Synthesis and Physico-chemical Properties of Cationic Derivatives of Phthalocyaninatocopper(II)†

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4,11,18,25-Tetra(chlorosulphonyl)phthalocyaninatocopper(II) and its 3,10,17,24-isomer have been used to prepare organo-soluble 4,11,18,25-tetra(2-pyridylmethylaminosulphonyl)-phthalocyaninatocopper(II) and its 3,10,17,24-isomer. These compounds in turn have been used to prepare water-soluble 4,11,18,25-tetra(*N*-methyl-2-pyridiniomethylaminosulphonyl)-phthalocyaninatocopper(II) tetra(methyl sulphate) and its 3,10,17,24-isomer. Spectrophotometric and e.s.r. measurements show that the organo-soluble forms and the water-soluble derivatives give rise to solute–solute interactions in their appropriate solutions. The relative amounts of each species in the monomer–dimer–polymer equilibria depends on the composition of the appropriate solutions. E.s.r. measurements on frozen solutions of each of the phthalocyaninatocopper(II) derivatives show clear evidence for the formation of dimeric forms of the chelates which are characterized by spectra arising from magnetic dipole–dipole coupling between the copper(II) centres, which form a triplet state. The e.s.r. spectral component attributed to the dimeric species is closely similar for all the compounds studied so that dimer formation is entirely determined by interactions between the phthalocyanine ring system. Computer simulation of the experimental e.s.r. spectra due to the dimeric species makes possible the determination of the spin-Hamiltonian parameters associated with the copper(II) centres as well as the distance between the copper(II) centres. Some comparisons of the measurements have been made with commercially available phthalocyaninatocopper(II) dyestuffs in their organo-soluble and cationic water-soluble forms.

The metallophthalocyanines and their derivatives are of promiscuous use in the dye and pigment industry.[1-3] Water solubility of these compounds may be achieved by the presence of hydrophilic exocyclic groups such as the pyridyl group which endows water solubility by quaternisation to cationic forms as a result of protonation in acidic media or methylation. The position of the pyridyl group in the phthalocyanine derivative may be one of attachment from a single carbon atom position or form part of the macrocyclic ring system, as in the pyridinoporphyrazines. The synthesis of compounds containing the pyridyl group directly attached to the phthalocyanine ring system has been achieved by condensation of 4-(2-, 3-, or 4-pyridyl)-1,2-dicyanobenzene and by reaction of 3,10,17,24-tetradiazophthalocyaninatocopper(II) with pyridine.[4] The implacement of the pyridyl group into the exocyclic functional group results from the condensation of tetrasulphonylphthalocyanine with 2-, 3-, or 4-aminopyridine[5] or from the reaction of 3,10,17,24-tetra(chloromethyl)phthalocyanine with pyridine.[6]

Reaction of metallophthalocyanines and in particular the copper(II) chelate with chlorosulphonic acid and thionyl chloride to introduce the chlorosulphonyl group into the ring system is one of the major routes in the synthesis of metallophthalocyanine derivatives. Reaction of the tetra(chlorosulphonyl)phthalocyanine with 2-(aminomethyl)pyridine presents the opportunity to build the pyridyl group into the exocyclic structure. This group in turn can be methylated to give a phthalocyanine derivative with peripheral cationic charges at some distance from the ring system. The solute–solvent axial interactions, and redox and catalytic properties of the metallophthalocyanines and their derivatives are influenced by their solute–solute interactions which are of ubiquitous occurrence in solutions containing the anionic tetrasulphonatophthalocyaninatometalates,[7,8] while absent in aqueous solutions containing tetracationic derivatives of tetra-2′,3′-pyrido[*b,g,l,q*]-5,10,15,20-tetra-azaporphyrin where the cationic charge is part of the ring system.[9] The purpose of the present investigation is to observe whether or not the solute–solute interactions persist when the peripheral positive charge resides on the exocyclic groups at some distance from the ring system and at different positions on the ring system.

Results

Preparation of Phthalocyaninatocopper(II) *Derivatives.*—The reactions which lead to the formation of water-soluble tetracationic derivatives of phthalocyaninatocopper(II) [Cu^{II}(pc)] are as follows. Taking the case involving substitution in the 4,11,18,25-positions of the ring, reaction of [Cu^{II}(pc)] with chlorosulphonic acid and thionyl chloride gives 4,11,18,25-tetra(chlorosulphonyl)phthalocyaninatocopper(II), 4,11,18,25-[Cu^{II}(tcspc)], which after treatment with 2-(aminomethyl)-pyridine leads to 4,11,18,25-tetra(2-pyridylmethylaminosulphonyl)phthalocyaninatocopper(II), 4,11,18,25-[Cu^{II}(tpmaspc)]. Finally reaction of the latter compound with dimethylformamide (dmf) containing dimethyl sulphate leads to the tetracationic derivative 4,11,18,25-tetra(*N*-methyl-2-pyridiniomethylaminosulphonyl)phthalocyaninatocopper(II), 4,11,18,25-[Cu^{II}(tmpmaspc)]$^{4+}$ isolated as its tetra(methyl sulphate) salt. The corresponding tetracationic 3,10,17,24-isomer may be prepared starting with tetrasodium 3,10,17,24-tetrasulphonatophthalocyaninatocuprate(II), Na_4[Cu^{II}(tspc)], which reacts with chlorosulphonic acid and thionyl chloride to produce 3,10,17,24-[Cu^{II}(tcspc)]. The properties of the neutral and tetracationic materials prepared here were compared with

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† *Non-S.I. unit employed:* mmHg = 133 Pa.

