Mark I, Hewlett-Packard Model 7001 AM x-y recorder, and a Hewlett-Packard frequency meter, Model X 532 B. Cooling was provided by using cold nitrogen gas and temperature was controlled to $\pm 2°$ using a Varian V-4557 variable-temperature accessory. The field and frequency calibrations were made using DPPH powder ($g = 2.0036$), field dial, and X532B frequency meter.

Electronic spectra were recorded on a Cary Model 14 recording spectrophotometer. Low temperature studies were performed with the aid of a Pyrex optical dewar obtained from Kontes Martin, Evanston, Ill. Infrared spectral studies were carried out on a Perkin-Elmer 421 grating spectrophotometer.

Results and Discussion

Epr Spectra of $Co^{II}TPP$ Adducts of CO, CH_3NC, and $(CH_3O)_3P$. Epr spectra for cobalt(II) tetraphenylporphyrin complexes with carbon monoxide, methylisonitrile, and trimethyl phosphite are shown in Figures 1 and 2. The associated g and hyperfine coupling parameters appear in Table I along with data on nitrogen donor ligands. Intensity measurements for a ${}^{13}C$ enriched (55%) carbon monoxide adduct of $Co^{II}TPP$ reveal that each peak in the ${}^{12}CO$ epr spectrum splits into two equal intensity components which demonstrates the presence of a 1 : 1 adduct (Figure 1). Phosphorus-31 hyperfine splitting similarly demonstrates that the $(CH_3O)_3P$ adduct of $Co^{II}TPP$ is a 1 : 1 complex (Figure 1). Epr spectra for the CO, CH_3NC, and $(CH_3O)_3P$ complexes can be analyzed in terms of an effective axially symmetric g tensor. In each complex the g values and cobalt coupling constants are consistent with a well-defined $(d_{xz,yz}, d_{xy})^6(d_{z^2})^1$ ground configuration. The appropriate relationships between electronic structure and magnetic parameters for this case are[15]

$$g_{||} = 2.002; \quad g_{\perp} = 2.002 - 6\xi_{eff}/\Delta E_{xz,yz \to z^2}$$

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Table I. Epr Parameters for Co[II]TPP·L [L = CO, CNCH₃, P(OCH₃)₃][a]

Ligand	$g_{\|\|}$	$g_\perp$	$A_{\|\|}$, cm⁻¹ [b] (G)	$A_\perp$, cm⁻¹ (G)	P, cm⁻¹ [c]	K [d]	$\Delta E_{zz,yz\to z^2}$, cm⁻¹
CO	2.017	2.217	0.00736 (77.6)	0.0034 (33)	0.0181	0.137	11,200
CNCH₃	2.025	2.247	0.00670 (70.9)	0.0037 (35.6)	0.0187	0.176	10,200
P(OCH₃)₃	2.024	2.244	0.00692 (73)	0.0028 (26.6)	0.0174	0.137	9,600
C₅H₅N [e]	2.027	2.324	0.00789	0.0013	0.0198	0.127	8,200
CH₃CN·O₂	2.076	2.004 [f] 1.995	0.00151 (15.6)	0.00166 (17.8)			

[a] Values for P, K, and $\Delta E_{zz,yz\to z^2}$ are based upon a $(xz,yz)^4(xy)^2(z^2)^1$ ground configuration for cobalt(II). The value of ξ_{eff} was estimated from the relation $\xi_{eff} = (P/P_0)\xi_0$ using $P_0 = 0.023$ cm⁻¹ and $\xi_0 = 515$ cm⁻¹. [b] $A_\perp$ and $A_{\|\|}$ are the cobalt hyperfine coupling components normal to and along the principal magnetic axis. $A_{\|\|}$ and $A_\perp$ are of opposite sign in all complexes except those containing oxygen. [c] $P = g_e\beta_e g_n\beta_n\langle r^{-3}\rangle_{3d} \cong 0.023$ for cobalt(II) free ion. [d] K is the Fermi contact term. [e] Reference 3. [f] Nonaxial symmetry.

