We suggest, following previous workers,[7] that the groups with the smaller R values are likely to be those subjected to larger nonbonded interactions, and thus the smaller alkyl proton coupling constants should be associated with the *endo* groups.

The suggestion[39] that deuterium does not hyperconjugate so effectively as protium could account for the observation that in both BDME$^+$ and TDE$^+$ the a_H/a_D ratio is *greater* than 6.514. However, diminishing the value of the resonance integral between the methyl carbon and the H_3 pseudoatom in the HMO calculations predicts a small *decrease* in the ethylenic carbon–nitrogen bond order.

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Electrochemical and Electron Paramagnetic Resonance Studies of Metalloporphyrins and Their Electrochemical Oxidation Products

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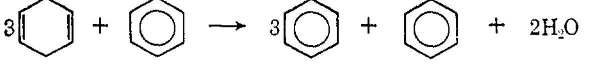
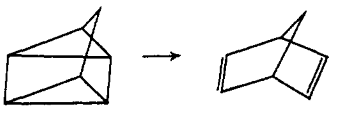
Abstract: The oxidation potentials of transition metal complexes of tetraphenylporphyrins (TPP) and phthalocyanine with bivalent Fe, Co, Ni, Cu, and Zn atoms were determined by cyclic voltammetry. The metallo TPP complexes and the products obtained by their controlled-potential electrochemical oxidation were studied by epr, magnetic susceptibility measurements, and optical spectroscopy. In the case of Fe, Co, and Ni, the first oxidation occurred at the central metal atom, whereas in the case of Cu and Zn, ligand oxidation was observed. Subsequent oxidations occurred at the ligand in all cases. The potentials of central metal oxidation showed a linear dependence on the third ionization potential of the ions. The ligand oxidation potentials were approximately independent of the metal ion for Fe, Co, and Ni, but dropped to a lower value for Cu and Zn, which was rationalized on theoretical grounds. A more or less stable Ni(III) square-planar complex was observed for the first time. ^{59}Co hf splitting of 5.7 G was observed in the epr spectrum of $[\mathrm{Co(III)TPP}]\cdot^{2+}$ where the unpaired electron is of π-ligand character. The decrease in the ^{14}N hyperfine lines after the two-electron oxidation of [Cu(II)TPP] gave quantitative information about Cu–N overlap change with oxidation. Although Fe(III)TPP acetate has five unpaired spins, its oxidation product $[\mathrm{Fe(III)TPP}]\cdot^{2+}$ has only two, one on the ligand and one on the central metal atom. For this kind of triplet species, which was also produced after the first oxidation of [Cu(II)TPP], no epr signal could be observed, but magnetic susceptibility measurements gave unequivocal evidence of their existence. The method of plotting oxidation potentials as a function of the third ionization potential of the metal ions appears to be of general importance and has been applied also to other complexes whose oxidation potentials had been reported in the literature.

Porphyrins and their metallo derivatives are significant in biological systems. Their properties and enzymatic activities have been studied extensively.[2] Recently Manassen and coworkers[3] demonstrated their catalytic activities in some pure chemical reactions, as oxidative dehydrogenation



(I)

and symmetry-forbidden rearrangements



(II)

Reaction I showed a decrease in conversion going from iron *via* cobalt to the nickel complex and then a slight increase going from nickel *via* copper to the zinc compound. In the rearrangement reaction, they found a high activity for the first three compounds and no reaction at all for the last two. In order to understand this behavior we have undertaken the current study of physical properties of some of the complexes by combining electrochemical with magnetic and optical spectroscopy measurements.

We have focused our attention on the complexes of tetraphenylporphyrins with first-row transition metal ions from iron to zinc, [M(II)TPP], and to a lesser degree to the corresponding phthalocyanine complexes, [M(II)Pc]. There are reports in the literature of electrochemical,[4] epr,[5,6] optical,[7-10] and combined electro-

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[6] P. T. Manoharan and M. T. Rogers in "Electron Spin Resonance

chemical, epr, and optical studies[11-14] of these and related complexes. However, except for the theoretical MO calculation of Zerner and Gouterman[15] no study covers the whole series of 3d^5–3d^{10} complexes with a given ligand.

Our method of investigation consists of oxidation potential measurements of the [M(II)TPP] complexes in solution by cyclic voltammetry of one-, two-, and three-electron transfer steps, coupled with coulometric determination of the number of electrons involved in each step. The products of controlled-potential oxidations were subjected to magnetic and optical measurements. Based on the spectroscopic data we were able to distinguish between metal and ligand oxidation, and consequently, to get a better correlation between catalytic activities of both the metallotetraphenylporphyrins and the metallophthalocyanines[3] and their oxidation potentials.

In the process of these experiments we were able to identify a square-planar trivalent nickel complex which was the subject of a separate note.[16]

Prior to proceeding to the work itself we would like to establish a common nomenclature for these complexes and their oxidation derivatives. Although through the ligand hyperfine (lhf) splittings in the epr spectra we have evidence for appreciable metal–ligand orbital overlap, the electrons are sufficiently localized to distinguish between epr signals of paramagnetic metal-ion complexes and organic free radicals. The optical spectra can be grouped into two distinct types parallel to the epr classification. Accordingly, we will distinguish between complexes which were oxidized at the metal atom and those which were oxidized at the ligand, *i.e.*, at the porphyrinic ring. For this reason we would like to adopt the following notation: [M(Roman numeral) ligand abbreviation]$^{m\cdot n+}$ for these complexes. The Roman numeral designates the oxidation state of the metal atom M, $n+$ indicates the total charge of the complex ion, and $m\cdot$ represents the number of unpaired electrons on the ligand. Thus, [Co(II)TPP] means a neutral complex of bivalent cobalt tetraphenylporphyrin, and [Co(III)TPP]$^{\cdot 2+}$ is the free-radical cation complex of trivalent cobalt tetraphenylporphyrin. Note that a two-electron oxidation will transform [Co(II)TPP] into [Co(III)TPP]$^{\cdot 2+}$, by extracting one electron from the metal and another one from the ligand, *i.e.*, a change of valency and a ligand oxidation process, respectively.

Experimental Section

Materials. Tetraphenylporphyrin and its metallo complexes were prepared and characterized by the method described in ref 7 and 17, respectively, except for the Ni complex which was synthesized according to ref 18. The phthalocyanine complexes were prepared according to ref 19.

Solutions of 0.002 *m* [M(II)TPP] complexes in 0.1 *m* n-Bu$_4$NClO$_4$/benzonitrile were prepared, except in few cases mentioned in Table I. The oxidized species were obtained by controlled-potential electrolysis which was stopped after the current had decreased to 1% of its initial value, which never took more than 15 min. Reversing the current gave in all cases, where cyclic voltammetry indicated reversibility, better than 95% of the original number of counts. The [M(II)Pc] complexes studied were saturated solutions in 0.1 *m* n-Bu$_4$NClO$_4$/1-chloronaphthalene. The solvents were purified by passing them over a column of alumina adsorbent just prior to their use.

