

The Synthesis and Characterisation of some MnL_nX_2 Complexes ($n = 1$, $L =$ pyridine, 4-pyrrolidinopyridine, $X = Cl, Br, I, NCS$; $n = 1$, $L = EtOH$, $X = Cl, Br$; $n = 2$, $L = EtOH$, $X = I, NCS$)

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Abstract

Mono-ligand complexes $MnLX_2$ ($L =$ pyridine, 4-pyrrolidinopyridine, $X = Cl, Br, I, NCS$) have been prepared. The pyridine complexes contain only bridging halide and pseudohalide groups, whereas the 4-py complexes contain both bridging and terminal bound anions. Ethanol is coordinated in $Mn(EtOH)X_2$ ($X = Cl, Br$) and $Mn(EtOH)_2X_2$ ($X = I, NCS$). Although the $MnLX_2$ complexes have the same stoichiometry as the $Mn(PR_3)X_2$ complexes none show any activity towards binding dioxygen either in the solid state or in solution.

Introduction

Complexes of manganese(II) with 'hard' ligands, such as those containing oxygen or nitrogen donor atoms, are well known. Until relatively recently it was thought that manganese in the +2 oxidation state did not form complexes with soft donors such as phosphorus and arsenic, but we [1–4] and others [5–9] have reported the synthesis and characterisation of several complexes of manganese(II) with such ligands. The formation of these complexes can only take place under vigorously anhydrous and anaerobic conditions.

Several studies have been reported on the reversible binding of dioxygen by $MnX_2(PR_3)$ [3, 5, 7] and $MnI_2(PEt_3)_2$ complexes. The reactivity of a given $MnX_2(PR_3)$ complex towards dioxygen appears to be dependent on the steric [10] and electronic properties of the phosphine ligand [11]. Because of the considerable interest that has been generated in the binding of small molecules such as dioxygen [3, 5–7], carbon monoxide [12], nitric oxide [13], carbon disulphide [14], and sulphur dioxide [15] by these manganese(II) phosphine complexes we have

examined other manganese(II) systems for potential in small molecule binding. We found, for example, that a range of manganese(II) selenocyanate complexes of a number of O-, N-, S- and P-donor ligands could be prepared, but they showed no such activity [16]. On the other hand, the manganese(II) iodide/triphenylphosphine system could bind sulphur dioxide to yield $Mn(OPPh_3)_4(OSO)_2$, in which the sulphur dioxide has inserted into a Mn–I bond; half of the sulphur dioxide is reversibly bound [17]. We have further extended our investigations of manganese(II) coordination chemistry and here report some new complexes of pyridine (py), 4-pyrrolidinopyridine (4-py) and ethanol.

Experimental

Two different experimental procedures were used for the preparation of the MnL_nX_2 complexes. For $L = py$ and 4-py the anhydrous [18] manganese salt was slurried with a stoichiometric quantity of the ligand (method a). For $L = EtOH$ the anhydrous salt was stirred with the neat ligand and the product precipitated by addition of diethylether (method b). Typical reaction conditions are described below.

(a) Preparation of $Mn(py)(NCS)_2$

Anhydrous manganese(II) thiocyanate (1.71 g, 10.0 mmol) was added to dry toluene (70 cm³) in flame-dried 250 cm³ flask equipped with a side-arm, under a dry argon atmosphere. Dry pyridine (0.86 cm³, 10.0 mmol) was added and the mixture was stirred for 72 h. The resulting complex was isolated using Schlenk techniques, dried *in vacuo*, and stored in a dry, inert atmosphere.

(b) Preparation of $Mn(EtOH)I_2$

Anhydrous manganese(II) iodide (2.0 g, 6.5 mmol) was dissolved in dry ethanol (50 cm³) in a flame-dried 250 cm³ flask equipped with a side-arm, under dry argon. The solution was stirred for 24 h. The volume

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of the solution was reduced *in vacuo* until an oil formed. Addition of dry diethylether (70 cm³) precipitated the orange–yellow complex, which was filtered using Schlenk techniques, dried *in vacuo*, and stored in a dry, inert atmosphere.

Physical Measurement

Infrared spectra were recorded as Nujol mulls in the range 4000–400 cm⁻¹ on a Perkin-Elmer 598 spectrophotometer and in the range 500–20 cm⁻¹ on a Beckman IR-720 m Fourier spectrophotometer.

Diffuse reflectance spectra were measured on a Beckman Acta M-IV spectrophotometer, and the ESR spectra were recorded on a Varian E9 spectrometer. Room temperature magnetic susceptibility measurements were carried out on a Newport Instruments Single Temperature Gouy balance system. Microanalyses were carried out by the UMIST Microanalytical Laboratory.

