

Spectral and electrochemical properties of deformed short-chain basket-handle iron (III) porphyrins

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Abstract. The spectral and electrochemical properties of series of deformed iron(III) derivatives of short-chain basket-handle porphyrins are reported. ¹H NMR and optical studies demonstrated that deformation arises because of the bridging of opposite phenyl groups by short chains. Axial ligation studies indicate that the straps present over both sides of the porphyrin ring do not prevent the entry of small ligands. Electrochemistry in four different solvents suggests the stabilisation of Fe(II) and Fe(I) over Fe(III) in strong coordinating solvents.

Keywords. Porphyrins; basket-handle iron; ¹H NMR; axial ligation; short-chain bridges.

1. Introduction

Iron is an essential metal ion for the function of heme proteins (Wilson and Erecinska 1979). The functional differentiation of hemoglobin, myoglobin, cytochromes, catalases and peroxidases which have the same prosthetic group, namely protoporphyrin IX, arises mainly from differences in axial ligation to the heme iron in addition to the differences in the protein environment surrounding the heme. Thus, the physiochemical properties of the complexes of iron porphyrins are of essential importance for understanding the properties of heme proteins. During the past few years, several superstructured iron porphyrins such as picket fence, capped, cyclophane, pocket crowned, strapped and basket-handle were synthesized and several factors affecting the thermodynamics and kinetics of the dioxygen and several other small molecules binding to these protected hemes investigated and discussed (Morgan and Dolphin 1987). We have recently reported the characterisation of a series of deformed short-chain basket-handle porphyrins in view of their biological importance (Reddy and Chandrashekar 1992; Reddy *et al* 1992, 1993; Ravikanth *et al* 1993; Ravikanth and Chandrashekar 1993, 1995). The observed unusual spectroscopic properties were related to the distortion of the porphyrin ring induced by the short bridging groups. In this paper, we report the characterisation of iron(III) derivatives of adjacent-*cis* and adjacent-*trans* isomers of short-chain basket-handle porphyrins (figure 1) and study the deformation effect on the chemistry of iron(III) porphyrins. The bridging chains selected include simple alkyl chain, alkyl chain containing aromatic ring and alkyl chain containing aromatic ring with electron-withdrawing substituents.

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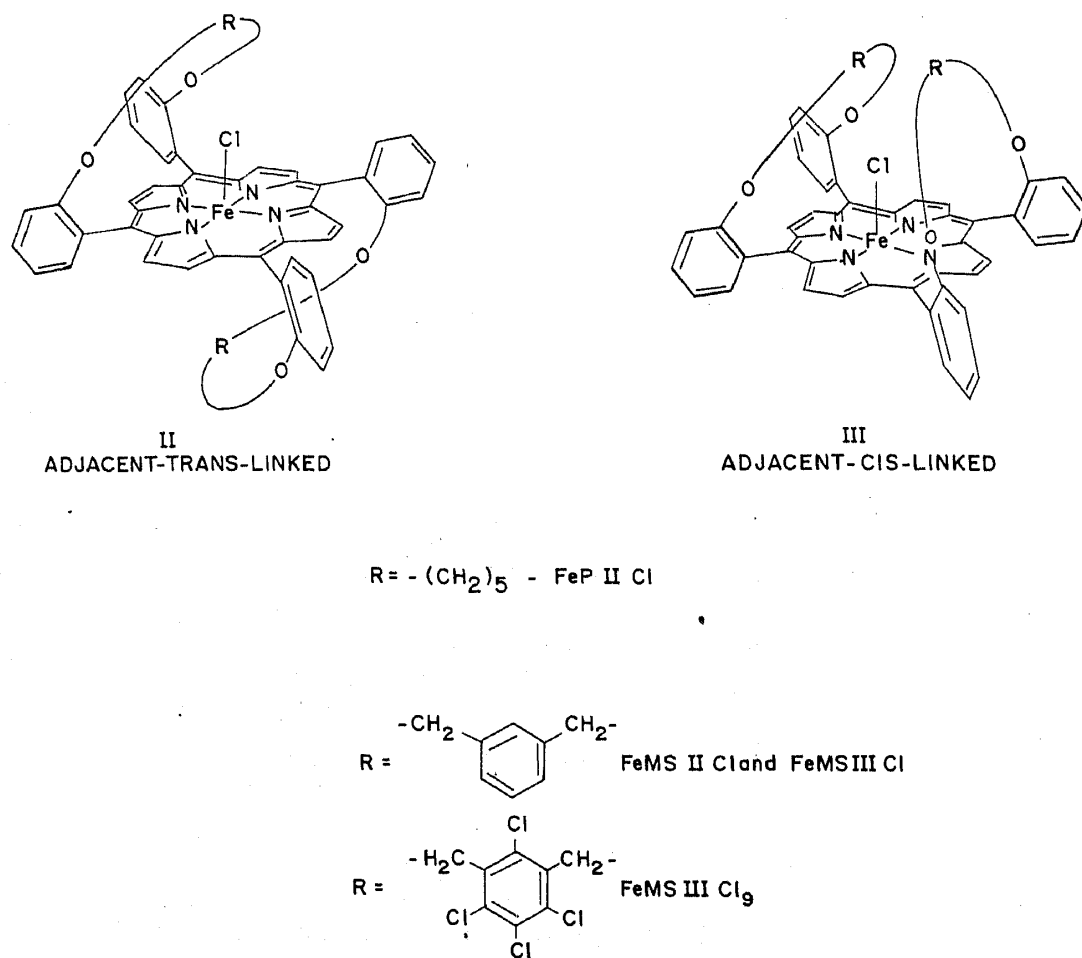


