Inorganica Chimica Acta, 39 (1980) 227–231

The Coordination Chemistry of Manganese. Part VI [1–4]. Bis(tetrahydrofuran)manganese(II) Halide Complexes; Synthesis and Characterisation

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Received August 7, 1979

The solid state structures of $Mn(THF)_2X_2$ (THF = tetrahydrofuran; X = Cl, Br, I) appear to be halide-bridged pseudooctahedral polymers which do not exhibit EPR signals. The EPR-active $Mn(THF)_2(NCS)_2$ is a pseudotetrahedral monomer. In tetrahydrofuran solution the $Mn(THF)_2X_2$ complexes react with $PPhMe_2$ to form a complex which can reversibly absorb/desorb molecular oxygen in a manner analogous to the authentic haem analogues $Mn(PPhMe_2)X_2$. However, reaction of $Mn(THF)_2X_2$ with $PPhMe_2$ in acetonitrile, followed by exposure to dioxygen, results in rapid decomposition to an EPR-inactive species, presumably manganese(III), accompanied by production of some $OPPhMe_2$. An authentic sample of $Mn(PPhMe_2)Br_2$ in acetonitrile also undergoes similar decomposition on exposure to dioxygen. Polarographic and other characterisation data are reported for the $Mn(THF)_2X_2$ complexes.

Introduction

During our development of a range of $Mn(PR_3)X_2$ complexes which reversibly coordinate molecular oxygen under very mild conditions [5] we have also observed that in some circumstances reaction of manganese(II) halides with tertiary phosphines in tetrahydrofuran (THF) leads to the isolation of $Mn(THF)_2X_2$ species. Of course $Mn(THF)_2X_2$ complexes do not reversibly bind molecular oxygen but they are nonetheless interesting complexes and have only been poorly characterised previously.

Manganese(II) is a typically 'hard acid' and, as such, forms strong complexes with oxygen-donor ligands such as sulphoxides [6], diphenylselenoxide [7], dimethylformamide [8], N,N-dimethylacetamide [9], pyridine-N-oxide [10], dimethylurea [11], phosphine oxides [2] and arsine oxides [2, 12]; nonetheless we have previously shown that, under rigorously anhydrous conditions Mn(II)–As and even Mn(II)–Sb bonds can be formed [4].

Here we wish to record our observations on the $Mn(THF)_2X_2$ (X = Cl, Br, I, NCS) complexes which form part of the periphery of our present development of the $Mn(PR_3)X_2$ compounds which are haemoglobin analogues [5]. It is remarkable to see that previous workers have isolated THF derivatives of stoichiometry $Mn(THF)_{1.5}Cl_2$ [13, 14] and $Mn(THF)Cl_2$ [14]. Some thermogravimetric measurements on $Mn(THF)_yX_2$ (X = Cl, Br; y = 0.25 - 2.00) have been reported [15]. Fowles *et al.* have also isolated and characterised some 1,4-dioxan adducts, *viz.* $Mn(dioxan)Cl_2$ and $Mn(dioxan)_2Br_2$ [16].

Experimental

The complexes were prepared by refluxing MnX_2 in tetrahydrofuran for 30 min, or until a clear solution was obtained. After cooling to room temperature stirring was continued for a further 2 h. The solution was concentrated under gentle evaporation of THF solvent leading to precipitation. Isolation was by filtration under a dinitrogen atmosphere. The complexes were dried *in vacuo* over P_2O_5.

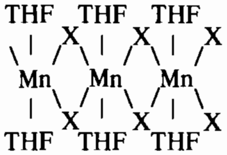
E.P.R. spectra were recorded at ambient temperature on a Varian E9 spectrometer in the X-band between 0 and 10,000 G. The following procedure was used to obtain polarographic data: Dry, deoxygenated tetrahydrofuran solutions of the $Mn(THF)_2X_2$ complexes were prepared. To ~15 cm^3 of each solution was added 0.25 g of tetrabutylammonium hexafluorophosphate support electrolyte and the mixture agitated by a stream of dinitrogen until dissolution occurred. Once dissolved the dinitrogen gas stream was redirected to give an inert blanket over the THF solution. The working electrode consisted of the hanging mercury drop system and the cell was completed by the platinum wire/mercury pool electrode. No reference electrode was available so the Pt/Hg pool was used as a dual purpose electrode. Changes in the amperage carried between the electrode through the solution by the ions were recorded on a chart recorder against voltage. Polarographic waves thus recorded were analysed in the usual way to give the half-wave potential corresponding to a particular oxidation or reduction reaction. By correcting this half-wave potential for the inherent potential of the mercury pool/Pt wire electrode it was possible to obtain the standard electrode potential for that oxidation/reduction reaction.

