acteristic Q bands (1533 cm^{-1} for *o*-hydroxy, 1590 cm^{-1} for *p*-hydroxy) were obtained from the percentage of Q found above and used to recalculate the constants. Results are given in Tables IV and V and plotted in Figures 6 and 7, with uv results.

Within the experimental errors, the K_T values obtained independently from infrared and ultraviolet measurements are similar. This seems to justify the assumptions made in their calculations. This agreement also supports the contention that the same phenomenon is measured by the two methods. Additional evidence is furnished by the study of the hydrolysis reaction of the Schiff bases under consideration. The rate constants measured by infrared and by ultraviolet, as well as the end product (*i.e.*, the anion of the aldehyde), were the same.

Conclusions

This study warrants the conclusion that the modifications observed in the ultraviolet spectra of *N*-salicylidene-2-aminopropane and of *p*-hydroxy-*N*-benzylidene-2-aminopropane are attributable to a displacement of the keto–enol equilibrium. Some of our results may be compared with the values obtained by Dudek and Dudek[5b] by nmr and by Bidegaray and Viovy[8] by ultraviolet for related compounds. At low temperature in ethanol, Dudek gives a percentage of 14% for the Q form of 2-(*N*-phenylformimidoyl)-phenol. In mixtures of propanol and water, Bidegaray and Viovy have found a curve similar to ours for the variation of K_T *vs.* the amount of water for *N*-salicylidene-1,1-dimethylethylamine. Their value for the absorptivity of the Q form at 387 μm (5900 cm^{-1} l. mol^{-1}) is comparable with the one we have found for *N*-salicylidene-2-aminopropane (7050 cm^{-1} l. mol^{-1}). Determination of the tautomeric constants in various solvents will help to analyze the factors promoting the appearance of the quinoid form.. Preliminary measurements already exclude the dielectric constant as a determining factor because the amount of the Q form in dimethylformamide is much less than that in methanol or propanol. The fact that the Q form is largely predominant in water has important consequences for the study of the hydrolysis reaction.[10]

The Redox Behavior of Metallo Octaethylporphyrins

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Abstract: The redox potentials of some 25 representative metalloporphyrins with different central ions have been measured by cyclic voltammetry. In many cases a ligand oxidation–reduction reaction could be discriminated from a metal reaction, through the utilization of visible absorption spectra and esr data. When such data are not available new rules concerning the conformity or nonconformity to redox regularities have been used. It was generally found that central metals are most stable in oxidation states 2+ and 3+ (except for main group IV elements, VO, MoO), and that the reactivity of the porphyrins undergoes substantial variations with different central metals and is determined by the electrostatic action of the central ion. A plot of first reduction *vs.* first oxidation potential of the porphyrin ring yielded a straight line relationship for all of the investigated metalloporphyrins, with the exceptions of Mn^{III}OEP(OH) and MoOOEP(OH). Ag^{III}OEP(ClO$_4$) was found to be stable, and CoOEP was the only compound where the metal could be reduced to the 1+ oxidation state. No special stabilization of low metal oxidation states, as might be expected for a "soft" ligand, was observed. Regularities found in the reduction and oxidation steps of the porphyrin ligand led to the formulation of new "induction parameters" for three- and four-valent metal ions.

Many biological redox systems use metal complexes of soft ligands as reaction centers. Prominent examples of such natural ligands are sulfide in ferredoxin, isoalloxazine in metalloflavoproteins, iron porphyrins in oxidases, cytochromes, and catalases, and magnesium chlorins in the chlorophylls. Highly polarizable ligands can influence the redox potentials and conduction of energy in various systems. The redox behavior of the metal complexes can be widely modified over a large potential range by changing the metal and/or the coordinating ligands. Furthermore, because of their highly conjugated character they are optimally suited for charge transfers to other electron systems. Also, these complexes may undergo addition reactions which may be reversible and serve the purpose of atom transfers (as in the case of flavins) or may be irreversible and serve in the modification or degradation of the ligand (as in the case of bile pigment formation).

During the past several years a number of electrochemical and spectroscopic studies have appeared in both aqueous and nonaqueous media.[2–13] In non-

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aqueous solutions it has been shown that the porphyrin ring can be reversibly oxidized in two one-electron steps, yielding π cation radicals and dications,[2,5] and reduced in two reversible steps, yielding π anion radicals and dianions.[3,4] Furthermore, in a number of cases the central metal could undergo an oxidation or reduction reaction changing from a plus two to a plus three ion.[2–5] The distinguishing of metal from ligand reaction was based for the most part on spectroscopic methods of identification.[4,5] In most of these studies various semiempirical correlations were put forth to rationalize the observed redox potentials, and a number of correlations were made between the porphyrin redox potential and the physical properties of the central metal (*e.g.*, electronegativity, ionization potential, ionic radius, etc.). However, all investigations have suffered from the fact that they were limited to a small number of available metalloporphyrins and, furthermore, in no case did any study cover both the oxidation and the reduction of the porphyrin ring.

