

Facile Aerial Oxidation of a Porphyrin. Part 3.† Some Metal Complexes of *meso*-Tetrakis-(3,5-di-*t*-butyl-4-hydroxyphenyl)porphyrin

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Metal complexes of the title porphyrin were prepared and their behaviour in basified dichloromethane solution examined using u.v.-visible and e.s.r. spectroscopy. The free base, Zn^{II}, Fe^{III}, and Co^{II} complexes undergo drastic colour changes with rapid and irreversible aerial oxidation. Acidification does not regenerate the porphyrin spectrum, but shaking with aqueous metabisulphite or dithionite does. The V^{IV}=O, Mn^{III}, Cu^I, Sn^{IV}, Pd^{II}, and Pt^{II} complexes also change colour but their metalloporphyrin u.v.-visible spectra largely return on acidification. Some deterioration over time in the returned *B* band intensity is noted, which is greatest for the Ni^{II} complex and is most likely due to autoxidation. E.s.r. spectra, arising from oxidation or autoxidation of the complexes to radical species, were observed for the Mn^{III}, Ni^{II}, Zn^{II}, and Sn^{IV} complexes, the latter in neutral dichloromethane. This gave a triplet e.s.r. spectrum that decayed with second-order kinetics. Addition of base to the Sn^{IV} complex quenched the e.s.r. spectrum. An explanation is offered in which the metal modulates electron transfer onto the macrocycle, from the phenoxy *meso*-substituents, *via* back-bonding and changes in porphyrin conformation.

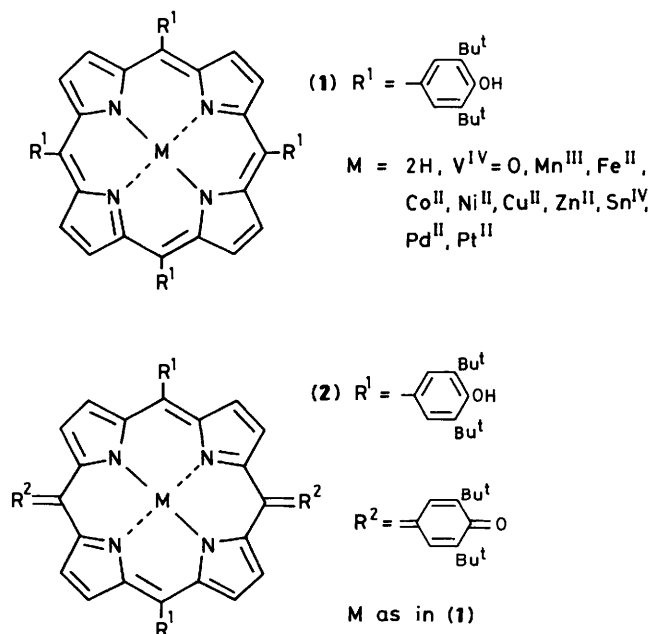
Synthetic metalloporphyrins are showing promise as novel oxygen-reduction catalysts,¹ in fuel cells, and as organic conductors and semiconductors.² This is primarily due to their ability to activate molecular oxygen and mediate electron transfer.³ Synthetic metalloporphyrins are also capable of modelling electron-transfer events in haemoproteins, such as cytochrome P450.^{3b} Consequently, readily oxidisable porphyrins such as (1), *meso*-substituted with suitable functional groups,⁴⁻⁷ could greatly facilitate investigations in these areas. Free-base porphyrin (1), for example, undergoes facile two-

electron aerial oxidation, in base, affording the porphodimethene-like compound (2). Reduction of (2) back to (1) is readily achieved, either chemically,⁴ or electrochemically,⁸ demonstrating that little or no oxidative disruption of the macrocycle has occurred. As we required metal complexes of (1), for studies in oxygen activation and electron transfer, we wished to examine how metal complexation affects the reactivity of the macrocycle to molecular oxygen. This paper reports our findings.

Results and Discussion

Metal insertion (of V^{IV}=O, Mn^{III}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Pd^{II}, Pt^{II}, and Sn^{IV}) into porphyrin (1) was by literature methods.⁹ With a few exceptions this was straightforward and similar to the preparation of the analogous TPP complexes. However, copper insertion [with copper(II) acetate and pyridine as solvent⁹] afforded a green solution that, on sodium dithionite reduction, turned red. This latter solution gave a u.v.-visible spectrum typical of a copper metalloporphyrin complex. Oxidation of the macrocycle, therefore, occurred during metal insertion. Copper insertion under inert atmosphere did not lead to macrocyclic oxidation. Attempts to insert silver by the same acetate method⁹ led to oxidation of the macrocycle, from (1) to (2) but no metal insertion, even under an inert atmosphere. Presumably silver(I) acetate is a powerful enough oxidising agent to convert (1) into (2).

Apart from the usual method of tin insertion,⁹ simply allowing tin(II) chloride to stand in contact with a pyridine solution of the oxidised porphyrin (2), under an inert atmosphere at room temperature, produced the tin(IV) complex of porphyrin (1). The reaction can be followed colorimetrically, by the gradual change from the mauve of (2) to the fluorescent, and dichroic, turquoise-red of the tin(IV) porphyrin. Presumably, as the tin(II) cation is inserted, an internal two-electron redox reaction reduces (2), while the tin(II) cation is oxidised to tin(IV). A similar procedure is currently under investigation as a possible route to Group V and hitherto unknown Group VI 'metallo' porphyrins.



† Part 2, ref. 6.

