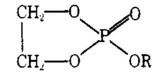
(37) (a) D. Hellwinkel, "Organo Phosphorus Compounds", Vol. 3, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N.Y., 1972, p 185; (b) R. Luckenbach, "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements", Georg Thieme Publishing Co., Stuttgart, 1973.

(38) J. A. Howard, D. R. Russell, and S. Trippett, *J. Chem. Soc., Chem. Commun.*, 856 (1973).

(39) D. A. Usher, E. A. Dennis, and F. H. Westheimer, *J. Am. Chem. Soc.*, 87, 2320 (1965), showed that the rapid hydrolysis of the monocyclic ester,



relative to its acyclic analog is explicable largely by a reduction in ring strain experienced by the cyclic ester on going to a pentacoordinate transition state with a preferred O–P–O angle of 90°. Consistent with our discussion, these results suggest that the difference in the acyclic TP level and monocyclic TP level shown in Figure 4 becomes compressed when dealing with saturated ring systems.

Effect of Extraplanar Ligands on the Redox Properties and the Site of Oxidation in Iron, Ruthenium, and Osmium Porphyrin Complexes

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Abstract: The redox properties of the complex Os(OEP)(CO)(py) (OEP^{2-} is the octaethylporphyrin dianion and py is pyridine) and related complexes of iron have been investigated in dichloromethane using electrochemical techniques. The osmium complex undergoes two electrochemically reversible oxidations. From spectral studies, the site of the first oxidation is at the osmium ion in contrast to related complexes of ruthenium where the first oxidation is at the porphyrin ring. Oxidation of the complex Fe(Etio I)(CO)(Im) (Etio I^{2-} is the etioporphyrin I dianion and Im is imidazole), which was prepared in situ, occurs at a potential $\sim$0.6 V higher than for oxidation of the analogous bisimidazole complex. Oxidation of Fe(Etio I)(CO)(Im) apparently also occurs at the central metal ion. The effect of CO as an extraplanar ligand in the iron, ruthenium, and osmium porphyrin complexes is discussed in terms of strong back-bonding with metal orbitals of dπ symmetry. In agreement with available crystallographic evidence, it is concluded that in the carbonyl complexes there is a significant tetragonal distortion. The variable site of oxidation in the porphyrin complexes is an example of an oxidation state isomerism in which the isomers differ with regard to the site of oxidation. Possible implications of the redox properties of the synthetic porphyrin–CO complexes for heme-based redox processes are discussed.

There have been few systematic studies of the effects of extraplanar ligands on the redox properties of metalloporphyrins.[1-3] We recently reported that changes in the extraplanar ligands can change not only reduction potentials but also the site of oxidation in ruthenium(II) porphyrins.[4] When pyridine occupies the extraplanar sites, oxidation occurs at the ruthenium ion. If CO is one of the extraplanar ligands, the site of oxidation is at the porphyrin ring.

The change in the site of oxidation with change in the extraplanar ligand is an interesting chemical problem. Qualitatively, the change has been explained in the ruthenium porphyrin complexes by stronger back-bonding to CO compared to pyridine. With strong back-bonding, the metal orbitals of dπ symmetry are lowered in energy below the porphyrin π levels which then become the valence MO's of the system.

It is a question of some interest in the metalloporphyrins as to whether or not the site of oxidation can be varied in a systematic way by synthetic modifications. In addition to variations in the extraplanar ligands it is possible to vary the central metal ion. The preparation of carbonyl complexes of osmium(II) octaethylporphyrin has been described by Buchler and coworkers,[5] and related complexes of iron have been characterized in solution. In the present paper we compare the redox properties of several iron, ruthenium, and osmium porphyrins with different ligands in the fifth and sixth coordination sites.

Experimental Section[6]

Measurements. Ultraviolet-visible spectra were obtained on a Cary Model 14 spectrophotometer. Infrared spectra were obtained on a Perkin-Elmer Model 421 spectrophotometer. All electrochemical measurements were vs. the saturated sodium chloride calomel electrode (SSCE) at 25 ± 2° and are uncorrected for junction potentials. Electrochemical measurements were made on an instrument previously described,[7] or a PAR Model 173 potentiostat was used for potential control with PAR Model 175 Universal Programmer as a sweep generator for voltammetric experiments. 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 the complete reaction. Reactions were judged to be complete when the current had fallen below 1% of its initial value. All voltammetric measurements were carried out at platinum electrodes. Electrochemical reversibility was determined, where possible, from plots of log $(i_1 - i)/i$ vs. E from stirred solution voltammetry. In some cases reversibility was determined by cyclic voltammetry. In a cyclic voltammetry experiment, reversibility was based on the ratio of anodic to cathodic peak currents (i_c/i_a) and the potential separation of the peaks (ΔE_p). The ratio i_c/i_a was usually $\sim$1.0, but ΔE_p ($\sim$70 mV) was higher than the theoretical value of 59 mV. The higher values most likely arise because of uncompensated solution resistance. Couples like ferrocene-ferricennium, which are known to be reversible, gave similar ΔE_p values in the same medium indicating that the $E_{1/2}$ values cited here are an accurate measurement of reduction potentials except for a usually negligible term involving the ratio of diffusion coefficients.