Elemental analyses were performed by the UMIST Microanalytical Service.

Results and Discussions

Room temperature magnetic moments obtained by the Gouy method for the $Mn(THF)_2X_2$ complexes (μ_{eff} = 5.32 (Cl), 5.60 (Br), 5.83 (I), 5.34 (NCS) μ_B) indicate the expected $^6A_{1g}$ ground term for divalent manganese(II), $3d^5$. There is no T.I.P. effect and no reduction of the moment below the spin-only value by spin–orbit coupling with higher ligand field terms expected for a complex having a $^6A_{1g}$ ground term. However, these moments are, for the most part, distinctly lower than that expected for a spin-only value, 5.92 μ_B (see later). The complexes are very pale in colour and their visible absorption spectra show very weak transitions typical of high-spin Mn(II) complexes.

The infrared spectra in the solid state show evidence for coordinated THF [17, 18]; two strong absorptions at *ca.* 1040 and 850 cm^{-1}. Uncoordinated THF exhibits similar bands at 1070 and 910 cm^{-1}. We do not observe any infrared bands in the region expected for either terminal Mn–Cl or Mn–Br stretching frequencies, but we observe bands at 240 cm^{-1} (Cl) and 190 cm^{-1} (Br) to which we assign ν(Mn–X–Mn). For the haloderivatives we confidently assign a polymeric halogen-bridged structure:



EPR evidence (see below) is consistent with this structure, as is our preliminary single-crystal X-ray data on $Mn(THF)_2Br_2$. This complex crystallises in the orthorhombic form (*a* = 7.6 Å, *b* = 18.3 Å, *c* = 4.05 Å; α = β = γ = 90°). For space group Pnn2 we estimate the Mn–Mn distance to be ~4 Å [19]. However, the $Mn(THF)_2(NCS)_2$ complex is clearly monomeric, and presumably tetrahedral in the solid state. No evidence exists for Mn–NCS–Mn bridges; indeed there is much infrared evidence for terminal Mn–NCS linkages, *viz.* ν(CN) 2100 br,s,ν(C–S) 790w, δ(NCS) 480 sb,w [20].

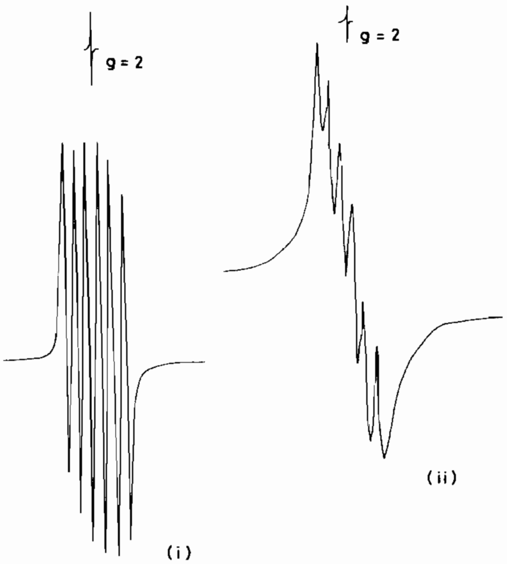


Fig. 1. (i) EPR spectrum of $Mn(THF)_2Br_2$ + $PPhMe_2$ in acetonitrile. (ii) EPR spectrum of $Mn(THF)_2Br_2$ + $PPhMe_2$ in acetonitrile 30 seconds after exposure to dioxygen.