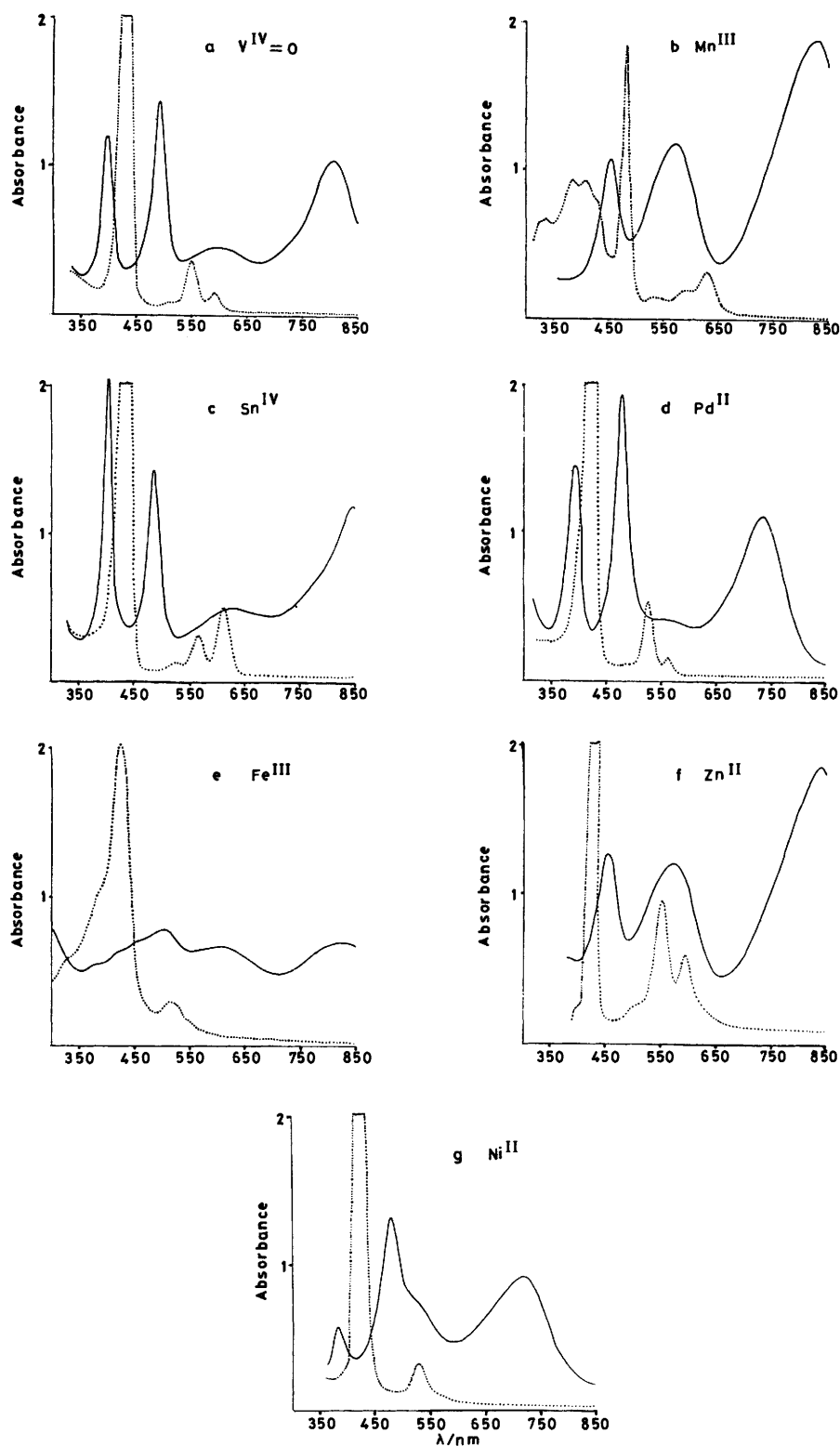


Figure 1. U.v.-visible spectra of representative metal complexes of (1) in neutral (····) and basified (—) dichloromethane

Metal complexes of (1), in dichloromethane, gave u.v.-visible spectra similar to the analogous TPP complexes.¹⁰ Addition of tetra-*n*-butylammonium hydroxide (1M solution in methanol; 3–4 drops) to these solutions, however, produced drastic colour and spectroscopic changes. The typical colours of the dilute metalloporphyrin solutions (pink for central metal cations 2H^+ , Zn^{II} , $\text{V}^{\text{IV}}=\text{O}$, Co^{II} , and Cu^{II} ; orange-brown for Fe^{III} ,

Ni^{II} , Pd^{II} , and Pt^{II} ; turquoise-red for Sn^{IV} ; green for Mn^{III}) were replaced by deep mauve, violet, or blue colours. This corresponded to a marked reduction in intensity and blue shift (from 420–435 to 380–410 nm for $\text{V}^{\text{IV}}=\text{O}$, Ni^{II} , Cu^{II} , Sn^{IV} , Pd^{II} , Pt^{II} , and from 483 to 455 nm for Mn^{III}), or complete removal (for H_2 , Zn^{II} , Fe^{III} , Co^{II}) of the metalloporphyrin *B* band, and the disappearance of the *Q* bands (see Figure 1 and Table 1). The

Table 1. U.v.-visible spectra of metal complexes of (1) in neutral and basic dichloromethane

Compound	Neutral CH ₂ Cl ₂ ^b	Basic CH ₂ Cl ₂ ^{b,c}	Class ^d
V ^{IV} =OP ^a	434 (481), 535.5 (26), 594 (11)	399.5 (86), 492 (105), 600 (br, 35), 807.5 (76)	A
Mn ^{III} P	325 (sh), 335 (36), 385 (50), 407 (50), 483 (99), 535 (8), 590 (11), 628 (17)	455 (58), 570 (63), 825 (100)	A
Fe ^{III} P	424 (114), 515 (16), 550 (sh)	300 (44), 505 (44), 825 (100)	B
Co ^{II} P	418 (331), 528 (23), 568 (sh)	465 (41), 532 (23), 820 (39)	B
Ni ^{II} P	421 (234), 532 (75), 570 (sh)	385 (31), 479 (70), 720 (50)	A-B
Cu ^{II} P	421 (536), 543 (27), 582 (10)	393 (53), 475 (98), 607 (40), 817 (73)	A
Zn ^{II} P	426 (600), 551 (54), 592 (34)	454 (72), 575 (68), 837 (104)	B
Sn ^{IV} P	439 (454), 525 (sh), 615 (30)	406 (126), 490 (88), 630 (br, 28), 845 (73)	A
Pd ^{II} P	424 (460), 529 (35), 564 (9)	391 (94), 475 (124), 734 (72)	A
Pt ^{II} P ^e	411 (302), 514 (26), 542 (sh, 2)		A

^a P is the dianion of the free-base porphyrin (1). ^b Absorption wavelengths in nm; decadic extinction coefficient ($\times 10^{-3}$) in parentheses. ^c Dichloromethane made basic by addition of a solution of tetra-*n*-butylammonium hydroxide in methanol (1M, 3–4 drops). ^d Class A complexes regain most of their Soret absorption on acidification; class B complexes do not. ^e See ref. 10.

latter were replaced by more intense bands at *ca.* 450–500, 540–630, and 700–850 nm. This last band is reminiscent of tetrapyrrole macrocycles with interrupted conjugation pathways,¹¹ *e.g.*, oxophlorins and isoporphyrins.

Acidifying these basified solutions, with several drops of trifluoroacetic acid (TFA) either (a) regenerated the metalloporphyrin spectrum to a greater (V^{IV}=O, Mn^{III}, Cu^{II}, Pd^{II}, Pt^{II}, and Sn^{IV}) or lesser (Ni^{II}) degree (termed class A behaviour) or (b) failed to regenerate the metalloporphyrin spectrum (H₂, Zn^{II}, Fe^{III}, and Co^{II}) (class B behaviour).

