Registry No. TU, 62-56-6; DT, 534-13-4; IT, 96-45-7; $IrCl_6^{2-}$, 16918-91-5; Cu^{2+}, 15158-11-9; $C_6H_{10}N_4S·HCl$, 68213-04-7.

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Contribution from the Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, E.R.A. au C.N.R.S. No. 468,
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Effects of Electron-Withdrawing Substituents on the Electrochemical Oxidation of Porphyrins

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Effects of β substitutions on the oxidation potentials of mesotetraphenylporphyrins are reported and compared with those observed in reduction of the same compounds. Remarkably, the magnitude of the redox potential shift induced by strong electron-withdrawing substituents (CN, NO_2) is different in oxidation from that in reduction. Typically, for the free-base tetraphenylporphyrin, the anodic shift resulting from four cyano substituents is +0.35 V in oxidation and +0.98 V in reduction. Also, at variance with results in reduction, the effects of β polysubstitution are nonadditive in oxidation, and for metalloporphyrins, these effects depend on the nonelectroactive central metal. These results may be interpreted by the existence of two sites for the electron transfer—the pyrrolic nitrogens in oxidation and the π-electron system in reduction.

A. Introduction

In nonaqueous media, the tetrapyrrolic macrocycle of the porphyrins is oxidized in successive monoelectronic steps[1–3] giving monocationic radicals and dications. The reduction of the tetrapyrrolic ring leads, by similar mechanisms, to monoanionic radicals and to dianions.[4,5] The half-wave potentials of these reversible reactions change with the electronegativity and the formal oxidation state of the central metal of the metalloporphyrins,[6] and they depend on the axial ligands[7,8] and the basicity of the tetrapyrrolic ring.[9] As a rule, the reduction of the porphyrin macrocycle becomes more difficult and its oxidation easier as the π-electron density increases. Recent studies have illustrated the variations of the electrochemical reactivity possible with changes in the chemical nature and the number of β and meso substituents on the porphyrin.[10–13]

The study[10,11] of the effects of β substitutions on the electroreduction energies of porphyrins revealed that these effects may be dramatic and illustrated the possibility of synthesizing porphyrins with "tailor-made" reduction potentials over a wide range (up to 1 V). Also, with para substituents on the phenyls of tetraphenylporphyrins (TPP), shifts in the oxidation–reduction potentials have been measured and analyzed.[12,13] In this latter type of substitution, the observed effects are 5–6 times smaller than for pyrrole-substituted porphyrins.[10,14] The comparative papers published up to now on the substituents' effects in porphyrins have reported analogous oxidation and reduction potential shifts.

While this work is primarily devoted to the analysis of the effects of electron-withdrawing β substituents on the oxidation potentials of the porphyrin, their reduction, which had previously been measured on mercury, is also reported for platinum. These effects are analyzed by correlation involving the Hammett parameters, whose interest has been recalled in recent papers[15,16] and which are quite different for oxidation and reduction. On the basis of these differences, an interpretation is proposed for the influence of the β substituents on the electrochemical reactivity of porphyrins.

The two first electrode reactions of the porphyrins, in oxidation and in reduction, may be described as in reactions 1–4.

Reduction

$$MP + e^- \rightleftarrows MP^{-\cdot} \quad \text{anion radical} \tag{1}$$

$$MP^{-\cdot} + e^- \rightleftarrows MP^{2-} \quad \text{dianion} \tag{2}$$

Oxidation

$$MP \rightleftarrows e^- + MP^{+\cdot} \quad \text{cation radical} \tag{3}$$

$$MP^{+\cdot} \rightleftarrows e^- + MP^{2+} \quad \text{dication} \tag{4}$$

In this reaction scheme, M is $(H)_2$ or the central metal in the metalloporphyrin, the central metal is chosen to be nonelectroactive (Cu^{II}, Pd^{II}, Zn^{II}), and P is the ligand por-

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Table I. Half-Wave Potentials and Potential Shifts (V/SCE ± 0.02 V) for β-Monosubstituted Porphyrins $H_2TPP(X)$ and $H_2T(p\text{-}C_6H_4CN)P$ in CH_2Cl_2 + 0.05 M THAP on a Pt RDE (2000 rev min^{-1})

	reduction			oxidation			
porphyrin	$E_{1/2}{}^{I}$	$\Delta E_{1/2}{}^{Ia}$	$\Delta E_{1/2}{}^{Ox-Red\,b}$	$E_{1/2}{}^{I}$	$E_{1/2}{}^{II}$	$\Delta E_{1/2}{}^{Ic}$	$E_{1/2}{}^{II} - E_{1/2}{}^{I}$
H_2TPP	−1.21	0	2.29	1.08	1.35	0	0.27
$H_2TPP(OEt)$	−1.26	−0.05	2.28	1.02	1.23	−0.06	0.11
$H_2TPP(Br)$	−1.13	0.08	2.29	1.16	1.26	0.08	0.10
$H_2TPP(Cl)$	-1.12^d	0.09	2.29	1.17	1.31	0.09	0.14
$H_2TPP(CN)$	-0.94^e	0.27	2.16	1.22	1.40	0.14	0.18
$H_2TPP(NO_2)$	−0.85	0.36	2.04	1.19	1.30	0.11	0.11
$H_2T(p\text{-}C_6H_4CN)P$	−1.03	0.18	2.32	1.29	1.43	0.21	0.14