Figure 1. Structures of iron(III) derivatives of adjacent-*trans* and adjacent-*cis*-linked isomers of short-chain basket-handle porphyrins.

2. Experimental

2.1 Syntheses

The synthesis of free base porphyrins has been described earlier.

FeMSIICl: A solution of free base porphyrin (0.100 g, 0.113 mmol) and excess of freshly prepared anhydrous ferrous chloride in dry DMF was heated under reflux for 6 hours in argon atmosphere. The progress of the reaction was monitored by absorption spectrum. The solution was filtered and evaporated to dryness under vacuo and the resultant solid was extracted with chloroform (100 ml). The organic layer was washed with dilute NaHCO_3 (3×100 ml) and evaporated to dryness. The crude iron(III) porphyrin was chromatographed over silicagel (60–120 mesh) using chloroform as the eluent. The fast-moving unreacted free base porphyrin band was collected first. The required iron(III) derivative then moved slowly as a dark brown band and was collected. The solution was evaporated and the resultant solid was dried under high vacuum (0.060 g, 45%). The compound was recrystallised from chloroform-methanol.

FAB Mass: Calculated for $\text{C}_{60}\text{H}_{40}\text{FeClN}_4\text{O}_4 = 974.30$; observed $m/z = 974$.

Analysis calcd. for $C_{60}H_{40}FeClN_4O_4$: C, 73.89; H, 4.10; N, 5.75%. Found: C, 72.93; H, 3.92; N, 5.68%.

The other iron(III) derivatives were also synthesized similarly.

FeMSIIICl: FAB Mass: Calculated for $C_{60}H_{40}FeClN_4O_4 = 974.30$; Observed $m/z = 974$.

Analysis calcd. for $C_{60}H_{40}FeClN_4O_4$: C, 73.89; H, 4.10; N, 5.75%. Found: C, 73.92; H, 4.20; N, 5.81%.

FePIICl: FAB Mass: Calculated for $C_{54}H_{44}FeClN_4O_4 = 904.27$; Observed $m/z = 904$.

Analysis calcd. for $C_{54}H_{44}FeClN_4O_4$: C, 71.72; H, 4.91; N, 6.20%. Found: C, 71.5; H, 4.82; N, 6.26%.

FeMSIIICl₉: FAB Mass: Calculated for $C_{60}H_{32}FeCl_9N_4O_4 = 1247.86$; Observed $m/z = 1248$.

Analysis calcd. for $C_{60}H_{32}FeCl_9N_4O_4$: C, 57.75; H, 2.59; N, 4.49%. Found: C, 57.95; H, 2.63; N, 4.57%.

2.2 Measurements

The UV/Vis and details of the cyclic voltammetry measurements in the present study are described in our earlier work (Ravikanth *et al* 1993b,c). 1H NMR spectra were recorded on a Bruker 400 MHz spectrometer and C, H, N analysis was done on a Heraeus Carlo Erba 1108 elemental analyser.

