Schiff bases of nickel(II), copper(II) porphyrins and dibenzo-18-crown-6 interspersed *bis*-metal porphyrins. Protonation studies

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Abstract. Schiff-base (SB) derivatives of Ni(II) and Cu(II) porphyrins endowed with various amine functions ($R-NH_2$), *n*-butylamine, *p*-anisidine and *m*-nitroaniline have been prepared from corresponding formyl porphyrins. Protonation studies of these SB derivatives reveal a marked red shift of the optical absorption bands in the visible region relative to the unprotonated imines. The magnitude of the observed red shifts in the protonated derivatives, (SBH^+) are found to depend on the electron-withdrawing or electron-donating nature of the R group of the amines. The results of the optical absorption, ^1H NMR, EPR, and cyclicovoltammetric studies are illustrative of the fact that protonation of the SB derivatives results in a localized positive charge, $P-C(H) = \overset{+}{N}(H)-R$ in the periphery of the porphyrin (p) system. The dibenzo-18-crown-6 interspersed *bis*porphyrin schiff bases have been prepared from *trans* 4,4'-diamino dibenzo-18-crown-6 and formyl porphyrins. The protonation of these SB derivatives is found to proceed in a concerted fashion. The cation complexation studies by the crown ether entity in the *bis*porphyrin systems have been investigated using optical absorption, magnetic resonance and electrochemical methods. The redox characteristics of the protonated dimeric SB porphyrins reveal that the first oxidation step involves a two-electron transfer reaction. This is important in view of their possible usage in multielectron transfer reactions of biological and catalytic interest.

Keywords. Schiff-bases of porphyrins; metal porphyrins; protonation studies; crown ether.

1. Introduction

In recent years considerable attention has been focussed on the protonation behaviour of Schiff-base porphyrins. Interest in these investigations lies in the observation of large red-shifts of the long wavelength absorption bands of the Schiff base porphyrins on protonation. These findings closely parallel the red shifts observed in the visible bands of *in vivo* chlorins and bacteriochlorins in plant and bacterial photosystems (Katz *et al* 1978; Sauer 1979). The red-shift of the long wavelength band of the protonated Schiff base (SBH^+) relative to the unprotonated imine (SB) has been explained in terms of localized positive charge in the vicinity of tetrapyrrole moiety (Ward *et al* 1984; Hanson *et al* 1984; Maggiora *et al* 1985). In all the model studies, the SB formation involves the condensation of the formyl/keto group (situated at the porphyrin periphery) with butyl amine. In view of the fact that the transition energies of the visible band of the SBH^+ species are

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affected by the extent of localization of the positive charge, it would be of interest to study the influence of the nature of the amines (electron-withdrawing and electron-donating) and metal ions on the optical absorption feature of the SBH^+ species. Moreover, the covalently linked *bis*porphyrins bearing Schiff-base linkages offer interesting models to probe into the changes in optical absorption features that can occur from cooperative interactions of the two constituent monomeric Schiff base units. In addition, these *bis*porphyrins provide an opportunity to study the mutual metal-metal interactions and the influence of a positive charge (in the periphery of SBH^+) on such interactions.

Here we report the synthesis and spectral properties of both monomeric and dimeric Ni(II) and Cu(II) Schiff base porphyrins and their protonated derivatives. The choice of Cu(II) and Ni(II) porphyrins are necessitated by their inertness towards demetallation. The SB porphyrins bear both aliphatic (butyl amine) and aromatic (*p*-anisidine and *m*-nitroaniline) amines to study the effect of electron-donating and electron-withdrawing groups on the protonation behaviour and the optical properties of the resulting SBH^+ species. Novel dimeric Ni(II) and Cu(II) porphyrin Schiff-bases wherein a crown ether, dibenzo-18-crown-6, moiety forms the Schiff base covalent bridge between the two porphyrin units have been prepared. In addition to investigating the possibility of step-wise protonation in these *bis*porphyrins, we explored the utility of crown-ether interspersed *bis*porphyrins as ionophores. The optical absorption, ^1H NMR and EPR spectral data of these SB and SBH^+ species provide valuable information concerning the mode of protonation of these SB porphyrins and their electronic structures.

2. Experimental

2.1 *Materials*

Nickel(II) and copper(II) meso-tetraphenyl porphyrin aldehydes MTPP-CHO were synthesised making use of the procedure of Momenteau *et al* (1979). The *trans* 4,4'-diamino-dibenzo-18-crown-6 was prepared according to the earlier described procedure (Thanabal and Krishnan 1981). The amines, *n*-butyl amine, *p*-anisidine and *m*-nitroaniline were procured from Aldrich Chemicals (USA) and used as received. All the solvents employed in the study were distilled and dried before use. Representative preparation of Schiff-base porphyrins are given below.

2.1a *Schiff base of NiTPP and p-anisidine*: A solution containing 0·10 g of NiTPP-CHO in 100 ml toluene and 0·20 g of *p*-anisidine dissolved in minimum amount of CH_3OH was refluxed for 4 h. At the end of this period, the solvent was removed under reduced pressure and the residue was quickly washed with CH_3OH to remove the excess amine. The product was crystallized from CH_3OH/CH_2Cl_2 (1:1 by vol) solvent mixture.