[a] $\Delta E_{1/2}{}^{I} = E_{1/2}{}^{X} - E_{1/2}{}^{H}$. [b] $\Delta E_{1/2}{}^{Ox-Red} = E_{1/2}{}^{I(Ox)} - E_{1/2}{}^{I(Red)}$. [c] $\Delta E_{1/2}{}^{I} = E_{1/2}{}^{I(X)} - E_{1/2}{}^{I(H)}$. [d] Second cathodic wave at −1.39 V/SCE. [e] Second cathodic wave at −1.31 V/SCE.

Table II. Half-Wave Potentials and Potential Shifts (V/SCE ± 0.02 V) for Metalloporphyrins $MTPP(CN)_x$ in CH_2Cl_2 + 0.05 M THAP on a Pt RDE (2000 rev min^{-1})($M = Zn^{II}, Cu^{II}, Pd^{II}; x = 0\text{–}4$)

	reduction			oxidation			
porphyrin	$E_{1/2}{}^{I}$	$\Delta E_{1/2}{}^{Ia}$	$\Delta E_{1/2}{}^{Ox-Red\,a}$	$E_{1/2}{}^{I}$	$E_{1/2}{}^{II}$	$\Delta E_{1/2}{}^{Ia}$	$E_{1/2}{}^{II} - E_{1/2}{}^{I}$
PdTPP	−1.34	0	2.54	1.20	1.61	0	0.41
$PdTPP(CN)_4$	−0.35	0.99	2.10	1.75		0.55	
CuTPP	−1.35	0	2.41	1.06	1.33	0	0.27
$CuTPP(CN)_4$	−0.34	1.01	1.76	1.41	1.70	0.35	0.29
ZnTPP	−1.42	0	2.24	0.82	1.13	0	0.31
$ZnTPP(CN)_4$	−0.44	0.98	1.55	1.11		0.29	

[a] See Table I for definition of these $E_{1/2}$'s.

phyrin. Reactions 1–4 have been characterized by spectral techniques.[2,5,6]

B. Experimental Section

The electrochemical measurements have been carried out at 25 °C on a platinum electrode (area = 3.14 mm^2). This platinum disk may be used as a rotating disk electrode (RDE), at rotation rates from 500 to 5000 rev min^{-1}. All measurements have been performed with an electrochemical device (Solea-Tacussel) comprising a potentiostat (PRT 20-2 X), a voltage pilot unit (Servovit 2), a millivoltmeter with a high-impedance input (S 6 B), and a potentiometric recorder (EPL 2). For cyclic voltammetric measurements, a signal generator (GSATP from Solea) was associated with the above units.

The determination of the number of faradays exchanged per mole of porphyrin in the two first oxidation steps (reactions 3 and 4) has been carried out by comparing the limiting currents of the oxidation waves (reactions 3 and 4) with the limiting currents of the two cathodic waves (reactions 1 and 2), in the same experimental run.

Throughout the measurements, the reference electrode was a calomel electrode in a saturated aqueous solution of KCl (SCE), electrically connected with the studied solution by a junction bridge (0.1 M tetra-*n*-hexylammonium perchlorate (THAP) in dichloromethane-*N*,*N*-dimethylformamide, 50%/50%). CH_2Cl_2 (Merck puriss) was used without further purification. The supporting electrolyte (THAP, 0.05 M) was purified before use by recrystallization in water after dissolution in methanol.

The studied porphyrins, prepared according to known procedures,[14,17,18] were (Figure 1) $H_2TPP(CN)_x$ and $CuTPP(CN)_x$, with x = 0–4, $H_2TPP(X)$, with X = OEt, H, Cl, Br, CN, and NO_2, PdTPP, $PdTPP(CN)_4$, ZnTPP, and $H_2T(p\text{-}C_6H_4CN)P$.

$ZnTPP(CN)_4$. The product was obtained on refluxing $H_2TPP(CN)_4$ (100 mg) and zinc acetate (500 mg) in chloroform–methanol (5:1; 120 mL) for 2 h. Evaporation followed by chromatography (silica gel in chloroform–ethyl acetate 95:5) and crystallization from chloroform–methanol gave $ZnTPP(CN)_4$ (48 mg). Mass spectrum: M^+, *m*/*z* 776. Anal. Calcd for ($C_{48}H_{24}N_8Zn\cdot 3H_2O$): C, 69.28; H, 3.63; N, 13.46. Found: C, 69.78; H, 3.56; N, 13.50.