Materials. Tetra(n-butyl)ammonium hexafluorophosphate was prepared by standard techniques,[8] recrystallized three times from hot ethanol-water mixtures, and vacuum dried at 80° for 12 hr. A sample of Os^{II}(OEP)(CO)(py) was kindly provided by Professor J. W. Buchler. Fe^{III}(Etio I)Cl was prepared by the method of Adler et al.[9] from FeCl$_2\cdot n$H$_2$O and etioporphyrin I.[10] Dichloromethane (Fisher "Spectroanalyzed") was used without further purification. Imidazole (Aldrich) was recrystallized from dichlomethane and

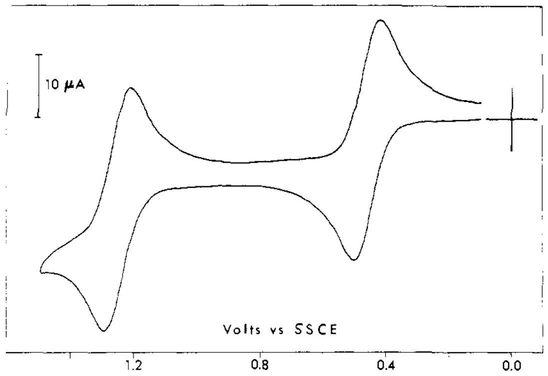

Figure 1. The 200 mV/sec cyclic voltammogram of Os(OEP)(CO)(py) in 0.1 *M* TBAH-CH_2Cl_2 solution.

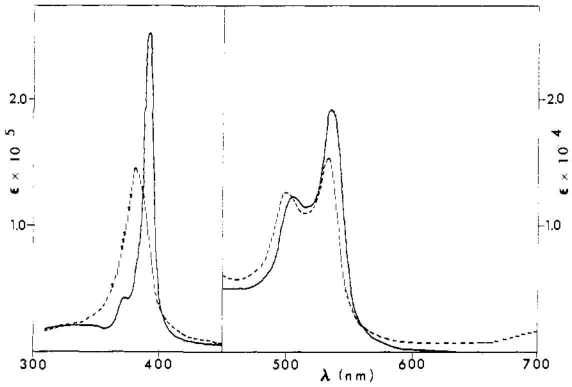

Figure 2. Electronic spectra of osmium octaethylporphyrin complexes in CH_2Cl_2 solution: (—) Os(OEP)(CO)(py); (- - -) Os(OEP)(CO)(py)$^+$.

then from benzene. All other chemicals were reagent or spectral grade and were used without further purification.

Preparation of Solutions. Os(OEP)(CO)(py)$^+$. Deaerated solutions of Os^{II}(OEP)(CO)(py) were exhaustively electrolyzed at +0.70 V vs. SSCE in 0.1 *M* TBAH-CH_2Cl_2 at a Pt mesh electrode. Aliquots were removed from solution to obtain infrared (ν_{CO}) and electronic spectra.

Fe^{III}(Etio I)(Im)$_2^+$. To a solution of Fe(Etio I)Cl (1.0×10^{-3} *M*) in 0.1 *M* TBAH-CH_2Cl_2 was added sufficient imidazole to make the concentration 2.5×10^{-2} *M*. At that level, there was sufficient imidazole present to drive the equilibrium

$$\text{Fe(Etio I)Cl} + 2\text{Im} \rightleftharpoons \text{Fe(Etio I)(Im)}_2^+ + \text{Cl}^- \quad (1)$$

completely to the right,[11] and the bisimidazole complex is by far the dominant form in solution.

Fe(Etio I)(CO)(Im). A solution of Fe(Etio I)Cl (1.0×10^{-3} *M*) and imidazole (2.1×10^{-2} *M*) in 0.1 *M* TBAH-CH_2Cl_2 was electrolyzed exhaustively at −0.70 V vs. SSCE on a Pt mesh electrode under an atmosphere of CO. The net reaction is

$$\text{Fe(Etio I)(Im)}_2^+ \xrightarrow[\text{CO}]{+e^-} \text{Fe(Etio I)(CO)(Im)} + \text{Im} \quad (2)$$

The electronic spectrum of the electrochemically reduced product was identical with that obtained by dithionite reduction. The presence of CO in the coordination sphere of Fe(II) was confirmed by the solution infrared spectrum which showed a strong ν_{CO} band at 1948 ± 2 cm^{-1}. *Caution: CO should only be used in a well-ventilated fume hood.*

