Inorganica Chimica Acta, *29* (1978) 25–36

The Multidentate Chemistry of Manganese(II). Part VI. Tridentate Nitrogenous Ligands Complexes

B. CHISWELL and D. S. LITSTER

Department of Chemistry, University of Queensland, Brisbane, Australia 4067

Received October 12, 1977

A large number of manganese(II) complexes of formulation $[Mn(ligand)X_2]$ *(where ligand = linear tridentate, quadridentate or quinquidentate nitrogenous ligand; X = Cl, Br, I or NCS) are described. The tridentate ligand compounds, in which X = Cl or NCS have been shown, in general, to be five coordinate on the basis of conductivity measurements, X-ray powder data and infrared spectral analysis; but in some cases the compounds may possess a polymeric octahedral structure.*

The quadridentate ligand compounds are octahedral, as are a series of complexes of formulation $[Mn(NNN)_2](ClO_4)_2$.

Introduction

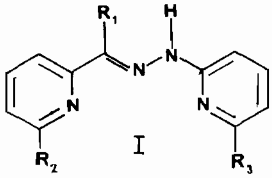
A previous paper [31] described the complexes of a large number of tridentate nitrogenous ligands with cobalt(II) and nickel(II) salts. It was pointed out in this paper that while the linear tridentates Ia, Ib, Ic, IIa, IIb, IIc, IIIa, IIIb, IVa, IVb, VIII and X gave five-coordinate $[Co(NNN)Cl_2]$ species, the similar nickel(II) complexes appeared to possess six-coordinate halogen bridged structures.

To extend the range of known five-coordinate manganese(II) complexes a large number of com-

TABLE I. Tridentate and Other Ligands.

Ligand No.	Formula	Substituents			Reference[a]
		R_1	R_2	R_3	
Tridentate Ligands					
Ia	I	CH_3	H	H	1
Ib	I	H	CH_3	H	1
Ic	I	H	H	CH_3	1
Id	I	H	CH_3	CH_3	2
IIa	II	H	H	–	3
IIb	II	CH_3	H	–	–
IIc	II	H	CH_3	–	–
IIIa	III	H	H	–	3
IIIb	III	H	CH_3	–	–
IIIc	III	CH_3	H	–	–
IVa	IV	H	H	–	4
IVb	IV	H	CH_3	–	5
Va	V	H	H	–	6
Vb	V	H	CH_3	–	5
Vc	V	CH_3	H	–	–
Ligands VI [1], VII, VIII, IX [7, 8], X and XI [9] shown in formulae					
Other Ligands					
XIIa	XII	CH_3	CH_3	H	10
XIIb	XII	CH_3	CH_3	CH_3	11
XIIc	XII	H	t-Bu	H	12
Ligand XIII [13] as in formula					

[a] Reference to prior preparation of ligand.



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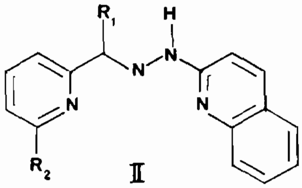

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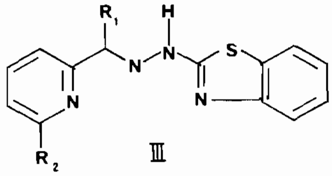

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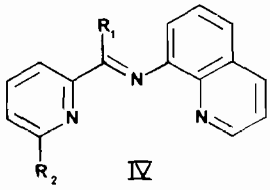

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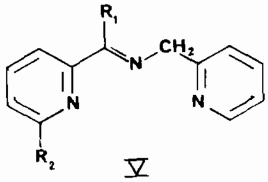

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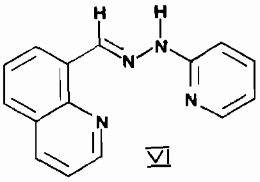

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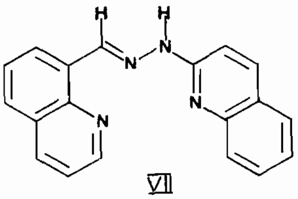

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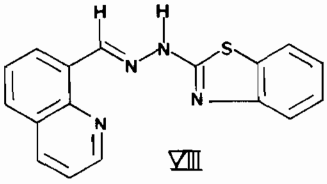

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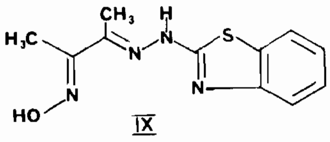

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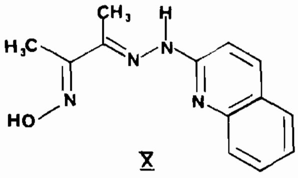

X

pounds of formulation $[Mn(NNN)X_2]$. (X = Cl, Br, I and NCS), have been prepared and studied.

Results and Discussion

Complexes of manganese(II) with the tridentate and other ligands of Table I have been prepared. The properties of these complexes are listed in Tables II to X.

The investigation of the structure of the manganese(II) complexes depends heavily on comparisons with cobalt(II) and nickel(II) complexes with corresponding ligands*. Unless single crystal X-ray diffraction data is available, the most effective method of structure determination is to compare the X-ray powder diffraction photographs with those of the corresponding nickel(II) and cobalt(II) complexes [14–19]. Infrared spectral data is useful in determining the structure of thiocyanato and nitrato complexes.

Halogeno Complexes of Manganese (II)

Complexes of the type $Mn(NNN)X_2$, (X = Cl, Br, I) have been prepared by various methods (Tables II, III and IV). The complexes range in colour from brown through orange to yellow. The solution chemistry of the complexes is limited because of their sparingly soluble nature, being soluble with difficulty in solvents such as nitrobenzene. In nitrobenzene, the complexes behave as non-electrolytes as illustrated by their molar conductivities. The iodo complexes appear to have a higher conductivity than either the chloro or bromo compounds. This is possibly due to a degree of decomposition in solution.

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*Reported previously [31].

TABLE II. Chloro Complexes of Manganese(II).

