

Mono- and Biscarbonyl Complexes of Iron(II) Tetraphenylporphyrin

B. B. Wayland,* L. F. Mehne, and J. Swartz

Contribution from the Department of Chemistry and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104.

Received June 16, 1977

Abstract: The mono- and biscarbonyl adducts of iron(II) tetraphenylporphyrin have been investigated spectroscopically. The equilibrium constants for the formation of the mono adduct and bis adduct were found to be 6.6×10^4 and 140 ± 3 , respectively. NMR studies of these complexes show that both the mono- and biscarbonyl adducts are diamagnetic. The exchange rate between FeTPP and FeTPPCO is estimated to be 10^5 – 10^6 s⁻¹. The mono- and biscarbonyl adducts have also been characterized by IR and electronic spectra.

Introduction

The coordination chemistry of diatomic molecules with metalloporphyrins has developed rapidly in recent years.^{1–10} The focus of attention on these materials has been promoted by interest in comparing the coordination properties of metalloporphyrins with heme proteins. Studies of carbon monoxide binding with heme proteins, metalloporphyrins, and related model complexes have been of particular interest in exploring the nature of the heme binding site. Our efforts in this area have been largely directed toward the systematic examination of the occurrence and properties of this class of diatomic molecule complexes.^{1–4} As part of these studies, we have examined the interaction of ferrous tetraphenylporphyrin with carbon monoxide.

Experimental Section

Materials. Samples of FeTPP were prepared under high vacuum (10^{-6} Torr) by reduction of FeTPPCl with sodium borohydride in a 1% methanol/toluene solvent which was then distilled off and replaced with pure toluene. The toluene was dried over freshly regenerated 4A molecular sieves. The FeTPPCl obtained from Strem Chemical was recrystallized from toluene. This material was then chromatographed as a benzene solution on Woelm neutral aluminum oxide, activity grade 1, and eluted with 2:1 benzene/chloroform. The isolated solid was then dissolved in toluene and treated with aqueous HCl in order to convert (FeTPP)₂O back into FeTPPCl. A sample of FeTPPCl prepared in this manner gave the following absorption spectrum at room temperature in toluene: 686 nm (ϵ 2.8), 660 (2.4), 572 (3.1), 507.5 (13.0), 419 (≥ 106), and 372 (49.3) (ϵ_{\max} in cm⁻¹ mM⁻¹).

CP grade carbon monoxide obtained from Matheson Co. was further purified of oxygen (max 5 ppm) by passing the gas through a column of Ridox obtained from Fischer Scientific. Perdeuterated toluene (99 atm %) and pyridine (95 atm %) obtained from Stohler Isotopic Chemicals were degassed and dried over molecular sieves.

Electronic Spectra. Variable temperature electronic spectra were obtained on a Cary 14 spectrophotometer using 0.3 cm i.d. quartz EPR tubes fitted with vacuum stopcocks. These tubes could be immersed in a liquid nitrogen filled Dewar without fracture. The Dewar was equipped with optical windows, making it possible to record the electronic spectra of the toluene glasses obtained by this technique. At room temperature, quantitative absorption measurements were made using standard quartz 1- or 5-mm spectrophotometric cells fitted with vacuum stopcocks. The solutions were prepared directly in the cells on the vacuum line.

NMR Spectra. Reference spectra of FeTPP and FeTPP(py-d₅)₂, as well as spectra of FeTPP(CO)_x, were obtained over a range of temperatures at 100 MHz using the Fourier transform mode of a Japan Electron Optics Laboratory JNM-PS-100 NMR spectrometer and associated EC-100 computer and Model JNM-VIT-3B temperature controller. Reference spectra of FeTPP and FeTPP(py-d₅)₂ were also obtained over a range of temperatures at 220 MHz using

the Fourier transform mode of a Varian Model HR-220 system 220-MHz NMR with superconducting magnet.

Samples under vacuum or known pressure of CO were prepared in NMR tubes directly on the vacuum line and sealed off. The spectra for FeTPP with CO were obtained from 0.8 mM solutions, since electronic spectra could be obtained at the same concentration. Chemical shifts were calculated with respect to tetramethylsilane by measuring shifts from the high-field component of the toluene phenyl resonances. The position of the reference peak was found to be temperature dependent; the shift at normal operating temperature (27 °C) was -6.973 ppm downfield from Me₄Si and was -6.933 ppm at -80 °C.

Typical instrumental parameters used to observe spectra of paramagnetic species, FeTPP, included collecting 4K data points from a single 90° pulse repeating at 0.5-s intervals. Data were collected from a bandwidth of 5000 Hz. These parameters caused the diamagnetic solvent peaks to become saturated, while the paramagnetic porphyrin peaks were unaffected owing to their fast relaxation times. For samples containing diamagnetic species or paramagnetic species of higher concentration the parameters used were 8K data points from a single 90° pulse repeating at 6-s intervals. Usually a bandwidth between 1000 and 2000 Hz was used and between 500 and 1000 transients were accumulated.

