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The Multidentate Chemistry of Manganese(II). I. Hybrid Tridentate Ligand Complexes

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The complex compounds obtained from the interaction of manganese(II) salts and four new tridentate ligands, each possessing the donor set NNAs, and prepared by the Schiff-base condensation of σ-dimethyl or σ-diethylarsinoaniline, are described.

Three types of complex were obtained: (i) [Mn ligand X_2] (where X = Cl, Br or I); ii, [Mn(ligand)$_2$]Y_2 (where Y = ClO_4 or BPh_4); (iii) Mn ligand $(NCS)_2$. Physical measurements have been used to demonstrate that in each case the ligands act as tridentates, and that type (i) complexes are five-coordinate, type (ii) complexes are octahedral, and type (iii) complexes are polymeric octahedral species.

Attempts to obtain manganese(II) complexes of various other ligands with the donor sets NNAs and ONAs were unsuccessful.

Introduction

Manganese(II) in its coordination compounds exhibits a marked preference for « hard » donor atoms such as oxygen and nitrogen. Manganese(II) complexes containing « soft » donor atoms (e.g. P, As) are scanty in number compared with those of other transition metals, presumably due to the difficulties encountered in preparing and preserving such complexes.[1]

Thus, triphenylarsine and triphenylphosphine have been reported to form high-spin four-coordinate complexes with manganese(II) halides, $MnX_2(ZPh_3)_2$ and $[Mn(ZPh_3)_4]X_2$ (Z = P or As).[2] However, when these preparations were repeated only complexes of triphenylphosphineoxide or triphenylarsineoxide were obtained.[3] On the other hand, *o*-phenylenebisdimethylarsine (diars) forms a series of high-spin octahedral complexes, $Mn(diars)_2X_2$ (X = Cl, Br or I), under anhydrous conditions.[4]

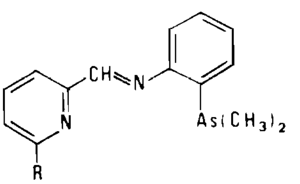
Some manganese(II) complexes with soft donors have been obtained from the oxidation of manganese(0) or manganese(I) carbonyl derivatives. Both $[Mn(CO)_3(diars)]$ and $[Mn(CO)_3(diars)]_2$ are oxidized by bromine with the formation of the manganese(II) complex, $[MnBr_2(CO)_2(diars)]$.[5]

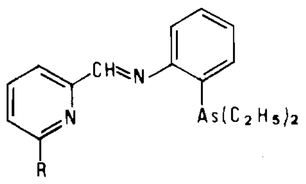
Examples of manganese(II) complexes containing hybrid ligands seem to be limited to a few compounds. (2′-pyridylamino)-diphenylphosphine forms a 3:1 complex with manganese(II) bromide.[6] The tripod quadridentate ligand, tris(α-picolyl)phosphine (tpp) forms, with manganese(II) chloride, a compound [Mn(tpp)Cl]Cl, which is postulated as a five-coordinate species on the basis of being a 1:1 electrolyte in nitromethane solution.[7] However, the magnetic moments of the two complexes above were not reported.

The interaction of manganese(II) bromide or perchlorate with *o*-(dimethylarsino)aniline (NAs) led to the formation of colourless crystalline complexes, $Mn(NAs)Br_2$ and $Mn(NAs)_2(ClO_4)_2$. The perchlorate compound was hydrolyzed rapidly in air. The magnetic moment of $Mn(NAs)Br_2$ was 5.78 B.M. at room temperature.[8]

Manganese(II) complexes of hybrid ligands containing an N-N-As donor sequence.

The interaction of equi-molecular quantities of manganese(II) halides and the appropriate ligands (NNAs(I), MeNNAs(II), NNAsEt(III) and MeNNAsEt(IV)) in mixed solvents (ethanol-benzene-heptane) gives orange-brown solutions, which upon refluxing and concentration yield large orange or yellow-brown crystals. (Table I).





