

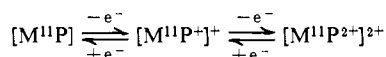
Metalloporphyrin Redox Chemistry. The Effect of Extraplanar Ligands on the Site of Oxidation in Ruthenium Porphyrins

Gilbert M. Brown, Frederick R. Hopf, John A. Ferguson, Thomas J. Meyer,* and David G. Whitten*

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. Received February 26, 1973

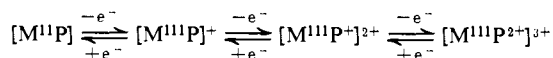
Abstract: Ruthenium(II) complexes of tetraphenylporphine, octaethylporphyrin, and etioporphyrin I undergo two reversible one-electron oxidations in dichloromethane. For the products of the first oxidation, electronic, epr, and infrared ($\nu(\text{CO})$) spectra indicate that oxidation occurs either at the metal ion or at the porphyrin ring depending on whether or not CO is an extraplanar ligand. Ruthenium(II) carbonylporphyrin complexes undergo ring oxidation to yield π -cation radicals similar in spectra and properties to the monomeric species formed by the one-electron oxidation of Cu(II), Co(III), Mg(II), Pb(II), and Zn(II). In contrast decarbonylated ruthenium(II) porphyrins are much more easily oxidized ($\Delta E_{1/2} \sim 0.6$ V) and the products are ruthenium(III) porphyrins with properties similar to the cobalt(III) and iron(III) porphyrins.

Recent work on the oxidation-reduction properties of metalloporphyrins has revealed several patterns of oxidation.¹⁻⁶ In divalent metal ion complexes in which the metal cannot be oxidized or is oxidized only with difficulty, oxidation proceeds by two reversible one-electron steps at the porphyrin ring



(M = Zn, Mg, Cd, or Cu; P = porphyrin or porphine dianion)

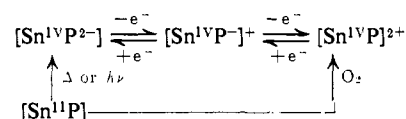
Tetraphenylporphine complexes of cobalt, nickel, and iron undergo an initial, reversible oxidation at the metal,^{2,7} which for cobalt and nickel is followed by successive one-electron oxidations at the porphine ring



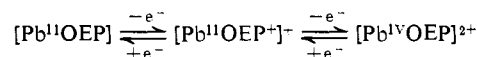
Recently, it was suggested that the second oxidation step for a variety of iron porphyrins leads to iron(IV) porphyrins⁸ instead of trivalent iron-ring-oxidized dications as suggested previously.

The oxidation-reduction properties of divalent tin⁹ and lead¹⁰ porphyrins are more complicated. For both metals the M(II) ions are too large¹¹ to fit into the central cavity of the porphyrin. Tin(II) complexes are converted thermally or photolytically into the more stable isomeric form $[\text{Sn}^{\text{IV}}\text{P}^{2-}]$ in which tin(IV) is in the plane of the porphyrin dianion. The more stable

$[\text{Sn}^{\text{IV}}\text{P}^{2-}]$ can also be prepared by electrochemical or light-catalyzed reduction of tin(IV) porphyrins



The electrochemical oxidation of lead(II) octaethylporphyrin (PbOEP) is rather unusual



An initial one-electron oxidation at the ring is followed by a second oxidation step in which both oxidation and internal electron transfer occur to give a lead(IV) porphyrin with chemical and physical properties similar to those of the ionic Ba^{2+} porphyrins.

Few systematic investigations of the effects of extraplanar ligands on the redox properties of metalloporphyrins have been reported. In this paper we report a study of the redox properties of ruthenium porphyrins which may have important implications for the biologically important iron porphyrin complexes.¹² In the ruthenium complexes the nature of the extraplanar ligands is not only crucial in determining redox potentials but, even more dramatically, the site of the redox reaction.