Results and Discussion

For L = py and 4-py only mono-ligand complexes MnLX₂ were isolated. For L = EtOH the Mn(EtOH)-X₂ (X = Cl, Br) form, but the bis-ligand Mn(EtOH)₂-X₂ (X = I, NCS) were also isolated, Table I.

The infrared spectra of the complexes of pyridine all show bands assignable to bridging halide (pseudo-halide) moieties [19] suggesting bridged polymeric structures. Such structures have been proposed for other manganese(II) halide–pyridine complexes. The bis-pyridine complexes Mnpy₂X₂ (X = Cl, Br, I, NCS) have been shown to be octahedral polymers [20–23]. Goldstein and Hughes [24] prepared Mn(py)Cl₂ and Mn(py)Br₂ by the thermal decomposition of the corresponding bis-pyridine complex and, on the basis of infrared data, concluded that the structures are cross-linked bridged polymers in which each manganese remains octahedrally coordinated. While

our method of preparation is significantly different from that of Goldstein and Hughes, the infrared spectra for Mn(py)Cl₂ and Mn(py)Br₂ prepared by the two methods are very similar and suggest similar structures. The crystal structure of Mn(PhPMe₂)₂ has recently been determined [4]. This complex also has a halide bridged polymeric structure with two PhPMe₂ ligands coordinated to alternate manganese(II) ions. Thus the manganese(II) ions are alternately octahedrally and tetrahedrally coordinated. The Mn(py)X₂ complexes prepared in this work are almost certainly halide bridged polymeric structures, although the exact structures are not known and attempts to grow crystals suitable for X-ray diffraction studies were not successful.

The Mn(4-py)X₂ and Mn(EtOH)_nX₂ appear to differ from the complexes of pyridine. The far infrared spectra (Table II) show bands assignable to both terminal and bridging M–X moieties [19], ($\nu(\text{Mn–Cl}) = 330\text{--}270\text{ cm}^{-1}$ and $290\text{--}200\text{ cm}^{-1}$; $\nu(\text{Mn–Br}) = 230\text{--}200\text{ cm}^{-1}$ and $190\text{--}150\text{ cm}^{-1}$; $\nu(\text{Mn–I}) = 200\text{--}190\text{ cm}^{-1}$ and $125\text{--}100\text{ cm}^{-1}$). These strongly suggest dimeric structures. Due to the extreme insolubility of the complexes in organic solvents such as toluene and methylene chloride, it was not possible to carry out molecular weight measurements. Solvents in which the complexes are soluble were found to initiate structural changes. However, it seems likely, on the basis of the infrared data, that the Mn(EtOH)_nX₂ and Mn(4-py)X₂ complexes differ from the Mn(PR₃)₂X₂ and the Mn(py)X₂ complexes discussed earlier.

Complexes of the type Mn(EtOH)_nX₂ ($n = 1$, X = Cl, Br; $n = 2$, X = NCS) have previously been reported [25–27]. There was some doubt expressed by the authors as to whether the ethanol ligand in Mn(EtOH)Cl₂ and Mn(EtOH)Br₂ was coordinated or was merely present as a solvent of crystallization. Our infrared results show a clear shift in (OH) to a lower frequency than that of the free ligand, suggesting that

TABLE I. Analytical Data of the Manganese(II) Complexes

Compound	%C ^a	%H ^a	%N ^a	%Hal ^a	%Mn ^a
Mn(py)Cl ₂	30.9(29.3)	2.6(2.4)	6.3(6.8)	32.6(34.6)	26.0(26.8)
Mn(py)Br ₂	23.4(20.4)	1.7(1.7)	5.6(3.8)	51.0(54.4)	16.8(18.7)
Mn(py)I ₂	16.9(15.5)	1.8(1.3)	3.8(3.6)	61.9(65.5)	13.1(14.2)
Mn(py)(NCS) ₂	32.6(33.5)	2.3(2.0)	16.0(16.8)		19.9(22.0)
Mn(4-py)Cl ₂	40.0(39.4)	4.1(4.4)	9.7(10.2)	25.5(25.9)	19.5(20.0)
Mn(4-py)Br ₂	30.2(29.8)	3.5(3.3)	8.0(7.7)	43.5(44.0)	16.0(18.2)
Mn(4-py)I ₂	24.0(23.6)	3.0(2.6)	6.0(6.1)	56.2(55.6)	11.6(12.0)
Mn(4-py)(NCS) ₂	42.0(41.4)	4.2(3.8)	18.0(17.6)		18.0(17.2)
Mn(EtOH)Cl ₂	12.6(13.9)	2.6(3.5)		40.6(41.3)	31.3(32.0)
Mn(EtOH)Br ₂	9.5(9.3)	2.4(2.3)		60.7(61.3)	19.3(21.0)
Mn(EtOH) ₂ I ₂	10.3(11.9)	2.6(3.0)		64.5(63.2)	13.5(13.7)
Mn(EtOH) ₂ (NCS) ₂	26.2(27.4)	4.5(4.6)	10.7(10.7)		20.9(20.9)

^a Found (calculated).