C. Results

1. Stationary Voltammetry on a Platinum Rotating Disk Electrode (RDE). Figure 2 shows a typical *I–E* curve of the studied porphyrins in the electroactivity range of the supporting electrolyte (i.e., from +1.8 V/SCE to −1.5 V/SCE for CH_2Cl_2 + 0.05 M THAP). Two reduction and two oxidation waves are observed, corresponding to reactions 1–4. The measured half-wave potentials are given in Tables I–IV. It may happen that less than four waves (oxidation plus reduction) are observed, either because one or two of the expected waves fall outside of the electroactivity range (e.g.: PdTPP and $PdTPP(CN)_4$) or as a result of passivation of adsorption processes occurring at the surface of the electrode.[19] These latter processes have been observed here only in the reduction steps.

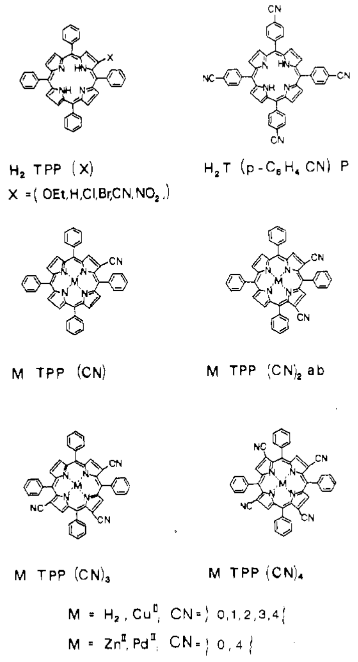

Figure 1. Porphyrins studied in this work.

The applicability of Levich's[20] relationship has been checked in all cases:

$$I_{lim} = 0.62nFAD^{2/3}\nu^{-1/6}\omega^{1/2}C$$

As the limiting currents, I_{lim}, are proportional to C and as the

Table III. Half-Wave Potentials and Potential Shifts (V/SCE ± 0.02 V) of Porphyrin Free Bases, in CH_2Cl_2 + 0.05 M THAP on a Pt RDE (2000 rev min^{-1}) and Their Electronic Transition Energies (Band III) (eV mol^{-1})

	reduction			oxidation				
porphyrin	$E_{1/2}^{I}$	$\Delta E_{1/2}^{I a}$	$\Delta E_{1/2}^{Ox-Red\ a}$	$E_{1/2}^{I}$	$E_{1/2}^{II}$	$\Delta E_{1/2}^{I a}$	$E_{1/2}^{II} - E_{1/2}^{I}$	$E_{h\nu}$(band III)
H_2TPP	−1.21	0	2.29	1.08	1.35	0	0.27	2.25 (550)[b]
$H_2TPP(CN)_1$	−0.94[c]	0.27	2.16	1.22	1.40	0.14	0.18	2.20 (560)
$H_2TPP(CN)_2$a,b	−0.71[d]	0.50	2.03	1.32	1.41	0.24	0.09	2.17 (568)
$H_2TPP(CN)_3$	−0.50[e]	0.71	1.86	1.36	1.54	0.28	0.18	2.11 (584)
$H_2TPP(CN)_4$	−0.23	0.98	1.66	1.43		0.35	0	2.06 (600)

[a] See Table I for definition of these $E_{1/2}$'s. [b] λ_{max}'s (nm) are given in parentheses. [c] Second cathodic wave at −1.31 V/SCE. [d] Second cathodic wave at −1.01 V/SCE. [e] Second cathodic wave at −0.61 V/SCE.

Table IV. Half-Wave Potentials and Potentials Shifts (V/SCE ± 0.02 V) of Copper Porphyrins in CH_2Cl_2 + 0.05 M THAP on a Pt RDE (2000 rev min^{-1}) and Their Electronic Transition Energies (Band III) (eV mol^{-1})

	reduction			oxidation				
porphyrin	$E_{1/2}^{I}$	$\Delta E_{1/2}^{I a}$	$\Delta E_{1/2}^{Ox-Red\ a}$	$E_{1/2}^{I}$	$E_{1/2}^{II}$	$\Delta E_{1/2}^{I a}$	$E_{1/2}^{II} - E_{1/2}$	$E_{h\nu}$(band III)
CuTPP	−1.35	0	2.41	1.06	1.33	0	0.27	2.29 (539)[b]
$CuTPP(CN)_1$	−1.10	0.25	2.33	1.23	1.48	0.17	0.25	2.27 (545)
$CuTPP(CN)_2$a,b	−0.86	0.49	2.15	1.29	1.61	0.23	0.32	2.23 (554)
$CuTPP(CN)_3$	−0.61	0.74	1.94	1.33	1.56	0.27	0.23	2.17 (570)
$CuTPP(CN)_4$	−0.34	1.01	1.75	1.41	1.70	0.35	0.29	2.10 (590)

[a] See Table I for definitions of these $E_{1/2}$'s. [b] λ_{max}'s (nm) are given in parentheses.