2.1b *Schiff base of NiTPP/CuTPP and diaminodibenzo-18-crown-6*: To a 0·50 g of CuTPP/NiTPP-(CHO) in 200 ml of toluene, 0·015 g of *trans* 4,4'-diamino-dibenzo-18-crown-6 in 10 ml of CH_3OH was added slowly over a period of 30 min. This solution was refluxed for 3 h and the solvent was removed under reduced

pressure. The residue was washed with CH_3OH several times to remove the unreacted amine. The product was taken in $CHCl_3$ and chromatographed on a neutral alumina column. The dimer was obtained after elution with $CHCl_3$.

The Schiff base complexes prepared in this study are shown in figure 1. The yields in all the cases were about 10% based on the porphyrin-aldehyde. It is found that repeated chromatography degrades the Schiff bases.

2.2 *Methods*

Schiff base protonation/deprotonation were performed according to the following procedure. Air, equilibrated over concentrated HCl was bubbled through a 100 ml solution of SB in $CHCl_3$. The progress in protonation was monitored by following the increase in absorbance at 620 nm. The protonation of SB is also accomplished by successive addition of CF_3COOH. The deprotonation reaction was carried out either by bubbling air saturated with triethyl amine or by the addition of pyridine in
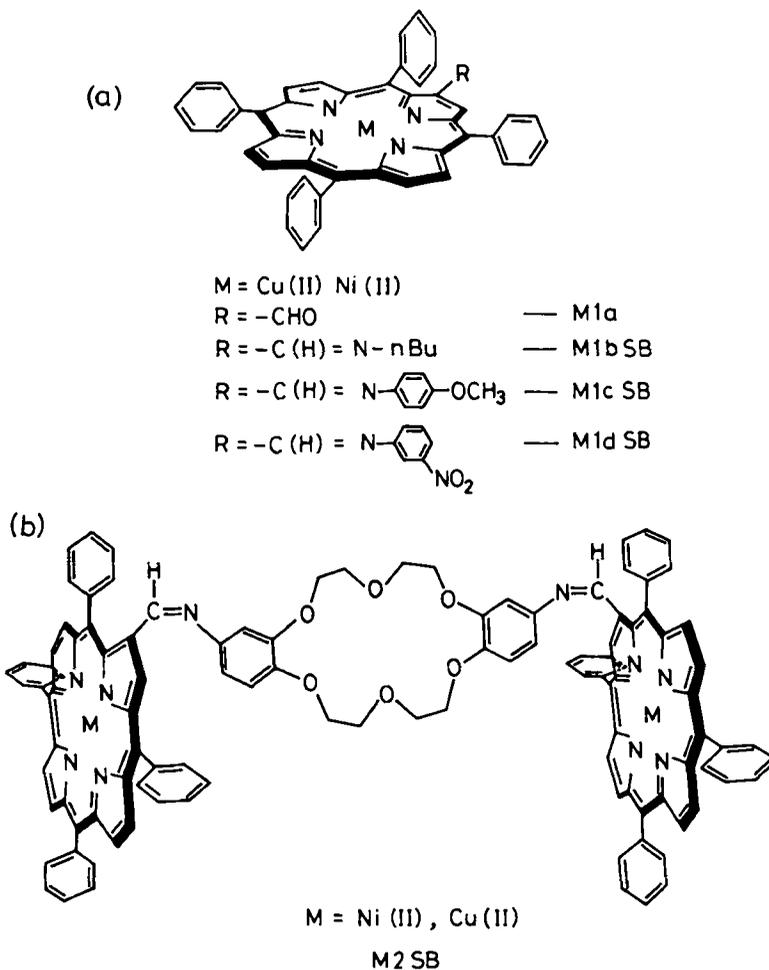
Figure 1. The chemical structures of (a) monomeric, and (b) dimeric Schiff-base complexes of Ni(II) and Cu(II) porphyrins.

dry ether to the acidified solution of SB. Sufficient care was taken to avoid the entrance of moisture when carrying out all the above reactions.

It is important to note that the features observed during the protonation/ deprotonation of dimeric SB porphyrins are essentially the same as that observed for monomeric SB porphyrins. We have not been able to identify any monoprotonated form of the dimeric SB porphyrin. Spectroscopic and electrochemical measurements were carried out on instruments described earlier (Bhaskar Maiya and Krishnan 1985).

3. Results and discussion

The SB derivatives of the metalloporphyrins have been synthesised from the corresponding formyl compounds. The structural integrity of these compounds has been established from the absorption spectral and ^{1}H NMR data.