Cyclic Voltammetry. The working electrode was a Beckman platinum disk electrode (Beckman No. 39273) and the auxiliary electrode, a piece of 0.5-mm diameter Pt wire. The saturated aqueous calomel electrode was separated from the solution by a fritted glass disk and a Luggin capillary. Cyclic potential sweeps were generated by a Hewlett–Packard 3300A function generator in conjunction with a Wenking 66TS10 potentiostat. Sweeps ranged from 1 to 150 V/min.

Controlled-Potential Coulometry. The working electrode was made of Pt mesh. The auxiliary and reference electrodes were as before. They were separated from the solution by salt bridges of a saturated solution of tetraethylammonium perchlorate in acetonitrile. This was sufficient to prevent water leakage into the oxidized solutions. The current was integrated using a voltage-to-frequency converter with an electronic counter.[20]

Electron Paramagnetic Resonance. The epr spectra were recorded on a Varian Associates X-band 4502 epr spectrometer, equipped with a dual cavity, 100-kc/sec modulation unit, and a Hewlett-Packard X530A frequency meter. The sample was introduced into one side of the cavity either in quartz flat cells or in a sealed quartz tube immersed in a liquid nitrogen dewar. As a standard a peroxylaminedisulfonate sample was placed in the other side of the cavity. The sample cells were purged with nitrogen prior to filling them with the samples.

Magnetic Susceptibility Measurements. The magnetic susceptibilities were measured using the method described by Evans,[21] by which one observes the paramagnetic relative shifts of the TMS signal added to both the complex solution and the solvent. From the difference in these shifts, the knowledge of the concentrations, and after corrections for the diamagnetism of the solvent one can calculate the μ of paramagnetic molecules. The instrument used was a Varian Associates A-60 nmr spectrometer equipped with concentric sample tubes.

Optical Spectra. The optical work was done on a Cary Model 14 spectrometer using a quartz cell of 0.01-cm optical path length.

Results

General. The measurement done by cyclic voltammetry showed well-resolved successive one-electron reversible oxidation steps, with a few exceptions. The [Ni(II)TPP] complex which was discussed previously[16] showed two overlapping one-electron transfer steps, the first being a reversible and the second an irreversible one. The nonmetallic H$_2$TPP molecule displayed a voltammogram with two irreversible one-electron oxidation steps. The oxidation potentials were determined at 85% of the maximum peak height of the oxidation half of the cycle, which coincided within experimental error with the position at 85% of maximum reduction peak height. We found that changing the electrolyte–solvent system caused a constant shift for all potentials. Hence, in 0.1 *m* n-Bu$_4$NBF$_4$/benzonitrile a shift of +0.1 V was measured with respect to 0.1 *m* n-Bu$_4$NClO$_4$/benzonitrile, and +0.2 V with respect to 0.1 *m* LiClO$_4$/butyronitrile, which was used by

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Table I. Oxidation Potentials of [M(II)TPP] Complexes[a]

Complex of	Metal oxidation, $2+ \rightarrow 3+$	Ligand oxidation First	Ligand oxidation Second
Fe	−0.32	1.18	1.50[b]
Co	0.52	1.19	1.42[b]
Ni	1.00[c]	1.10[c]	1.40[c]
Cu		0.99	1.33
Zn		0.79	1.10
H_2		1.00[c]	1.20[c]

[a] 0.002 m in 0.1 m solution of n-Bu_4NClO_4 in benzonitrile in V *vs.* sce; accuracy ±0.01 V unless otherwise stated. [b] Measured in 0.1 m n-Bu_4NBF_4/benzonitrile solution, and corrected for electrolyte effect. [c] Accuracy ±0.02 V.

Table II. Epr Parameters of the [M(II)TPP] Complexes and Their Oxidation Derivatives

No.	Complex	Temp, °K	$\langle g \rangle$[a,b]	$g_{\parallel}$	$g_{\perp}$	$\langle A \rangle$, gauss		$A_{\parallel}$		$A_{\perp}$		Half-life	Ref[d]
1	$[\mathrm{Zn(II)TPP}]^{\cdot +}$					^{14}N	^{1}H						13
		295	2.0026			1.63	0.26					~14 days	
		77	2.0026					Not observed					
2	[Cu(II)TPP]					$^{63,65}Cu$	^{14}N	Cu	N	Cu	N		5, 6
		295	2.105			92	16.8						
		77	*2.093*	2.180	2.050	*91*	*11.0*	203	17.5	35 ± 5	16.0		
3	$[\mathrm{Cu(II)TPP}]^{2+}$	295	2.112			89	15.4						
		77	*2.108*	2.195	2.064	*88*	15.5	195		35 ± 5			
4	$[\mathrm{Ni(II)TPP}]^{\cdot +}$	295	2.0269									5 min	
		77	*2.0265*	2.0306	2.0244								
5	$[\mathrm{Ni(III)TPP}]^{+}$	295	Not observed					Not observed					
		77	*2.235*	2.116	2.295							45 min	
6	[Co(II)TPP]	295	Not observed					Not observed					5b
						^{59}Co		Co		Co			
		77	*2.066*	2.187	2.005	*41.4*		*96.7*		13.7			
7	$[\mathrm{Co(III)TPP}]^{\cdot 2+}$	295	2.0035			5.7						7.5 hr	
		77	2.0109			5.7							
8	$[\mathrm{Fe(III)TPP}]^{+}$	295	Not observed					Not observed					
		77	6.0 ± 0.5 (anisotropic)[c]										
9	$[\mathrm{H_2TPP}]^{\cdot +}$	295	2.0111									16 min	
		77	*2.0113*	2.0085	2.0127								

[a] Accuracy ±2 units of the last digit unless otherwise stated in the table. [b] Italics are the average values calculated from the components. [c] Our instrument was unreliable at this low-field value. [d] These complexes were measured previously. Our results are basically in agreement with them; differences can be explained by considering the different conditions.

Stanienda and Biebl.[4] The results for the TPP complexes are given in Table I and, when the above-mentioned shift is taken into account, agree very well with Stanienda and Biebl's oxidation potentials. The electrochemical measurements give only the potentials and the number of electrons removed from the complexes. The organization of the table to metal or ligand oxidation is due to the epr, nmr, and optical experiments.

In general, just by inspection of the epr spectra we could distinguish between free-radical type and metallic-paramagnetic-center-type complex ions. At room temperature the green solutions of the cation radicals, $[\mathrm{Co(III)TPP}]^{\cdot 2+}$, $[\mathrm{Ni(II)TPP}]^{\cdot +}$, $[\mathrm{Zn(II)TPP}]^{\cdot +}$, and the nonmetallic ion, $[\mathrm{H_2TPP}]^{\cdot +}$, displayed highly isotropic epr signals. In some cases this isotropy was preserved even in the glassy solid solution at liquid nitrogen temperature. On the other hand, the complexes with metallic paramagnetic centers, $[\mathrm{Fe(III)TPP}]^{+}$, [Co(II)TPP], $[\mathrm{Ni(III)TPP}]^{+}$, [Cu(II)TPP] and $[\mathrm{Cu(II)TPP}]^{2+}$, were brown and gave anisotropic spectra at 77°K only. The copper complexes showed, in addition, an isotropic signal at room temperature. The epr parameters are summarized in Table II, together with lifetimes of the species determined by following the decay in the epr signal intensity. The spin Hamiltonian used, and the assumptions made, will be discussed for each complex separately.