IR Spectra. Infrared spectra of FeTPP(CO) and FeTPP(CO)₂ were obtained on a Perkin-Elmer 521 infrared grating spectrophotometer from Nujol mulls supported between salt plates. Wavelengths were calibrated using a polystyrene film. Samples were prepared by exposing a solution of FeTPP in toluene to 760 mm of CO overnight to precipitate the red-violet solid, FeTPP(CO)₂. The solid was removed from the reaction vessel and milled with degassed Nujol inside a glove bag filled with CO. After recording the initial IR spectrum, the mull between NaCl plates was stored under vacuum and periodically removed to record the spectral changes.

Equilibrium Constant Measurement. The multiple equilibrium expressions were solved, using data obtained by recording the absorbance of a toluene solution of FeTPP at 518 nm as a function of CO pressure. The apparatus consisted of a 1- or 5-mm path length spectrophotometric cell connected to a ~100-mL glass bulb and stopcock. A solution of FeTPP in toluene was prepared in the cell and its concentration determined spectrophotometrically (ϵ_{\max} 11 564 \pm 97 cm⁻¹ M⁻¹ at 20.0 °C and 538 nm) before sequentially adding measured pressures of CO and measuring the absorbance. The apparatus was thermostated at all times to 20.0 \pm 0.1 °C. Gas/liquid equilibrium was assured by shaking the apparatus until no further change was observed in the electronic spectrum. The absorbance data were corrected for the absorption of the cell and solvent. The measured CO pressures were corrected for the amount of CO which dissolved, as well as the vapor pressures of toluene, which was found to be 20.89 \pm 0.02 Torr at 20.0 °C. The range of pressures used was 2–780 nm. No correction was necessary for the amount of CO which was bound by the iron complex, since the large gas volume of the cell and low iron complex concentration provided an effective buffer against any significant change. The corrected CO pressures were converted to concentrations using the value 7.242 mM/atm for the solubility of CO in toluene at 20 °C.¹¹

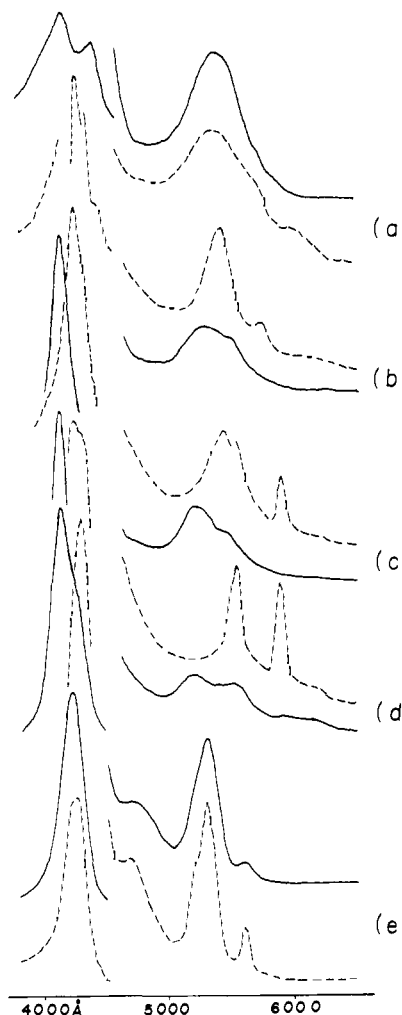
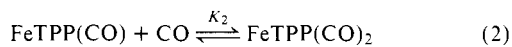


Figure 1. Electronic spectra for $\text{Fe}^{\text{I}}\text{TPP}$ complexes in toluene, (—) 296 K, (---) 77 K: (a) $\text{Fe}^{\text{I}}\text{TPP}$; (b) $\text{Fe}^{\text{I}}\text{TPP} + 50$ Torr CO; (c) $\text{Fe}^{\text{I}}\text{TPP} + 100$ Torr CO; (d) $\text{Fe}^{\text{I}}\text{TPP} + 760$ Torr CO; (e) $\text{Fe}^{\text{I}}\text{TPP}(\text{py})_2$.

The equilibrium constants for the reactions



are given by the expressions

$$K_1 = \frac{[\text{FeTPP}(\text{CO})]}{([\text{FeTPP}]_0 - [\text{FeTPP}(\text{CO})] - [\text{FeTPP}(\text{CO})_2])[\text{CO}]} \quad (3)$$

$$K_2 = \frac{[\text{FeTPP}(\text{CO})_2]}{[\text{FeTPP}(\text{CO})][\text{CO}]} \quad (4)$$