For some time now we have been interested, in our laboratories, in the reversible and irreversible redox behavior of metalloporphyrins[7–20] and chlorins, which have redox potentials fully 300 mV lower than the respective metalloporphyrins.[16]

Initial results of our measurements, coupled with electron spin resonance spectra, have indicated that metalloporphyrins with stable two-valent central metal ions (Mg, Zn, Cu, Pd) can be reversibly oxidized to radicals with the unpaired electron on the ligand and that the midpoint potential of the oxidation ($E_{1/2}$) is proportional to the electronegativity of the central ion.[14,15] However, if the oxidation state of the central metal is different from 2+ (Fe^{3+}, Al^{3+}, Si^{4+}, etc.) no prediction could be made. Manassen's[5a] suggestion that the $(n + 1)$ ionization potential of the metal, where n is the ion charge, can be used to predict the ring and metal oxidation potentials at first seemed to be correct for three or four selected transition metal porphyrins but falls apart when considering more than his three examples. Thus, the purpose of this present study was to establish reduction and oxidation potentials of the metalloporphyrin ring and the central ions at the same time under the same conditions and to find physical and theoretical correlations of potentials in terms of the total electron system of the porphyrin. This was done over a much wider range of central ions than had ever been tried, namely the ions of groups IIa, IIIa, IVa, and Va, the whole first period of the transition metals, and several examples of the second transition period. Having classified and characterized the electron transfer reactions, we could then look for interesting irreversible reactions which might give hints on the chemical and photochemical behavior of the respective metalloporphyrins.

Our method of investigation consisted of measuring the redox potentials of the metal complex through the use of cyclic voltammetry. The $E_{1/2}$'s were measured as that potential lying midway between the oxidation and the reduction peak of a given couple (for example, $MOEP \rightleftarrows MOEP^+$), where OEP stands for the dianion of octaethylporphyrin and M for a 2+ metal). For reversible reactions, the cathodic peak potential is $0.029/n$ V more cathodic than $E_{1/2}$, and the anodic peak potential is $0.029/n$ V more anodic than $E_{1/2}$. This is the potential where i, the current, is equal to 85.17% of the diffusion peak current and is virtually interchangeable with the classical polarographic $E_{1/2}$ and in these cases the thermodynamically significant E^0.[21]

The usefulness of cyclic voltammetry over the potentiometric and classical polarographic method is that both the starting material and generated reaction product can be simultaneously investigated *in situ* verifying the absence of chemical reactions coupled to the electron transfer (which if present would tend to shift the chemical equilibrium, giving erroneous values of $E_{1/2}$). In those cases where a chemical reaction (*e.g.*, dimerization, dismutation) might occur after the electron transfer, one could increase the scan rate to that experimental time interval where only the electron transfer occurred.[22] The classification of reactions as belonging to either the ring or the metal could be determined by known visible and esr spectra as well as by the relationships we have developed in this paper.

In the course of these experiments we were able to identify and classify several unusual metal oxidation states which are the subject of a separate note.[12]

Experimental Section

I. **Preparation of Metallo Octaethylporphyrins** (MOEP). H_2OEP was kindly supplied by Professors H. Pommer and H. H. Inhoffen and was prepared according the procedure of Siedel[23] and of Inhoffen,[24] *et al.*

The following complexes have been prepared by literature procedures: MgOEP,[15] CaOEP,[15] TlOEP(OH),[25] SiOEP$(OH)_2$,[26] PbOEP,[27] SbOEP(OH),[28] ScOEP(OH),[29] CrOEP(OH),[30] Mn-

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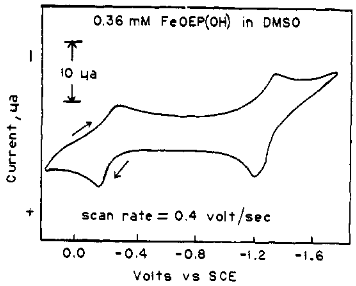

Figure 1. A cyclic voltammogram of $Fe^{III}OEP(OH)$ showing the $Fe^{3+} \rightleftarrows Fe^{2+}$ transition at −0.24 V and $Fe^{II}OEP \rightleftarrows Fe^{II}OEP^-$ at −1.33 V.

OEP(OH), CoOEP,[27] NiOEP,[27] ZnOEP,[27] AgOEP,[27] and CdOEP.[27] The axial OH^- ligand was introduced in the course of the chromatography on dry alumina (Woelm), alumina with activity grade III, or silica gel and in all cases was tested to be more than 90% OH^-. Chloride tests were negative. All preparations were uniform on thin layer chromatography and produced the reported uv-visible extinction coefficients within an experimental error of ±5%.

New or modified procedures have applied to the following complexes.

$Fe^{III}OEP(OH)$ and $Fe^{III}OEP(Cl)$. One gram of H_2OEP was dissolved with 1 g of $FeCl_3$ in 200 ml of acetic acid; a trace of sodium acetate was added and the solution was then refluxed for 90 min. Subsequent standing at room temperature yielded $Fe^{III}OEP(Cl)$ crystals. These were washed with methanol, water, dilute HCl, and water again after which the crystals were dried.

Anal. Calcd for $C_{36}H_{44}N_4FeCl$ (624.1): C, 69.28; H, 7.11; N, 8.97; Cl, 5.68. Found: C, 69.46; H, 7.01; N, 8.91; Cl, 7.00.

The $Fe^{III}OEP(OH)$ was formed from the above crystals by dissolving them in chloroform, shaking the solution with 1 *N* KOH, then washing with water, and crystallizing from chloroform–methanol. Chloroform solutions of this material gave the typical spectra of a monomeric $Fe^{III}OEP$ salt. The same material was obtained when $Fe^{III}OEP(Cl)$ was chromatographed on silica gel with a chloroform–methanol (100:3) mixture: spectra in chloroform, FeOEP(OH), 638, 580, 538, 509 mm; spectra in dichloromethane, FeEtioP(Cl), 635, 580, 535, 505 mm.