Magnetic susceptibility measurements helped to determine in controversial cases whether the epr signal was broadened beyond detection or the sample was actually diamagnetic. The results are tabulated in Table III. The accuracy of μ_{eff} for the oxidized species is limited because of the slight uncertainty in the actual concentration, and because of the neglect of the diamagnetic correction due to the solvent and the electrolyte. However, the results leave no doubt with regard to the correct assignment of the number of unpair electrons.

The optical spectra support the magnetic observations. Here, too, there was a marked difference between species in which the metal was oxidized and those which had undergone ligand oxidation. All the neutral molecules, [M(II)TPP], and the metal-oxidized complex ions $[\mathrm{M(III)TPP}]^{+}$ of iron and cobalt display the characteristic metalloporphyrin spectrum;[8] see curves A

Table III. Magnetic Susceptibilities

Complex	μ_{eff}, BM	S
[Fe(II)TPP]	0.00	0
$[\mathrm{Fe(III)TPP}]^{+}$	5.10	$^5/_2$
$[\mathrm{Fe(III)TPP}]^{\cdot 2+}$	2.71	1
[Cu(II)TPP]	1.64	$^1/_2$
$[\mathrm{Cu(II)TPP}]^{\cdot +}$	2.88	1

Table IV. Soret Band Peak Positions[a]

	A [M(II)TPP]	B $[\mathrm{M(III)TPP}]^{+}$	C $[\mathrm{M(II)TPP}]^{\cdot +}$ or $[\mathrm{M(III)TPP}]^{\cdot 2+}$
Fe	4140	4190	3960
Co	4150	4380	4160
Ni	4170		4080
Cu	4190		4110
Zn	4270		4120

[a] In Å; accuracy ±10 Å.

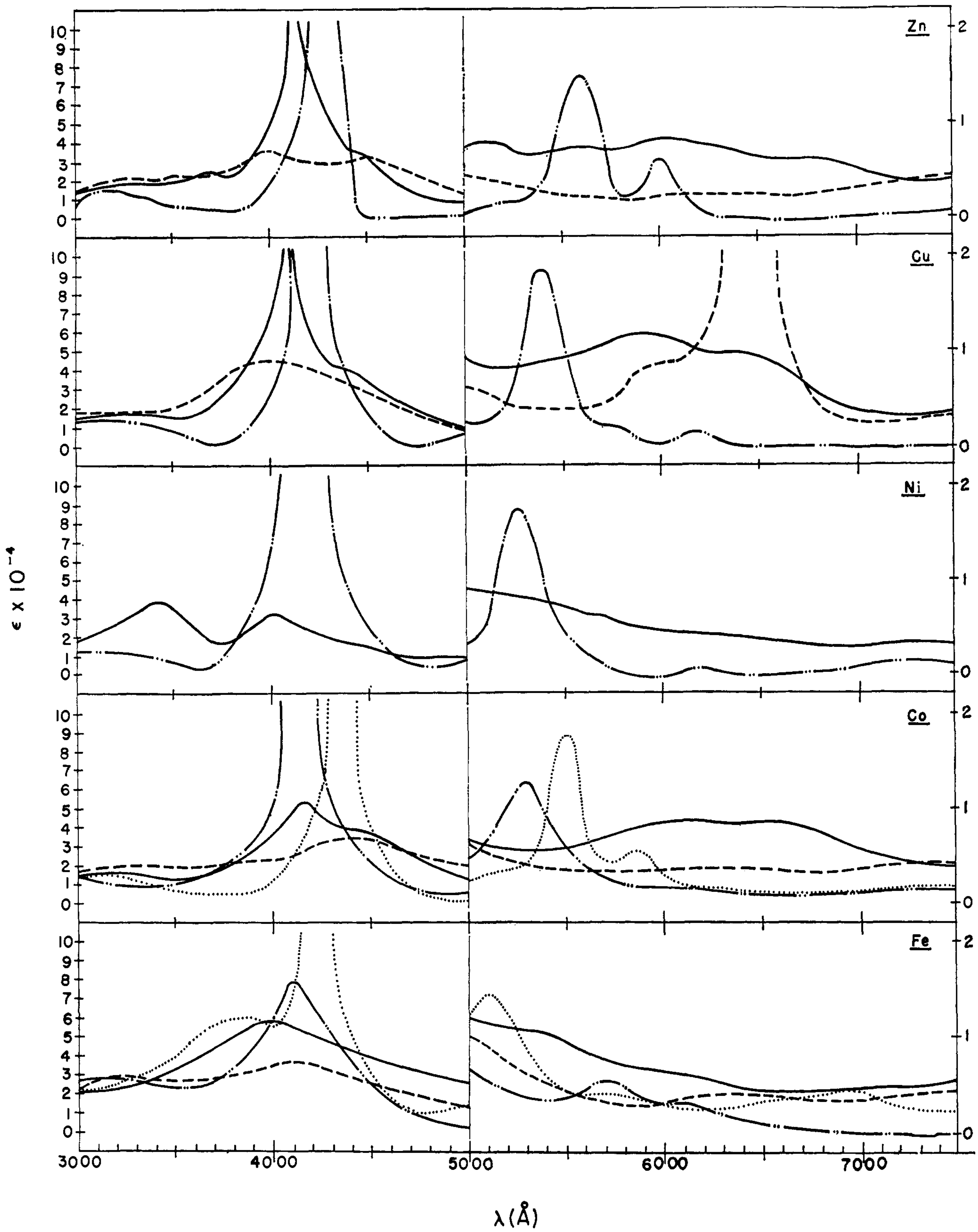

Figure 1. Optical spectra of the [M(II)TPP] complexes and their electrochemical oxidation derivatives: A (—··—··) [M(II)TPP], B (··········) metal oxidation products $[M(III)TPP]^+$, C (——) first ligand oxidation $[M(II)TPP]\cdot^+$ or $[M(III)TPP]\cdot^{2+}$, and D (------) second ligand oxidation $[M(II)TPP]^{2+}$ or $[M(III)TPP]^{3+}$.

and B in Figure 1, with their visible peaks at 5500 Å, and the very intense Soret band in the near-uv at approximately 4200 Å (Table IV). When oxidation takes place at the ligand we see that in the first step the visible peak decreases markedly in intensity (curve C) and disappears in the second step (curve D). The

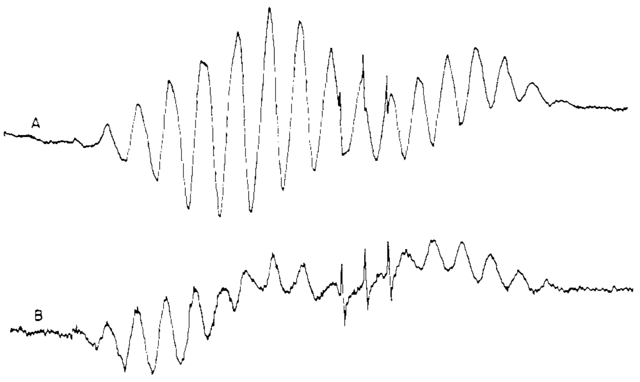

Figure 2. Epr first derivative of the high-field hf line spectra of A, [Cu(II)TPP], and B, $[Cu(II)TPP]^{2+}$. Spectra recorded at 77°K, magnetic field increases from left to right; the three narrow lines 13.0 G apart belong to peroxylamine disulfonate.