Table II. Ligand Hyperfine Coupling Constants and Derived Spin Densities for Co[II]TPP Complexes

Complex	$a_{\|\|}$, cm⁻¹ [a] (G)	$a_\perp$, cm⁻¹ (G)	a_{dip}, cm⁻¹ [b]	$\langle a_{iso}\rangle$, cm⁻¹ [c]	ρ_s [d]	ρ_p	ρ_p/ρ_s [e]
P(OCH₃)₃	0.0295 (312)	0.0276 (264)	0.0013	0.02823	0.083	0.068	0.82
CO	0.00597 (63.5)	0.00553 (53.5)	0.00030	0.00567	0.054	0.049	0.91

[a] $a_{\|\|}$ and $a_\perp$ are the ligand hyperfine coupling constants along and normal to the principal magnetic axis. [b] $a_{dip} = a_{\|\|} - a_{iso}$. [c] $a_{iso} = (a_{\|\|} + 2a_\perp)/3$. [d] ρ_s and ρ_p are the spin densities in the s and p atomic orbitals of the ligand donor species. [e] Ratio of p/s character in the ligand donor orbital.

$$A_{\|\|} = P[-K + (^4/_7) - (^1/_7)(g_\perp - 2.002)]$$

$$A_\perp = P[-K - (^2/_7) + {}^{45}/_{42}(g_\perp - 2.002)]$$

Electronic parameters that result from solving these expressions for the π-acceptor ligands and several nitrogen donors are given in Table I. Reduction of cobalt P values ($P = g_e g_n\beta_e\beta_n\langle r^{-3}\rangle_{3d}$) by 20–30% from the free ion value is largely caused by the redistribution of the odd electron population from cobalt to the ligands. Magnetic and electronic parameters for CO and CH₃NC show that they are closely related. The phosphite ligand is found to have larger spin density as evidenced by both the P values and ³¹P hyperfine coupling (Tables I and II). Despite the known smaller σ-donor properties of CO, the calculated $\Delta E_{zz,yz\to z^2}$ is somewhat larger than the other ligands which probably results from the superior π-acceptor properties leading to a lowering of the occupied $d_{zz,yz}$ relative to the d_{z^2}. The observed $g_{\|\|}$ values in all reported Co[II]-TPP adducts are slightly larger than the theoretical value of 2.002, which may result from a small contribution of the $d_{z^2-y^2}$ to the ground state.[16] The observation that $g_{\|\|}$ increases as the d_{z^2} is elevated in going from 1:1 to 2:1 complexes of nitrogen donors[3] is consistent with this orbital mixing.

Ligand hyperfine coupling constants (¹³C and ³¹P) for CO and (CH₃O)₃P are found in Table II. The ligand hyperfine coupling in both cases is larger in the $g_{\|\|}$ region than in the $g_\perp$ which is characteristic of an axially ligated complex where the ligand hyperfine and g tensors are nearly coincident.

The ¹³C and ³¹P coupling constants are quite large and provide an opportunity to examine the nature of the ligand σ-donor orbital used in bonding the metal. Using the isotropic ¹³C coupling constant in the CO adduct and the C_{2s} atomic value[17] of 0.1054 cm⁻¹ leads

to a C_{2s} spin density of ~0.054 (Table II). Under ideal conditions the anisotropic ¹³C coupling constants can be used to evaluate the C_{2p} spin density. In this case where only frozen solution data can be obtained, interpretation of the data is limited by uncertainty of the orientation of the principal values of the ligand hyperfine tensor. Assuming that the g and hyperfine tensors are coincident results in a C_{2p} spin density of 0.049 ($\rho C_{2p} \cong A_{\|\|}(^{13}C) - \langle A(^{13}C)\rangle/A_{C_{2p}}; A_{C_{2p}} = 0.00615$ cm⁻¹).[17] The carbon monoxide donor orbital that binds with the cobalt d_{z^2} has a carbon 2p/2s ratio ~0.91. This ratio is close to the expected sp hybrid donor orbital for carbon monoxide. The highest occupied σ-donor orbital for carbon monoxide is ~78% C from SCF calculations[18] so that the spin density reaching the CO molecule is ~0.13.