Johnson and Bowen have reported equations for solution of these expressions using absorption data collected at a wavelength at which only two products absorb.¹² Their equations were modified for use in the case considered here. A simplification was introduced by designing the apparatus to contain a large gas volume so that the approximation $[\text{CO}]_0 \approx [\text{CO}]_{\text{final}} = [\text{CO}]_0 - [\text{FeTPP}(\text{CO})] - [\text{FeTPP}(\text{CO})_2]$ would be accurate to better than 99.9% under all experimental conditions. Using this approximation and the material balance relation, the absorbance at any point is given by the Beer-Lambert law as

$$A = e_0P[\text{Fe}]_0 + (e_1 - e_0)P[\text{Fe}]_0B + (e_2 - e_0)P[\text{Fe}]_0[\text{CO}]B \quad (5)$$

where e_0 , e_1 , and e_2 are the molar extinction coefficients of FeTPP , $\text{FeTPP}(\text{CO})$, and $\text{FeTPP}(\text{CO})_2$, respectively, at the wavelength corresponding to A , P is the path length of the spectroscopic cell being used, and B is equal to $1/(1 + K_2[\text{CO}] + (K_1[\text{CO}])^{-1})$.

In order to extract values for K_1 and K_2 from eq 1, a series of three independent experimental runs was carried out at 20 °C in toluene

Table I. Spectrophotometric Data for $\text{Fe}^{\text{I}}\text{TPP}$ Equilibrium with CO

P_{CO} , Torr ^a	$[\text{CO}]$, M $\times 10^3$	A/l , o.d./cm ^b	$[\text{FeTPP}]_0$
0	0	1.05	0.13
1.8	0.017	1.39	
8.6	0.082	1.69	
25.8	0.246	1.65	
49.9	0.475	1.62	
89.6	0.853	1.57	
168.2	1.602	1.48	
288.0	2.745	1.33	
423.6	4.037	1.29	
538.2	5.128	1.23	
624.4	5.949	1.19	
0	0	1.20	0.15
2.8	0.027	1.56	
15.4	0.147	1.90	
31.9	0.304	1.92	
55.2	0.526	1.88	
83.9	0.800	1.84	
136.8	1.304	1.77	
231.6	2.203	1.66	
344.2	3.279	1.56	
461.6	4.399	1.47	
561.5	5.350	1.42	
644.9	6.145	1.38	
709.2	6.756	1.34	
773.7	7.372	1.32	
0	0	6.20	0.79
2.5	0.02	8.74	
7.9	0.075	8.94	
16.6	0.158	9.28	
27.1	0.258	9.29	
40.2	0.383	9.12	
54.0	0.514	8.91	
71.1	0.677	8.76	
91.9	0.875	8.44	

^a P_{CO} is the equilibrium partial pressure of CO. ^b The path length, l , was 0.5 cm for $[\text{FeTPP}]_0 = 0.13$ and 0.15 mM and was 0.1 cm for $[\text{FeTPP}]_0 = 0.79$ mM.

in which the change in absorption at 518 nm was measured as a function of carbon monoxide pressure. The data are found in Table I. A total of 31 data points were collected and fitted to eq 5, using a standard nonlinear least-squares computer program to give a set of best values for e_1 , e_2 , K_1 , and K_2 . The other variable, e_0 , was determined independently from solutions containing known concentrations of FeTPP . The final values obtained for the extinction coefficients were held constant to force all errors into the equilibrium constants. The calculated extinction coefficients are 12 442 $\text{cm}^{-1} \text{M}^{-1}$ for $\text{FeTPP}(\text{Cl})$ and 4914 $\text{cm}^{-1} \text{M}^{-1}$ for $\text{FeTPP}(\text{CO})_2$. The resulting equilibrium constants are $K_1 = (6.6 \pm 0.3) \times 10^4$ and $K_2 = 140 \pm 3$ at 20.0 °C in toluene. The error limits used represent the 95% confidence level and were obtained from the standard deviations observed in the fit of K_1 and K_2 , assuming a normal error distribution. The average difference between the observed and calculated absorbance values was 2.4%.

Results and Discussion

Electronic Spectra. Electronic spectra for toluene solutions of $\text{Fe}^{\text{I}}\text{TPP}$ in the presence of carbon monoxide are shown in Figure 1. The spectral changes accompanying increases in CO pressure suggest the formation of two CO complexes, $\text{FeTPP}(\text{CO})$ and $\text{FeTPP}(\text{CO})_2$. The distinctive electronic spectra for these two new species are clearly resolved in toluene glass media (77 K) (Figure 1). The mono-CO adduct is characterized by visible bands at 570 and 537 nm and a Soret band centered at 419 nm, while the corresponding peak maxima in the bis-CO adduct occur at 578, 551, and 426 nm. The electronic spectral changes in forming these CO complexes are closely related to those associated with formation of the diamagnetic bispyridinate ($\text{Fe}^{\text{I}}\text{TPP}(\text{py})_2$), Figure 1. Thorough removal of CO resulted in the reappearance of the spectrum

