Electron Spin Resonance Study of the Species formed by Reduction of Manganese(II) Chelates of Tetrasodium 3,10,17,24-Tetrasulphonatophthalocyanine in Aqueous Solution

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E.s.r. spectroscopy has been used to identify the products formed by reduction of the low-spin manganese(II) chelates of tetrasodium 3,10,17,24-tetrasulphonatophthalocyanine Na_4(tspc) on addition of various reducing agents. Addition of hydrazine to an aqueous solution containing $[Mn^{II}(tspc)]^{4-}$ leads to the formation of low-spin $[Mn^{0}(tspc)]^{6-}$ which is also formed on addition of sodium sulphide or dithionite to an aqueous solution of the manganese(II) chelate containing 10% v/v of pyridine. The addition of sodium tetrahydroborate to an aqueous solution of $[Mn^{II}(tspc)]^{4-}$ is thought to lead to diamagnetic $[Mn^{I}(tspc)]^{5-}$. When pyridine or imidazole are present in an aqueous solution of $[Mn^{II}(tspc)]^{4-}$, the addition of $Na[BH_4]$ leads to a free-radical species, which is thought to involve the phthalocyanine ring system. The magnetic parameters associated with the e.s.r. spectrum due to $[Mn^{0}(tspc)]^{6-}$ have been determined by computer simulation of the experimental spectrum. The values of these magnetic parameters, together with the absence of extra hyperfine interactions due to certain axial ligands, lead to the proposal of a $3d_{xy}$ ground-state configuration for the low-spin manganese(0) chelate.

CONSIDERABLE recent interest has been shown in the oxidation and reduction properties of metal phthalocyanines and porphyrins.[1-25] Reduction corresponds to the successive addition of electrons to vacant or partially occupied orbitals of the metal complex. For complexes

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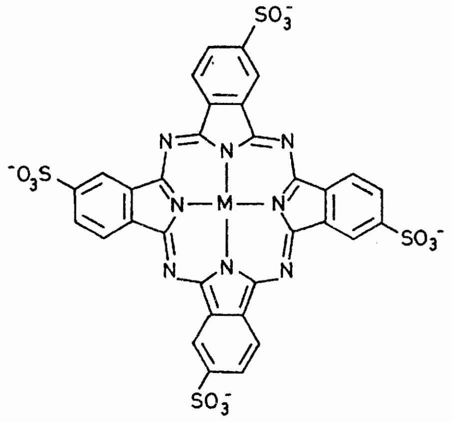
with closed-shell central metal ions (Mg^{2+} or Zn^{2+}), electron addition is confined to the π orbitals of the ligand system. It has been shown that up to four electrons can be donated to these systems,[9,17,19] and these are added to the lowest-vacant e_g orbital of the ring system.[14] On the other hand, the metal 3*d* orbitals in a transition-metal complex lie close to the highest-filled a_{1u} orbital of the ring system, and it is therefore possible for reduction of the metal ion to take place.

A number of e.s.r. studies have been made [12,21] on the reduction of phthalocyanines. Clack *et al.*[21] obtained results which indicated that magnesium(II), aluminium(III), zinc(II), copper(II), and nickel(II) phthalocyanines are reduced by addition of electrons to the ring system, whereas in cobalt(II) phthalocyanine at least one electron is added to a metal orbital. Guzy *et al.*[12] made similar studies of chromium, iron, nickel, copper, and metal-free phthalocyanines which indicated that electrons are added to a ring orbital for the copper, nickel, and metal-free phthalocyanines, and to a metal orbital in formation of the one-electron reduction products of chromium and iron phthalocyanines. In the case of chelates, [3,10,17,24-tetrasulphonatophthalocyanine(2-)]metal, $[M(tspc)]^{4-}$ (1), reduction of copper(II), nickel(II), and metal-free complexes appears only to involve the ligand,[11] whereas reduction of $[Co^{II}(tspc)]^{4-}$ may be interpreted on the basis of the first reduction step yielding $[Co^{I}(tspc)]^{5-}$.[7,8,11]