R=H NNAs IR=H NNAsEt III
R=Me MeNNAs IIR=Me MeNNAsEt IV

The thiocyanate complexes, $MnL(NCS)_2$ n(solvate) (L = I, II, III and IV), were obtained in a similar manner to the corresponding halide complexes, howe-

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Table I. Analytical data and physical properties of Manganese(II) complexes

Complex		Analysis (%)					Magnetic data		
		C	H	N	T°K	$10^6\chi_g$	$10^6\chi_M'$	μ_{eff}(B.M.)	Λ_M *
$\mathrm{Mn(NNAs)Cl_2}$	Found	40.3	3.6	6.6	299.3	36.7	15360	6.07	2.4
	Calc.	40.6	3.7	6.8					
$\mathrm{Mn(NNAs)Br_2}$	Found	33.5	2.9	5.5	299.3	29.15	14.870	6.00	4.0
	Calc.	33.5	3.0	5.6					
$\mathrm{Mn(NAAs)I_2\frac{1}{2}EtOH}$	Found	29.2	2.7	4.6	298.8	23.60	14879	5.99	11.8
	Calc.	29.1	2.9	4.5					
$\mathrm{Mn(NNAs)(NCS)_22EtOH}$	Found	43.9	3.4	10.5	298.8	26.45	14.831	5.96	i.s.
	Calc.	43.6	4.9	10.2					
$\mathrm{Mn(MeNNAs)Cl_2}$	Found	42.5	4.1	6.2	299.3	33.15	14.370	5.88	3.6
	Calc.	42.2	4.0	6.6					
$\mathrm{Mn(MeNNAs)Br_2}$	Found	35.2	3.3	5.2	299.3	27.60	14482	5.90	6.0
	Calc.	34.9	3.3	5.4					
$\mathrm{Mn(MeNNAs)I_2\frac{1}{2}EtOH}$	Found	30.6	3.0	4.4	298.8	23.60	15211	6.03	9.5
	Calc.	30.2	3.2	4.4					
$\mathrm{Mn(MeNNAs)(NCS)_2}$	Found	43.3	3.8	11.7	299.8	29.15	13980	5.81	i.s.
	Calc.	43.2	3.6	11.9					
$\mathrm{Mn(MeNNAs)_2(ClO_4)_2}$	Found	42.4	3.9	6.3	299.8	16.65	14640	5.93	178
	Calc.	42.1	4.0	6.6					
$\mathrm{Mn(MeNNAs)_2(BPh_4)_24H_2O}$	Found	68.6	5.8	4.0	299.8	16.65	14640	5.93	142
	Calc.	68.6	6.0	4.1					
$\mathrm{Mn(NNAsEt)Cl_2}$	Found	43.1	4.4	6.1	295.3	31.90	14290	5.82	3.2
	Calc.	43.5	4.3	6.4					
$\mathrm{Mn(NNAsEt)Br_2}$	Found	36.5	3.8	5.1	295.3	30.15	16202	6.20	3.6
	Calc.	36.2	3.6	5.3					
$\mathrm{Mn(NNAsEt)I_2EtOH}$	Found	32.1	3.4	3.9	295.3	23.60	16082	6.18	10.8
	Calc.	32.2	3.7	4.2					
$\mathrm{Mn(NNAsEt)(NCS)_2\frac{1}{2}C_6H_6}$	Found	48.1	4.5	10.6	205.3	23.48	12593	5.45	i.s.
	Calc.	48.0	4.2	10.7					
$\mathrm{Mn(MeNNAsEt)Cl_22H_2O}$	Found	41.9	4.8	5.6	295.3	3.100	15300	5.97	7.0
	Calc.	41.6	5.10	5.7					
$\mathrm{Mn(MeNNAsEt)Br_2\frac{1}{2}C_6H_6}$	Found	41.0	4.3	4.6	295.3	26.15	15.490	6.05	2.9
	Calc.	41.3	4.1	4.8					
$\mathrm{Mn(MeNNAsEt)I_2}$	Found	31.7	3.1	4.5	295.3	24.80	14840	6.12	9.9
	Calc.	32.0	3.3	4.4					
$\mathrm{Mn(MeNNAsEt)(NCS)_2EtOH}$	Found	46.6	4.6	10.4	295.3	26.63	14839	5.96	i.s.
	Calc.	46.2	5.0	10.3					
$\mathrm{Mn(MeNNAsEt)_2(ClO_4)_2H_2O}$	Found	4.15	4.5	5.6	295.3	13.32	13530	5.69	199
	Calc.	41.6	4.5	5.7					
$\mathrm{Mn(MeNNAsEt)_2(BPh_4)_24H_2}$	Found	69.3	6.1	3.8	295.3	10.70	15.600	6.08	140
	Calc.	69.2	6.3	3.9					

