Electron-spin Resonance Studies of Manganese(II) 4,4′,4,″4‴-Tetrasulphophthalocyanine

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E.s.r. measurements on manganese 4,4′,4″,4‴-tetrasulphophthalocyanine, [Mn^{II}(tspc)], confirm earlier reports that in the solid state this complex is obtained as a manganese(II) chelate. Measurements on aqueous solutions containing [Mn^{II}(tspc)] show that disaggregation of the chelate occurs as a result of small additions (5—10% v/v) of polar organic solvents such as *NN*-dimethylformamide. In these circumstances the e.s.r. spectrum has been assigned to a mixture of low-spin forms of the manganese(II) chelate. The solute–solute interactions which occur as a result of the addition of [Ni^{II}(tspc)] or [Zn^{II}(tspc)] to aqueous solutions of [Mn^{II}(tspc)] are characterized by the appearance of e.s.r. signals at 77 K attributable to a high-spin form of the manganese(II) chelate. The presence of ligands such as cyanide, pyridine, or imidazole, which are capable of axial interactions with [Mn^{II}(tspc)] promotes autoxidation of the manganese chelate in aqueous solution. Measurements at room temperature and 133 K provide evidence for a change in the spin state of the metal ion in the chelates as a result of changes in the pH of the solutions.

A NUMBER of investigations have been concerned with the tendency of metal complexes of 4,4′,4″,4‴-tetrasulphophthalocyanine (tspc) to form aggregates in solution.[1-9] For example, e.s.r. measurements involving water–*NN*-dimethylformamide (dmf) solutions of copper(II) and vanadium(IV) and tspc have provided evidence for the formation of dimeric species in these solutions. Computer simulation of the e.s.r. lineshapes attributed to dimeric forms of these chelates made possible a determination of the metal-ion separations, which in turn gave a measure of the interplanar distance in the dimeric chelates.[8] Similarly, e.s.r. studies of frozen aqueous dmf solutions containing binary mixtures of cobalt(II), nickel(II), copper(II), and zinc(II) and tspc have been used to discern various solute–solute interactions.[10]

These results reinforce the general conclusion that depolymerization of the dye molecules is critically dependent on the solvent composition and the nature of the metal ion. The advantage of e.s.r. spectroscopy in these investigations is that it is possible, in principle, to monitor the distribution of polymeric, dimeric, and monomeric forms of the chelates, and to obtain structural information about the dimeric forms by observation of the appropriate signals. In favourable cases e.s.r. can also provide detailed information about the nature of any axial interactions which occur at the metal site. It seems a logical step, therefore, to extend these investigations to a system in which the aggregation process is less well understood, namely the manganese(II) chelate of tspc. An additional complication which may arise here is that the valence state of the manganese ion could depend on the nature of the groups co-ordinating to the ion in the positions above and below the plane, similar to the changes observed by Calvin and his co-workers [11,12] for manganese(II) phthalocyanine. As well as the solute–solute and solute–solvent interactions which occur in solution, there will be the possibility of acid–base interactions with the degree of association and/or the co-ordination to the out of plane positions being affected by the pH of the solution.

Phthalocyanine (H_2pc) and its metal derivatives are only readily soluble in highly acidic media such as concentrated sulphuric acid. Conductimetric measurements indicate that in chlorosulphuric acid solutions of [Cu(pc)], [Ni(pc)], and [Zn(pc)] all the bridging nitrogen atoms are protonated but the results for Cu^{II} suggest that the two central tertiary nitrogen atoms are not protonated.[13,14] In contrast to phthalocyanine, tspc and its metal derivatives are extremely soluble in aqueous solution. However, little information is available concerning the acid–base behaviour of these complexes.

This paper reports the results of an investigation of solute–solute, solute–solvent, axial-ligand, and acid–base interactions in manganese(II) tetrasulphophthalocyanine.