$[M(tspc)]^{4-}$ (1)

In view of the limited information available on the reduction of tspc complexes in aqueous solution, the present investigation was undertaken in order to study the effects of solvent composition on the reduction process of $[Mn^{II}(tspc)]^{4-}$ and to study the effect of the reducing agent on the site of reduction in these complexes, *i.e.* metal ion or ligand. An earlier study dealt with solute–solute and solute–solvent interactions in aqueous solutions containing the manganese(II)–tspc chelate.[26]

RESULTS

Addition of hydrazine to an aqueous solution of $[Mn^{II}(tspc)]^{4-}$ resulted in an immediate colour change from blue to violet. The visible absorption-spectral changes associated with this reaction are shown in Figure 1. Subsequent exposure of the violet solution to oxygen resulted in rapid decolouration of the solution, apparently due to oxidative degradation of the ligand.[27]

The e.s.r. spectrum of the violet solution (Figure 2) bears some resemblance to that of a low-spin $3d^7$ complex such as $[Co^{II}(tspc)]^{4-}$, with the difference being that $I = \frac{5}{2}$ here rather than $I = \frac{7}{2}$ as for cobalt(II). A consideration of the prevailing chemical condition points to the formation of a manganese(0)–tspc complex resulting from two-electron reduction of $[Mn^{II}(tspc)]^{4-}$. A second species of Mn^0 is thought to be responsible for the additional weak transitions discerned in the 300—350 mT region. On exposure to oxygen the e.s.r. spectrum due to the manganese(0) complex changed quite significantly as shown in Figure 3(*a*). The

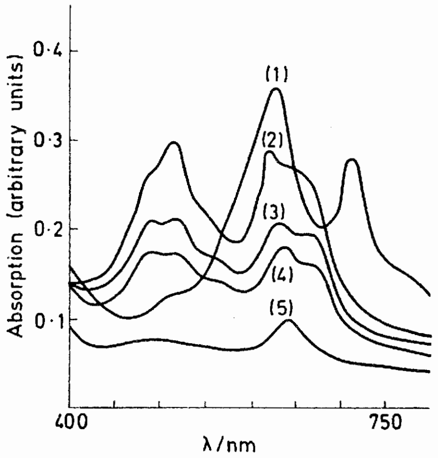


FIGURE 1 Absorption spectra of: (1) an aqueous solution of $[Mn^{II}(tspc)]^{4-}$ (1.0×10^{-4} mol dm^{-3}); (2) the same solution containing 2% v/v of hydrazine and left in air for 5, 35 (3), 50 (4), and 160 min at room temperature (5)

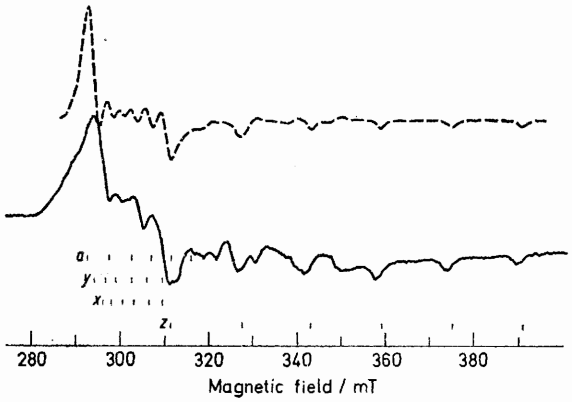


FIGURE 2 *X*-Band e.s.r. spectrum at −140 °C of an aqueous solution of $[Mn^{II}(tspc)]^{4-}$ (1.0×10^{-3} mol dm^{-3}) containing 5% v/v of hydrazine. The broken curve represents the computer simulation of the experimental spectrum using the parameters listed in the Table. Stick spectra relate to *x*, *y*, and *z* axes as well as to the direction corresponding to the angular anomaly (designated *a*)

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sharp line at *g ca.* 2 indicates the formation of a free-radical species in solution. The solution eventually became pale green and gave the spectrum shown in Figure 3(*b*) which differs from Figure 3(*a*) in the absence of the sharp radical line. Addition of more hydrazine to this solution affected neither its colour nor its e.s.r. spectrum. The rate at which colouration of the solution occurred increased with increasing hydrazine concentration, indicating that hydrazine is probably playing a part in the eventual degradation of the ligand.[27] The nature of the free-radical species is uncertain.