* measured in ca. 10^{-3} nitromethane solution; in $\mathrm{ohm^{-1}cm^2mole^{-1}}$. i.s. insufficiently soluble.

ver they do not immediately separate upon mixing the ligands and the thiocyanate salt. This is in contrast to the instant separation of the corresponding nickel(II) thiocyanate complexes under similar conditions.[9]

Furthermore, the interaction of equi-molecular quantities of manganese(II) perchlorate and ligand I or III gave red-brown iols. The bis-ligand manganese(II) complexes with ligands II and IV, $\mathrm{MnL_2Y}$ $\mathrm{nH_2O}$ (L = MeNNAs, MeNNAsEt; Y = $\mathrm{ClO_4}$), crystallized only after keeping them under refrigeration for several days. The corresponding bis-complexes of cobalt(II) and nickel(II) separate instantly in ethanol.[9] All attempts to prepare the nitrate complexes of manganese(II) with ligands I-IV were unsuccessful and led to the isolation of oily masses.

All the complexes obtained are yellow-orange to orange-brown in colour in the solid state and stable in dry air. Except for the thiocyanates they are readily soluble in common organic solvents such as ethanol, acetone and nitromethane, but the solutions become turbid on standing.

The magnetic moments of the complexes measured at room temperature are all of the high-spin type ranging from 5.45 to 6.20 B.M.

The values of molar conductivities measured at 25°C in approx. $10^{-3}M$ nitromethane solution indicate that:

(i) the halide complexes $\mathrm{MnLX_2}$ (L = I-IV; X = Cl, Br, I) are pratically non-electrolytes in that solvent;

(ii) the bis-ligand complexes, $\mathrm{MnL_2Y_2}$ (L = II, IV; Y = $\mathrm{ClO_4}$, $\mathrm{BPh_4}$), show molar conductivities typical of 1:2 electrolytes;

(iii) the thiocyanate complexes, $\mathrm{MnL(NCS)_2}$ (L = I-IV), are invariably not sufficiently soluble in common organic solvents for the measurements of molar conductivities.

The solid state spectra of these complexes in the visible region (140 - 400 nm) gave similar patterns.

Some of them are shown in Figure 1. The halide complexes exhibit a broad band around 500 nm, and its displacement can be correlated with the spectrochemical position of the respective halide ion. On the basis of the fact that the nature of electronic transitions in all the high-spin manganese(II) com-

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[9] B. Chiswell and K.W. Lee, to be published; K.W. Lee, Ph.D. Thesis, University of Queensland, 1971. (Microfilm copies of the Thesis can be obtained).

Table II. Electrolyte types of cobalt(II), nickel(II) and manganese(II) complexes *.

Ligand(L)	Cobalt(II)	Nickel(II)	Manganese(II)
NNAs(I) NNAsEt(III)	$[CoL_2][CoX_4]$ 1 : 1 electrolyte	$NiLX_2$** poor electrolyte	$MnLX_2$ poor electrolyte
MeNNAs(II) MeNNAsEt(IV)	$CoLX_2$ poor electrolyte	$NiLX_2$ poor electrolyte	$MnLX_2$ poor electrolyte
	$[CoL_2][Co(NCS)_4]$ 1 : 1 electrolyte L = I, II	$NiL(NCS)_2$ insoluble L = I-IV	$MnL(NCS)_2$ insoluble L = I-IV
	$CoL(NCS)_2$ non-electrolyte L = IV		

* X = Cl, Br, I. ** $NiLX_2$ (L = I, III, X = I; L = III, X = Br), 1 : 1 electrolyte in nitromethane.

plexes are spin-forbidden, this band is presumably due to halide to metal charge transfer band.

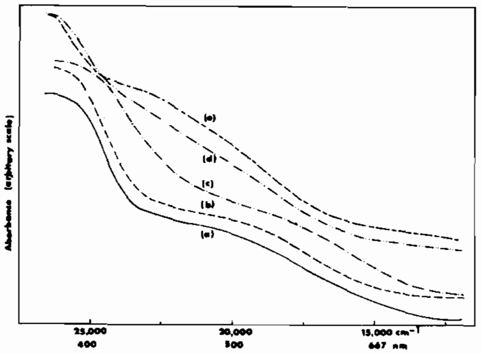

Figure 1. Reflectance sepctra of Manganese(II) complexes of the type $Mn(MeNNAsEt)X_2$. (a) X = Cl, (b) X = Br, (c) X = I. (d) X = NCS, (e) $Mn(MeNNAsEt)_2(ClO_4)_2$.