3. Results and discussion

3.1 1H NMR

The pyrrole region of the 1H NMR spectra of various deformed high spin iron(III) porphyrins in $CDCl_3$ is displayed in figure 2 and the chemical shift data of various deformed short-chain basket-handle iron(III) porphyrins presented in table 1. The observed large downfield shift of pyrrole protons in iron(III) porphyrins is attributed to σ -spin delocalisation in $d_{x^2-y^2}$ orbital (La Mar and Walker 1979). The notable features in table 1 are: (1) the multiplet structure for pyrrole protons unlike singlet observed for unstrapped FeTPPCl, and (2) the chemical shift values in iron(III) basket handle porphyrins do not vary much relative to FeTPPCl. Observed multiplet structure for pyrrole protons suggests that all four pyrrole rings are displaced up and down from the mean plane due to deformation created in the porphyrin ring by the bridging meso phenyl groups with short chains. Furthermore, similar asymmetry in the porphyrin skeleton is also noted in the corresponding free bases (Reddy and Chandrashekar 1992; Ravikanth *et al* 1993a). The splitting of pyrrole signal in free base porphyrins suggests that there is retainment of deformation in the porphyrin ring upon insertion of iron(III) metal ion into its core. However, the shifts are minor relative to FeTPPCl indicating that the tension imposed by the bridging adjacent phenyl groups is not effective. The support for this observation comes from the spectral and electrochemical properties of the corresponding free bases relative to H_2 TPP (Reddy and Chandrashekar 1992; Reddy *et al* 1992, 1993; Ravikanth *et al* 1993; Ravikanth and Chandrashekar 1993, 1995).

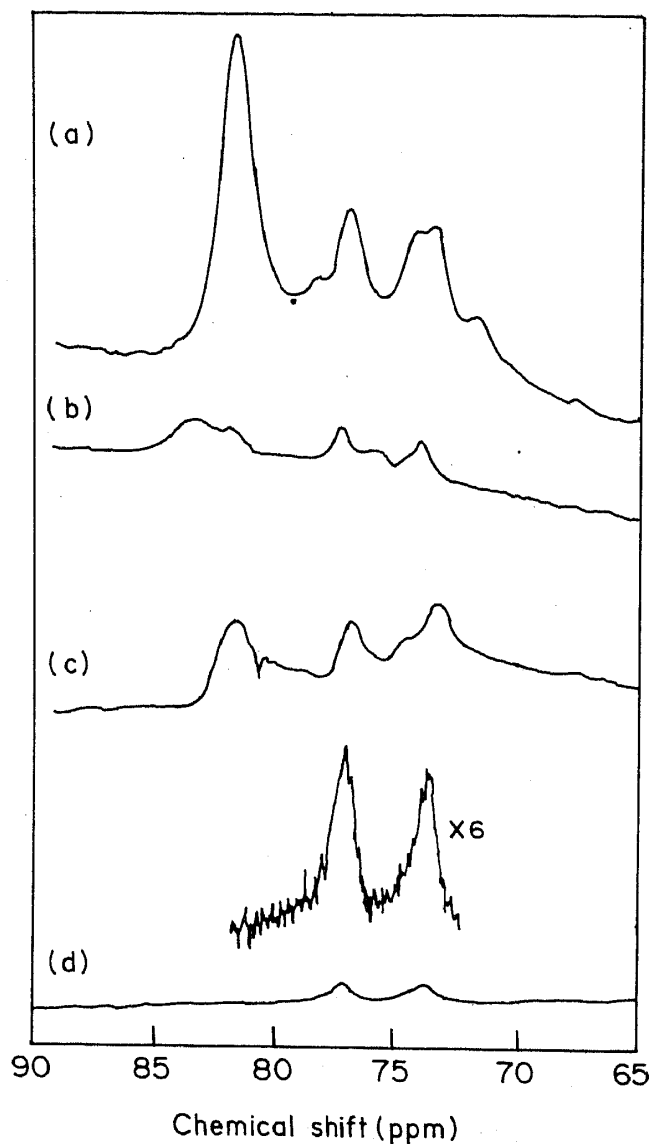


Figure 2. ^1H NMR spectra in pyrrole region of (a) FePIICl , (b) FeMSIICl_2 , (c) FeMSIICl and (d) FeMSIICl in CDCl_3 at 300 K.

Table 1. ^1H NMR chemical shifts (ppm) of high spin iron(III) porphyrins in CDCl_3 at 300 K.

