Water-soluble Thiaporphyrins and Metallothiaporphyrins; Synthesis, Characterization, Ground- and Excited-state Properties†

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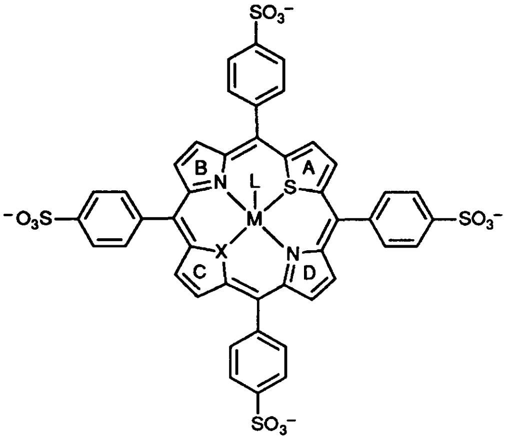
The synthesis and characterization of two anionic water-soluble thiaporphyrins 5,10,15,20-tetrakis-(4-sulfonatophenyl)-21-thiaporphyrin (Htsptp^{4-}) and 5,10,15,20-tetrakis(4-sulfonatophenyl)-21,23-dithiaporphyrin (tspdtp^{4-}) and derivatives of the former with Cu^{2+} and Ni^{2+} {[Cu(tsptp)Cl]$^{4-}$ and [Ni(tsptp)Cl]$^{4-}$} have been carried out. Both Htsptp^{4-} and tspdtp^{4-} show aggregation in aqueous solution. Addition of cation and 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) to dilute monomeric solutions of either results in cofacial dimer formation similar to that observed for normal anionic water-soluble porphyrins. The electronic absorption spectra of both the paramagnetic metal derivatives of the monothiaporphyrin show a split Soret band and a complex pattern of Q bands due to reduced symmetry. The fluorescence of the two thiaporphyrins is quenched considerably relative to H_2tspp^{4-}[5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin], the magnitude of quenching depending on the number of sulfur atoms in the porphyrin core. Electrochemical studies indicate harder oxidations and easier reductions for Htsptp^{4-} and tspdtp^{4-} relative to H_2tspp^{4-}. Addition of a first electron to [Cu(tsptp)Cl]$^{4-}$ or [Ni(tsptp)Cl]$^{4-}$ results in the reduction of the metal centre suggesting that the metal $d_{x^2-y^2}$ orbital is lower in energy than the empty porphyrin $e_g(\pi^*)$ orbitals in contrast to those of [Cu(tspp)]$^{4-}$ and [Ni(tspp)]$^{4-}$.

The electronic structure of the porphyrin skeleton can be influenced significantly by a suitable modification of the porphyrin core. Thiaporphyrins, in which one or more pyrrole rings are replaced by thiophene ring(s) represent one class of such core-modified porphyrins.[1–3] Development of elegant synthetic methodologies[4,5] for the synthesis of thiaporphyrins has attracted many studies on their complexing ability,[6] electrochemical behaviour[7] and aromatic character.[4,8] Monothiaporphyrins have been extensively used as ligands and X-ray crystal structures of a few transition-metal derivatives have revealed many interesting co-ordination properties of these ligands.[9–11] However, no studies have so far been made on water-soluble analogues of thiaporphyrins. In view of this, we have synthesised two anionic water-soluble thiaporphyrins 5,10,15,20-tetrakis(4-sulfonatophenyl)-21-thiaporphyrin (Htsptp^{4-}) and 5,10,15,20-tetrakis(4-sulfonatophenyl)-21,23-dithiaporphyrin (tspdtp^{4-}) and prepared copper- and nickel-(II) derivatives with the former. The spectroscopic and electrochemical properties of these derivatives are studied. Comparison of the properties of thiaporphyrins with normal porphyrins has revealed both similarities and differences with respect to aggregation behaviour, magnetic properties and redox behaviour.



X	M	L	
NH	–	–	Htsptp^{4-}
N	Cu^{2+}	Cl^-	[Cu(tsptp)Cl]$^{4-}$
N	Ni^{2+}	Cl^-	[Ni(tsptp)Cl]$^{4-}$
S	–	–	tspdtp^{4-}

Results and Discussion

Sulfonation of porphyrins by chlorosulfonic acid employed in the preparation of the two new thiaporphyrins has many advantages over the traditional method utilizing sulfuric acid. These include milder reaction conditions, shorter reaction times, higher yields, and easier purification of products. The sulfonation of many delicate porphyrins such as basket handle- and bridged-porphyrins has been achieved by this method.

Proton NMR spectroscopy has been used to identify the new thiaporphyrins. The ^1H NMR spectra of Htsptp^{4-} and tspdtp^{4-} in $(CD_3)_2SO$ are shown in Fig. 1 and chemical shifts and coupling constants are listed in Table 1. For tspdtp^{4-} all the four thiophene protons and the four pyrrole protons resonate as sharp singlets as a consequence of the high symmetry of the molecule. The phenyl protons appear as an AB quartet with coupling constants comparable to those of *para*-substituted benzenes. On the other hand, the reduced symmetry of the monothiaporphyrin Htsptp^{4-} results in the inequivalence of the pyrrole protons, the two pyrrole protons of ring C resonate as a singlet while the four pyrrole protons of rings B and D resonate as an AB quartet. Two sets of quartets in the region δ 8.0–8.3 are due to the phenyl protons. Thus, the NMR spectrum clearly confirms that sulfonation has taken place at the *para* position of the *meso*-phenyl ring.