RESULTS AND DISCUSSION

Solid State and Doped Powders.—In the polycrystalline form, [Mn^{II}(tspc)] had the e.s.r. spectrum at 133 K shown in Figure 1(*a*). Diamagnetic dilution into the corresponding zinc(II) or nickel(II) chelate gave the spectrum shown in Figure 1(*b*), which is interpreted as arising from a high-spin [Mn^{II}(tspc)] complex with a spin of $\frac{5}{2}$. The six strong lines spaced at *ca.* 90 G intervals

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and centered around $g = 2.0$ arise from the $M_S = \frac{1}{2} \rightarrow -\frac{1}{2}$ ($\Delta m_I = 0$) transitions.* The weak lines observed at high spectrometer gain in between these six intense lines arise from 'forbidden' transitions with $\Delta m_I = \pm 1$, which become 'allowed' as a result of state mixing by the fine structure term DS_Z^2 in the spin Hamiltonian for high-spin Mn^{II}.[15] The absence of features due to the other fine structure lines, *i.e.* those with $M_S = \pm\frac{3}{2} \rightarrow \pm\frac{5}{2}$ and $\pm\frac{3}{2} \rightarrow \pm\frac{1}{2}$ is probably due to small variations in D which result in the 'smearing out' of these lines due to the large anisotropy. The partly resolved peaks in Figure 1(*b*) suggest that the manganese hyperfine structure is slightly anisotropic.

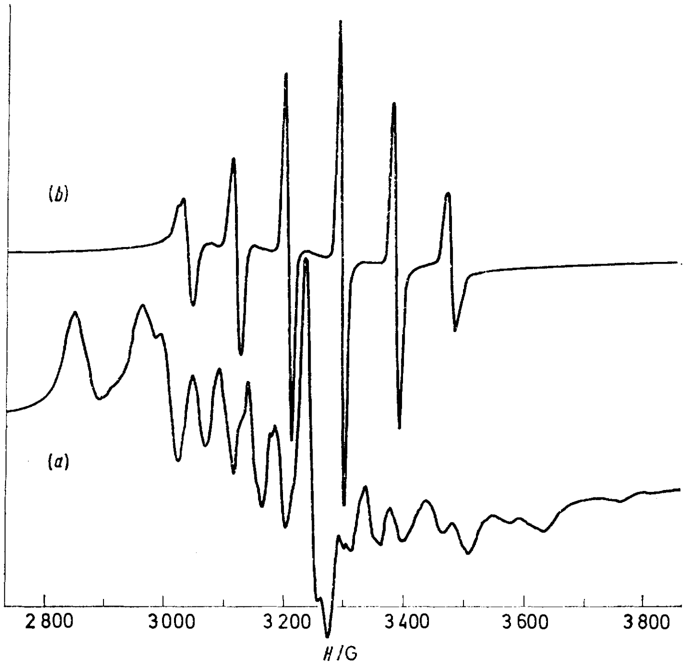

FIGURE 1 *X*-Band e.s.r. spectrum at 133 K due to [Mn^{II}(tspc)] (microwave frequency 9 143 MHz): (*a*) solid powder; (*b*) doped into corresponding zinc chelates in a ratio of 1 : 20

The configuration of the undiluted polycrystalline [Mn^{II}(tspc)] is not so clearly establised, although the positions and spacings of the resonances suggest that it is low spin with an effective spin of $\frac{1}{2}$. This would be in agreement with the conclusions of Weber and Busch,[16,17] which were derived from magnetic-susceptibility measurements. The results do, however, establish that the complex contains Mn^{II} rather than Mn^{III} as postulated by Fenkart and Brubaker.[18]

It is also proper to consider whether some of the spectra reported herein may, in fact, arise from Mn^{II} with a spin $\frac{3}{2}$ ground state. However, as pointed out by Griffith,[19] it is likely that resonance will be observed only in the lowest doublet which may be described by an effective spin of $\frac{1}{2}$, $g_\parallel$ *ca.* 2, and $g_\perp$ *ca.* 4. None of our results falls into this category. Alternatively, if the zero-field splitting between the $M_S = \pm\frac{1}{2}$ and $M_S = \pm\frac{3}{2}$ doublet is small, the strongest transitions will be $M_S = \frac{1}{2} \rightarrow -\frac{1}{2}$ with $g_\parallel$ and $g_\perp$. An estimate of possible g values may be made from susceptibility data for manganese(II) phthalocyanine [20] from which it is found that $g_\parallel$ *ca.* 2.1 and $g_\perp$ *ca.* 2.3. As for the high-spin $S = \frac{5}{2}$ case, the outer transitions, $M_S = \frac{3}{2} \rightarrow \frac{1}{2}$ and $-\frac{1}{2} \rightarrow -\frac{3}{2}$, may be broadened beyond detection. It is clear that none of our results fits into this latter category. Therefore, we conclude that our results may be described either in terms of the usual high-spin ($\frac{5}{2}$) or low-spin ($\frac{1}{2}$) configurations for Mn^{II}.