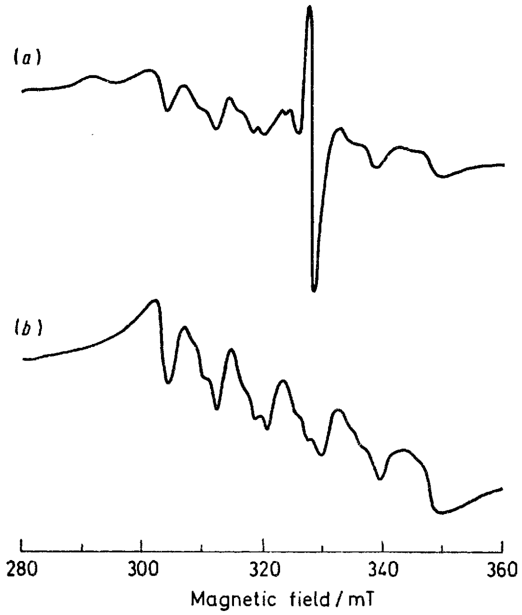

FIGURE 3 *X*-Band e.s.r. spectra at −140 °C of an aqueous solution of $[Mn^{II}(tspc)]^{4-}$ (1.0×10^{-3} mol dm^{-3}) containing 5% v/v of hydrazine after standing in air at room temperature for (*a*) 60 and (*b*) 180 min

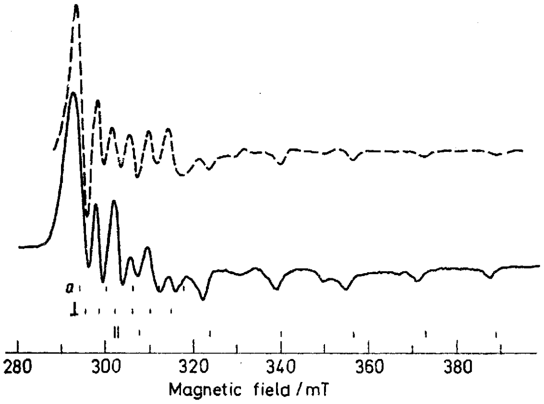

FIGURE 4 *X*-Band e.s.r. spectrum at −140 °C of a 10% pyridine–water solution of $[Mn^{II}(tspc)]^{4-}$ (1.0×10^{-3} mol dm^{-3}) containing 5% v/v of hydrazine. The broken curve represents the computer simulation of the experimental spectrum using the parameters listed in the Table (for stick spectra see Figure 2)

It may result from the formation of another reduced manganese(II)–tspc species or from a degradation process involving the production of free-radical species.

The effect of extraplanar ligands on the reduction process is demonstrated in Figure 4 in which a spectrum attributed to low-spin Mn^0 is given. Weak lines towards the high-field end appear to be due to a second species present in low concentrations. Addition of hydrazine to a 10% pyridine–water solution of $[Mn^{II}(tspc)]^{4-}$ gave a green solution, indicating that a new complex may be formed under these circumstances. However, no nitrogen superhyperfine splitting was detected in the ' parallel ' region of the spectrum. When hydrazine was added to a solution of $[Mn^{III}(tspc)(OH)]^{4-}$, produced by oxidation of a pyridine–water solution of $[Mn^{II}(tspc)]^{4-}$, an identical spectrum was obtained, presumably as a result of a three-electron reduction process.

The presence of imidazole or *NN*-dimethylformamide (dmf) had little effect on the spectrum shown in Figure 2. However, the rate of the subsequent oxidation process increased as indicated by the rapid rate of decolouration of these solutions in the presence of oxygen.