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† *Non-SI units employed:* G = 10^{-4} T, eV ≈ 1.6×10^{-19} J.

Table 1 Chemical shifts and coupling constants (*J*/Hz) of $Htsptp^{4-}$ and $tspdtp^{4-}$ in $(CD_3)_2SO$

		Pyrrole (H^P)		Phenyl		
Porphyrin	Thiophene (H^T)	Ring C	Ring B and D	*o*-H	*m*-H	N-H
$Htsptp^{4-}$	9.8 (s)	8.98 (s)	8.78 (d) 8.60 (d) $J_{AB} = 4.08$	8.24 (d) 8.13 (d) $J_{AB} = 6.12$	8.21 (d) 8.05 (d) $J_{AB} = 6.12$	−2.81 (s)
$tspdtp^{4-}$	9.78 (s)	8.69 (s)		8.28 (d) $J_{AB} = 8.16$	8.13 (d) $J_{AB} = 8.16$	—

Table 2 Electronic absorption spectral data λ/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1}) of free-base and metallothiaporphyrins *

		Q bands			
Porphyrin	Soret band	IV	III	II	I
$Htsptp^{4-}$	425 (187)	514 (14.9)	548 (4.7)	608 (2.5)	667 (2.8)
$tspdtp^{4-}$	431 (96)	514 (11.1)	547 (3.90)	625 (1.4)	687 (2.3)
$[Cu(tsptp)Cl]^{4-}$	434 (100) 463 (sh)	—	557 (5.9)	616 (4.1)	686 (2.6)
$[Ni(tsptp)Cl]^{4-}$	445 (61) 458 (56)	—	560 (5.1)	633 (4.1)	690 (3.2)

* sh = Shoulder.

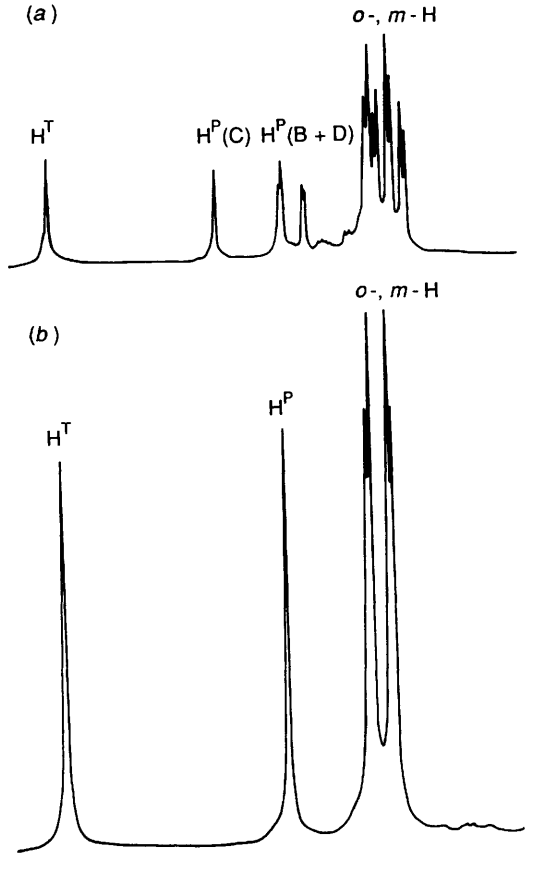

Fig. 1 Proton NMR spectra of (*a*) $Htsptp^{4-}$ and (*b*) $tspdtp^{4-}$ in $[^2H_6]$dmso at 25 °C ($c = 5 \times 10^{-4}$ mol dm^{-3})

Optical Spectra.—Sulfonation of the free-base thiaporphyrins does not affect significantly the peak positions or intensities of the Soret or Q bands (Table 2). However, the free-base thiaporphyrins do show extensive aggregation in aqueous solution.

Table 3 Dimerization-induced absorption band shifts[a] (nm) and the exciton splitting parameter (*V*) for free base- and metallo-thiaporphyrins in the presence of cation and 18-crown-6

	Q bands				
Porphyrin	I	II	III	IV	V^b/cm^{-1}
$Htsptp^{4-}$	23	11 (sh)	14	9	1025
$tspdtp^{4-}$	22	5 (sh)	15	9	905
H_2tspp^{4-}	22	15 (sh)	12	9	1065
$[Ni(tsptp)Cl]^{4-}$	2	0	2		63
$[Cu(tsptp)Cl]^{4-}$	6	−3	9		232

[a] Positive value indicates red shift. [b] Calculated from shift of Q(1) band.

Beer's law studies indicate that $Htsptp^{4-}$ and $tspdtp^{4-}$ obey Beer's law in the concentration range 1.5×10^{-5}–3×10^{-4} mol dm^{-3} for the former and 1.1×10^{-5}–4.4×10^{-4} mol dm^{-3} for the latter. Metalloporphyrins generally show only two Q bands, Q(0,0) and Q(1,0) arising from D_{4h} symmetry.[12] The fact that the copper- and nickel-(II) derivatives of the monothiaporphyrin $Htsptp^{4-}$ show split Soret bands and complex patterns of Q bands (Fig. 2) suggests a low symmetry probably indicating non-planarity in the porphyrin core. Both $[Cu(tsptp)Cl]^{4-}$ and $[Ni(tsptp)Cl]^{4-}$ are paramagnetic with the former showing an axial EPR signal (MeOH, 100 K), $g_{\parallel} = 2.187$, $g_{\perp} = 2.043$ $A_{\parallel}^{Cu} = 168$ G and $A_{\perp}^{N} = 12.0$ G. These values are closer to those observed for 21-methyl-5,10,15,20-tetraphenylporphyrinatocopper[13] than for $[Cu(tspp)]^{4-}$ $[H_2tspp^{4-}$ = 5,10,15,20-tetrakis(4-sulfonatophenyl)-porphyrin].[14] The magnetic moment for $[Ni(tsptp)Cl]^{4-}$ measured by the Evans NMR method[15] in water at 27 °C is 3.5 which corresponds to a high-spin ground state with $S = 1$.