Solute–Solvent Interactions.—The e.s.r. spectrum at 133 K of a 1.0×10^{-3} mol dm^{-3} aqueous solution of [Mn^{II}(tspc)] in the range pH 6.5—10.0 could only be observed at high spectrometer gain. Addition of small amounts of dmf (up to 5% v/v) resulted in a ten-fold increase in signal intensity, and gave the spectrum shown in Figure 2(*a*). No further increase in signal intensity was observed for additions of dmf above 5% v/v. Similar results were obtained on addition of dimethyl sulphoxide (dmso) and ethylene glycol, although addition of 10% v/v of acetone or acetonitrile did not change the signal from that observed in frozen aqueous solution.

The spectrum observed in 5% dmf–water is interpreted as arising from a number of low-spin monomeric [Mn^{II}(tspc)] species with anisotropic g values. In pure water

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* 1 G = 10^{-4} T.

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most of the [Mn^{II}(tspc)] is in a polymeric form, which gives no e.s.r. signal. However, the polymer is readily disaggregated by addition of quite small amounts of dmf. No e.s.r. signals were observed at room temperature from either the pure aqueous solution containing 1.0×10^{-3} mol dm^{-3} [Mn^{II}(tspc)] or from aqueous solutions containing 1.0×10^{-3} mol dm^{-3} [Mn^{II}(tspc)] to which 5% v/v dmf had been added. The signal shown in Figure 2 did however appear on freezing the solution. This behaviour would be consistent with the interpretation of the spectra in terms of low-spin Mn^{II}.

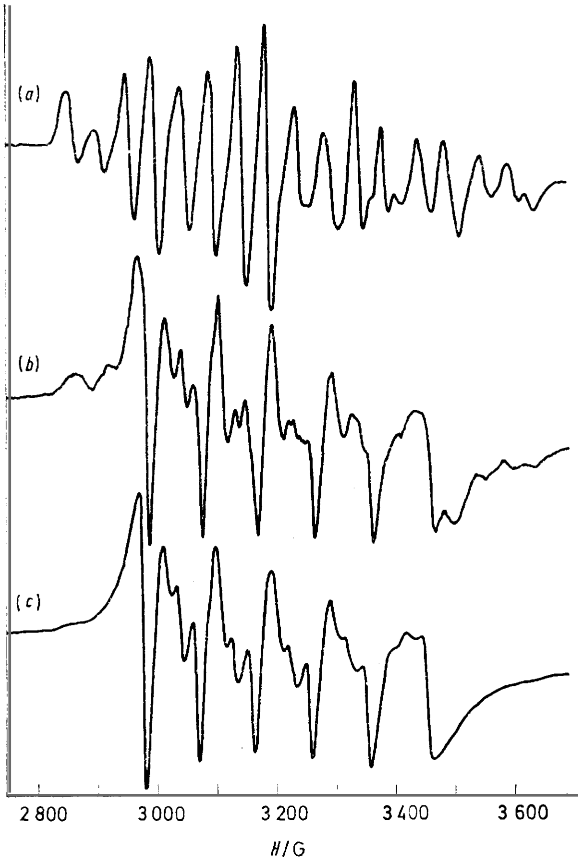

FIGURE 2 X-Band e.s.r. spectra at 133 K due to a 15% dmf–water solution of [Mn^{II}(tspc)] (1.0×10^{-3} mol dm^{-3}), pH: (*a*) 6.5—10.0, (*b*) 5.5, (*c*) 2.0—4.4; microwave frequency 9 143 MHz

An explanation of the spectrum in terms of a dimeric species may be discounted because first no resonances were observed near $g = 4$, and secondly the number, intensity, and spacing of the lines at *g ca.* 2 is not compatible with that expected from dimeric species. Thus the explanation in terms of a mixture of low-spin [Mn^{II}(tspc)] species appears most probable, a conclusion in accordance with the magnetic-susceptibility data of Weber and Busch,[16] where a magnetic moment of 1.80 B.M. was obtained for [Mn^{II}(tspc)] in solution.