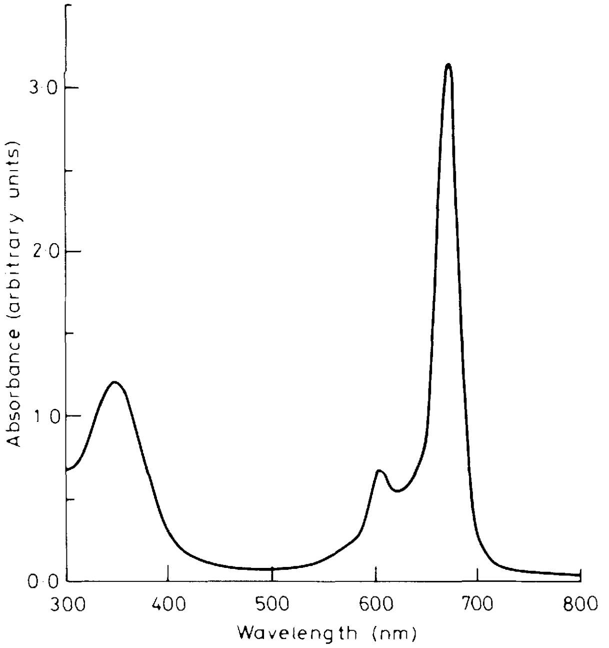

Figure 1. Electronic absorption spectrum of 4,11,18,25-[Cu^{II}(tpmaspc)] (2.002×10^{-6} mol dm^{-3}) in dmf in a 10-cm quartz cell

those containing neutral and cationic sulphonamide groups available commercially. The neutral compound made available by Hoechst Farbewerken AG possesses the formula 4,11,18-$(SO_2NHCH_2CH_2CH_2NMe_2)_3$-phthalocyaninatocopper(II) ('4,11,18-Hoechst') while the water-soluble cationic derivative was made available by Bayer AG and represented as [4,11,18,25-$(SO_2NHCH_2CH_2CH_2NMe_3)_{3.3}$-phthalocyaninatocopper(II)]$[CH_3SO_4^-]_{3.3}$ ('4,11,18,25-Bayer'). The latter material is thought to be a mixture of tri- and tetra-substituted [Cu^{II}(pc)].

Electronic Spectra of the Phthalocyaninatocopper(II) *Derivatives.*—The phthalocyaninatocopper(II) derivatives give rise to intense blue solutions when dissolved in certain organic solvents. A typical example of their electronic absorption spectra in the visible region is shown in Figure 1, which depicts the results for a dmf solution of 4,11,18,25-[Cu^{II}(tpmaspc)] (2.002×10^{-6} mol dm^{-3}). The molar absorption coefficients for the remaining compounds in dmf, pyridine, and chloroform are given in Table 1. It is of interest to note the difference in solubility properties of the 4,11,18,25- and 3,10,17,24-isomers with respect to chloroform. Addition of water to dmf solutions containing 4,18,11,25-[Cu^{II}(tpmaspc)] results in a progressive diminution of the absorption at 678 nm (Figure 2) and the emergence of a broader much less intense band in the 620 nm region, which indicates the presence in solution of solute–solute interactions. A comparison of the extent to which solute–solute

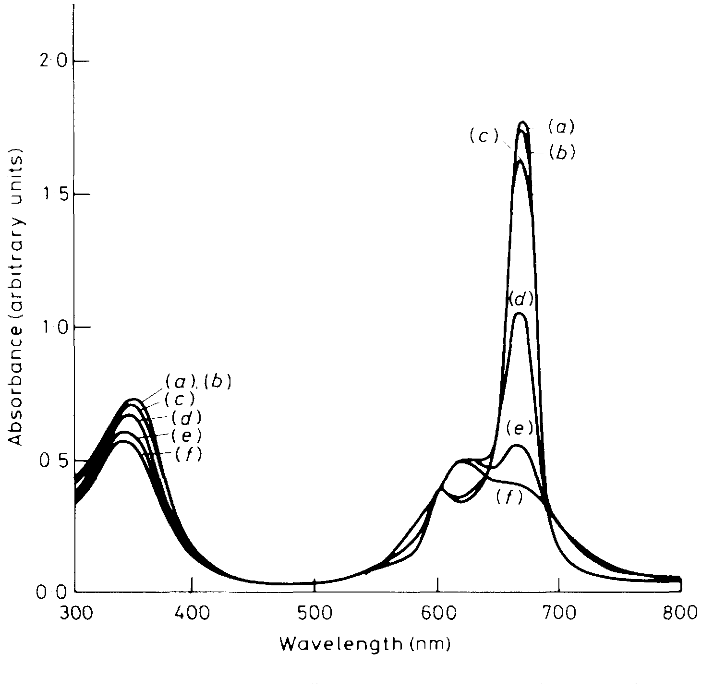

Figure 2. Electronic absorption spectra of solutions of 4,11,18,25-[Cu^{II}(tpmaspc)] (2.166×10^{-6} mol dm^{-3}) in dmf with increasing amounts of water added, recorded in a 10-cm quartz cell: (*a*) dmf alone; (*b*) dmf–water (95:5 v/v); (*c*) dmf–water (80:20 v/v); (*d*) dmf–water (60:40 v/v); (*e*) dmf–water (40:60 v/v); (*f*) dmf–water (20:80 v/v)

Table 1. Molar absorption coefficients (dm^3 mol^{-1} cm^{-1})* of the phthalocyaninatocopper(II) derivatives

Solvent	3,10,17,24-[Cu^{II}(tpmaspc)]	4,11,18,25-[Cu^{II}(tpmaspc)]	4,11,18-Hoechst
dmf	11.9×10^4 (678)	15.7×10^4 (673)	14.7×10^4 (671)
Pyridine	12.0×10^4 (684)	15.5×10^4 (675)	14.5×10^4 (674)
Chloroform	Not soluble	15.5×10^4 (673)	14.6×10^4 (671)

* Wavelengths of maximum absorption (nm) are given in parentheses.

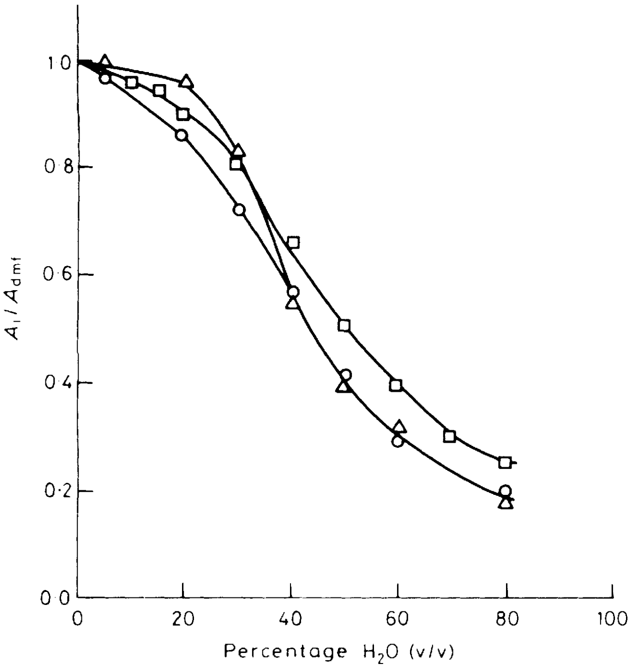

Figure 3. Plot of the absorbance of the monomer band (~670 nm) as a function of the percentage of water in the dmf solution. The absorbance readings, A_i, have been normalized with respect to the absorbance of the chelate in dmf alone, A_{dmf}. Concentrations of the chelates were 1.0 × 10^{-6} mol dm^{-3} and 10-cm quartz cells were used. (△) 4,11,18,25-Bayer; (○) 4,11,18,25-[Cu^{II}(tspc)]; (□) 3,10,17,24-[Cu^{II}(tspc)]