It is well established that dilute solutions of water-soluble porphyrins tend to dimerize in aqueous solution in the presence of electrolytes and our earlier studies[16] have shown that dimerization can be induced by addition of alkali-metal cations and 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane). The inset in Fig. 3 shows the effect upon the intensity of a prominent Q band upon titration of K^+ into dilute solutions of various thiaporphyrins ($\approx 1 \times 10^{-5}$ mol dm^{-3}) containing 0.05 mol dm^{-3} 18-crown-6. Dimerization is most apparent by a broadening and decrease in the absorption coefficients of the Soret band and a red shift of all the Q bands. A comparison of

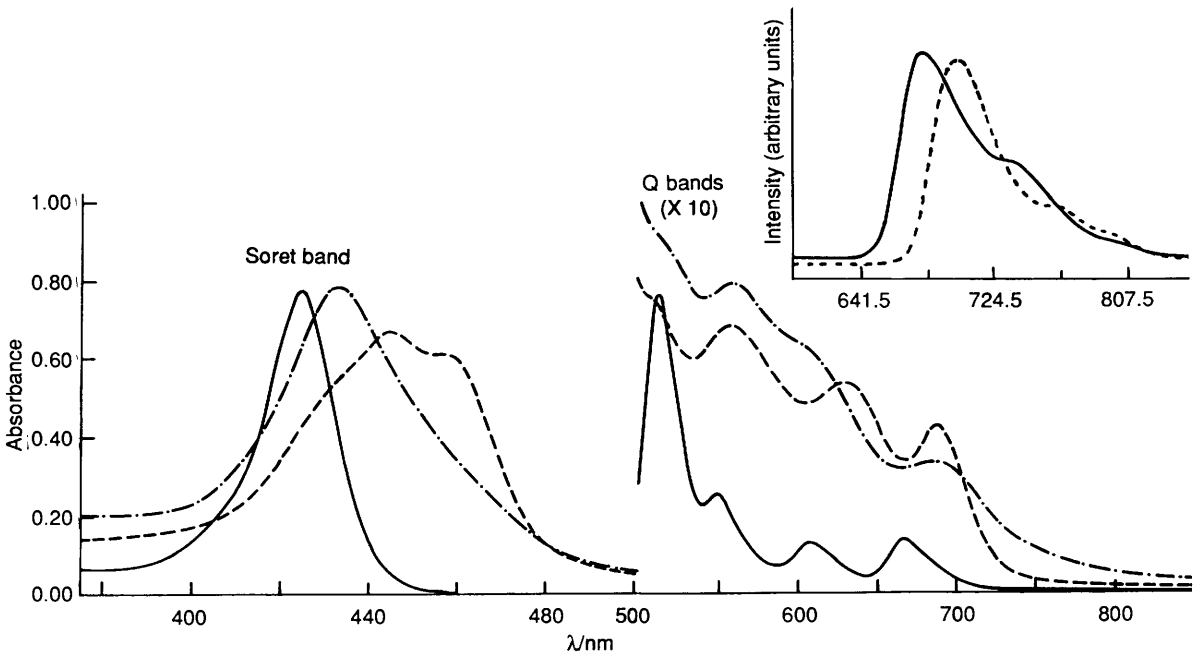

Fig. 2 Electronic absorption spectra of Htsptp^{4-} (——), [Cu(tsptp)Cl]$^{4-}$ (— · — · —) and [Ni(tsptp)Cl]$^{4-}$ (– – – –) in water ($c \approx 1 \times 10^{-5}$ mol dm^{-3}). The inset shows the fluorescence spectra of Htsptp^{4-} (——) (4.90×10^{-5} mol dm^{-3}) and tspdtp^{4-} (– – – –) (5.2×10^{-5} mol dm^{-3}) in water