Experimental Section

Measurements. Ultraviolet-visible spectra were recorded on either a Cary Model 14 or Cary Model 17 spectrophotometer, epr spectra on a Varian E-3 spectrometer,¹³ and infrared spectra on a Perkin-Elmer 421 spectrometer. All electrical measurements were vs. the saturated sodium chloride calomel electrode (ssce) at $25 \pm 2^\circ$ and are uncorrected for junction potentials. In all electrochemical experiments standard three electrode operational amplifier circuitry was used as described previously.¹⁴ Values of n , where n is the total number of electrons transferred in exhaustive electrolyses at constant potential, were calculated after measuring the total areas under current vs. time curves for complete reaction. Reactions were judged to be complete when the current had fallen below

(1) A. Stanienda and G. Biebl, *Z. Phys. Chem. (Frankfurt am Main)*, **52**, 254 (1967).

(2) A. Wolberg and J. Manassen, *J. Amer. Chem. Soc.*, **92**, 2982 (1970).

(3) J. H. Fuhrup and D. Mauzerall, *ibid.*, **91**, 4174 (1969).

(4) R. H. Felton, D. Dolphin, D. C. Borg, and J. Fajer, *ibid.*, **91**, 196 (1969).

(5) J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, *ibid.*, **92**, 3451 (1970).

(6) C. E. Castro and H. F. Davis, *ibid.*, **91**, 5405 (1969).

(7) A. Wolberg and J. Manassen, *Inorg. Chem.*, **9**, 2365 (1970).

(8) R. H. Felton, G. S. Owen, D. Dolphin, and J. Fajer, *J. Amer. Chem. Soc.*, **93**, 6332 (1971).

(9) D. G. Whitten, J. C. Yau, and F. A. Carroll, *ibid.*, **93**, 2291 (1971); D. G. Whitten and J. C. Yau, *Tetrahedron Lett.*, 3077 (1969).

(10) J. A. Ferguson, T. J. Meyer, and D. G. Whitten, *Inorg. Chem.*, **11**, 2767 (1972).

(11) A. M. Schaffer and M. Gouterman, *Theor. Chim. Acta*, **18**, 1 (1970).

(12) D. Dolphin and R. H. Felton, *Accounts Chem. Res.*, in press. We thank Professor Dolphin for a reprint of this manuscript.

(13) The magnetic field was calibrated with a nuclear resonance (H, Li) gaussmeter.

(14) J. A. Ferguson and T. J. Meyer, *Inorg. Chem.*, **10**, 1025 (1971).

Table I. Electrochemical, Epr, and $\nu(\text{CO})$ Values for the Neutral and Oxidized Porphyrin Compounds

Compound	$E_{1/2}(1)$, V ^a	$E_{1/2}(2)$, V ^a	$n(1)^b$	g after oxidation at (1) ^c	$\nu(\text{CO})$, cm ⁻¹ , neutral compd ^d	$\nu(\text{CO})$, cm ⁻¹ , after oxidation at (1) ^d
H ₂ TPP	0.95	1.28	1.15	2.004		
Ru(TPP)CO	0.82	1.21	0.90 ^e	2.004	1930	1945
Ru(TPP)(CO)(py)	0.81	1.36	1.01	2.007	1943	1970
Ru(TPP)(py) ₂	0.21	1.26	0.94			
H ₂ OEP	0.83	1.39	1.19	2.004		
Ru(OEP)CO	0.64	1.21	0.88 ^e	2.004	1917	1950
Ru(OEP)(py)(CH ₃ CN) ^g	0.08	1.05	<i>f</i>			
H ₂ Etio I	0.78	1.34	0.97	2.004		
Ru(Etio I)(CO)	0.61	1.11	0.88 ^e	2.004	1917	1940

^a Potential measurements are *vs.* the ssce in 0.1 M TBAH-CH₂Cl₂ at 25 ± 2°. ^b n values, where n is the equivalent number of electrons passed in an exhaustive electrolysis, are the average of at least three determinations. ^c g values were determined at 77°K in frozen 0.1 M TBAH-CH₂Cl₂ solutions. The estimated error in the g values is ±0.001. ^d Ir spectra were obtained in 0.1 M TBAH-CH₂Cl₂ solutions. ^e n values were calculated on the basis of a five-coordinate molecule whereas a molecule of THF (from recrystallization) is likely in the sixth coordination site. As a result the reported n values are low. ^f Reduction of the ruthenium(III) porphyrin to Ru(II) results in formation of the dimeric complex [Ru(OEP)(py)]₂ on a time scale slower than the voltammetry experiment.²⁴ ^g All measurements on this ion were carried out in 0.1 M TBAH-CH₃CN.