TABLE II. Spectral Data for $Mn(L)_nX_2$

Compound	Ligand	Infrared spectra			Colour	μ_{eff} (BM)	λ (nm)
		$\nu(\text{Mn-L})$	$\nu(\text{Mn-X})$	$\nu(\text{NCS})$			
Mn(py)Cl ₂	627(m) ^a 412(w)	215(br)	235(m)		pale pink	5.5	518, 480, 410, 385(sh)
Mn(py)Br ₂	629(m) 419(w)	219(br)	200(sh)		pale pink	5.6	526, 475, 405, 385(sh)
Mn(py)I ₂	629(w) 416(w)	205(br)	116(s)		yellow	5.4	525(sh), 470, 415(sh)
Mn(py)(NCS) ₂	624(s) 418(w)	256(s) 201(m)		2125(s)	pale yellow	5.4	540, 475, 402, 360
Mn(4-py)Cl ₂	1025(m) ^b 815(w)	215(br)	270(m) 200(s)		off white	5.6	
Mn(4-py)Br ₂	1028(m) 820(w)	219(br)	190(m) 156(s)		pink	5.8	530, 480, 405, 380
Mn(4-py)I ₂	1030(w) 825(w)	206(br)	200(m) 125(s)		pale yellow	5.7	540, 465, 400, 365
Mn(4-py)(NCS) ₂	1025(s) 815(s)	260(s) 255(sh)		2100(sh) 2060(s)	pale yellow	5.5	522, 465, 418, 362(sh)
Mn(EtOH)Cl ₂	3425(s) ^c	412(w) ^b 435(sh)	324(w) 238		pale pink	5.8	
Mn(EtOH)Br ₂	3400(s)	420(sh) 350(sh)	226(sh) 196(sh)		white	5.7	
Mn(EtOH) ₂ I ₂	3350(s)	414(sh) 346(sh)	193(br) 106(sh)		orange-yellow	5.5	530(sh), 460, 420, 320
Me(EtOH) ₂ (NCS) ₂	3390(s)	412(sh) 345(sh)		2130(s) 264(s)	pale green	6.0	

^aFree py absorbs at 618 cm^{-1} and 412 cm^{-1} . ^bFree 4-py absorbs at 980 cm^{-1} and 790 cm^{-1} . ^cFree EtOH absorbs at 3450 cm^{-1} .

the EtOH ligand is indeed coordinated. The results obtained for $Mn(\text{EtOH})_2(\text{NCS})_2$ were essentially the same as those previously reported [27].

Further evidence for the bridging structures of the $Mn(L)_nX_2$ complexes comes from the room temperature, solid state X-band ESR spectra which show single, intense signals at $g = 2.0$. Although not totally unambiguous, this suggests a high spin d^5 manganese(II) system in which the bridged structure induces spin-pairing effects [28]. The room-temperature magnetic moments, Table II, also show some evidence for spin-pairing.

Unlike the $Mn(\text{PR}_3)X_2$ complexes previously reported [3, 4], these MnL_nX_2 complexes show no reaction, either reversible or irreversible, with dioxygen. There is no colour change on exposure to O_2 either in the solid complexes or in solutions of appropriate organic solvents (e.g. THF toluene). No appreciable uptake beyond that of the THF blank is observed using gas burette techniques [3]. At ambient pressures of O_2 these samples show no activity whatsoever towards the binding of O_2 .

The work described shows that it is possible to prepare a wide variety of complexes with the general formula MnL_nX_2 . Complexes have been prepared in which the donor atom of the ligands L is O, or N, as well as our phosphine [3, 4] and isocyanide [29] complexes. While many of the complexes appear to be structurally similar to the active phosphine complexes only the latter bind molecular oxygen. The ability of the manganese complexes to bind O_2 is clearly very ligand dependent. These results are consistent with the observation that within the series of phosphine complexes, reactivity towards O_2 is sensitive to relatively small structural changes within the phosphine ligand [11].

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