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An Electron Spin Resonance Study of the Formation of a Molecular Oxygen Adduct of the Manganese(II) Chelate of Tetra-sodium 3,10,17,24-tetrasulphonatophthalocyanine

STUART W. OLIVER, THOMAS D. SMITH

Chemistry Department, Monash University, Clayton, Vic. 3168, Australia

and JOHN R. PILBROW

Physics Department, Monash University, Clayton, Vic. 3168, Australia

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Abstract

Treatment of the manganese(II) chelate of tetrasodium 3,10,17,24-tetrasulphonatophthalocyanine (tspc) with alkaline aqueous solution in air followed by the addition of ethanol leads to formation and precipitation of an ESR non-detectable form of the chelate. When the material is dissolved in slightly alkaline aqueous solution and allowed to stand under nitrogen or air for two hours, a product is formed with the ESR spectral characteristics of a manganese(II) molecular oxygen complex. Treatment of this material with ferrocyanide leads to an ESR non-detectable form of manganese tspc formed by a one electron transfer process while titration with sodium ascorbate leads to the formation of low-spin manganese(0) tspc by a two electron transfer.

Introduction

An earlier study of the manganese chelate of tetrasodium 3,10,17,24-tetrasulphonatophthalocyanine (Na_2tspc) provided some evidence that the compound prepared by the method of Weber and Busch [1] is obtained as a manganese(II) chelate, Though it was not recognized at the time, the procedure used for the preparation of the chelate leads to products which contain manganese in a high oxidation state [2]. More recently it has been shown that manganese(II) tspc can be prepared and that it exists in aqueous solution in high-spin and low-spin forms, with the latter being favoured in slightly alkaline solution and showing tendency to take up molecular oxygen [3].

Studies by Lever *et al.* [4] have shown that exposure of a dimethylacetamide solution of manganese(II) phthalocyanine to molecular oxygen leads to the formation of a stable 1:1 molecular oxygen adduct of the chelate which is characterized by an approximately eighteen line ESR spectrum. This critically important observation suggests that a quite similar ESR spectrum due to manganese tspc species may be due to a molecular oxygen adduct formed in aqueous solution. On the other hand work describing the formation of manganese(II) tspc adduct with dioxygen does not include the observation of the 18-line spectrum among its ESR spectral results [5]. The present investigation was undertaken to study the nature of the manganese tspc chelate produced by the synthesis outlined by Weber and Busch [1] and to examine more closely the circumstances leading to the formation of the species responsible for the ~18-line ESR spectrum observed in certain frozen aqueous solutions of the manganese chelate.

Experimental

The ESR measurements at room temperature and of frozen solutions were made on a Varian E12 spectrometer at a microwave frequency ~9.15 GHz. In experiments involving the addition of various reducing agents the original mixing of solutions and subsequent transfer operations were carried out under a nitrogen atmosphere. Absorption spectra in the visible region were recorded on a Varian 635 spectrophotometer operating at room temperature with 1 cm path length glass and silica cells.

Preparation of Manganese tspc and Associated Measurements

The monosodium salt of 4-sulphophthalic acid, urea (43.5 g), ammonium chloride (3.5 g), ammonium molybdate (0.5 g) and manganese(II) sulphate (8.7 g) were ground together until finely powdered and blended. The reaction mixture was introduced into a glass lined steel bomb, flushed with carbon dioxide or nitrogen prior to sealing and heated to

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180 °C. The reaction mixture was subject to heating for 6 h, after which the product mixture was withdrawn from the bomb and washed with 300 ml of 1 M hydrochloric acid which was 10% with respect to sodium chloride. This process removed unreacted manganese salt. The ESR and UV–Vis spectra of the product in various aqueous solutions were recorded. The product was divided into two portions, one of which was dissolved in water and chromatographed on a Sephadex G10 column and collected in an aqueous phase from which the manganese(II) tspc was isolated by removal of water at diminished pressure. *Anal.* Found: C, 37.72; H, 1.60; N, 10.96. Calc. for $C_{32}H_{12}N_8O_{12}S_4MnNa_4 \cdot 2H_2O$: C, 37.98; H, 1.58; N, 11.08%. The purified material gave the same ESR spectra observed in samples prior to the chromatographic purification process. The second portion was dissolved in 400 ml of 0.1 M sodium hydroxide, heated to 80 °C in air, filtered and cooled to room temperature. Ethanol was added to the filtrate to precipitate the phthalocyanine and the slurry heated to 80 °C until the evolution of ammonia had ceased. The solid was purified further by precipitation from an aqueous solution by addition of ethanol. The ESR and UV–Vis spectra of various aqueous solutions of the product of this final stage were recorded.

Preparation of Potassium Hexacyanatomanganese(II)

This material was prepared by the method outlined by Meyer [6].