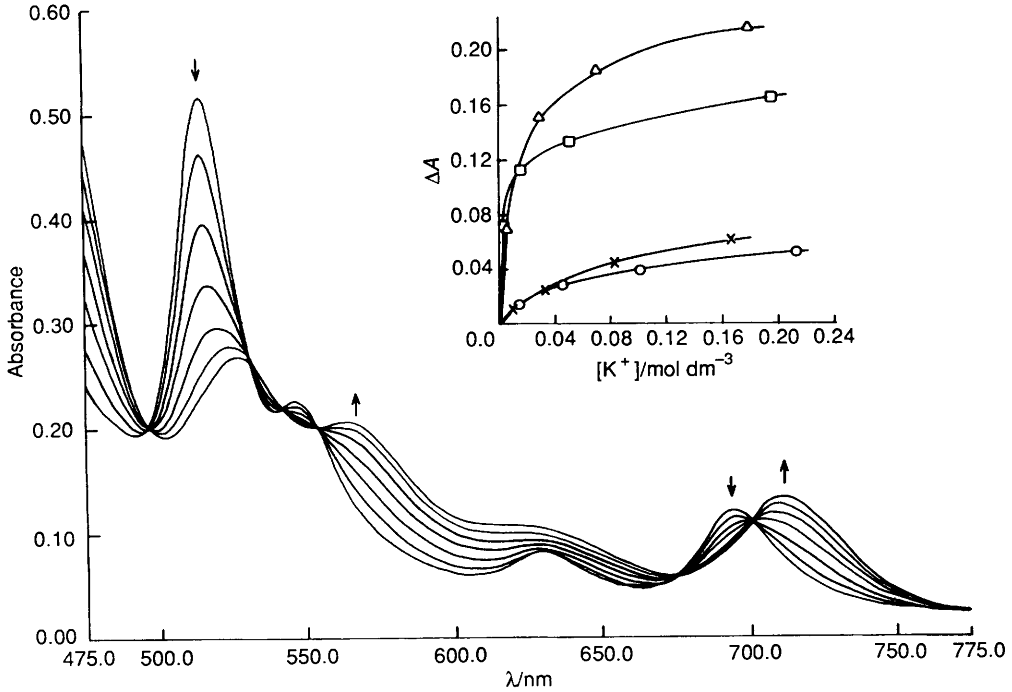

Fig. 3 Effect of temperature on Q bands of tspdtp^{4-} (5.55×10^{-5} mol dm^{-3}) containing 18-crown-6 (0.05 mol dm^{-3}) and K$^+$ (0.196 mol dm^{-3}) in water; T = 10, 20, 30, 40, 50, 60 and 70 °C. Arrows indicate changes on decreasing temperature. The inset shows the absorbance changes of a prominent Q band of Htsptp^{4-} (△), tspdtp^{4-} (□), [Cu(tsptp)Cl]$^{4-}$ (×) and [Ni(tsptp)Cl]$^{4-}$ (○) in solutions containing 18-crown-6 (0.05 mol dm^{-3}) upon increasing concentrations of K$^+$ ions

the dimerization-induced red shift for Htsptp^{4-} and tspdtp^{4-} with the structurally similar non-thiaporphyrin H$_2$tspp^{4-} indicates similar magnitudes of dimerization (Table 3) and the exciton splitting parameter calculated from the available spectral data is comparable to those observed recently for cation-induced dimerization of crowned phthalocyanins[17] and porphyrins.[16c] The magnitude of the red shift and the intensity decrease for the metal derivatives [Cu(tsptp)Cl]$^{4-}$ and [Ni(tsptp)Cl]$^{4-}$ are much less relative to the free-base derivatives. This is ascribed to the non-planarity of the porphyrin core in the metal derivatives resulting in a decreased π–π interaction (which is at least in part responsible for the red shift) between the two rings in a cofacial geometry.[18]

The effect of temperature on an aqueous solution containing tspdtp^{4-} (5.55×10^{-5} mol dm^{-3}), 18-crown-6 (0.05 mol dm^{-3}) and K$^+$ (0.196 mol dm^{-3}) is shown in Fig. 3. The presence of well defined isosbestic points is indicative of a monomer–dimer equilibrium in solution. Evidently, small changes in temperature have a large effect on the extent of dimerization with lower temperatures favouring the formation of the dimer while higher temperatures shift the equilibrium towards the monomer.

The shapes of the curves in Fig. 3 (inset) reveal that the

Table 4 Redox potentials[a] of free base- and metallo-thiaporphyrins

Porphyrin	Solvent	Oxidation $E_{\frac{1}{2}}$ (1)	Reduction $E_{\frac{1}{2}}$ (M^{2+}–M^{+})	$E_{\frac{1}{2}}$ (1)	$E_{\frac{1}{2}}$ (2)	Δ(Redox)[b]
H_2tspp^{4-}	dmf	+1.10	—	−0.964	−1.536	2.064
$Htsptp^{4-}$	dmf	+1.164	—	−0.845	−1.364	2.009
	dmso	—	—	−0.845	−1.382	—
$tspdtp^{4-}$	dmf	+1.240	—	−0.745	−1.245	1.985
	dmso	—	—	−0.745	−1.254	—
$[Cu(tsptp)Cl]^{4-}$	dmf	—	−0.099[c]	−0.946	−1.40	—
	dmso	—	−0.095[c]	−0.945	−1.382	—
$[Ni(tsptp)Cl]^{4-}$	dmf	—	−0.346[d]	−0.768[c]	—	—
	dmso	—	−0.400[d]	−0.719[c]	−1.391	—

[a] Unless indicated otherwise $E_{\frac{1}{2}}$ values correspond to peak potentials for irreversible process. [b] Δ(redox) = $E_{\frac{1}{2}}$ (1) (ox) − $E_{\frac{1}{2}}$ (1) (red). [c] $E_{\frac{1}{2}}$ value for reversible process. [d] $E_{\frac{1}{2}}$ value for quasi-reversible process.