Results and Discussion

Oxidation of Os(OEP)(CO)(py). The cyclic voltammogram in Figure 1 shows that Os^{II}(OEP)(CO)(py) undergoes two chemically reversible one-electron oxidations in 0.1 *M* TBAH-CH_2Cl_2. The oxidations are also electrochemically reversible so that half-wave potentials are formally reduction potentials in the medium used. The reduction potentials refer to reactions 3 and 4.

$$[\text{Os(OEP)(CO)(py)}]^+ + e \rightarrow [\text{Os(OEP)(CO)(py)}],\ E_{1/2} = 0.48 \quad (3)$$

$$[\text{Os(OEP)(CO)(py)}]^{2+} + e \rightarrow [\text{Os(OEP)(CO)(py)}]^+,\ E_{1/2} = 1.48 \quad (4)$$

Reaction 3 is chemically reversible and solutions of Os(OEP)(CO)(py)$^+$ can be generated by exhaustive electrolysis at 0.70 V vs. SSCE in 0.1 *M* TBAH-CH_2Cl_2 (n = 0.91). Cyclic voltammograms after the oxidation and again after rereduction to Os(OEP)(CO)(py), indicated that no decomposition had taken place. The electronic spectrum before oxidation and again after reduction also showed that the conversion was reversible. Similar results were obtained for the first oxidation in Ru^{II}(OEP)(CO)(THF).[4]

The second oxidation of Os(OEP)(CO)(py), reaction 4, is chemically reversible on the cyclic voltammetry time scale but not on longer time scales. Electrolysis on the diffusion plateau of the second wave gave $n > 10$. The electronic spectrum showed that extensive decomposition of the porphyrin ring system had occurred as evidenced by a large decrease in the intensity of the Soret transition. The same behavior was observed in the second oxidation for the carbonylruthenium(II) porphyrins.[4]

The ν_{CO} stretching frequency in Os^{II}(OEP)(CO)(py) is at 1896 cm^{-1} in 0.1 *M* TBAH-CH_2Cl_2. Upon oxidation to [Os(OEP)(CO)(py)]$^+$, ν_{CO} shifts to 2014 cm^{-1}. The large value for $\Delta\nu_{CO}$ (118 cm^{-1}) indicates that the site of oxidation is at the osmium atom and not at the porphyrin ring system. This is in contrast to the corresponding ruthenium porphyrin complexes where $\Delta\nu_{CO}$ = 15–33 cm^{-1}.

That the site of oxidation is at the metal and not at the porphyrin π system is confirmed by the electronic spectra shown in Figure 2. The electronic transitions for [Os^{III}(OEP)(CO)(py)]$^+$ in the visible region of the spectrum are still sharp and shifted only a small amount from that of the neutral complex, Os^{II}(OEP)(CO)(py). In systems containing a porphyrin π-cation radical, the spectra characteristically have broad transitions covering almost all of the visible region.[1]

Redox Properties of Iron Etioporphyrin I Complexes. Iron prophyrins have several properties which complicate a study of their redox chemistry as a function of the extraplanar ligands. Hoard and coworkers have shown from X-ray crystallographic studies that in high-spin iron(III) porphyrins the metal atom is out of the plane of the porphyrin ring.[12–14] It has also been suggested that the complexes are essentially five-coordinate in solution. In contrast, low-spin iron(II) and iron(III) porphyrins are six-coordinate,[15,16] and the iron atom is essentially in the plane of the porphyrin ring.[17,18]

The energy difference between six-coordinate, low-spin and five-coordinate, high-spin iron(III) porphyrins and the energy barrier to their interconversion are both apparently small in solution. The formation constants for six-coordinate complexes are somewhat low and the extraplanar ligand sites are labile. In order to prepare solutions of iron(III) porphyrins where the dominant form is the six-coordinate complex, it is necessary to add relatively large concentrations of the desired extraplanar ligand.[11,19]

Cyclic voltammograms for some iron etioporphyrin I complexes are shown in Figure 3. The complex Fe^{III}(Etio I)Cl is expected to be five-coordinate and high-spin since Fe^{III}(TPP)Cl is five-coordinate and high-spin. Fe^{III}(Etio I)Cl (Figure 3A) undergoes an electrochemically reversible oxidation in 0.1 *M* TBAH-CH_2Cl_2 ($E_{1/2}$ = 0.94 V). In related iron porphyrins, the oxidation has been attributed to the oxidation of iron(III) to iron(IV).[20] A reduction (iron(III) → iron(II)) occurs at $E_{1/2} = -0.57$ V which is irreversible as shown by cyclic voltammetry.