aggregation occurs as a result of addition of water to dmf solutions containing the various phthalocyaninatocopper(II) derivatives may be made by plotting the intensity of the main absorption band $A_{H_2O\text{-}dmf}$ normalized with respect to the intensity of the main absorption band observed in dmf, A_{dmf}. The results are shown in Figure 3 which indicates that water has a somewhat greater influence on solute–solute interactions in dmf solutions containing the 4,11,18,25-isomer but that in all cases there is substantial conversion to aggregated forms when the solution contains 80% v/v of water.

The electronic spectrum in the visible region of the water-soluble complex 4,11,18,25-[Cu^{II}(tmpmaspc)]$^{4+}$ (Figure 4) comprises the broad spectrum centred at 623 nm attributable to aggregated forms of the chelate and gives rise to a band of greater intensity centred at 671 nm due to the formation of monomeric species in solution upon addition of dmf. Similar additions of ethanol are much less effective in bringing about disaggregation of chelate in aqueous solution.

The addition of dmf to aqueous solutions containing 4,11,18,25-Bayer phthalocyaninatocopper(II) again results in the emergence of an intense peak at 672 nm due to the monomeric form of the chelate to about the same extent as that observed for 4,11,18,25-[Cu^{II}(tmpmaspc)]$^{4+}$. On the other hand additions of dmf to aqueous solutions containing 3,10,17,24-[Cu^{II}(tmpmaspc)]$^{4+}$ bring about modest spectral changes such that the intensity of the absorption at *ca.* 670 nm is about half of that of the 4,11,18,25-isomer for an addition of 80% v/v of dmf. Clearly the aggregated form of 3,10,17,24-[Cu^{II}(tmpmaspc)]$^{4+}$ is able to resist the presence of dmf in its aqueous solution much better than the 4,11,18,25-isomer with respect to breaking up to monomeric species.

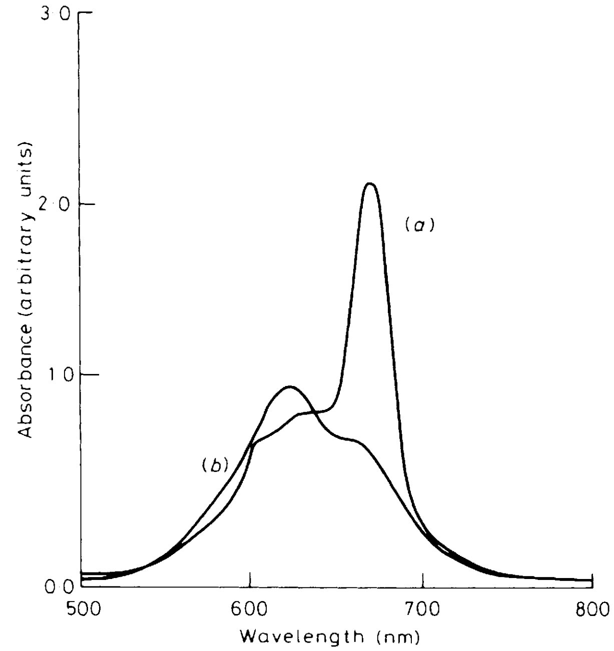

Figure 4. Electronic absorption spectrum of 4,11,18,25-[Cu^{II}(tmpmaspc)][CH_3SO_4]$_4$ (10 cm quartz cell): (*a*) 2.0 × 10^{-6} mol dm^{-3} in dmf water (80:20 v/v); (*b*) 2.0 × 10^{-6} mol dm^{-3} in water

E.S.R. Spectral Measurements.—A typical example of the e.s.r. spectra due to 4,11,18,25-[Cu^{II}(tpmaspc)] in dmf at 77 K is shown in Figure 5. In frozen chloroform glass, the spectrum in the $g = 2$ region is that expected from a mixture of a minor component of monomeric species together with dimeric species in which the magnetic dipolar coupling gives rise to a triplet state resulting in broader resonances in this region. This broader resonance is due to the $\Delta M_s = \pm 1$ transition. At $g = 4$, a well resolved signal is observed attributable to the corresponding $\Delta M_s = \pm 2$ transition and which is diagnostic of the presence of dimeric forms of the chelate. The e.s.r. spectral results for the chelate in frozen dmf or pyridine show a greater preponderance of the signal due to the monomeric form, though the component due to the dimeric species is easily discerned with very clear resolution of the low-field ($g = 4$, $\Delta M_s = \pm\frac{1}{2}$) component of the spectrum. The e.s.r. spectrum of the chelate in frozen 1-chloronaphthalene shows a greater contribution by the monomeric species though the presence of the dimeric form is still apparent. Largely similar e.s.r. spectral results are obtained from frozen (77 K) solutions of 3,10,17,24-[Cu^{II}(tpmaspc)] in dmf and pyridine with the spectra showing a rather larger contribution from the monomeric species compared with the 4,11,18,25-isomer. The e.s.r. spectra of 4,11,18-Hoechst phthalocyaninatocopper(II) in frozen (77 K) solutions of chloroform, dmf, or pyridine are interpretable in terms of monomeric and dimeric forms of the chelate with a greater amount of the dimeric form being present compared with 4,11,18,25-[Cu^{II}(tpmaspc)].

