The Synthesis and Characterization of Some Manganese(II) Complexes Containing Tetrahydrothiophene Ligands

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Anhydrous manganese(II) salts, MnX_2 (X = Cl, Br, I, NCS), react with tetrahydrothiophene in refluxing toluene to form $MnX_2(THT)_2$ complexes. These complexes have been characterized by spectroscopic techniques and appear to be anion-bridged polymers (X = Cl, Br, I) or, for $Mn(NCS)_2(THT)_2$, a pseudo-tetrahedral monomer.

Introduction

In recent years the interest in the co-ordination chemistry of manganese(II) has grown rapidly. Our own studies have concentrated on complexes of soft group 5 donors such as tertiary phosphines or the hard Schiff base O,N donor ligands. The former complexes can reversibly bind small molecules such as dioxygen [1] or nitric oxide [2], and the latter are proving to be interesting as models for the active site of photosystem II in green plant photosynthesis [3].

In our studies with group 5 donors we have shown that, by employing strictly anhydrous manganese(II) salts and solvents, it is possible even to stabilise Mn^{II}–As and Mn^{II}–Sb bonds [4]. Here we present our results of studies using a soft group 6 donor ligand, tetrahydrothiophene (THT).

Results and Discussion

Refluxing anhydrous manganese(II) salts, MnX_2 (X = Cl, Br, I, NCS) with an excess of THT in toluene under an inert atmosphere leads to the isolation of the $MnX_2(THT)_2$ complexes; microanalytical data confirming their formulation, Table I. Room temperature magnetic moments obtained by the Gouy method clearly indicate the presence of manganese(II). The values obtained, Table I, are, however, for the most part lower than that expected for a strictly spin-free value, 5.92 μ_B (see later). The complexes are very pale in colour and their visible spectra show only very weak bands typical of high spin manganese(II) complexes, Table II.

The far infrared spectra are typical of those previously reported for $MnX_2(THF)_2$ (THF = tetra-

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TABLE I. Some Physical and Analytical Data for the Manganese Complexes.

Complex	Colour	μ_{eff}^a	%C^b	%H^b	%X^b	%S^b	%Mn^b
$MnCl_2(THT)_2$	Off-white	5.35	32.0(31.8)	6.0(5.3)	23.0(23.5)	21.5(21.2)	18.0(18.2)
$MnBr_2(THT)_2$	Pink	5.55	25.0(24.6)	4.0(4.6)	40.4(40.9)	15.8(16.3)	14.5(14.1)
$MnI_2(THT)_2$	Buff	5.80	20.0(19.8)	3.5(3.3)	52.0(52.4)	13.5(13.2)	11.0(11.3)
$Mn(NCS)_2(THT)_2$	Cream	5.41	35.0(34.6)	5.0(4.6)	8.5(8.1)^c	37.0(36.9)	16.2(15.9)

$^a\mu_b$; ^{b}Found (calculated); ^{c}%N.

TABLE II. Spectroscopic Data for the $MnX_2(THT)_2$ Complexes.

Complex	Electronic Spectra (nm)^a	Infrared Spectra (cm^{-1})^b	
		ν(Mn–X–Mn)	ν(Mn–S)
$MnCl_2(THT)_2$	525, 445, 420, 390	240	330
$MnBr_2(THT)_2$	528, 450, 410, 400sh	190	320
$MnI_2(THT)_2$	535, 470, 430, 390	130	320
$Mn(NCS)_2(THT)_2$	510, 460, 450, 380	^{c}	315

^{a}Diffuse reflectance spectra. ^{b}Nujol mulls; ^{c}ν(CN) 2100; ν(C–S) 790; δ(NCS) 480 cm^{-1}.

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hydrofuran) complexes [5]. No bands are present which could be assigned to terminal Mn–X (X = Cl, Br, I) stretching frequencies, but bands are present which can be assigned to bridging ν(Mn–X–Mn) vibrations. In addition ν(Mn–S) are clearly visible, indicating co-ordination of the THT ligands. The magnetic moments obtained at room temperature are consistent with antiferromagnetic interactions (such interactions increasing in the order $I < Br < Cl$) arising from Mn–X–Mn bridges. Moreover, the complexes do not exhibit ESR spectra, further evidence for strong Mn–X–Mn interactions. We thus assign these complexes the pseudoctahedral polymeric structure, similar to that assigned to their THF analogues [5].

The structure of the $Mn(NCS)_2(THT)_2$ complex is different, however. Only a single ν(CN) band is seen, and this in the region expected for terminal Mn–NCS linkages [6]. This complex also exhibits an ESR spectrum comprising a single broad line in the $g = 2$ region with no fine structure being observed at room temperature. These data are consistent with a monomeric pseudotetrahedral structure, although μ_{eff} is low for a complex with no antiferromagnetic interactions.

Experimental

Microanalyses were performed by the UMIST Microanalytical Service. The spectrometers used were: Varian E9 (X-band), ESR; Perkin Elmer 598, IR; Beckman IR 720M, far IR; Beckman Acta M4, electronic spectra. Reagents and solvents were dried by methods reported previously [7]. All manipulations were performed under an atmosphere of dry argon.

Synthesis of the $Mn(X_2(THT)_2$ Complexes

Typically, an MnX_2 salt (0.4 mmol) was refluxed with a 10% excess of THT in toluene (50 cm^3) overnight. On cooling the complex precipitated, was filtered, washed with toluene (5×10 cm^3) and dried *in vacuo*.

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