Results

It has been shown already that the synthesis of manganese tspc from a reaction mixture consisting of manganese(II) sulphate, the tri-sodium salt of 4-sulphophthalic acid, urea, ammonium chloride and trace amounts of ammonium molybdate under nitrogen atmosphere with washing of the product mixture with hydrochloric acid and chromatographic separation using a Sephadex G10 column leads to the isolation of the manganese(II) chelate, characterized by its low-spin form which exists in slightly alkaline aqueous solution, its inability to take up molecular oxygen and reduction to manganese(0) tspc by hydrazine [3].

The product obtained after washing with hydrochloric acid was subsequently dissolved in 0.1 M sodium hydroxide and precipitated from solution by addition of ethanol. The ESR spectrum of a frozen aqueous solution containing material obtained from this procedure and recorded almost immediately after preparation consisted of the complex 18 line spectrum, though the intensity of the signal was low. It was noted that if the solution was allowed to stand at room temperature while samples were withdrawn

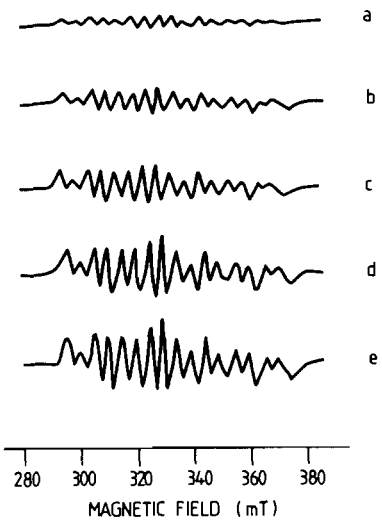


Fig. 1. The ESR spectra of an aqueous solution of manganese tspc (1.0×10^{-3} mol dm^{-3}) containing 10% *v/v* of dmf recorded over a period of 90 min. Temperature of frozen solution 133 K, microwave frequency 9.148 GHz: a = 0, b = 20, c = 50, d = 70, e = 90 min.

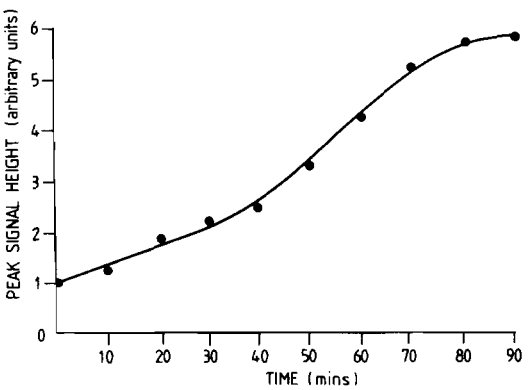


Fig. 2. Plot of relative intensity of the most prominent line in the ESR spectrum due to the manganese(II) tspc superoxide complex against time of standing of the aqueous solution containing the manganese tspc chelate (1.0×10^{-3} M). The aqueous solution contained 10% *v/v* of dmf.

to record the ESR spectrum in the frozen state at intervals of about 10 min there is a progressive increase in the intensity of the signal. Thus the ESR spectra recorded over a period of ninety minutes are depicted by Fig. 1. At the time of initial solution preparation a barely discernable ESR signal, consisting of less than 5% of the signal expected for a 1.0×10^{-3} M solution of the chelate, was obtained indicating that initially most of the manganese tspc is in some ESR non-detectable form. A plot of the growth of height of the most intense peak in the complex spectrum with time is shown in Fig. 2 which indicates that the concentration of the ESR detectable species increases six fold after 90 min

and thereafter remains constant. The progressive increase in the intensity of the ESR signal takes place in the same way and rises to the same ultimate level in 90 min when the solution of manganese tspc was carefully prepared and stored under nitrogen or argon. Again identical results were obtained for solutions which had been prepared and stored in the dark. The immediate conclusion of these results is that the increasing presence of the ESR detectable species does not depend on exposure to molecular oxygen and is not of photochemical origin.