Class B behaviour corresponds to oxidation of the macrocycle. For the free-base porphyrin, this leads to formation of a dioxoporphodimethene-like compound⁴ that is e.s.r.-silent [Nolan *et al.*, however, report observation of a weak e.s.r. triplet and paramagnetic broadening in the n.m.r. spectrum of (2)^{5b}]. The zinc metalloporphyrin, on the other hand, oxidises to an e.s.r.-active species.⁵ Compared with the three-banded u.v.-visible spectra of the free base^{4,5} and the zinc oxidised-porphyrin (see Figure 1f), the spectra of the Fe^{III} (see Figure 1e) and Co^{II} oxidised macrocycles are broad and relatively featureless. Reduction with sodium metabisulphite largely regenerates the metalloporphyrin spectrum, with its typical intense *B* band, for all of the class B-type oxidised species. For the Fe^{III} and Co^{II} complexes, this regenerated *B* band showed some loss in optical density compared with the original starting metalloporphyrin. This implies that, although the integrity of the macrocyclic ring has largely been maintained on initial oxidation, some further oxidative ring opening has occurred.

Class A spectra consist of three main bands (see Figure 1a–d, g), two of these are sharp and straddle (370–410 and 460–495 nm) the position occupied by the original metalloporphyrin *B* band, but at much reduced intensity. These bands are reminiscent of hyperporphyrin spectra obtained by the interaction of partially filled metal *p* or *d* orbitals with the

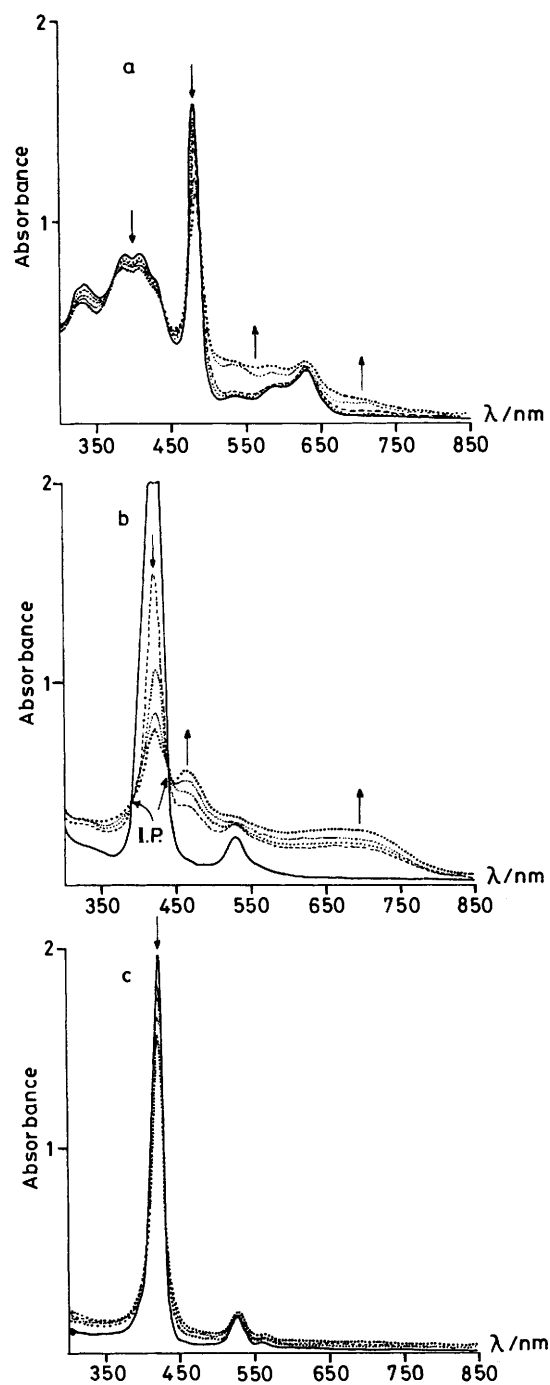


Figure 2. Decrease in regenerated metalloporphyrin *B* band optical density for: a, Mn^{III} complex; b, Ni^{II} complex (isosbestic points at 395 and 435 nm); c, Pd^{II} complex

porphyrin π -system.¹² There is also a strong, broad band, further to the red (720–850 nm) that is reminiscent of oxophlorin and oxyporphyrin spectra. The exact positioning of these bands seems to change with the central metal cation (Table 1).

Class A behaviour corresponds to only small amounts of aerial oxidation. This was assessed by neutralisation of the basified porphyrin solutions. Stock solutions of the metalloporphyrins were prepared and a few drops of methanolic tetra-*n*-butylammonium hydroxide solution added. The observed colour changes were complete within 30 s. Portions of these

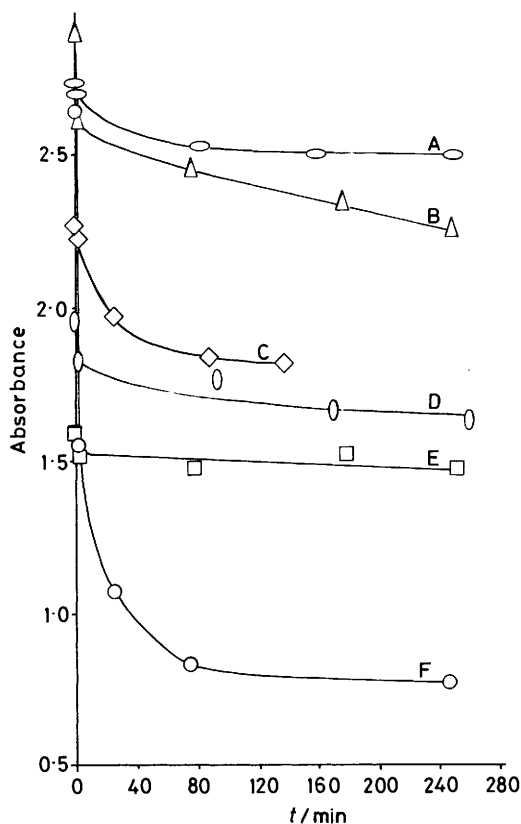


Figure 3. Decrease in regenerated metalloporphyrin *B* band optical density, the abscissa representing time elapsed after addition of base ($t = 0$), before neutralisation with TFA: Sn^{IV} complex, A; Cu^{II} complex, B; $\text{V}^{\text{IV}}=\text{O}$ complex, C; Pd^{II} complex, D; Mn^{III} complex, E; Ni^{II} complex, F

stock solutions were withdrawn at intervals, placed in a 1 cm cuvette and neutralised with TFA. It was noticed that the optical density of the regenerated *B* band decreased compared with the original *B* band prior to the addition of base. This decrease continued the longer the stock solution was left before neutralising with TFA (Figures 2 and 3). Eventually, however, the decrease stopped so that a constant regenerated *B* band optical density was obtained (Figure 3). For the Ni^{II} porphyrin, the optical density of the regenerated *B* band fell sharply before reaching its constant value, giving isosbestic points at 395 and 435 nm (Figures 2b and 3). These effects are probably caused by autoxidation of the metalloporphyrins by dissolved oxygen. Several of these compounds, in fact, give weak e.s.r. signals, on addition of base, again suggesting some autoxidation in solution.

