Coordination behaviour of metalloporphyrins with intramolecularly linked thiolate ligand

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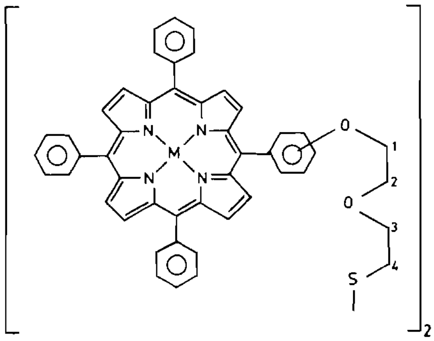
(Received February 5, 1990; revised May 15, 1990)

Abstract

meso-Tetraphenylporphyrin was derivatized at different positions of one of the *meso* aryl groups to obtain interesting bisporphyrin systems bearing a disulfide group. Various metal (VO(IV), Ni(II), Co(II), Cu(II), Zn(II) and Ag(II)) derivatives of these porphyrins have been prepared. *In situ* reduction of these derivatives results in well-defined five coordinate complexes with thiolate as the axial ligand exhibiting hyperporphyrin spectra. The relative extent of thiolate coordination to the metal ion depends on the nature of the substitution as $o>m>p$. The electrochemical redox behaviour of these systems reveals the existence of the disulfide group and spectroelectrochemical studies unambiguously show the formation of negatively charged pentacoordinate porphyrin complexes. Possible structures have been proposed for the *o*, *m* and *p* substituted porphyrin derivatives based on the ^{1}H NMR data.

Introduction

Metalloporphyrins bearing peripheral organic substituents form important model compounds for the study of the mechanism of various biological reactions, viz. hemeoxygenation, cytochrome oxidase and peroxidase functions and others. Of particular interest are the model studies on the cytochrome-P_{450} function. Many elegant synthetic structural models to reproduce the optical spectral features of the different intermediates involved in the catalytic cycle of cytochrome-P_{450} have been reported. These include porphyrins bearing covalently linked thiol [1] and/or imidazole moieties [2] and 'strapped' porphyrins [3] wherein the thiol group is constrained in the bridging portion. In addition, studies on intermolecular complexes of iron and a few non-iron porphyrins with thiolate ligands have been reported [4].



M = 2H, VO(IV), Co(II), Ni(II), Cu(II), Zn(II), Ag(II)

ortho : ($\underline{o}$- MP ~ S$)_2$; meta : ($\underline{m}$- MP ~ S$)_2$; para : ($\underline{p}$- MP ~ S$)_2$.

Fig. 1. Structure of disulfide linked bisporphyrins.

Porphyrins bearing thiol functional group are inherently unstable and hence in the present study the disulfide group is intentionally chosen as the covalent linkage. The strategy adopted is to generate a potentially ligating thiolate group *in situ* by reduction of the disulfide. To accomplish this, we synthesized porphyrin derivatives, $(H_2P\sim S)_2$, in which two porphyrin units are linked through a disulfide moiety (Fig. 1). This was prepared from the reaction of NaSH with (*o*, *m* and *p*) 1-bromo-4-phenoxydiethylether triphenylporphyrins ($H_2P\sim Br$). The selection of a bisethyleneoxide bridge over an alkyl chain is preferred since the former is known to exist in the *all gauche* conformation favorable for metal–ligand binding. The *o*, *m* and *p* substituted derivatives are chosen to position the thiolate group at the preferred distance and orientation to promote coordination to the metal ion in the porphyrins. Spectroscopic and electrochemical studies of the various metal (VO(IV), Ni(II), Co(II), Cu(II), Zn(II) and Ag(II)) derivatives of these porphyrins have provided interesting struc-

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tural information on the nature of coordination of sulfur bearing ligands.

Experimental

5-(*o*, *m* and *p*)hydroxyphenyl-10,15,20-triphenylporphyrins were synthesized according to the published procedure [5]. Dibromo diethylether was prepared from the reaction of dihydroxy diethylether and PBr_3 [6]. NaSH was obtained by passing H_2S over sodium ethoxide solution [7].

