E.S.R. Studies of Some Working Haem Analogues Mn(PR₃)X₂ and Their Dioxygen Adducts

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The reversible dioxygenation of $Mn(PR_3)X_2$ (R = n-butyl, n-pentyl; X = Cl, Br, I) has been studied in solution by e.s.r. spectroscopy; the dioxygenated species, '$Mn(PR_3)(O_2)X_2$,' have the highly unusual spin state $S = 5/2$.

The e.s.r. spectra of the haem analogues $Mn(PR_3)X_2$[1] have not previously been reported. We recently reported the preparation and properties of the 'parent' $Mn(PPh_3)X_2$ (X = Cl, Br, I, NCS) species which are inactive to dioxygen.[2] The e.s.r. spectra of these complexes in the solid state and in solution show only a broad absorption at $g = ca.$ 2, except for $Mn(PPh)_3I_2$ in the solid state and in frozen dichloromethane solution at 77 K and $Mn(PPh_3)(NCS)_2$ in frozen tetrahydrofuran (THF) solution at 77 K which showed extra broad lines down to $g = 6$. Comparison of the spectra with the published graphs of Dowsing and Gibson[3] indicated an essentially tetrahedral environment for the species in the solid state and in frozen dichloromethane solution, and an essentially octahedral environment for the species in frozen THF.

Here we report preliminary data on the e.s.r. spectra of the dioxygen-active species $Mn(PR_3)X_2$ (R = n-butyl, n-pentyl; X = Cl, Br, I) in THF and toluene solutions, and

also report evidence for an intermediate state in the uptake of dioxygen by these complexes. The uptake of dioxygen by the $Mn(PR_3)X_2$[4] and $Mn(PPhR_2)X_2$[5] (X = Cl, Br, I[4,6], NCS;[5] R = alkyl) complexes in THF and toluene proceeds very rapidly and is reversible. The absorption of dioxygen can be followed by a gas burette and desorption by collection in a gas burette or Toepler apparatus.[7] Absorption results in a 1:1 $Mn(PR_3)(O_2)X_2$ complex[4-6] and there is no subsequent O–O bond breaking on desorption.[7]

In general, the dioxygenated species were prepared in THF at −60 °C, and samples for e.s.r. spectroscopy were taken by syringing a portion into cooled (to −60 °C) dioxygen-filled e.s.r. tubes with careful exclusion of moisture.[†] The solutions were rapidly frozen by plunging into liquid nitrogen and their

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† For discussion of drying techniques in the preparation and handling of these compounds, see refs. 2 and 4.

Table 1. E.s.r. data for the dioxygenated manganese complexes in solution.

Complex	Colour	Temp. /°C	Solvent	E.s.r. line positions/G
$Mn(PBu_3^n)(O_2)Cl_2$	Pink	—60	THF	Strong broad line ca. 3 300, 5 500 m 0—3 000[a] numerous lines
	Purple	0	THF	Same as at —60 °C except that intensity of broad lines at ca. 3 300 is stronger
$Mn(PBu_3^n)(O_2)Br_2$	Deep pink	—60	THF	1 125[a] s, 1 600[a] m, 2 200[a] m, 3 300 m, 5 700 m, 8 500 w
	Blue	0	THF	Same as at —60 °C
$Mn(PBu_3^n)(O_2)I_2$	Purple– brown	—60	THF	950[a] s, 1 400[a] m, 3 300 m, 5 350 m
$Mn(PPe_3^n)(O_2)Cl_2$[b]	Purple	0	Toluene	1 650 w, 3 300 s
$Mn(PPe_3^n)(O_2)Br_2$	Blue	0	Toluene	1 500 s, 3 300[a] s
$Mn(PPe_3^n)(O_2)I_2$	Green	0	Toluene	1 600 s, 3 310 s

[a] Split into six by hyperfine coupling to ^{55}Mn ($I = 5/2$). [b] $Pe^n =$ n-pentyl.

e.s.r. spectra recorded at 77 K. In addition, for the $Mn(PBu_3^n)$-$(O_2)X_2$ (X = Cl, Br) complexes in THF, the solutions were warmed to 0 °C under 1 atm of dioxygen and the e.s.r. spectra were again recorded, because of colour changes associated with the change in temperature (see Table 1). The Mn-${P(n-pentyl)_3}(O_2)X_2$ (X = Cl, Br, I) were prepared by stirring toluene solutions of Mn${P(n-pentyl)_3}X_2$ under 1 atm of dioxygen for ca. 2 h at 0 °C.