Soret band decreases in peak height, becomes broader, reveals some structure, and shifts slightly (see Table IV). These changes are in agreement with oxidized zinc or alkaline earth metalloporphyrins reported in the literature.[13,14] Dolphin, *et al.*,[22] in their study showed that in some cases the two-electron electrochemical oxidation products might chemically interact with nucleophiles like water or methanol even if they are present in trace amounts only. The isoporphyrins obtained in this reaction have very similar spectra to our D-type optical spectra, and upon two-electron electrochemical reduction will yield the starting [M(II)TPP] complexes. Therefore, we have to keep in mind that some of the dication radicals $[M(II)TPP]^{2+}$ and trication radicals $[M(III)TPP]^{3+}$ might actually be their isoporphyrin derivatives. Some of the more detailed features and exceptions will be pointed out in our complex-by-complex description.

The oxidation potentials of the phthalocyanines are given in Table V. The concentrations were very low, and therefore the signals much weaker than those for the [M(II)TPP] complexes.

Table V. Oxidation Potentials of [M(II)Pc] Complexes[a]

Complex of	Oxidation potential	Type of electron transfer
Fe	0.19	Metal 2+ → 3+ oxidation
Co	0.77	Metal 2+ → 3+ oxidation
Ni	1.05	Either or both (?)
Cu	0.98	Ligand oxidation
Zn	0.68	Ligand oxidation
H_2	1.10	Ligand oxidation

[a] Filtered saturated solution in 0.1 *m* n-Bu_4NClO_4/1-chloronaphthalene; in V *vs.* sce; accuracy ±0.02 V.

[Zn(II)TPP]. Very recently, a brief note[13] described the epr hf splittings of the paramagnetic one-electron oxidation product. We have measured the potentials of both the one- and two-electron transfer steps.

$$[Zn(II)TPP] \xrightarrow{0.79\ V} [Zn(II)TPP]\cdot^{+} \xrightarrow{1.10\ V} [Zn(II)TPP]^{2+}$$

As expected, only the monocation radical, $[Zn(II)TPP]\cdot^{+}$, gave an epr signal. We have determined the g value as well as the hf parameters (which do agree with Felton, *et al.*) in liquid solution at room temperature and in frozen glassy solid solution at 77°K. The room-temperature spectrum was compared to a computer simulation[23] of an isotropic signal with hf splittings due to both hydrogen and nitrogen nuclei assuming a Lorentzian line shape. This, similar to Felton's report, gave a better fit than with gaussian line shape or by considering one nucleus only. Although the overall line width at the low temperature decreased from 7.2 to 4.9 G no hf structure was observed. Fajer more recently[24] was able to prove by isotopic labeling that the hydrogen hf structure is due to the eight equivalent *ortho* hydrogens on the phenyl group rather than the eight equivalent porphyrinic hydrogens. This explains why in the liquid phase, where there is more freedom of rotation, the phenyl groups might some of the time be in the plane of the porphyrinic ring and contribute more strongly to the hf structure, whereas in the solid glassy phase their out-of-plane arrangement completely decouples the hydrogen nuclei from the porphyrinic π electrons. The g values of both signals were determined by direct measurement from the spectrum. The optical spectra show the typical A curve of [M(II)TPP] complexes prior to oxidation and C and D curves after one- and two-ligand electron oxidation, respectively.

[Cu(II)TPP]. The cyclic voltammetry combined with the coulometric measurement indicate two successive one-electron reversible electron-transfer steps.

$$[Cu(II)TPP] \xrightarrow{0.99\ V} [Cu(II)TPP]\cdot^{+} \xrightarrow{1.33\ V} [Cu(II)TPP]^{2+}$$

This assignment of ligand oxidation rather than metal valency change $[Cu(II)TPP] \rightarrow [Cu(III)TPP]^{+} \rightarrow [Cu(III)TPP]\cdot^{2+}$ is based on the magnetic and optical data. As in the case of two-electron reduction of the sulfonated copper phthalocyanine complex,[12] we observed almost identical epr spectra for the neutral and the two-electron oxidation product (see Figure 2) except for a small shift and a slight difference in the splittings. In both cases the Cu^{2+} characteristic spectra of spin $^1/_2$ and hyperfine (hf) splittings due to the copper nuclei with spin $^3/_2$ were observed. The room-temperature spectra were isotropic, and those in the solid phase at 77°K anistropic. In both cases the high-field hf line showed nitrogen lhf splittings (Figure 2). The first oxidation product did not show any epr signal at both temperatures.

The magnetic susceptibility measurement demonstrated unequivocally that the lack of an epr signal is not due to diamagnetism but rather to broadening of the triplet species $[Cu(II)TPP]\cdot^{+}$. The lack of an epr signal in the similar case of the oxidized copper octaethylporphyrin, [Cu(II)OEP], apparently led Fuhrhop and Mauzerall[14] to postulate that their oxidation product is the diamagnetic $[Cu(III)OEP]^{+}$ with a $3d^8$ electronic configuration rather than the more plausible paramagnetic triplet, $[Cu(II)OEP]\cdot^{+}$, with one unpaired electron on the metal ($3d^9$ configuration) and the other on the ligand. Rollmann and Iwamoto[12] also could not detect the triplet monoreduced sulfonated copper phthalocyanine with an X-band epr spectrometer.

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(22) D. Dolphin, R. H. Felton, D. C. Borg, and J. Fajer, in preparation. The authors are grateful to Dr. D. Dolphin for communicating these results prior to publication.

(23) The program for simulating isotropic epr spectra with a number of hf interactions was written by Dr. J. M. Fritsch, Monsanto Co.

(24) J. Fajer, private communication.

However, Taube and Arfert[25] established the existence of a triplet by magnetic susceptibility measurement of the lithium salt of $[\mathrm{Cu(II)Pc}]^{\cdot -}$ radical anion.

The room-temperature parameters of the epr signals were measured directly from the spectra, and the low-temperature parameters were obtained by comparing experimental slightly overmodulated curves with simulated ones. The overmodulation did not distort the hf lines but was sufficient to broaden the lhf structure. The simulation was done by a computer program which assumes axial symmetry with a common axis for the g and A tensors and Lorentzian line shape, and which includes up to second-order terms in the spin Hamiltonian.[26] The program neglects nuclear Zeeman and quadrupole interactions. It seems that this neglect is not too serious in light of Rollman's results on the sulfonated cobalt phthalocyanines,[12,27] where, after including quadrupole and forbidden transitions, appreciable change was detected for $A_{\perp}$ only. The lhf of the nitrogens showed fairly isotropic well-resolved lines and were determined directly from the spectra.

The optical spectra are similar to those observed for the [Zn(II)TPP] series, with the exception that the two-electron oxidation product curve D shows an extra peak at 6450 Å. Curve C also supports the assignment of the first electron transfer as ligand oxidation rather than valency change.