The dimer spectra is quite different, so even though a dimer might be expected by analogy with FeTPP, this is not the case.

Anal. Calcd for $C_{36}H_{44}N_4FeOH$ (605.6): C, 71.40; H, 7.33; N, 9.25. Calcd for $(C_{36}H_{44}N_4Fe)_2O$ (1192.6): C, 72.52; H, 7.45; N, 9.40. Found: C, 72.45; H, 7.36; N, 9.19; Cl, negative.

TiOOEP. A 200-mg portion of H_2OEP was suspended in 100 ml of diethylene glycol with 1 g of dicyclopentadienyltitanium dichloride and refluxed for 120 min. Quantitative reaction of H_2OEP was verified with a hand spectroscope. The solution was cooled to room temperature, mixed with 500 ml of chloroform, and thoroughly washed with dilute hydrochloric acid, sodium bicarbonate solution, and water. The concentrated chloroform solution was applied to a column containing dry alumina (Woelm) and eluted with chloroform. The yield of large rhombic crystals was 160 mg. Another 50 mg of fine needles was obtained from the mother liquid. Tsutsui[31] used diphenyltitanium and an inert atmosphere for the same reaction.

$GeOEP(OH)_2$. A 100-mg portion of H_2OEP was dissolved in 9 ml of pyridine together with 200 mg of germanium dichloride (Alfa). The mixture was treated for 14 hr at 170° in a sealed glass tube. An 80% yield of chromatographically pure (dry column alumina-$CHCl_3$) and crystallized material (from CH_3Cl/CH_3OH) was obtained. Germanium tetrachloride can be utilized instead of the more expensive dichloride.

GaOEP(OH) and InOEP(OH). These complexes were prepared in the same manner as $GeOEP(OH)_2$ using the respective trichlorides.

AlOEP(OH). A suspension of 300 mg of H_2OEP in 200 ml of carbon disulfide was prepared. Three 1-g additions of solid aluminum bromide (or chloride) were made within 10 min; the mixture was stirred in a dry atmosphere at room temperature. Chromatography on dry column alumina ($CHCl_3$) and crystallization from methanol yielded 60% AlOEP(OH).

$Ag^{III}OEP(ClO_4)$. A 100-mg portion of AgOEP was dissolved in 300 ml of chloroform and mixed with a solution of iron(III) perchlorate in a few milliliters of methanol. The color of the solution changed from a bright red to brownish red. It was immediately washed with water and evaporated to dryness. The residue was recrystallized from chloroform–methanol. Yields of $Ag^{III}OEP(ClO_4)$ were quantitative.

The product was more soluble in methanol than in chloroform. It could be redissolved in methanol and no rereduction to the silver(II) complex was then observed. The quantitative electronic excitation spectrum of the Ag(III) complex was quite similar to the Ag(II)–OEP: $Ag^{III}OEP(ClO_4)$, 552 nm (25,200), 516 nm (9800), 404 nm (131,000); $Ag^{II}OEP$, 560 nm (18,300), 526 nm (12,500), 409 nm (219,000); mass spectrum, mol peak at *m/e* 740.

Anal. Calcd for $C_{36}H_{44}N_4AgClO_4$ (740): C, 58.37; H, 6.00; N, 7.57; Ag, 14.59. Found: C, 59.15; H, 6.32; N, 7.05; Ag, 15.03.

The bulk susceptibility was measured with 400 mg of crystalline material on a conventional Gouy balance. The sample was diamagnetic.

II. **Cyclic Voltammetry.** All cyclic voltammetric measurements were made with a three-electrode potentiostatic circuit constructed from operational amplifiers. Construction of this apparatus is described elsewhere.[12] The working electrode was a platinum button of area 4.3 mm.[3] A commercial saturated calomel electrode was used as the reference electrode and a platinum wire sealed in the bottom of the cell served as the auxiliary electrode. The reference electrode was separated from the bulk of the solution by a bridge filled with the solution to be investigated. The bridge was then placed in another tube ending in a luggin capillary tip. This arrangement thus prevented aqueous contamination from entering the solution *via* the calomel electrode. The total volume of the electrolysis cell was 2–5 ml and porphyrin concentrations were between 10^{-3} and 10^{-4} *M*. Sweep rates varied between 0.01 and 100 V/sec. Deaeration of the solution was performed before commencing the experiment and a stream of high quality purified nitrogen was passed above the solution throughout. All experiments were carried out in a controlled temperature room of 20.0 ± 0.1° and potentials are reported with respect to the saturated calomel electrode (sce). Reagent butyronitrile was used as a solvent for oxidations and dimethyl sulfoxide (DMSO) for reductions, unless otherwise noted. Tetrabutylammonium perchlorate (TBAP) was the supporting electrolyte in all cases at a concentration of 0.1 *M*. For spectra work a larger Pt electrode was used in a three-compartment cell. Provision was made to transfer solutions under nitrogen.[7] Some oxidations and reductions were carried out chemically.

III. **Esr Spectroscopy.** Esr spectra were recorded on a Bruker 414s X-band spectrometer equipped with a 100-kHz field modulator and a 25-cm magnet. All samples were measured in chloroform. Titrations of $Ag^{II}OEP$ with Fe^{3+} were followed simultaneously on the esr spectrophotometer and a Zeiss DMR 21 spectrophotometer. Porphyrin concentrations were 2–4 × 10^{-5} *M*.