Complex[a]		Analysis (%)				Λ_M cm^2 ohm^{-1} mol^{-1}	Prep.	μ_{eff} (B.M.)	Infrared νM–N cm^{-1}
		C	H	N	Mn				
$\mathrm{Mn(ligIa)Cl_2}$	Found	42.6	3.7	16.6	16.3	0.03	B	5.93	–
	Calc.	42.6	3.6	16.6	16.2				
$\mathrm{Mn(ligIb)Cl_2}$	Found	42.5	3.7	16.4	16.0	0.1	A	5.90	310s
	Calc.	42.6	3.6	16.6	16.2				
$\mathrm{Mn(ligIc)Cl_2}$	Found	42.5	3.7	16.1	16.1	0.1	A	5.84	290m
	Calc.	42.6	3.6	16.6	16.2				
$\mathrm{Mn(ligId)Cl_2}$	Found	44.2	4.1	15.9	15.5	0.31	A	5.74	310s
	Calc.	44.3	4.0	16.0	15.6				
$\mathrm{Mn(ligIIa)Cl_2}$	Found	48.1	3.3	14.8	14.8	0.1	A	5.96	295s
	Calc.	48.4	3.2	15.0	14.7				
$\mathrm{Mn(ligIIb)Cl_2}$	Found	48.8	3.8	13.6	14.2	0.2	B	6.14	290s
	Calc.	49.5	3.6	14.4	14.2				
$\mathrm{Mn(ligIIc)Cl_2}$	Found	49.2	3.8	14.2	14.0	0.1	C	5.94	305s
	Calc.	49.5	3.6	14.4	14.2				
$\mathrm{Mn(ligIIIa)Cl_2}$	Found	41.2	2.8	14.4	14.6	0.1	A	5.96	290m
	Calc.	41.1	2.6	14.7	14.5				
$\mathrm{Mn(ligIIIb)Cl_2}$	Found	42.9	3.2	14.3	14.3	0.1	C	6.05	305m
	Calc.	42.6	3.0	14.2	14.0				
$\mathrm{Mn(ligIIIc)Cl_2}$	Found	42.4	3.3	14.0	14.1	0.1	B	6.03	290m
	Calc.	42.6	3.0	14.2	14.0				
$\mathrm{Mn(ligVI)Cl_2}$	Found	47.9	3.4		14.8	0.04	A	5.93	300s
	Calc.	48.4	3.2		14.7				
$\mathrm{Mn(ligVIII)Cl_2}$	Found	53.2	3.4	12.6	12.8	0.12	A	5.80	300m
	Calc.	53.8	3.3	13.2	13.0				
$\mathrm{Mn(ligVIII)Cl_2}$	Found	47.4	3.1	12.4	12.7	0.13	C	5.57	295m
	Calc.	47.4	2.8	13.0	12.8				
$\mathrm{Mn(ligVa)Cl_2}$	Found	45.1	3.8	13.0	16.9	0.50	B	5.59	295s
	Calc.	44.6	3.4	12.9	17.0				
$\mathrm{Mn(ligVb)Cl_2}$	Found	46.2	4.0	11.8	16.2	0.34	B	5.88	310s
	Calc.	46.3	3.9	12.5	16.3				
$\mathrm{Mn(ligVc)Cl_2}$	Found	45.9	3.9	12.5	16.3	0.37	B	5.76	300s
	Calc.	46.3	3.9	12.5	16.3				
$\mathrm{Mn(LigIVa)Cl_2}$	Found	50.2	3.2	11.6	15.2	0.92	B	5.60	305s
	Calc.	50.1	3.1	11.7	15.3				
$\mathrm{Mn(ligIVb)Cl_2}$	Found	51.3	3.5	10.9	14.5	0.52	B	5.83	315s
	Calc.	51.5	3.5	11.3	14.8				
$\mathrm{Mn(ligX)Cl_2}$	Found	42.5	3.8	15.2	15.0	0.04	C	5.92	305s
	Calc.	43.0	3.9	15.4	15.2				
$\mathrm{Mn(ligXI)Cl_4}$	Found	31.0	2.4	12.2	23.2	insol.	A	–	–
	Calc.	31.2	2.2	12.1	23.8				

[a] lig = ligand, the reference system used is given in Table I.

TABLE III. Bromo Complexes of Manganese(II).

Complex		Analysis (%)				Λ_M cm^2 ohm^{-1} mol^{-1}	Prep.	μ_{eff} (B.M.)	Infrared νM–N cm^{-1}
		C	H	N	Mn				
$\mathrm{Mn(lig\ Ia)Br_2}$	Found	33.5	2.9	13.2	12.8	0.12	B	6.11	–
	Calc.	33.7	2.8	13.1	12.9				
$\mathrm{Mn(lig\ Ib)Br_2}$	Found	33.7	2.9	12.9	12.8	0.16	A	5.77	296s
	Calc.	33.7	2.8	13.1	12.9				
$\mathrm{Mn(lig\ Ic)Br_2}$	Found	33.8	2.9	13.1	12.9	0.20	A	6.01	304m
	Calc.	33.7	2.8	13.1	12.9				

(continued overleaf)

TABLE III. *(continued)*

Complex		Analysis (%)				Λ_M cm^2 ohm^{-1} mol^{-1}	Prep.	μ_{eff} (B.M.)	Infrared νM–N cm^{-1}
		C	H	N	Mn				
Mn(lig Id)Br_2	Found	353.	3.2	12.8	12.3	0.32	A	5.76	305s
	Calc.	35.3	3.2	12.7	12.5				
Mn(lig IIa)Br_2	Found	38.9	2.6	11.6	12.0	0.27	A	6.12	290s
	Calc.	38.9	2.6	12.1	11.9				
Mn(lig IIb)Br_2	Found	40.6	3.2	11.5	11.4	0.29	B	6.03	290s
	Calc.	40.3	2.9	11.7	11.5				
Mn(lig IIc)Br_2	Found	39.0	3.3	11.4	11.4	0.04	C	5.96	305s
	Calc.	40.3	2.9	11.7	11.5				
Mn(lig IIIa)Br_2	Found	33.3	2.2	11.6	11.7	0.29	A	5.92	290s
	Calc.	33.3	2.1	11.9	11.7				
Mn(lig IIIb)Br_2	Found	35.2	2.6	11.4	11.5	0.13	C	5.96	298s
	Calc.	34.8	2.5	11.6	11.4				
Mn(lig IIIc)Br_2	Found	35.0	2.1	11.4	11.5	0.19	B	6.01	165w
	Calc.	34.8	2.5	11.6	11.4				
Mn(lig VII)Br_2	Found	43.9	3.0	10.5	10.6	0.30	A	5.53	285m
	Calc.	44.4	2.8	10.9	10.7				
Mn(lig VIII)Br_2	Found	39.1	2.6	10.6	10.4	0.13	C	5.90	280m
	Calc.	39.3	2.3	10.8	10.6				
Mn(lig Va)Br_2	Found	35.6	2.8	10.3	13.2	1.22	B	5.73	270m
	Calc.	35.0	2.7	10.2	13.4				
Mn(lig Vb)Br_2	Found	36.8	3.2	9.8	12.8	1.07	B	5.70	300m
	Calc.	36.6	3.1	9.9	12.9				
Mn(lig Vc)Br_2	Found	36.6	3.1	9.7	12.9	1.58	B	5.71	300s
	Calc.	36.6	3.1	9.9	12.9				
Mn(lig IVa)Br_2	Found	40.3	2.7	9.5	12.0	0.65	B		285m
	Calc.	40.2	2.5	9.4	12.3				
Mn(lig IVb)Br_2	Found	41.3	2.8	10.3	11.8	2.28	B		290s
	Calc.	41.6	2.8	9.1	11.9				