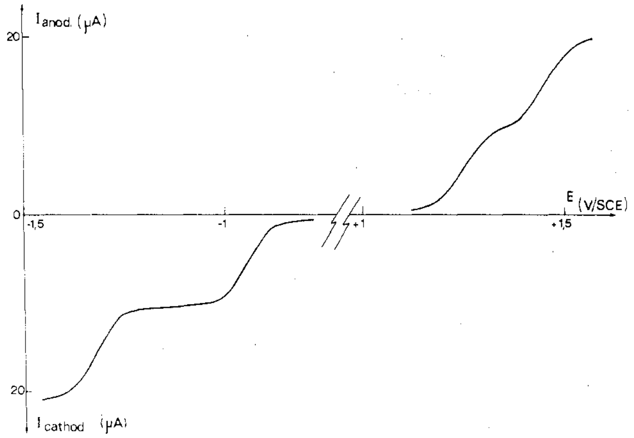

Figure 2. I-E curve on Pt rotating disk electrode for 4 × 10^{-4} M $H_2TPP(CN)_1$ in CH_2Cl_2 + 0.05 M THAP (N = 2000 rev min^{-1}).

$1/I_{lim}$ vs. $1/\omega^{1/2}$ plots are straight lines crossing the origin of the axes, all of the cathodic and anodic limiting currents are diffusion controlled.

Previous studies on mercury electrodes[10,11,14] revealed that the first two reduction steps are monoelectronic. On a platinum RDE, the identical heights of the recorded cathodic and anodic waves demonstrated that the oxidation steps are also monoelectronic.

2. Cyclic Voltammetry on a Platinum Disk Electrode. For the first two oxidation steps, two anodic peaks are observed, with the corresponding reduction peaks. For each oxidation step the peak potentials' difference $\Delta E_p = E_{p_a} - E_{p_c}$ between corresponding anodic and cathodic peaks has the constant value of 57 mV at low scan rates (v < 0.1 V s^{-1}), which indicates that the two monoelectronic oxidation steps are reversible.

On the other hand, the reduction gives qualitatively the same results as previously obtained on mercury electrodes, namely, a reversible cathodic electron transfer for each of the first two reduction steps (reactions 1 and 2).

D. Discussion

1. Effect of the Chemical Nature of the β Substituent. By reduction on the platinum electrode in CH_2Cl_2, the same conclusions may be drawn as on mercury electrodes in dimethylformamide (DMF),[10,11,14] although the half-wave potentials here are about 100 mV more cathodic than on mercury in DMF. This effect may be ascribed to the different solvents used.[12] Figure 3 represents the shifts of the half-wave potentials $E_{1/2}^{I(Red)}$ corresponding to the first reduction step of mono-β-substituted free-base porphyrins (Table I) vs. the Hammett parameters σ_p^-, σ_p, and σ_m[24] of the substituents. The observed shifts of the $E_{1/2}^{I(Red)}$ reveal, as expected, that the reduction of the porphyrin ligand becomes easier as the electron-withdrawing character of the substituent increases. The better correlation observed with σ_p^- expresses the resonant interaction of the substituent with the porphyrin macrocycle, as previously illustrated by Raman spectral measurements[22] and by the axial coordination ability of the central metal in metalloporphyrins.[23] This conclusion is consistent with the additivity of the positive potential shifts measured on increasing the number of β-substituents on a porphyrin ring (Tables III and IV). The value of the ligand characteristic ρ_π, given by the slope of the $E_{1/2}^{I(Red)}$ vs. σ_p^- plot,[24] is +0.28 V. The same value, ρ_π = +0.28 V, has been calculated from reduction measurements on a Hg electrode, in DMF.[14]

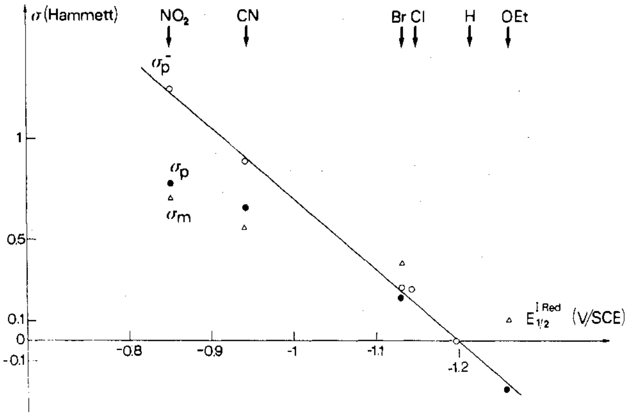

Figure 3. Free energy plot for the first reduction step of $H_2TPP(X)$ (X = NO_2, CN, Br, Cl, H, OEt): ○, σ_p^-; ●, σ_p; △, σ_m.