Synthesis of 5(o, m and p)-1-bromo-4-phenoxy diethylether-10,15,20-triphenylporphyrin, $H_2P \sim Br$

The synthesis of the title compound was accomplished by the condensation of 5(*o*, *m* or *p*)hydroxyphenyl-10,15,20--triphenyl porphyrin (100 mg) with dibromodiethylether (500 mg) in dimethylformamide (250 ml) in the presence of dry K_2CO_3 (2 g) for about 8 h at 25 °C. The condensed product was washed with water and the solvent evaporated. The residue was taken in CH_2Cl_2 and column chromatographed on basic alumina using CH_2Cl_2 as eluent. The bromo derivatives were obtained in good yields (~60%). ^1H NMR in $CDCl_3$ (δ in ppm) (nature of the multiplet, number of protons in the specified group): (i) *o*-$H_2P \sim Br$: 8.83 (m, 8H, pyrrole H), 8.20 (m, 6H, triphenyl *ortho* H), 7.76 (m, 9H, triphenyl *meta* and *para* H), 8.04, 7.34 (m, 4H, substituted phenyl H), 4.08, 3.84, 3.63, 3.45 (four triplets, 8H, ether CH_2), −2.79 (s, 2H, imino H). (ii) *m*-$H_2P \sim Br$: 8.92 (m, 8H, pyrrole H), 8.19 (m, 6H, triphenyl *ortho* H), 7.75 (m, 9H, triphenyl *meta* and *para* H), 7.23, 7.59 (m, 4H, substituted phenyl H), 4.28, 3.81, 3.40 (t, p, t, 8H, ether CH_2), −2.78 (s, 2H, imino H). (iii) *p*-$H_2P \sim Br$: 8.83 (m, 8H, pyrrole H), 8.22 (m, 6H, triphenyl *ortho* H), 7.76 (m, 9H, triphenyl *meta* and *para* H), 8.10, 7.28 (d, d, 4H, substituted phenyl H), 4.43, 4.02, 3.14, (t, m, t, 8H, ether CH_2), −2.76 (s, 2H, imino H).

Synthesis of bis[5-(o, m and p)-1-thio-4-phenoxy diethylether-10,15,20-triphenylporphyrin], $(H_2P \sim S)_2$ and its metal derivatives, $(MP \sim S)_2$

The $H_2P \sim Br$ derivative (*o*, *m* and *p*) (30 mg) was dissolved in 50 ml of a mixture of ethanol and dimethylformamide (1:1 vol./vol.) and refluxed. To this NaSH (100 mg) was added slowly and the refluxing continued for 2 h. At the end of this period, the solvent was evaporated under reduced pressure and the residue was extracted with dry benzene to remove unreacted NaSH and one of the products of the reaction, NaBr. The solvent benzene was removed under reduced pressure and the $CHCl_3$ solution of the residue was chromatographed on a neutral alumina column using $CHCl_3$ as an eluent. The first fraction was found to contain the desired compound (yield ~70%). The purified product revealed a *m/e* peak at 1465 (calculated 1466). The FT-IR spectra of these dimers revealed a peak around 475 cm^{-1} characteristic of the S–S stretching [8]. ^1H NMR in $CDCl_3$: (i) *o*-$(H_2P \sim S)_2$: 8.78 (m, 8H, pyrrole H), 8.11 (m, 6H, triphenyl *ortho* H), 7.57 (m, 9H, triphenyl *meta* and *para* H), 7.90 (m, 4H, substituted phenyl H), 3.46, 2.37, 1.80, 0.88 (four t, 8H, ether CH_2), −2.84 (s, 2H, imino H). (ii) *m*-$(H_2P \sim S)_2$: 8.75 (m, 8H, pyrrole H), 8.11 (m, 6H, triphenyl *ortho* H), 7.57 (m, 9H, triphenyl *meta* and *para* H), 6.97, 7.90 (m, 4H, substituted phenyl H), 4.14, 3.72, 2.84 (t, m, t, 8H, ether CH_2) −2.77 (s, 2H, imino H).(iii) *p*-$(H_2P \sim S)_2$: 8.81 (m, 8H, pyrrole H), 8.20 (m, 6H, triphenyl *ortho* H), 7.74 (m, 9H, triphenyl *meta* and *para* H), 8.19, 7.52 (d, d, 4H, substituted phenyl H), 3.98, 3.56, 2.87 (t, m, t, 8H, ether CH_2), −2.77 (s, 2H, imino H).