The absorption spectral profiles of CuTPP, CuTPP(CHO), and Cu1bSB in CHCl$_3$ are shown in figure 2. It is observed that the Q bands of the porphyrins are red-shifted on formylation. The porphyrin Schiff bases exhibit absorption bands at shorter wavelengths relative to the formylated products. Dramatic changes in the absorption spectral features of SB porphyrins are observed on protonation of these compounds with CF$_3$COOH/HCl. Successive addition of the acid to the SB derivatives of Cu(II) and Ni(II) porphyrins results in very large spectral shifts of the Q bands to the red region and a splitting/broadening of B bands (figure 3). The absorption data of all SB porphyrins and their protonated analogues are given in table 1. It can be seen that SBH$^+$ species [Ni(II) and Cu(II) derivatives of Ic and Id, and dimeric SB] endowed with aromatic side groups exhibit a larger red shift (40 nm) of the Q bands relative to the SBH$^+$ compounds bearing aliphatic side groups [Ni(II)/Cu(II)1bSB]. It is found that the magnitudes of these red shifts are independent of the nature of the metal ion. This suggests that the changes in the absorption profiles are due to the localized charges on the periphery of the porphyrins and absence of any M-N (σ or π bond) interaction with the peripheral charge. Significantly, addition of bases, pyridine or triethylamine, to the SBH$^+$ species returns the original spectrum of SB indicating that the protonation is a completely reversible process. It is of interest to note that the magnitude of the spectral shifts and the shapes of the red-shifted bands observed on protonation of the bisporphyrin Schiff-bases are not different from the corresponding monomeric protonated Schiff bases. This implies that the protonation occurs in a concerted fashion and the spectral changes are a consequence of the electronic structure of the SBH$^+$ species. The origin of the spectral shifts in SBH$^+$ could be either due to the delocalization of the positive charge on the ring or to the localization of the hole on the periphery in an electron-deficient group in conjugation with the ring. In order to investigate the effect of the latter, we synthesized an ethylcyanoacetate adduct of CuTPP(CHO)/NiTPP(CHO) in which the substituent at the periphery of the porphyrin is electron-withdrawing but coulombically neutral. The absorption spectral features of these adducts closely resemble the features observed for SBH$^+$ derivatives (table 1). This suggests that the charge in SBH$^+$ is localized on the macrocycle. The presence of a positive charge in the porphyrin periphery can lead to the lowering of the energy of the π orbital of –C(H) = $\overset{+}{N}$ (H)–R entity of SBH$^+$

causing a perturbation of π^* (e_g) orbitals of the porphyrin macrocycle resulting in the red-shift of the Q bands of SBH^+. These effects are investigated using magnetic resonance spectroscopy.