Porphyrin	Pyrrole	ortho ^a	meta ^a	para ^a	-OCH ₂
FeTPPCI	79.4	8.0	13.3	6.35	
FePIICl	78.5	5.0	12.2		
	(<i>m</i> , 4H)	6.67	15.3(<i>m</i> , 4H)	4.67	-4.5
FeMSIICl	75.8	7.50	12.7(<i>m</i> , 4H)	(<i>m</i> , 4H)	(<i>m</i> , 10H)
	(<i>m</i> , 8H)	(<i>m</i> , 4H)	13.3	4.83	-4.0
FeMSIICl	78.3	6.90	(<i>m</i> , 8H)	(<i>m</i> , 4H)	(<i>m</i> , 8H)
	(<i>m</i> , 8H)	(<i>m</i> , 4H)	13.6	4.65	-4.65
FeMSIICl_2	79.5	7.24	(<i>m</i> , 8H)	(<i>m</i> , 4H)	(<i>m</i> , 8H)
	(<i>m</i> , 8H)	(<i>m</i> , 4H)	14.5	5.34	-3.45
			(<i>m</i> , 8H)	(<i>m</i> , 4H)	(<i>m</i> , 8H)

^aortho, meta and para protons of meso phenyl group of porphyrin.

Table 2. Electronic spectral data of various deformed iron(III) porphyrins in dichloromethane.

Porphyrin	Soret band $B(0,0)$ λ_{\max}/nm ($10^{-4}\epsilon/\text{dm}^3$ $\text{mol}^{-1}\text{cm}^{-1}$)	Q -bands, λ_{\max}/nm ($10^{-3}\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$)			
		I	II	III	IV
FeTPPCL	417(110)	511(13.4)	577(13.3)	658(2.8)	690(3.2)
FePIICl	420(70.5)	512(11.03)	586(3.39)	656(2.30)	698(2.36)
FeMSIICl	420(58.9)	513(7.24)	583(2.02)	656(1.51)	701(1.32)
FeMSIICl	423(54.3)	511(8.34)	589(2.50)	657(1.68)	698(1.57)
FeMSIICl ^a	420	511	589	656	697

^a ϵ values are not evaluated due to poor solubility

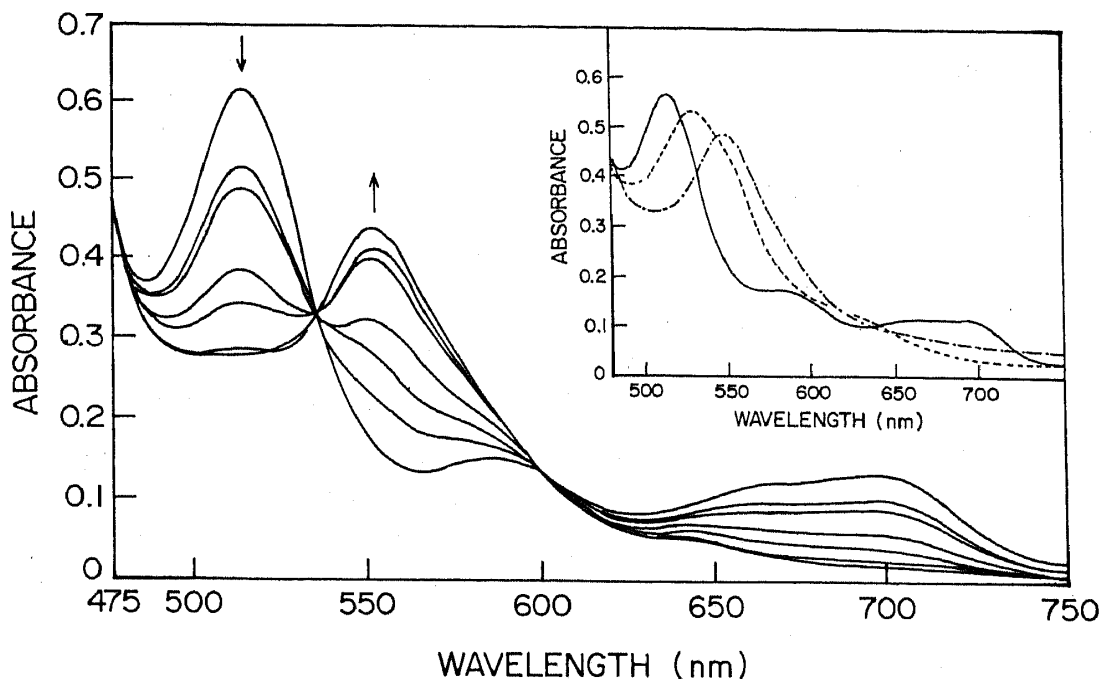


Figure 3. Absorption spectral changes of FeMSIICl ($7.2 \times 10^{-5} \text{ mol dm}^{-3}$) upon addition of increasing concentrations of imidazole. The concentrations of imidazole used were 2.2×10^{-5} , 4.4×10^{-5} , 6.6×10^{-5} , 1.5×10^{-4} and $2 \times 10^{-4} \text{ mol dm}^{-3}$. The arrows indicate the direction of spectroscopic change. The inset shows the absorption spectra of FeMSIICl ($5 \times 10^{-5} \text{ mol dm}^{-3}$) (—); after reduction with sodium dithionite to Fe(II) derivative (---) and on addition of $4 \times 10^{-4} \text{ mol dm}^{-3}$ imidazole ligand $[\text{Fe(II)MSII}(\text{Im})_2]$ (-·-·-)