Two methods were employed to obtain the metal derivatives of $(H_2P \sim S)_2$. In the first method the metal derivatives of $H_2P \sim Br$ were synthesized using metal acetates as the metal carrier in a $CHCl_3$:CH_3OH (70:30 vol./vol.) mixture, except in the case of vanadyl porphyrins where vanadium sulfate was used as the metal carrier [9]. The metallated porphyrins, $MP \sim Br$ were converted to disulfide derivatives by the reaction with NaSH using the method mentioned above. In the second method, the disulfide linked porphyrin $(H_2P \sim S)_2$ was metallated using the above procedure. The products obtained by both these methods gave identical spectral features. The mass spectrum of a representative sample of the nickel(II) derivative gave a *m/e* peak at 1763 (calculated 1764).

The absorption spectra of the porphyrins were recorded on a Hitachi U-3400 spectrometer. Emission spectra were monitored using a Hitachi 650-60 fluorescence spectrometer. The right angle detection technique was employed. ^1H NMR spectra were recorded on a Bruker 270 MHz FT NMR spectrometer using $CDCl_3$ or CD_3CN as solvent. EPR measurements were carried out on a Varian E-109 spectrometer. DPPH was used as a 'g' marker.

Electrochemical studies were performed using a BAS-100A electrochemical analyzer. A three electrode assembly with a glassy carbon working electrode (BAS MF-2012), a platinum wire auxiliary electrode and a Ag/AgCl reference electrode was employed. Porphyrin solutions (10^{-3} M) in acetonitrile containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte were employed for redox potential measurements. Thin layer spectroelectrochemical studies were carried out using a home built setup. The cell was constructed using gold minigrid as working electrode enclosed in an annular space with optical flats on either side of the electrode. Another piece of gold minigrid was used as auxiliary electrode and Ag/AgCl as a reference electrode. The path length of the cell determined spectrophotometrically was found to be 0.12 cm with nearly 80% optical transparency. Electrolysis of the solutions was performed using this cell with a Bank Electronic (F.R.G.) Model MP-81 potentiostat. The potential drift during electrolysis was less than ±5 mV. The performance of this cell was evaluated from electrochemical reduction measurements of methylviologen in propylene carbonate solution as described by Blubaugh and Doane [10].

The porphyrin solutions were completely degassed with argon prior to all spectral measurements. This precaution is necessary to eliminate any traces of oxygen to avoid oxidation of the thiolate group.