On the other hand, the oxidation half-wave potentials (Tables I–IV) show that the electron-withdrawing substituents

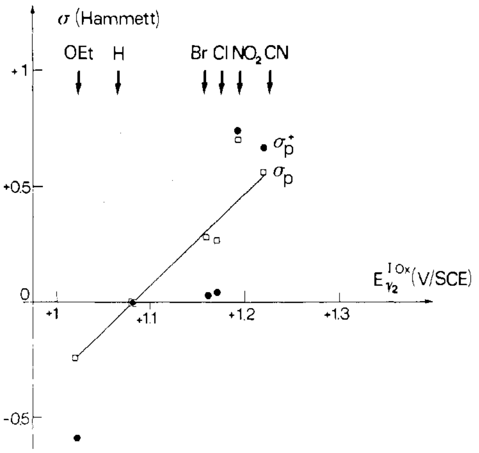

Figure 4. Free energy plot for the first oxidation step of $H_2TPP(X)$ (X = NO_2, CN, Cl, Br, H, OEt): ●, σ_p^+; □, σ_p.

make the oxidation of the porphyrin ligand more difficult. The difficulty of oxidation increases along the following sequence of monosubstitution:

$$\mathrm{OEt} < \mathrm{H} < \mathrm{Br} < \mathrm{Cl} < \mathrm{NO_2} < \mathrm{CN}$$

That corresponds to the increase of the electron-withdrawing character of the substituents, with an inversion between NO_2 and CN. This inversion has been also observed with para substituents on the phenyls of TPP.[13] However, it shall be noted (Table I) that, for a given substituent, the anodic shift is always smaller in oxidation than in reduction for the strong electron-withdrawing substituents, namely, if

$$\Delta E_{1/2}{}^{\mathrm{I(Ox)}} = E_{1/2}{}^{\mathrm{I(Ox)}}(\mathrm{H_2TPP(X)}) - E_{1/2}{}^{\mathrm{I(Ox)}}(\mathrm{H_2TPP})$$

and

$$\Delta E_{1/2}{}^{\mathrm{I(Red)}} = E_{1/2}{}^{\mathrm{I(Red)}}(\mathrm{H_2TPP(X)}) - E_{1/2}{}^{\mathrm{I(Red)}}(\mathrm{H_2TPP})$$

Thus

$$\Delta E_{1/2}{}^{\mathrm{I(Ox)}} < \Delta E_{1/2}{}^{\mathrm{I(Red)}}$$

We have plotted in Figure 4 the oxidation (first step) half-wave potentials $E_{1/2}{}^{\mathrm{I(Ox)}}$ (Table I) of the mono-β-substituted free-base porphyrins vs. the Hammett parameters σ_p and σ_p^+ of the substituents. The plot exhibits better correlation with σ_p than with σ_p^+. The slope of the straight line $E_{1/2}{}^{\mathrm{I(Ox)}}$ vs. σ_p is $\rho = +0.17$ V, which is consistent[24] with the increased difficulty of oxidizing the porphyrins as the electron density is decreased over the macrocycle.

These latter results are consistent with the conclusions of Baker et al.,[23] who demonstrated that good correlations between the protonation constants of the porphyrins and the σ Hammett parameter of the substituents were only obtained by choosing σ corresponding to the absence of direct conjugation between the substituent and the reaction site. These results imply that the β substituents of the pyrroles have mostly inductive effects on to the reaction site, which is therefore not the π-electron system of the porphyrin, in oxidation.

Thus the clear-cut difference between the oxidation and reduction behavior, as a result of strong electron-withdrawing substituents, may be ascribed primarily to a difference in the relevant reaction sites. The reductive electron transfer may be considered as a direct transfer to the π electrons of the conjugated system[25,26] with which the β substituents are in direct resonant interaction.[22,23] On the contrary, the results obtained in oxidation preclude an electron transfer from the π-electron system and favor the interpretation that the lone electron pairs of the pyrrolic nitrogens are involved. As the potential shifts due to the strong electron-withdrawing β substituents (CN, NO_2) are smaller in oxidation than in reduction (Tables I–IV), the pyrrolic nitrogens may indeed be the oxidative reaction site. Since the interactions of these nitrogens with the substituents are mostly inductive and inductive interactions are weaker than the conjugation (resonant) ones,[21] the smaller effects observed in oxidation than in reduction are expected. This interpretation is in agreement with the conclusions of Stanienda[1,27] on the electrochemical reactivity of porphyrins and metalloporphyrins.