The solid complexes $Mn(THF)_2X_2$ (X = Cl, Br, I) exhibit no EPR spectra, consistent with the bridging polymeric structure proposed. However, upon dissolution in THF or CH_3CN strong signals close to g = 2 are obtained, with the Br and I complexes exhibiting nuclear hyperfine coupling to manganese (*ca.* 110 G). On the other hand the solid complex $Mn(THF)_2(NCS)_2$ does exhibit an EPR spectrum; a single line close to g = 2. Upon dissolution in THF or CH_3CN nuclear hyperfine coupling to manganese (*ca.* 100 G) is also observed. Addition of Me_2PPh in the presence of dioxygen to the CH_3CN solutions of each of the complexes caused the lines to broaden and the nuclear hyperfine coupling was lost, Fig. 1. These new signals slowly decayed (more rapidly in the case of X = I) over a period of several minutes.

These results are consistent with the solid complexes (X = Cl, Br, I) existing as halogen-bridged polymeric manganese(II) species exhibiting no EPR spectra. In the case of X = NCS the solid complex is monomeric and EPR active. In coordinating solvents such as THF or MeCN the Mn–X–Mn bridges are broken and monomeric species result which are EPR active. In acetonitrile addition of phosphines produces a transient manganese(II) complex which rapidly decays to an EPR inactive species, probably manganese(III).

We have examined the interaction of $Mn(THF)_2Br_2$ with $PPhMe_2$ and dioxygen in both THF and MeCN solutions (Figs. 2–4). When to a solution of $Mn(THF)_2Br_2$ in THF is added one molar equiv-

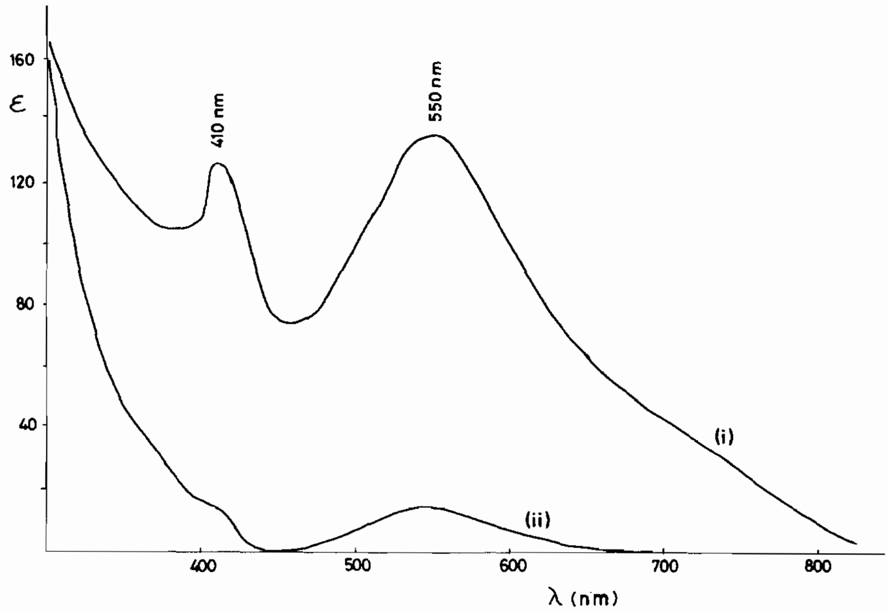


Fig. 2. Electronic spectrum in THF at room temperature of $Mn(PPhMe_2)Br_2$; (i) plus dioxygen; (ii) almost deoxygenated. N.B. The $Mn(THF)_2Br_2 + PPhMe_2$ system in THF, subsequently oxygenated and deoxygenated, gives identical spectra.