No e.s.r. spectrum was obtained at −140 °C from an aqueous solution of $[Mn^{II}(tspc)]^{4-}$ to which sodium sulphide had been added, even though a colour change from blue to violet occurred. It is possible therefore that under these conditions reduction to $[Mn^{I}(tspc)]^{5-}$ has occurred. Addition of Na_2S to a 10% pyridine–water solution of $[Mn^{II}(tspc)]^{4-}$ resulted in an e.s.r. spectrum similar to those shown in Figures 2 and 4, indicating a two-electron reduction to $[Mn^{0}(tspc)]^{6-}$.

The redox processes associated with sodium dithionite led to a spectra attributed to Mn^0 (Figure 5). Similar results were obtained when Na_2S was used. Sodium tetrahydroborate, on the other hand, caused a departure from the trend that is emerging as far as reduction to a manganese(0) chelate is concerned. Thus, addition of $Na[BH_4]$ to an aqueous solution of $[Mn^{II}(tspc)]^{4-}$ resulted in almost complete loss of the signal. It is tentatively proposed that this occurs as a result of reduction to a diamagnetic $[Mn^{I}(tspc)]^{5-}$ species. The solution rapidly oxidizes in air and the e.s.r. spectrum indicates the presence of a high-spin manganese(II) complex. The marked decrease in intensity of the colour of the solution is indicative of ligand degradation, as was observed in solutions containing hydrazine. In the presence of pyridine or imidazole the e.s.r. spectra shown in Figure 6 were obtained. In this case, reduction to a manganese(0) species is not evident. The presence of a free-radical signal

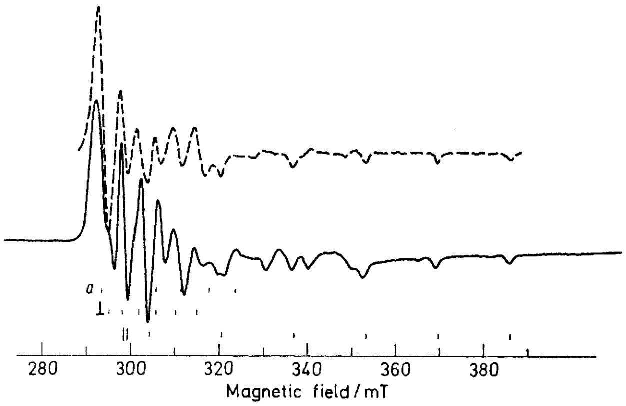

FIGURE 5 *X*-Band e.s.r. spectra at −140 °C of a 10% pyridine–water solution of $[Mn^{II}(tspc)]^{4-}$ (1.0×10^{-3} mol dm^{-3}) to which sodium dithionite had been added. The broken curve represents the computer simulation of the experimental spectrum using the parameters listed in the Table (for stick spectra see Figure 2)

at *g* 2.00 indicates that reduction of the phthalocyanine ring has taken place. However, no ligand superhyperfine splitting was observed, even at high spectrometer gain.

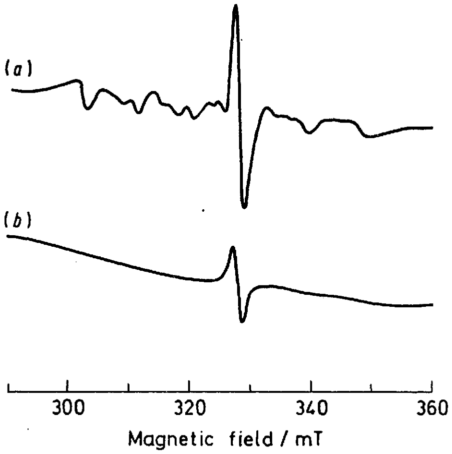

FIGURE 6 *X*-Band e.s.r. spectra at −140 °C of an aqueous solution of $[Mn^{II}(tspc)]^{4-}$ (1.0×10^{-3} mol dm^{-3}) containing (*a*) 10% v/v of pyridine and (*b*) 1.0×10^{-2} mol dm^{-3} imidazole, to which $Na[BH_4]$ had been added