The proton NMR spectra of NiTPP(CHO), NilcSB and the corresponding SBH^+ in $CDCl_3$ are shown in figure 4. It is found that all the proton resonances, β-pyrrole (8·90–8·60 ppm), o-mesoaryl (8·00–7·80 ppm) and *m* and *p meso* aryl (7·78–7·60 ppm) groups of the porphyrin aldehyde are shifted marginally in the corresponding Schiff bases. Of particular interest is the shift in the proton resonance of NiTPP(*CHO*) at 9·20 ppm to 9·30 ppm on imine, $-C(H) = N-R$, formation. The resonances originating from the R group are assigned based on comparison with the resonance spectrum of NiTPP(CHO). We observed dramatic changes in the proton resonances of SB on protonation. It is found that the
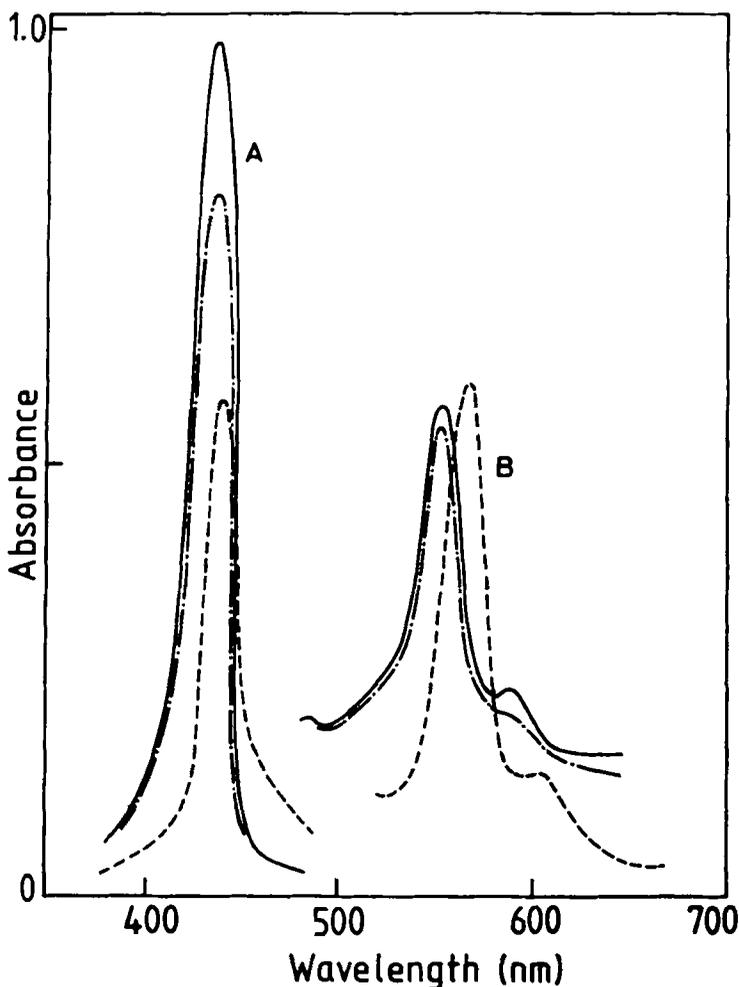
Figure 2. Optical absorption spectral profiles of CuTPP(——), CuTPPCHO(- - -) and CulbSB(-·-·-) in $CHCl_3$ at 298 K. (A) The concentrations employed are 1·0 to 4·0 μM. (B) The concentrations employed are 0·1 to 0·4 mM.
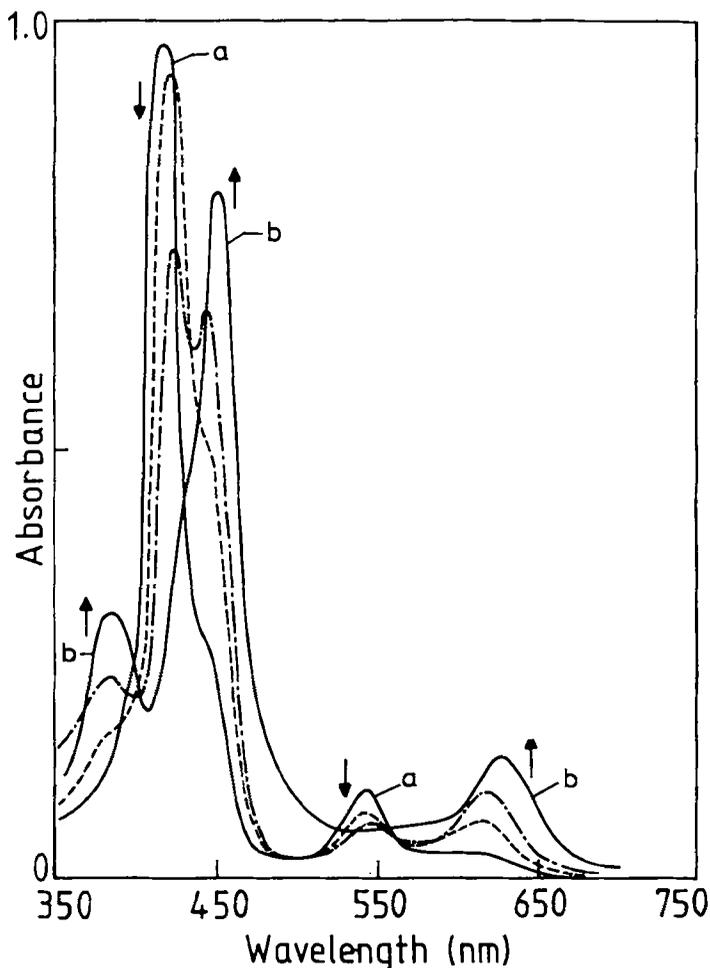
Figure 3. Optical absorption spectral changes observed on successive addition of CF_3COOH to Cu1bSB in $CHCl_3$ at 298 K. (a) Cu1bSB and (b) completely protonated derivative Cu1b2SH$^+$. The concentration of Cu1bSB employed is 1.0–2.0 μM.

resonances of the protons close to the positive charge, $-C(H) = \overset{+}{N}(H)R$, are progressively shifted to higher fields and broadened. On the other hand, the β-pyrrole and *meso* aryl proton resonances occur around the same field as that observed for the SB indicating that these protons are less affected by protonation. Interestingly, the proton bonded to the carbon in $-C(H) = \overset{+}{N}(H)R$ resonates in the upfield region relative to its position at 9·30 ppm in the SB. We ascribe this to the shielding effect induced on protonation and to the π-electron anisotropy experienced by the $-C(H) = \overset{+}{N}(H)-R$ group. It is noteworthy that the presence of a positive charge on the nitrogen of the SBH$^+$ results in the deshielding and broadening of the proton resonances of the R group. The latter decreases with increasing distance between the positive charge and the R group. These findings

**Table 1.** Visible spectral data on Schiff-base complexes and their protonated species in CHCl₃ at 298 K[a].

Compound	λ(nm)			
	Q₁	Q₂	B₂	B₁
CuTPP	580	541	417	
Cu1a	590	551	429	
Cu1bSB	580	545	419	
Cu1bSBH⁺	628		452	387
Cu1cSB	587	549	425	
Cu1cSBH⁺	643		476	397
Cu1dSB	587	547	431	
Cu1dSBH⁺	648		476	396
Cu2SB6	587	549	425	
Cu2SBH⁺ᵇ	646		474	394
NiTPP	573	528	416	
Ni1a	576	538	428	
Ni1bSB	575	536	422	
Ni1bSBH⁺	615		446	380
Ni1cSB	580	540	426	
Ni1cSBH⁺	638		472	390
Ni1dSB	583	541	429	
Ni1dSBH⁺	640		475	395
Ni2SBb	580	537	427	
Ni2SBH⁺ᵇ	650		475	380
Ni-ethyl cyano acetate adduct	667		448	

[a] Protonation was achieved by adding HCl or CF₃COOH;
[b] Addition of Cs⁺ to these dimeric porphyrins does not alter the spectral features.

collectively show that the protonation of the SB is similar to the effect of creating an exceptionally strong electron-withdrawing group in the periphery of the macrocycle.