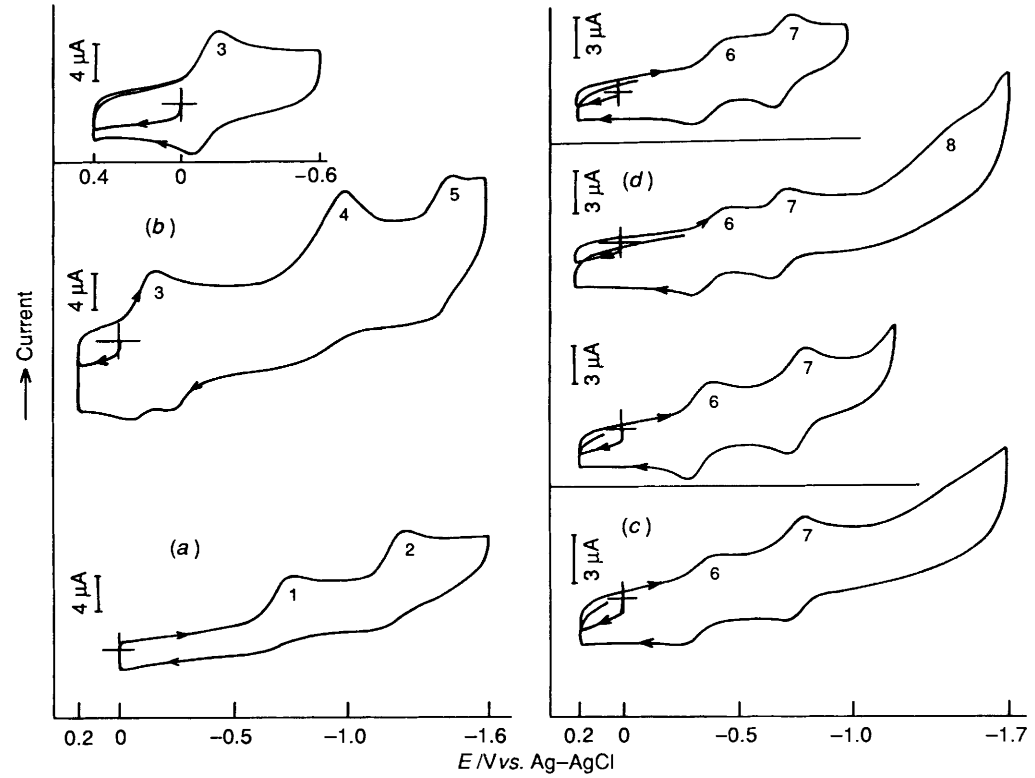

Fig. 4 Cyclic voltammograms of (*a*) $tspdtp^{4-}$ (≈6.9 × 10^{-4} mol dm^{-3}) in dmf, v = 100 mV s^{-1}; (*b*) $[Cu(tsptp)Cl]^{4-}$ (≈5.7 × 10^{-4} mol dm^{-3}) in dmf, v = 300 mV s^{-1} (inset shows the reversible nature of Cu^{II}–Cu^{I} reduction); (*c*) $[Ni(tsptp)Cl]^{4-}$ (≈5.4 × 10^{-4} mol dm^{-3}) in dmf, v = 100 mV s^{-1}; and (*d*) $[Ni(tsptp)Cl]^{4-}$ (≈6.5 × 10^{-4} mol dm^{-3}) in dmso, v = 100 mV s^{-1}. The insets to (*c*) and (*d*) show the quasi-reversible and reversible nature of waves 6 and 7 respectively

process of formation of the dimer involves more than one step. Two types of dimer can be visualised upon addition of cation–crown ether complex; a 'non-sandwich' dimer of the type porphyrin–(cation-crown ether)–porphyrin involving only one cation–crown ether complex per dimer and a cofacial or sandwich dimer which involves two or more cation–crown ether complexes per dimer. At lower concentrations of K^+, the intensity decrease is sharp probably indicating the formation of a non-sandwich dimer with a very high formation constant. At higher concentrations of K^+, a transformation of non-sandwich dimer to a cofacial dimer occurs by encapsulating a second cation–crown ether complex. Since two more sites are still available in the cofacial dimer for saturation, it is possible that the encapsulation continues at higher concentration until the two porphyrin units bind four cation–crown ether moieties. The formation constants evaluated by the method described earlier[16c] vary as $Htsptp^{4-}$ (log K = 10.6) > $tspdtp^{4-}$ (log K = 9.5) and the magnitudes are similar to those observed for related anionic porphyrins.

Electrochemistry.—Cyclic voltammetry was used to examine the redox reactions of the free mono- and di-thiaporphyrins and of the metalloderivatives. Both $Htsptp^{4-}$ and $tspdtp^{4-}$ exhibit one-electron irreversible oxidations which are shifted positively by 64 and 140 mV respectively relative to H_2tspp^{4-} in dimethylformamide (dmf).[19] Reductions were examined in dmf and dimethyl sulfoxide (dmso). A typical cyclic voltammogram of $tspdtp^{4-}$ in dmf is shown in Fig. 4(*a*). Waves 1 and 2 correspond to two one-electron reductions, both of which are chemically irreversible. The monothiaporphyrin $Htsptp^{4-}$ in dmf shows similar behaviour but with an additional cathodic peak at −0.2 V. This peak is observed at low scan speed (20–200 mV s^{-1}) and disappears at higher scan speeds (>500 mV s^{-1}) indicating a coupled chemical reaction. The two reductions observed for the free-base derivatives correspond to the formation of mono- and di-anions of the porphyrin ring. These results are parallel to those observed for the non-thia H_2tspp^{4-}[19,20] except that the potentials are shifted to more positive values upon heteroatom substitution and a regular decrease in Δ(redox) is observed for the series. It has been well established that in thiaporphyrins both the highest occupied- (HOMO) and lowest unoccupied- (LUMO) molecular orbitals are stabilized by different mechanisms.[7]