Using the observed ³¹P hyperfine splitting for the (CH₃O)₃P adduct and the atomic hyperfine parameters[17] ($A_{P_{3s}} = 0.3396$ cm⁻¹; $A_{P_{3p}} = 0.01922$ cm⁻¹) and assuming coincidence of the hyperfine and g tensors results in phosphorus 3s and 3p spin densities of 0.083 and 0.068, respectively. These results indicate that the phosphorus donor orbital has 55% P₃ₛ character. SCF calculations have predicted that the p character of the phosphorus donor orbital should increase substantially with decreasing values of the substituent electronegativity.[19] This trend has been experimentally confirmed by examining a series of phosphorus donor adducts of Co[II]TPP. Phosphorus-31 hyperfine splitting in the tributylphosphine complex in the $g_{\|\|}$ (2.02) and $g_\perp$ (2.24) regions of 234 (0.0221 cm⁻¹) and 176 G (0.0184 cm⁻¹), respectively, transcribe into spin densities for the P₃ₛ and P₂ₚ orbitals of 0.058 and 0.130,

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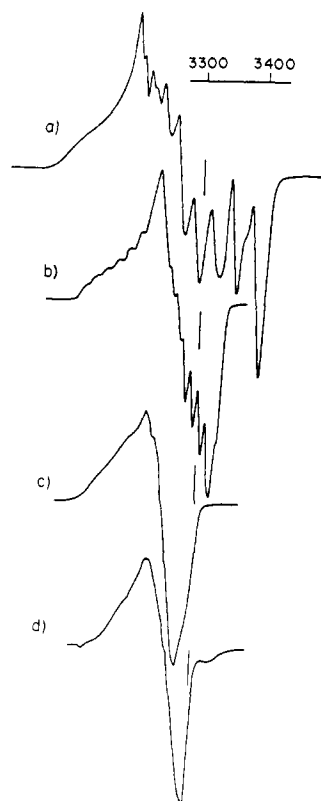
Figure 3. Epr spectra for oxygen complexes of Co^{II}TPP and Co^{II}TPP·B adducts (B = CH$_3$CN, (Bu)$_3$P, and CO) in toluene glass (−150°): (a) Co^{II}TPP·O$_2$ (toluene solvate) ($g_1 \cong$ 2.05, $g_2 \cong$ 1.988, $g_3 =$ 1.993; $A_1 \sim$ 0.0012, $A_2 \sim$ 0.0027, $A_3 =$ 0.0028 cm^{-1}), (b) Co^{II}TPP·CH$_3$CN·O$_2$ ($g_1 =$ 2.076, $g_2 =$ 2.004, $g_3 =$ 1.995; $A_1 =$ 0.00151, $A_2 \cong A_3 =$ 0.00166 cm^{-1}), (c) Co^{II}TPP·(Bu)$_3$P·O$_2$ ($g_1 \sim$ 2.07, $g_2 \sim g_3 \cong$ 2.014; $A_1 \sim$ 0.0012, $A_2 \sim A_3 =$ 0.00092 cm^{-1}), (d) Co^{II}TPP·CO·O$_2$ ($g_1 \sim$ 2.07, $g_2 \sim g_3 \cong$ 2.014; $A_1 \sim$ 0.0012, $A_2 \sim A_3 =$ 0.00090 cm^{-1}).

respectively, which corresponds to a donor orbital with 31% s character.

Epr Spectra of Oxygen Complexes. Oxygen interacts with Co^{II}TPP and Co^{II}TPP·B (B = CH$_3$CN, (Bu)$_3$P, CO) to form 1:1 dioxygen complexes. Representative epr spectra and magnetic parameters are in Figure 3 and Table I.

Most previously reported cobalt(II) dioxygen complexes have contained a nitrogen donor in the sixth-coordination position trans to oxygen. In these cases no ^{14}N hyperfine splitting is observed in the epr.[2,3] Replacing the nitrogen donor by a phosphorus donor with its much larger atomic hyperfine values provides a more sensitive probe for spin delocalization to the axial ligand in cobalt–dioxygen complexes. The epr spectrum for Co^{II}TPP·(Bu$_3$P)·O$_2$ in toluene glass does not show well-resolved ^{31}P hyperfine; however, a small ^{31}P hyperfine is observed in the solution isotropic spectra ($\langle a \rangle^{31}$P = 18.3 G, $\langle A \rangle^{59}$Co = 8.5 G). The presence of only a small ^{31}P hyperfine provides further indirect evidence for a high degree of odd electron localization in the O$_2\pi^*$ orbital in Co^{II}TPP·B·O$_2$ complexes.