Results

A typical cyclic voltammogram is displayed in Figure 1. All voltammograms were similar in shape and form, being characteristic of reversible one-electron transfers. The results of the electrochemical measurements are given in Table I. The criteria we employed for crediting various redox steps to the experimentally observed electron transfer reactions were the following.

1. Electronic excitation spectra with two sharp bands between 500 and 600 nm are invariably indicative of a metalloporphyrin with an uncharged porphyrin ring.[27] Thus, if an oxidation step was observed but the product still retained the typical metalloporphyrin spectrum, it could be deduced that only oxidation of the central metal occurred (*e.g.*, $Ag^{2+} \rightleftarrows Ag^{3+}$, $Pb^{2+} \rightleftarrows Pb^{4+}$, $Co^{2+} \rightleftarrows Co^{3+}$). In the same fashion the reductions of central metals could be postulated (*e.g.*, $Fe^{3+} \rightleftarrows Fe^{2+}$, $Mn^{3+} \rightleftarrows Mn^{2+}$).

2. If, on oxidation, the visible spectrum was trans-

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Table I. Summary of Redox Potentials for Octaethylporphyrin and Metallo Octaethylporphyrin ($E_{1/2}$'s in volts *vs.* Sce)

	Ligand oxidation[a]			Ligand reduction[b]	
	$E_{1/2}$ (2)	$E_{1/2}$ (1)	Metal[b] $E_{1/2}$	$E_{1/2}$ (1)	$E_{1/2}$ (2)
H_2OEP	1.30	0.81		−1.46	−1.86
H_4OEP^{2+}		1.65			
Mono-*N*-MeOEP		1.37		−0.73	−1.17
Mono-*N*-MeOEP$^-$		0.86		−1.37	
AgOEP			0.44 III ⇄ II	−1.29[d]	
AlOEP(OH)	1.28	0.95		−1.31	
CaOEP	0.86	0.50		−1.68	
CdOEP	1.04	0.55		−1.52	
CoOEP		1.00	Irreversible III ⇄ II −1.05 II ⇄ I		
CrOEP(OH)	1.22	0.99	0.79 IV ⇄ III −1.14 III ⇄ II	−1.35	
CuOEP	1.19	0.79		−1.46	
FeOEP(OH)	1.24	1.00	−0.24 III ⇄ II	−1.33	
GaOEP(OH)	1.32	1.01		−1.34	−1.80
$GeOEP(OH)_2$	1.36	1.09		−1.31	
InOEP(OH)	1.36	1.08		−1.19	−1.59
MgOEP	0.77	0.54		−1.68	
MnOEP(OH)	>1.4	1.12	−0.42 III ⇄ II	−1.61	
MoOOEP(OH)		1.43	−0.21 V ⇄ IV	−1.30	−1.72
NiOEP		0.73[d,e]		−1.5[d]	
PbOEP	0.91[d]	0.65[d]	See ref 33	−1.30	
PdOEP		0.82		−1.53[c]	
SbOEP(OH)	>1.4	0.75		−1.07	
ScOEP(OH)	1.03[d]	0.70[d]		−1.54	
$SiOEP(OH)_2$	1.19	0.92		−1.35	
$SnOEP(OH)_2$	>1.4	≥1.4		−0.90	−1.30
TiOOEP	1.32	1.03		−1.21	−1.69
TlOEP(OH)	1.31	1.00		−1.24	
VOOEP	1.25	0.96		−1.25	−1.72
ZnOEP	1.02	0.63		−1.61	

[a] 0.1 *M* TBAP in butyronitrile. [b] 0.01 *M* TBAP in DMSO. [c] 0.1 *M* TBAP in DMF. [d] 0.1 *M* TBAP in benzonitrile. [e] The exact nature of this product is in controversy; see A. Wolberg and J. Manassen, *Inorg. Chem.*, **9**, 2365 (1970); J. B. Raynor, *Nature (London)*, **230**, 179 (1971).

formed from the characteristic two-banded spectrum to a single broad band covering the whole visible range, then a one-electron ligand oxidation could be formulated[5b] (*e.g.*, MgOEP ⇄ $MgOEP^+$, ZnOEP ⇄ $ZnOEP^+$, and PdOEP ⇄ $PdOEP^+$).

3. In a number of cases esr spectra were run on the starting metalloporphyrin and its oxidation products. Single-line signals with a line width of less than 10 G were taken to have been indicative of porphyrin ring π cation radicals (*e.g.*, Mg, Zn, Ni, Pd), while much broader signals with extensive hyperfine splitting were characteristic of metalloporphyrins containing a single electron on the metal. Lack of an esr signal was taken either to signify a diamagnetic complex (*e.g.*, Mg, Ni, Zn) or a complex having unpaired electrons on both the porphyrin ring and the metal (*e.g.*, $CuOEP^+$).[5a]

4. The bulk susceptibilities of some chemical oxidation products were determined directly on a Gouy balance (*e.g.*, $Ag^{III}OEP(ClO_4)$, $ZnOEP(ClO_4)$). From these data of the solid products the oxidation states of the central ion and the ligand could be deduced. In other cases susceptibilities were obtained by the usual nmr measurements as subsequently explained.