When more than 40% v/v dmf was added to aqueous solutions of [Mn^{II}(tspc)] there was a decrease in spectral intensity on standing in air at room temperature such that no signal was observed at 133 K after 2—3 h. The greater the amount of organic solvent added, the more rapidly did the signal intensity decrease with time. This is explained in terms of oxidation to a manganese(III) complex, as found by Fenkart and Brubaker.[18] The manganese(III) complex is not expected to give an e.s.r. signal.

Rather less concentrated solutions of [Mn^{II}(tspc)] are required for the optical-absorption spectroscopy measurements, namely 1.0×10^{-4} compared with the 1.0×10^{-3} mol dm^{-3} solutions for e.s.r. However, weak e.s.r. signals could be detected at these lower concentration levels, and the spectral peaks had the same relative intensities as at the higher concentrations.

The visible-absorption spectral data associated with the changes described above are shown in Figure 3. An aqueous solution of [Mn^{II}(tspc)] had two main bands in its visible absorption spectrum at 636 and 718 nm. Addition of dmf [Figure 3(*b*)] resulted in an increase in the absorption at 718 nm. This effect parallels the results previously observed for the vanadyl, cobalt(II), and copper(II) chelates and has been shown to arise from an increasing concentration of the monomeric forms of these chelates in solution. The manganese(II) case, however, is complicated by oxidation processes and Figure 3(*c*) shows the effect of exposure to air of a 1.0×10^{-4} mol dm^{-3} solution of [Mn^{II}(tspc)] in water to which 10% v/v of dmf had been added. Under these circumstances, the absorption at 718 nm again increased and has been assigned to [Mn^{II}(tspc)(OH)]$^{4-}\cdot$H$_2$O.[11]

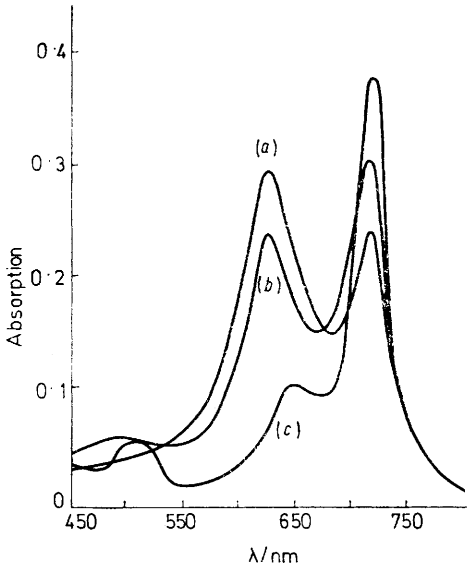

FIGURE 3 Absorption spectrum at room temperature due to [Mn^{II}(tspc)] in (*a*) aqueous solution, (*b*) 5% dmf–water, and (*c*) 5% dmf–water after standing in air for 100 min [absorption scale twice that in (*a*) and (*b*)]

Solute–Solute Interactions.—Addition of Ni^{II} to an aqueous solution of [Mn^{II}(tspc)] has a profound influence on the e.s.r. spectrum observed in frozen solution (Figure 4). The six strong lines separated by *ca.* 90 G are characteristic of the high-spin form of [Mn^{II}(tspc)], whilst the other fine structure lines were not observed presumably for the same reasons as discussed previously. The sharp line at $g = 2.003$ arises from a free-radical species associated with [Ni^{II}(tspc)]. Addition of [Zn^{II}(tspc)] instead of [Ni^{II}(tspc)] gave a spectrum which differed only in the absence of the free-radical line. When small amounts of dmf (*ca.* 1—2% v/v) were added the spectrum indicates that there is a mixture of high- and low-spin species in solution, whilst addition of 10% v/v dmf gives the low-spin spectrum observed in the absence of nickel or zinc species. These results provide evidence for an interaction between [Mn^{II}(tspc)] and the corresponding zinc or nickel species in aqueous solution similar to that observed between [Cu^{II}(tspc)] or [Co^{II}(tspc)] and [Ni^{II}(tspc)]. The surprising result is that involving [Zn^{II}(tspc)] and [Mn^{II}(tspc)], since in both the copper(II) and cobalt(II) cases the interactions between 'like' chelates [*i.e.* copper(II)–copper(II) or cobalt(II)–cobalt(II)] appears to be favoured over that involving 'unlike' chelates [*i.e.* copper(II)–zinc(II) or cobalt(II)–zinc(II)]. In contrast to the systems involving [Cu^{II}(tspc)] and [Co^{II}(tspc)], the strength of the solute–solute interactions involving [Mn^{II}(tspc)], as demonstrated by the case of regeneration of the low-spin spectrum on addition of dmf, appears to be the same for both the manganese(II)–nickel(II) and manganese(II)–zinc(II) systems.