For the $\text{V}^{\text{IV}}=\text{O}$, Fe^{III} , Co^{II} , and Cu^{II} complexes, the paramagnetism of the central metal cation masks any contribution from oxidised macrocycle, and the palladium and platinum complexes are e.s.r.-silent under these conditions. However, the Mn^{III} , Ni^{II} , and Zn^{II} complexes do give weak e.s.r. signals (see Figure 4) in base that are attributable to oxidation of the macrocycle or its *meso*-substituents. The Mn^{III} and Zn^{II} complexes have e.s.r. spectra that may be interpreted as collapsed 1:1:1 triplets, while the Ni^{II} complex gives a complicated spectrum that may be interpreted as two radical species with overlapping spectra, one a 1:2:1 triplet, while the other is a doublet. The Sn^{IV} complex is unusual in that it gives a weak triplet e.s.r. signal in neutral dichloromethane ($g\ 2.0066 \pm 0.0006$, $a_{\text{H}}\ 1.78$, $\Delta H_{\text{pp}}\ 1.20\ \text{G}$; see Figure 4a) which disappears on addition of the methanolic base. Neutralisation, with TFA, partially regenerates the triplet e.s.r. spectrum.

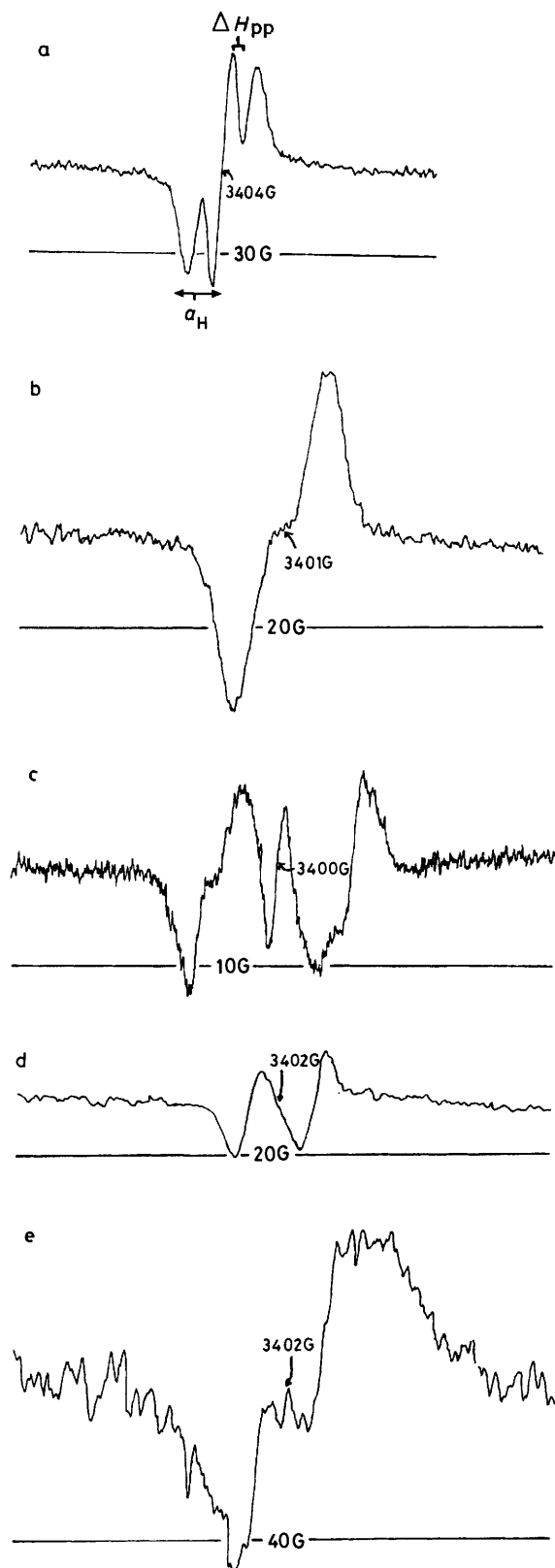


Figure 4. E.s.r. spectra of some metallocomplexes of (1): a, Sn^{IV} complex in neutral dichloromethane ($g\ 2.0066 \pm 0.0006$, $a_{\text{H}}\ 1.78\ \text{G}$, $\Delta H_{\text{pp}}\ 1.20\ \text{G}$); b, Mn^{III} complex in basified dichloromethane ($g\ 2.0088 \pm 0.0006$); c, Ni^{II} complex immediately after addition of base ($g\ 2.00745 \pm 0.0006$); d, Ni^{II} complex, 20 min after addition of base ($g\ 2.0074 \pm 0.0006$); e, Zn^{II} complex after addition of base ($g\ 2.0078 \pm 0.0006$). See text for best-fit a_{H} , a_{N} , and ΔH_{pp} values

Table 2. Half-wave potentials (*V* versus s.c.e.^a) of porphyrin (1) and its metal complexes in neutral and basic^b dichloromethane (DCM) compared with equivalent TPP^c complexes

Metal	Porphyrin half-wave potentials					
	TPP		P in DCM		P in basic DCM	
	First wave	Second wave	First wave	Second wave	First wave	Second wave
H ₂	0.95	1.28	0.79		0.27	0.48
V ^{IV} =O	1.00	1.22	1.00	1.22	0.24	
Mn ^{III}			1.01	1.24	0.18	0.35
Fe ^{III}	1.40		1.10			
Co ^{II}	1.06	1.26	0.83	1.10	0.10	0.55
Ni ^{II}	1.10	1.40	1.05		0.70	
Cu ^{II}	0.90	1.16	0.90	1.15	0.23	
Zn ^{II}	0.71	1.03	0.63	0.97	0.16	0.63
Sn ^{IV}			>1.3			
Pd ^{II}	1.02	1.47	0.98	1.24	0.22	0.80

^a Saturated calomel electrode. ^b By addition of sodium ethoxide. ^c *meso*-Tetraphenylporphyrin: see R. H. Felton and D. G. Davies, ref. 12b.

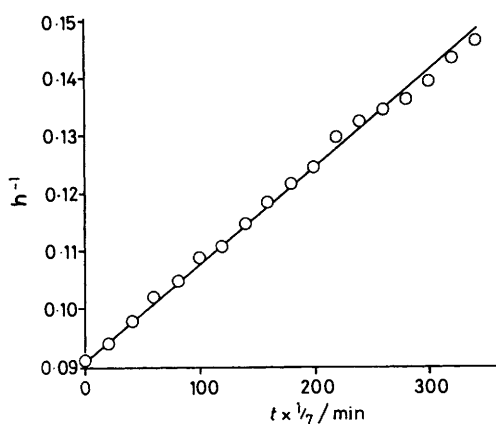


Figure 5. Decay of Sn^{IV} radical e.s.r. spectrum in neutral dichloromethane. The decay follows second-order kinetics according to the rate expression $\frac{1}{2}d[A]/dt = k[A]^2$, where $[A]$ = concentration of radical and is proportional to intensity of e.s.r. spectrum. Integration gives $[A]_0^{-1} - [A]^{-1} = 2kt$. A plot of h^{-1} (inverse height of the main e.s.r. triplet) against time gives a straight line whose slope = $2k$ (k is the rate constant for radical decay). From the graph, k $0.98 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

Decay of the Sn^{IV} complex's e.s.r. spectrum in neutral dichloromethane followed second-order kinetics (see Figure 5) with respect to the radical. A possible mechanism for this decay (see Scheme) envisages radical dimerisation, *via* a peroxy link, followed by heterolytic disproportionation of the dimer to give the two-electron-oxidised product and the starting metalloporphyrin. In base, the Sn^{IV} complex is e.s.r.-silent. This is envisaged as a small amount of autoxidation leading to diradical formation. This is followed by intramolecular electron pairing to form oxidised Sn^{IV} porphyrin. On the whole, the e.s.r. behaviour of these metalloporphyrins on addition of base is generally similar to that of oxophlorins,¹³ which tend to be contaminated with small amounts of radicals by autoxidation.