3.2 Electronic spectra

The optical absorption spectral data of various high-spin iron(III) basket-handle porphyrins presented in table 2 reveals a bathochromic shift of absorption maxima with reduction in extinction coefficients as compared to FeTPPCL suggesting a retention of deformation in the porphyrin skeleton in solution on metallation. Furthermore,

since in adjacent *trans* isomer, the straps are on both sides of the porphyrin ring, the entry of the axial ligand may not be possible due to hindrance provided by straps. But in adjacent *cis* isomer, both the straps are on the same side of the porphyrin ring and therefore the axial ligand can approach from the less hindered side of the porphyrin. To know the feasibility of axial ligation in iron(III) derivatives of adjacent-*trans* isomer, the titration of $\approx 5 \times 10^{-5} \text{ mol dm}^{-3}$ of FeMSIICl with different amounts of imidazole is carried out as shown in figure 3. Additions of increasing concentrations of imidazole to chloroform solutions of FeMSIICl at room temperature result in dramatic visible region spectral changes (UV-Vis λ_{max} (nm) 425 and 551) with little change in Soret band maxima. The *Q*-bands are shifted towards higher wavelengths with well-defined isosbestic points indicating the existence of equilibrium between the two species. Since prior to addition of imidazole ligand, the iron(III) derivative is penta coordinate, certainly the species formed with the addition of imidazole is hexa coordinate due to binding of imidazole ligands to iron(III) centre. The binding constant was evaluated by plotting the reciprocal of optical difference (ΔA^{-1}) against $[\text{Im}]^{-1}$. The plot followed a straight line and binding constant was found to be $93 \mu\text{M}$.

Similar spectral changes have been observed upon addition of imidazole to high spin iron(II) derivative of basket-handle porphyrins (Grazynski *et al* 1982; Collman *et al* 1983; Suslick *et al* 1984). The electronic spectral changes that accompany the reduction of iron(III) to iron(II) in FeMSIICl (UV-Vis λ_{max} (nm)(CH_2Cl_2) 424 and 541) under argon atmosphere by sodium dithionite followed by the addition of imidazole is shown in figure 3 (UV-vis λ_{max} (nm)(CH_2Cl_2) for FeMSII(Im): 426 and 553). The red shift observed upon reduction of high spin FeMSIICl is due to formation of four coordinate iron(II) species which takes up two molecules of imidazole and forms a symmetric six coordinate species. The magnitude of red shifts observed upon addition of excess of imidazole to iron(III) derivative as well as to iron(II) derivative are the same, further confirming the formation of six coordinate species by binding imidazole molecules to

Table 3. Electrochemical redox data (in volts) of iron(III) derivatives of short-chain basket-handle porphyrins in different solvents.

Porphyrin	Solvent	Oxidation		Reduction		
		I	II	I	II	III
FeTPPCI	CH_2Cl_2	1.14	1.40	-0.23	-1.07	-1.60
	$\text{CH}_3-(\text{CH}_2)_2-\text{CN}$	1.14		-0.27	-1.05	
	DMF	1.17		-0.19	-1.03	-1.61
	DMSO			-0.11	-1.14	-1.68
FePIICl	CH_2Cl_2	1.09	1.40	-0.28	-1.18	
	$\text{CH}_3-(\text{CH}_2)_2-\text{CN}$	1.12		-0.26	-1.10	
	DMF	1.11		-0.22	-1.12	
	DMSO	0.98		-0.023	-1.31	-1.73
FeMSIICl	CH_2Cl_2	1.04	1.46	-0.32	-1.16	
	$\text{CH}_3-(\text{CH}_2)_2-\text{CN}$	1.11		-0.31	-1.04	
	DMF	1.00		-0.25	-1.11	
	DMSO	0.98		-0.030	-1.35	
FeMSIICl	CH_2Cl_2	1.02	1.44	-0.39	-1.19	
	$\text{CH}_3-(\text{CH}_2)_2-\text{CN}$	1.12		-0.28	-1.10	
	DMF	1.08		-0.20	-1.10	
	DMSO	0.98		-0.030	-1.35	

the iron centre. Thus, the preliminary optical studies reported here indicate that the straps present over the porphyrin skeleton not only prevent the μ -oxo dimer formation but also allow the incoming axial ligands. This suggests that reactions with small molecules such as O_2 and CO will be certainly helpful in understanding the mechanism by which oxygen carrier heme proteins regulate dioxygen and carbon monoxide binding. Such studies are in progress and will be reported elsewhere.