$[Fe^{III}(Etio\ I)(Im)_2]^+$ is expected to be low spin by analogy with the related low-spin complex $[Fe^{III}(TPP)(Im)_2]Cl$.[21] As indicated by the cyclic voltammogram in Figure 3B, the bisimidazole complex undergoes an electrochemically reversible one-electron reduction in 0.1 *M* TBAH-CH_2Cl_2 ($E_{1/2} = -0.52$ V). Under the experimental conditions used, the dominant form of the iron complex is expected to be $[Fe^{III}(Etio\ I)(Im)_2]^+$. A large excess of imidazole was used, and if the formation constant for the bisimidazole complex is not substantially lower than that for $[Fe^{III}(TPP)(Im)_2]^+$, the bisimidazole complex will be the only important iron porphyrin species in solution. The attempted preparation of $Fe^{II}(Etio\ I)(Im)_2$ by controlled-potential electrolysis was frustrated by the reaction between the Fe(II) complex and trace amounts of oxygen in solution. The difficulty in isolating bisimidazole iron(II) porphyrin complexes has been noted previously in related systems.[21]

Solutions of $Fe^{II}(Etio\ I)(CO)(Im)$ were generated by exhaustive, controlled-potential reduction of solutions containing $Fe^{III}(Etio\ I)Cl$ and excess imidazole which had been saturated with CO. The stoichiometry of the net reaction is given by eq 2. The visible spectrum of the product is identical with that produced by dithionite reduction under similar conditions. The spectrum is qualitatively the same as the spectra of other CO-containing complexes of iron(II) porphyrins. The presence of CO in the coordination sphere of the iron(II) was confirmed by infrared spectroscopy ($\nu_{CO} = 1948 \pm 2\ cm^{-1}$). Although iron(II) is known to be low spin in carbonyl iron(II) porphyrins, the CO group is not tightly bound and can be removed, even in the solid state, with a stream of an inert gas such as nitrogen.[22]

Steady-state cyclic voltammograms of $Fe^{II}(Etio\ I)(CO)(Im)$ in 0.1 *M* TBAH-CH_2Cl_2 are shown in Figure 3C. $Fe^{II}(Etio\ I)(CO)(Im)$ undergoes an electrochemically irreversible oxidation at $E_p = 0.32$ V which is remarkable when compared to the potential for the bisimidazole couple ($E_{1/2} = -0.52$ V). The large increase in potential is consistent with the fact that solutions of the iron(II) carbonyl complex are not especially air sensitive and can be stored for long periods under CO. The bisimidazole iron(II) complex is extremely air sensitive as mentioned previously.

The oxidation wave for the process

$$Fe(Etio\ I)(CO)(Im) \xrightarrow{-e^-} [Fe(Etio\ I)(CO)(Im)]^+ \quad (5)$$

is irreversible; a corresponding reduction wave is not observed even at a scan rate of 50 V/sec. The oxidation at +0.32 V and the reduction at −0.41 V are not connected. The peak potential for the oxidation wave is well defined and independent of sweep rate over the range 0.1 to 2.0 V/sec. Since E_p for the oxidation is independent of sweep rate, the electrode reaction is apparently a well-defined, diffusion-controlled electron transfer process. Oxidation is apparently followed by a rapid chemical reaction. For this case the E_p value represents a *lower* limit for the $E_{1/2}$ of the hypothetical, electrochemically reversible $[Fe(Etio\ I)(Im)(CO)]^{+/0}$ couple.[23]

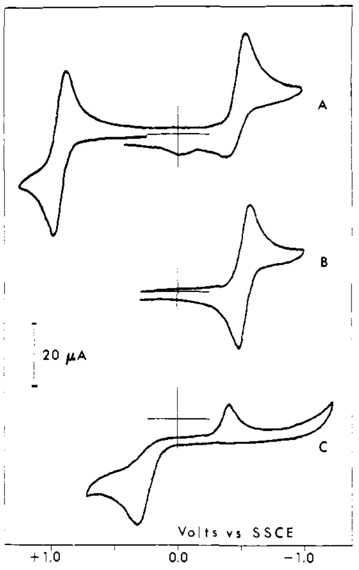

Figure 3. The 200 mV/sec cyclic voltammograms of iron etioporphyrin I complexes in 0.1 *M* TBAH-CH_2Cl_2 solution: (A) Fe(Etio I)Cl, (B) $[Fe(Etio\ I)(Im)_2]Cl$, (C) Fe(Etio I)(CO)(Im).

Scheme I

$E_{1/2}$, V	Couple
>0.64	$[Ru^{III}(Etio\ I)(CO)]^+ - [Ru^{II}(Etio\ I)(CO)]^a$
0.64	$[Ru^{II}(Etio\ I^+)(CO)]^+ - [Ru^{II}(Etio\ I)(CO)]^a$
0.61	$[Ru^{II}(OEP^+)(CO)]^+ - [Ru^{II}(OEP)(CO)]^a$
0.48	$[Os^{III}(OEP)(CO)(py)]^+ - [Os^{II}(OEP)(CO)(py)]$
$E_p = 0.32$	$[Fe(Etio\ I)(CO)(Im)]^{+/0}$
0.08	$[Ru^{III}(OEP)(py)_2]^+ - [Ru^{II}(OEP)(py)_2]^b$
0	(SSCE)
−0.52	$[Fe^{III}(Etio\ I)(Im)_2]^+ - [Fe^{II}(Etio\ I)(Im)_2]$

[a] The Etio I and OEP complexes have a tetrahydrofuran molecule in the sixth coordination site, ref 4. [b] In ref 4, this couple was incorrectly identified as the $Ru(OEP)(py)(CH_3CN)^{+/0}$ couple; see ref 28.