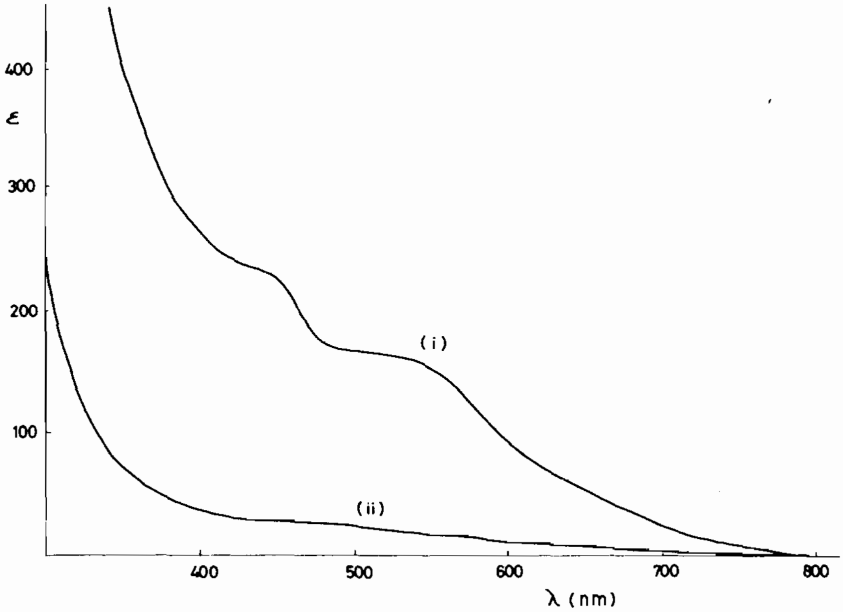


Fig. 3. Electronic spectrum of $Mn(THF)_2Br_2$ + $PPhMe_2$ in acetonitrile; (i) in the presence of dioxygen; (ii) in the absence of dioxygen. N.B. Rapid decomposition was occurring as spectrum 3(i) was run; thus, extinction coefficients are very approximate.

alent of $PPhMe_2$ and exposed to dioxygen a deep purple colour is observed the spectrum of which, Fig. 2, is identical to that of an *authentic* haem analogue, $Mn(PPhMe_2)Br_2 \cdot O_2$ in THF, Fig. 2(i) [21]. This observation should be contrasted with the spectral behaviour of the authentic haem analogue $Mn(PPhMe_2)Br_2$ in MeCN to which dioxygen is added. An immediate purple colouration develops which rapidly begins to fade (Fig. 4(i) is a plot of such a spectrum mid-way through its disappearance). Although this spectrum exhibits a band at 575 nm, quite close in energy to that of $Mn(PPhMe_2)Br_2 \cdot O_2$ (Fig. 1) at 550 nm, it is distinctly different from the latter complex in not exhibiting a band at 410 nm. As can be seen from Fig. 2, the repeated oxygenation and deoxygenation of $Mn(PPhMe_2)Br_2$ results in the

TABLE I. Analytical Data for the $Mn(THF)_2X_2$ complexes.

Complex	Colour	%C[a]	%H[a]	%X[a]	%Mn[a]
$Mn(THF)_2Cl_2$	white	34.8(35.6)	5.7(5.9)	25.5(26.3)	18.9(20.3)
$Mn(THF)_2Br_2$	white	26.0(26.7)	4.1(4.5)	44.4(44.5)	15.0(15.3)
$Mn(THF)_2I_2$	buff	20.0(21.2)	2.9(3.5)	56.9(56.1)	11.8(12.1)
$Mn(THF)_2(NCS)_2$	pale cream	37.4(38.1)	4.4(5.1)	8.7(8.9)[b]	17.1(17.4)

[a] Found (Calculated). [b] %N.