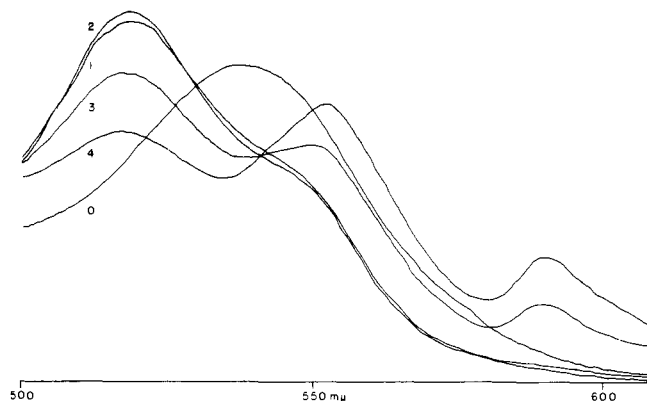


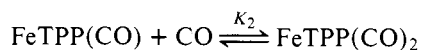
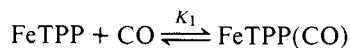
Figure 2. Electronic spectra of Fe^{II}TPP and varying amounts of CO, at 293 K: (0) 0 Torr CO; (1) 73 Torr CO; (2) 107 Torr CO; (3) 356 Torr CO; and (4) 760 Torr CO.

for Fe^{II}TPP, demonstrating the facile reversibility of CO complex formation.

IR Spectra. A saturated solution of Fe^{II}TPP exposed to an atmosphere of CO results in precipitation of a red-purple solid. Nujol mulls of this red solid prepared in a nitrogen atmosphere show two ν_{CO} bands (2042 and 1973 cm^{-1}). The relative intensities of these two bands were found to depend on the extent of grinding and length of exposure to the nitrogen atmosphere. Nujol mulls prepared in a CO atmosphere contained only a single sharp ν_{CO} band at 2042 cm^{-1} . Exposing this mull to vacuum resulted in the loss of intensity and eventual disappearance of the 2042- cm^{-1} band and appearance of a band at 1973 cm^{-1} . Prolonged exposure to high vacuum leads to the disappearance of all IR bands attributable to carbon monoxide. The IR bands at 2042 and 1973 cm^{-1} are respectively assigned to FeTPP(CO)₂ and FeTPP(CO). Reduction of the CO stretching frequency from the free ligand value (2143 cm^{-1}) results from populating the CO π^* with metal $d\pi$ electrons. Entrance of the second CO ligand substantially increases ν_{CO} as a result of competitive π bonding between trans CO groups. The ν_{CO} values for RuTPP(CO) (1945 cm^{-1}) and RuTPP(CO)₂ (2005 cm^{-1}) also show the influence of competitive π bonding. The lower ν_{CO} for complexes of RuTPP,¹³ compared with those of FeTPP, is in line with increased π bonding for 2nd transition series metal ions.

Equilibrium Studies of 1:1 and 2:1 Adducts of CO with Fe^{II}TPP. The effects of varying CO pressures on visible electronic spectra for toluene solutions of Fe^{II}TPP are depicted in Figure 2. At low CO pressures there is substantial absorption by three species, Fe^{II}TPP, FeTPP(CO), and FeTPP(CO)₂. At the higher CO pressures there are effectively only two absorbing species, FeTPP(CO) and FeTPP(CO)₂, which result in the presence of an isosbestic point at 541 nm (Figure 2).

The known pressure dependence for the concentration of carbon monoxide in toluene at 20 °C has been used in conjunction with the electronic spectral changes in determining the equilibrium constants for the following reactions:



Solving the multiple equilibrium equations (Experimental Section) for 31 data points taken at 518 nm results in $K_1 = (6.6 \pm 0.3) \times 10^4$ and $K_2 = 140 \pm 3$ at 20 °C in toluene. These values are comparable to those recently reported for iron(II) deuteroporphyrin dimethyl ester with carbon monoxide in benzene (25 °C) [$K_1 = (5.0 \pm 0.5) \times 10^4$, $K_2 = 21.0 \pm 2$].¹⁴ The accurate fit achieved to this multiple equilibrium model