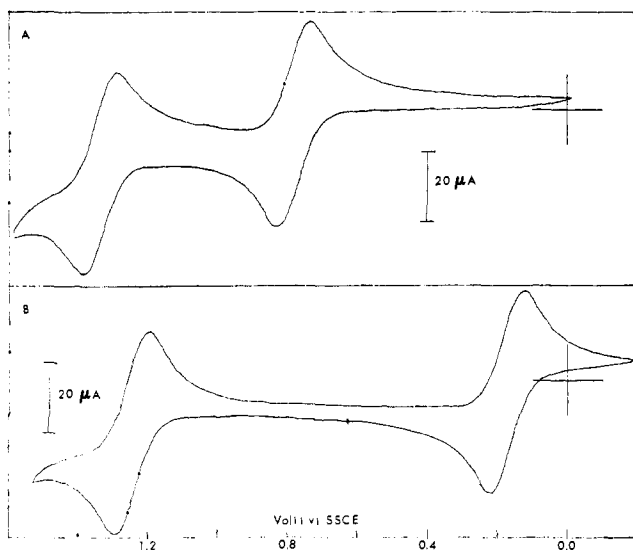


Figure 1. 200 mV/sec cyclic voltammograms in 0.1 M TBAH-CH₂Cl₂: (A) Ru(TPP)(CO)(py). (B) Ru(TPP)(py)₂.

1% of its initial value. All voltammetric measurements were carried out at platinum bead electrodes.

Materials. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by standard techniques¹⁵ recrystallized three times from hot ethanol-water mixtures, and vacuum dried at 70° for 10 hr. Ruthenium(II) carbonyloctaethylporphyrin, Ru^{II}(CO)-OEP,¹⁶ ruthenium(II) carbonyletioporphyrin I, Ru^{II}(CO)Etio I, and ruthenium(II) carbonyltetraphenylporphyrin, Ru^{II}(TPP)CO, were prepared from ruthenium carbonyl and octaethylporphyrin,¹⁷ etioporphyrin I,¹⁸ and tetraphenylporphyrin,¹⁹ respectively, according to the procedure of Tsutsui, *et al.*²⁰ The monopyridinate of Ru^{II}TPP(CO), Ru^{II}TPP(CO)(py), was prepared by recrystallization from pyridine, followed by vacuum drying at 70° for 24 hr. The dipyridinate of Ru^{II}TPP(CO), Ru^{II}TPP(py)₂, was prepared *via* the procedure of Chow and Cohen,²¹ and vacuum dried for

(15) W. Lange and E. Müller, *Chem. Ber.*, **63**, 1058 (1930).

(16) Abbreviations used: H₂TPP = tetraphenylporphyrine, TPP = tetraphenylporphyrine dianion, H₂OEP = octaethylporphyrin, OEP = octaethylporphyrin dianion, H₂Etio I = etioporphyrin I, Etio I = etioporphyrin I dianion, py = pyridine.

(17) H. W. Whitlock and R. Hanauer, *J. Org. Chem.*, **33**, 2169 (1968).

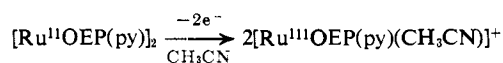
(18) G. Engelsma, A. Yamamoto, E. Markham, and M. Calvin, *J. Phys. Chem.*, **66**, 2517 (1962).

(19) A. Adler, F. Longo, J. Finarelli, J. Goldmacher, J. Assour, and L. Kausakoff, *J. Org. Chem.*, **32**, 476 (1967).

(20) (a) M. Tsutsui, D. Ostfeld, and L. M. Hoffman, *J. Amer. Chem. Soc.*, **93**, 1820 (1971); (b) M. Tsutsui, D. Ostfeld, J. N. Francis, and L. M. Hoffman, *J. Coord. Chem.*, **1**, 115 (1971).

(21) B. C. Chow and I. A. Cohen, *Bioinorg. Chem.*, **1**, 57 (1971).