The u.v.-visible data may be interpreted in the following way. Base deprotonates the hydroxy groups, generating phenoxide anion substituents which, because of their greater electron-releasing power,¹⁴ can interact strongly with the porphyrin π -system.¹⁵ The extent of this interaction will depend on the relative coplanarity of the phenoxide anion substituents to the macrocycle, but it will have a two-fold effect. (a) It creates a

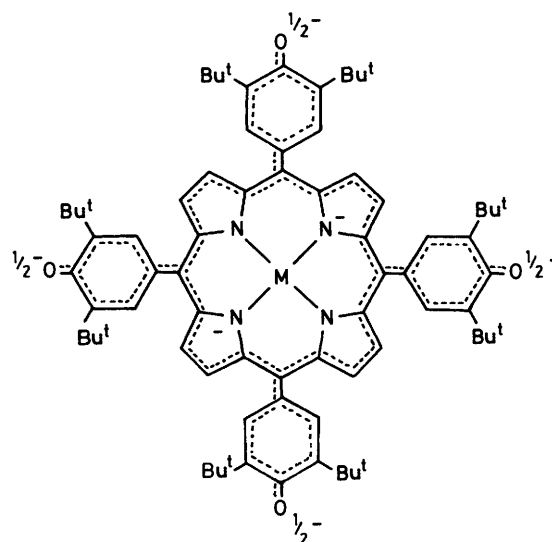
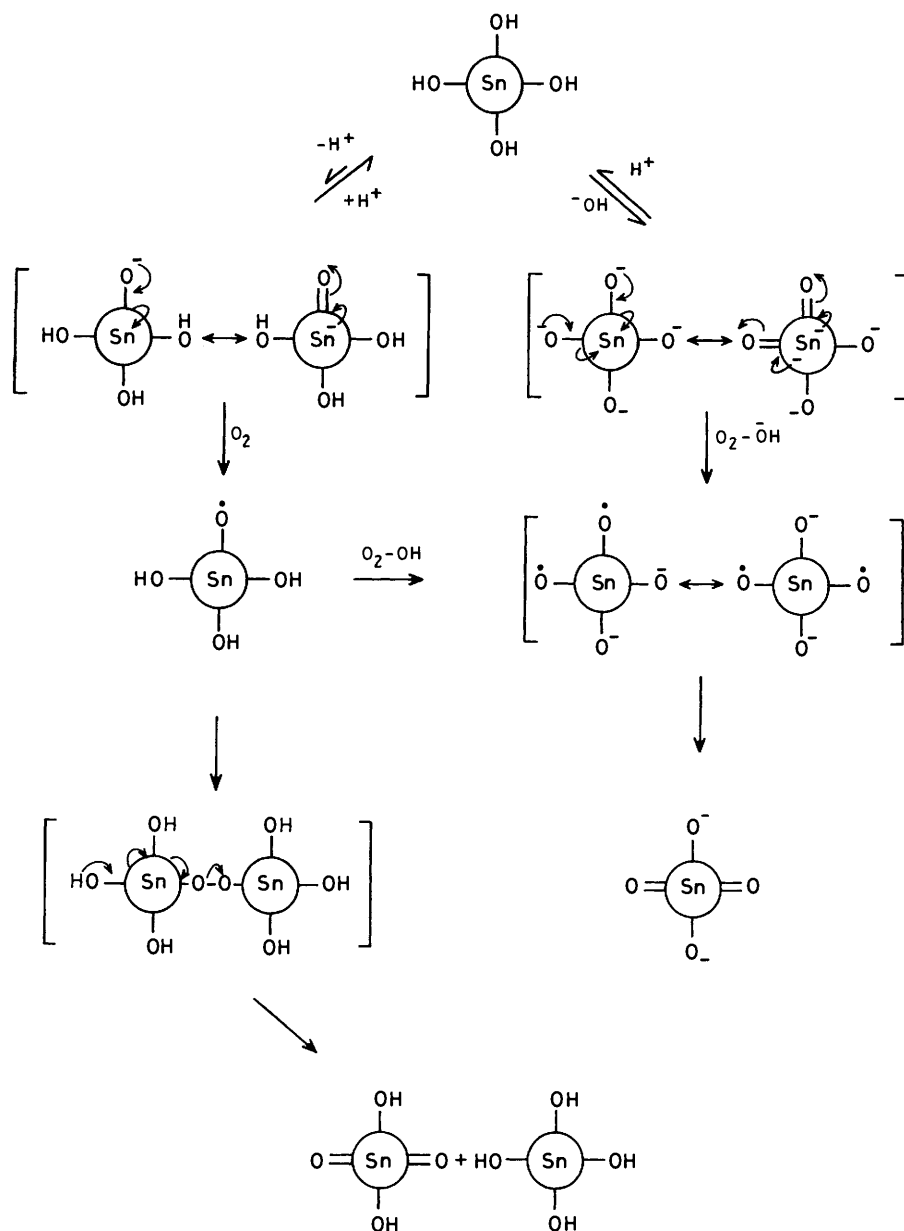


Figure 6. New chromophore formed by π -orbital overlap of phenoxide anion substituents with the porphyrin macrocycle

new chromophore (*e.g.* see Figure 6) from the interaction of phenoxide anion substituents with porphyrin π - and π^* -molecular orbitals (Figure 7); this would produce some formal double-bond character between the phenoxide anion substituent(s) and the macrocycle, so that the chromophore would be expected to have some features resembling those of oxophlorins,¹¹ *e.g.*, a broad band at long wavelength. (b) Increasing electron density over the porphyrin macrocycle would lower the redox potential for oxidation of the whole system, a point illustrated by the cyclic voltammetric data shown in Table 2.

In neutral dichloromethane, the average difference between the first and second oxidation waves is *ca.* 260 mV, which is comparable to the analogous TPP complexes.^{12b} This shows that the metal complexes of (1) behave as expected of a substituted TPP during cyclic voltammetry. However, on addition of base (sodium ethoxide) both oxidation waves occur at much lower potentials, indicating increased ease of electron removal. This must be due to greater electron availability on the macrocycle.