It would be of interest to study whether there exists any electronic coupling of the π-system and the peripheral positive charge. The Schiff bases of Cu(II) porphyrins are chosen to study these effects using EPR spectroscopy. The EPR spectra of Cu1dSB and the corresponding SBH⁺ in toluene at 100 K are shown in figure 5. The spectra were analysed using the spin Hamiltonian for axial symmetry (Assour 1965). The values of g and A tensors have been calculated for all the monomeric and dimeric SB derivatives, and their corresponding protonated species (table 2). It is found that the EPR spectral features of SB and SBH⁺ species are similar and the magnitudes of the g and A values do not markedly change in SB and in the protonated SBH⁺ complexes. These two observations indicate that the hole created at the porphyrin periphery is not electronically coupled with the π-system so as to create a perturbation at the Cu(II) centre. This also suggests the absence of any Cu(II)-Cu(II) interaction in the crown ether interspersed dimeric Schiff base derivatives of Cu(II) porphyrins (Thanabal and Krishnan 1982). The possibility of axial coordination of the added proton donors CF₃COOH/HCl to the Cu(II) centre is discarded since the g and A values do not increase in the SBH⁺ species relative to
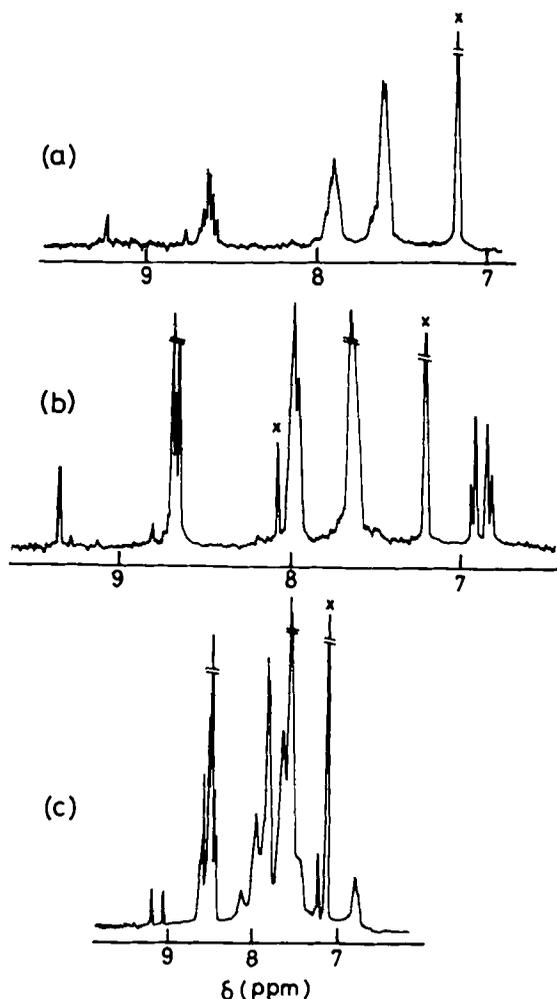
Figure 4. The ^{1}H NMR spectra of (a) NiTPPCHO, (b) NilcSB and (c) NilcSBH$^+$ in CDCl$_3$ at 298 K. NilcSBH$^+$ is produced on addition of CF$_3$COOH to NilcSB. Solvent impurity peaks are marked X.

those observed for the corresponding SB (Chandrashekar and Krishnan 1981, 1982). The marginal changes in EPR parameters in SBH$^+$ relative to SB can be ascribed to the inductive effects of the peripheral electron-withdrawing group, $-C(H) = \overset{+}{N}(H)-R$.