When CO and O$_2$ are simultaneously exposed to toluene solutions of Co^{II}TPP at low temperature, an epr spectrum characteristic of a dioxygen complex of Co^{II}TPP·donor is observed (Figure 3). This complex is believed to contain both CO and O$_2$ coordinated with Co^{II}TPP, [Co^{II}TPP·CO·O$_2$], and can be viewed as a carbon monoxide adduct of a cobalt(III) porphyrin

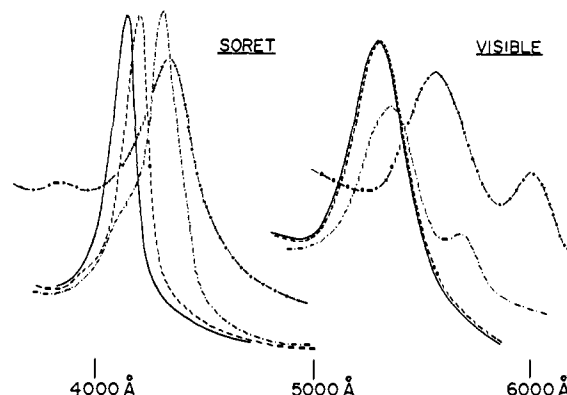**Figure 4.** Electronic spectra for Co^{II}TPP and 1:1 adducts with pyridine and methylisonitrile in toluene. Concentrations of Co^{II}TPP used in recording the visible band region are tenfold larger than used for the Soret region: (—) Co^{II}TPP (toluene solution, 25°), (- - - - -) Co^{II}TPP (77°K), (−·−·−) Co^{II}TPP·C$_5$H$_5$N (77°K), (-▲-▲-) Co^{II}TPP·CH$_3$NC (77°K).

which is formally analogous to the CO complex of methylcobaloxime(III).[20]

Cobalt-59 hyperfine splitting in these oxygen complexes arises primarily from dπ population in the predominantly oxygen π* odd electron orbital. Both σ-donor and π-acceptor ligands reduce the ^{59}Co hyperfine coupling from the values for CoTPP·O$_2$ (toluene solvate) (Figure 3). σ-Donors indirectly influence the ^{59}Co coupling in two interrelated ways. Donor adduct formation elevates the d_{z^2} which tends to localize Co–O$_2$ σ-bonding electrons on oxygen and promote larger bending of the Co–O$_2$ fragment. Both increased negative charge and increased bending tend to reduce the cobalt dπ–oxygen π* bonding. Presence of the π-acceptor ligand (carbon monoxide) trans to O$_2$ results in smaller ^{59}Co hyperfine coupling as reflected in the smallest total resonance width (Figure 3). Isotropic ^{59}Co coupling in Co^{II}TPP·PBu$_3$·O$_2$ ($\langle A \rangle^{59}$Co = 8.5 G, 0.00080 cm^{-1}) is significantly smaller than in the corresponding pyridine adduct (Co^{II}TPP·C$_5$H$_5$N·O$_2$) ($\langle A \rangle^{59}$Co = 12.4 G, 0.00117 cm^{-1}). In addition to the σ-donor effect, these ligands have π-acceptor properties which lower the $d_{xz,yz}$ and thus further reduce the cobalt–oxygen back-bonding.

Electronic Spectra for Co^{II}TPP and Adducts with CO, NO, O$_2$, CH$_3$NC, and C$_5$H$_5$N. Electronic spectra for Co^{II}TPP and a series of adducts are displayed in Figures 4 and 5. Electronic spectra for metalloporphyrins including Co^{II}TPP are characterized by a uv (Soret) and visible absorption bands.[21] 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. The two bands in Co^{II}TPP are currently considered to arise from transitions from the ground ^{2}A$_{1g}$ to two excited ^{2}E$_u$ states which are heavily mixed by configuration interaction. In the limiting case where the two ^{2}E$_u$ states are degenerate, configuration interaction mixes the states such that one electronically allowed band (Soret) and one forbidden band (visible) result.[22–25]