The Site of Oxidation and The Influence of CO in Iron, Ruthenium, and Osmium Porphyrins. Scheme I summarizes voltammetric data for the first oxidation wave for the Etio I or octaethylporphyrin complexes of iron, ruthenium, and osmium studied here or in our previous work. Comparisons are made interchangeably between OEP and Etio I complexes since the two ligand systems are known to give metalloporphyrin complexes which have nearly identical spectral and redox properties.[1] The potential values quoted in Scheme I are reduction potentials in dichloromethane vs. the SSCE at 25 ± 2°. Comparisons made using E_p for the $Fe(Etio\ I)(CO)(Im)^{+/0}$ couple are somewhat in doubt because the couple is chemically irreversible.

Spectroscopic studies presented here and in our previous work have shown that the site of oxidation in the ruthenium(II) carbonyl complexes is at the porphyrin ring,

$$Ru^{II}(OEP)(CO)(THF) \xrightarrow{-e^-} [Ru^{II}(OEP^+)(CO)(THF)]^+ \quad (6)$$

and in $Os^{II}(OEP)(CO)(py)$, at the osmium,

$$Os^{II}(OEP)(CO)(py) \xrightarrow{-e^-} [Os^{III}(OEP)(CO)(py)]^+ \quad (7)$$

Because of the chemical irreversibility of the oxidation of $Fe^{II}(Etio\ I)(CO)(Im)$, the site of oxidation in the oxidized, +1 ion cannot be determined by direct spectral observation.

For a series of divalent metal complexes of octaethylporphyrin, Fuhrhop, Kadish, and Davis have found that a reasonably linear correlation exists between $E_{1/2}$ for the first oxidation at the ring and the electronegativity of the central metal ion.[24] The electronegativities of iron (1.8), ruthenium

(2.2), and osmium (2.2) are similar. If the data of Fuhrhop, Kadish, and Davis are applicable to the systems studied here, the potentials for oxidation at the ring should be the same within ~0.10 V for the iron, ruthenium, and osmium porphyrins. The potential for ring oxidation in the Ru(Etio I)(CO)(THF)$^{+/0}$ couple (0,64 V) is considerably higher than E_p for the oxidation of Fe(Etio I)(CO)(Im) (0.32 V). The large difference implies that oxidation of Fe(Etio I)(CO)(Im) occurs at iron, giving [Fe^{III}(Etio I)(CO)(Im)]$^+$. Oxidation at iron is also consistent with the fact that oxidation of Os(OEP)(CO)(py) occurs at a higher potential (0,48 V) than for the iron complex, and that in the osmium complex, oxidation occurs at the metal.

Potential values for the series of couples [M^{III}(P)(CO)(L)]$^+$-M^{II}(P)(CO)(L) (P is OEP or Etio I; L is py, THF, or Im) are E_p = 0.32 V (M = Fe), 0.48 V (M = Os), and >0.64 V (M = Ru). Only a lower limit can be given for the ruthenium$^{+/0}$ potential since the site of oxidation is at the porphyrin. The observed trend in potentials, Ru > Os > Fe, is that sometimes found for metal complexes in which back-bonding from ligand to metal is important, For example, the potentials for the M(CN)$_6{}^{3-/4-}$ couples in aqueous solution (vs, NHE) are: 0.36 (M = Fe), 0.75 (M = Os), and 0.86 (M = Ru). On the basis of thermochemical arguments, the trend arises because the third ionization potential, which decreases in the series Fe > Ru > Os, is counterbalanced by increased back-bonding in the series Os > Ru > Fe.[25] Increased back-bonding tends to stabilize the M(II) state over the M(III) state.

As in the osmium carbonyl system (Figure 1), there is a second electrochemically reversible oxidation at >1.2 V for ruthenium carbonyl porphyrins.[4] Also as in the osmium system, the twice-oxidized complexes are unstable for periods longer than the cyclic voltammetry time scale, and it is not possible to use conventional spectral techniques to determine the site of oxidation. The second oxidation may occur at ruthenium, or at the ring,

$$[\mathrm{Ru^{II}(P^+)(CO)}]^+ \xrightarrow{-e^-} [\mathrm{Ru^{II}(P^{2+})(CO)^{2+}}]$$

If oxidation is at the metal, the potential gives an unreasonably high estimate for a Ru^{III}(P)(CO)$^+$-Ru^{II}(P)(CO) couple, but would represent an upper limit.