TABLE IV. Iodo Complexes of Manganese(II).

Complex		Analysis (%)				Λ_M cm^2 ohm^{-1} mol^{-1}	Prep.	μ_{eff} (B.M.)	Infrared νM–N cm^{-1}
		C	H	N	Mn				
Mn(lig IIa)I_2	Found	32.4	2.2	10.2	10.0	6.9	D	5.39	310m
	Calc.	32.3	2.2	10.1	9.9				285w
Mn(lig IIc)I_2	Found	33.6	2.5	9.9	9.7	17.1	D	6.11	285w
	Calc.	33.6	2.5	9.8	9.6				
Mn(lig IIIa)I_2	Found	27.7	1.8	9.6	9.7	6.9	D	5.95	295m
	Calc.	27.7	1.8	10.0	9.8				
Mn(lig IIIc)I_2	Found	28.9	2.1	9.7	9.7	9.44	D	5.91	–
	Calc.	29.1	2.1	9.7	9.5				
Mn(lig Va)I_2	Found	28.5	2.3	8.2	10.6	8.4	D	5.81	310m
	Calc.	28.5	2.2	8.3	10.9				
Mn(lig VII)I_2	Found	37.8	2.5	9.0	9.2	2.2	D	5.86	285s
	Calc.	37.6	2.3	9.2	9.1				

The conductivity in solvents of higher polarity such as methanol shows a marked increase which is compatible with a decomposition of the type

$$2MnligX_2 \rightarrow [Mnlig_2]^{2+} + Mn^{2+} + 4X^-$$

The spectra in methanol is similar to that of the bis-ligand perchlorate complex in acetone, which is consistent with the above decomposition.

The magnetic moments are, as expected, close to the high spin value (5.92 B.M.) for manganese(II) complexes and are of no consequence in elucidating the structure of the complexes.

TABLE V. X-ray Powder Diffraction Data for Manganese(II), Cobalt(II), Nickel(II) Complexes.