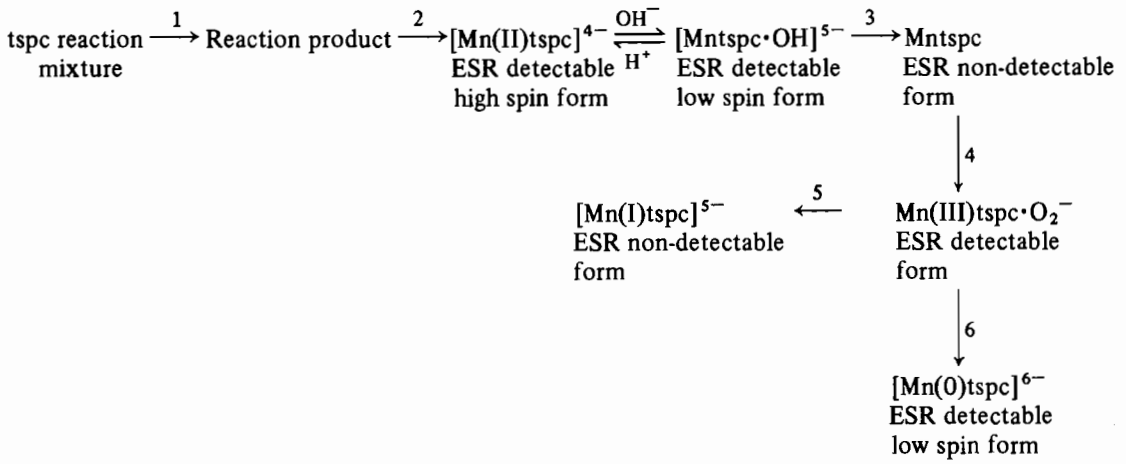
If a sufficient quantity of an aqueous solution of potassium ferrocyanide is added to a freshly prepared aqueous solution of manganese tspc obtained after the second stage of purification to completely eliminate the 18 line ESR signal, the subsequent storage of the solution for a short time (about 10 min) results in the ability to detect the ESR signal due to the manganese tspc molecular oxygen adduct. The further addition of potassium ferrocyanide would once more eliminate this signal. However if the original manganese tspc solution is kept at room temperature for about 2 h prior to the addition of potassium ferrocyanide, to allow for the full formation of the signal to the manganese tspc molecular oxygen adduct, the titration with potassium ferrocyanide, monitored by the loss of intensity of the 18 line ESR signal, indicates that this signal is eliminated at the point where one-electron equivalent of potassium ferrocyanide (1.0×10^{-3} M) to manganese tspc molecular oxygen adduct (1.0×10^{-3} M) is reached. The results point to the fact that a one electron change is sufficient to form an ESR non-detectable species, presumably Mn(I) tspc and to the fact that only the ESR detectable species is titrated by the potassium ferrocyanide.

A similar titration of an aqueous solution of the manganese tspc molecular oxygen adduct (1.0×10^{-3} M), prepared as before by allowing an aqueous solution of the manganese tspc chelate, obtained from the second stage of purification, to stand for about two hours, with an aqueous solution of sodium ascorbate (1.0×10^{-3} M) such that all solutions were 10% *v/v* with respect to dmf and 0.1 M with respect to sodium hydroxide, was performed under nitrogen. The results showed that when a half-molar ratio of ascorbate to manganese tspc oxygen adduct was added, the signal due to the oxygen adduct was difficult to detect. Subsequent addition of ascorbate resulted in the appearance of the ESR signal due to a low spin manganese tspc assigned previously to manganese(0) tspc. The increase in intensity of this signal, which is a measure of the two-electron reduction of the manganese tspc molecular oxygen adduct, is reached when the molar ratio of the redox components reached 1:1. The ESR changes are accompanied by a change of blue to violet as described previously [3].

Discussion

The various chemical changes concerning the manganese tspc species are summarised in Scheme 1.

Exposure of manganese(II) tspc to a combination of alkaline aqueous solution (0.1 M sodium hydroxide), organic solvent (ethanol) and air, provide the conditions necessary to form the ESR non-detectable oxidised species which on standing in aqueous solution gives rise to the ESR detectable manganese tspc species possessing a complex ESR spectrum, and which is formally due to the molec-



Scheme 1. (1) Heated in controlled atmosphere; (2) 0.1 M HCl/10% NaCl; (3) 0.1 M NaOH in air precipitation by ethanol; (4) Stand in H_2O for 2 h; (5) $Fe(CN)_6^{4-}$; (6) Na ascorbate.

ular oxygen adduct of manganese(II) tspc. The formation of the oxidised form of manganese tspc in these circumstances is compatible with earlier findings that the presence of organic solvent (dmf, such that it comprises 50% of the solvent media) and strong ligand field ligands [2] promotes the autoxidation of manganese tspc.

The material formed as a result of the oxidation of manganese(II) tspc in alkaline aqueous solution to which a sufficient quantity of ethanol is added to precipitate the sulphonated metallo–phthalocyanine, is still of uncertain composition though it presumably contains manganese in high oxidation state and incorporates oxygen in the form of a peroxo group. The reaction sequence leading to the formation of the equivalent of a molecular oxygen adduct of manganese(II) tspc is undefined. The pathway is so far unique in allowing the formation of the molecular oxygen adduct and is all the more noteworthy since the product is not formed by the direct interaction of molecular oxygen with low spin manganese(II) tspc. Recent work has shown that dichloromanganese(IV) complexes with bidentate Schiff's bases react with water to liberate molecular oxygen [7].