The e.s.r. spectra in the $g = 2$ region of frozen (77 K) aqueous solutions of 4,11,18,25-[Cu^{II}(tmpmaspc)]$^{4+}$ containing various amounts of dmf are given in Figure 6 which shows the contributions made to the spectra by monomeric and dimeric forms of the chelate. The dmf content of the solution has to reach 80% v/v before a well resolved spectrum due to the monomeric species can be observed. In the case of similar aqueous solutions containing the 3,10,17,24-isomer, additions of dmf as large as 50% v/v are necessary for the observation of a well resolved spectrum due to monomeric species. The e.s.r. spectrum of the frozen (77 K) solution resembles that of curve (*a*) of Figure 6 while for an 80% v/v content of dmf the e.s.r.

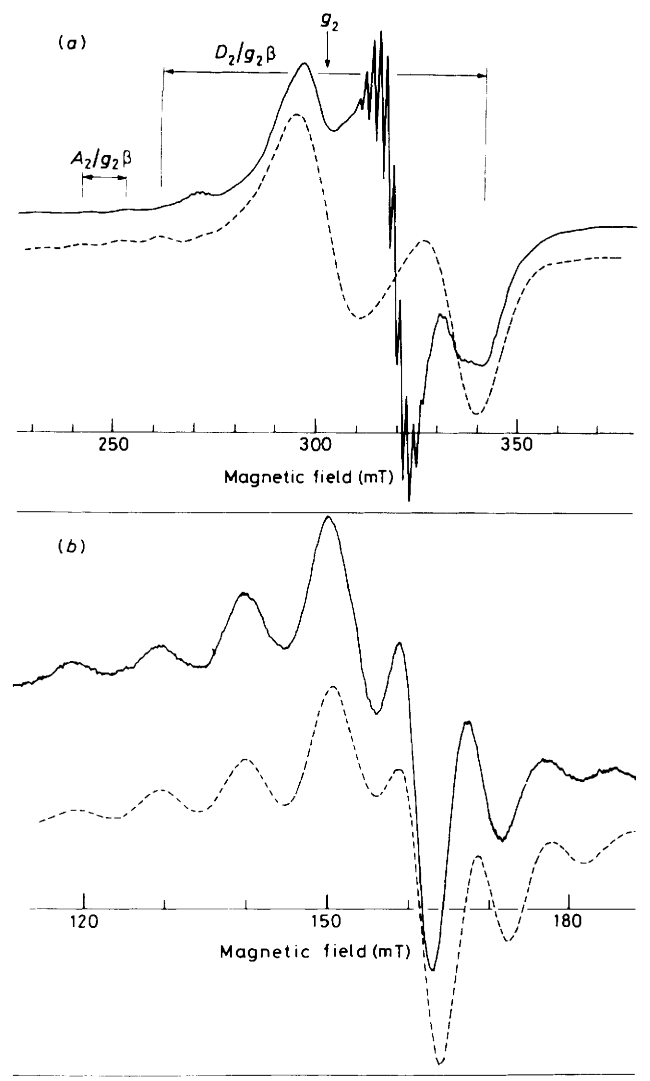

Figure 5. E.s.r. spectra of 4,11,18,25-[Cu^{II}(tpmaspc)] in dmf at *ca.* 77 K. (*a*) $\Delta M_s = \pm 1$ dimer monomer mixture ($M_{\parallel}$, $M_{\perp}$) recorded at 9.139 GHz (——). Weak hyperfine lines seen at low-field end of dimer spectrum and in wings of high-field dimer peak. Simulated spectrum ( ) obtained using program GNDIMER; [7,10,11] parameters are given in Table 2. Parameters D_2 and g_2 [16–19] also indicated on diagram (from Chikira H. Yokoi and T. Isobe, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 2208). (*b*) $\Delta M_s = \pm 2$ spectrum recorded at 9.12 GHz (——); baseline drift not corrected. Simulated spectrum ( ) based upon program GNDIMER and using parameters given in Table 2

spectrum is like that of curve (*b*). Clearly the presence of dmf in frozen aqueous solutions of 3,10,17,24-[Cu^{II}(tmpmaspc)]$^{4+}$ is not as effective in producing a monomeric form of the chelate in frozen solution compared with the 4,11,18,25-isomer. This is equally true for frozen aqueous solutions of 4,11,18,25-Bayer phthalocyaninatocopper(II) where again the presence of dmf was not as effective in producing the monomeric form of the chelate.

The complex 4,11,18,25-[Cu^{II}(tpmaspc)] is absorbed from its chloroform solution by silica gel, Y-type zeolite (Linde SK40), or γ-alumina. The e.s.r. spectra due to the adsorbed species clearly indicate the presence of both monomeric and dimeric species. The water-soluble chelates 4,11,18,25-[Cu^{II}(tmpmaspc)]$^{4+}$ and 4,11,18,25-Bayer are absorbed from boiling aqueous solutions by cotton. The e.s.r. spectra of the dyes adsorbed on cotton show that they are present as polymeric and dimeric forms. The existence of the dye on the cotton surface in its aggregated form would be expected to contribute to the light-fastness of these dyes on the cotton.

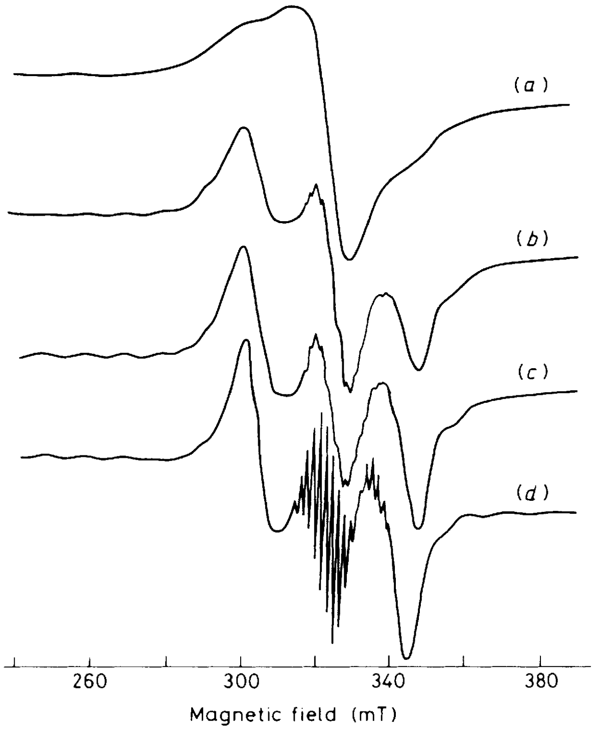

Figure 6. E.s.r. spectra of 4,11,18,25-[Cu^{II}(tmpmaspc)][CH$_3$SO$_4$]$_4$ (1 × 10^{-3} mol dm^{-3}) in water with increasing amounts of dmf: (*a*) 0%, (*b*) 10%, (*c*) 50%, and (*d*) 80% v/v. Spectra recorded at 9.14 GHz and *ca.* 77 K