When the meso phenyls are para substituted, instead of the pyrroles, the results obtained on mesotetrakis(para-cyanophenyl)porphine, $H_2T(p\text{-}C_6H_4CN)P$, show that the positive potential shift is about the same in oxidation as in reduction. This result does not contradict the hypothesis of two distinct reaction sites in oxidation and in reduction. $H_2T(p\text{-}C_6H_4CN)P$, the electron-withdrawing cyano groups are actually substituted on the meso phenyls which are not coplanar with the tetrapyrrolic ring.[28,29] Thus, the conjugation is weakened between the cyano groups and the π-electron system of the porphyrin as illustrated by comparing the cathodic half-wave potential $E_{1/2}{}^{\mathrm{I(Red)}}$ of H_2TPP with those of $H_2TPP(CN)_4$ and $H_2T(p\text{-}C_6H_4CN)P$. The comparison reveals that the interaction of cyano substituents with the π-electron system is only about one-fifth as large if the substituents are on the para position of the meso phenyls instead of on the pyrroles.[10-14] Thus, the weakened interaction of the four CN's with the tetrapyrrolic ring, in $H_2T(p\text{-}C_6H_4CN)P$, may very well explain the equal potential shifts observed in reduction and in oxidation, since both the reduction and the oxidation sites have neither direct nor resonant interactions with the cyano substituents. Furthermore, the effect of the cyano on the porphyrin is exerted through the phenyl–porphyrin bonds and thus the Hammett correlations are linear only if the nonresonant parameter σ_p is used.[12,30]

2. Influence of the Central Metal on the Redox Properties of Metalloporphyrins. In the studied porphyrins, metalation of the free base makes the electrochemical oxidation easier when $M^{II} = Cu^{II}$ or Zn^{II} and more difficult when $M^{II} = Pd^{II}$ (Tables II–IV), with respect to the free base.

In the nonsubstituted porphyrins examined here the increase, from Zn to Cu to Pd, of the energy required for the electrochemical oxidation has been discussed by several authors, in terms of the electronegativity of the central metal[6] and of its number of d electrons[1] and also in terms of the basicity of the metalloporphyrin.[9] Along the sequence Zn, Cu, Pd, the amine character of the pyrrolic nitrogens decreases from the zinc to the palladium porphyrin. Also from Zn to Pd, the porphyrin macrocycle becomes more planar, thus allowing a better conjugation of the porphyrin and a reinforcement of the d–π metal–macrocycle interactions. Also, the increased difficulty to demetalate the porphyrins, from Zn to Pd, demonstrates that the pyrrolic nitrogens become then less reactive toward the protons. These effects account for the experimental observation that the electrochemical oxidation of metalloporphyrins becomes more difficult along the sequence Zn^{II}, Cu^{II}, Pd^{II}.

Among the substituted porphyrins studied here, it is observed also that, for a given identical substitution—$(CN)_4$—the sensitivity of the oxidation potential toward the β substituents changes with the nature of the central metal: the positive shift of the first oxidation half-wave potential, induced by the four cyano groups, increases from zinc to palladium (Table II). This result is indeed expected from the reinforced d–π interactions between the metal and the porphyrin macrocycle, from Zn to Pd.[31]

Unlike the results obtained in oxidation, the effects of the substituents on the reduction potentials are almost independent

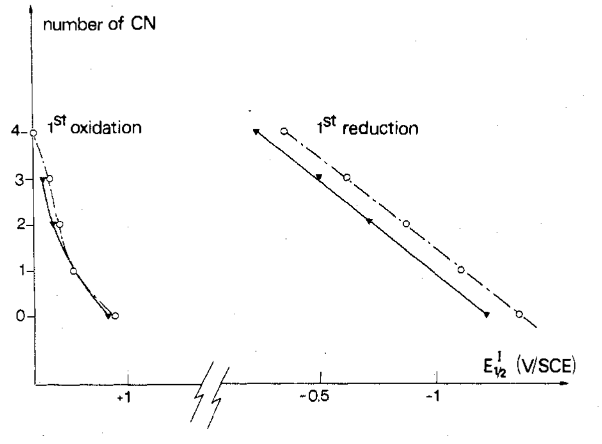

Figure 5. Comparison of the $E_{1/2}{}^{I}$ shifts, in the first oxidation and in the first reduction of $H_2TPP(CN)_x$ and $CuTPP(CN)_x$ (x = 0–4): ▼, $H_2TPP(CN)_x$; ○, $CuTPP(CN)_x$.

of the central metal. This is not surprising, as the reduction of the porphyrin involves the π-electron system of the ligand, which is in direct resonant interaction with the β substituents.

3. Effect of the Number of β Substituents. For a given substituent, successive β substitutions on the porphyrin affect the reduction and the oxidation potentials differently (Tables III and IV). We have plotted in Figure 5 the half-wave potentials corresponding to the first oxidation and to the first reduction of the free-base porphyrin and of the copper porphyrin vs. the number of cyano substituents.

For the reduction, the previously known linear plot[10] is again observed for H_2TPP and CuTPP. The net effect of the four cyanos is to facilitate the reduction of the porphyrin at about 1 V.