Results and discussion

The optical absorption spectra of the free-base porphyrin dimers $(H_2P{\sim}S)_2$ in CH_3CN exhibited normal *etio* type spectrum. The presence of disulfide linkage in $(H_2P{\sim}S)_2$, is not discernible in the absorption spectra of the dimers. Also, reduction of the disulfide, $(H_2P{\sim}S)_2$ with $NaBH_4$ and/or KH (in benzo-15-crown-5) revealed no perceptible changes in the absorption spectrum indicating poor involvement of H-bonding of the thiolate group with imino protons of the porphyrin ring. Interestingly, reduction of the disulfide bridge in the metalloporphyrin dimers (zinc(II) and cobalt(II)) showed dramatic changes in the visible absorption spectra (Fig. 2). The appearance of a split Soret band and red shifted visible bands in the reduced species suggest thiolate coordination to the metal ions. Similar observations have been made by Nappa and Valentine [4e], and others [4f–h] in their intermolecular complexation studies. The spectral data are summarized in Table 1. The hyperbands of the zinc derivatives appear around 360 nm while in the cobalt derivatives this band is apparently shifted by 10 nm to the red region (~370 nm). It is of interest to note that the presence of the hyperband is observed only in the *o* and *m* derivatives whereas in cobalt porphyrins there is a marginal shift of the hyperbands towards the red region in going from *o* to *p* substituted derivatives. This suggests that the thiolate coordination is more favoured in the *o* substituted derivative of $(ZnP{\sim}S)_2$, relative to *m* and *p* derivatives owing to the proximity of the ligating group to the metal ions. The relative extent of the splitting of the Soret band and the red shift of the visible bands in the reduced species of zinc(II) and cobalt(II) derivatives of the disulfide bisporphyrins, follow the order $o>m>p$. It is possible that the thiolate group (generated by the chemical reduction) of the dimeric porphyrin disulfide is involved in intermolecular binding to the metal ions. In the present study we observed no significant changes in the absorption spectral bands of the reduced species with increasing concentration of the porphyrins indicating an absence of intermolecular coordination of the thiolate ligand. The metal derivatives (VO(IV), Ni(II), Cu(II) and Ag(II)) of $(H_2P{\sim}S)_2$, did not show any significant changes in optical absorption spectra on reduction indicating the poor coordination of the thiolate group to these metal ions. In addition, it is also noted that the ^1H NMR spectra of the reduced diamagnetic porphyrin disulfides reveal the absence of a broadening or shift in the proton resonances with increase in concentration of the porphyrins (10^{-4} to 10^{-3} M). This suggests that the intermolecular association is not present in the reduced species unlike those reported for the ammine substituted porphyrins [11].

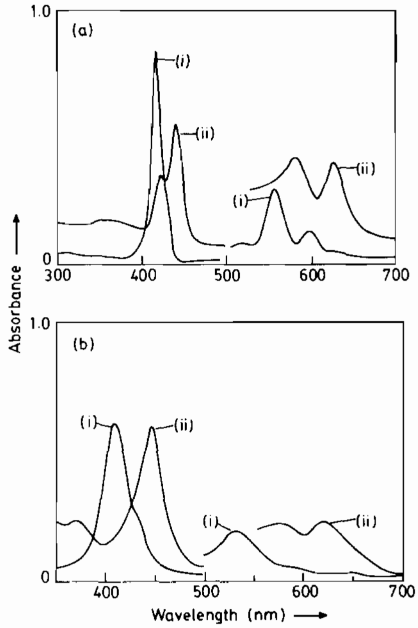

Fig. 2. Optical absorption spectra of (a) (i) $(o\text{-}ZnP{\sim}S)_2$ and (ii) $o\text{-}ZnP{\sim}S^-$; (b) (i) $(o\text{-}CoP{\sim}S)_2$ and (ii) $o\text{-}CoP{\sim}S^-$ in CH_3CN at 25 °C. The spectra in the range 500–700 nm are expanded for clarity. The reduced complexes are obtained by chemical reduction (see text).

The fluorescence spectra of $(H_2P{\sim}S)_2$ and its zinc(II) derivatives revealed emission bands around 654 and 720 nm, and 594 and 652 nm, respectively. It may be noted that the reduction of $(H_2P{\sim}S)_2$ in CH_3CN does not result in any change in the quantum yield of the emission bands. However, a marked decrease in the quantum yield of the emission bands was observed on the reduced $(ZnP{\sim}S)_2$ species (Fig. 3). Interestingly, the relative decrease in the quantum yields is found to be dependent on the nature of the substitution as $o>m>p$ in various disulfide bis-

TABLE 1. Optical absorption data (λ in nm) of intramolecularly bound thiolate complexes of metalloporphyrins in CH_3CN at 298 K[a]

Compound	Hyper band	B_1	Q_1	Q_2	Q_3	Q_4
$o H_2P \sim S^-$		419	650	592	550	514
o-$ZnP \sim S^-$	362	418(sh), 442		625	579	
m-$ZnP \sim S^-$	365(sh)	422, 432		613	569	
p-$ZnP \sim S^-$		423		599	558	
o-$CoP \sim S^-$	371	446		620	577	
m-$CoP \sim S^-$	373	445		618	540	
p-$CoP \sim S_-$	376	442		615	540	
o-$CuP \sim S^-$		413			540	
o-$AgP \sim S^-$		423			541	
o-$VOP \sim S^-$		420			546	
o-$NiP \sim S^-$		411			525	

[a] The thiolate complexes are obtained by *in situ* reduction of the corresponding disulfide derivatives using $NaBH_4$ or KH (crown ether complexed).

