Manganese 4,4′,4″,4‴-Tetrasulphonated Phthalocyanine, its Dioxygen Adduct, and E.s.r. Evidence for Intramolecular Electron Transfer in Solution

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Summary In the solid state the dioxygen adduct of manganese 4,4′,4″,4‴-tetrasulphonated phthalocyanine (MnTsPc) is best formulated as $\mathrm{Mn^{III}TsPcO_2^{-}}$ and in solution the e.s.r. spectrum as a function of pH indicates that there is an intramolecular electron transfer between $\mathrm{Mn^{II}TsPcO_2}$ and $\mathrm{Mn^{III}TsPcO_2^{-}}$; the superoxide is only stable between a pH of *ca.* 11·5 and 13·5 and evidence of oxidase activity is observed at pH > *ca.* 14.

The ability of manganese phthalocyanine (MnPc) to bind molecular oxygen to generate an exceptionally stable 1 : 1 adduct $\mathrm{MnPc(O_2)}$ and formulated as a $\mathrm{Mn^{III}}$ superoxide species has been reported recently by Lever *et al.*[1] We have now isolated and characterized manganese tetrasodium 4,4′,4″,4‴ tetrasulphonated phthalocyanine (MnTsPc) and its dioxygen adduct and have monitored the solution e.s.r. spectrum as a function of pH. This has provided new evidence on the electronic structure and possible electronic and/or structural rearrangements in these complex manganese dioxygen compounds.

The product which is obtained from the Weber–Busch synthesis[2] of 'MnTsPc' is a mixture of species. The product from our preparation, purified by dialysis through a cellulose membrane, is the dioxygen adduct with a characteristic absorption in the optical spectrum at 718 nm. The reactions of $\mathrm{MnTsPc(O_2)}$ in solution were followed conveniently by changes in the u.v. spectrum.[1] Solid $\mathrm{MnTsPc(O_2)}$ and MnTsPc have also been isolated and characterized. An intermediate product, presumed to be the μ-peroxo compound similar to that postulated in the Mn–tetraphenylporphyrin oxygen system,[3] has been identified ($\lambda_{\max}$ 632 nm) but not isolated. Reaction of $\mathrm{MnTsPc(O_2)}$ with hydrazine hydrate produces MnTsPc directly[4] with no intermediate products although excess of hydrazine produces a purple reduction product ($\lambda_{\max}$ 660 nm). The 1 : 1 Mn : O ratio has been confirmed by oxygen absorption studies, the rate of oxygen absorption increasing with $\mathrm{H^+}$ concentration indicating proton-activated oxygenation. The Raman spectra of the $^{16}\mathrm{O}$ and $^{18}\mathrm{O}$ adducts *in the solid state* confirm that the dioxygen adduct is a superoxide because the peak at 1135 $\mathrm{cm^{-1}}$ in the $^{16}\mathrm{O}$ spectra is shifted to 1050 $\mathrm{cm^{-1}}$ in the $^{18}\mathrm{O}$ spectra.[3,5,6] The *solid state* e.s.r. spectrum of $\mathrm{MnTsPc(O_2)}$ has a single peak at *g* 1·99 and is typical of the spectra expected for $\mathrm{O_2^{-}}$ species.[7] The magnetic moment of solid MnTsPc is temperature dependent (5·9 μ_{B} at 299 K, 3·55 μ_{B} at 4·42 K) and is only compatible with a spin equilibrium between the high, low, and intermediate spin states of the $\mathrm{d^5}$ ion. The magnetic moment of $\mathrm{MnTsPc(O_2)}$ in the solid state varies from 4·6 μ_{B} at 280 K to 3·2 μ_{B} at 4·3 K and is similar to $\mathrm{Mn^{III}PcO_2^{-}}$.[1] A small interaction between the $S = 2$ $\mathrm{d^4}$ $\mathrm{Mn^{III}}$ ion and the unpaired electron on $\mathrm{O_2^{-}}$ is the only model consistent with these data. All the above evidence suggests that in the solid state the dioxygen adduct is best formulated as $\mathrm{Mn^{III}TsPcO_2^{-}}$.

The solution e.s.r. spectrum of MnTsPc($\mathrm{O_2}$) at 300 K is an intense well resolved 6 line spectrum, very characteristic of a Mn$^{\mathrm{II}}$ species and must be due to the dioxygen adduct because dialysis should remove any free Mn^{2+} ion. When the pH of the solution is raised several significant changes in the spectra occur (Figure). First, the appearance of a sharp line at $g = 1{\cdot}97$ becomes noticeable at pH *ca.* 11·5 and increases in intensity at the expense of the original 6-line spectrum, to a pH of *ca.* 13·5. This line is characteristic of the spectrum expected for the $\mathrm{O_2^-}$ species and observed by us in the solid state and by Uchida[7] in solution. Secondly, on further addition of $\mathrm{OH^-}$ the intensity of this sharp line begins to decrease as the pH rises until at pH $>$ *ca.* 14 there is little or no signal at all. If acid is now added to the solution (to say pH 3) in the presence of oxygen and the e.s.r. spectrum is monitored as a function of time, the original 6-line spectrum reappears and grows in intensity over a period of some hours paralleling our oxygen absorption studies. We have observed identical behaviour for MnPcO$_2$ at slightly different pH values which was not reported previously.[1]