An increased difficulty is observed for the oxidation of the porphyrin as the number of cyano substituents increases. However, the effects of the substituents are not additive, and the specific potential shift induced, per cyano, decreases as the number of cyanos on the porphyrin ring increases. This weakening in the specific effect of the successive β substituents may be rationalized in terms of antagonistic inductive effects of these substituents on the lone pairs of the pyrrolic nitrogens.

As a consequence, the potential difference $\Delta E_{1/2}{}^{\text{Ox-Red}}$ between the first oxidation wave and the first reduction wave of the porphyrin ligand decreases as the number of cyano substituents increases (Tables III and IV). The same trend is observed in Table I, where the $\Delta E_{1/2}{}^{\text{Ox-Red}}$ of mono-β-substituted porphyrins decreases as the electron-withdrawing character of the substituent increases. Thus, $\Delta E_{1/2}{}^{\text{Ox-Red}}$ may be considered as characteristic of a series of porphyrins as proposed by Fuhrhop and Kadish,[6] only when the various substituents exert small or equivalent effects in oxidation and in reduction.

On the other hand, in contradistinction with the results on $CuTPP(CN)_x$—where the difference $\Delta E_{1/2}{}^{\text{Ox}} = E_{1/2}{}^{\text{II}} - E_{1/2}{}^{\text{I}}$ = 0.28 ± 0.05 V in oxidation—this difference decreases with the increase of x in the series $H_2TPP(CN)_x$, and the two oxidation waves merge finally in a unique bielectronic wave at $E_{1/2} = +1.43$ V/SCE for $H_2TPP(CN)_4$.

4. Effect of Electron-Withdrawing Substituents on the Electronic Spectra. As already observed,[10,33] these substituents decrease the energy of the transitions in the electronic absorption spectra.

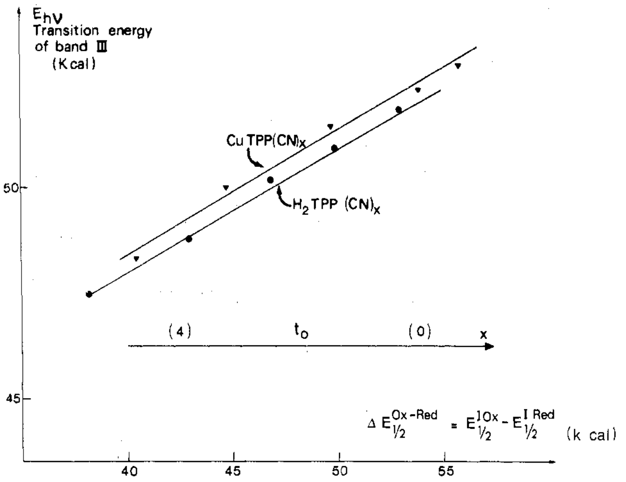

Figure 6. Effects of electron-withdrawing substituents CN: correlated decrease of the ligand field strength ($\sim\Delta E_{1/2}{}^{\text{Ox-Red}}$) and of the electronic transition energy ($E_{h\nu}$(band III)) in $CuTPP(CN)_x$ (▼) and in $H_2TPP(CN)_x$ (●) (x = 0–4).

In the substituted porphyrins studied here, the effect of the strong electron-withdrawing substituents on the low-energy transitions (Tables III and IV) is illustrated by a decrease in the ligand field of the porphyrin, as exemplified in Tables I, III, and IV, by the change of $\Delta E_{1/2}{}^{\text{Ox-Red}} = E_{1/2}{}^{\text{I(Ox)}} - E_{1/2}{}^{\text{I(Red)}}$, whose parallelism is well-known with the energy difference of the HOMO and LUMO orbitals.[27,34,35]

Also, the shifts of $E_{1/2}{}^{\text{I(Red)}}$ and $E_{1/2}{}^{\text{I(Ox)}}$ in Tables III and IV reveal clearly the increase of the electron affinity of the porphyrins with the number of cyano electron-withdrawing groups[10,11] as well as an increase of the ionization energy of these porphyrins with the number of substituents.

Figure 6 illustrates the good correlation between $\Delta E_{1/2}{}^{\text{Ox-Red}}$[36] and the energy ($E_{h\nu}$) corresponding to the spectral band III[33] of the porphyrins $CuTPP(CN)_x$ and $H_2TPP(CN)_x$ with x = 0–4.

The possibility of using ad hoc β substituents to control the spectral and redox properties of metal macrocycle complexes, recently exemplified for nonporphyrinic systems,[37] is thus demonstrated for free-base porphyrins and for metalloporphyrins.

E. Conclusion

In porphyrins, it is remarkable to observe that β substitutions of pyrroles by strong electron-withdrawing groups have pronounced and different effects on the electrochemical oxidation and reduction potentials. Such a difference had not previously been observed, as the substituted porphyrins studied in previous works did not bear strong electron-withdrawing β substituents. This is ascribed to a difference in the nature of the oxidation site (pyrrolic nitrogens) and of the reduction site (π electrons), which is reflected in a difference of their interaction with the substituents. The electron-withdrawing β substituents weaken the ligand field of the porphyrins and analogously the energies of the first bands of their visible spectra.