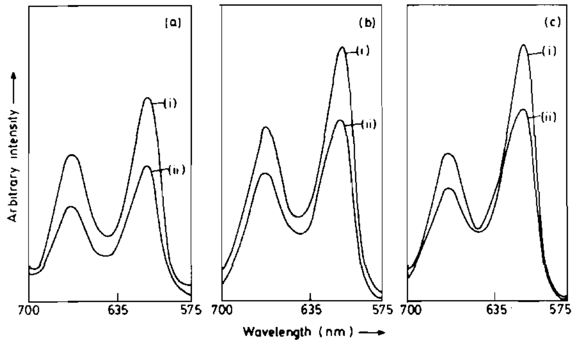

Fig. 3. Fluorescence spectra of (a) (i) $(o\text{-}ZnP \sim S)_2$ and (ii) $o\text{-}ZnP \sim S^-$; (b) (i) $(m\text{-}ZnP \sim S)_2$ and (ii) $m\text{-}ZnP \sim S^-$; (c) (i) $(p\text{-}ZnP \sim S)_2$ and (ii) $p\text{-}ZnP \sim S^-$ in CH_3CN at 25 °C. The reduced complexes are obtained by chemical reduction (see text).

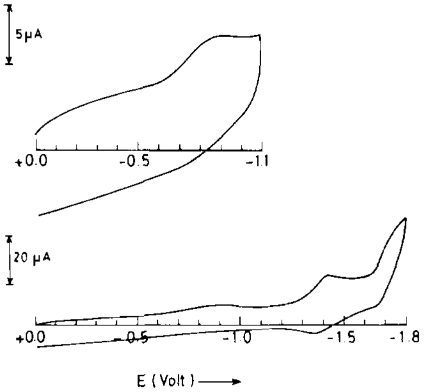

Fig. 4. Cyclic voltammogram of $(m\text{-}ZnP \sim S)_2$ in CH_3CN containing 100 mM of TBAP at 25 °C. Scan rate 100 mV/s.

porphyrins. This observation is similar to that obtained in the optical absorption data. The decrease in the quantum yield observed in the present study is interpreted due to the presence of a five coordinated negatively charged zinc porphyrin complex.

The cyclic voltammogram of a representative porphyrin disulfide dimer, $(m\text{-}ZnP \sim S)_2$ is shown in Fig. 4. It is observed that the disulfide group in the porphyrin dimer undergoes one electron irreversible reduction around -0.85 V (on a glassy carbon electrode). The observed reduction potential is similar to that found for diphenyldisulfide in CH_2Cl_2 (-0.77 V versus Ag/AgCl). All the synthesized compounds reveal a characteristic reduction potential ~ -0.85 V on a glassy carbon electrode indicating the presence of a disulfide group in these compounds. The reduction potential of the disulfide is not markedly changed with the nature of substitution as well as the nature of the metal ion in the different porphyrins. The optical absorption spectrum of the reduced zinc derivative of $(o\text{-}H_2P \sim S)_2$ in a thin layer spectroelectrochemical cell is shown in Fig. 5. It can be seen that the reduction of disulfide at -0.9 V results in a spectrum similar to that obtained from chemically reduced species indicating the formation of a pentacoordinate zinc(II) porphyrin–thiolate complex. This suggests that the chemically or electrochemically reduced zinc(II) derivatives of $(H_2P \sim S)_2$ exhibit intramolecular binding of the thiolate ligand to zinc ion.