[Ni(II)TPP]. Our observation of this complex was reported previously.[16] The following oxidation mechanism was proposed.

$$[\mathrm{Ni(II)TPP}] \xrightarrow{1.00\ \mathrm{V}} [\mathrm{Ni(III)TPP}]^{+} \xrightarrow{1.10\ \mathrm{V}} [\mathrm{Ni(III)TPP}]^{\cdot 2+} \xrightarrow{1.40\ \mathrm{V}} [\mathrm{Ni(III)TPP}]^{3+}$$

The oxidation product decomposed back to the original material. The $[\mathrm{Ni(III)TPP}]^{+}$ cation, which had a lifetime of 45 min, decomposed to [Ni(II)TPP] *via* an intermediate radical cation, $[\mathrm{Ni(II)TPP}]^{\cdot +}$. The rate constant ratio of these two decomposition reactions was about ten. The observation of the epr signals of both the monocation $[\mathrm{Ni(III)TPP}]^{+}$ and the cation radical $[\mathrm{Ni(II)TPP}]^{\cdot +}$ is of great interest owing to the controversy over the existence of a Ni(III) square-planar species in solution (see discussion in ref 16). The optical observations show definite behavior of A- and C-type spectra for the [Ni(II)TPP] and $[\mathrm{Ni(III)TPP}]^{\cdot 2+}$ species, respectively. The epr results indicate that curve C might be a mixture of the oxidation and decomposition products.

[Co(II)TPP]. The cyclic voltammogram distinctly showed three one-electron reversible oxidation steps.

$$[\mathrm{Co(II)TPP}] \xrightarrow{0.52\ \mathrm{V}} [\mathrm{Co(III)TPP}]^{+} \xrightarrow{1.19\ \mathrm{V}} [\mathrm{Co(III)TPP}]^{\cdot 2+} \xrightarrow{1.42\ \mathrm{V}} [\mathrm{Co(III)TPP}]^{3+}$$

The neutral species is paramagnetic, with an effective spin $^{1}/_{2}$ compatible with a square-planar $3d^7$ configuration. The epr signal was observed at the low temperature only, and its parameters were calculated by comparing the observed spectrum with a simulated one, based on the same program used for the copper low-temperature spectra. The results agree with those reported in the literature for the same complex in different environments.[5] The first oxidation product, $[\mathrm{Co(III)TPP}]^{+}$, is very stable, and showed no epr spectrum, which is consistent with a square-planar $3d^6$ configuration. This change from a $3d^7$ to a $3d^6$ configuration implies metal atom oxidation rather than the ligand oxidation which was observed for the zinc and copper complexes. This effect was realized by Stanienda and Biebl, too.[4] The second oxidation species, $[\mathrm{Co(III)TPP}]^{\cdot 2+}$, showed a definite free radical type epr spectrum. It was isotropic and was observed at both room temperature in the liquid solution and at liquid nitrogen temperature in solid solution. We have used the same program which was used for the zinc spectrum to simulate a theoretical spectrum. Figure 3 displays the experimental curve at room temperature with two simulated curves, one assuming gaussian and the other Lorentzian line shapes. The Co hf parameter is actually a lhf-type phenomenon. Usually in transition-metal complexes with unpaired electron(s) the metal is the paramagnetic center, and if its nucleus has a nuclear spin, one expects to resolve hf splittings. In the case that the nuclei of the ligands bonded to the metal have a nuclear spin one expects to observe lhf splittings. Hence, lhf structure is an indication of the chemical bond between the metal and the usually nonmetallic ligand atom in the complex. In our case, the unpaired electron is part of the π system of the porphyrin ring and hf splitting would be expected to be from the nitrogen atoms, as was the case in the $[\mathrm{Zn(II)TPP}]^{\cdot +}$ complex. Thus, structure due to the cobalt nuclei is of "lhf type" and indicates overlap of the porphyrin π electron with a 3d electron of neighboring cobalt atom. Similar phenomena were reported for alkali-metal ions with free radicals;[28] however, this might be the first reported case in a covalent molecule with a transition-metal atom. The life time of this complex was found to be 7.5 hr. The third oxidation species $[\mathrm{Co(III)TPP}]^{3+}$ is expected to be diamagnetic, and indeed no signal was observed.

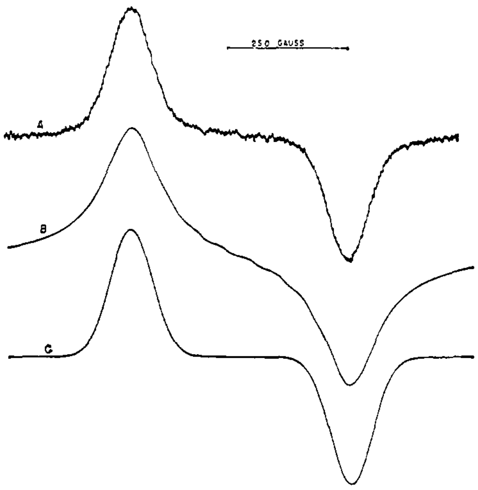

Figure 3. Epr first-derivative spectra of $[\mathrm{Co(III)TPP}]^{2+}$ at room temperature with magnetic field increasing from left to right: A, experimental; B, simulated assuming Lorentzian line shape; and C, simulated assuming gaussian line shape.

The optical spectra of all four species were observed and recorded. We see very clearly that the first oxidation caused only minor changes in the [Co(II)TPP]

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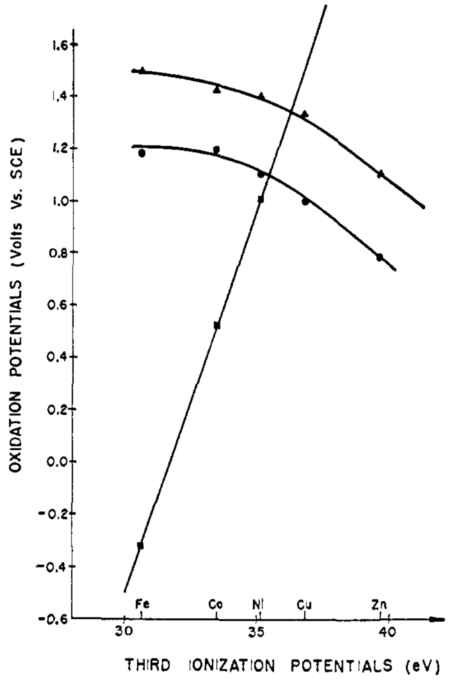

Figure 4. Oxidation potentials of the [M(II)TPP] complexes (Table I) plotted against third ionization potentials of the metal atoms (C. E. Moore, "Atomic Energy Levels," Vol. II, National Bureau of Standards, U. S. Government Printing Office, Washington, D. C., 1952): ■, metal valency change; ●, first ligand oxidation; and ▲, second ligand oxidation.

spectrum (see curves A and B). The following oxidation steps gave rise to C and D type spectra. One notes the shift of both the Soret and visible peaks toward higher wavelengths in the Co(III) complex with respect to those in the Co(II), a phenomenon pointed out by Corwin, *et al.*[10] They suggest that this is a general phenomenon for square-planar porphyrins bonded to ligands in the octahedral positions. It seems reasonable that the [Co(III)TPP]$^+$ cation will more readily interact with the electrolyte anions than the neutral molecule does.