The effect of the binding of CO in an extraplanar site can be seen very clearly in the data summarized in Scheme I. The increase in potential for the [M^{III}(porphyrin)L$_2$]$^+$-M^{II}(porphyrin)L$_2$ couple when a N-base ligand (py or Im) is replaced by a CO is ~0.8 V when M = Fe and >~0.6 V when M = Ru. The increase in potential for the osmium system cannot be estimated since we have investigated only the osmium-carbonyl system. However, it can be predicted that the potential for a couple like Os(OEP)(py)$_2{}^{+/0}$ will fall in the range between the potentials for the Fe(Etio I)(Im)$_2{}^{+/0}$ (−0.52 V) and Ru(OEP)(py)$_2{}^{+/0}$ (0.08 V) couples.[48]

What appears to be a reasonable orbital interpretation of the effect of CO leads to a rather surprising conclusion about the relative energies of the metal d orbitals. The metalloporphyrin complexes can be treated as a tetragonally distorted ligand field case. If the z axis is taken along the extraplanar ligand axis perpendicular to the plane of the porphyrin, by symmetry arguments, only the d_{zx} and d_{zy} orbitals can interact with the CO π^* orbitals, The electrochemical results show that the metal electronic levels involved in net electron transfer are significantly affected by the introduction of CO, which suggests that these levels are the degenerate pair d_{zx} and d_{zy}. The only pattern of d levels which is consistent with this observation places d_{z^2} below d_{zx} and d_{zy} in the octahedral complex (Figure 4) and a large tetragonal distortion caused by the porphyrin ring must occur. A significant tetragonal distortion has been observed in the crystal structure of Ru^{II}(TPP)(CO)(py)·1.5 toluene.[26] The axial Ru-N(pyridine) bond distance (2.193 (4) Å) is unusually long, and the Ru-C(CO) bond distance (1.838 (9) Å) falls at the upper end of the range of Ru-C(CO) distances found in various mononuclear organometallics. A large tetragonal distortion is also consistent with the known kinetic lability of the L group in Ru^{II}(TPP)(CO)L complexes.[27] In the bispyridine complex, Ru^{II}(OEP)(py)$_2$, an X-ray study has shown[28] that the tetragonal distortion is considerably smaller, and it is not apparent as to which of the metal d orbitals ($d_{zx,zy}$, d_{xy}, d_{z^2}) is the highest filled orbital. It should also be noted that a schematic MO diagram has been given recently[29] for Fe(TPP)(NO)Cl in which d_{z^2} lies above both d_{xy} and $d_{zx,zy}$.

The effect of an extraplanar CO group on the metal d levels can be seen in Scheme I, In the iron and osmium complexes, the effect of the added CO is to stabilize the valence d levels by back-bonding, and perhaps to change the pattern of the d orbital energies. The same effect occurs for ruthenium. However, for the ruthenium-carbonyl complexes, the d_{zx} and d_{zy} levels are sufficiently stabilized so that porphyrin π levels become the valence levels of the system and the site of oxidation changes.

The redox properties outlined above are remarkable since they indicate that in the M(II)-porphyrin complexes there are two *different* sites for oxidation: at the metal and at the porphyrin ring. Oxidation at the two different sites gives rise to two distinctly different states, e.g., [Ru^{III}(OEP)(py)$_2$]$^+$ and [Ru^{II}(OEP$^+$)(CO)(THF)]$^+$, with their own chemical and physical properties. For a given central metal ion (ruthenium), both states are accessible by varying the extraplanar ligands.

For a given complex the two possible states represent a case of *oxidation state isomerism*, in which the isomers differ with regard to the site of oxidation, e.g., [Ru^{II}(OEP$^+$)(CO)(THF)]$^+$ and [Ru^{III}(OEP)(CO)(THF)]$^+$. Other cases of oxidation state isomerism have been suggested to exist in a closely related cobalt-tetraazaannulene system,[30] ligand-bridged metal complexes where there are chemically different sites,[31] in certain metal nitrosyl complexes,[32] in the products arising from the addition of SnCl$_4$ and CH$_3$SnCl$_3$ to a square-planar Ir(I) complex,[33] and in tin(IV) porphyrins, and perhaps, oxidized Pb(II) porphyrins.[34]

A high energy oxidation state isomer like [Ru^{III}(OEP)(CO)(THF)]$^+$ is analogous to a thermally equilibrated MLCT excited state. However, from the data in Scheme I, it is apparent that the energy differences between the ground and excited states are probably small for the ruthenium-carbonyl cases and for cases like [Os^{III}(OEP)(CO)(py)]$^+$ → [Os^{II}(OEP$^+$)(CO)(py)]$^+$ or [Ru^{III}(OEP)(py)$_2$]$^+$ → [Ru^{II}(OEP$^+$)(py)$_2$]$^+$. In principle, the existence of a low-lying oxidation state isomer may be observable spectroscopically, and experiments are currently being carried out to test this idea. Such a state could also influence the chemistry of a system, perhaps by providing a normally inaccessible, low energy pathway for reaction.

Implications for Heme-Based Redox Processes. Carbon monoxide is well known for its ability to bind to heme-type iron proteins. Coordinated CO has the effect of disrupting the normal functions of the metalloproteins.