The ^1H NMR spectra of the disulfide linked bisporphyrins, $(H_2P \sim S)_2$ and its divalent metal derivatives exhibit characteristic spectra permitting structural elucidation. All the proton resonances of the synthesized porphyrin derivatives are suitably apportioned and assigned, with the aid of a model compound 1-bromo-4-phenoxydiethylether, $Ph \sim Br$ (1) and the precursor 1-bromo-4-phenoxydiethylether-triphenylporphyrin derivatives, $(H_2P \sim Br)$. The occurrence of well separated signals of ethyleneoxide protons in $(H_2P \sim S)_2$ and its zinc(II) and nickel(II)

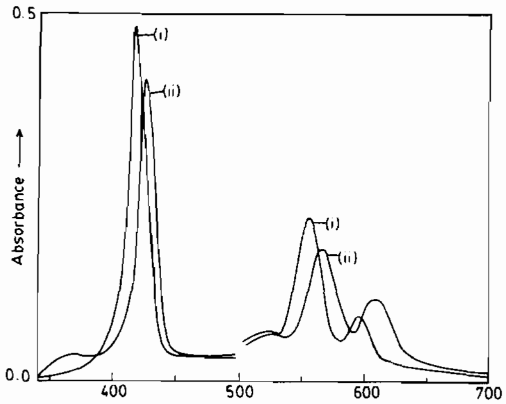

Fig. 5. Thin layer optical absorption spectra of (i) (o-$ZnP\sim S)_2$ and (ii) its reduced product after 10 min in CH_3CN containing 100 mM TBAP. Potential held at -0.9 V (vs. Ag/AgCl).

derivatives arise from ring current anisotropy of the porphyrin core [12]. This is supported by the shielding effect experienced by these protons relative to the resonances observed for the model compound. A comparison of the 'side arm' ethyleneoxide proton resonances of $(H_2P\sim S)_2$ with the corresponding resonances of the precursor $H_2P\sim Br$ reveals that the CH_2 proton resonances are shifted upfield. It is seen that the CH_2 protons of the 'side arm' resonate as four distinct triplets in the *ortho* substituted porphyrin while these resonances occur as complex multiplets in the *m* and *p* substituted porphyrins. Moreover, the magnitude of the shielding experienced by these protons in $(H_2P\sim S)_2$ and its zinc(II) and nickel(II) metal derivatives are found to be much larger in the *o* substituted derivatives compared to *m* and *p* derivatives (Table 2). This is rationalized in terms of greater ring current anisotropy experienced by these protons in the *o* substituted derivatives due to proximity effect. The ^1H NMR spectra of the disulfide linked bisporphyrins have been useful in arriving at the possible solution-averaged structures of these compounds. Molecular modelling using the CART program employing the crystal structure data of porphyrins [13] and related crown ether complexes [14] reveals three probable structures with minimum molecular strain for the dimer $(H_2P\sim S)_2$ (Fig. 6). It can be seen that in case of the *para* substituted dimer the 'extended' conformation (Fig. 6(b) and (c)) seems to be most likely while a 'strapped' conformation with the disulfide group disposed in-between the porphyrin cavity is preferred for the *ortho* substituted dimers (Fig. 6(a)). The greater shielding of the ethyleneoxide protons in the *ortho* substituted porphyrins supports the proposed 'strapped' conformation. The ^1H NMR spectra of the reduced species are complicated due to the large number of peaks arising from $NaBH_4$ and KH in the crown ether. Hence, more reliance is placed on optical absorption spectral changes for studying the intramolecular binding of thiolate with metalloporphyrins.

The EPR spectra of Cu(II), Ag(II) and VO(IV) metallated disulfide bridged bisporphyrins have been studied in toluene at liquid nitrogen temperature. The spectra are analyzed using the procedure described in the literature [15]. It is found that the EPR parameters of the dimers show marginal changes in the 'g' and hyperfine (A) tensor values relative to the MTTPs (Table 3). The absence of the half-field signal in these derivatives indicates no metal–metal interaction between the two porphyrins units. The EPR spectra of the chemically reduced species, however, show marginal changes in the 'g'

TABLE 2. Chemical shift (δ) and ring current shifts ($\Delta\delta$) of the side arm CH_2 protons in porphyrin monomers, $H_2P\sim Br$ and dimers, $(H_2P\sim S)_2$ in $CDCl_3$[a]