3.3 Electrochemistry

Half-wave potentials measured for three iron(III) derivatives of basket handle porphyrins in nonaqueous solvents with dielectric constants ranging from 8.9(CH_2Cl_2) to 46(DMSO) are presented in table 3 and a few representative cyclic voltammograms are

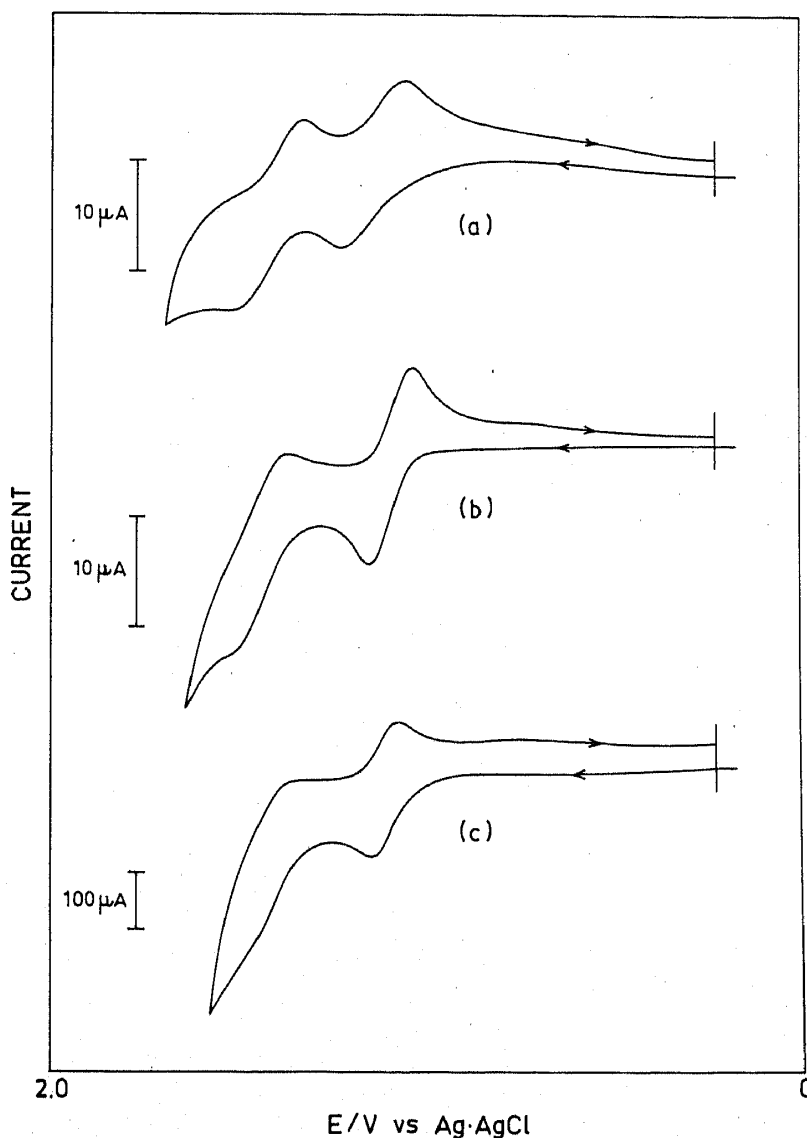


Figure 4. Cyclic voltammograms of (a) FePIICl, (b) FeMSIICl and (c) FeMSIIICl in CH_2Cl_2 . The concentrations used were $5 \times 10^{-3} \text{ mol dm}^{-3}$. Scan rate is 100 mV/s . The potentials are versus Ag/AgCl with TBAP as the supporting electrolyte.

shown in figures 4, 5 and 6. Generally, the number of oxidations and reductions in iron(III) derivatives depends on the nature of the solvent. For example in FePIICl, two oxidations and two reductions are observed in CH_2Cl_2 whereas in DMSO, one oxidation and three reductions are observed. The first and second oxidation steps are assigned to the formation of iron(III) porphyrin cation radical and dication and the reduction process to the formation of Fe(II) and Fe(I) porphyrin derivatives respectively. The extra reduction observed for FePIICl in DMSO is due to formation of Fe(I) porphyrin anion radical. These assignments are based on similar reactions observed for FeTPPCl in the respective solvent systems (Kadish 1982). An inspection of table 3 reveals the following observations: (1) oxidation potentials are shifted towards less positive and reduction potentials to more negative values in iron(III) derivative of basket handle porphyrins compared to FeTPPCl and (2) the potentials for the iron(III) oxidation are found to be independent of the nature of the solvent and reduction potentials appears to be solvent directed.