10 hr at room temperature. The acetonitrile-pyridinate complex of ruthenium(III) octaethylporphyrin, [Ru^{III}OEP(py)(CH₃CN)]⁺, was electrolytically generated *in situ* from the previously reported²² photodimer of Ru^{II}OEP(CO)(py) by the reaction sequence^{23,24}

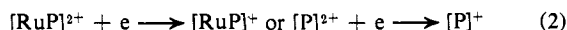
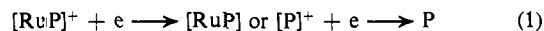


Acetonitrile (MCB "Spectrograde") was dried over activated alumina before use. Dichloromethane (Fisher, Spectrograde) was used without further purification. Pyridine was freshly distilled from potassium hydroxide. All other chemicals were reagent, spectra, or polarographic grade and were used without further purification.

Solutions and Reactions. All experiments were carried out under an atmosphere of dry, deaerated nitrogen. Approximately millimolar solutions of the neutral porphyrin complex were prepared in dichloromethane or acetonitrile which was 0.1 M in TBAH. The solutions were exhaustively electrolyzed at a potential sufficient to ensure complete one-electron oxidation. Aliquots of this solution were removed for determination of ultraviolet-visible, infrared, and epr spectra. Identical solutions were used for potential measurements and massive electrolysis.

Results

Electrochemistry. As indicated by the cyclic voltammograms in Figure 1, the ruthenium(II) tetraphenylporphyrin complexes in dichloromethane undergo two one-electron oxidations in the potential region 0–1.6 V *vs.* the ssce. The cyclic voltammetric behavior of the OEP and Etio I complexes is analogous to those shown. The reversible half-wave potentials (measured voltammetrically or calculated from cyclic voltammetry data given in Table I) are reduction potentials and refer to the reactions



where P refers to the various porphyrins.

Reaction 1 is chemically and electrochemically reversible. Solutions of the ruthenium porphyrin monocations can be prepared by exhaustive electrolysis in 0.1 M TBAH-CH₂Cl₂ solution. The starting neutral

(22) G. W. Sovocool, F. R. Hopf, and D. G. Whitten, *J. Amer. Chem. Soc.*, **94**, 4350 (1972).

(23) Cyclic voltammograms for the acetonitrile complexes were obtained on solutions of the ruthenium(III) complexes [Ru^{III}(P)(py)(CH₃CN)]⁺. The waves are reversible on the cyclic voltammetry time scale. However, on longer time scales, for example in coulometric experiments, the final reduction product was the dimeric complex [Ru^{II}(P)(py)]₂, formed by dimerization of the ruthenium(II) acetonitrile complex: 2[Ru^{III}(P)(py)(CH₃CN)]⁺ → [Ru^{II}(P)(py)]₂ + 2CH₃CN.²⁴

(24) F. R. Hopf and G. M. Brown, to be submitted for publication.

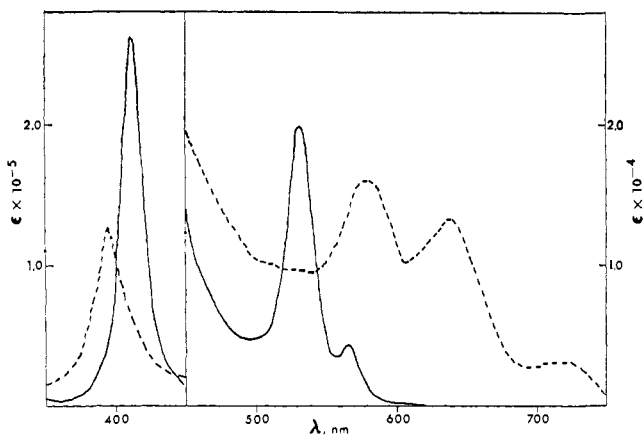


Figure 2. Spectra of ruthenium tetraphenylporphine complexes in CH_2Cl_2 solution: (—) $\text{Ru}(\text{TPP})(\text{CO})(\text{py})$, (-----) $[\text{Ru}(\text{TPP})(\text{CO})(\text{py})]^+$.

complex could be recovered quantitatively by exhaustive reduction. This was verified by oxidation and reduction coulometric n values and by visible spectra (Figures 2 and 3) which will be discussed more fully in a later section. Cyclic voltammograms after exhaustive oxidation and then on the re-reduced solutions were identical, indicating that the complexes had not decomposed on the time scale of the experiment.