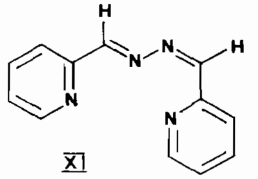
Complex	'd' Spacings (Å)
Co(lig Ia)Cl_2[a]	9.5m, 7.5s, 7.2m, 6.2s, 5.9m, 5.2m, 4.7m, 4.4w, 4.2w, 3.9m, 3.5m, 3.3m, 3.2m, 2.55m
Mn(lig Ia)Cl_2[a]	9.5w, 8.9s, 7.5s, 6.2m, 5.9w, 5.0m, 4.4w, 4.0w, 3.6m, 3.5m, 3.4m, 3.2m
Ni(lig Ia)Cl_2	8.0s, 7.0m, 6.8m, 5.2s, 4.9m, 4.6m, 4.0s, 3.6s, 2.6m, 2.45m
Co(lig Ib)Cl_2[a]	7.1w, 6.9s, 6.2s, 5.2w, 4.7w, 4.2w, 3.8m, 3.7m, 3.6m, 3.2m
Mn(lig Ib)Cl_2[a]	7.4w, 6.9m, 6.2s, 5.3w, 4.7w, 4.1w, 3.8m, 3.7m, 3.6m, 3.2w
Ni(lig Ib)Cl_2	9.2s 7.6m, 6.9s, 6.0m, 5.2s, 4.2s, 3.9m, 3.6w, 3.2s
Co(lig Ic)Cl_2[a]	7.1m, 6.9s, 6.1s, 5.2m, 4.5m, 4.2m, 3.8m, 3.6s, 3.4s, 3.2m
Mn(lgi Ic)Cl_2[a]	7.3 m, 6.8s, 6.2s, 5.2w, 4.6w, 4.1w, 3.7m, 3.6w, 3.4m, 3.2m
Ni(lig Ic)Cl_2	10.0s, 7.9s, 7.4s, 6.8s, 6.7m, 5.2s, 4.8w, 4.0s, 2.8m
Co(lig IIa)Cl_2[a]	9.7s, 7.0s, 6.2s, 6.7s, 4.9m, 4.6m, 3.9m
Mn(lig IIa)Cl_2[a]	9.5s, 7.0s, 6.2s, 5.1m, 4.5w, 4.2m, 3.6w, 3.2m, 2.6w
Ni(lig IIa)Cl_2	11.0s, 8.5s, 7.9m, 6.7s, 4.9m, 4.6m, 3.9m, 3.6s, 2.7m
Co(lig IIb)Cl_2[a]	10.0w, 8.7s, 7.1w, 5.2m, 5.1w, 5.0m, 4.3m, 4.1m, 3.5w, 3.4s, 2.7s
Mn(lig IIb)Cl_2[a]	8.7s, 7.1w, 5.2m, 5.1m, 4.4m, 4.2m, 3.5w, 3.4s
Co(lig IIIa)Cl_2[a]	9.5w, 7.6w, 6.8s, 6.0m, 5.2w, 4.8m, 4.6w, 4.2w, 4.05w, 3.85w, 3.55m
Mn(lig IIIa)Cl_2[a]	6.85s, 6.2m, 5.0m, 4.7w, 3.95m, 3.6w, 3.2s
Co(lig IIIb)Cl_2	7.3s, 6.6s, 6.0s, 5.7m, 4.6m, 4.1m, 3.8s, 3.6s, 3.2m, 2.3m, 1.9m
Mn(lig IIIb)Cl_2	9.8s, 6.9m, 6.4s, 5.8s, 5.4m, 5.1w, 4.9m, 4.3m, 4.1s, 3.7w, 3.6w, 3.5s, 3.3s
Co(lig X)Cl_2	8.5s, 7.0w, 6.8w, 5.6s, 4.8s, 4.2m, 3.8m, 3.3s
Mn(lig X)Cl_2	7.5m, 6.6s, 6.4w, 6.2w, 4.8w, 3.8m, 3.3s
Co(lig VII)Cl_2	9.4s, 8.4m, 7.4m, 6.8s, 6.7m, 5.4w, 5.3m, 5.0s, 4.4m, 4.1m, 3.5s
Mn(lig VII)Cl_2	9.5s, 8.5w, 6.0m, 5.6m, 4.9m, 4.6s, 4.4m, 3.4s
Ni(lig VII)Cl_2[a]	10.7m, 9.5s, 8.5s, 7.4m, 7.0s, 6.7m, 5.4w, 5.3m, 5.0s, 4.4m, 4.1m, 3.5s
Co(lig VIII)Cl_2[a]	9.3s, 8.0w, 7.2w, 6.2s, 5.8m, 4.7s, 4.4s, 4.2m, 4.0m, 3.6m, 3.4s, 3.3s, 2.75m
Mn(lig VIII)Cl_2[a]	9.5s, 7.3w, 6.2m, 5.6w, 4.8m, 4.6w, 3.4s, 2.8m
Co(lig IVb)Cl_2[a]	9.5s, 7.0m, 5.9s, 5.6m, 5.2m, 4.6w, 3.6s, 3.5s, 3.3s
Mn(lig IVb)Cl_2[a]	9.5s, 7.0w, 6.0s, 5.6m, 5.2m, 4.7w, 3.8s, 3.6w, 3.5w, 3.3s
Co(lig IIIc)Cl_2	8.7s, 7.0w, 5.7s, 5.2w, 5.0s, 4.7m, 4.3m, 4.1m, 4.0s, 3.5s, 3.4s, 2.8s, 1.9s
Mn(lig IIIc)Cl_2	8.2w, 7.5s, 7.0s, 6.2w, 5.6m, 5.1m, 4.9w, 4.32, 4.0m, 3.9m, 3.7w, 3.6s, 3.5s, 3.3s
Co(lig IIc)$(NCS)_2$[a]	8.7s, 8.0w, 7.2m, 6.4m, 5.3m, 5.2m, 5.0m, 4.4m, 4.3s, 3.5s, 3.3m
Mn(lig IIc)NCS)$_2$[a]	8.8s, 8.0w, 7.2w, 6.4m, 5.6w, 5.2w, 5.0m, 4.4m, 3.6s, 3.3m
Ni(lig IIc)$(NCS)_2$	8.7s, 8.2w, 7.7m, 7.4m, 7.0w, 6.4s, 5.8s, 5.2m, 4.8m, 4.3s, 3.6s, 3.5s
Co(lig IIIb)$(NCS)_2$[a]	8.7s, 7.3s, 6.2m, 5.5m, 5.0m, 4.4m, 3.8w, 3.6s, 3.4m
Mn(lig IIIb)$(NCS)_2$[a]	8.7s, 7.2m, 6.2m, 5.3m, 5.0m, 4.3w, 3.7w, 3.6s, 3.4m
Ni(lig IIIb)$(NCS)_2$	8.5s, 8.0s, 6.8s, 6.2m, 5.2s, 4.9s, 4.5w, 3.8w, 3.5s, 3.4s, 3.1m, 2.8m, 2.7m

(continued overleaf)

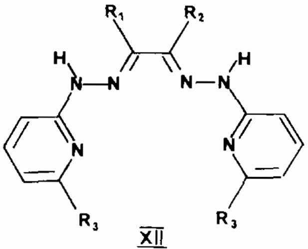
TABLE V. *(continued)*

Complex	'd' Spacings (Å)
Cu_2(lig XI)Cl_4	6.8s, 6.0m, 5.4w, 4.4w, 4.0w, 3.8w, 3.6w, 3.5s, 3.1m, 2.8w, 2,6w, 2.4w
Mn_2(lig XI)Cl_4	8.4s, 5.7s, 5.4w, 5.0w, 4.2w, 4.0w, 3.2w, 2.9s, 2.8m, 2.7w, 2.6w, 2.5m

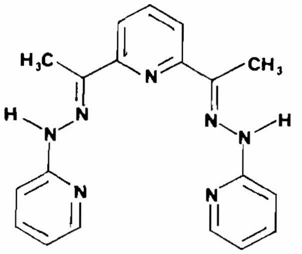
[a] Denotes isomorphous complexes of same ligand.



XI



XII



XIII

Comparison of X-ray powder diffraction photographs ('d' spacing data: Table V) of cobalt(II), nickel(II) and manganese(II) complexes of the same empirical formula [M(lig)Cl_2] show that for ligands Ia, Ib, Ic, IIa, IIb, IIIa, IVb and VIII the manganese(II), and cobalt(II) complexes are isostructural.

In those instances where a photograph of a corresponding nickel(II) complex was obtained there was no similarity of the X-ray powder diffraction photographs to either the cobalt(II) or manganese(II) complexes. As the relevant cobalt(II) complexes have been assigned a five-coordinate geometry [31], the corresponding manganese(II) complexes are assigned this configuration.

The X-ray powder diffraction photographs of the following manganese(II) complexes are different to those of the corresponding cobalt(II) complexes: (a) Mn(ligIIIb)Cl_2; (b) Mn(ligIIIc)Cl_2; (c) Mn(ligVII)Cl_2; (d) Mn(ligX)Cl_2. These complexes are therefore not isostructural with the cobalt(II) complexes of the corresponding ligand.

d–d Electronic absorption bands of manganese(II) complexes are spin forbidden and therefore weak in intensity. In many cases therefore, the diffuse reflectance spectrum is of little value in a study of the manganese tridentate complexes, since the intense charge transfer bands of the ligand mask any d–d bands which may be present. However, in a few instances, the spectrum shows three shoulders on a rising ligand absorption band in the region 16.5–20 kK. These bands have been observed by Lions, Dance and Lewis [14] in Mn(PAPHY)X_2 (X = Cl, Br, NCS; PAPHY = I, $R_1 = R_2 = R_3$ = H) which have been proposed as five coordinate compounds.

