

SPECTRAL CHARACTERIZATION OF MANGANESE(II) COMPLEXES

6.1. Introduction

Manganese is the twelfth most abundant element by weight in the earth's crust. Traces of manganese are found in many plants and bacteria, and a healthy human adult has about 10-20 mg of manganese in his body. It is an essential trace element, forming the active sites of a number of metalloproteins. In these metalloproteins, manganese can exist in any of the five oxidation states or in mixed valence states. For inorganic chemists, metalloproteins with two or even more manganese atoms per sub unit are particularly interesting. The most important natural role of manganese is in the oxidation of water in green plant photosynthesis where its presence in photosystem II is essential [1].

Manganese shows oxidation states ranging from (-III) to (+VII). The (+II) state is the most common and Mn^{2+} ions exist in the solid, in solution and as complexes. This Chapter deals with the synthesis, magnetic, spectral and biological studies of two Mn(II) complexes synthesized using the two ligands HL^1 and HL^2 .

6.2. Experimental

6.2.1. Materials

The details regarding the synthesis of ligands HL^1 and HL^2 are discussed in Chapter 2. Manganese acetate and manganese sulphate are used for the synthesis of the complexes. The solvents are purified by standard methods of purification.

6.2.2. Synthesis of complexes

$[Mn(L^1)_2] \cdot H_2O$ (17)

Manganese acetate (1 mmol, 0.2449 g) dissolved in 20 ml ethanol and HL^1 (2 mmol, 0.676 g) dissolved in 30 ml hot ethanol were mixed and stirred for 3 hrs. The yellow colored solids, which separated on cooling, were filtered, washed with hot ethanol and ether and dried over P_4O_{10} *in vacuo*.

$[Mn(L^2)_2]$ (18)

Manganese sulphate (1 mmol, 0.169 g) dissolved in a mixture of hot water and methanol and HL^2 (2 mmol, 0.664 g) dissolved in 30 ml hot methanol were mixed and stirred for 3 hrs. The yellow colored solids, which separated, were filtered, washed with hot ethanol and ether and dried over P_4O_{10} *in vacuo*.

6.3. Results and discussion

6.3.1. Physical measurements

The two Mn(II) complexes are yellow powders, clearly soluble in chloroform, dimethylformamide and dimethylsulphoxide. The two complexes synthesised using the two ligands have the same stoichiometry MnL_2 i.e. a structure in which two anionic ligands are coordinated to the Mn(II) ion. The details of the elemental analysis, physical characteristics and magnetic properties are given in Table 6.1.

Table 6.1 Analytical data

Compound	Empirical formula	Colour	Found (Calculated) %			Λ_M^* (in DMF)	μ B.M.
			C	H	N		
$[\text{Mn}(\text{L}^1)_2] \cdot \text{H}_2\text{O}$ (17)	$\text{C}_{38}\text{H}_{44}\text{N}_8\text{S}_2\text{OMn}$	Yellow	61.78 (61.15)	5.96 (5.88)	14.92 (14.95)	1.8	5.94
$[\text{Mn}(\text{L}^2)_2]$ (18)	$\text{C}_{38}\text{H}_{30}\text{N}_8\text{S}_2\text{Mn}$	Yellow	63.27 (63.70)	4.30 (4.17)	15.46 (15.57)	5.02	5.79

*Molar conductivity of 10^{-3}M solution, in $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-2}$

6.3.2. Magnetic moments

Because of the additional stability of the half filled d shell, Mn(II) generally forms high spin complexes with an orbitally degenerate 6S ground state term and the spin only magnetic moment of 5.92 B.M., which will be independent of the temperature and stereochemistry, is expected [3]. The magnetic moments of the two Mn(II) complexes are calculated from the magnetic susceptibility measurements and using the diamagnetic corrections. The magnetic moments of the two complexes $\text{Mn}(\text{L}^1)_2$ and $\text{Mn}(\text{L}^2)_2$ are 5.94 and 5.79 B.M. respectively, indicating the presence of five unpaired electrons and hence these are high spin complexes [4].