It is known that the redox properties of the porphyrins are strongly influenced by the electron-donating or -withdrawing nature of the substituents (Felton 1978). The cyclic voltammograms (CV) of the various SB and their protonated complexes have been studied to elucidate the effect of the substituents on the redox potentials. The CV of CulbSB and its derivatives in the anodic region are shown in figure 6. The two reversible peaks observed in the region 0–1·50 V correspond to the successive one-electron transfers from the porphyrin ring. This is confirmed by the analysis of
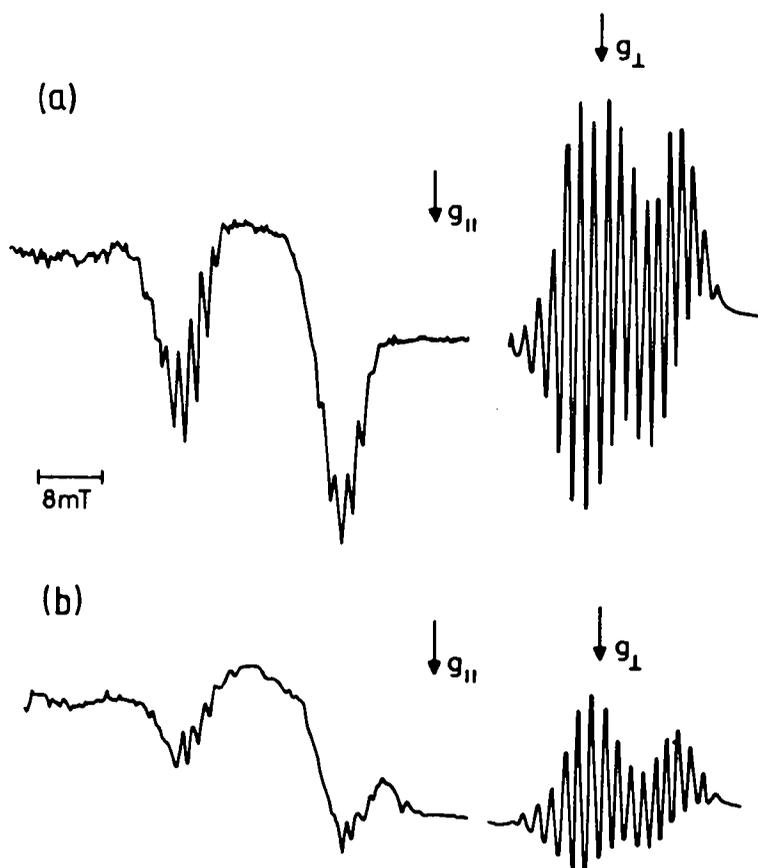
Figure 5. EPR spectra of (a) CuldSB, and (b) CuldSBH$^+$ in toluene at 100 K. CuldSBH$^+$ is produced by addition of HCl to CuldSB.

Table 2. EPR data on Cu(II) derivatives of Schiff-base complexes and their protonated analogues in toluene at 100 K.

	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}^{Cu}$	$A_{\perp}^{Cu}$	$A_{\parallel}^{N}$	$A_{\perp}^{N}$
				$(\times 10^{-4}\ cm^{-1})$		
CuTPP	2·185	2·047	208·0	31·5	14·8	16·0
Cula	2·152	2·013	196·0	31·0	14·3	15·5
CulbSB	2·167	2·029	198·0	31·9	14·3	16·0
CulbSBH$^+$	2·173	2·023	198·0	31·1	14·4	15·7
CulcSB	2·157	2·022	201·0	31·3	14·3	15·5
CulcSBH$^+$	2·160	2·020	205·0	30·0	14·6	15·4
CuldSB	2·158	2·020	200·0	31·2	14·3	15·6
CuldSBH$^+$	2·159	2·024	201·0	31·2	14·4	15·5
Cu2SB	2·138	1·989	207·0	31·1	15·0	15·6
Cu2SBH^{+a}	2·160	2·019	*	31·4	*	15·7
Cu2SBH$^+$ + Cs^a	2·138	1·985	207·0	30·8	15·1	15·7

^{a} Spectra were taken in $CH_3OH:CH_2Cl_2$ (1:1, V/V) solvent mixture; * Spectrum is not well resolved to calculate these values.
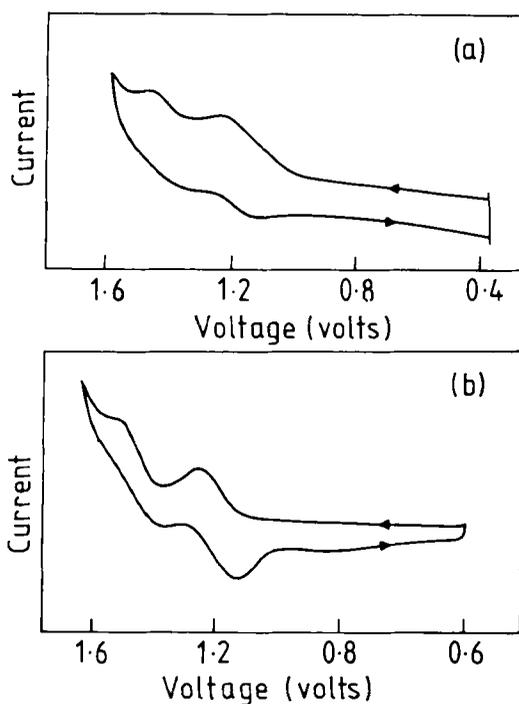
Figure 6. Cyclic voltammograms of (a) CulbSB, and (b) CulbSBH⁺, in CH_2Cl_2 containing 100 mM TBAP at 298 K. Scan rate 50 mV/s. CulbSBH⁺ was produced on addition of CF_3COOH to CulbSB. Potentials are with respect to SCE.

current-voltage profiles at different scan rates. The electrochemical data obtained for all other Cu(II) and Ni(II) derivatives are given in table 3. An inspection of the table reveals that the SB porphyrins exhibit ring oxidation potentials in a lower anodic region relative to that of the porphyrin-aldehyde, while on protonation, the SBH⁺ species exhibit ring oxidation at a higher anodic potential relative to the SB. This shows that the addition of acid renders the electron removal from the porphyrin more difficult suggesting that the $-C(H) = \overset{+}{N} (H)-R$ group situated at the periphery of the porphyrin is indeed a strong withdrawing group.