The stereochemistries of these manganese(II) complexes, as expected, could not be deduced from the magnetic moments and electronic spectra. However, their stereochemistry might be deduced by the comparison of their physical properties with those of the corresponding cobalt(II) and nickel(II) complexes. In carrying out the comparison it is assumed that:

(i) the ligands (I-IV) act as tridentate ligands as in the corresponding complexes of cobalt(II) and nickel(II)[9] and

(ii) the manganese(II) complexes (except thiocyanate complexes) are not polymeric on the basis of their steady solubility in common organic solvents.

It may be possible to assign the stereochemistries of the manganese(II) complexes by comparison of the solution behaviour (the molar conductivities) of the cobalt(II) and nickel(II) complexes. It can be seen from Table II that the electrolyte type of manganese(II) complexes are very similar to those of the nickel(II) complexes. In particular, of the complexes of the ligands NNAs and NNAsEt, those of cobalt(II) halides and thiocyanate are typical 1:1 electrolytes having the formula $[CoL_2][CoX_4]$ in nitromethane, while those of manganese(II) and nickel(II) halides are practically non electrolytes and the corresponding thiocyanate complexes are practically insoluble in that solvent.

It may therefore be assumed that the manganese(II) complexes have the same stereochemistries as those of the corresponding nickel(II) complexes:

(i) halide complexes $MnLX_2$ = I, II, III or IV; X = Cl, Br, I) are five-coordinate;

(ii) bis-ligand complexes MnL_2Y_2 (L = II, IV; Y = ClO_4, BPh_4) are high-spin octahedral;

(iii) thiocyanate complexes $MnL(NCS)_2$ (L = I, II, III, IV) are polymeric octahedral by the intermolecular bridging of the thiocyanate group (see Figure 2).

However, it should be noted that there is a possibility of the formation of a four-coordinate square-planar or tetrahedral complex if the potential tridentate ligand (I-IV) act as bidentates in the manganese(II) halide complexes described above.

The infrared spectra (Table III) of the thiocyanate complexes do exhibit two strong bands at 2093-2112 cm^{-1} and 2066-2070 cm^{-1} (C–N stretching), two medium bands in the range 465-480 cm^{-1} (N–C–S bending) and a very strong broad band around 260 cm^{-1} (Mn–NCS stretching), which might be indicative of the presence of an N–bonded terminal and a bridging thiocyanate group.[10,11,12] The insolubility of these complexes in solvents such as nitromethane and the close similarity of the infrared spectra of the manganese(II) and nickel(II) complexes with corresponding ligands, are in accordance with the hypothesis that the thiocyanate complexes have polymeric octahedral stereochemistry.

The three tridentate hybrid ligands derived from the condensation of *o*-(dimethylarsino)aniline and

(i) *o*-dimethylaminobenzaldehyde (donor set NNAs)

(ii) 2-pyrrolealdhyde (donor set NNAs)

(iii) salicylaldehyde (donor set ONAs)

yield with manganese(II) bromide and thiocyanate, oily masses, and do not give an isolable amount of

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Table III. Infrared spectral data of manganese(II) thiocyanate complexes.

Complex	ν(C—N)	ν(C—S	ν(NCS)	ν(Mn—N)
$Mn(NNAs)(NCS)_2 2EtOH$	2093s, 2070s	814w	465w, 480m	~250vs br
$Mn(MeNNAs)(NCS)_2$	2112s, 2066s		483m, 465m	~260vs.vbr
$Mn(NNAsEt)(NCS)_2 \frac{1}{2}C_6H_6$	2102s, 2070s	810vw	480m, 470m	~250vs.br
$Mn(MeNNAsEt)(NCS)_2 EtOH$	2110s, 2070s		477m, 469m	~260vs.br
$MnPy_2(NCS)_2$ * (Ref. 10)	2095s	787w	475m, 468w	254vs
$MnPy_4(NCS)_2$ (Ref. 10)	2066s	798m	428m, 479sh	253vs
$(BuPh_3P)_2[Mn(NCS)_4]$ (Ref. 11)				287vs.br
$(QH)_4[Mn(NCS)_6]$ (Ref. 11)				~222vs.br

* polymeric octahedral. Intensity: s strong; m medium; w weak; sh shoulder; v very; br broad.