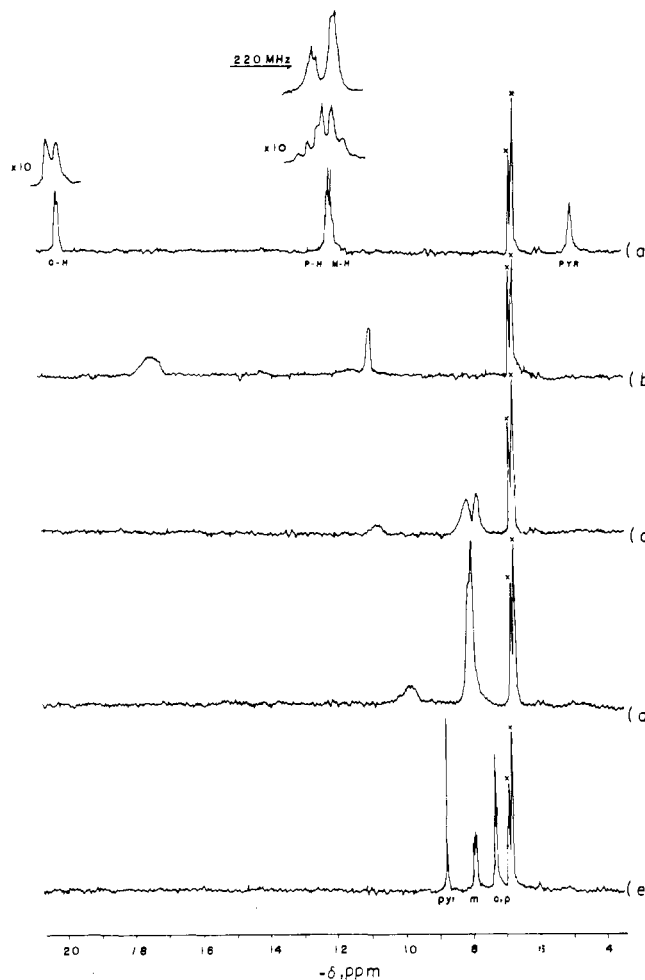


Figure 3. NMR spectra for the fast exchange between FeTPP, FeTPPCO, and FeTPP(CO)₂ at 293 K: (a) FeTPP; (b) FeTPP + 0.41 Torr CO; (c) FeTPP + 5 Torr CO; (d) FeTPP + 7 Torr CO; (e) FeTPP(py)₂. Peaks marked X are due to deuteriotoluene.

further supports the presence of both mono- and bis-CO complexes of FeTPP in solution. Previous studies using pyridine and imidazole have resulted in K_1 being substantially smaller than K_2 .¹⁴ Carbon monoxide is distinctly different from the nitrogen donors in that the first equilibrium constant (K_1) is much larger than the second (K_2).

NMR Studies. ¹H NMR spectra for Fe^{II}TPP in deuteriotoluene are shown in Figure 3. The spectral assignments were assisted by determining the NMR at both 100 and 220 MHz. Definitive assignment of the pyrrole proton was made by comparing the NMR spectra of FeTPP and FeT(py-d₅)P. Temperature dependence of the phenyl and pyrrole protons contact shifts is illustrated in Figure 4. The contact shifts of phenyl protons, measured relative to the corresponding resonance in the diamagnetic complex FeTPP(py-d₅)₂, follow Curie behavior and show that the complex (Fe^{II}TPP) is not involved in a spin state equilibrium in toluene solution in the temperature range from 20 to -70 °C.

Figure 3 depicts the effects on ¹H NMR when Fe^{II}TPP interacts with CO at several pressures of CO at 20 °C. As the pressure of CO increases, the proton resonances move toward the positions associated with diamagnetic TPP complexes such as FeTPP(py)₂ and FeTPP(CO)₂. The concentrations of FeTPP, FeTPP(CO), and FeTPP(CO)₂ in toluene solution (20 °C) are known as a function of CO pressure from our equilibrium studies. The NMR spectra shown in Figure 3b correspond to a solution (0.8 mM FeTPP, 0.41 Torr CO) calculated to contain 79.5% FeTPP, 20.5% FeTPPCO, and 0%

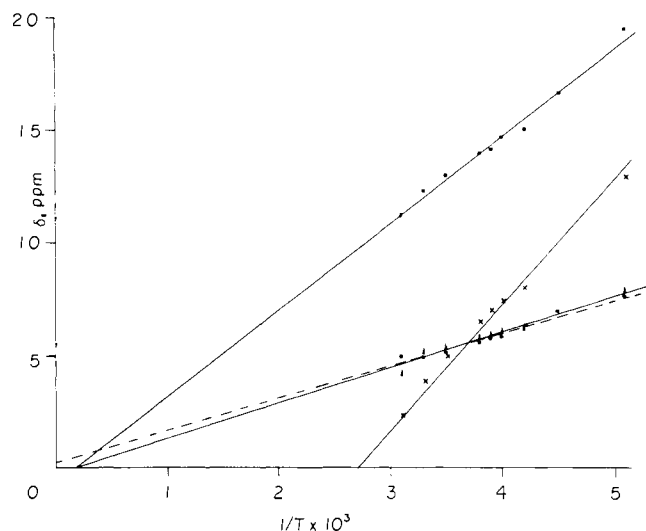


Figure 4. Temperature dependence of the proton contact shifts of $\text{Fe}^{\text{II}}\text{TPP}$ in toluene- d_6 : ortho (-■-■-■-), meta (-●-●-●-), para (-▲-▲-▲-), pyrrole (-X-X-X-). The shift scale is negative for the ortho, meta, and para protons and positive for the pyrrole protons.