The metal can modulate the flow of electron density onto the macrocycle in two ways. First, by complexing with the por-



Scheme.

phyrin, the metal imposes some constraint on the macrocycle's ability to become deformed about its pyrrole α -carbons.¹⁶ This would increase the phenoxide anion substituents' activation energy for rotation,^{17,18} possibly hindering their approach to coplanarity with the macrocycle which, in turn, could curtail interaction of the porphyrin and phenoxide anion π -systems. Even so, *meso*-aryl-substituent rotation in metalloTPPs has been shown to occur^{17,18} and could be enhanced especially where accommodation of the metal by the macrocycle causes 'ruffling' of the macrocycle (e.g., Ni^{II}). Secondly, the metal may itself be interacting strongly with the porphyrin π -system¹² (e.g., Pd, Pt, and Mn).

On the simplest view, the extra electron density flowing onto the macrocycle from the phenoxide anion substituents would undermine the integrity of the porphyrin aromatic ($4n + 2$; $n = 4$) π -system, mixing in some antiaromatic ($4n$; $n = 5$), triplet character into the porphyrin singlet ground state (see Figure 7b). Clearly, this would render the whole system more amenable to oxidation, especially by molecular oxygen (free

base, Zn^{II}, Fe^{III}, and Co^{II} complexes). That the *meso*-substituent(s) do not oxidise without assistance from the macrocycle, is suggested by the following argument.

The compound 3,5-di-*t*-butyl-4-hydroxybenzaldehyde has an electron-withdrawing ($-\text{CH}=\text{O}$) group *para* to the hydroxy group. The ¹H n.m.r. spectrum of this material in CDCl₃ shows no paramagnetic broadening on addition of methanolic base (1M-tetra-*n*-butylammonium hydroxide in methanol). Also there was no appearance of colour when the base was added. Both these observations indicate that aerial oxidation has not taken place, which suggests that the electron-withdrawing substituent stabilises the molecule by delocalising the phenoxide negative charge. Now the *meso*-carbons of porphyrins are well known to be electron deficient, due to the electron-withdrawing effect of the neighbouring pyrroline-type rings.⁹ Consequently, it may be argued that the *meso*-carbons of (1) would have the same stabilising, electron-withdrawing effect on the phenoxide *meso*-substituents as the formyl group. As mentioned above, however, the macrocycle would be destabilised

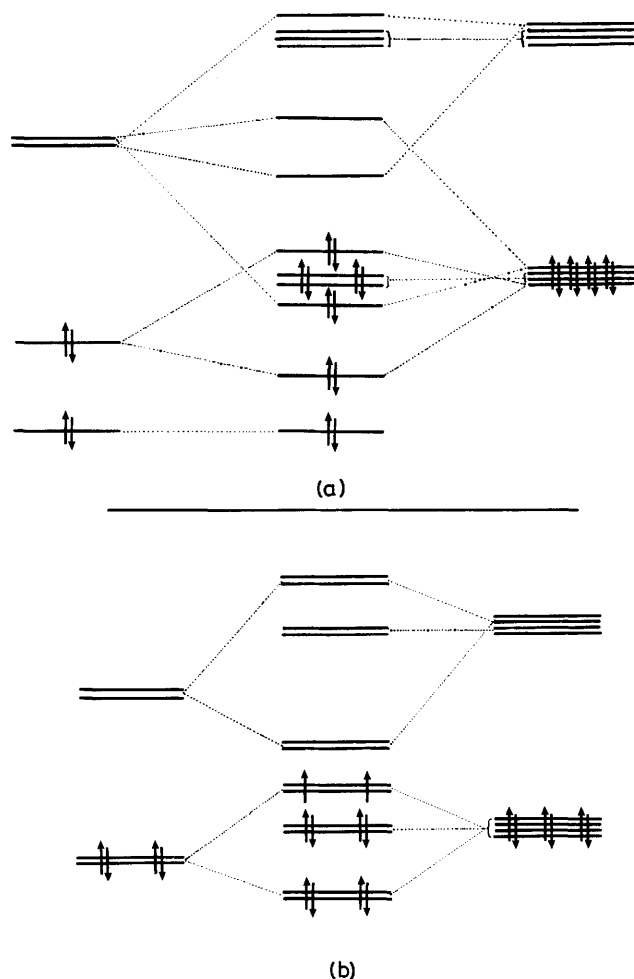


Figure 7. Possible molecular orbitals formed by overlap of *meso*-phenoxy substituents with: a, porphyrin macrocycle; b, oxidised macrocycle

by this coupling of the porphyrin and *meso*-substituent(s) π -systems. Oxidation of the macrocycle would lead to oxidation of the whole system.

Where the central metal possesses vacant, or partially vacant, *d*- or *p*-orbitals of the appropriate energy,^{12a} then the extra electron density on the macrocycle could conceivably be accommodated here. This would lower the formal oxidation state of the metal, stabilisation of which could be achieved by *d*- π^* (or *p*- π^*) back-bonding from the metal to the porphyrin π^* orbitals. For the Fe^{III} and Co^{II} complexes, oxygen bound to the metal would provide a site for oxidation.^{12b}

The net effect of intramolecular electron-transfer from the phenoxide anion substituents onto the porphyrin macrocycle is to (a) raise the energy of the π^* orbitals, which leads to a blue shift in the porphyrin *B* band (*i.e.*, increase in energy of the π - π^* transition¹⁰), as observed, typical of hyper-type porphyrin spectra,^{12a} (b) shorten the excited-state lifetime of the porphyrin by promoting an extremely rapid reaction to the porphyrin optical state (*cf.* as in quinone-porphyrins,¹⁹ but here electron transfer is in the opposite direction, from the porphyrin to the *meso*-substituent). This would lead to uncertainty broadening of the transition, and a reduction in its oscillator strength, and therefore extinction coefficient, as discussed elsewhere.^{19b}

We obtained weak e.s.r. spectra for the Mn^{III}, Ni^{II}, and Zn^{II} complexes in basified dichloromethane, and for the Sn^{IV} complex in neutral dichloromethane, which we ascribed to oxo-

phlorin-like autoxidation. Traylor *et al.*^{5b} also obtained a radical species for the zinc complex, which they observed as a 1:2:1 triplet and represent as a diradical. By contrast, in this work we obtain for the zinc complex an e.s.r. spectrum that is best described as a collapsed 1:1:1 triplet (see Figure 4e).

Traylor *et al.*^{5b} represent the diradical using the conventional porphyrin formulation that envisages the macrocycle with an 18-membered conjugation pathway. This consists of two pyrrole and two pyrroline units. Inspection of this conjugated system shows that two unpaired electrons on two *meso*-substituents could pair up through the porphyrin π -system, yielding an e.s.r.-silent oxidised zinc porphyrin.