The e.s.r. spectra consist of several groups of six lines arising from the coupling to $^{55}Mn(I = 5/2)$ together with

broad features in which hyperfine coupling was not resolved. The magnetic field at the centre of each sextuplet or broad line for the dioxygen adducts are shown in Table 1. The $Mn(PBu_3^n)(O_2)X_2$ (X = Br, I) complexes exhibit a strong sextuplet at g = ca. 6 together with other broad absorptions, as indicated in Table 1. The shape and position of this line is characteristic of $g_\perp$ signals observed in six-co-ordinate high spin (S = 5/2) complexes with axial symmetry, and this is supported by the well resolved hyperfine couplings to ^{55}Mn in this region (80—90 G).‡[9,10] Thus, the most likely structure of the dioxygenated species in the THF is that which involves co-ordinated THF with the halogens in *trans* positions.

The unoxygenated species $Mn(PBu_3^n)X_2$ (X = Br, I) in frozen THF show spectra in the high field region very similar to those of the dioxygenated species. The spectra in the low field region show the same strong g = ca. 6 absorption, but there are more absorptions in this region than for the dioxygenated case, and they are all split by coupling to ^{55}Mn, making determination of precise field positions difficult.§

The bonding between the manganese and the dioxygen can be described by using the guidelines of Hoffman et al.[11] In order to have five unpaired electrons in manganese d-orbitals,

‡ See, e.g. spectrum of Mn(tetraphenylporphyrin)(pyridine) in ref. 12.