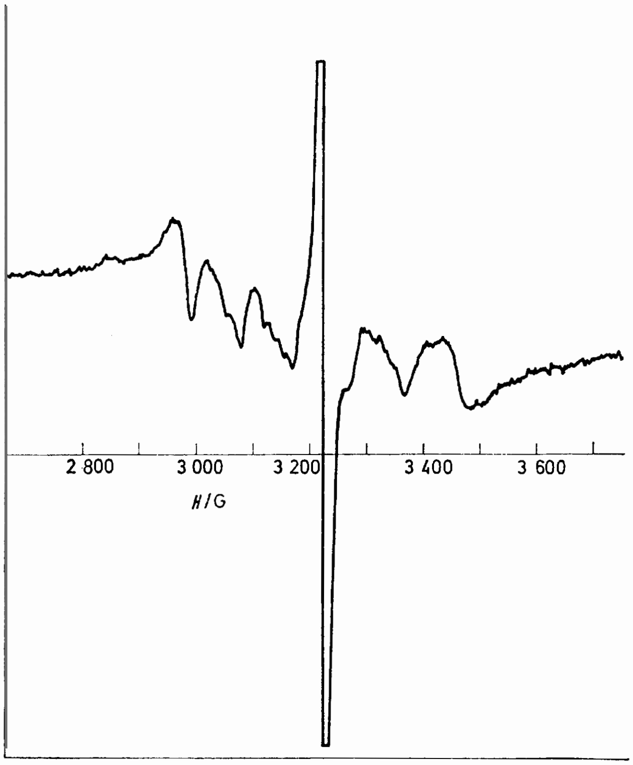

FIGURE 4 *X*-Band e.s.r. spectrum due to a frozen aqueous solution at 133 K containing [Mn^{II}(tspc)] (1.0×10^{-3} mol dm^{-3}) and [Ni^{II}(tspc)] (5.0×10^{-3} mol dm^{-3}); microwave frequency 9 145 MHz {Sharp line at $g = 2$ due to free-radical impurity in [Ni^{II}(tspc)]}

Axial Interactions.—The e.s.r. spectrum at a sample temperature of 133 K of a 1.0×10^{-3} mol dm^{-3} aqueous solution of [Mn^{II}(tspc)] to which 5% v/v of pyridine had been added prior to freezing is shown in Figure 5. It can be seen that the spectrum is very similar to those obtained on addition of 5% v/v of dmf or ethylene glycol and may be interpreted as arising from a mixture of low-spin species. Although only a tentative identification can be made at this stage, the spectrum appears to be due to two species of low-spin manganese(II) ions, with tentative g and hyperfine constants as indicated on Figure 5.

Upon addition of imidazole, a spectrum was only observed at high spectrometer gain, and here again a mixture of species appeared to be present. In both cases, exposure to oxygen resulted in a colour change of the solutions from blue to green and a loss of the e.s.r. signal. This results from oxidation to a [Mn^{III}(tspc)] complex, which, by analogy with [Mn^{II}(pc)],[21] may have the general formula [Mn^{III}(tspc)(OH)L] where L is the axial ligand.

Similar results were obtained on addition of sodium cyanide or sodium azide. The rate of the oxidation process increased with increasing concentration of axial ligand. There was no evidence for the presence of an oxygen complex, which might be expected as an intermediate in the oxidation reaction. The strong ligand-field extraplanar ligands promote the autoxidation of the manganese(II) ion to the trivalent state. This indicates that the highest-energy 3*d* electron of the manganese(II) species occupies an orbital that becomes increasingly antibonding as the strength of binding to the unidentate ligands increases. In this connection, it should also be noted that, despite the e.s.r. evidence that an axial interaction is occurring, no superhyperfine structure arising from interaction with out-of-plane nitrogen nuclei was observed.