Now, metalloporphyrin formation is known to generate a formal porphyrin dianion which stabilises an 18 π 16-membered delocalisation pathway.^{16,20} Using this formalism, two different diradical species for the oxidised zinc porphyrin may be envisaged, in which the unpaired electrons reside on *meso*-substituents either '*cis*' or '*trans*' to each other²¹ (see Figures 8a and b). These might have slightly different e.s.r. parameters, which could account for the asymmetry observed in the e.s.r. spectrum of the oxidised zinc complex (see Figure 4e). Alternatively, the same formalism could explain our observation of an apparent 1:1:1 triplet e.s.r. spectrum for this species. Such triplets would be observed if the unpaired electron(s) interact with *one* atom with nuclear spin, $S = 1$, *e.g.*, a nitrogen atom. Thus, the e.s.r. spectrum suggests that the unpaired electron density resides mainly on a central nitrogen atom. The asymmetry could then be a result of some mixing in of the 1:2:1 triplet e.s.r. spectrum [in which unpaired electron density resides on the *meso*-substituent(s)].

For the platinum and palladium complexes of (1), extensive *d*- π^* backbonding^{10,22} may be thought of as stabilising a 22 π 20-membered pathway (Figure 8c). In any diradical formed during autoxidation, it is possible for electron pairing to occur through the macrocycle.

The tin(IV) complex of (1) forms a small amount of radical in neutral dichloromethane. Presumably, the inductive effect of the tin(IV) cation (plus a trace of water) would be enough to cause ionisation of one of the porphyrin's aryl hydroxy groups, which would be followed by autoxidation as in the Scheme. Addition of base would further deprotonate the *meso*-aryl substituents as before, autoxidation generating a diradical. An 18 π , 18-membered delocalisation pathway would allow two unpaired electrons on *meso*-aryl substituents to pair through the macrocycle, leading to loss of the e.s.r. signal (see Figure 8d).

The Mn^{III} complex of (1) in basic dichloromethane gives a weak e.s.r. spectrum. This can be satisfactorily modelled⁶ as a collapsed 1:1:1 triplet, using the experimentally determined *g* value (2.0088 ± 0.0006) and best-fit hyperfine splitting constant (a_N 1.11 G) and peak-to-peak width (ΔH_{pp} 1.27 G). As with the zinc complex, this implies that unpaired electron density is being localised on *one* of the central nitrogens. The porphyrin 'frontier' orbitals include either four (a_{2u}), two (e_g or b_{1u}), or none (a_{1u}) of the central nitrogens.²³ An orbital embracing only one nitrogen can be tentatively envisaged if electron density flows onto the macrocycle from a phenoxy substituent (see Figure 8e). Presumably, the Mn^{III} cation can synergistically back-donate excess of electron density *via* its already extensive interaction^{12a} with the macrocycle π^* system. Thus, the Mn^{III} cation would stabilise a formal 'oxidised' macrocycle, while it is 'reduced'. Neutralisation, with TFA, would cause electron density to flow back to the *meso*-substituents (*via* protonation of the phenoxy groups), so accounting for this compound's group A behaviour. However, in basic dichloromethane, autoxidation would leave unpaired electron density on a central nitrogen atom (Figure 8e).

The Ni^{II} complex gives a weak e.s.r. spectrum, in basic dichloromethane, that is strongly asymmetric. This suggests the

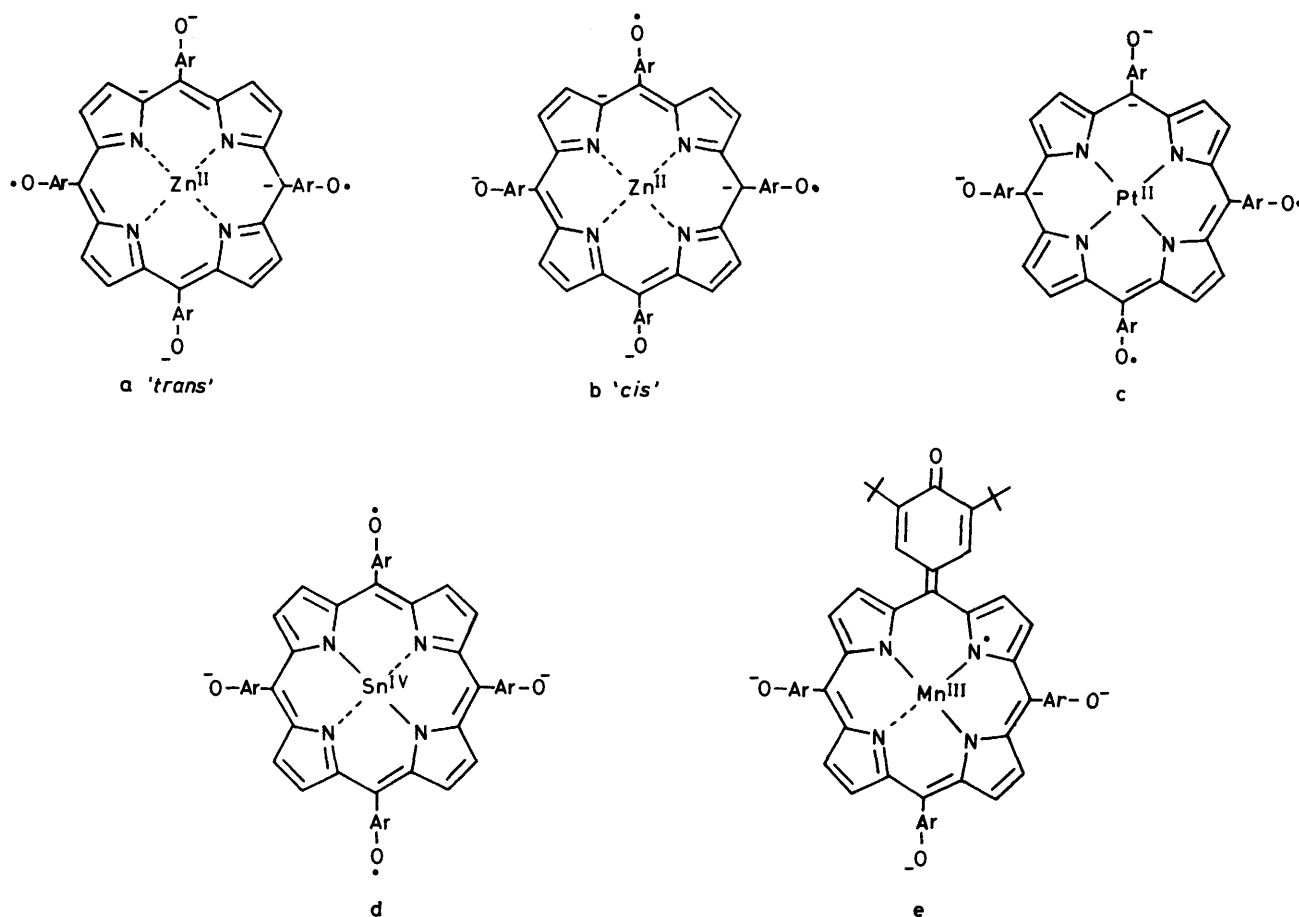


Figure 8. Effect of metals on conjugation pathways: a and b, Zn^{II} stabilises an 18π 16-membered path; c, Pd^{II} and Pt^{II} , a 22π 20-membered path; d, Sn^{IV} , an 18-membered path; e, Mn^{III} complex, radical has unpaired electron density on one nitrogen