Infrared spectral data of the manganese(II) complexes indicate similar behaviour to the cobalt(II) and nickel(II) complexes [31]. Hence for complexes containing the N–H group, the bands due to ν_{N-H} are of varied intensity and are of little consequence in providing structural information. Bands in the 1550–1650 cm^{-1} have been used by other workers [13, 20–24] to deduce if pyridine rings (when present in the ligand) are coordinated to the metal atom. In such ligands two pyridine ring vibrations are observed in the infrared spectrum of the free ligand: (i) at approx. 1600 cm^{-1} (Py I), and (ii) at 1570–1580 cm^{-1} (Py II). On coordination the 1600 cm^{-1} band shifts by 10–20 cm^{-1} to a higher wavenumber, while Py II remains unchanged.

In all the compounds [Mn(NNN)X_2] (X = Cl, Br or I) in which the ligand contains pyridine or methyl-substituted pyridine residues, infrared evidence indicates that there are no uncoordinated pyridine nitrogen atoms (thus, for example, in the complexes Mn(LigVa)X_2, (X = Cl, Br, I), Mn(ligVb)X_2 (X = Cl, Br) and Mn(ligVc)X_2, (X = Cl, Br) the infrared spectra show only two bands in the region which may be attributed to Py I and Py II vibrations). This is consistent with all the pyridine rings being coordinated to the manganese atom since a free pyridine ring

TABLE VI. Thiocyanato Complexes of Manganese(II).

Complex		Analysis (%)				Λ_M cm^2 ohm^{-1} mol^{-1}	Prep.	μ_{eff} (B.M.)	Infrared	
		C	H	N	Mn				νM–N	νC≡N cm^{-1}
Mn(lig Ib)(NCS)$_2$	Found	43.9	3.3	20.9	14.4	0.59	D	6.13	290m	2070s
	Calc.	43.6	3.1	21.8	14.4					2095s
Mn(lig Ic)(NCS)$_2$	Found	43.5	3.3	21.3	14.3	0.77	D	5.70	310w	2080s
	Calc.	43.9	3.1	21.9	14.4					2110s
										2125s
Mn(lig Id)(NCS)$_2$	Found	45.1	3.6	20.9	13.7	0.65	D	5.86	303s	2060s
	Calc.	45.4	3.5	21.1	13.9					2095s
Mn(lig IIa)(NCS)$_2$	Found	48.3	3.0	19.8	12.9	0.90	D	6.02	310m	2060s
	Calc.	48.7	2.9	20.1	13.1				295sh	2085s
Mn(lig IIb)(NCS)$_2$	Found	49.5	3.5	19.2	12.6	1.04	D	5.88	290s	2070s
	Calc.	49.9	3.2	19.4	12.7					
Mn(lig IIc)(NCS)$_2$	Found	49.6	3.4	19.0	12.6	0.30	D	5.96	310m	2070s
	Calc.	49.4	3.2	19.4	12.7					
Mn(lig IIIa)(NCS)$_2$	Found	42.3	2.5	20.0	12.8	0.35	D	5.96	290m	2080s
	Calc.	42.4	2.4	19.8	12.9					2110s
Mn(lig IIIb)(NCS)$_2$	Found	43.6	2.9	18.9	12.4	0.38	D	6.10	310s	2070s
	Calc.	43.7	2.7	19.1	12.5					2090sh
Mn(lig IIIc)(NCS)$_2$	Found	43.8	2.9	18.5	12.3	1.10	D	5.71	300w	2070s
	Calc.	43.7	2.7	19.1	12.5					2110s
Mn(lig VI)(NCS)$_2$	Found	48.2	3.0	19.7	13.0	1.55	D	5.82	290m	2060s
	Calc.	48.7	2.9	20.1	13.1					2080s
Mn(lig VII)(NCS)$_2$	Found	53.0	3.3	17.3	11.8	2.64	D	5.77	270w	2060s
	Calc.	53.7	3.0	17.9	11.7					2080s
Mn(lig VIII)(NCS)$_2$	Found	47.3	2.6	17.2	11.7	1.45	D	5.61	285m	2080s
	Calc.	48.0	2.5	17.7	11.6					2100sh
Mn(lig IVa)(NCS)$_2$	Found	50.4	2.8	17.1	13.4	1.59	D	5.84	285m	2060s
	Calc.	50.5	2.7	17.3	13.6					2080sh
Mn(lig IVb)(NCS)$_2$	Found	51.7	3.2	16.3	13.0	1.36	D	5.64	290s	2075s
	Calc.	51.7	3.1	16.8	13.2					2100sh
Mn(lig Vb)(NCS)$_2$	Found	47.0	3.7	17.1	14.1	3.80	D	5.96	300m	2080s
	Calc.	47.1	3.4	18.3	14.4					
Mn(lig Vc)(NCS)$_2$	Found	46.1	3.6	18.6	14.2	2.75	D		305m	2080s
	Calc.	47.1	3.4	18.3	14.4					2100sh

and a coordinated pyridine ring would produce three bands due to pyridine ring vibrations in the 1550–1650 cm^{-1} region.

The complex Mn(ligX)Cl$_2$ may be considered to be coordinated through the nitrogen atoms in the ligand since the presence of a ν_{O-H} band in the spectrum indicates that the oxime-OH is not coordinated to the metal.

There is no direct evidence to indicate the geometry of bromo and iodo complexes. In other five coordinate series, the bromo and iodo complexes are usually of the same geometry as the chloro complex [14].

Thiocyanato Complexes of Manganese(II)

These compounds are of the type Mn(NNN)(NCS)$_2$ (Table VI). Their magnetic properties indicate that all the complexes are high spin and their molar conductivities in nitrobenzene show that the complexes are non-electrolytes.

Infrared spectral data show that all the complexes with the exception of Mn(ligIc)(NCS)$_2$ have a band or bands attributed to $\nu_{C\equiv N}$ with a frequency less than 2110 cm^{-1}. These absorption bands may be associated with terminal thiocyanate groups [25] which implies that the complexes are likely to be monomeric and therefore of five-coordinate geometry. The complex Mn(lig Ic)(NCS)$_2$ has infrared absorption bands at 2080, 2110 and 2125 cm^{-1}. The absorption pattern is indicative of the presence of bridging thiocyanato groups which would result in a six-coordinate, thiocyanato bridged molecular species [25].