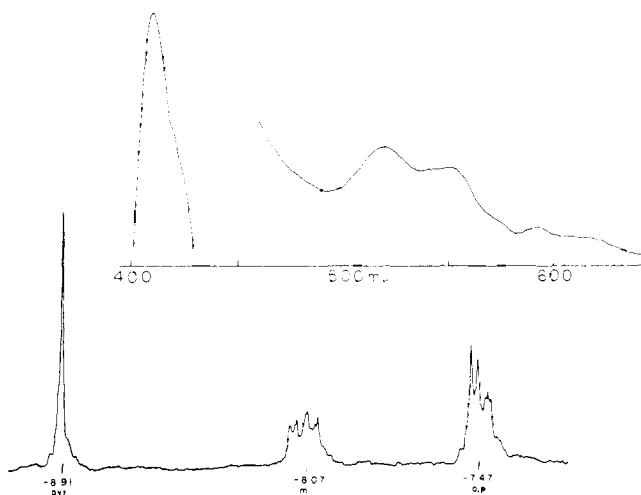


Figure 5. Electronic and NMR spectra for solution of 50% FeTPPCO and 50% $\text{FeTPP}(\text{CO})_2$. The spectra were both recorded using the same sample of 0.8 mM FeTPP , 760 Torr CO .

$\text{FeTPP}(\text{CO})_2$. The positions of the resonances, which lie between those for FeTPP and $\text{FeTPP}(\text{CO})_2$, are consistent with the limiting fast exchange of CO between the paramagnetic complex FeTPP (75%) and the diamagnetic complex $\text{FeTPP}(\text{CO})$ (25%). Similarly, the NMR spectrum in Figure 3c corresponds to a solution (0.8 mM FeTPP , 5.0 Torr CO) calculated to contain 24.0% FeTPP , 75.5% FeTPPCO , and 0.5% $\text{FeTPP}(\text{CO})_2$. Experimentally the positions of the resonances were found to be consistent with a solution containing 23% FeTPP and 77% diamagnetic sites ($\text{FeTPP}(\text{CO})$ and $\text{FeTPP}(\text{CO})_2$) based on the limiting fast exchange of carbon monoxide. The NMR spectral positions in Figure 3d indicate 14% paramagnetic sites (FeTPP) and 86% diamagnetic sites ($\text{FeTPP}(\text{CO})$ and $\text{FeTPP}(\text{CO})_2$) while the calculated concentrations are 16.4% FeTPP , 82.7% FeTPPCO , and 0.9% $\text{FeTPP}(\text{CO})_2$. Line broadening of the proton resonances in this system is consistent with a CO exchange rate of 10^5 – 10^6 s^{-1} .¹⁵ Increasing the CO pressure to 760 Torr produces the NMR in Figure 5. This solution is calculated to contain 0% FeTPP , 50% $\text{FeTPP}(\text{CO})$, and 50% $\text{FeTPP}(\text{CO})_2$. The observed spectrum is very similar to that of $\text{FeTPP}(\text{py}-d_5)_2$ and consistent with fast exchange between two diamagnetic complexes,

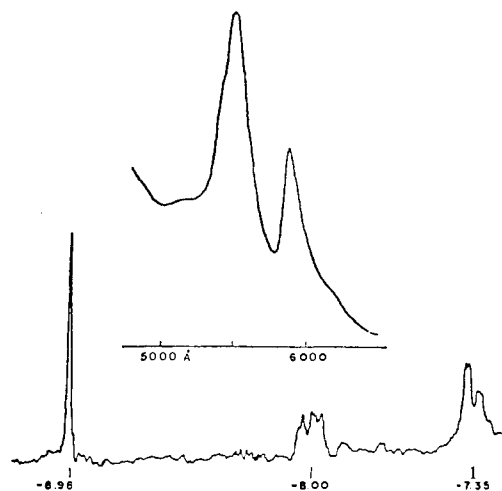
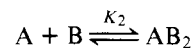
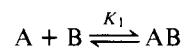


Figure 6. Low-temperature (193 K) electronic and NMR spectra for 0.8 mM FeTPP and 760 Torr CO . Both spectra were recorded using the same sample.

$\text{FeTPP}(\text{CO})$ and $\text{FeTPP}(\text{CO})_2$. The nature of the solution equilibria makes it impossible to obtain the NMR of pure $\text{FeTPP}(\text{CO})$; however, by going to low temperatures (193 K) the NMR for $\text{FeTPP}(\text{CO})_2$ can be recorded (Figure 6). The exclusive presence of $\text{FeTPP}(\text{CO})_2$ under these conditions was confirmed by the electronic spectrum of this solution at 193 K, which shows only peaks associated with $\text{FeTPP}(\text{CO})_2$ (Figure 6). The NMR data for $\text{FeTPP}(\text{CO})_2$ and the fast-exchanging mixture of $\text{FeTPP}(\text{CO})$ and $\text{FeTPP}(\text{CO})_2$ indicate that both species are diamagnetic.