5. The remainder of the cases were those in which the metalloporphyrin radicals were too unstable to be isolated and no data were hitherto available. In these cases, ring redox assignments could be made on the basis of simple arguments which indicate that the central metal is rather stable to changes in oxidation states (*e.g.*, Al(III), Si(IV)). Furthermore, all cases could be interpreted by our finding[12] that the difference in $E_{1/2}$'s between the first ring oxidation yielding π cation radicals and the first ring reduction yielding π anion radicals was invariably 2.25 ± 0.15 V. It can also be seen from Table I that the normal difference between the first and second ring oxidation was 0.29 ± 0.05 V and the first and second ring reductions was 0.42 ± 0.5 V. This also aided in assigning redox steps to the metal of the ring.[4,12] The only exceptions to this observed rule were Mn and MoOEP, and in these cases the "deviations" are easily rationalized on theoretical grounds.

In Table II some hitherto unreported or unusual oxidation states of central ions are listed, as well as those normally found. Some specific evidence leading to some of the unusual assignments has been discussed (Ag(III),[12,13,32] Pb(IV),[33] Fe(IV),[34] Cr(II) and Cr(IV),[12] and Co(I)[35–37]). The suggestion that Fe(III) porphyrins can be oxidized to a Fe(IV) species[34] is neither confirmed nor denied by our electrochemical experiments, although they do support the other assignments. The iron and chromium porphyrins certainly need more detailed work before definite conclusions can be drawn.

Table II. Summary of Oxidation States of Central Metal Ions of Octaethylporphyrins

Central Metals That Are Stable to Electrochemical Oxidation or Reduction	
(a) Monovalent	Alkaline metals
(b) Divalent	Alkaline earth metals, Pd, Cu, Zn, Cd
(c) Trivalent	Sb, Sc, Al, Ga, In, Tl
(d) Quadrivalent	Si, Ge, Sn, TiO, VO
Central Metals Which Undergo Redox Reactions	
(a) I ⇄ II	Co
(b) II ⇄ III	Mn, Fe, Co, Cr, Ag, Ni(?)
(c) II ⇄ IV	Pb
(d) III ⇄ IV	Cr, Fe
(e) IV ⇄ V	MoO

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(32) J. Fajer, ref 13.

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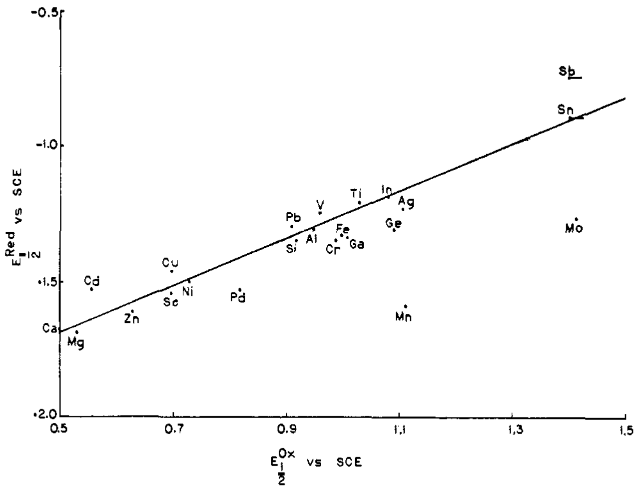

Figure 2. A plot of $E_{1/2}$ for the first ring oxidation *vs.* $E_{1/2}$ for the first ring reduction. This figure shows the inverse trend in the ease of metalloporphyrin ring oxidation *vs.* reduction.

Discussion

The arguments made for the assignment of metal and/or porphyrin ring reactions can be discussed in terms of both theoretical calculations on metalloporphyrins and their known chemistry.

A two-banded visible absorption spectrum is characteristic of all metalloporphyrins;[27] at times it may be broadened somewhat by intramolecular charge transfer to extra ligands (*e.g.*, Fe^{3+}, $TiOH^{+}$),[38,39] but in these cases the intact porphyrin π electron system is easily recognized by an unsplit, intensive Soret band. Only in the cases of Mn[40] and Mo[41] does this band show "abnormal" behavior, the Soret band being split into two bands having a separation of about 150 nm. We refer here to major splits rather than the short wavelength bumps often observed. (These two cases are also abnormal in their redox behavior.) The near uv Soret band contains an $a_{2u}e_g$ configuration with high π electron density on the nitrogens. Therefore, the usual observation of an unsplit and unshifted Soret band in metalloporphyrins indicates that, as a first approximation, the interaction between metal $d(\pi)$ and porphyrin ring (π) orbitals is minimal,[42] with the exception of the two noted cases. On the other hand, it is known that porphyrin ring cation radicals show only one band covering the whole visible range up to the near infrared,[3] while anion radicals produce intensive bands in the region over 700 nm.[6,43] This fact is easily rationalized by the results of MO calculations.[44] The highest occupied orbital (usually a_{2u} or a_{1u}) lies so close in energy to other porphyrin π orbitals that removal of one electron from the highest occupied orbital results in a loss of its energy through diminution of the electron–electron repulsion term, mixing these orbitals thoroughly with lower ones. This then leads to the participation of many different configurations to the excited state and to broad absorptions. On the other hand, the addition of an electron to an unoccupied e_g orbital leads to new low energy transitions producing intensive bands in the near infrared.