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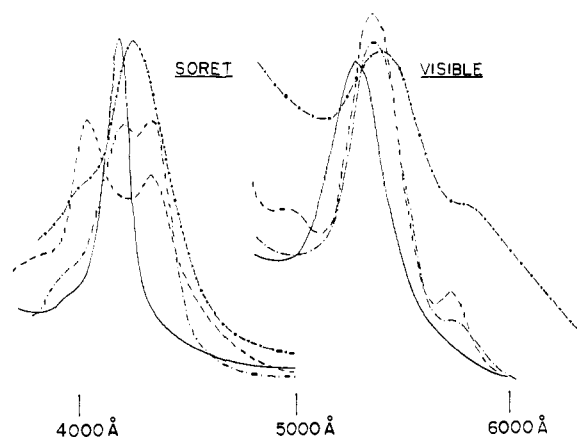(23) M. Gouterman, G. H. Wagniere, and L. C. Snyder, J. Mol. Spectrosc., 11, 108 (1963).

Figure 5. Electronic spectra for Co^{II}TPP and its 1:1 adducts with diatomic molecules in toluene. Concentrations of Co^{II}TPP used in recording the visible band region are tenfold larger than used for the Soret region: (—) Co^{II}TPP (toluene glass, 77°K), (- - - - -) Co^{II}TPP·CO (77°K), (- · - · -) Co^{II}TPP·NO (77°K), (-▲-▲-) Co^{II}TPP·O$_2$(77°K).

Figure 6. Schematic molecular orbital diagram for linear and bent adducts of diatomic molecules with cobalt(II) porphyrins [AB = CO (π^{*0}), NO (π^{*1}),O$_2$ (π^{*2}); cobalt(II)(d^7), iron(II)(d^6)].

Electronic spectra for Co^{II}TPP in toluene solution and glass (77°K) are shown in Figure 4. The Soret band shifts 360 cm^{-1} in the toluene glass media. This shift probably results from specific toluene–Co^{II}TPP interactions which are also manifested in toluene glass epr spectra.

Complex formation shifts the Co^{II}TPP Soret and visible bands to lower energy (Figures 4 and 5). The Soret band width appears normal for Co^{II}TPP and the C$_5$H$_5$N adduct; however, substantial broadening or splitting occurs in complexes with potential π-acceptor ligands (CO, NO, O$_2$, CH$_3$NC) (Figures 4 and 5). Complex formation also produces one or more new bands in the visible region. The visible band becomes electronically allowed in the maximum effective adduct symmetry (C_{4v}) which permits observation of additional bands (0–0, 0–2, etc.) irrespective of possible removal of ^{2}E orbital degeneracy.

Two well-defined bands are observed in the Soret region for toluene glass spectra of Co^{II}TPP·B (B = CO, NO) (Figure 5). One or more weaker bands are also discernible on the high energy side of the Soret region. The relative intensities of these Soret region bands in the CO adduct are insensitive to CO pressure or toluene glass temperature. Epr spectral studies on the same toluene glass (−140°) used in recording the electronic spectra demonstrate that only one Co^{II}TPP species is present. Spectral studies at 28° where there is very little CO complex formed demonstrate both the complete reversibility of CO adduct formation and the absence of observable quantities of a Co^{III}TPP complex. These observations indicate that a single molecular species results in multiple transitions in the Soret region.