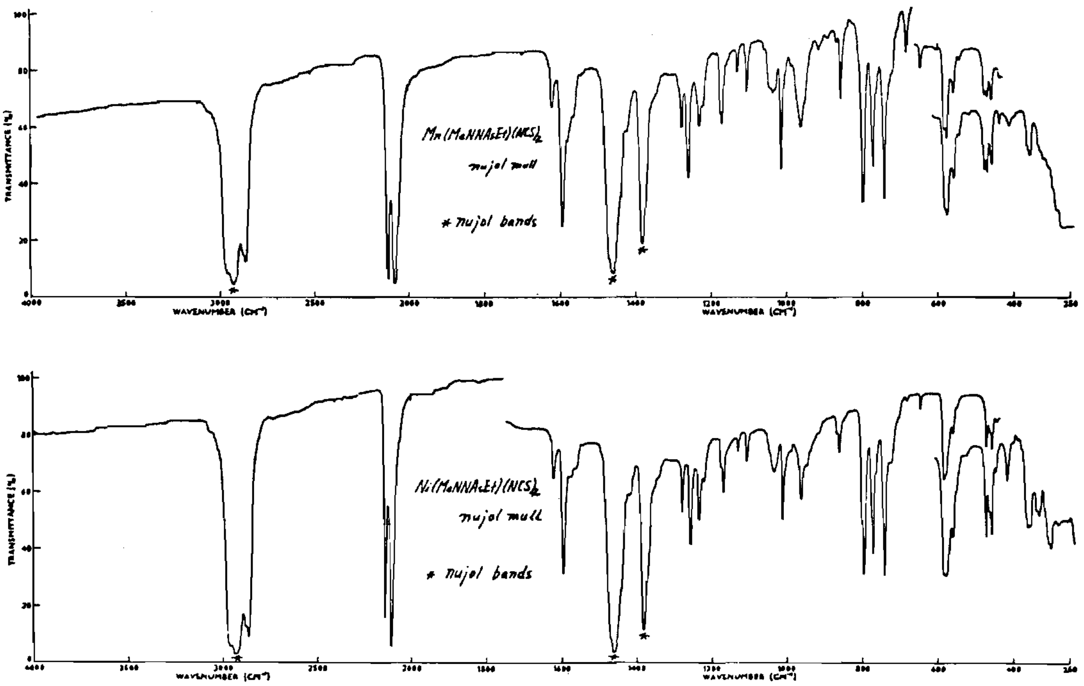

Figure 2. Infrared spectra of Manganese(II) and Nickel(II) thiocyanate complexes of ligand MeNNAsEt.

crystalline precipitate in ethanol or mixed solvents such as ethanol-benzene (1:3).

Experimental Section

Preparation of Ligands. The required aldehyde was reacted with either *o*-dimethyl or *o*-diethyl-arsinoaniline[13] in aqueous ethanol with a few drops of glacial acetic acid added. Upon cooling of the solution, the required ligand crystallised. Recrystallisation was from aqueous ethanol.

Preparation of Complexes. All of the complexes were prepared by mixing the required manganese(II) halide or perchlorate in ethanol with an equi-molecular quantity of the ligand in 50/50 benzene/heptane solvent. The mixture was refluxed, filtered while hot, and upon cooling yielded the required complex. In cases where the compound deposited during refluxing, the hot solution was not filtered.

The tetraphenylborate salts were obtained by adding a slight excess of lithium tetraphenylborate to the reaction mixture of manganese(II) chloride and the ligand.

Spectra. Infrared spectra were measured using a Perkin-Elmer model 457 spectrometer, while a Unicam SP800 spectrophotometer with a diffuse reflectance attachment was used to repord the electronic spectra.

Magnetic Moments. Magnetic susceptibility measurements were taken on a Faraday magnetic balance described elsewhere.[14] The authors are grateful for Dr. R. C. Marshall for undertaking these measurements.

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