However, the dication (reaction 2) was only stable on a cyclic voltammetric time scale. In all cases, attempts to generate solutions of the dication were unsuccessful due to decomposition of the complex. Exhaustive electrolysis yielded n values $\gg 2$, and visible spectra indicated decomposition of the porphyrin ring.

Epr. Electron paramagnetic resonance spectra were obtained for the monocations of the ruthenium porphyrin complexes containing CO. Solutions of the monocations were generated by exhaustive electrolysis, and spectra were obtained in frozen solutions at 77°K . The isotropic g values for these complexes are given in Table I along with g values for the corresponding monocations of the free base porphyrins. These g values are characteristic of oxidation at the porphyrin ring.^{3,12} Resonances were not observed for the ruthenium porphyrin monocations which did not contain CO. The difficulty in obtaining epr spectra of d^5 ruthenium(III) complexes has been noted previously.²⁵ Epr spectra were, however, not observed for the monocations of the complexes containing CO at room temperature.

Infrared Spectra. Also given in Table I are the $\nu(\text{CO})$ bands in CH_2Cl_2 solution for the neutral and singly oxidized porphyrin complexes which contain CO. The shift in $\nu(\text{CO})$ from the neutral to the singly oxidized complexes, $\Delta\nu(\text{CO}) = \nu(\text{CO}, \text{RuP}^+) - \nu(\text{CO}, \text{RuP})$, are in the range $15\text{--}33\text{ cm}^{-1}$. The shifts to higher frequency upon oxidation are consistent with the increase in positive charge on the complexes. However, the shifts appear to be smaller than expected if oxidation were occurring at the metal ($\text{Ru(II)} \rightarrow \text{Ru(III)}$). For example, $(\text{NH}_4)_2[\text{Ru}^{\text{II}}(\text{CO})(\text{H}_2\text{O})\text{Cl}_4]$ has $\nu(\text{CO})$ at 1950 cm^{-1} whereas $(\text{NH}_4)_2[\text{Ru}^{\text{III}}(\text{CO})\text{Cl}_5]$ has $\nu(\text{CO})$ at 2059 cm^{-1} .²⁶

(25) B. A. Goodman and J. B. Raynor, *Advan. Inorg. Chem. Radiochem.*, **13**, 278 (1970).

(26) J. Halpern, B. R. James, and A. L. W. Kemp, *J. Amer. Chem. Soc.*, **88**, 5142 (1966).

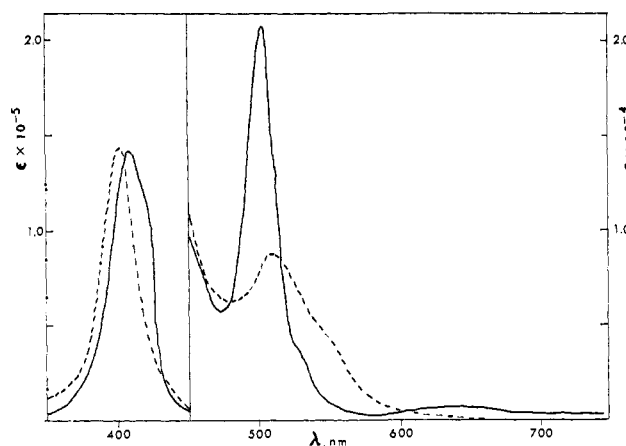


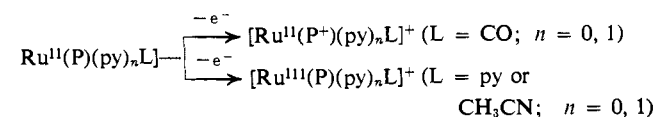
Figure 3. Spectra of ruthenium tetraphenylporphine complexes in CH_2Cl_2 solution: (—) $\text{Ru}(\text{TPP})(\text{py})_2$, (-----) $[\text{Ru}(\text{TPP})(\text{py})_2]^+$.