Interpretation of the E.S.R. Spectra due to the Dimeric Species.—The phthalocyaninatocopper(II) derivatives used in the present investigation are present in solution as a mixture of monomeric, dimeric, and higher aggregated species the relative proportions of which depend on the solvent composition. The e.s.r. spectra due to the monomeric species are essentially the same as those reported previously.[7] The $\Delta M_s = \pm 1$ spectra due to dimeric species which, in most of the examples studied are readily recognised in the presence of the spectra due to monomeric species as well as the half-field $\Delta M_s = \pm 2$ transitions, provide sufficient data for computer simulation. Attention is drawn to the spectra in Figure 5. The computed lineshape which may be compared with the experimental spectrum makes possible the determination of the spatial relationship of the magnetic axes of the copper(II) ions within the dimeric species which includes their distance apart and angular disposition with respect to each other. In addition the values of the spin-Hamiltonian magnetic parameters, *g* and *A*, pertinent to the copper(II) centres within the dimeric species are obtained and may be compared with those due to monomeric species. The effects on these parameters that may accrue as a result of any axial interactions on the copper(II) centres, which may occur as a result of or be the cause of dimer formation, may be determined. As noted previously,[10,11] it is not always possible to obtain complete agreement particularly for $g_{\parallel}$ (or g_z) values because of the different levels of adequacy of perturbation theory for $\Delta M_s = \pm 1$ ($g \sim 2$) and $\Delta M_s = \pm 2$ ($g \sim 4$) spectra.

Computer simulations of $\Delta M_s = \pm 1$ spectra when there is no

Table 2. E.s.r. parameters for the dimeric forms of the 3,10,17,24- and 4,11,18,25-isomers of [Cu^{II}(tpmaspc)] and [Cu^{II}(tmpmaspc)]$^{4+}$, 4,11,18-Hoechst, and 4,11,18,25-Bayer

			Hyperfine constants		Linewidths				Relative intensity[a] ($\Delta M_s = \pm 1/\Delta M_s = \pm 2$)	
	$g_{\parallel}$	g	$10^{-4}A_{\parallel}$ cm^{-1}	$10^{-4}A_{\perp}$ cm^{-1}	$W_{\parallel}$ mT	$W_{\perp}$ mT	$\xi/^{\circ}$	r/Å	Expt.[b]	Theory[c]
$\Delta M_s = \pm 1$	2.210 ±0.005	2.035 ±0.005	210 ±5	10 ±10	3.5 ±0.5	5.5 ±0.5	20 ±2	4.4 ±0.1	53 ±1	65 ±12
$\Delta M_s = \pm 2$	2.153 ±0.005	2.015 ±0.005	210 ±5	10 ±10	2.5 ±0.5	3.0 ±0.5	20 ±2	4.4 ±0.2		
Monomer[d]	2.189 ±0.002	2.056 ±0.002	210 ±3	~0	—	—				

[a] Ratio of main peaks. [b] Corrected for different signal gains and 100-kHz modulation amplitudes. [c] Corrected for the $1/g$ factor of Aasa and Vanngard.[12,13] [d] From ref. 7.

exchange coupling ($J = 0$) do not give the correct seven-line hyperfine spectrum at the low-field end of Figure 5(*a*). Clearly $|J|$ is very much larger than the microwave energy (~ 0.3 cm^{-1}). For purposes of simulation, J was taken to be either ± 10 cm^{-1}, the simulation being unable to distinguish positive and negative values.[10,11]

Considerable effort was put into trying to obtain good linewidth estimates because of the desirability of checking the model by comparing experimental and simulated intensity ratios for $\Delta M_s = \pm 1/\Delta M_s = \pm 2$. The best fits yielded linewidths of ~ 5 mT for $\Delta M_s = \pm 1$ and ~ 2.5 mT for $\Delta M_s = \pm 2$ transitions. This is consistent with many previous observations[10,11] and in this case the product of g values (~ 2 for $\Delta M_s = \pm 1$ and ~ 4 for $\Delta M_s = \pm 2$) and the linewidths in field units (~ 5 mT for $\Delta M_s = \pm 1$ and ~ 2.5 mT for $\Delta M_s = \pm 2$) is a constant. This illustrates a more general principle noticed recently by one of the authors.[12]

A comparison of the ratios of peak intensities in experimental $\Delta M_s = \pm 1$ and $\Delta M_s = \pm 2$ spectra with those derived from the final simulated lineshapes is shown in Table 2. Theoretical values have been divided by 2 ($\Delta M_s = \pm 1$) and 4 ($\Delta M_s = \pm 2$) to approximate the $1/g$ correction introduced by Aasa and Vanngard.[13] The intensity of $\Delta M_s = \pm 2$ transitions varies as r^{-6}, so small errors in r (distance between the magnetic centres) will have a large effect compared with the $\Delta M_s = \pm 1$ spectrum. Bearing in mind these factors, the agreement is very satisfactory.

The final parameters given in Table 2 were obtained after an extensive range of simulations were carried out in which the angle between the phthalocyanine normal and the internuclear axis, ξ, was varied from 0 to 60°. Variations of 2° were noticeable for $\Delta M_s = \pm 2$ spectra. The $\Delta M_s = \pm 1$ peak positions were, as expected, much more sensitive to variations in r of 0.1 Å than were $\Delta M_s = \pm 2$ transitions. A satisfactory fit to the peak at ~ 159 mT was possible only for values of ξ close to 20°. Differences in $g_{\parallel}$ values related to limitations of second-order perturbation theory.