6.3.3. IR spectra

The infrared spectral assignments (cm^{-1}) of ligands HL^1 and HL^2 and their Mn(II) complexes are given in Table 6.2. The bonding sites of the thiosemicarbazone to the metal ion have been deduced by comparing the spectra of the complexes with the spectra of the ligands.

The $\nu(\text{C}=\text{N})$ band of thiosemicarbazones are found to be shifted to higher frequencies in the spectra of the complexes suggesting the coordination of the

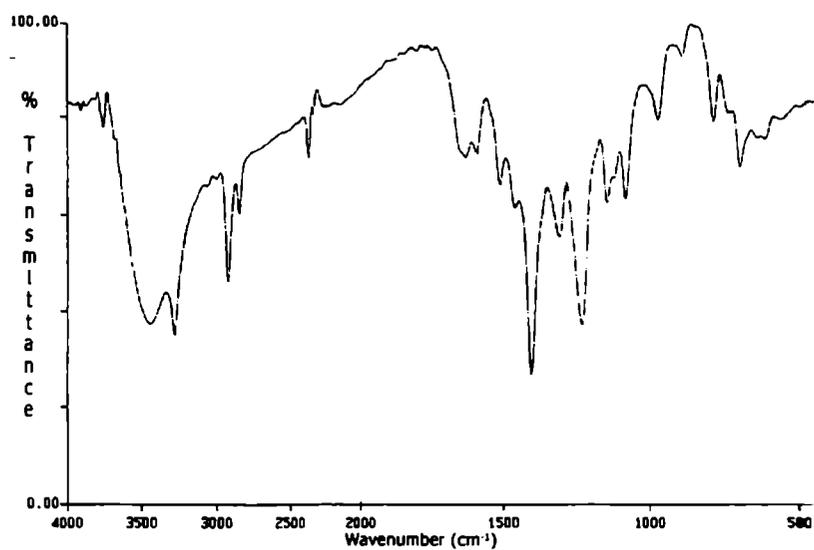


Fig.6.1. IR spectrum of compound 17

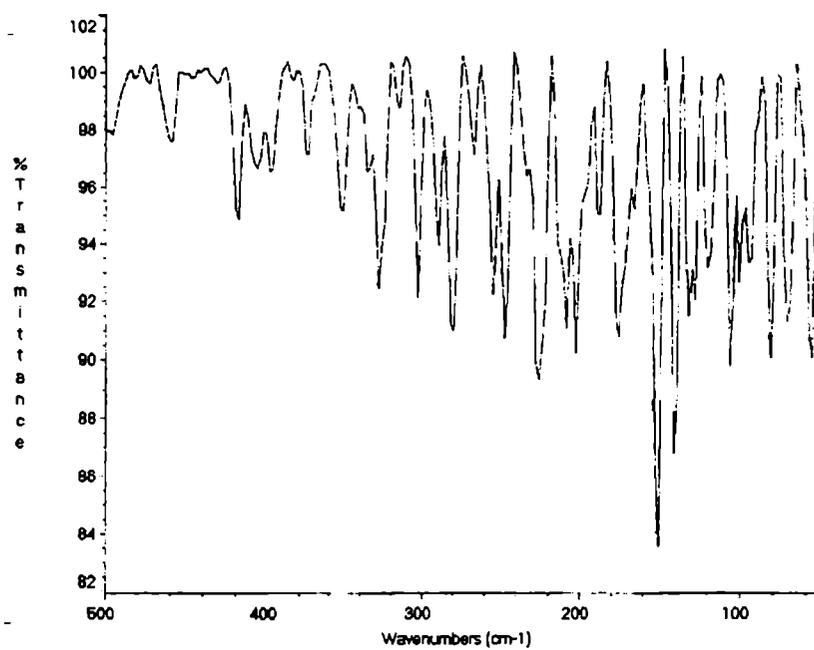


Fig.6.2. Far IR spectrum of compound 17

azomethine nitrogen to the Mn(II) ion. The involvement of this nitrogen in bonding is also supported by a shift in $\nu(\text{N}-\text{N})$ to higher frequencies. The $\nu(\text{C}=\text{S})$ bands in the ligands appear at *ca.* 1370 and 834 cm^{-1} . These are found to be shifted to *ca.* 1319 and 784 cm^{-1} in the complexes. This large negative shift of the $\nu(\text{C}=\text{S})$ band indicates the coordination of the ligand via the thiolate sulfur to the manganese atom. The coordination of the nitrogen atom of the pyridine ring to the Mn(II) ion in the complexes is indicated by the shifting of the pyridine ring vibrations at 607 and 622 cm^{-1} of HL¹ and HL², respectively, to higher frequencies in their manganese complexes [5,6]. In the far IR spectra of the complexes, the bands at *ca.* 470, and 424 cm^{-1} are assigned to the $\nu(\text{Mn}-\text{N})$ and $\nu(\text{Mn}-\text{S})$ modes [7] respectively.

6.3.4. Electronic spectra

The electronic spectra of the two Mn(II) complexes are recorded in polycrystalline state and the spectral data are given in Table 6.3. The solid state electronic spectra of the two Mn(II) complexes contain a broad band at 435 nm which is a typical charge transfer transition as expected for an octahedral Mn(II) complex. The ground state term for high spin d^5 configuration is 6S . Since there are no other terms of sextet spin multiplicity, all the $d-d$ transitions in high spin d^5 complexes are not only Laporte forbidden but also spin forbidden [8]. The ground state of the high spin octahedrally coordinated Mn^{2+} ion is ${}^6A_{1g}$. The ground state (${}^6A_{1g}$) is the only state with a multiplicity of 6. The d^5 configuration gives rise to the 4G , 4D and 4P excited states. The diffuse reflectance spectra of the Mn(II) complexes exhibit weak absorption bands at *ca.