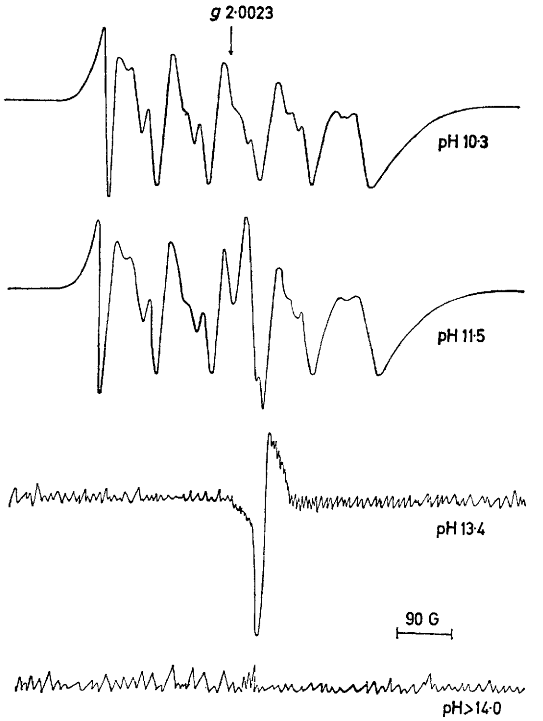
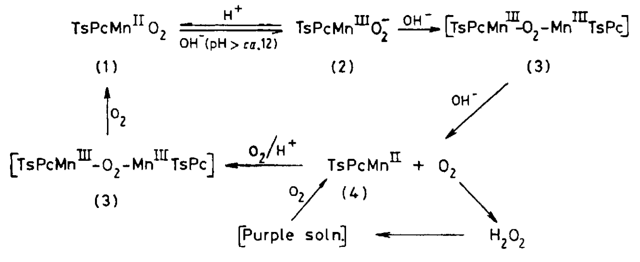


FIGURE. E.s.r. spectra of the MnTsPc–O$_2$ system as a function of pH.

Our postulated mechanism for this behaviour is shown in the Scheme. In solutions with pH $<$ 12 the predominant species is Mn$^{\mathrm{II}}$TsPcO$_2$ which gives a 'normal' Mn$^{\mathrm{II}}$ 6-line spectrum whereas when the pH increases above 12 Mn$^{\mathrm{III}}$TsPcO$_2^-$ becomes the preferred electronic arrangement. At still higher pH both (**3**) and/or (**4**) are not expected to possess an easily observable e.s.r. spectrum at 300 K. [We have observed a 6-line spectrum for (**4**) in frozen solution but only at 4·2 K]. The u.v. spectra of (**1**)—(**4**) are all compatible with the proposed reaction scheme. The solution i.r. spectrum is more revealing because the differences between the ^{16}O and ^{18}O adducts as a function of pH show clearly the presence of MnTsPcO$_2$ and Mn$^{\mathrm{III}}$TsPcO$_2^-$.[3,5,6] For example at a pH *ca.* 9 the peak at 1702 cm^{-1} in the ^{16}O spectra is shifted to *ca.* 1655 cm^{-1} in the ^{18}O spectra suggesting that the dioxygen in (**1**) is formally a neutral O$_2$.[5]



SCHEME

One remarkable feature of the conversion of (**2**) into (**4**) is that little or no oxygen could be detected by pressure changes or mass spectrometry. After some hours *in vacuo* the blue solution (**4**) changed to that of the same but as yet uncharacterized purple product seen in the over-reduction of MnTsPcO$_2$ with hydrazine hydrate. Tests using the usual *O*-dianisidine peroxidase reagent showed the presence of hydrogen peroxide. On the other hand if CN$^-$ is added in the conversion of (**2**) into (**4**) nearly the stoicheiometric quantity of molecular oxygen can be recovered. This then is good evidence for oxidase activity.

A very qualitative M.O. diagram[5] shows that (**1**) contains three unpaired metal-based electrons (compatible with the solution magnetic moment of 3·9 μ_{B} using Evans' method) whereas (**2**) also has one unpaired electron in the highest-occupied and mainly oxygen-based π^* orbital. This difference is controlled by the relative energies of the $d_{x^2-y^2}$ and π^* orbitals and suggests that the molecular geometries of (**1**) and (**2**) may be different.

We thank Dr D. James (University of Queensland) for the use of Raman facilities, Dr R. Bramley for the *X*-band e.s.r facilities, Professor A. M. Sargeson and Dr P. Lay for discussion, the Australian Research Grants Committee for financial support (A.K.G.) and the Commonwealth Government for a Postgraduate Scholarship (N.T.M.).

(*Received*, 16*th September* 1980; *Com.* 1013.)

[1] A. B. P. Lever, J. T. Wilshire, and S. K. Ouan, *J. Am. Chem. Soc.*, 1979, **101**, 3668.
[2] J. H. Weber and D. H. Busch, *Inorg. Chem.*, 1965, **4**, 469.
[3] J. A. Fee and J. S. Valentine, 'Superoxide and Superoxide Mutases,' Academic Press, New York, 1977.
[4] I. Okura, N. K. Thuan, and T. Keii, *J. Mol. Catal.*, 1979, **5**, 125.
[5] R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, 1979, **79**, 139.
[6] C. G. Barraclouth, G. A. Lawrence, and P. A. Lay, *Inorg. Chem.*, 1978, **17**, 3317.
[7] K. Uchida, S. Nanto, M. Soma, T. Onishi, and K. Tamaru, *J. Chem. Soc., Chem. Commun.*, 1978, 217.