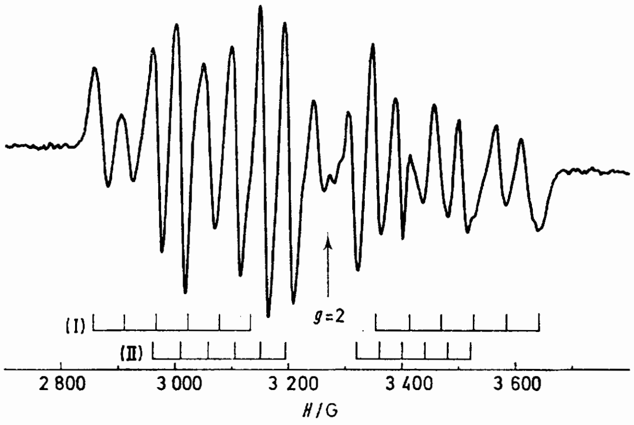

FIGURE 5 *X*-Band e.s.r. spectrum at 133 K due to a 5% pyridine–water solution of [Mn^{II}(tspc)] (1.0×10^{-3} mol dm^{-3}); microwave frequency 9 143 MHz. Species (I): $g_{\parallel} = 1.87$, $g_{\perp} = 2.18$, $A_{\parallel} = 0.0049$ cm^{-1}, and $A_{\perp} = 0.0055$ cm^{-1}. Species (II): $g_{\parallel} = 1.91$, $g_{\perp} = 2.12$, $A_{\parallel} = 0.0036$ cm^{-1}, and $A_{\perp} = 0.0045$ cm^{-1}

Acid–Base Interactions.—Dissolution of [Mn^{II}(tspc)] in a highly acidic medium, *e.g.* 3—5 mol dm^{-3} HCl,

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[21] L. H. Vogt, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, 1967, **6**, 1725.

resulted in demetallation of the chelate. The e.s.r. spectrum of the resulting solution indicates the presence of free manganese(II) ions. The complex [Mn^{II}(tspc)] does however survive the extremes of pH which are involved in its preparation, *i.e.* 1.0 mol dm^{-3} HCl to 0.5 mol dm^{-3} Na[OH].

Addition of 10% v/v of dmf to an aqueous solution of [Mn^{II}(tspc)] provides the best circumstances for the observation at 133 K of the e.s.r. spectrum of the monomeric form of the complex. The effect of changing acidity on such a solution is demonstrated in Figure 2. Results for addition of 5% v/v of dmf to aqueous solution are almost exactly identical. Quite pronounced changes were observed, particularly in the range pH 2.0—4.4, where the spectra point to a high-spin configuration for [Mn^{II}(tspc)]. The low-spin spectrum, observed at pH >6.0, can be regenerated by addition of sodium hydroxide. The cycle can be repeated, indicating that the phthalocyanine is not undergoing any major structural change.

The room-temperature spectra due to aqueous solutions of [Mn^{II}(tspc)] at low pH consisted of six lines centred on $g = 2.00$, a result expected for high-spin forms of Mn^{II}. As the pH was increased, the signal decreased in intensity until it was no longer observed at pH >6.5. Similar results were obtained with the room-temperature and frozen-solution spectra of aqueous solutions, although the high-spin spectrum observed at low temperature was not well defined due to its large linewidth.

The effect of changing pH on the absorption spectrum of a 5% dmf–water solution of [Mn^{II}(tspc)] was investigated. Addition of acid to a neutral solution resulted in an increase in the absorption at 718 nm and a corresponding decrease in the absorption at 636 nm. In alkaline solutions, the absorption at 718 nm was not observed and the main absorption was at 630 nm with a shoulder at 672 nm.

Conclusions.—The ease with which the addition of polar organic solvents can break down the aggregated form of the manganese(II) chelate indicates that attachment of dmf to the axial sites of the chelate is more important than solvation of the sulphonic acid groups. This contrasts with the case of [Co^{II}(tspc)] where it is envisaged that the initial role of the polar organic solvent is to diminish the forces holding the polymeric form together, by clustering around the sulphonic acid groups on the periphery of the molecule.[10] In the [Co^{II}(tspc)] case, the axial positions are initially occupied by weakly co-ordinated water molecules which are ultimately displaced by the organic solvent.[10] However, one must consider in the case of the manganese(II) chelates the possibility of the presence of both five- and six-co-ordinate species. It is clear from the results that, unlike the case of [Co^{II}(tspc)], the e.s.r. spectra are unable to distinguish readily between five- and six-co-ordinate species. This is also clear from examination of the signals obtained after addition of pyridine and imidazole to aqueous solutions. However, addition of [Ni^{II}(tspc)] or [Zn^{II}(tspc)], which appear to form a molecular complex with the manganese(II) chelate, gives rise to a high-spin spectrum.