§ For the $Mn(PBu_3^n)(O_2)Cl_2$ and $Mn(PBu_3^n)X_2$ (X = Cl, Br, I) complexes in THF the intensities and the resolved separation of the lines in the low field region sometimes vary slightly depending on how the THF solutions are frozen. Further studies using 2-MeTHF, which forms a glass are in progress, but interpretation is not helped because of the large number of lines in this region, all of which show coupling to ^{55}Mn. The $Mn(PBu_3^n)(O_2)X_2$ (X = Br, I) species show the same spectra irrespective of how the solutions are frozen.
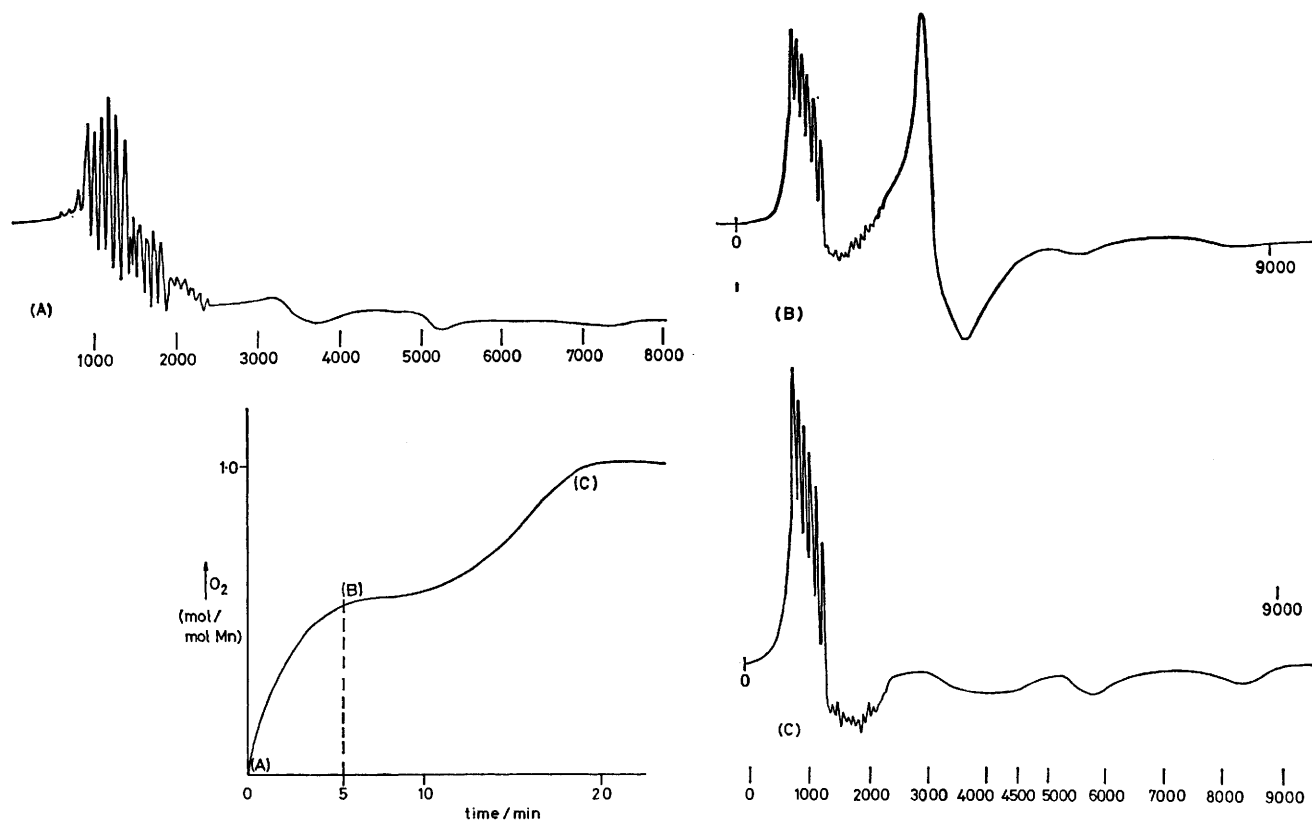
Figure 1. Plot of dioxygen uptake vs. time for the $Mn(PBu_3^n)Br_2$ complex in THF at —60 °C, correlated with the e.s.r. spectra. (A) Unoxygenated, (B) 5 min after mixing with dioxygen, (C) fully dioxygenated.
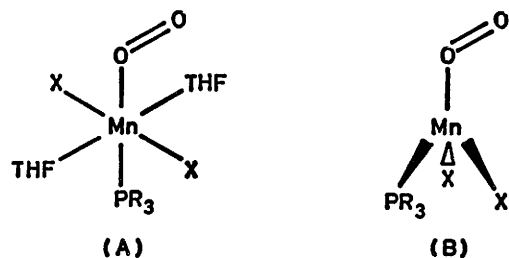
Figure 2. Suggested structures for the oxygenated complexes in (A) THF and (B) toluene.

it is necessary to have a 'bent' dioxygen so as to remove the degeneracy of the d_{xz}, d_{yz} orbitals which would be inevitable with 'end on' dioxygen.

Under certain conditions there is a distinct plateau in the graph of mole fraction dioxygen uptake $vs.$ time, shown in Figure 1 for the reaction of dioxygen with $Mn(PBu_3^n)Br_2$ in THF at $-60\,^{\circ}C$. The position of this plateau appears to depend on the concentration of the solution. For $Mn(PBu_3^n)X_2$ (X = Br, I) we have been able to isolate a species with new e.s.r. signals by syringing out samples of the solution into e.s.r. tubes at different stages of the uptake and freezing them rapidly in liquid nitrogen.

All our evidence suggests that the structures shown in Figure 2 are the most likely for the dioxygenated species in THF or toluene. We find no evidence for Mn^{III} or Mn^{IV} [12] in the dioxygen adducts, and the e.s.r. spectra are readily interpreted in terms of a ^6S state. Such a system is highly unusual because there is no reduction in the number of unpaired electrons as occurs in all other systems which add dioxygen.[13] That the dioxygenated $Mn(PR_3)(O_2)X_2$ species are unusual is further shown by the room temperature magnetic moments in the solid state ($\mu_{eff} = ca.\ 6.9\mu_B$).[1,5] It may well

be that the magnetic properties of these manganese(II)–phosphine complexes and of their adducts with O_2 is partly responsible for the ease with which the $Mn(PR_3)X_2 + O_2 \rightleftharpoons Mn(PR_3)(O_2)X_2$ equilibrium reverses when compared to other haem mimic systems.[14]

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