[Fe(II)TPP]. The stable species at room temperature and atmosphere is the monocation, [Fe(III)TPP]$^+$; hence, in this case we measured both oxidation and reduction of the acetate salt.

$$[\mathrm{Fe(II)TPP}] \xleftarrow{-0.32\ \mathrm{V\ (red)}} [\mathrm{Fe(III)TPP}]^+ \xrightarrow{1.18\ \mathrm{V\ (ox)}}$$
$$[\mathrm{Fe(III)TPP}]\cdot^{2+} \xrightarrow{1.50\ \mathrm{V}} [\mathrm{Fe(III)TPP}]^{3+}$$

The [Fe(III)TPP]$^+$ gave an anisotropic epr signal at very low magnetic field, at liquid nitrogen temperature. The rest of the iron species did not show any epr signals. The magnetic information about their spin states was obtained by nmr measurements using Evans'[21] technique. Table III indicates that the reduction product [Fe(II)TPP], with electronic configuration 3d^6, is indeed diamagnetic, consistent with the absence of an epr signal. The stable [Fe(III)TPP]$^+$ complex ion with electronic configuration 3d^5 is a high-spin species, but the ligand monooxidation product [Fe(III)TPP]$\cdot^{2+}$ is in a triplet state similar to the one observed in [Cu(II)-TPP]$\cdot^+$, *i.e.*, with one unpaired electron on the ligand and the other on the metal atom. The epr signal of this triplet also was not detected. The *g* value of [Fe(III)TPP]$^+$ was determined using our program for axial symmetry with Lorentzian line shape.

The optical spectra of the iron series are very similar to those of cobalt. Here, too, the Soret band moved slightly toward higher wavelength upon oxidation from Fe(II) to Fe(III) complex; however, the visible peaks showed a reverse trend.

[H$_2$TPP]. For comparison purposes we have run the nonmetallic compound too. Here we observe two one-electron irreversible oxidation steps.

$$[\mathrm{H_2TPP}] \xrightarrow{1.00\ \mathrm{V}} [\mathrm{H_2TPP}]\cdot^+ \xrightarrow{1.20\ \mathrm{V}} [\mathrm{H_2TPP}]^{2+}$$

At room temperature the green solution of the paramagnetic cation radical [H$_2$TPP]$\cdot^+$ had an isotropic *g* value, with no hf structure; hence we determined its value by direct measurement. At the low temperature in the glassy form slight anisotropy was detected. In this case we used our program for axial symmetry with Lorentzian line shape described previously. An estimate of the life time of the oxidation products from the irreversible cyclic voltammogram indicated values of less than 10^{-2} sec, in contrast to the value of 16 min measured from the intensity decay of the epr signal. This might indicate either a decomposition mechanism different at the electrode than in the solution or that our epr spectra concern a decomposition product rather than the [H$_2$TPP]$\cdot^+$ cation radical itself.

Discussion

Oxidation Trends. In the series of iron through zinc TPP we could classify the oxidation products as paramagnetic cation radicals or paramagnetic metal-center complex ions. The zinc monocation and the cobalt dication were of the first kind, whereas the copper dication, the iron monocation, and the neutral copper and cobalt complexes were of the second kind. It was fairly easy to assign ligand oxidation in the case of the zinc and copper complexes, and a metal valency change followed by ligand oxidation in the case of the cobalt complex. The rest of the classification was based on trends in the oxidation potentials and was consistent with the rest of the epr, magnetic susceptibility, and optical data.

Our results show that the first oxidation potentials increase upon going from iron to nickel and then slightly decrease for the copper and zinc complexes. Stanienda and Biebl[4] did realize that the first low value of the cobalt complex is due to a change in oxidation state of the metal atom and, therefore, excluded this value from their plot of oxidation potentials *vs.* the second ionization potentials, which now show a decrease in potentials for the cobalt through zinc series, with a sharp discontinuity at the copper complex. We believe that it would be more proper to plot the oxidation potentials *vs.* the third ionization potentials, because in the metalloporphyrins the metal atom is already in the 2+ oxidation state, and if it will be further oxidized, the potential should be related to a free ion property describing the same change. Inspection of Figure 4 shows that, indeed, those complexes which have undergone a metal atom oxidation show a strictly linear dependence of their oxidation potentials on the third ionization potentials, whereas those which were oxidized at the ligand do not show this dependence, but instead reveal a more complicated trend. This plot tends to confirm that the identification of the [Ni(III)-TPP]$^+$ cation[16] was correct; moreover, it warned against the oversimplified approach, that if one-electron oxidation produces a Ni(III) species, a two-electron oxidation process will produce a Ni(IV) complex.[29]

The linear dependence for the iron, cobalt, and nickel complexes indicates that, although the TPP ligand strongly influences the metal atom which is incorporated in it, the free ion properties retain their trends. Both the first and the second ligand oxidations have many features in common. They both show a decrease with an increase in the number of d electrons, and do not show any discontinuity upon going from ions with a bivalent atom to ones with a trivalent one. This might serve as an evidence for the strong covalency of these complexes which have a metal-to-ligand bond, of σ and π character. The σ bond is composed of a metal atom dsp^2 hybrid and four pairs of electrons from the nitrogen in-plane sp^2 hybrid. When the $3d_{x^2-y^2}$ orbital is empty as in the iron, cobalt, and nickel complexes, the molecular σ orbital accommodates the ligand electrons. Upon filling the $3d_{x^2-y^2}$ orbital in the copper and the zinc complex, the extra charge on the metal makes it easier to ionize the ligand, hence reducing the oxidation potential of the whole complex. This clearly demonstrates the important role of the strong covalent σ bond in the metalloporphyrins which completely overshadows any effects expected from a change in oxidation state.

The optical data fit very well into the overall picture. Curves A and B are characteristic for metalloporphyrins and C and D for metalloporphyrins which have undergone electron removal from the ligand. Hence, a step corresponding to a change from A to B indicates metal oxidation, whereas a change from A or B to C and from C to D indicates ligand oxidation.

In Figure 5 we show how oxidation potentials of transition metal complexes, which are recorded in the literature, can be related to the third ionization potentials similar to Figure 4. 5A is a plot of the [M(II)Pc] series which we have measured (Table V); 5B plots sulfonated metallophthalocyanines, taken from ref 12; 5C and 5D show Stanienda and Biebl's[4] results on metallo-etio-I-porphyrins, [M(II)Etio-I], and [M(II)-TPP], respectively. Note the agreement between Stanienda and Biebl's plot 5D with our plot in Figure 4 Most of these data are incomplete, but plotting them this way gives an indication of what kind of oxidation was measured and where to look for values that are missing. Fe(III) porphyrins are known to be reduced to Fe(II) porphyrins at much lower potentials than the corresponding iron phthalocyanines. Comparison of the slope of 5A with that of 5D shows this to be caused by the slope of the straight line correlating oxidation potentials with third ionization potential. This difference therefore fits into a general trend and is not some peculiarity of the iron porphyrins.[15]

An attempt to generalize this approach to complexes other than porphyrins is given in plots 5E and 5F. Here we plot the oxidation potentials of the metallo-1,2-dithiolates, $[M(II)(S_2C_2R_2)_2]^{2-}$ with R = CN (plot 5E) and R = CF_3 (plot 5F).[30] These plots suggest that in the case of the very strong electronegative