Discussion

The interactive forces between the macrocyclic chelate molecules are responsible for the solute–solute interactions in solution, the occurrence of which is monitored by the amounts of dimeric forms of the phthalocyanine derivatives. Essentially the amount of dimeric species present in a given set of solution circumstances and their persistence in changing solution composition is influenced by the nature of the peripheral substituents and their position in the exocyclic structure. The electronic and e.s.r. spectral results show that in solution as well as frozen solution the dimeric form of 4,11,18,25-[Cu^{II}(tpmaspc)] is more stable than the dimeric form of the 3,10,17,24-isomer. For the tetracationic phthalocyaninatocopper(II) derivatives, the dimeric form of 3,10,17,24-[Cu^{II}(tmpmaspc)]$^{4+}$ is more stable compared with that of the 4,11,18,25-isomer. However, in all cases the e.s.r. spectral results show that the dimeric forms of the phthalocyaninatocopper(II) derivatives share common structural and magnetic parameters. Early *X*-ray crystallographic studies of [Ni^{II}(pc)] have shown that the perpendicular distance between the planes of parallel molecules is 3.38 Å, which represents the distance of closest approach.[14] A later study of [Pt^{II}(pc)] showed that the platinum atom gives as much clearance as possible to the nearest atom in the parallel molecules, the vertical distance between the complexes in the plane being 3.41 Å.[15] Table 3 summarizes the structural features of the dimeric forms of various metalloporphyrins and metallophthalocyanines. It can be seen that there are some instances where the interplanar distances measured from observations of n.m.r. spectra in solution or e.s.r. spectra in frozen solution are not very different from those expected from closest approach of the macrocyclic planar structures in the crystalline state. However, in the majority of cases the internuclear distance between the metal centres is larger and in a large number of cases is in the region of *ca.* 4.3 Å. A distance of this order was found for the complexes studied here and the centre of one of the macrocyclic planes is displaced by about 1.5 Å with respect to the centre of the plane of the other macrocycle. The distance of closest approach of the chelates studied here is *ca.* 4.1 Å.

Close π–π bond stacking has been suggested to be of importance in the structure of the 'chlorophyll a special pair,' where macrocycle parallel stacking provides the intermolecular π–π bond overlap necessary to promote delocalization of the unpaired electron of the *in vivo* radical over two chlorophyll a π-systems.[16] The structural features outlined in this proposal have gained weight as a result of nuclear spin relaxation and ring-current shift measurements on chlorophyll a dimers.[17] In the dimer of chlorophyll a formed in chloroform, one macrocycle is perpendicular with respect to the other[18] while in the special pair of chlorophyll a, a dimer formed in water or ethanol has the macrocyclic components parallel to one another as suggested in the Shipman–Katz geometry.[16] Thus in common with a number of systems, solute–solvent interactions play an important role in determining the formation and structure of the dimer.

Metallophthalocyanine sub-units have been used to constitute the rigid core of discotic mesophases which may function as liquid crystalline one-dimensional conductors.[19] Preliminary

Table 3. Structural features of some metallo-porphyrins and -phthalocyanines

Compound forming dimeric species	Conditions	Method of determination	Intermetallic distance (r/Å)	Interplanar distance (r/Å)	Ref.
Porphine	Crystalline	*X*-ray		3.4	*a*
[Cu^{II}(tpp)]	Crystalline	*X*-ray		3.76	*b*
[Ni^{II}(dmcetmp)]	Crystalline	*X*-ray	3.7	3.5	*c*
H_2tmcetmp I	$CHCl_3$ solution	^1H n.m.r.		8.5	*d*
H_2tmcetmp II	$CHCl_3$ solution	^1H n.m.r.		8.5	*d*
H_2tmcetmp III	$CHCl_3$ solution	^1H n.m.r.		7.5	*d*
H_2tmcetmp IV	$CHCl_3$ solution	^1H n.m.r.		7.5	*d*
H_2dedmcetmp	$CHCl_3$ solution	^1H n.m.r.		10	*e*
[Ni^{II}(dedmcetmp)]	$CHCl_3$ solution	^1H n.m.r.		7.9	*e*
[Fe^{III}(CN)$_2$(dcetmdvp)]$^-$	CD_3OD (−80 °C)	^1H n.m.r.		~4.5	*f*
[Fe^{III}Cl(tpp)]	$CDCl_3$–$CHCl_3$ (0 °C)	^1H n.m.r.		5.0	*g*
[Tl^{III}(OH)(tcetmp I)]	$CHCl_3$ solution	^1H n.m.r.		8.5	*h*
[Tl^{III}(OH)(tcetmp IV)]	$CHCl_3$ solution	^1H n.m.r.		8.1	*h*
[Zn^{II}(oettfaop)]	$CDCl_3$ solution	^1H n.m.r.		4.5	*i*
[Zn^{II}(oenp)]	$CDCl_3$	^1H n.m.r.		4.5	*j*
[Zn^{II}(oednp)]	$CDCl_3$	^1H n.m.r.		4.5	*j*
[Cu^{II}(cyt)]	H_2O, pH < 4	e.s.r.	4.4	3.37	*k*
[Cu^{II}(cyt-pep)]	H_2O, pH > 11.5	e.s.r.	4.3	3.90	*k*
	H_2O, pH 7—12	e.s.r.	4.3	3.90	
[Cu^{II}(dcetmdvp)]	mim–dmf	e.s.r.	4.1	3.72	*k*
[Cu^{II}(tcetcmp)]	NH_3–H_2O	e.s.r.	3.5		
[Cu^{II}(dcetmdvp)]	dmf solution	e.s.r.	4.3		*l*
	PO(OMe)$_3$ solution	e.s.r.	5.0		*m*
[Cu^{II}(dmcetmdvp)]	$CHCl_3$ solution	e.s.r.	3.7		*n*
[Cu^{II}(dmcetmp)]	$CHCl_3$ solution	e.s.r.	3.9		*n*
[Cu^{II}(dbcetmp)]	$CHCl_3$ solution	e.s.r.	3.9		*n*
[Cu^{II}(dhedmcetm)]	$CHCl_3$ solution	e.s.r.	3.9		*n*
[Cu^{II}(dbdmcetmp)]	$CHCl_3$ solution	e.s.r.	4.4		*n*
[VO(dmcetmp)]	$CHCl_3$ solution	e.s.r.	3.4		*n*
[VO(dbcetmp)]	$CHCl_3$ solution	e.s.r.	3.5		*n*
[VO(dmcetmdvp)]	$CHCl_3$ solution	e.s.r.	3.5		*n*
[VO(tetmp)]	CH_2Cl_2 solution	e.s.r.	5.6		*o*
[Cu^{II}(tetmp)]	CH_2Cl_2 solution	e.s.r.	4.1		*o*
	Pyridine solution	e.s.r.	4.7		*o*
[Cu^{II}(dedmcetmp)]	Toluene solution	e.s.r.	4.0		*p*
[Cu^{II}(dedmcetmp)]	tce solution	e.s.r.	4.1		*q*
[Ag^{II}(dedmcetmp)]	tce solution	e.s.r.	5.0		*q*
[Cu^{II}/Ag^{II}(dedmcetmp)]	tce solution	e.s.r.	4.5		*q*
[Cu^{II}(oenp)]	Toluene solution	e.s.r.	4.16	3.93	*r*
[Cu^{II}(oednp)]	Toluene solution	e.s.r.	4.24	3.25	*r*
[Cu^{II}(oednp)]	Toluene solution	e.s.r.	4.17	4.06	*r*
[Cu^{II}(oep)]	Toluene solution	e.s.r.	4.19	3.96	*r*
Na_4[Cu^{II}(tspp)]	dmf H_2O	e.s.r.	4.5		*s*
Na_4[Cu^{II}(tcpp)]	dmf H_2O	e.s.r.	4.5		*s*
[Fe^{III}(oenp)]$^+$	Toluene solution	e.s.r.	7.2		*t*
Na_4[Cu^{II}(tspc)]	dmf H_2O	e.s.r.	4.4		*u*
Na_4[VO(tspc)]	dmf H_2O	e.s.r.	4.5		*u*
Na_4[Cu^{II}/Co^{II}(tspc)]	dmf H_2O	e.s.r.	4.5		*v*
Na_4[Cu^{II}(tspc)]	Wool	e.s.r.	4.4		*w*
Na_4[Cu^{II}(tspc)]	Sephadex DEAE A25 anion exchanger	e.s.r.	4.5		*x*
Na_4[VO(tspc)]	Sephadex DEAE A25 anion exchanger	e.s.r.	5.5		*x*