X-ray diffraction powder photographs of the manganese(II), cobalt(II) and nickel(II) thiocyanates of IIIb and IIc support the above conclusions (Table V). The monomeric, five-coordinate manganese(II) and cobalt(II) complexes are isostructural, but both are different to the thiocyanato bridged nickel(II) complexes.

TABLE VII. Complexes of the Type Mn(NNN)$_2$(ClO$_4$)$_2$.

Complex		Analysis (%)				Λ_M cm^2 ohm^{-1} mol^{-1}	Prep.	μ_{eff} (B.M.)	Infrared νM–N cm^{-1}
		C	H	N	Mn				
Mn(lig Ia)$_2$(ClO$_4$)$_2$	Found	42.0	3.6	15.1	8.1	58.1	E	5.86	320w
	Calc.	42.4	3.5	16.5	8.0				
Mn(lig Ib)$_2$(ClO$_4$)$_2$·H$_2$O	Found	41.2	3.9	15.1	7.9	61.6	E	5.97	290s
	Calc.	41.4	3.7	16.0	7.9				
Mn(lig Ic)$_2$(ClO$_4$)·2H$_2$O	Found	40.6	4.1	15.3	7.8	61.0	E	6.02	290m
	Calc.	40.3	3.9	15.6	7.7				
Mn(lig Id)$_2$(ClO$_4$)$_2$·H$_2$O	Found	43.3	4.1	16.1	7.8	51.7	E	5.88	300s
	Calc.	43.1	4.1	15.5	7.6				
Mn(lig IIa)$_2$(ClO$_4$)$_2$·3H$_2$O	Found	45.1	3.4	13.5	7.0	51.0	E	5.80	290w
	Calc.	44.8	3.7	13.9	6.8				
Mn(lig IIb)$_2$(ClO$_4$)$_2$·2H$_2$O	Found	47.3	3.9	13.5	6.8	56.5	E	6.18	290s
	Calc.	47.3	3.9	13.2	6.8				
Mn(lig IIc)$_2$(ClO$_4$)$_2$·H$_2$O	Found	48.6	4.3	14.2	6.9	47.0	E	–	305s
	Calc.	48.3	3.8	14.1	6.9				
Mn(lig IIIc)$_2$(ClO$_4$)$_2$·2H$_2$O	Found	40.3	3.3	13.3	6.6	54.5	E	6.02	290w
	Calc.	40.7	3.5	13.6	6.6				
Mn(lig IVa)$_2$(ClO$_4$)$_2$·H$_2$O	Found	49.0	3.2	11.0	7.5	68.6	E	6.12	290m
	Calc.	48.8	3.3	11.4	7.5				
Mn(lig IVb)$_2$(ClO$_4$)$_2$	Found	51.3	3.6		7.3	66.2	E	–	290m
	Calc.	51.3	3.5		7.4				
Mn(lig VI)$_2$(ClO$_4$)$_2$·2H$_2$O	Found	46.0	3.6	13.8	7.0	56.4	E	–	280m
	Calc.	45.8	3.6	14.3	7.0				
Mn(lig VII)$_2$(ClO$_4$)$_2$·2H$_2$O	Found	51.4	3.5	12.5	6.1	46.9	E	5.76	300w
	Calc.	51.5	3.6	12.6	6.2				

TABLE VIII. Deprotonated Complexes of Manganese(II).

Complex		Analysis (%)				Infrared νM–N cm^{-1}
		C	H	N	Mn	
Mn(lig Ib–H)$_2$	Found	61.2	5.1	24.2		290w
	Calc.	60.4	4.6	24.4		
Mn(lig Ic–H)$_2$·½C$_6$H$_6$	Found	62.4	4.9	21.8		290w
	Calc.	62.0	4.8	21.4		
Mn(lig IIa–H)$_2$	Found	65.5	4.1	18.8	9.6	285s
	Calc.	65.6	4.0	20.4	10.0	

Bis-ligand Perchlorates of Manganese(II)

Bis-ligand perchlorates (Table VII) of the type [Mn(NNN)$_2$](ClO$_4$)$_2$ range in colour from yellow to deep red. The complexes are soluble in organic solvents such as acetone, ethanol and nitrobenzene. Conductivity measurements (Table VII) in the latter solvent show no deviation from the expected values for 1:2 electrolytes. Magnetic moments are close to the expected value for manganese high spin complexes.

Infrared spectra indicate bands at ~1100 cm^{-1} (br) and 625 cm^{-1} (s) which are those due to ionic perchlorate. No bands due to coordinated water are observed. Where the pyridine ring vibrations are observed, they indicate that both pyridine rings in the ligand are bound to the manganese. This suggests that the ligand acts only in a tridentate capacity.

Deprotonation of Manganese(II) Complexes

Deprotonation of mono-ligand complexes yielded only bis-ligand deprotonated complexes in low yield (Table VIII). The reactions produced copious quantities of manganese dioxide which made purification difficult. As the reaction was performed in polar solvents using ethanolic sodium hydroxide, it is probable that decomposition of the mono-ligand complexes occurs, with the formation of a bis-ligand complex which is subsequently deprotonated. This situation is similar to that found by Lions *et al.* [14]. Complexes of ligands formed from 2-acetyl-

TABLE IX. Metal–Ligand Vibrations in Cobalt Nickel, Iron, Copper and Zinc Complexes.