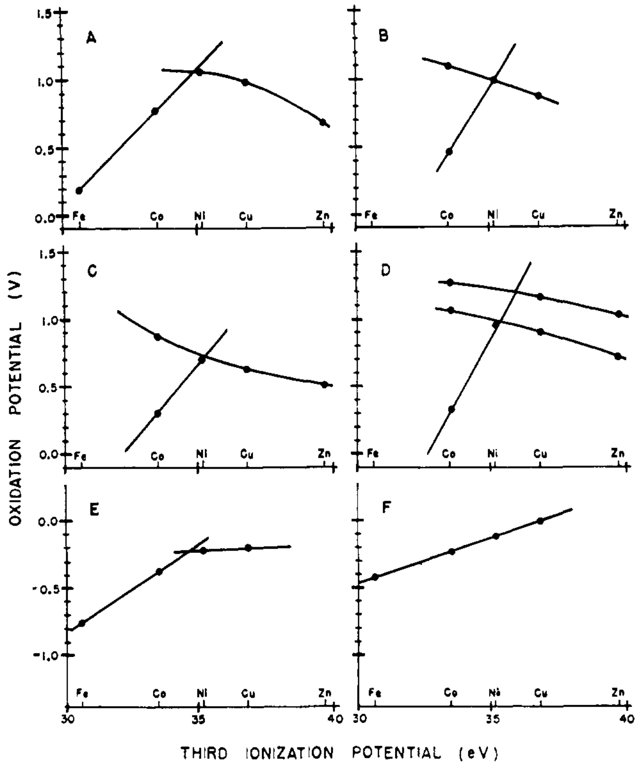

Figure 5. Oxidation potentials of six series of organometallic complexes as a function of the third ionization potentials of their metal atoms: A, [M(II)Pc] (Table V); B, sulfonated [M(II)Pc] (ref 12); C, [M(II)Etio-I] (ref 3); D, [M(II)TPP] (ref 3); E, $[M(II)S_4C_4(CN)_4]$ (ref 30); and F, $(M(II)S_4C_4(CF_3)_4]$ (ref 30).

CF_3 group even a Cu(III) species can be stabilized, whereas with the cyano group a metal oxidation seems to occur for iron and cobalt only. This, of course, is a tentative prediction which, if substantiated by further work, would prove the general utility of our technique for locating the oxidation in organometallic compounds.

Catalytic Results. In the introduction we mentioned that our motivation for conducting this study was to elucidate the catalytic activity of the metalloporphyrins, and indeed we had some success. The results of this study are used in ref 3. Here we will consider one example only. In reaction I we find that the higher the oxidation potential of the complex the lower its catalytic activity, but for a given potential a catalyst which undergoes metal valency change is the more effective one.

Biological Consequences. We would like to point out an interesting consequence of our study to the understanding of the enzymatic activity of chlorophyll and hemoglobin. The chlorophyll which is a magnesium complex of a porphyrin derivative acts as radiant energy absorber. Its active site is on the ligand. On the other hand, the heme which is a ferrous complex of porphyrin derivative acts as an oxygen transport agent through direct metal–molecular oxygen bonding. This enzymatic behavior ties very well with the two cases of valency change and ligand oxidation which we have observed in the MTPP series. A free radical could be formed from a nonmetallic molecule, but as the irreversible voltammogram of the H_2TPP indicates, the Mg serves to stabilize the molecule and also to reduce the oxidation potential which is an indicator of the photosensitivity of the pigment.

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Molecular Orbital Considerations. Until now we have emphasized the idea of having electrons in certain orbitals and have distinguished between metal and ligand electrons. The terms we have used were taken from crystal-field theory as opposed to molecular-orbital or ligand-field theory. We would like to point out, however, the evidence in our own work for the formation of strong molecular orbitals. The lhf interactions of the nitrogen atoms with the copper atom indicate that the unpaired copper $3d^9$ electron spends some time at the nitrogen nuclei. On the other hand, the cobalt lhf structure of the free-radical unpaired π-type electron of the ligand indicates that a porphyrin electron spends some time at the metal nucleus.

The MO treatment of the [Cu(II)TPP] was developed by Assour[5b] and recently reworked in greater detail by Manoharan and Rogers.[6] According to these authors the unpaired electron is in a molecular orbital

$$\psi(b_{1g}) = \alpha|d_{x^2-y^2}\rangle - {}^1/_2\alpha'(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$$

where the σ_i's are the sp^2 hybrid orbitals of the ith nitrogen atom of the porphyrinic ring, $d_{x^2-y^2}$ is the metal orbital, and α' and α are the mixing coefficients which satisfy the normalization condition

$$\alpha^2 + \alpha'^2 - 4\alpha\alpha'S = 1$$

where S is the metal ligand overlap integral $\langle d_{x^2-y^2}|\sigma_i\rangle$. According to Manoharan and Rogers,[6] if we use Assour's value[5b] of $S = 0.046$, then $\alpha' = 0.548$ and $\alpha = 0.888$. The decrease in the lhf coefficient of the nitrogens in the copper complex spectra from 16.8 to 15.4 G on oxidation of [Cu(II)TPP] to $[\text{Cu(II)TPP}]^{2+}$ will cause a decrease in α' from 0.548 to 0.525, which corresponds to an 8% decrease in the electron distribution on the nitrogen atoms of the ligand. Note that the electrons were removed from the π system and here we are discussing how this change affects the σ bonds. The change in α is more difficult to evaluate because we do not know how the two electron oxidation changes the overlap integral S. We have assumed two extremes, one that there is no change in S and the other that the overlap integral decreases by more than 10% to 0.040. Accordingly, α will be equal 0.901 and 0.894, which correspond to a relative increase of 3 and 1.4% in electron charge distribution in the metal orbital, respectively.

The cobalt lhf structure observed in the $[\text{Co(III)TPP}]^{\cdot 2+}$ cation radical cannot be explained by simple MO theory. If we use the π-type molecular orbitals

$$\psi(e_g) = \begin{cases} \epsilon|d_{xz}\rangle - \dfrac{1}{\sqrt{2}}\epsilon'(p_1 - p_3) \\ \epsilon|d_{yz}\rangle - \dfrac{1}{\sqrt{2}}\epsilon'(p_2 - p_4) \end{cases}$$

where p represents the nitrogen p_z orbitals, which form part of the ring's π system, d_{xz} and d_{yz} are the metal orbitals, and ϵ and ϵ' are the mixing coefficients, there is no way to describe any charge due to the unpaired π electron of the ligand at the cobalt nucleus. To explain this interaction we would have to invoke the empirical concepts of core polarization, or to assume that through the dsp^2 hybridization for the σ bonds, or due to the nonplanarity of the porphyrins, there is some 4s mixing into the metal $3d_{xz}$ and $3d_{yz}$ orbitals, and this would introduce too many assumptions for a meaningful calculation.