Electronic Spectra. The visible spectra of the neutral and singly oxidized complexes of $\text{Ru}(\text{TPP})(\text{CO})(\text{py})$ and $\text{Ru}(\text{TPP})(\text{py})_2$ are shown in Figure 2 and Figure 3, respectively. The spectra of the related OEP and Etio I complexes are similar. As illustrated in Figure 2, the visible spectra of the monocations of the CO containing complexes are consistent with porphyrin ring oxidation, showing the two broad absorptions in the range $550\text{--}700\text{ nm}$ observed for ring-oxidized zinc(II), cobalt(III), and copper(II) porphyrins.² Conversely, the spectra of the monocations of the non-CO containing complexes are characteristic of ruthenium oxidation as illustrated by Figure 3. This spectrum is quite similar to those of $\text{Fe}^{\text{III}}\text{TPP}$ and $\text{Co}^{\text{III}}\text{TPP}$ with an intense Soret peak and characteristic, reasonably sharp visible transitions (550 and 510 nm for $\text{Fe}^{\text{III}}\text{TPP}$).²

Discussion

From the $E_{1/2}$ values given in Table I, it is clear that when compared with pyridine or acetonitrile, the presence of CO in ruthenium porphyrins causes large anodic shifts for the first oxidation, e.g., $\Delta E_{1/2} = E_{1/2}[\text{Ru}(\text{TPP})(\text{CO})(\text{py})] - E_{1/2}[\text{Ru}(\text{TPP})(\text{py})_2] = 0.60\text{ V}$, making the carbonyl complexes much more difficult to oxidize. Even more striking is the related observation that the site of oxidation—at the porphyrin ring or at the ruthenium ion—is also controlled by the presence or absence of CO.

The infrared ($\nu(\text{CO})$), electronic, and epr spectra of the singly oxidized carbonyl complexes— $\text{Ru}(\text{TPP})(\text{CO})^+$, $\text{Ru}(\text{TPP})(\text{CO})(\text{py})^+$, $\text{Ru}(\text{OEP})(\text{CO})^+$, $\text{Ru}(\text{Etio I})(\text{CO})^+$ —are all consistent with the first oxidation having occurred at the porphyrin ring giving Ru(II)-ring oxidized complexes. For the non-CO containing complexes— $\text{Ru}(\text{TPP})(\text{py})_2^+$ and $\text{Ru}(\text{OEP})(\text{py})(\text{CH}_3\text{CN})^+$ —the available data clearly indicate that oxidation has occurred at ruthenium giving ruthenium(III) porphyrins with properties similar to analogous cobalt(III) and iron(III) complexes. The redox behavior at the first oxidation wave is summarized in the diagram



Oxidation of ruthenium(II) porphyrins gives products

in which the electron has been removed from either a metal d orbital or a porphyrin π_{MO} . The relative ordering of the levels depends on the extraplanar ligand. For acetonitrile or pyridine, metal d lies highest; for CO as the extraplanar ligand, porphyrin π_{MO} is highest. Undoubtedly an important factor contributing to the relative ordering is the strong effect of CO on metal d- π levels by back-bonding. A large difference between CO and pyridine (or acetonitrile) in π back-bonding ability might be sufficient to depress the metal d orbitals of π symmetry below π_{MO} of the porphyrin and change the site of oxidation.

Recent pmr studies have shown that the second extraplanar coordination site in ruthenium(II) carbonyl porphyrins is unusually labile²⁷ even though the ruthenium ion is presumably squarely in the porphyrin plane.²⁸ Apparently, the CO group in the ruthenium complexes acts both to control the site of oxidation and it also exerts a strong trans labilizing effect.

The $E_{1/2}$ values for the second oxidation of the ruthenium porphyrins (Table I) do not show the large extraplanar ligand effects on $\Delta E_{1/2}$ values that were observed for the first oxidation. The nature of the oxidation products obtained at the second oxidation wave are clearly of interest since depending on the extraplanar ligand the site of oxidation could be at the ruthenium

(27) S. S. Eaton, G. R. Eaton, and R. H. Holm, *J. Organometal. Chem.*, **39**, 179 (1972).