The electrochemical redox data has provided information on the relative energy difference between the HOMO and the LUMO in the various synthesized porphyrin aldehydes, Schiff bases and their corresponding protonated species. The difference between the first oxidation potential and the reduction potential of the porphyrin ring can be approximated to the energy difference betwen the HOMO and the LUMO in the porphyrins (Fuhrhop 1974). It is observed that the energy difference between the HOMO and the LUMO in the SB porphyrins are marginally higher than the porphyrin aldehydes. This affords an explanation of the blue shift of the Q bands observed on SB formation. It was earlier suggested that in the SBH⁺ species, there is considerable mixing of the π^* orbital of the substituent with the e_g (π^*) orbital of the porphyrin ring leading to the stabilization of the latter orbital. This suggests that the reduction of the substituent group should occur at a higher cathodic potential relative to the free state. Though we are unable to probe into the reduction of the substituent electrochemistry, the trend in the oxidation

Table 3. Redox potentials of Schiff-base and their protonated complexes in CH_2Cl_2 at 298 K[a].

Compound[b]	$P \longrightarrow P^{+\cdot}$, V	$P^{+\cdot} \longrightarrow P^{2+}$, V	$P \longrightarrow P^{-\cdot}$, V
CuTPP	1·01	1·26	−1·29
Cu1a	1·08	1·32	−1·11
Cu1bSB	1·15	1·38	−1·26
Cu1bSBH⁺	1·18	1·36	
Cu1cSB	1·14	1·45	−1·21
Cu1cSBH⁺	1·16	1·49	
Cu1dSB	1·16	1·37	−1·16
Cu1dSBH⁺	1·26	1·43	
Cu2SB	1·01	1·35	−1·19
Cu2SBH⁺	0·94[c]		
NiTPP	1·18		−1·21
Ni1a	1·15		−1·10
Ni1bSB	1·19		−1·22
Ni1bSBH⁺	1·23		−1·26
Ni1cSB	1·25		−1·22
Ni1cSBH⁺	1·26		
Ni1dSB	1·25		−1·20
Ni1dSBH⁺	1·21		
Ni2SB	1·19		−1·16
Ni2SBH⁺	1·12[c]		

[a] Potentials are reported with respect to SCE, Error: ± 20 mV.
[b] P, $P^{+\cdot}$, P^{2+} and $P^{-\cdot}$ refer to neutral, monocation radical, dication and monoanion radical species of the corresponding porphyrins, respectively.
[c] Represents two-electron transfer.

potentials of the SBH⁺ species indicate that the energy differences between the HOMO and the LUMO are lower than in the corresponding SB porphyrins. This provides an explanation of the red shift of the Q bands observed for SBH⁺ species.

Of special interest is the electrochemical behaviour of dimeric SBH⁺ derivatives of Cu(II) porphyrins. Earlier studies on *bis* Cu(II) systems reveal that the Cu(II)-Cu(II) interactions are easily manifested in the magnitudes of the oxidation/reduction potentials (Collman *et al* 1979; Liu *et al* 1983). The CV of the *bis* Cu(II) derivative, Cu2bSB, in CH_2Cl_2 exhibits a reversible peak (figure 7) at 1·01 V involving one-electron oxidation of the porphyrin ring. This shows that the porphyrin rings are essentially non-interacting in the *bis* Cu(II) derivatives (Collman *et al* 1980; Leznoff *et al* 1984). Interestingly, on protonation, the SBH^{2+} species exhibit a potential at 0·94 V involving a two-electron oxidation in contrast to the one-electron oxidation of the corresponding non-protonated Schiff base (figure 7). This seems to suggest that the presence of a positive charge on the periphery of the porphyrins in the *bis* Cu(II) derivatives possibly alters the mechanism of heterogenous electron transfer (Nicholson 1965). We believe that the two porphyrin rings in the dimer respond to oxidation independently and that the interaction between them is weak since the two rings are separated by more than 10 Å and the covalent bridge that exists between them is conformationally rigid.

In our earlier studies, we demonstrated the utility of cavity-bearing porphyrins as efficient ionophores (Dasgupta *et al* 1982). We investigated the ionophore
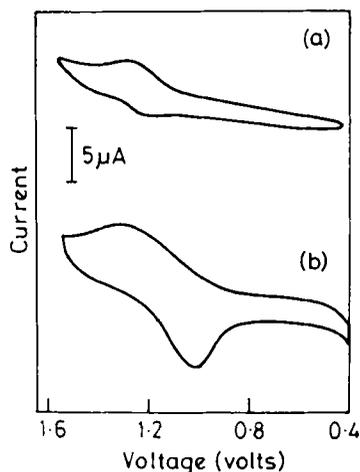
Figure 7. Cyclic voltammograms of (a) Cu2bSB, and (b) Cu2bSBH$_2^{2+}$, in CH$_2$Cl$_2$ containing 100 mM TBAP at 298 K. Scan rate 50 mV/s. SBH$_2^{2+}$ was produced on addition of CF$_3$COOH to SB. Potentials are with reference to SCE.