Interpretation of the E.S.R. Spectra of Low-spin $[Mn^0(tspc)]^{6-}$.—The e.s.r. spectra due to monomeric $[Mn^0(tspc)]^{6-}$ species may be described by the spin Hamiltonian (1), where

$$\begin{aligned}\mathscr{H} = {} & [g_xS_xB_x + g_yS_yB_y + g_zS_zB_z] \\ & + A_xS_xI_x + A_yS_yI_y + A_zS_zI_z \\ & + P[I_z^2 - \tfrac{1}{3}I(I + 1)] \qquad (1)\end{aligned}$$

all the terms have their usual meaning and for Mn^0 we take $S = \frac{1}{2}$ and $I = \frac{5}{2}$. Computer simulations of the spectra were carried as described previously[28] using analytic expressions for transition fields and intensities derived using perturbation theory. For axial symmetry, when for example $g_x = g_y$ and $A_x = A_y$, the perturbation solutions reduce to those of Bleaney.[29,30]

There are additional transitions which may occur due to the presence of finite quadrupole and nuclear Zeeman interactions, the so-called forbidden transitions. These are of the type in which the nuclear quantum number *m* changes, *i.e.* $\Delta m = \pm 1$ or ± 2. A detailed discussion of these transitions including the correct derivation of transition fields in the case of axial symmetry has previously been given.[28] It suffices to point out that such effects are not required in the cases described in this paper. Inclusion of values of the axial quadrupole parameter *P* of up to 0.0005 cm^{-1} gave no significant improvement. Values of *P* larger than this are not permitted in the present perturbation theory where $|P| \ll |A_x|$ and $|A_y|$. In particular, the additional lines seen in Figures 2, 4, and 5 are not due to such forbidden transitions but appear to have a natural explanation in terms of additional species present in small concentrations. The e.s.r. parameters due to these weak species have not been allowed for in the spectral fitting.

It is clear that the computed spectra do not match the experimental results perfectly and this is attributed to the influence of the weaker spectra in the 280—320 mT region. Nevertheless there can be no doubt that the spectra in Figures 2, 4, and 5 are indeed due to low-spin Mn^0 ($3d^7$). Errors quoted in the Table are based on variations of the parameters of equation (1) which still give rise to acceptable results. Linewidth anisotropies required were 0.8—1.2 mT in the *z* direction and 1.6—2.0 mT in the *xy* plane. Further alteration in linewidths did not produce improvement in the overall spectral shape.

Spin-hamiltonian parameters for manganese(0) complexes of tspc

Solvent for $[Mn^{II}(tspc)]^{4-}$ (1×10^{-3} mol dm^{-3})	Reducing agent	±0.005			Hyperfine constants ±5 × 10^{-4} cm^{-1}		
		g_x	g_y	g_z	A_x	A_y	A_z
Water	N_2H_4	2.154	2.161	1.859	28	32	138
		$g_\perp$		$g_\parallel$	$A_\perp$		$A_\parallel$
10% Pyridine–water	N_2H_4	2.135		1.874	39		142
10% Pyridine–water	$Na_2S_2O_6$	2.135		1.888	40		145

DISCUSSION

The various chemical changes brought about by addition of reducing agents to aqueous solutions of $[Mn^{II}(tspc)]^{4-}$, together with related solute–solute, solute–solvent, and axial protonation reactions, are summarized in the Scheme.