$\text{FeTPP}(\text{CO})$, which cannot be examined in the pure form in solution or in the solid, has been inferred to be diamagnetic from NMR studies in conjunction with solution equilibrium measurements. All previously studied five-coordinate adducts of $\text{Fe}^{\text{II}}\text{TPP}$ have been high spin. Weak donor ligands such as tetrahydrofuran and *N,N*-dimethylformamide only form five-coordinate complexes and have solution moments in the range 4.8–5.2 μ_B .¹⁶ The sterically hindered 2-methylimidazole ligand forms a high-spin 1:1 complex with $\text{Fe}^{\text{II}}\text{TPP}$ which has been fully characterized.¹⁶ Steric requirements prohibit formation of the six-coordinate complex. Strong σ donor ligands such as pyridine and imidazole form six-coordinate diamagnetic complexes with $\text{Fe}^{\text{II}}\text{TPP}$; however, solution equilibrium studies indicate the presence of intermediate five-coordinate (1:1) complexes. The magnetic properties of these complexes have not been directly determined, but they are thought to be high spin. $\text{FeTPP}(\text{CO})$ is the only five-coordinate complex of this type which has been shown to be low spin.

In general an acceptor species in forming 1:1 and 2:1 complexes will have $K_1 > K_2$.



Entrance of the first donor molecule reduces the acceptor ability of the Lewis acid and results in $K_2 < K_1$. This generality applies to all known addition reactions which occur without change in spin state. When a change in spin state occurs, the relative values of K_1 and K_2 are complicated by the energy changes associated with the spin states and differences of M–L binding for different spin states. In the case of diamagnetic NiTPP , the d_{z^2} orbital is filled and is thus a poor σ acceptor molecule. In the excited high spin form the d_{z^2} is only half filled and thus a better acceptor orbital. The combined binding of two donor molecules is usually needed to induce the high-spin form, and for this case K_2 is usually larger than K_1 .¹⁷ In the

case of high-spin $Fe^{II}TPP$ the d_{z^2} is half filled, while the low-spin form has an empty d_{z^2} and thus improved σ acceptor properties. The low-spin configuration also has improved metal $d\pi$ donor properties owing to the filled $d_{xz,yz}$ orbitals, which is important for π acceptor ligands like carbon monoxide. Formation of a high- or low-spin five-coordinate complex depends on a trade-off between the promotion energy for producing the low-spin state and the resulting improved $d\sigma$ acceptor and $d\pi$ donor properties. A low-spin five-coordinate complex will result only when covalent σ and π bonding are dominant characteristics of the ligand, as is the case for CO. Apparently the covalent bonding from single nitrogen or oxygen donor is generally insufficient to promote formation of a diamagnetic complex.

The diamagnetism of $FeTPP(CO)$ is one more example of an emerging general rule that diatomic molecule adducts of planar metal complexes are low spin. Some examples of this behavior are [$S = 0$: $MnTPPNO$, $FeTPP(Cl)(NO)$,² $FeTPP(NO)_2$,² $CoTPP(NO)$, $FeTPP(CO)$, $FeTPP(CO)_2$, $S = 1/2$: $CrTPP(NO)$, $MnTPP(NO)(Cl)$,^{3,4} $CoTPP(CO)$, $FeTPP(NO)$,^{2,5} $CoTPP(O_2)$]. This generality probably results from the necessity of a filled $d_{xz,yz}$ in order to provide maximum metal–diatomic ligand $d\pi$ bonding. The only published exceptions to this generality which appear authentic are $MnTPP(O_2)$ ($S = 3/2$)¹⁹ and $CrTPP(O_2)$ ($S = 1$).²⁰ These complexes deserve more complete characterization, for an unusual form of metal–diatomic molecule bonding may be present.

Acknowledgment. This work was supported by the NSF MRL program under Grant DMR 76-80994 and PHS Grant AM 17533.