presence of more than one radical species. Indeed, the spectrum (Figure 4c and d) changes with time (Figure 4c is the spectrum immediately after the addition of base, while 4d is 20 min later), indicating the two species have different life-times. The overall spectrum (Figure 4c) is best modelled by assuming there are two paramagnetic species present in a 2:1 ratio, the first gives a triplet e.s.r. spectrum, with Gaussian lineshape, having g 2.00745 ± 0.0006 , hyperfine splitting constant a_H 1.21 G, and linewidth ΔH_{pp} 0.47 G. This would arise from unpaired electron density on the *meso*-aryl substituent (which has two hydrogen nuclei). The second component can be modelled as a partially resolved doublet, again with a Gaussian lineshape, due to splitting from a nucleus of spin $s = \frac{1}{2}$. The e.s.r. parameters are g 2.0074 ± 0.0006 , a_H 2.35, and ΔH_{pp} 0.94 G. As yet, we are unable to account satisfactorily for this spectrum in terms of any known structural features. However, because the Ni^{II} cation is slightly too small to fit into the central 'hole' of the porphyrin,²⁴ Ni^{II} porphyrins, in the solid state, crystallise in two polymorphic forms, triclinic and tetragonal. In the former, the Ni^{II} cation is paramagnetic and centred in a flat porphyrin ring, while in the latter the Ni^{II} cation is diamagnetic and the macrocycle experiences extensive ruffling. If the two forms persist in solution for any length of time then several radical species could arise. Further work on the Ni^{II} complex is in progress.

Conclusions.—Metal complexation of porphyrin (1) modulates its reactivity towards aerial oxidation in basic dichloromethane solutions. The phenoxy groups labilise the macrocycle towards oxidation. Consequently, where there is no strong interaction between the metal and the porphyrin (Zn^{II}), the

macrocycle undergoes a two-electron oxidation^{5b} as in the metal-free porphyrin. However, if this oxidation leads to a diradical species, this is because the metal stabilises a macrocyclic conjugation pathway that inhibits electron pairing. When there is a strong electronic interaction between the central metal cation and the porphyrin, aerial oxidation can occur if the oxygen can co-ordinate to the metal (Fe^{III} and Co^{II}). Otherwise, the metal deals with excess of electron density on the macrocycle by back-bonding into the porphyrin π^* system. Although some autoxidation can still occur (as witnessed by the e.s.r. behaviour of some of these complexes), with the exception of the Ni^{II} complex, the macrocycle remains largely intact to aerial oxidation. Consequently, some of these metal complexes could find practical utility as, for example, coatings for modified electrodes in fuel cells *etc.*, where their stability to being cycled through several oxidation states will be beneficial. Experiments along these lines are in progress. Preliminary results⁸ indicate that modification of a glassy carbon electrode with several of these porphyrins improves its electrochemical performance during oxygen reduction. These and other results will be reported elsewhere.

Experimental

Porphyrin (1) was synthesised by a literature method.^{4,5}

Metals were inserted into porphyrin (1) by literature methods.⁹ The following analytical data were recorded.

Vanadyl(IV) complex of (1) (Found: C, 74.3; H, 7.9; N, 4.7. $C_{76}H_{92}N_4O_4 \cdot VO \cdot H_2O$ requires C, 75.4; H, 7.8; N, 4.6%).

Manganese(III) complex of (1) (Found: C, 72.6; H, 7.4; N, 4.4.

$C_{76}H_{92}N_4O_4 \cdot MnCl \cdot 2.5H_2O$ requires C, 72.4; H, 7.7; N, 4.45%.
Iron(III) complex of (1) (Found: C, 74.6; H, 7.7; N, 4.5).
 $C_{76}H_{92}N_4O_4 \cdot FeCl \cdot 0.5H_2O$ requires C, 74.5; H, 7.6; N, 4.6%.
Cobalt(II) complex of (1) (Found: C, 75.5; H, 7.8; N, 4.7).
 $C_{76}H_{92}N_4O_4 \cdot Co \cdot 1.5H_2O$ requires C, 75.4; H, 7.85; N, 4.6%.
Nickel(II) complex of (1) (Found: C, 76.6; H, 7.8; N, 4.8).
 $C_{76}H_{92}N_4O_4 \cdot Ni \cdot 0.5H_2O$ requires C, 76.5; H, 7.7; N, 4.7%.
Copper(II) complex of (1) (Found: C, 76.9; H, 7.9; N, 4.6).
 $C_{76}H_{92}N_4O_4 \cdot Cu$ requires C, 76.8; H, 7.75; N, 4.7%.
Palladium(II) complex of (1) (Found: C, 73.1; H, 7.6; N, 4.6).
 $C_{76}H_{92}N_4O_4 \cdot Pd \cdot H_2O$ requires C, 73.05; H, 7.53; N, 4.5%.
Tin(IV) complex of (1) (Found: C, 67.7; H, 7.3; N, 4.3).
 $C_{76}H_{92}N_4O_4 \cdot SnCl_2 \cdot 2H_2O$ requires C, 67.6; H, 7.1; N, 4.15%.

For u.v.-visible spectroscopy, stock solutions of the porphyrins were prepared in dichloromethane ($10^{-4}M$; 100 cm^3) and their spectra run on a Pye-Unicam SP7-500 u.v.-visible spectrophotometer, fitted with a Philips PM 8040 X-Y recorder. A solution of tetra-n-butylammonium hydroxide in methanol (1M; 3–5 drops) was then added to each stock solution and their spectra rerun. Neutralisation (to test the amount of autoxidation) was performed by withdrawing portions of these basic solutions, placing in a cuvette, and adding trifluoroacetic acid (1–2 drops). The u.v.-visible spectrum was then re-recorded.

E.s.r. spectra were obtained on a Bruker ER 200t instrument, using freshly prepared solutions of the metalloporphyrins in dichloromethane (as supplied), to which had been added several drops of 1M-tetra-n-butylammonium hydroxide in methanol. A solid solution of Mn^{II}-doped (190 p.p.m.) MgO was used as reference. Computer simulations of these spectra were performed on a CDC mainframe computer. Fitting was performed using experimentally determined values of g and 'best-guess' values of splitting constants (a_H and a_N) and line widths (ΔH_{pp}). The relative peak heights and shapes could be fitted using Gaussian line shapes.

Cyclic voltammograms were performed in neutral and basic nitrogen-degassed, dried dichloromethane, with tetra-n-butylammonium fluoroborate (0.1M) as supporting electrolyte. For the basic solutions, sodium ethoxide in ethanol ($10^{-2}M$) was added, after purging with nitrogen.

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