For [Mn^{II}(tspc)] in its low-spin form with spin $\frac{1}{2}$, no superhyperfine structure from either the four in-plane nitrogens or from an out-of-plane nitrogen, *e.g.* from a pyridine or imidazole molecule, is observed. This implies that the unpaired electron is neither in the in-plane $d_{x^2-y^2}$ orbital {*cf.* [Cu^{II}(tspc)]} nor in the out-of-plane $d_{3z^2-r^2}$ orbital {*cf.* [Co^{II}(tspc)]}.[22] Thus the possible ground-state orbitals are d_{xy}, d_{yz}, and d_{xy}. The g values expected from the first two are, as a first approximation, $g_{\parallel} = 4$ and $g_{\perp} = 0$, or both $g_{\parallel} = 0$ and $g_{\perp} = 0$, whilst for the d_{xy} orbital one may expect both $g_{\parallel}$ and $g_{\perp}$ to be close to 2. (For a detailed discussion see ref. 15, section 7.8.) In view of the assignment of a d_{xy} ground state to [$Mn^{II}(pc)(py)_2$] (py = pyridine)[12] and the order of the levels proposed for manganese(II) phthalocyanine by Barraclough *et al.*,[20] the proposed d_{xy} ground state does not seem unreasonable.

The g values and hyperfine constants given for the pyridine complex in Figure 5 are consistent with those expected from a d_{xy} ground state. Similar g and hyperfine values would apply to the spectra observed in the frozen solutions containing, for example, dmf and ethylene glycol, in which the spectra are more complex than in pyridine.

The change from a low- to a high-spin configuration of [Mn^{II}(tspc)] on acidification of aqueous solutions may be explained in two ways. The first explanation relates to a change in the axial ligand bound to the metal ion. The nature of the axial ligand co-ordinated to planar metal complexes has a marked effect on the spin state of the metal ion. For example, in an e.s.r. study of ferrihemoglobin [23] the aqua- and fluoro-derivatives of this iron(III) complex were shown to be high spin whereas the azido-, cyano-, and hydroxo-derivatives were low spin. The classification of each derivative was related to the strength of the interaction between the iron(III) ion and the axial ligand. E.s.r. studies at 77 K of sperm-whale ferrimyoglobin,[24] as a function of pH, showed a transition from a predominantly high-spin form to a low-spin form at pH 10. This result was shown to correspond to replacement of iron(III)-bound water by hydroxide ion. A similar change could occur for [Mn^{II}(tspc)].

A second explanation is related to the possibility of protonation of the tspc chelates. Demetallation of tspc chelates in strong acid presumably results in the formation of metal-free tspc, H_2tspc, in which two of the inner basic nitrogen atoms are protonated. Addition of sodium hydroxide to a highly acidic solution of [Mn^{II}(tspc)] results in hydrolysis of the free metal ion, indicating that re-insertion of the metal ion does not take place under these circumstances.

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The state of the tspc chelate prior to demetallation is the key to the explanation of the spin configurational change. Protonation of one or both of the inner nitrogen atoms of the manganese(II) complex would be expected to produce dramatic sterochemical changes as a result of steric crowding and electrostatic repulsion.[25] Under such conditions, the metal ion is likely to move out of the plane of the cyclic ligand and consequently would be weakly bound by the ring nitrogen atoms, resulting in a change in the spin state of the metal ion. Further acidification of the solution would then result in complete demetallation of the complex. This result is surprising in view of the extreme conditions required to protonate metal phthalocyanines, *i.e.* concentrated chlorosulphuric acid, and the remarkable stability of these complexes in such a medium.

EXPERIMENTAL

The manganese(II) chelate of 4,4′,4″,4‴ - tetrasulphophthalocyanine was prepared by the method of Weber and Busch.[16] The corresponding nickel(II) and zinc(II) chelates were prepared in an identical manner using the appropriate metal sulphate. In all cases the composition of the products was established by elemental analysis.

Measurements of pH were made using a Radiometer model 22 pH meter fitted with a glass electrode and a saturated calomel electrode. Visible absorption spectra were recorded at room temperature on a Varian 635 u.v.–visible spectrophotometer. *X*-Band e.s.r. measurements were made at room temperature and 133 K using a Varian E12 spectrometer.

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