References and Notes

- (1) B. B. Wayland, J. V. Minkiewicz, and M. E. Abd-Elmageed, *J. Am. Chem. Soc.*, **96**, 2795 (1974).
- (2) B. B. Wayland and L. W. Olson, *J. Am. Chem. Soc.*, **96**, 6037 (1974).
- (3) B. B. Wayland and L. W. Olson, *Inorg. Chim. Acta*, **11**, L23–L24 (1974).
- (4) B. B. Wayland, L. W. Olson, and Z. U. Siddiqui, *J. Am. Chem. Soc.*, **98**, 94 (1976).
- (5) W. R. Scheidt and M. E. Frisse, *J. Am. Chem. Soc.*, **97**, 17 (1975); P. L. Piculio, G. Rupprecht, and W. R. Scheidt, *ibid.*, **96**, 5293 (1974).
- (6) H. Kon and N. Kataoka, *Biochemistry*, **8**, 4759 (1969).
- (7) C. H. Barlow, J. C. Maxwell, W. J. Wallace, and W. S. Caughey, *Biochem. Biophys. Res. Commun.*, **55**, 91 (1973).
- (8) D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 4087 (1973).
- (9) D. L. Anderson, C. J. Weschler, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 5599 (1974); C. K. Chang and T. G. Traylor, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 2647 (1973); *J. Am. Chem. Soc.*, **95**, 5810 (1973); W. S. Brinigar, C. K. Chang, J. Geibel, and T. G. Traylor, *ibid.*, **96**, 5597 (1974); J. E. Baldwin and J. Huff, *ibid.*, **95**, 5757 (1973); J. A. Almoy, J. E. Baldwin, R. L. Dyer, J. Huff, and C. J. Wilkerson, *ibid.*, **96**, 5600 (1974).
- (10) J. P. Collman and C. A. Reed, *J. Am. Chem. Soc.*, **95**, 2048 (1973); J. P. Collman, R. R. Gagne, T. R. Halbert, J. Marchon, and C. A. Reed, *ibid.*, **95**, 7868 (1973); J. P. Collman, R. R. Gagne, H. B. Gray, and J. W. Hare, *ibid.*, **96**, 6522 (1974); S. S. Eaton, G. R. Eaton, and R. H. Holm, *J. Organomet. Chem.*, **39**, 179 (1972).
- (11) G. Just, *Z. Phys. Chem. (Leipzig)*, **37**, 342 (1901).
- (12) G. Johnson and R. Bowen, *J. Am. Chem. Soc.*, **87**, 1655 (1965).
- (13) J. Bonnet, S. Eaton, G. Eaton, R. Holm, and J. Ibers, *J. Am. Chem. Soc.*, **95**, 2141 (1973); G. Eaton and S. Eaton, *ibid.*, **97**, 235 (1975).
- (14) M. Rougee and D. Brault, *Biochem. Biophys. Res. Commun.*, **55**, 1364 (1973); M. Rougee and D. Brault, *Biochemistry*, **14**, 4100 (1975).
- (15) H. R. O. Hill and P. Day, "Physical Methods in Advanced Inorganic Chemistry," Interscience, New York, N.Y., 1968, p 487.
- (16) D. Brault and M. Rougee, *Biochemistry*, **13**, 4598 (1974); H. Kobayashi and Y. Yanagawa, *Bull. Chem. Soc. Jpn.*, **45**, 450 (1972).
- (17) J. P. Collman and C. A. Reed, *J. Am. Chem. Soc.*, **95**, 2048 (1973); D. Brault and M. Rougee, *Biochem. Biophys. Res. Commun.*, **57**, 654 (1974).
- (18) B. D. McLees and W. S. Caughey, *Biochemistry*, **7**, 642 (1968); F. A. Walker, E. Hui, and J. M. Walker, *J. Am. Chem. Soc.*, **97**, 2390 (1975).
- (19) B. M. Hoffman, C. J. Weschler, and F. Basolo, *J. Am. Chem. Soc.*, **98**, 5473 (1976).
- (20) S. K. Cheung, C. J. Grimes, J. Wong, and C. A. Reed, *J. Am. Chem. Soc.*, **98**, 5028 (1976).

Kinetics and Mechanism of the Quenching of the Emission of Substituted Polypyridineruthenium(II) Complexes. Reactions of RuL_3^+ , $*RuL_3^{2+}$, and RuL_3^{3+} with the Copper(I)–Copper(II) Couple

M. A. Hoselton, C-T. Lin, H. A. Schwarz, and N. Sutin*

Contribution from the Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973. Received July 11, 1977

Abstract: The series of complexes RuL_3^{2+} , where L is a bipyridine or phenanthroline derivative, has been used to study the mechanism of the quenching of the luminescent excited state of RuL_3^{2+} by copper(II) ions in aqueous solution. The quenching rate constants were obtained from emission intensity measurements. A pulsed dye laser was used to generate the electron-transfer products RuL_3^{3+} and copper(I) and the rate constants for the reactions of these products to re-form RuL_3^{2+} and copper(II) were measured. Rate constants for the quenching of some OsL_3^{2+} complexes were also determined. The rate constants for the reaction of copper(II) with RuL_3^+ , generated by pulse radiolysis, were measured and compared with the rate constants for the reaction of copper(II) with $*RuL_3^{2+}$. On the basis of these results and spectroscopic considerations it is concluded that the quenching of $*RuL_3^{2+}$ by copper(II) proceeds by an electron-transfer mechanism. The free-energy dependence of the quenching reactions is smaller than expected for an electron-transfer mechanism and possible reasons for this behavior are discussed. The quantum yields for the formation of separated electron-transfer products are analyzed in terms of the electron-transfer rates within the primary cages and the rates of the thermal back reactions.

Introduction

The predominant process occurring when $Ru(bpy)_3^{2+}$ absorbs visible or ultraviolet light is the formation of a relatively long lived, charge transfer to ligand excited state.¹ This excited state decays to the ground state, in part, by the emission of

radiation. The quenching of this emission by added substrates has been the subject of a large number of studies.^{2,3} These studies have shown that the quenching may proceed by an energy transfer mechanism or by oxidation or reduction of the complex. An added reason for the current interest in the re-