Arguments based on esr signals can be taken directly from the experimental results; the first derivative signals of porphyrin anion[3] and cation radicals[5b,15] have often been shown to be sharp single lines with line widths of about 5 G, while paramagnetic metals usually show esr absorptions where the unsplit signal is at least 20 G broad and which often produce additional anisotropic splittings.[45–47] Interactions of two unpaired electrons, *e.g.*, one on the porphyrin ring and the other on the metal, leads to undetectable esr signals[5a,15] in triplet or high spin states, but in these cases measurements of the susceptibilities by .nmr measurements,[5a,48] or on the solid compound on the Gouy balance,[49] if taken together with other evidence, can give particulars on the metal oxidation states in solution, if the paramagnetism of the sample is not canceled out by aggregation. Hyperfine splittings by constituents of the porphyrin ligand need not be discussed here.

The metal oxidation states preferred in a ligand field of the porphyrin can easily be rationalized. All central metals are in the oxidation state of 2+ or 3+ except for the main group IV ions, ions with double-bonded oxygen (which are 4+) and Co(I). No general trend of special stabilization of low oxidation states, *e.g.*, of the 2+ state, was observed as might be expected for complexes of the soft ligand porphyrin base. The special stabilization of d^8 ions (Ag^{3+}, Co^{+}) is common in square-planar complexes although the extent of this stabilization seems exceptional with metalloporphyrins.

Reactions of the Porphyrin Ring. The porphyrin ring reductions and oxidations are governed by the activation or deactivation of the π electron conjugated system through the electrostatic action of the central ions. The inverse trends in the case of the metalloporphyrin ring reduction and oxidation (shown in Figure 2) can be explained simply as a variation in the electrostatic forces which are introduced into the porphyrin cavity by the different metal ions. A possible parameter which can describe the $E_{1/2}$'s in terms of such an electrostatic field is the electronegativity of the central metal ion. It is shown that, when considering stable two-valent central metal ions, plots of either reduction or of oxidation potentials *vs.* electronegativity yield linear relationships (see Figure 3). However, when similar plots are made for central metal ions with oxidation number 3+ or 4+, no obvious relationship is observed. It appears that in these later cases, when metal ions with an oxidation number of 3+ or 4+ are introduced into the porphyrin cavity, the extra positive charge has a much greater influence on the porphyrin π system (and its redox properties) than would be suggested by the only slightly higher values of electronegativities. However, in all cases one can

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speak of induction effects of the central metal as determining the ring redox potential.

In order to systematize the data and show the redox reactivity of each complex as a function of the inductive effects of the metal, we have defined an induction (or reactivity) parameter *h*. This parameter is identical with electronegativity in the case of 2+ central metal ions, but for the 3+ and 4+ ions "*h*" is a hypothetical "working" value derived from the extrapolation of the data for 2+ ions (Figure 3), yielding overall *h*'s between 1.0 and 5.2. Thus PdOEP, with ring reactions at 0.82 and −1.53 V, is shown to have an inductive value of 2.0 for both oxidation and reduction (which is identical with its electronegativity), while for AlOEP the reactions at 0.95 and −1.31 V yield inductive parameters of 2.9 and 2.8, respectively. All of the induction values are summarized in Table III. With the use of this table, one can determine a working order of metalloporphyrin reactivity to chemical oxidation and/or electrophilic addition or substitution (similar to the activity table of metals) and, after verifying its validity on known systems, make predictions of a number of other reactions.

Table III. Summary of Induction Parameters[a]

Central metal ion of OEP	*h* (from first ring oxidation)	*h* (from first ring reduction)
Ca(II)	(1.0)	(1.0)
Mg(II)	(1.0)	(1.0)
Mn(II)	(1.4)	(1.4)
Cd(II)	(1.5)	(1.5)
Zn(II)	(1.5)	(1.5)
Ni(II)	(1.8)	(1.8)
Sc(III)	1.9	1.8
Pd(II)	(2.0)	(2.0)
Fe(II)		2.5
Si(V)	2.7	2.7
Al(III)	2.9	2.8
V(IV)	3.0	3.0
Tl(III)	3.1	3.1
Ga(III)	3.2	2.7
Fe(III)	3.2	
Co(III)	3.2	
Ti(IV)	3.3	3.2
In(III)	3.5	3.4
Ge(IV)	3.6	2.9
Sn(IV)	>4.7	4.8
Sb(III)	>4.7	5.2

[a] Values in parentheses are actual electronegativities.[b] The metal ions are arranged in order of the reactivity of their porphyrin ring as explained in the text. [b] W. Gordy and W. J. O. Thomas, *J. Chem. Phys.*, **24**, 439 (1956).

Furthermore, since roughly the same values of induction parameters are obtained from ring oxidation and ring reduction experiments, this reinforces our belief that simple inductive effects are at work and can be described by a simple parameter, *h*, for most metals. Since we have found that the difference between the first ring oxidation and reduction is constant, this manipulation is valid and numerical addition of the ring oxidation and reduction potential will yield that potential lying midway between the HOMO and LUMO. It can also be stated that our experimental difference, $E_{1/2}^{ox} - E_{1/2}^{red} = 2.25 \pm 0.15$ V, is in excellent agreement with the theoretically calculated value of 2.18 eV for the difference between the HOMO and LUMO in most metalloporphyrins.[44]