Abbreviations: H_2tpp = 5,10,15,20-tetraphenylporphyrin, H_2dmcetmp = 13,17-di(methoxycarbonylethyl)-2,7,12,18-tetramethylporphyrin, H_2tmcetmp I = 3,8,13,18-tetra(methoxycarbonylethyl)-2,7,12,17-tetramethylporphyrin, H_2tmcetmp II = 3,7,13,17-tetra(methoxycarbonylethyl)-2,8,12,18-tetramethylporphyrin, H_2tmcetmp III = 3,18,13,17-tetra(methoxycarbonylethyl)-2,7,12,18-tetramethylporphyrin, H_2tmcetmp IV = 3,8,12,17-tetra(methoxycarbonylethyl)-2,7,13,18-tetramethylporphyrin, H_2dedmcetmp = 3,8-diethyl-13,17-di(methoxycarbonylethyl)-2,7,12,18-tetramethylporphyrin, H_2dcetmdvp = 13,17-di(carboxyethyl)-2,7,12,18-tetramethyl-3,8-divinylporphyrin, H_2tcetmp I = 3,8,13,18-tetra(carboxyethyl)-2,7,12,17-tetramethylporphyrin, H_2tcetmp IV = 3,8,12,17-tetra(carboxyethyl)-2,7,13,18-tetramethylporphyrin, H_2oettfaop = 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetrakis(trifluoroacetoxy)porphyrin, H_2oenp = 2,3,7,8,12,13,17,18-octaethyl-5-nitroporphyrin, H_2oednp = 2,3,7,8,12,13,17,18-octaethyl-5,10-dinitroporphyrin, H_2cyt = cytochrome C, H_2cyt-pep = cytochrome C undeca- and octa-peptide, H_2tcetcmp = 3,8,13,17-tetra(carboxyethyl)-2,7,12,18-tetra(carboxymethyl)porphyrin, H_2dmcetmdvp = 13,17-di(methoxycarbonylethyl)-2,7,12,18-tetramethyl-3,8-divinylporphyrin, H_2dbcetmp = 13,17-di(butoxycarbonylethyl)-2,7,12,18-tetramethylporphyrin, H_2dhedmcetm = 3,8-di(1-hydroxyethyl)-13,17-di(methoxycarbonylethyl)-2,7,12,18-tetramethylporphyrin, H_2dbdmcetmp = 3,8-dibromo-13,17-di(methoxycarbonylethyl)-2,7,12,18-tetramethylporphyrin, H_2tetmp = 3,8,13,18-tetraethyl-2,7,12,17-tetramethylporphyrin, H_2oep = 2,3,7,8,12,13,17,18-octaethylporphyrin, tspp = 5,10,15,20-tetra(*p*-sulphonatophenyl)porphyrinate(6−), tcpp = 5,10,15,20-tetra(*p*-carboxylatophenyl)porphyrinate(6−), tspc = 3,10,17,24-tetrasulphonatophthalocyaninate(6−), tce = 1,1,1-trichloroethane mim = 1-methylimidazole. [a] S. Silvers and A. Tulinsky, *J. Am. Chem. Soc.*, 1964, **86**, 927; M. J. Hamoe, T. A. Hamor, and J. L. Hoard, *ibid.*, p. 1934. [b] E. B. Fleischer, C. K. Miller, and L. E. Webb, *J. Am. Chem. Soc.*, 1964, **86**, 2342. [c] T. A.