In dmf $[Cu(tsptp)Cl]^{4-}$ shows three one-electron reductions [Fig. 4(*b*)]. The first reduction (wave 3) is reversible in both dmf ($\Delta E_p = 72$ mV, $i_{pc}/i_{pa} \approx 1$) and dmso ($\Delta E_p = 63$ mV, $i_{pc}/i_{pa} \approx 1$) when scanned separately [Fig. 4(*b*) (inset)]. The $E_{\frac{1}{2}}$ values corresponding to this couple are much more anodic than the corresponding reductions for free $Htsptp^{4-}$ (Table 4), and thus can be assigned to a metal-centred process leading to the formation of $[Cu^I(tsptp)Cl]^{5-}$. This is in contrast to the behaviour of $[Cu(tspp)]^{4-}$ where the first electron reduction corresponds to a ligand-centred process, leading to the formation of $[Cu^{II}(tspp^{\bullet -})]^{5-}$.[21] Addition of a second electron to $[Cu^I(tsptp)Cl]^{5-}$ results in the formation of $[Cu^I(tsptp^{\bullet -})Cl]^{6-}$ (wave 4) and addition of a further electron gives $[Cu^I(tsptp^{2-})Cl]^{7-}$ (wave 5). Both these reductions are chemically irreversible. The absolute potential difference between the two successive ring reductions is 0.454 V in dmf and 0.437 V in dmso, which is within the range of 0.45 ± 0.05 V expected for two successive ring reductions as found for a variety of metallo derivatives of 2,3,7,8,12,13,17,18-octaethylporphyrin and 5,10,15,20-tetraphenylporphyrin.[22] Furthermore, upon scan reversal, an additional cathodic peak is observed at around −0.2 V similar to that observed for the free porphyrin $Htsptp^{4-}$. On repetitive scans at constant scan speed, there is an enhancement of this peak. This is ascribed to the instability of the $Cu^I(tsptp^{2-})$ moiety resulting in demetallation of copper from the porphyrin. A similar decomposition was observed[23] upon electrode reduction of $[Cu(tptp)]^+$ (Htptp = 5,10,15,20-tetraphenyl-21-thiaporphyrin).

The cyclic voltammograms of $[Ni(tsptp)Cl]^{4-}$ in dmf and dmso are shown in Fig. 4(*c*) and (*d*). Two well defined reductions (waves 6 and 7) and a broad ill defined anodic peak (wave 8) at 1.391 V (in dmso) are observed. The first reduction in both the solvents is quasi-reversible [$\Delta E_p = 91$ mV (dmf) and 128 mV (dmso), $i_{pc}/i_{pa} \approx 1$, Fig. 4(*c*) and (*d*) (inset)]. As for the copper derivative, the $E_{\frac{1}{2}}$ value for this reduction is not in the range of the first reduction of the free porphyrin, so discounting the possibility of ring reduction. Instead, this process is ascribed to a metal-centred reduction corresponding to the formation of $[Ni^I(tsptp)Cl]^{5-}$. This behaviour is in contrast to that observed for $[Ni(tspp)]^{4-}$ where addition of the first electron results in formation of a porphyrin radical.[24] It is pertinent that the first reduction of [Ni(tptp)Cl] in thf gives the nickel(I) species $[Ni^I(tptp)Cl]^-$. Two cathodic waves observed at −0.23 and −0.52 V were assigned to the formation of $[Ni^I(tptp)]$ and $[Ni^I(tptp)Cl]^-$ based on the dependence of the peak current on addition of LiCl as source of chloride ligand.[25] However, in the present study only one couple (wave 6) was observed in both the solvents for the nickel(II)–nickel(I) couple and addition of LiCl had no appreciable effect on the peak current of wave 6 indicating that the axial chloride ligand is not dissociated under our experimental conditions.

The addition of a second electron results in the formation of the porphyrin radical $[Ni^I(tsptp^{\bullet -})Cl]^{6-}$ and this reduction is reversible in both dmf and dmso (wave 7) ($\Delta E_p = 64$ mV, 73 mV, $i_{pa}/i_{pc} \approx 1$ respectively). Addition of a further electron results in the formation of $[Ni^I(tsptp^{2-})Cl]^{7-}$ (wave 8). The absolute potential difference between the two successive ring reductions is 0.57 V which is slightly more than the expected value of 0.45 ± 0.05 V. Because of the broadness and irreversible nature of this peak (wave 8) only peak potentials are reported while for the first ring redution (wave 7) the $E_{\frac{1}{2}}$ value corresponds to midpoint of the anodic and cathodic peaks. This probably accounts for the small observed difference.

It is well known that the site of reduction of the metalloporphyrin complexes with redox-active metals depends on the relative energies of the empty porphyrin $e_g(\pi^*)$ orbitals and the filled metal d orbitals. Consideration of the first reduction potentials of H_2tspp^{4-} and $Htsptp^{4-}$ indicates that the $e_g(\pi^*)$ orbitals of the latter are lower in energy by about 119 mV relative to that of the former. Despite this, the first electron addition to copper- or nickel-(II) derivatives of the monothiaporphyrin results in metal-centred reduction suggesting that the metal $d_{x^2-y^2}$ orbitals in both the metals are in fact lower in energy than the $e_g(\pi^*)$ orbitals of the porphyrin ring. The reverse is true for the non-thiaporphyrin derivatives $[Cu(tspp)]^{4-}$ and $[Ni(tspp)]^{4-}$. The following explanation is offered for this observation. The structures of the monothiaporphyrin complexes [Cu(tptp)Cl][3,6] and [Ni(tptp)Cl][6,10] have revealed that the porphyrin plane is non-planar and the thiophene ring is sharply bent out of the plane of the porphyrin. The shape of the porphyrin resembles that seen in metal complexes of porphyrin *N*-oxides[26] and *N*-alkylporphyrins.[13b] The introduction of SO_3^- groups at the *p*-phenyl rings should not affect the distorted geometry around the metal ion in $[Cu(tsptp)Cl]^{4-}$ and $[Ni(tsptp)Cl]^{4-}$. The observation of split Soret bands and a complex pattern of Q bands in the electronic spectra also suggests such a conclusion. On the other hand, both of the non-thia porphyrin complexes $[Ni(tspp)]^{4-}$ and $[Cu(tspp)]^{4-}$ have planar porphyrin cores.[12b] Thus, this difference in the structures of the porphyrin core around the metal ion in going from the non-thia to mono-thia derivatives is probably responsible for the reversal of order of energy levels.