The magnetic susceptibilities of the iron complexes lead to some surprising conclusions. The reduction product [Fe(II)TPP] is diamagnetic with $S = 0$. The low-spin ground state ${}^1A_{1g}$ is due to a $3d^6$ configuration. The stable $[\text{Fe(III)TPP}]^+$ cation is paramagnetic with a spin of ${}^5/_2$. This high-spin complex has an ${}^6A_{1g}$ ground state term due to a $3d^5$ configuration. The ligand oxidation product $[\text{Fe(III)TPP}]^{\cdot 2+}$, on the other hand, is a paramagnetic low-spin triplet, $S = 1$, rather than a high-spin heptet with $S = 3$. From Gouterman and coworkers' theoretical MO computations[31] such behavior might have been expected. In their paper the possibility that certain iron porphyrins assume high, low, or even intermediate spin states is explored. Their calculations show that nonplanarity or coordination in the out-of-plane positions might produce the difference required to transform a low-spin state into a high-spin one. In our series the different oxidation states are able to coordinate in the 5 and 6 positions with the acetate or the electrolyte ClO_4^- anions. Thus, in the series

$$[\text{Fe(II)TPP}] \longrightarrow [\text{Fe(III)TPP}]^+ \longrightarrow [\text{Fe(III)TPP}]^{\cdot 2+}$$

a change from square-planar to distorted octahedral *via* a pyramidal symmetry might occur with large changes in local field and consequent changes in energy levels.

Note that the difference in energy between the visible and Soret absorbtions changes from 6610 cm^{-1} for [Fe(II)TPP] to 4255 cm^{-1} for $[\text{Fe(III)TPP}]^+$ and back to 6730 cm^{-1} for $[\text{Fe(III)TPP}]^{\cdot 2+}$. These are not the energy levels involved directly in populating the low- and high-spin levels, but give a fairly good indication of fluctuations in valence levels with changes in spin number.

The current work can be used as a test for the theoretical computations of Zerner and Gouterman.[15,31] The calculations account pretty well for the observed electronic transitions. Even though at times it seems that according to their calculations we should expect metal oxidation, whereas our experiment indicates ligand oxidation, this might not be a contradiction. One has to realize that electronic transitions obey the Frank–Condon principle while electrochemical electron transfer allows for the whole molecule to rearrange itself. Therefore, only after applying their theory to the oxidized species and checking its consistency with both the optical and magnetic data for each molecule and the predicted trends of oxidation for a given metal complex series will we have a better theoretical and experimental understanding of these systems.

Conclusion

The oxidation potentials of the [M(II)TPP] (M = Fe, Co, Ni, Cu, and Zn) complexes, when plotted *vs.* the appropriate (third in this case) ionization potentials, provide a tool for localizing the electron removal in organometallic complexes. This distinguishes between metal valency change and ligand oxidation. The trend, when studied over a sufficiently broad section of the periodic table, furnishes valuable information which

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(31) M. Zerner, M. Gouterman, and H. Kobayashi, *Theor. Chim. Acta*, **6**, 363 (1966).

could not be extracted from an erratic study of complexes with different metal atoms and ligands.

In particular one can (1) explain the stability of the [Fe(II)Pc] complex *vs.* the iron porphyrins, in which the stable iron complex is the trivalent one; (2) find an interesting magnetic transition between low and high spin upon oxidizing the [Fe(II)TPP] complex; (3) find hf interaction of a ligand unpaired π electron with the nuclear spin of the cobalt; (4) identify a Ni(III) square-planar complex in solution; and (5) find triplet states with one unpaired electron on the metal atom (Fe and Cu) and the other on the ligand. Most of the experimental results agree with Gouterman's theoretical calculations; however, they point out that upon removal of one ligand electron the whole energy level scheme is affected.

The assignments of the electrochemical trends were proven by spectroscopic (optical and magnetic) measurements; therefore, it would be gratifying if future studies could prove the existence of the predicted Cu(III)–dithiolate complex, and thus generalize our observations beyond the metalloporphyrins.

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Ligand Binding by Metalloporphyrins. I. Thermodynamic Functions of Porphyriniron(II)–Pyridine Complexes

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Abstract: Enthalpy, entropy, and free energy values for the addition of a series of substituted pyridine ligands to a number of porphyriniron(II) dimethyl esters in benzene solution were measured spectrophotometrically. Variations in free energy of reaction with the changes in ligand and metalloporphyrin were not great but changes in enthalpy and entropy of reaction were large. The results obtained best fit a model in which the ligand is bound by both σ bonding from the pyridine nitrogen to the metal atom and π bonding by back-donation from the iron atom to the pyridine. While π bonding becomes more important in the order 4-methyl < 4-vinyl < pyridine < 4-carboxybutyl ester < 4-cyanopyridine, σ bonding is most important for 4-methylpyridine and decreases in importance in the same order. π bonding was not as important for 2,4-diacetyldeuteroporphyriniron(II) dimethyl ester as it was for the meso-, deutero-, and protoporphyrin complexes. Entropies of reaction were large and variable and were well correlated with the enthalpy changes observed. This and the compensatory nature of the entropy change in relation to the enthalpy change gave an isoequilibrium temperature of 340°K. The close proximity of this to the temperature at which the reactions were studied led to the small changes observed in the free energy of reaction.

Recent work[2] on the addition of ligands to metalloporphyrins highlights the need for an explanation of the physiochemical properties in terms of the electronic structures involved. This is of both chemical and biochemical importance. In the latter case there is a need to be able to explain in electronic and structural terms the changes in properties of hemoproteins when the same heme (usually protoheme) is attached to various proteins and various ligands.

It has been suggested that the affinity of iron porphyrins for ligands is partly explained in terms of π bonding occurring by back-donation of electrons from the metal atom to the π system of the ligand.[3] The suggestion was prompted by the changes observed in the stability constants of heme–pyridine complexes as the ligand changes from 4-aminopyridine, through pyridine, to 4-cyanopyridine—a potent π acceptor. However, there are strong objections to using stability constant data alone to derive conclusions about the nature of chemical bonding.

The effect of the entropy term is usually unknown, but comparison of a series of stability constants to obtain information about bonding presupposes that the effect of entropy is negligible. This is not so in zinc and nickel tetraphenylporphyrin complexes where the entropy terms are large and variable.[4] Complete enthalpy and entropy data as well as free-energy changes (stability constants) are needed before reactions of metalloporphyrins with basic ligands can be properly understood.

In this study the equilibrium constant for the reaction between metalloporphyrin and ligand symbolized by the equation

$$\mathrm{MP} + n\mathrm{L} \longrightarrow \mathrm{MPL}_n$$

was determined spectrophotometrically. The equilibrium constant $K = [\mathrm{MPL}_n]/[\mathrm{MP}][\mathrm{L}]^n$ can be evaluated readily provided the ratio of the two metalloporphyrin species can be determined and the equilibrium concentration of ligand is known. In the systems studied here the concentration of ligand is so far in excess of the metalloporphyrin concentration that the amount of ligand added may be taken as the equilibrium concentration.

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(1) (a) University of Newcastle, N.S.W., Australia; (b) Avondale College, Cooranbong, N.S.W., Australia.

(2) (a) J. E. Falk in "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., New York, N. Y., 1964, p 41; (b) W. S. Caughey, W. Y. Fujimoto, and B. P. Johnson, *Biochemistry*, 5, 3830 (1966).

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(4) S. J. Cole, unpublished results, 1967.