The easier oxidations and difficult reductions observed for iron(III) derivatives of basket handle porphyrins relative to FeTPPCl can be attributed to nonplanarity in the porphyrin ring caused by short bridging groups. This is consistent with our earlier observations. The electrochemical data clearly demonstrates that solvent has a marked

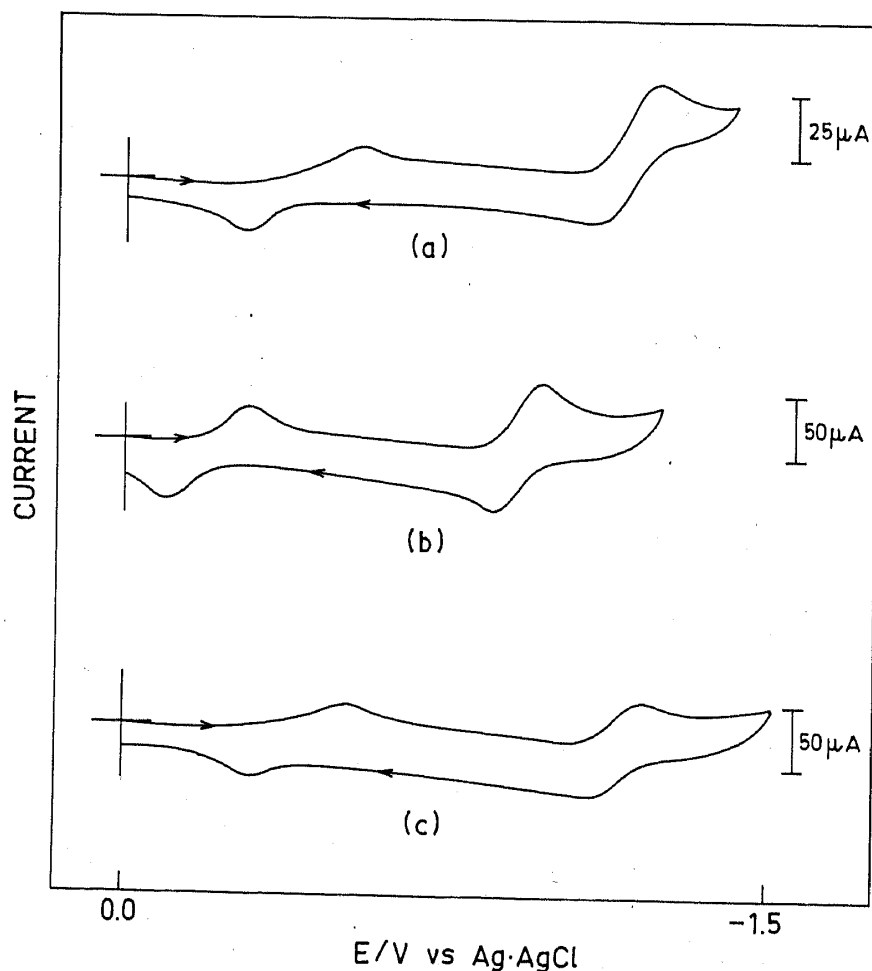


Figure 5. Cyclic voltammograms of (a) FePIICl, (b) FeMSIICl and (c) FeMSIIICl in DMF. The concentrations used were $5 \times 10^{-3} \text{ mol dm}^{-3}$. Scan rate is 100 mV/s.