Electronic spectra for Co^{II}TPP solutions in the presence and absence of CO suggest that the total intensity for Co^{II}TPP·CO in the Soret region is not substantially different from the intensity for the single Soret band in Co^{II}TPP. This observation may provide evidence that the ^{2}E state in Co^{II}TPP·CO is split or that a second transition gains intensity from the Soret.
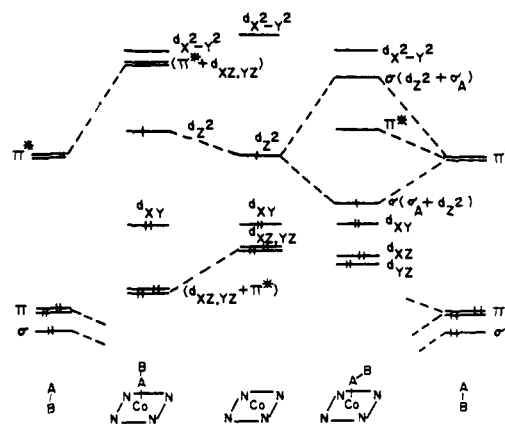
Presence of an axially coordinated ligand could introduce new charge transfer bands or shift existing M → L or L → M bands into the Soret region.[25,26] One charge transfer state expected to occur in this region arises from the e(d$_{zz,yz}$) → b$_1$(π^*)[^{2}A$_1$ → ^{2}E].[25] The intensity in the Soret region could be redistributed through mixing of states of this type with the Soret. Another possibility is that the ^{2}E(Soret) state is split by a ligand field or Jahn–Teller mechanism. The real symmetry for Co^{II}TPP·CO may be low enough to permit splitting the ^{2}E even though epr observations indicate effective axial symmetry (C_{4v}). The Soret region spectra for Co^{II}TPP·CO closely resemble predictions for a Jahn–Teller split ^{2}A → ^{2}E transition using an adiabatic potential surface modified by a pseudocentrifugal term.[27] The relatively high energy positions of the bands, distribution of intensities, presence of weaker bands at high energy, and the absence of resolved vibronic structure are all consistent with this mechanism.[27] The origin of multiple band maxima in the Soret region of Co^{II}TPP·CO is at present speculative and remains a fertile area for further experimental and theoretical studies.

Bonding Model for Adducts of Diatomic Molecules with Cobalt(II) and Iron(II) Porphyrins. Carbon monoxide, nitric oxide, and oxygen form 1:1 complexes with Co^{II}TPP. This series of complexes with diatomic ligands provides an opportunity to examine the effects of the π^* orbital energy and occupancy (COπ^{*0}, NOπ^{*1}, O$_2\pi^{*2}$) on the electronic structure of the resulting complexes with Co^{II}TPP.

A molecular orbital scheme is formulated in Figure 6 as a guide in correlating the principal electronic features in complexes of diatomic molecules with planar metal complexes. Nitric oxide complexes have recently been described using similar molecular orbital (MO) models.[28,29] The MO diagram is highly abbreviated to permit focusing on the principal valence levels (i.e., metal d orbital and the diatomic π^*). A single

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generalized molecular orbital diagram is used in depicting the interaction of diatomics with planar metal complexes; however, the MO energies and electron populations will be different in each complex. One important difference between the diatomic ligands which is not reflected in the generalized MO diagram is that the energy of the π^* level decreases monotonically from CO to NO to O_2.[18,30] Several of the principal features of the MO scheme are (1) linear diatomic-metal bonding maximizes $d\pi-p\pi$ bonding, (2) bent diatomic–metal bonding removes the ligand π^* double degeneracy to produce one MO that is essentially a diatomic π^* orbital and a second orbital appropriate for 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 diatomic π^* level are partially occupied, and (4) the extent of bending will depend on the relative importance of the σ-electronic system which is maximized at $120°$ and π back-bonding which is maximized at $180°$.

The MO diagram (Figure 6) has orbital occupancies appropriate for $Co^{II}TPP \cdot CO$ [seven electron case; Co(II) (d^7), CO (π^{*0})]. Epr data for the carbon monoxide complex of $Co^{II}TPP$ place the odd electron in a MO which is predominantly cobalt d_{z^2} (0.87) with 0.13 in the carbon monoxide σ orbital. Single occupancy of a MO with cobalt d_{z^2} and CO σ character should result in a bent Co–CO fragment. A nonaxially symmetric g tensor and bent Fe–NO unit in the isoelectronic FeTPP·NO complex show that this electron configuration can be associated with a bent metal–diatomic unit.[31,32] Epr spectral parameters for CoTPP·CO including ^{13}C hyperfine can be readily interpreted in terms of a near axially symmetric species. These data indicate that the Co–CO bending if any is less than the Fe–NO bending in FeTPP·NO. This is consistent with the MO model which predicts that the effectiveness of covalent σ bonding and interrelated degree of bending depends on the $d_{z^2} \rightarrow \pi^*$ energy separation which is much smaller and thus more favorable for σ bonding in the case of NO compared to CO. Metal d_{z^2} (σ) odd electron population of $\sim$0.87 in $Co^{II}TPP \cdot CO$ and $\sim$0.4–0.5 in FeTPP·NO[32] and myoglobin·NO[33] provide experimental support for this model.