Complex	ν_{M-L}	Complex	ν_{M-L}	Complex	ν_{M-L}
Co(lig Ia)Cl$_2$	290s				
Co(lig Ib)Cl$_2$	325s	Ni(lig Ib)Cl$_2$	335m	Fe(lig Ib)Cl$_2$	305
Co(lig Ib)Br$_2$	315	Ni(lig Ib)Br$_2$	335s	Zn(lig Ib)Cl$_2$	315s
Co(lig Ib)(NCS)$_2$	320	Ni(lig Ib)I$_2$·H$_2$O	330s	Zn(lig Ib)Br$_2$	305m
Co(lig Ic)Cl$_2$	315s	Ni(lig Ic)Cl$_2$	325m	Zn(lig Ib)I$_2$	305s
Co(lig IIa)Cl$_2$	300m	Ni(lig IIa)Cl$_2$	310m	Zn(lig Ib)(NCS)$_2$	320m
Co(lig IIb)Cl$_2$	290br, w			Cu(lig Ib)Cl$_2$	320m
Co(lig IIc)Cl$_2$·H$_2$O	320m	Ni(lig IIc)Cl$_2$·H$_2$O	320m	Cu(lig Ib)Br$_2$	320m
Co(lig IIc)Br$_2$·H$_2$O	310m	Ni(lig IIc)Br$_2$	340m	Cu(lig Ib)(NCS)$_2$	328m
Co(lig IIc)(NCS)$_2$	320m	Ni(lig IIc)(NCS)$_2$	320m		
Co(lig IIIa)Cl$_2$	315s				
Co(lig IIIb)Cl$_2$	320br, m	Ni(lig IIIb)(NCS)$_2$	285w		
			325m		
			340m		
Co(lig IIIb)Br$_2$	320br	Ni(lig IIIc)Cl$_2$	310m		
Co(lig IIIb)(NCS)$_2$	325m				
Co(lig IIIc)Cl$_2$	305m				
Co(lig VII)Cl$_2$	310s	Ni(lig VII)Cl$_2$·H$_2$O	315m		
			285m		
Co(lig VIII)Cl$_2$	325m				
Co(lig IVb)Cl$_2$	330s				
	310s				
Co(lig X)Cl$_2$	290m				

pyridine and quinoline-8-aldehyde decomposed on deprotonation, while those deprotonated complexes of ligands with a benzothiazyl group could not be isolated. As expected no deprotonated complexes show bands in the ν_{N-H} region.

Far Infrared Spectra of Manganese Complexes

The far infrared spectra of manganese(II) complexes contain bands which may be attributed to metal ligand vibrations. All complexes contain bands in the region 250–350 cm^{-1}, the bands being of medium to strong in intensity. Investigations by Postmus, Ferraro and Wozniak [26], Bamfield, Price and Miller [27], Bryson and Nuttall [28] have associated bands in this region with metal halogen vibrations. In each case there are two bands due to metal halogen vibrations. The separation of these bands in a number of metal complexes, both five and six coordinate, has been postulated as being an indication of the stereochemistry of the metal complex. It has also been suggested [28] that the metal halogen frequencies for five coordinate complexes are intermediate between those of six and four coordinate compounds. Bamfield and co-workers have found that a separation of 15–21 cm^{-1} occurs in five coordinate complexes of the M(NNN)X$_2$ (X = Cl, Br) with distorted trigonal bipyramidal geometry and a greater separation 27–42 cm^{-1} in complexes intermediate between the two idealized five coordinate geometries [27]. It has also been suggested that more a complex spectrum in this region is indicative of halogen bridged complex.

Complexes of the ligand 2,6-(dibenzothiazol-2-yl)-pyridine have two bands in the far infrared region which are not present in the ligand. The first of these bands occurs in the region 271–325 cm^{-1} for chloro complexes only, and is described as a metal-chlorine stretching frequency. The other, which occurs in the region 365–369 cm^{-1} for all complexes has been assigned as a metal–nitrogen stretching frequency [16].

The bands in the far infrared region of the spectra of the complexes under review are shown in Tables II–IV and VI–VII. Infrared bands for some cobalt, nickel, iron, copper and zinc complexes are shown for comparison of the spectra with manganese complexes of the same ligand (Table IX).

The absorption in the region (250–350 cm^{-1}) are suggested as being due to ν_{M-N} vibrations for the following reasons.

(a) The bands are not present in the spectra of the ligands.

(b) The bands are not greatly sensitive to a change in halogen.

TABLE X. Complexes of Manganese(II) with Ligands IX, XIIa, XIIb, XIIc and XIII.

Complex		Analysis (%)				Λ_M cm^2 ohm^{-1} mol^{-1}	Prep.
		C	H	N	Mn		
Mn(lig IX)$_2$(H$_2$O)$_2$Cl$_2$	Found	40.2	4.2		8.4	0.18	C
	Calc.	40.1	4.3		8.4		
Mn(lig XIIc)Cl$_2$	Found	45.2	4.8	19.0	12.9	2.90	A
	Calc.	45.5	4.7	19.9	13.0		
Mn(lig XIII)Br$_2$	Found	40.6	3.5		9.8	2.10	A
	Calc.	40.7	3.4		9.8		
Mn(lig XIIa)Cl$_2$	Found	42.7	4.3	21.1	13.9	5.1	A
	Calc.	42.6	4.1	21.3	14.0		
Mn(lig XIIa)Br$_2$	Found	34.7	3.4	17.4	11.4	7.4	A
	Calc.	34.8	3.3	17.4	11.4		
Mn(lig XIIa)(NCS)$_2$	Found	43.8	3.7	26.0	12.6	17.1	D
	Calc.	43.7	3.6	25.4	12.5		
Mn(lig XIIb)Cl$_2$	Found	45.2	4.7	19.5	13.0	7.2	A
	Calc.	45.4	4.7	19.9	13.0		
Mn(lig XIIb)Br$_2$	Found	37.5	4.1	16.1	10.7	8.7	A
	Calc.	37.6	3.9	16.4	10.8		
Mn(lig XIIb)(NCS)$_2$	Found	46.3	4.4	23.5	11.8	8.5	D
	Calc.	46.3	4.3	23.9	11.8		

(c) The bands are not greatly sensitive to a change in metal atom in the complex.

(d) The bands occur at the same, or close to the same frequency in bis-ligand perchlorate complexes.

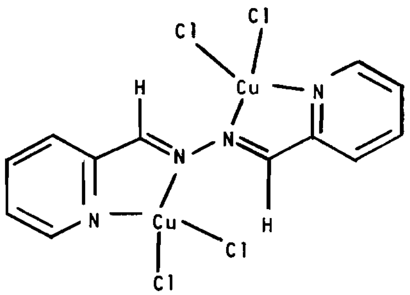
Miscellaneous Complexes of Manganese(II)