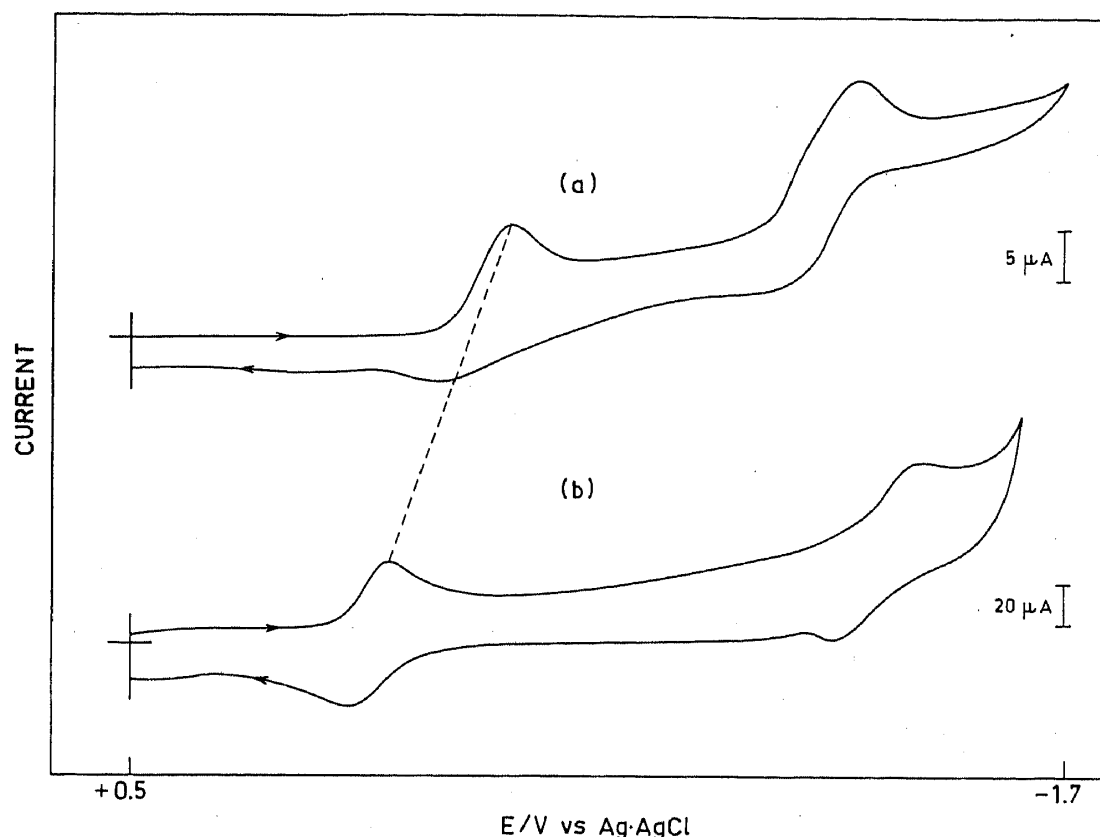


Figure 6. Cyclic voltammograms of FeMSIICl in (a) CH₂Cl₂, and (b) DMSO. The concentrations used were 5×10^{-3} mol dm⁻³. Scan rate is 100 mV/s. The dotted line represents the shift in first reduction potential in two different solvents.

effect on the redox potentials of iron(III) basket-handle porphyrins. The potential shifts seem to be dependent on the coordinating ability of the solvent and site of reaction (figure 6) (Kadish 1986). As seen from the table 3, the half wave potentials for oxidation of iron(III) basket handle porphyrins are invariant and this is assigned to porphyrin ring centred oxidation rather than metal centred oxidation. The support for above conclusion comes from the observed negligible magnitude of shift in the oxidation potentials even though the coordinating ability of the solvent has increased. For example, the first reduction is observed at -0.023 V in DMSO for FePIICl but in CH₂Cl₂, it is shifted to -0.28 V. The easier reduction in DMSO compared to CH₂Cl₂ suggests the stabilisation of Fe(II) over Fe(III) since DMSO is a strong coordinating solvent and therefore can act as an axial ligand. It binds axially to the iron centre by displacing counter ions and forms a symmetrical six-coordinate iron(II) species. However, the second reduction which is attributed to Fe(II)/Fe(I) appears to be insensitive to changes in the solvent, presumably because Fe(I) is noncomplexing (Kadish 1982). In addition, it is interesting to note here that the difference in half wave potentials between the first and second reductions in all iron(II) derivatives remains constant in dichloromethane, butyronitrile and dimethylformamide (900 mV). This difference in redox potentials between various solvents further reflects different stabilisation effects of various solvents on reduced forms of iron(III) derivatives reported here.

4. Conclusion

In conclusion, the introduction of a metal into the porphyrin core does not affect the degree of distortion. Axial ligation studies suggest that strapping groups on both sides of the porphyrin do not prevent the entry of small ligands to bind axially to iron metal ion. This led us to do controlled experiments with oxygen and other small molecules, binding studies and results will be reported elsewhere. Finally, electrochemistry of iron(III) porphyrins in different solvent systems suggests the stabilisation of iron(II) and iron(I) over iron(III) in strong coordinating solvents.

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