The anticipated electron configuration for $Co^{II}TPP \cdot NO$ (eight electron case; Co(II) d^7, NO (π^{*1})) is obtained by placing one additional electron in the MO scheme (Figure 6). The MO model suggests that a linear Co–NO unit is associated with an effective reduction of cobalt(II) [Co^INO^+]. Enemark and Feltham[34] have demonstrated these features in the related [Co(NO){o-phenylenebis(dimethylarsine)}$_2$][ClO$_4$]$_3$ complex. Scheidt and Hoard have shown that the Co NO fragment in $Co^{II}TPP \cdot NO$ is bent.[35] Bending the NO group splits the π^* orbital degeneracy and produces a singly occupied orbital (Figure 6) with proper symmetry to σ-bond with the metal d_{z^2}. A two-electron

normal covalent bond can then form between cobalt and nitric oxide. It is useful to think of the NO bending so as to take full advantage of the cobalt(II) property of forming normal covalent bonds as manifested in the familiar alkyl and hydride compounds of vitamin B_{12} and related complexes.[36,37] The effective oxidation state of cobalt in the bent nitric oxide complex depends on how the pair of covalent bonding electrons is distributed between cobalt and nitric oxide and also on the extent of $d\pi \rightarrow p\pi$ back-bonding. Back-bonding decreases with bending and is probably closely related to the charge distribution in the σ-orbitals. In the limiting case of $Co^{III}NO^-$, back-bonding will be relatively insignificant. The Co^{II}–NO unit is isoelectronic with the Fe^{II}–O_2 unit and the structure and bonding of these species should prove to be closely related. Scheidt and Hoard[35] have recently used isoelectronic arguments related to those of this MO model in discussing the relationship of Co^{II}–NO complexes with heme–O_2 complexes.

The electron configuration for the oxygen complex, $Co^{II}TPP \cdot O_2$ [nine electron case; Co(II)(d^7), O_2(π^{*2})], is generated by adding two electrons to the MO diagram (Figure 6). This places the single unpaired electron in an oxygen based essentially π^* orbital as observed in epr studies. Resolution of three g values in the epr of $Co^{II}TPP \cdot O_2$ and related oxygen adducts[7,38] is indicative of a bent cobalt–oxygen unit. X-Ray structure determination for $Co(bzacen)(pyridine)O_2$ demonstrates the bending in that closely related complex.[39] The principal cobalt–oxygen bonding can be described in analogy with the nitric oxide and alkyl compounds as resulting from covalent bonding of the singly occupied cobalt(II) d_{z^2} and the singly occupied oxygen σ-orbital that results from splitting the π^* degeneracy. The effective oxidation state for cobalt and degree of Co–O_2 bending is dependent on how the pair of σ-bonding electrons is distributed and on back-bonding. As the Co–O_2 unit bends the electron pair tends to localize on oxygen effectively approaching $Co^{III}O_2^-$ and back-bonding decreases. Most cobalt–oxygen complexes contain a sixth axial donor such as pyridine. A donor molecule elevates the metal d_{z^2} and will tend to localize the covalent σ pair on oxygen causing both further bending of the Co–O_2 unit and a decline in cobalt–oxygen $d\pi \rightarrow p\pi$ bonding. Cobalt-59 hyperfine coupling in the Co–O_2 complexes is sensitive to the $d\pi$ population in the singly occupied π^*. The ^{59}Co hyperfine for $Co^{II}TPP \cdot O_2$ (toluene solvate) is substantially larger and more anisotropic than in $Co^{II}TPP \cdot CH_3CN \cdot O_2$ (Figure 3) consistent with larger odd electron $d\pi$ population and thus more back-bonding in the absence of an N donor. π-Acceptor ligands further reduce the importance of M$\rightarrow O_2$ back-bonding by lowering the $d_{xz,yz}$ (vide ante).