Fluorescence Spectra.—Both $Htsptp^{4-}$ and $tspdtp^{4-}$ exhibit room-temperature fluorescence [Fig. 2 (inset)] in dilute aqueous solution and the emission maxima are red-shifted relative to the free base H_2tspp^{4-} consistent with the reduction in Δ(redox). The magnitude of the red shift and the intensity quenching depends on the number of S atom(s) in the porphyrin core. The fluorescence quantum yield calculated by a comparative method[27] using H_2tspp^{4-} as standard ($\varphi_f = 0.08$), the natural radiative lifetime (τ_o) estimated from the absorption and the emission spectra using Birks–Dyson[28] modification of the Strickler–Berg equation,[29] the rate of intersystem crossing (K_{isc}) and the rate of fluorescence radiative decay (K_f) are in Table 5. The general features of these findings can be summarized as follows: (*a*) the quantum yield decreases in the series $H_2tspp^{4-} > Htsptp^{4-} > tspdtp^{4-}$, τ_o and K_{isc} increase in the order $H_2tspp^{4-} < Htsptp^{4-} < tspdtp^{4-}$ and (*b*) there is a small decrease in K_f in the order $H_2tspp^{4-} > Htsptp^{4-} > tspdtp^{4-}$. The decrease in quantum yield can be ascribed in part to the increase in K_{isc} and τ_o due to the introduction of heavy sulfur atom(s) into the porphyrin core. The heavy-atom effect[12] is known to increase the rate of K_{isc} and the increase in K_{isc} upon thia substitution is consistent with this. However, in porphyrin systems, internal conversion (ic) is known to be one of the major decay pathways from the S_1 state.[12] A rough estimate of φ_{ic} for H_2tspp^{4-} from known values of φ_f (0.08) and φ_T (0.78)[20] suggests that internal conversion accounts for about 14% of the decay. In the absence of φ_T values for thiaporphyrins, estimates of the contribution of internal conversion to decay of the S_1 state is difficult. Nevertheless, a contribution from internal conversion to decay of the S_1 state is expected on the basis of theoretical calculations by Gouterman and co-workers[30] which predict the absence of any low-lying charge-transfer state for 5,10,15,20-tetraphenyl-21,23-dithiaporphyrin (tpdtp).[30] Thus, it is reasonable to presume that the combined effect of increase in K_{isc} rates and internal conversion accounts for the decrease in the quantum yield upon substitution of nitrogen by sulfur.

The singlet excited-state potentials estimated from the

Table 5 Singlet excited-state parameters of thiaporphyrins

Porphyrin	Emission band maxima/nm Q(0,0)	Q(0,1)	Quantum yield φ_f	τ_0/ns	10^{-6} K_f/s^{-1}	10^{-8} K_{isc}/s^{-1}	E_{0-0} (P–P*)/eV	*$E°$ (P$^+$–*P)^a/V	*$E°$ (*P–P$^-$)^b/V
Htsptp^{4-}	678	742	0.0055	234	4.3	7.77	1.83	−0.666	+0.985
	(686)	(776)							
tspdtp^{4-}	703	768	0.0042	278	3.6	8.53	1.76	−0.520	+1.015
	(720)	(800)							
H$_2$tspp^{4-}	645	700	0.08	203	4.9	0.56	1.92	−0.82	+0.956
	(669)	(750)							

Values in parentheses correspond to emission maxima of dimers. [a] Excited-state oxidation potential. [b] Excited-state reduction potential.

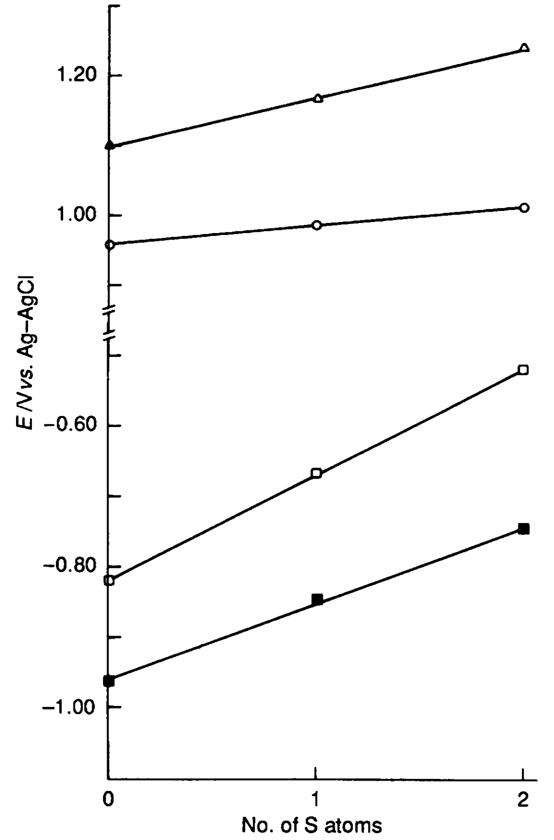

Fig. 5 Plots of ground-state potentials $E°$(P$^+$–P) (△), $E°$(P–P$^-$) (■) and excited-state potentials $E°$(*P–P$^-$) (○), $E°$(P$^+$–*P) (□) *versus* the number of sulfur atoms in the porphyrin core