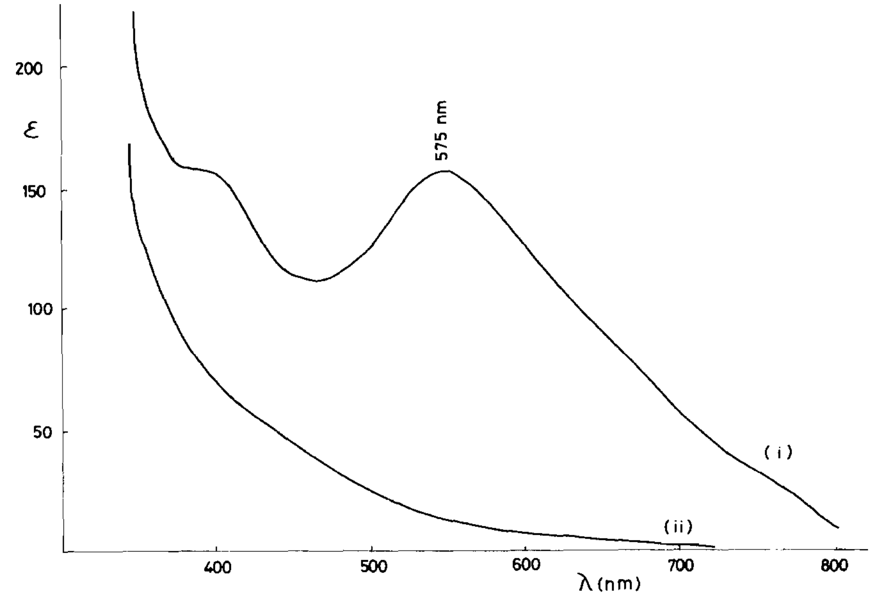


Fig. 4. Electronic spectrum of $Mn(PPhMe_2)Br_2$ in acetonitrile; (i) in the presence of dioxygen; (ii) in the absence of dioxygen. N.B. Rapid decomposition was occurring as the spectrum was run, thus, extinction coefficients are very approximate.

growth and disappearance of *both* these bands. Moreover, although $Mn(PPhMe_2)Br_2$ in THF can be repeatedly oxygenated and deoxygenated without decomposition we observe no such behaviour with $Mn(THF)_2Br_2 + PPhMe_2$ in MeCN. Once the transient colour has faded addition of further O_2 does not regenerate the dioxygen-adduct species. In the decomposition products we find some infrared evidence for $OPPhMe_2$ and thus conclude that essentially what happens in MeCN is:

$$Mn(THF)_2Br_2 + PPhMe_2 + O_2 \xrightarrow{MeCN} \text{transient Mn(II)}$$
$$\xrightarrow{\text{rapidly}} Mn(III) + OPPhMe_2 + \text{other products}$$

We would stress that MeCN is a solvent to be completely avoided for investigations of $Mn(II)/PR_3$ complexes. Attempts to react $Mn(THF)_2Br_2$ with $PPhMe_2$ in MeCN in the presence of dioxygen again shows a transient deep blue/purple colour which fades very rapidly, Fig. 3.

We have also made polarographic measurements on the $Mn(THF_2)X_2$ complexes. A total of four waves was obtained for each complex, two of which can be assigned, Table II. For the change $Mn^{2+} \rightarrow Mn^{3+} + e^-$, the standard electrode potential is –1.50 v, but for our THF complexes the measured potential for this change varied from –1.3908 to –1.5255 v in the order $Br < NCS < I < Cl$. For the change $Mn^{2+} + 2e^- \rightarrow Mn^0$ the standard electrode potential is –1.029 v, but for our THF adducts we find values between –0.8826 and –1.0602 v, varying in the order $Cl \cong NCS < I < Br$.

Analyses of the current–voltage curves for the polarographic waves of these two processes indicate that they meet the criterion for reversibility [22], *i.e.*, $E_{3/4} - E_{1/4} = 56$ mv/n, the oxidation corresponding to a one-electron process and the reduction corresponding to a two-electron process. It is likely that the polarographic reactions seen here

TABLE II. Summary of Polarographic Measurements.

Complex	E_0 value (v)	Process
$Mn(THF)_2Cl_2$	−0.8826	$Mn^{2+} \rightarrow Mn^0$
	−1.5255	$Mn^{2+} \rightarrow Mn^{3+}$
$Mn(THF)_2Br_2$	−1.0602	$Mn^{2+} \rightarrow Mn^0$
	−1.3908	$Mn^{2+} \rightarrow Mn^{3+}$
$Mn(THF)_2I_2$	−0.9989	$Mn^{2+} \rightarrow Mn^0$
	−1.4643	$Mn^{2+} \rightarrow Mn^{3+}$
$Mn(THF)_2(NCS)_2$	−0.8826	$Mn^{2+} \rightarrow Mn^0$
	−1.4153	$Mn^{2+} \rightarrow Mn^{3+}$

obey the Nernst equation since the half-wave potentials are independent of manganese concentration.

We have not yet assigned the other two waves recorded for each complex: they may be due to the reaction of the $Mn(THF)_2X_2$ complexes with the support phosphate electrolyte or be associated with a reaction of the Pt wire with halide present.

Acknowledgements

We are grateful to the National Research Development Corporation and the Science Research Council for financial support.

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