Partitioning of the electron population between the metal and diatomic in the σ-covalent bond primarily depends on the relative energies of the metal d_{z^2} and the diatomic π^* level. There is a substantial decrease in the π^*-orbital energy in going from CO to NO to

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O_2 and thus the fraction of σ bonding electron density on the diatomic is expected to increase in that order. Epr data for the $Co^{II}TPP \cdot CO$ (Table I) show that the σ electron is primarily ($\sim 85\%$) on cobalt. Photoelectron spectra for the related Co(benacen) complexes of NO and O_2 show that the effective oxidation state of cobalt in the O_2 complex is close to (III) while the NO complex is intermediate between (II) and (III).[40]

Success of this MO bonding model in describing the principal electronic features of cobalt(II) porphyrin adducts of CO, NO, and O_2 provides justification for extending this model to the corresponding iron(II) porphyrins which may permit comment on the biologically important myoglobin and hemoglobin complexes. Iron(II) porphyrin complexes (d^6 case) have one electron less than the corresponding cobalt(II) complexes.

Just considering the metal–diatomic bonding, carbon monoxide should form linear complexes with iron(II) porphyrins. Both the Fe(II) d_{z^2} and the CO π^* are empty (six electron case), and thus there is no gain in the σ covalent bonding through bending the Fe–CO unit. There are no reported structures for iron(II) porphyrin--CO complexes, but the closely related $Fe(C_{22}H_{22}N_4)$-$(NH_2NH_2)(CO)$ and an isoelectronic $RuTPP \cdot CO \cdot CH_3$-OH have essentially linear structures.[41,42] X-Ray structure studies of the CO adducts of Lamprey and Chironomus thummi thummi hemoglobin have, however, been interpreted in terms of a strongly bent Fe–CO unit.[43,44] Presence of a bent Fe–CO fragment can be taken as an indication of protein interactions in the hemeprotein complexes.

Nitric oxide complexes of iron(II) porphyrins are isoelectronic with the carbon monoxide complexes of cobalt(II) porphyrins (seven electron case). Epr studies demonstrate a bent Fe–NO unit in the myoglobin adduct.[33] In this case the presence of a single electron in the NO π^* is expected to result in a bent complex irrespective of protein interactions. This point is illustrated by the observation of three g values in the epr

spectra for $Fe^{II}TPP \cdot NO$[31] and the complete structure determination by Scheidt and Frisse.[45] According to the MO diagram (Figure 6) the Fe^{II}–NO complex should contain a one-electron covalent bond with the single unpaired electron in a MO of principally NO (σ_N) and Fe d_{z^2} character. Observation of ^{14}N hyperfine splitting from both NO and axial nitrogen donors in $FeTPP \cdot NO \cdot$(piperidine) and myoglobin$\cdot$NO demonstrates that this bonding model is essentially correct.[32,33,46]

Extending this model to O_2 complexes of Fe(II) (eight electrons, d^6, π^{*2}, i.e., oxymyoglobin and oxyhemoglobin) leads to the anticipation of a bent diamagnetic O_2 complex that contains essentially singlet O_2 binding Fe(II) by the empty d_{z^2}. Fe^{II}–O_2 complexes are isoelectronic with the familiar Co^{II}–NO complexes and are probably isostructural. In the $Fe^{II}O_2$ case, however, both σ-bonding electrons originate on oxygen so that covalent bonding with the empty Fe d_{z^2} induces positive charge in the oxygen σ orbitals. This charge effect coupled with the already low position of the oxygen π^* should produce substantial $d\pi \rightarrow p\pi$ backbonding, a point which has been particularly emphasized by Scheidt and Hoard.[35] Once again the effective metal oxidation state is determined by the net electron distribution resulting from transfer in the σ orbital to the iron and back-bonding from metal to oxygen through the π orbital. In the same manner as in the previously discussed nitric oxide complexes bending the Fe–O_2 unit will tend to localize the σ-bonding pair ($d_{z^2} + \sigma_0$) on oxygen producing a σ distribution approaching singlet oxygen, and accompanied by a corresponding decline in π back-bonding. Although the net effect should be negative charge on oxygen, we believe that Fe^{II}–O_2 complexes are best described as containing coordinated singlet oxygen.[47]

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