While the evidence of e.s.r. and chemical change points to the two-electron reduction product of $[Mn^{II}(tspc)]^{4-}$ being a low-spin manganese(0)–tspc species, *i.e.* the additional electrons are both placed in metal orbitals, the actual ground state of the manganese(0) complex is not so readily established. It has been generally accepted that the equivalent $[Co^{II}(tspc)]^{4-}$ (also $3d^7$) has its unpaired electron in the d_{z^2} orbital, directed with its main lobes normal to the plane, along the *z* axis. At first sight, the same ground-state orbital would appear to be appropriate for manganese(0)–tspc. However, a more critical appraisal indicates that this may not be so. First, addition of pyridine to a 5% hydrazine–water solution of $[Mn^0(tspc)]^{6-}$, which results in a colour change from violet to green and values of $g_\parallel$ *ca.* 1.87 and $g_\perp$ *ca.* 2.13, does not give rise to the observation of nitrogen superhyperfine splitting. This would be expected if the pyridine molecules were co-ordinated to the Mn^0 in the out-of-plane positions and if, in the ground state, the electrons were in an essentially d_{z^2} orbital. It should be noted that addition of either pyridine or hydrazine to $[Co^{II}(tspc)]^{4-}$ results in the observation of nitrogen superhyperfine structure, whereas nitrogen superhyperfine structure is not observed for any of the manganese(0) species, even under conditions favourable for its observation.

Secondly, when the value of $g_\parallel < 2$ in cobalt(II) phthalocyanine complexes, $g_\perp$ is considerably different from 2.0 and is usually close to 3. It is clear that this is

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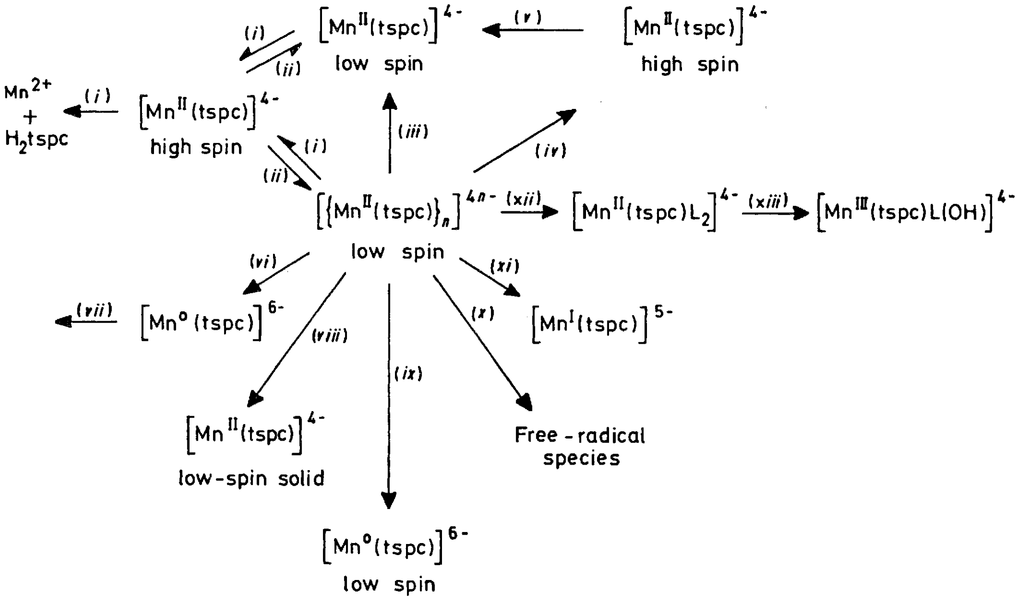
not the case for $[\mathrm{Mn^0(tspc)}]^{6-}$. Thus doubt must be cast on any interpretation of the ground state in terms of a d_{z^2} orbital. Of the other possible ground states, a $d_{x^2-y^2}$ orbital $\{cf.\ [\mathrm{Cu^{II}(tspc)}]^{4-}\}$ may be ruled out as no nitrogen hyperfine structure is observed from the four in-plane nitrogens. Furthermore, it is unlikely that a ground state resulting from some combination of d_{xz} and d_{yz} orbitals could have appropriate *g* values. The remaining possibility is d_{xy}. This is attractive for it would have, on a simple calculation, both *g* values close to 2.0 and one would not expect to observe nitrogen superhyperfine coupling from either in-plane or out-of-plane ligands. Although such an orbital has been considered as a possible ground state for cobalt(II) complexes, no experimental confirmation has been reported. However, the calculations of Engelhardt and Green[31] show that the d_{xy} orbital may indeed be lower in energy than d_{z^2}. Indeed, their calculations indicate that the *g* values obtained here could be accounted for on the basis of a d_{xy} orbital. The specific conditions required are a cubic-field model with a strong tetragonal distortion and particular relations between the parameters *Ds* and *Dt* of the tetragonal crystal field.[32] It must be borne in mind that the orbitals are not really one-electron orbitals, d_{xy}, *etc.*, at all, but seven-electron (or three-hole) Slater determinants which transform under the symmetry at the ion site in the same way. However, for the present purpose, no problem arises in using the one-electron nomenclature.