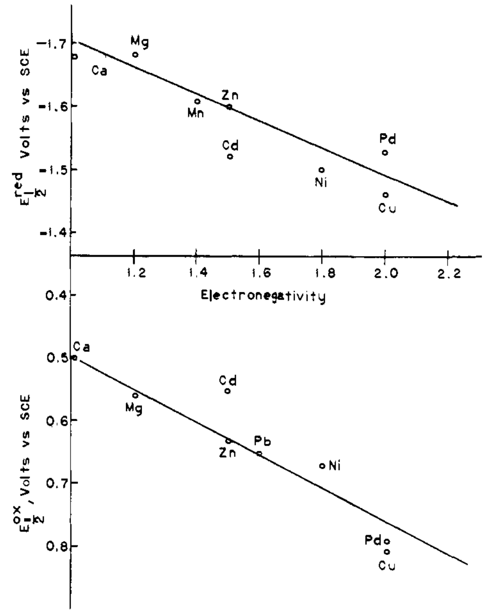

Figure 3. A plot of the first ring reduction, $E_{1/2}(\mathrm{I})^{red}$ and $E_{1/2}(\mathrm{I})^{ox}$ *vs.* the electronegativity of the central metal ion. Linearity is obtained only for the case of divalent metal ions.

The domination of inductive effects of the central ions over conjugative effects has earlier been formulated by Gouterman[42] mainly on the basis of the observed electronic excitation spectra. Our results confirm this conclusion with experiments on the ground state. Gouterman has also calculated the porphyrin ring charges for a number of different metalloporphyrins.[44,50,51] As might be predicted, plots of these charges *vs.* our experimental porphyrin ring oxidation and reduction potentials yield a quite linear relationship (Figures 4 and 5).

The inductive action of the metals can be taken into account in MO calculations by simply changing the Coulomb parameters of the central nitrogens. Results of Hückel calculations performed in this way indicated that large differences in the chosen Coulomb integrals indeed yielded shifts of the HOMO and LUMO eigenvalues in the correct direction, but of an order of magnitude too small when compared with experimental differences from the redox data. Figure 6 is a schematic representation of the experimental data but no definite values of the Coulomb potentials can be assigned to these changes so far. Gouterman's calculations also show only slight changes of the energy eigenvalues of the frontier orbitals of the porphyrin π electrons by different central metal ions[44] contrary to experimental results.

Finally, the above conclusions on metalloporphyrins are confirmed by several measurements of porphyrin anion and cation redox potentials (Table I); the oxidation of H_4OEP^{2+} dication occurs at a potential of 1.65 V, while the free base, H_2OEP, oxidation occurs at the much lower value of 0.81 V. Thus the oxidation behavior of the dication can be compared with the

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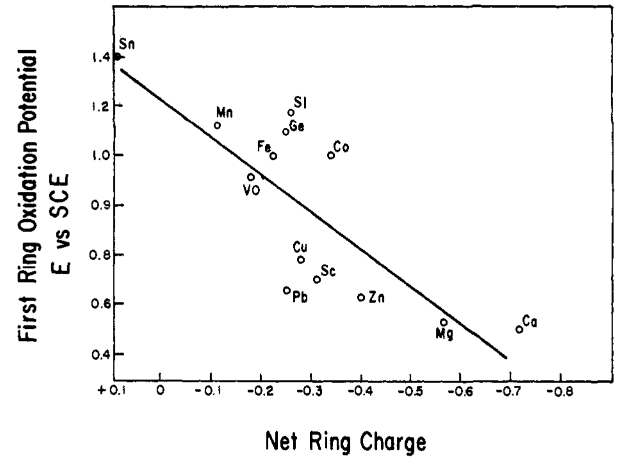

Figure 4. A plot showing linearity of first ring oxidation, $E_{1/2}(I)^{ox}$ *vs.* the calculated porphyrin ring charge.

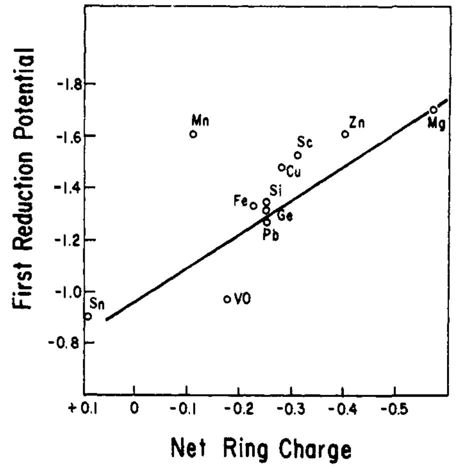

Figure 5. A plot showing linearity of first ring reduction, $E_{1/2}(I)^{red}$ *vs.* the calculated prophyrin ring charge.

$Sn^{IV}OEP(OH)_2$ and the free base behaves similar to PdOEP. Looking at the reduction potentials it is seen that the difference between the reduction of H_2OEP and N-$(CH_3)OEP^-$ is 640 mV (reduction potentials −0.73 and −1.37, respectively), and this difference roughly approximates that between the extremes in potential between MgOEP and $Sn^{IV}OEP(OH)_2$. Thus, protonation or deprotonation of the central porphyrin cavity introduces positive or negative charges into the porphyrin ring and, by the use of inductive forces, produces a porphyrin reactivity similar to that of any given metalloporphyrin.