The present results confirm that the increased interest of β substitutions with strong electron-withdrawing groups on the pyrroles of the porphyrins, already demonstrated in reduction,[14] has led to a better understanding of their redox behavior.

Registry No. H_2TPP, 917-23-7; $H_2TPP(CN)_1$, 54247-32-4; $H_2TPP(CN)_2$, 54247-33-5; $H_2TPP(CN)_3$, 54247-35-7; $H_2TPP(CN)_4$, 52353-92-1; CuTPP, 14172-91-9; $CuTPP(CN)_1$, 54329-85-0; $CuTPP(CN)_2$, 54329-84-9; $CuTPP(CN)_3$, 54329-87-2; $CuTPP(CN)_4$, 54329-88-3; PdTPP, 14187-13-4; $PdTPP(CN)_4$, 57948-04-6; ZnTPP, 14074-80-7; $ZnTPP(CN)_4$, 68307-56-2; $H_2TPP(NO_2)$, 63160-31-6; $H_2TPP(Br)$, 17260-22-9; $H_2TPP(Cl)$, 31905-99-4; $H_2TPP(OEt)$, 54247-28-8; $H_2T(p\text{-}C_6H_4CN)P$, 14609-51-9.

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Notes

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Biological Analogues. A Planar Quadridentate Ligand with an Axial Thioether Tail

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Planar quadridentate systems with an attached tail containing a donor functionality capable of axial coordination have been the subject of considerable recent interest.[1] Such combinations of planar quadridentate and axial coordination occur frequently in biological systems; examples include the axial imidazole and planar heme in hemoglobin and myoglobin[2] and the axial benzimidazole and quasi-planar corrin in vitamin B_{12}.[3] Cytochrome *c* is a six-coordinate system containing a planar heme with the axial sites occupied by histidine imidazole and methionine thioether.[4]

Prompted by the last, we have synthesized the ligand (*S*)-*N*,*N*′-[(2-(methylthio)ethyl)ethylene]bis(salicylidenimine), salmetH_2, a derivative of *N*,*N*′-ethylenebis(salicylidenimine), salenH_2, containing a thioether tail (Figure 1). The purpose was to determine the coordinating ability of the thioether tail, since, although thioether coordination occurs in the biological system, under normal circumstances thioether ligands coordinate only weakly with the first transition elements in their usual oxidation states.[6] We wished to know whether the chelate effect achieved by tail incorporation would enhance the stability or whether other factors were necessary.

Synthesis and Stereochemical Considerations

The synthesis, originating from (*S*)-methionine, is shown in Figure 1, as is the structure of the sought-after metal complexes. The structural requirement for the tail coordination, namely, that the tail carbon atom emanating from the ethylenediamine backbone be axially disposed, is consistent with observations on substituted salen complexes for which it has been found that the ethylenediamine substituents prefer an axial disposition.[5]

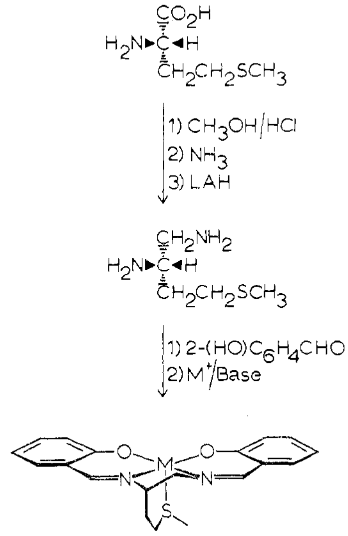

Figure 1. Method of preparation of the salmetH_2 ligand and its complexes.

Results

We have isolated crystalline salmet complexes of copper(II), nickel(II), and iron(III), the latter containing two *N*-methylimidazole (*N*-meim) ligands without which a crystallizable compound could not be obtained. The solid crystalline complexes [Cu(salmet)] and [Ni(salmet)] are dark blue and deep red, respectively, and are quite unlike the colors obtained for the corresponding [Cu(salen)] and [Ni(salen)] complexes. The color of the copper complex is consistent with thioether coordination[6], but new absorption bands could arise in square-planar Cu(II) and Ni(II) salen and salmet complexes because of oxygen–metal interaction between neighboring molecules in the solids. So it is not possible to confidently transfer information from the solid to solution where we show there is no evidence for thioether coordination.

Electronic spectra of [Cu(salmet)] were recorded in chloroform, benzene, methanol, dioxane, dichloromethane, and nitrobenzene. In all cases the visible spectrum (300–800 nm) was identical with that of [Cu(salen)] in the same solvent, indicating lack of coordination of the sulfur in these media. Similarly, electronic spectra of [Ni(salmet)] (diamagnetic)

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