SCHEME (*i*) $\mathrm{H^+}$; (*ii*) $\mathrm{OH^-}$; (*iii*) 5% v/v dmf; (*iv*) $[\mathrm{Ni^{II}(tspc)}]^{4-}$ or $[\mathrm{Zn^{II}(tspc)}]^{4-}$; (*v*) 10% v/v dmf; (*vi*) $\mathrm{N_2H_4}$; (*vii*) $\mathrm{O_3}$, ligand degradation; (*viii*) water; (*ix*) 10% v/v py plus $\mathrm{S^{2-}}$, $\mathrm{S_2O_6^{2-}}$, or $\mathrm{N_2H_4}$; (*x*) $\mathrm{BH_4^-}$ plus py or imidazole; (*xi*) $\mathrm{BH_4^-}$; (*xii*) py or imidazole plus $\mathrm{CN^-}$ or $\mathrm{N_3^-}$; (*xiii*) $\mathrm{O_2}$

Reduction to a manganese(0) species with sodium sulphide or dithionite requires the presence of an extraplanar ligand such as pyridine. It is possible, therefore, that the reduction process involves the initial formation of a five- or six-co-ordinate species which in turn reduces the redox potential for the two-electron reduction step. In addition to acting as a reducing agent, hydrazine is also capable of co-ordinating to tspc chelates, as shown in the cases of $\mathrm{Fe^{III}}$ and $\mathrm{Co^{II}}$. The reaction, in water, of hydrazine and $[\mathrm{Mn^{II}(tspc)}]^{4-}$ probably involves initial formation of a $[\mathrm{Mn^{II}(tspc)}]^{4-}\cdot\mathrm{N_2H_4}$ adduct, followed by reduction of this complex to the manganese(0) species. However, due to the extremely rapid reaction rate, the presence of such an intermediate was not detected.

The mechanisms of electron-transfer reactions in chemical and biological systems have been extensively investigated.[33-39] In a recent article by Sutin[39] it was shown that electron-transfer reactions involving ferricytochrome C may occur *via* the edge of the porphyrin ring system or directly at the metal-ion centre. This distinction is important when considering possible mechanisms for the reactions of $[\mathrm{Mn^{II}(tspc)}]^{4-}$ with $\mathrm{N_2H_4}$ and $\mathrm{Na[BH_4]}$. In the case of hydrazine, electron transfer at the metal-ion centre occurs, whereas electron transfer on to the phthalocyanine ring occurs under similar circumstances with $\mathrm{Na[BH_4]}$, highlighting the marked dependence of the reduction process not only on solution conditions but also on the nature of the reducing agent.

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EXPERIMENTAL

The manganese(II) chelate of 3,10,17,24-tetrasulphonatophthalocyanine was prepared by the method outlined by Weber and Busch.[40] In each case, the reducing agent was used in excess to ensure complete reaction with $[Mn^{II}(tspc)]^{4-}$ and to reduce the rate of reoxidation. The original mixing and subsequent transfer operations were carried out under a nitrogen atmosphere.

The e.s.r. measurements, at room temperature and −140 °C, were made on a Varian E-12 spectrometer at a microwave frequency of 9 143 MHz.

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