Compound	Chemical shift δ (ppm)				$\Delta\delta$ (ppm)			
	1	2	3	4	1	2	3	4
1	4.08	3.84	3.63	3.45				
o-$H_2P\sim Br$	4.03	3.03	2.23	1.90	0.05	0.81	1.41	1.55
m-$H_2P\sim Br$	4.28	3.80[b]		3.40	−0.20	0.04		0.05
p-$H_2P\sim Br$	4.43	4.02[b]		3.14	−0.32	−0.18	−0.39	0.31
2[c]	4.17	3.82	3.75	2.79				
$(o$-$H_2P\sim S)_2$	3.46	2.37	1.80	0.88	0.71	1.45	1.95	1.91
$(m$-$H_2P\sim S)_2$	4.14	3.72[b]		2.84	0.03	0.10		−0.05
$(p$-$H_2P\sim S)_2$	3.98	3.56[b]		2.87	0.19	0.26		−0.08

The numbering of CH_2 protons is according to Fig. 1. [a]The relative intensities are in agreement with the predicted values. The negative and positive values in ($\Delta\delta$) indicate upfield and downfield shifts respectively. [b]The proton resonances of 2 and 3 overlaps. [c]Disulfide derivative of **1**.

TABLE 3. EPR parameters for the disulfide metallobisporphyrins and their reduced thiolate bound metalloporphyrins in toluene at 100 K[a]

Compound	$g_\parallel$	$g_\perp$	$A_\parallel^M$	$A_\perp^M$ ($10^4\times\text{cm}^{-1}$)	$A_\parallel^N$	$A_\perp^N$
CuTPP	2.185	2.047	208.1	31.5	14.7	15.7
$(o\text{-CuP}{\sim}\text{S})_2$	2.193	2.033	198.0	34.1	14.0	17.1
$o\text{-CuP}{\sim}\text{S}^-$	2.191	2.031	197.2	34.0	14.0	17.0
AgTPP	2.109	2.038	49.2	26.4		
$(o\text{-AgP}{\sim}\text{S})_2$	2.102	2.010	48.0	25.0		
$o\text{-AgP}{\sim}\text{S}^-$	2.110	2.000	47.2	24.8		
VOTPP	1.960	1.992	165.8	57.8		
$(o\text{-VOP}{\sim}\text{S})_2$	1.968	1.997	164.3	57.5		
$o\text{-VOP}{\sim}\text{S}^-$	1.962	1.995	164.0	56.9		

[a] The thiolate complexes are obtained by *in situ* reduction of the corresponding disulfide using NaBH_4 or KH (crown ether complexed).

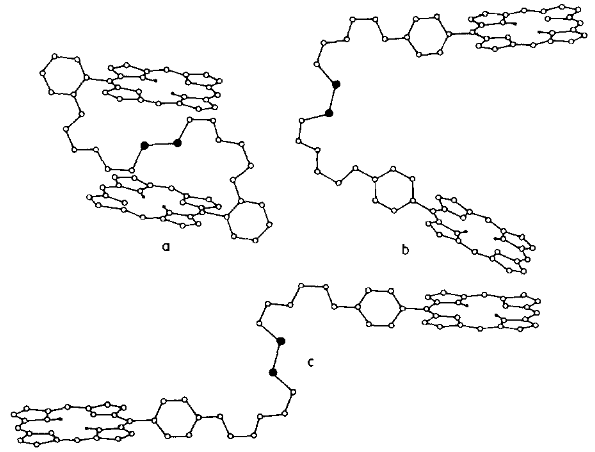

Fig. 6. Schematic representation of the possible solution-averaged structures for the *o* and *p* substituted disulfide linked bisporphyrins; (a) strapped (b) close and (c) extended conformations are shown.

and '*A*' tensors indicating the poor coordinating ability of the generated thiolate with the metalloporphyrins.

Acknowledgements

The authors thank the Department of Science and Technology and Department of Non-Conventional Energy Sources, Government of India, for their financial support.

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