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Table 4. Analysis (%) of compounds *

Compound	C	H	N	S
[Cu(pc)]	66.8 (66.7)	2.75 (2.80)	19.5 (19.45)	
Na_4[Cu(tspc)]	37.5 (37.65)	1.70 (1.60)	10.9 (11.0)	12.5 (12.55)
4,11,18,25-[Cu(tcspc)]	39.55 (39.6)	1.30 (1.25)	11.5 (11.55)	13.15 (13.2)
3,10,17,24-[Cu(tcspc)]	39.75 (39.6)	1.30 (1.25)	11.6 (11.55)	13.2 (13.2)
4,11,18,25-[Cu(tpmaspc)]	53.6 (53.5)	2.95 (3.20)	17.75 (17.85)	10.2 (10.2)
3,10,17,24-[Cu(tpmaspc)]	53.5 (53.5)	2.80 (3.20)	17.75 (17.85)	10.25 (10.2)
4,11,18,25-[Cu(tmpmaspc)][CH_3SO_4]$_4$	43.6 (43.65)	3.50 (3.65)	12.8 (12.7)	14.5 (14.55)
3,10,17,24-[Cu(tmpmaspc)][CH_3SO_4]$_4$	43.8 (43.65)	3.55 (3.65)	12.7 (12.7)	14.65 (14.55)

* Calculated values are in parentheses.

large-angle *X*-ray diffraction measurements on these systems point to a 3.8-Å stacking of the macrocyclic sub-units. The solute–solute interactions which exist in solutions of 4,11,18,25-[Cu^{II}(tpmaspc)] and its 3,10,17,24-isomer persist when these chelates are absorbed from solutions in organic solvents by γ-alumina, silica, or zeolites, such that the chelates are present on the solid surface as a mixture of monomeric, dimeric, and polymeric forms. The surface acid sites present on these solids presumably contribute to the absorption of the phthalocyaninatocopper(II) derivatives from solution.

A study of the adsorption of carbon monoxide, dinitrogen, and dioxygen by Y-type zeolite containing cobalt(II), nickel(II), or copper(II) phthalocyanines shows that the chelates exist largely in the monomeric state in the large cavities of the zeolite and allow attachment of adsorbate on both sides of the macrocycle.[20] A later publication revealed that the metallophthalocyanines were distributed on the zeolite by treating the zeolite in the transition-metal ion exchanged form with phthalonitrile.[21] It would be of interest to pursue the heterogeneous catalytic properties of the phthalocyanines studied here distributed on silica, alumina, or zeolite surfaces.[22] The distribution of monomeric, dimeric, and polymeric forms of the phthalocyaninatocopper(II) derivatives studied here on silica is in keeping with photoacoustic measurements on methylene blue which show that the dye, adsorbed onto silica from its aqueous solution where it is known to exist in dimeric form, occurs once more in dimeric form.[23]

Experimental

The e.s.r. spectra, recorded as the first derivatives of absorption, were obtained using a Varian E-12 spectrometer with an E-101 microwave bridge at *X*-band frequency (*ca.* 9.15 GHz). Magnetic fields were calibrated against ^1H n.m.r. frequencies measured using a Hewlett Packard HP5254L frequency counter. Absorption spectra of the coloured solutions were recorded on a Varian 635 spectrometer at room temperature using 1-cm glass cells. Microanalyses were carried out by the Commonwealth Scientific and Industrial Research Organisation Microanalytical Service, Melbourne. The analytical results for the various chelates are summarised in Table 4.

The phthalocyaninatocopper(II) derivative, soluble in organic solvents, 4,11,18-Hoechst, kindly donated by Hoechst Farbewerken AG (F.D.R.), was used without further purification. The structurally related water-soluble derivative, 4,11,18,25-Bayer, kindly donated by Bayer AG (F.D.R.) as product OCD-9626, was also used as received. This product is presumably a mixture of tri- and tetra-substituted phthalocyaninate at the 4,11,18,25-positions.

Preparation of 4,11,18,25-*Tetra(chlorosulphonyl)phthalocyaninatocopper*(II) *and its* 3,10,17,24-*Isomer*.—The tetra(chlorosulphonyl) derivatives of phthalocyaninatocopper(II) were prepared by the method outlined in the literature.[24] It is believed that in the derivatives obtained by sulphonylation or chlorosulphonylation of phthalocyanine the functional groups occupy the 4,11,18,25-positions of the phthalocyaninate ring system. Thus phthalocyaninatocopper(II) (5.0 g), prepared as described previously,[25] was treated with chlorosulphonic acid. The yellow-green reaction mixture was stirred for 1 h at 75 °C and for a further 6 h at 140 °C. After cooling to 80 °C, thionyl chloride (20 cm^3) was added over 30 min while the bright green mixture was stirred for a further 2 h at 80 °C. The product was isolated by pouring the cooled reaction mixture onto crushed ice. The fine blue precipitate was washed until the washings were of neutral pH, and finally washed with acetone. The product was dried at 80 °C under reduced pressure (1 mmHg).

3,10,17,24-Tetra(chlorosulphonyl)phthalocyaninatocopper(II) was prepared by treatment of tetrasodium 3,10,17,24-tetrasulphonatophthalocyaninatocuprate(II) synthesised as described previously[26] with chlorosulphonic acid and thionyl chloride as outlined above.

Preparation of 4,11,18,25-*Tetra(2-pyridylmethylaminosulphonyl)phthalocyaninatocopper*(II) *and its* 3,10,17,24-*Isomer*.—The 4,11,18,25-tetra(2-pyridylmethylaminosulphonyl) derivative of [Cu^{II}(pc)] and its 3,10,17,24-isomer were prepared by addition of an excess of 2-(aminomethyl)pyridine (30 cm^3) to the appropriate tetra(chlorosulphonyl) derivative (5.0 g) with stirring for 2 h at 40 °C. The products were isolated by pouring the product mixture onto crushed ice (500 g), washing with water, and then hot ethanol (~ 50 °C), and drying at 80 °C (1 mmHg).

Preparation of 4,11,18,25-*Tetra*(N-*methyl-2-pyridinomethylaminosulphonyl*)*phthalocyaninatocopper*(II) *Tetra*(*methyl sulphate*) *and its* 3,10,17,24-*Isomer*.—A dimethylformamide solution (100 cm^3) of the appropriate tetra(2-pyridylmethylaminosulphonyl)phthalocyaninatocopper(II) complex (5.0 g) was treated with dimethyl sulphate (20 cm^3). The reaction mixture was stirred at 40 °C for 4 h after which the product mixture was cooled to room temperature and poured into cold (0 °C) acetone (500 cm^3). After further washing with acetone the products were dried at 80 °C (1 mmHg).

The molar absorption coefficients at the wavelengths of maximum absorption of 3,10,17,24-[Cu^{II}(tpmaspc)], 4,11,18,25-[Cu^{II}(tpmaspc)], and 4,11,18-Hoechst in various solvents characterize these materials and are summarized in Table 1.

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