* 555, 435 and 385 nm. The three lowest energy bands are assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$, ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g} \rightarrow {}^4E_g(G)$, ${}^4A_{1g}(G)$ transitions. The pair of transitions ${}^6A_{1g} \rightarrow {}^4E_g(G)$, ${}^4A_{1g}(G)$, are degenerate in octahedral symmetry whose energies are given by $10B+5C$.

Table 6.2 IR spectral assignments of HL¹, HL² and Mn(II) complexes

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{N})$	$\nu(\text{C}-\text{S})$	$\rho(\text{py})$	$\nu(\text{Mn}-\text{N})$	$\nu(\text{Mn}-\text{S})$	$\nu(\text{Mn}-\text{N})$ py
HL ¹	1582m	1118s	1370s,833m	607m	--	--	--
[Mn(L ¹) ₂].H ₂ O	1632m	1149m	1313s,786s	643w	459s	418s	303s
HL ²	1591s	1102s	1369s,835m	622m	--	--	--
[Mn(L ²) ₂]	1625m	1128s	1325s,782m	630s	489s	428m	316s

Table 6.3: Electronic spectral Data of Mn(II) complexes (nm)

Compound	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$	${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g, {}^4\text{A}_{1g}(\text{G})$	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	B	10Dq (cm ⁻¹)	C (cm ⁻¹)	$\beta = \text{B}/\text{B}_0$
[Mn(L ¹) ₂].H ₂ O	550sh	437	386sh	334	271	692	8060	3058	0.8046
[Mn(L ²) ₂]	546sh	433	389sh	329	277	667	8000	2948	0.775

These assignments are obtained by fitting the observed spectrum to the Tanabe Sugano diagram [9]. The energies corresponding to the above transitions and the values of Racah parameters B and C and Dq calculated are given in Table 6.3. The extent of covalence in the metal-ligand bond may be evaluated from the electronic spectrum by estimating $\beta = B/B_0$. The value of B_0 for Mn^{2+} is 860 cm^{-1} [10]. The absorption bands observed at ~ 350 and 270 nm are the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the ligand which remain unaltered in the complexes.