The molecular oxygen adduct is characterised by the complex ESR spectrum which serves as an essential link in the identification of the species formed in aqueous solution from the oxidised ESR silent species of manganese tspc with the molecular oxygen adduct of manganese(II) Pc. An intriguing comparison of this ESR spectrum may be made with that obtained by dissolution of potassium hexacyanato manganese(II), which in the solid state is one of the few low spin manganese(II) compounds, in aqueous–methanol solution, and recording the ESR of the frozen solution [8]. The ESR spectrum due to the manganese cyanide species in these circumstances bears a close similarity to that due to the dioxygen adduct of manganese(II) Pc with the spacing of the major lines being close to 4 mT. The spectrum was attributed to a dinuclear intermediate product formed in the decomposition pathway of the hexacyanato manganese(II) anion and was thought to arise from the magnetic interaction between the paramagnetic manganese(II) atoms through a bridging cyanide group. It is tempting to suggest that the spectrum arises from the formation of a molecular oxygen adduct of a manganese cyanide species. To confirm this point, various aqueous solutions of potassium hexacyanato manganese(II) were prepared under nitrogen or oxygen atmosphere and subsequently frozen to record the ESR spectra. Unfortunately, despite many attempts we were unable to observe the well-defined ESR spectra reported previously. While this does not invalidate the earlier work we did not proceed further with this avenue of investigation.

Among the possible explanations of the ESR observed for oxygenated manganese tspc is one involving a coupling between an unpaired electron on O_2 and Mn(III). The former would possess a spin of $S_1 = ½$ and the latter a value of $S_2 = 2$. Firstly in zero magnetic field we begin by considering an axial model for the Mn(III) configuration whose ground state can be represented by the spin Hamiltonian:

$$\mathcal{H}_{Mn} = D_2\left[S_{2z^2} - \frac{1}{3}S_2(S_2+1)\right] + A_{2\parallel}S_{2z}I_{2z} + A_{2\perp}(S_{2x}I_{2x} + S_{2y}I_{2y}) \quad (1)$$

Suppose the Mn(III) and the superoxide were coupled by an isotropic exchange interaction,

$$\mathcal{H}_{ex} = -JS_1 \cdot S_2 \quad (2)$$

where $|J| \gg |D|$, $|A_\parallel|$, $|A_\perp|$. By a process familiar in literature calculations of the Landé interval rule, there are two resultant states: $S = S_1 + S_2 = 5/2$ and $S = S_1 - S_2 = 3/2$. To obtain the first order value of the splittings between the 5/2 and 3/2 levels we consider:

$$-JS_1 \cdot S_2 = -\frac{1}{2}J[S(S+1) - S_1(S_1+1) - S_2(S_2+1)]$$

$$= -J \text{ for } S = 5/2$$

and

$$= +\frac{3}{2}J \text{ for } S = 3/2.$$

If J is negative, *i.e.* antiferromagnetic then we would have $S = 3/2$ lowest.

When the Zeeman interactions are added, the spin Hamiltonian for the resulting $S = 3/2$ multiplet becomes:

$$\mathcal{H} = \beta\Sigma_i g_i S_i B_i + D\left[S_{z^2} - \frac{1}{3}S(S+1)\right] + A_\parallel S_z I_{2z} + A_\perp(S_x I_{2x} + S_y I_{2y}) \quad (3)$$

where g-values are close to 2. The resulting g-values may be related to the individual Mn(III) and O_2^- g-values [9], where D can be shown to be:

$$D = \frac{7}{5}D_2 \quad (4)$$

The complete analysis of this problem is not yet available as it is complicated by the fact that perturbation theory solutions are hard to obtain because $-JS_1 \cdot S_2$ and the individual Zeeman interactions cannot easily be accommodated in either of the two

obvious basis sets of wave functions. In addition the manganese hyperfine interaction requires careful calculation in the coupled system. The measured hyperfine splittings in the coupled system will differ from the A_2-values in eqn. (1) for isolated Mn(III).

While there is danger in comparing chemical simplicity with the circumstances of biological complexity, the formation of a molecular oxygen adduct of manganese(II) tspc by an electron transfer pathway from manganese in a higher oxidation state is worthy of comparison with some aspects of dioxygen evolution from the manganese cluster component of Photosystem II [10, 11]. An ESR study of the intermediates of a polynuclear manganese centre involved in the photosynthetic oxidation of water involves a cluster containing at least two and possibly four manganese centres in the photosynthetic oxidation of water [12]. The present work shows that in principle a manganese–dioxygen centre can be formed in aqueous solution making a useful contribution to the proposal by Renger that in the photosynthetic system oxygen is ultimately formed by oxidation of complexed superoxide [13]. It has been shown that visible light irradiation of a number of manganese(III) tetradentate Schiff base chelates leads to a liberation of oxygen [14], a finding which may be compared with earlier work [7]. However the relevance of this observation to the photosynthetic production of oxygen in Photosystem II is misleading.

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