(28) J. J. Bonnet, S. S. Eaton, G. R. Eaton, R. H. Holm, and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 2141 (1973).

ion giving Ru(III) (L = CO) or Ru(IV) (L = py or CH₃CN) or at the porphyrin giving Ru(II)(P²⁺) (L = CO) or Ru(III)(P⁺) (L = py or CH₃CN). Although the doubly oxidized complexes are stable in dichloromethane on the time scale of the cyclic voltammetry experiment (seconds), on longer time scales they are unstable and react, probably with solvent or solvent impurities, giving the singly oxidized complexes and uncharacterized decomposition products.

Carbon monoxide is well known for its ability to coordinate to hemoglobin as well as to other heme-type enzymes. Moreover, CO is known to stabilize the iron(II) state with respect to oxidation to iron(III) in porphyrin environments, and in this manner inhibits the actions of biological systems. For instance, Fe^{II}(heme)(CO)(py) is resistant to oxidation by molecular oxygen in solution.²⁹ It seems reasonable to expect that the effects of CO on the redox properties of spin-paired iron(II) porphyrins should be related to the effects observed here, in electronically similar ruthenium complexes.

Acknowledgments. Acknowledgments are made to the National Science Foundation (Grant No. GP 17083), the National Institutes of Health (Grant No. GM 15238), and to the Materials Research Center of the University of North Carolina for support of this research.

(29) J. H. Wang, A. Nakahara, and E. B. Fleischer, *ibid.*, **80**, 1109 (1958).

Metal Ion Porphyrin Interactions. II. Evidence for the Nonexistence of Sitting Atop Complexes in Aqueous Solution¹

Hilary Baker, Peter Hambright,* and Lorenz Wagner

Contribution from the Department of Chemistry, Howard University, Washington, D. C. 20001. Received April 12, 1973

Abstract: *meso*-Tetrapyrrolylporphine (TPyP) has been postulated to form "sitting-atop" (SAT) complexes in aqueous solution, 1:1 adducts between metal ions and porphyrins which are presumed to be universal intermediates in metal ion incorporation. The completely water soluble and monomeric tetrakis(*N*-methylpyridyl)porphine (TMTPyP), which is similar to TPyP, has been reported to show no SAT properties. To clarify the SAT problem, a study of the kinetics of Cu²⁺ incorporation into TMTPyP was done at 26°, from pH 0.5 to 3.5, as a function of ionic strength (NaNO₃). The rate law was of the form: rate = $k[\text{Cu}^{2+}][\text{NO}_3^-][\text{TMTPyP}]/(1 + (\text{H}^+)/K_3 + (\text{H}^+)^2/K_3K_4)$. From equilibrium pH studies, K_3 and K_4 are the monocation-free base and dication-monocation dissociation constants, which increase with an increase in ionic strength. The rate determining step involves Cu²⁺, NO₃⁻, and only the free base form of the porphyrin. The results indicate that SAT complexes do not exist in aqueous solution with TMTPyP or TPyP. The SAT phenomena previously observed with TPyP can be explained by (1) an unusual anion term in the rate law, (2) the strong increase in pK_3 and pK_4 upon increase in ionic strength, and (3) the lack of reactivity of mono- and dication forms toward metal ions. The fact that all porphyrins do not incorporate metal ions by a single mechanism is discussed.

Over the past 12 years, a considerable effort has been made to determine the mechanisms by which metal ions insert into porphyrin molecules to form metalloporphyrins.²



(1) Part I concerns metal ion substitution and exchange reactions: H. Baker, P. Hambright, L. Wagner, and L. Ross, *Inorg. Chem.*, **12**, 2200 (1973).

(2) P. Hambright, *Coord. Chem. Rev.*, **6**, 247 (1971).

A particularly attractive idea was that of "sitting-atop" complexes,³ which were observable adducts of metal ions with free base (PH₂) porphyrins that form prior to metal ion incorporation. Evidence for SAT complexes has been presented in two types of systems. In methanol-chloroform mixtures, protoporphyrin dimethyl ester³ and various transition metal ions pro-

(3) E. B. Fleischer and J. H. Wang, *J. Amer. Chem. Soc.*, **82**, 3498 (1960).