behaviour of *bis*Cu(II)/Ni(II) porphyrins bearing a dibenzo-18-crown-6 cavity. Of special importance is the study of the complexation behaviour of *bis*porphyrins with those cations which require two dibenzo-18-crown-6 cavities, since the cation encapsulation can result in the dimeric derivatives of the *bis* Cu(II)/Ni(II) porphyrins similar to the cation-induced dimers of crown ether porphyrins (Thanabal and Krishnan 1982). It is known that the Cs$^+$ ion forms 1:2 (cation : dibenzo-18-crown-6) complexes with crown ether (Pedersen 1967). It is observed that the addition of CsCl/CsCNS solution (CH$_3$OH : CHCl$_3$ 1:1 by vol) to the Cu2SB/Ni2SB or their protonated derivatives in the same solvent mixture does not produce any shifts in Q or B absorption bands of the porphyrins. However, the ^{1}H NMR spectra of a solution containing Ni2SB/Ni2SBH^{2+} in CD$_3$OD/CD$_3$CN and Cs$^+$ ion reveal broadening of the proton resonances of the ether fragments in the region 3·00–4·00 ppm suggesting Cs$^+$ complexation with the crown ether (Live and Chan 1976). Owing to poor resolution of the ^{1}H NMR spectrum, it is difficult to assess the extent of complexation in these systems. We investigated the EPR spectra of Cs$^+$ complexes of Cu2SBH/Cu2SBH^{2+} in toluene at 100 K in the anticipation of detecting axial dimers of *bis* Cu(II) SB and its promoted derivatives. The EPR parameters of the Cs$^+$ complexes reveal no significant change in g and A tensor values and show the absence of $\Delta m = \pm 2$ transitions. This indicates that the complexation of Cs$^+$ ion does not result in dimers of *bis* Cu(II) SB derivatives possessing axial symmetry. The presence of Cs$^+$ ion in the dibenzo-18-crown-6 cavity of the *bis* Cu(II)/Ni(II) SB porphyrins and their protonated species does not alter the ring oxidation/reduction potentials of these porphyrins. It is of interest to note that the oxidation potentials of Cs$^+$ complexes of protonated derivatives involve a two-electron process. The Cs$^+$ complexes of these porphyrins, though formed in solution, do not exhibit any marked changes in the spectral features. This can be due to two reasons: (i) the effect of ion-dipole (of the ether oxygens) interactions are not transmitted to the porphyrin π-manifold because of large distance and/or absence of conjugation to the ring and (ii) the dimers of the *bis*

Cu(II)/Ni(II) SB porphyrins as a consequence of Cs^+ ion complexation do not possess the axial symmetry, and/or the distance between the two *bis*porphyrins in the dimer are very large.

4. Conclusions

It is shown that protonation of the Schiff-base derivatives of Ni(II) and Cu(II) porphyrins endowed with various amines, $R-NH_2$, with varying R produces a red-shift of 40 nm in the Q bands of the porphyrin. The observed red-shift in these model compounds are analogous to the shift observed between the *in vivo* and *in vitro* chlorophyll molecules. This suggests that the structurally modified porphyrins form viable alternatives to the special-pair model of P680 in plant-bacterial photosynthetic systems. It is reasonable to assume that a protein residue can enter Schiff base formation with a formyl/keto group of the tetrapyrrole derivatives of P680. Protonation of this can lead to the observed red-shift in the primary donor in P680 relative to the isolated *in vitro* monomeric pigments. It is recognized that the plant pigments possess Mg ions in the macrocycle and the *in vitro* studies containing Mg ions are sensitive to demetallation on protonation. Moreover, the pigments bearing Mg are fluorescent while the Cu(II)/Ni(II) derivatives reported here are non-fluorescent. Interestingly, however, the observed two-electron oxidations in the protonated *bis*-Cu(II)SB porphyrins is encouraging in view of the recent studies in the search for multielectron catalytic systems of biological interest.

It is illustrated that the red-shift in the Q bands observed for the protonated SB derivatives essentially arise from the localized positive charge, $(-CH=\overset{+}{N}HR)$, in the periphery of the macrocycle. Several lines of evidence have been presented for the non-interacting positive charge in these systems. We demonstrate here that the Schiff base formation need not necessarily arise from formyl porphyrins (where the formyl group is situated in one of the β-pyrrole rings) and an amine. Instead, a porphyrin amine, mono p-aminophenyl triphenyl porphyrin can be used for SB formation with benzaldehyde. The protonation of the latter leads to the red-shifts of the Q bands similar to that observed in the formyl-porphyrin Schiff bases (unpublished). This shows that the presence of a positive charge in any remote position can lead to the red shifts of the Q bands, arising from the perturbation/mixing of the π^* orbital of the substituent with the LUMO of the porphyrins.

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