Another more general relationship is observed between metalloporphyrins and a purely organic system of simple alternating hydrocarbons. It has been demonstrated that the redox potentials for a series of increasing alternating hydrocarbons will vary linearly with the wave number of the L_a absorption band.[52] The metalloporphyrins fit very well such a relationship which is described by the equation $\nu_{exp} = -11{,}900 - (19{,}400)E_{1/2}^{red}$, where the wave numbers are expressed in cm^{-1}. Thus, if we consider metalloporphyrin behavior to approximate that of an alternating hydrocarbon, we can, for example, from the $E_{1/2}^{red} = -1.53$, predict for PdOEP a wave number of 18,300 cm^{-1} (546 nm), which is the exact value found experimentally. Another relationship has been proposed between the redox potential of a conjugated π electron system and its absorption spectrum,[53] that is, $E_{1/2}^{ox} - E_{1/2}^{red} - (h\nu) = 0.01$, where $h\nu$ is energy in electron volts of the long wavelength band. This equation has been found to hold true for all of the metal complexes which fall on our straight line of Figure 2.

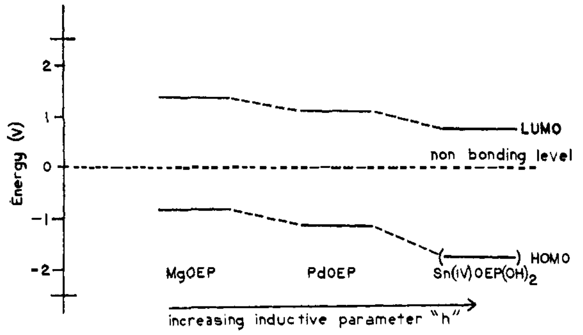

Figure 6. A schematic representation of redox potentials showing the energy distribution of the porphyrin reaction as a function of the charge on the central metal ion.

The major result of this work consists of the finding that when a main group or transition metal is introduced into a porphyrin (yielding the corresponding metalloporphyrin) only the σ shell of the porphyrin is shifted in energy, changing both the e_g and a_{2u} orbitals in the same direction by approximately the same amount due to purely inductive interactions. Two exceptions to this were found (Mn^{3+} and Mo^{5+}) where exceptional interactions of the $d(\pi)$ metal electrons with the π electrons of the porphyrin ring also occurred. This is also evidenced by the split of the Soret band in the electronic excitation spectra of these compounds. These interactions probably raise the energy of the e_g orbitals by partially populating them with metal electrons.[40,54]

Comparison of Redox Behavior and Chemical Reactivity of Metalloporphyrins. From the regularities found in the redox behavior of the porphyrin ring of metalloporphyrins one may try to predict the chemical reactivity of the macrocycle. Porphyrin rings which bear a relatively negative ring charge should easily undergo chemical oxidation and other electrophilic additions or substitutions. On the other hand, an electropositive ring should be easy to reduce and should undergo nucleophilic additions and substitutions. Known experimental facts are generally in accord with this view.

For instance, photooxygenation of the porphyrin ring is only possible with the dianion, the magnesium or the calcium complexes.[55,56] The zinc complex does not react but zinc octaethylchlorin does.[56] It is known that the latter has an oxidation potential some 300 mV lower that zinc porphyrin.[16] Thus oxidation potentials of 0.55 V or less are a requirement for photooxygenation.

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Magnesium and zinc porphyrins are too easily hydrolyzed to withstand the usual strongly acidic conditions of electrophilic substitutions. The next most reactive metal complexes as predicted by the redox data are those of nickel and copper. These have indeed been shown to be reactive in Vilsmeir formylation.[57,58] The dication of octaethylporphyrin, which is formed under acidic conditions from the porphyrin, does not react. The positively charged tin(IV) complex likewise is unreactive.[59] Reagents such as NO_2^+, H_2O_2, and Br_2 are such powerful oxidants that little metal specificity is observed. It has been found, however, that the tin(IV) porphyrin is stable in the presence of Br_2.[18]

The most electropositive metalloporphyrin investigated so far is the tin(IV) complex. While it is stable against electrophilic attack as shown above, it is very reactive with reducing agents. The porphyrin ligand of tin(IV) porphyrins can easily be photohydrogenated to phlorine[18,59] and chlorins,[18,59,60] and it is the only metalloporphyrin that can be chemically reduced by diimide in diglyme to a chlorin.[60] On the other hand, the role of iron(II) in the frequently used procedure of Eisner[61,62] to produce chlorins with sodium in amyl alcohol is not clear since the reduction of Fe(II) porphyrins should not be particularly easy. That the photoreduction procedure leading to α,γ-dihydroporphomethenes first described by Krasnovskii is usually carried out on porphyrin dications[63] fits the picture presented here, but the also described high reactivity of the zinc complex[63] seems contradictory. It would be desirable to carry out further experiments comparing the reactivities of relatively electropositive and electronegative metal complexes.

It should also be mentioned that Buchler[64] has found that the dianions of different metalloporphyrins undergo mesodimethylation with methyl iodide.

$$MeP^{2-} + 2CH_3I = MeP(CH_3)_2 + 2I^-$$

The yield of the dimethylation reaction is roughly proportional to the size of the negative charge on the ring of the starting metalloporphyrin.

Some general predictions on the chemical behavior of the porphyrin ring of metalloporphyrin can now be made: antimony porphyrins, which can be demetalated in acids, should be subject to nucleophilic attack and reductive additions; manganese and molybdenum porphyrins should undergo radical reactions whereas magnesium, calcium, and alkali metal porphyrins should be ideally suited for oxidations. The photochemistry of metalloporphyrins also follows the predictions obtained from the redox patterns, unless quenching through metal orbitals prevents such reactivity.

Future work will involve further checks but it is already evident that the straightforward electrostatic picture usually describes metalloporphyrin reactivities and, as well, that variation of the central metal can dramatically change these reactivities.

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