ground-state redox potentials and the singlet excited-state energies[31] (Table 5) reveal the following features: (*a*) thiaporphyrins are better oxidants (by 150–200 mV) and poorer reductants in the first singlet excited state relative to H$_2$tspp^{4-}; (*b*) tspdtp^{4-} is a better oxidant (by 146 mV) than Htsptp^{4-}. It is interesting that the $E_{\frac{1}{2}}$ values evaluated both for ground- and excited-states can be correlated with the number of sulfur atom(s) in the porphyrin core. Such a plot, shown in Fig. 5, is consistent with the observation that thiaporphyrins are harder to oxidize and easier to reduce both in the ground and excited states than are ordinary porphyrins.

Conclusion

The analysis of the various spectroscopic data of water-soluble free-base thiaporphyrins and their metal derivatives presented here has clearly outlined the similarities and differences between H$_2$tspp^{4-} and its thia analogues. It has been shown that similarities exist with respect to dimerization, absorption and emission characteristics and in redox behaviour. Many differences however occur between the copper- and nickel-(II) derivatives of the thiaporphyrin Htsptp^{4-} and of H$_2$tspp^{4-} relating to their magnetic properties and electrochemical behaviour. The former in fact show similar behaviour to copper- and nickel-(II) derivatives of *N*-substituted metalloporphyrins.[13] Further studies are in progress to stabilize the nickel- and copper-(I) derivatives of Htsptp^{4-} by chemical reduction using mild reducing agents. Preliminary results in this direction are quite encouraging.

Experimental

The ligands Htptp and tpdtp were synthesised and purified as described in our earlier work.[11]

Synthesis of [NH$_4$]$_4$[Htsptp].—The porphyrin Htptp (0.200 g, 0.317 mmol) was dissolved in chloroform (30 cm^3) in a 100 cm^3 three neck flask. Chlorosulfonic acid (1.408 g, 0.8 cm^3 12.09 mmol) was slowly added with vigorous stirring and the mixture was heated for 1 h at 45 °C. The stirring was continued until the evolution of HCl gas ceased. Excess of chlorosulfonic acid was decomposed by addition of ice-cold water (20 cm^3). The mixture was cooled to 5 °C for 3 h and filtered. The green precipitate was washed three times with ice-cold water (3 × 2 cm^3), several times with acetone and dried in an oven at 65 °C for 2 h. The precipitate was dissolved in dry methanol (150 cm^3) and ammonia gas was passed through the solution until its green colour changed to yellow orange. The solution was filtered and the volume of the methanol solution was reduced to 20 cm^3 under reduced pressure. Dry acetone (70 cm^3) was added to precipitate the porphyrin which was purified by three successive reprecipitations from methanol with acetone. The black-violet crystals (0.255 g) obtained were dried *in vacuo* in an oven at 80 °C for 18 h: yield 79%.

The dithiaporphyrin [NH$_4$]$_4$[tspdtp] was also prepared by the above method.

Synthesis of [NH$_4$]$_4$[Cu(tsptp)Cl].—The porphyrin salt [NH$_4$]$_4$[Htsptp] (0.05 g, 0.0491 mmol) and CuCl$_2$·2H$_2$O (0.030 g, 0.1760 mmol) in methanol (120 cm^3) was refluxed for 8 h. The progress of the reaction was monitored by optical absorption spectroscopy. Upon completion the solvent was evaporated under reduced pressure to 20 cm^3 and dry acetone (70 cm^3) was added to precipitate the complex which was purified by three successive reprecipitations from methanol upon addition of acetone. The black crystals (0.046 g) obtained were dried *in vacuo* in an oven at 75 °C for 12 h: yield 84%.

Synthesis of [NH$_4$]$_4$[Ni(tsptp)Cl].—The porphyrin salt [NH$_4$]$_4$[Htsptp] (0.05 g, 0.0491 mmol) was dissolved in methanol (175 cm^3) and the solution refluxed for 15 min. Nickel(II) dichloride hexahydrate (0.045 g, 0.1893 mmol) in methanol (25 cm^3) was added to the solution and refluxing was continued for 26 h. The progress of the reaction was monitored by optical absorption spectroscopy. Upon completion the solvent was evaporated under reduced pressure to 25 cm^3 and dry acetone (90 cm^3) was added to precipitate the porphyrin which was washed with acetone and purified by three successive reprecipitations from methanol upon addition of acetone. The black crystals (0.043 g) obtained were dried *in vacuo* in an oven at 75 °C for 18 h: yield 79%.

18-Crown-6 (Aldrich, USA) was used as received. All the solvents were purified and dried before use. Doubly distilled water was used for studies in aqueous media.

Fluorescence spectra were recorded on a Jobin Yvon model (Jy. 3CS) spectrofluorometer. The details of other spectrometers are the same as described earlier.[32] The magnetic susceptibility measurements were done in water using the peak of water as the reference.

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