The complex Mn(LigXIIc)Cl$_2$ as prepared by the reactions of manganese(II) chloride and the potentially quadridentate ligand XIIc in ethanol, is a deep orange colour similar to Mn(ligIa)Cl$_2$ and related compounds. The compounds Mn(ligXIIa)X$_2$ and Mn(ligXIIb)X$_2$ (X = Cl, Br, NCS) were prepared and were found to be olive green in colour. It is suggested that in Mn(ligXIIc)Cl$_2$ the ligand is acting in a tridentate manner whereas the ligands XIIa and XIIb act as quadridentates. Investigation of the infrared spectra of ligands and complexes in the 1550–1650 cm^{-1} region suggest that for complexes of ligands XIIa and XIIb, both pyridine rings are bound to the metal atom. The assigned Py I band increases in frequency from 1600–1620 cm^{-1} on coordination while the py II band remains in the region 1570–1580 cm^{-1}. No third band in the region of 1600 cm^{-1} exists in these complexes. [Mn(lig XIIA)Br$_2$] was incorrectly reported previously [32] to have the Py I band at 1591 cm^{-1}. The correct position of this band is some 30 cm^{-1} higher. [Mn(ligXIIc)Cl$_2$] has bands in this region at 1620, 1605, 1576 cm^{-1} whereas the associated ligand (XIIc) has bands at 1605 and 1578 cm^{-1}. This suggests that one pyridine ring is unbound and the ligand is acting as a tridentate. It is possible that the bulky tertiary butyl group prevents a pyridine ring from coordinating by steric interaction with a pyridyl hydrazone side chain adjacent to the t-butyl group. The pyridine ring would be pushed out of position for coordination on an octahedral site.

The complex Mn(lig XIII)Br$_2$ is prepared from the potentially quinquedentate ligand XIII. This complex is also orange brown in colour. Infrared spectral data in this case, however, suggests that all pyridine rings are bound. As the complex is very insoluble, it may be that the ligand itself is acting in a bridging capacity. X-ray diffraction studies of complexes of ligand XIII with cobalt(II) and zinc(II) salts, [Co(lig XIII)(H$_2$O)$_2$]Cl$_2$, [Zn(lig XIII)(H$_2$O)$_2$]Cl$_2$, indicate that the ligand acts as a quinquedentate, the complexes being of pentagonal bipyramidal structure [29, 30]. The zinc complex on deprotonation yields a complex in which the deprotonated ligand acts in a bridging capacity.

The complex Mn(lig IX)$_2$Cl$_2$(H$_2$O)$_2$ occurs as a pale pink compound. On heating at 110 °C for two days no loss in weight occurs and it is assumed that the ligand functions as a unidentate. This is confirmed by the molar conductivity in nitrobenzene (Λ_M = 0.18 at 25 °C) indicating the complex to be a non-electrolyte. The oxime group oxygen is not coordinated as the infrared spectra of ligand and complex have bands at 3300 and 3270 cm^{-1} respectively. The presence of a sharp band at 3420 cm^{-1} (ν_{OH}) supports the proposition that the water molecules are coordinated and hence that the complex is octahedral in structure.

The yellow insoluble complex Mn$_2$(lig XI)Cl$_4$ is probably polymeric. A copper complex Cu$_2$(lig XI)Cl$_4$ has been proposed as being of structure [20].



However X-ray powder diffraction photographs of the manganese and copper complexes are completely dissimilar indicating the compounds are not isostructural (Table V).

Experimental

Preparation of Ligands and Metal Complexes

Ligand preparations are described in an earlier paper [31] or in the relevant reference of Table I.

The preparation of metal complexes may be classified into several standard types as follows:

Method A

A hot, filtered, ethanolic solution of the ligand was added slowly to a hot, filtered, ethanolic solution of the metal salt (the metal salt being in a slight excess of a 1:1 molar ratio of ligand:metal). The metal complex crystallized immediately or on slight evaporation of solvent.

Method B

This method is the same as method A except that the ligand is prepared *in situ* from the appropriate aldehyde or ketone and hydrazine or amine and used without isolation.

Method C

The ligand and metal salt were suspended in ethanol and refluxed together for at least one hour. The metal complex separated out, was allowed to digest for 30 minutes and filtered off after cooling.

Method D

The hot filtered ethanolic solution of the ligand prepared either as in method A or B was added to a hot filtered ethanolic solution of the metal salt (in slight excess) prepared *in situ*. The metal salt was prepared *in situ* by adding an appropriate lithium salt in ethanol to a solution of the metal perchlorate in ethanol. As above, the metal complex crystallized immediately or on slow evaporation. In some cases, acetone was preferred to ethanol as a solvent, the metal complex perchlorates being less likely to crystallise from this solvent than from ethanol.

Method E

A hot, filtered, ethanolic solution of the metal perchlorate was added to a hot, filtered, ethanolic solution of the ligand, the mole ratio of ligand: metal being in a slight excess of 2:1. The bis-ligand complex perchlorates crystallized on cooling and were recrystallized from either ethanol or aqueous ethanol.

Deprotonation of Manganese Complexes

1.0–1.5 g of the manganese(II) complex (mono or bis ligand) were dissolved in warm aqueous ethanol, the solution cooled to room temperature and a calculated quantity of ethanolic sodium hydroxide added. A deep red coloration was produced. The solution was extracted several times with benzene to separate the deprotonated complex from the manganese dioxide formed during the reaction. The benzene extracts were dried over anhydrous sodium sulphate, the benzene removed under reduced pressure and the red product thus obtained recrystallized from benzene–petroleum ether mixed solvent.

Conductance Measurements

Conductivity measurements were made using a Philips PR9501 conductivity bridge with platinum "dip-type" electrodes. Conductivity measurements were made at 25 °C in pure nitrobenzene. The concentration of the nitrobenzene solutions of the metal complexes was in the range 10^{-4}–10^{-3} *M*. For some complexes, conductivity measures in A.R. methanol were made under the same conditions. Molar conductivities (Λ_M) were expresssed in ohm^{-1} cm^2 mol^{-1}.

Magnetic Susceptibility Measurements

Magnetic susceptibility measurements were made using the Gouy method. The magnetic field was produced by a permanent magnet of field strength 6.58 kG and the force developed on the sample measured using a Mettler balance with digital readout to 0.01 mg. Measurements were made at room temperature. The apparatus was calibrated using mercury-(II) tetrathiocyanatocobaltate(II), $Hg[Co(NCS)_4]$. Magnetic moments are given in Bohr Magnetons at room temperature (289–304 K).

X-ray Powder Diffraction Photographs

X-ray powder diffraction photographs were taken using a Philips PW1400 vacuum X-ray spectrometer and a Debye–Scherrer powder camera. The radiation used was cobalt Kα radiation wavelength 1.7902 Å. The photographs of the manganese(II) complexes were found to be slightly fogged due to fluorescence of the manganese atoms.

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