It is an interesting fact that for the synthetic system Fe(OEP)(CO)(Im) in CH$_2$Cl$_2$, ν_{CO} is at 1948 ± 2 cm^{-1}. For CO bound to eight normal hemoglobins, ν(CO) has been found to be 1951 ± 1 cm^{-1}.[35,36] The similarity in ν(CO) values suggests that the electronic environment around the iron atom is similar in both the synthetic and the hemoglobin systems.

CO is known to interfere with O_2 binding in the hemoglobins. Another effect of CO in heme-based redox processes may come from its effect on the iron(III)-iron(II) redox potentials in the hemes. In the synthetic system, the replacement of an imidazole group by CO results in an increase in the iron(III)-iron(II) reduction potential by ~0.8 V. The binding of CO to a heme group in the cytochrome electron transfer sequence would probably have a similar effect. A large increase in one or more of the iron(III)-iron(II) heme potentials in the cytochromes could disrupt the normally rapid passage of reducing equivalents through the cytochrome chain.

The possibility of different sites of oxidation in the metalloporphyrins is important with regard to the electron transfer properties of ferri and ferrocytochrome *c*'s. Crystallographic studies[37] have shown that in cytochrome *c*, an edge of the porphyrin group is exposed to the exterior of the protein sheath. It has been suggested that electron transfer can occur to the metal ion through the exposed edge of the porphyrin.[38,39] It has been further suggested that in the oxidation of ferrocytochrome *c*, complete removal of an electron may occur initially, giving the ferrocytochrome *c* porphyrin π-cation radical.[40] Some experimental evidence is available which indicates the possible intermediacy of a porphyrin π-cation radical in iron porphyrin redox reactions.[41]

$$\mathrm{Fe^{II}(Cyt\ c)} \xrightarrow[k_1]{-e^-} \mathrm{Fe^{II}(Cyt\ c^+)} \xrightarrow[k_2]{} \mathrm{Fe^{III}(Cyt\ c)} \qquad (8)$$

If the mechanism in eq 8 is correct, the net rate of electron transfer

$$\mathrm{Fe^{II}(Cyt\ c)} \xrightarrow[k]{-e^-} \mathrm{Fe^{III}(Cyt\ c)}$$

will be determined in part by the free energy difference between the reductant couple and the oxidation state isomer couple, $\mathrm{Fe^{II}(Cyt\ c^+)^+}$-$\mathrm{Fe^{II}(Cyt\ c)}$, and not by the free energy difference between the reductant couple and the ground state couple $\mathrm{Fe^{III}(Cyt\ c)^+}$-$\mathrm{Fe^{II}(Cyt\ c)}$. The rate of intramolecular electron transfer, k_2, should be exceedingly rapid as evidenced by the characteristically rapid rates of internal conversion for charge transfer excited states.

In principle, the increased barrier imposed by initial oxidation at the porphyrin could be minimized by selection of appropriate extraplanar ligands. Strong back-bonding ligands should minimize the barrier by minimizing the free energy difference between oxidation at the porphyrin and oxidation at the metal. A mechanism involving initial oxidation at the porphyrin may hold for outer-sphere electron transfer paths involving cytochrome *c*. However, there is no compelling need to invoke it. Electron transfer between large transition metal complexes such as the iron, ruthenium, and osmium polypyridines, e.g.,

$$\mathrm{Fe(bpy)_3^{2+} + Fe(bpy)_3^{3+} \rightarrow Fe(bpy)_3^{3+} + Fe(bpy)_3^{2+}} \qquad (9)$$

are known to be rapid[42] even though the complexes have large molecular diameters (12-16 Å).[43] In reactions like (9), electrons are exchanged between metal d-π orbitals which contain some ligand π^* character.[43] Even for such large complexes, overlap between dπ orbitals on the reacting ions is sufficiently large so that electron transfer is apparently adiabatic.[44,45] Overall electron transfer processes involving such complexes are characteristically very rapid.[46,47] There is no reason to believe that similar orbital pathways are not available for the metalloporphyrin complexes.

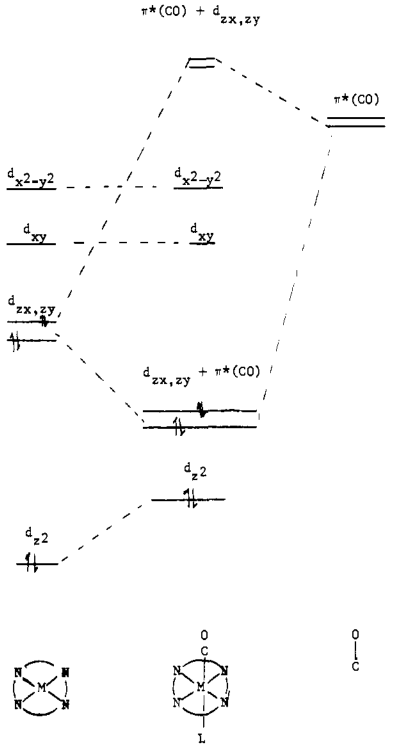

Figure 4. Schematic MO diagram for M(P)(CO)(L) (P is OEP or Etio I; M is Fe, Ru, or Os; L is a neutral ligand).

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(6) Abbreviations used here and later in the text include: TBAH = tetra(*n*-butyl)ammonium hexafluorophosphate, OEP^{2-} = octaethylporphyrin dianion, Etio I^{2-} = etioporphyrin I dianion, py = pyridine, Im = imidazole, TPP^{2-} = tetraphenylporphine dianion, tetrahydrofuran = THF.
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(48) Note Added in Proof: The potential for this couple was found to be −0.40 V (J. W. Buchler and G. Deserno, unpublished).

Natural Solid State Optical Activity of Tris(ethylenediamine)metal(II) Nitrates. II. Single-Crystal Circular and Linear Dichroism Spectra of Tris(ethylenediamine)cobalt(II) Nitrate[1]

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Abstract: The electronic structure of tris(ethylenediamine)cobalt(II) nitrate has been investigated by measurement of the linear dichroism (LD) and circular dichroism (CD) spectra of cobalt-doped Zn(en)$_3$(NO$_3$)$_2$ and of pure Co(en)$_3$(NO$_3$)$_2$ single crystals. Spectra have been measured at ambient and cryogenic temperatures in the region from 7 to 35 kK. Cotton effects associated with all ligand field transitions are observed to have the same sign in the axial CD of a given crystal. Polarizations in the orthoaxial LD indicate that the ground state is $^4A_2$ in the trigonal field. The main source of absorption spectral band intensity is a vibronic mechanism, whereas the CD intensity is primarily static in origin. The crystals of both the cobalt and zinc compounds appear to be completely isomorphous with Ni(en)$_3$(NO$_3$)$_2$. The CD results show clearly that all three compounds represent unusual instances of spontaneous resolution of tris(bidentate) chelates by crystallization. The absolute configuration of the host crystal is deduced by reference to that of the kinetically inert Ru(en)$_3^{2+}$ ion and from this the chirality and signs of rotational strength of Co(en)$_3^{2+}$ as well as of Cu(en)$_3^{2+}$, Ni(en)$_3^{2+}$, and Mn(en)$_3^{2+}$ in the crystal have been correlated.

Spectroscopic interest in trisethylenediamine complexes has generally centered on the dichroism,[2-4] the source and magnitude of the trigonal field splitting,[5-8] the source of absorption band intensity,[9-11] and/or the optical activity.[3,11-18] Among the first-row transition metal complexes of ethylenediamine, only Cr(en)$_3^{3+}$, Co(en)$_3^{3+}$, Ni(en)$_3^{2+}$, and Cu(en)$_3^{2+}$ have been studied intensively owing to the air sensitivity of the other members of the series. Among these, studies of optical activity have been limited to Cr(en)$_3^{3+}$ and Co(en)$_3^{3+}$ because of the lability of the high spin divalent metal ion complexes, which effectively prevents isolation of the pure enantiomers (except as solid diasteroisomers). Ru(en)$_3^{2+}$ (low spin d^6) appears to be the only divalent trisethylenediamine complex to have been resolved.[17] Besides Ru(en)$_3^{2+}$ and several α-diimine complexes of low spin iron(II), ruthenium(II), and osmium(II),[18] verified natural optical activity measurements of *chiral* divalent transition metal complexes have previously been reported only for tris(1,10-phenanthroline)nickel(II) and tris(2,2′-bipyridine)nickel(II) ions.[19] Natural optical activity measurements have also been made on the intrinsically *achiral* hexaaquo complexes of manganese(II), iron(II), cobalt(II), nickel(II), and copper(II) in various enantiomorphous lattices.[20-28]

As part of a continuing study of natural solid state optical activity, we have measured the circular dichroism (CD) and linear dichroism (LD) of the divalent transition metal ions Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, and Ru^{2+} doped into Zn(en)$_3$(NO$_3$)$_2$. In the cases of nickel and cobalt, measurements on the isomorphous pure crystals have also been made. Previous reports of the LD of the nickel complex have been made by Karipides[3] and by Dingle and Palmer[10] and of the copper complex by Karipides.[3] LD of the copper complex in the sulfate crystal has also been measured.[29] The solution CD of the kinetically inert complex Ru(en)$_3^{2+}$ has been reported by Elsbernd and Beattie.[17] In this paper we report our results for Co(en)$_3$(NO$_3$)$_2$ and Zn(Co)(en)$_3$(NO$_3$)$_2$. A preliminary account of this work has been published,[1] and detailed results for nickel, copper, manganese, and ruthenium are reported separately.[30]

The crystals of Co(en)$_3$(NO$_3$)$_2$ and Zn(en)$_3$(NO$_3$)$_2$ are apparently completely isomorphous with their nickel ana-