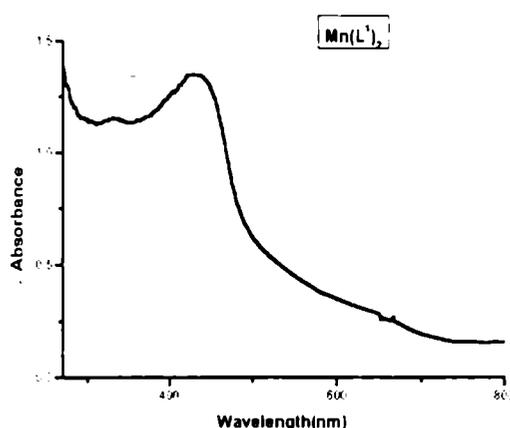


Fig.6.3. Electronic spectrum of compound 17

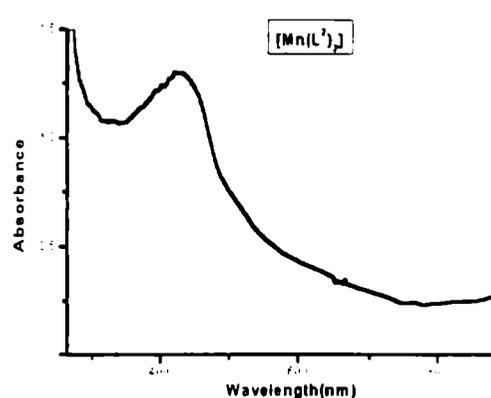


Fig.6.4. Electronic spectrum of compound 18

In the Tanabe-Sugano diagram for d^5 octahedral complexes the ground state ${}^6A_{1g}$ is taken as the abscissa, with the energies of the other states being plotted relative to it. Inter electronic repulsion is expressed in terms of the Racah parameters B and C, which are linear combinations of certain coulomb and exchange integrals pertaining to the uncomplexed ion. The parameter B is usually sufficient to evaluate the difference in energy between states of the same spin multiplicity; however, both the parameters are necessary for terms of different multiplicities [8].

6.3.5. EPR spectra

The high spin Mn(II) has ${}^6S_{5/2}$ ground state term which should not interact with the electric field in the first order case. The spin-Hamiltonian (\hat{H}) for Mn(II) can be defined as

$$\hat{H} = g\beta H_s + D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2)$$

where H is the magnetic field vector, g is the spectroscopic splitting factor, β the Bohr magneton, D is the axial zero field splitting term, E is rhombic zero field splitting parameter and S is the electron spin vector [11].

If D and E are very small, compared with $g\beta H_s$, five EPR transitions should be obtained with g value of ~ 2.0 given by the Bra-Ket notations

$$\begin{aligned} | +5/2 \rangle \leftrightarrow | +3/2 \rangle, & \quad | +3/2 \rangle \leftrightarrow | +1/2 \rangle, & \quad | +1/2 \rangle \leftrightarrow | -1/2 \rangle, & \quad | -1/2 \rangle \leftrightarrow | -3/2 \rangle, \\ | -3/2 \rangle \leftrightarrow | -5/2 \rangle. & \end{aligned}$$

However, only if D is very large, the transition between $| +1/2 \rangle \leftrightarrow | -1/2 \rangle$ will be observed. If D or E is very large, the lowest doublet has effective g value $g_{\parallel} \sim 2.0$, $g_{\perp} \sim 6.0$ for $D \neq 0$ and $E = 0$, but for $D = 0$ and $E \neq 0$ middle Kramer's doublet has an isotropic g value of 4.29. Depending on the values of A and D , the number of lines appear in the spectra are 6, 24 or 30 [12].

For $S = 5/2$ and noting the selection rule $\Delta m_s = \pm 1$, the allowed transitions should arise when field separations are dependent on θ , the angle between the applied magnetic field and the symmetry axis. These transitions are:

$$\Delta m_s = \pm 5/2 \leftrightarrow 3/2; H = H_0 = 2D(3 \cos^2 \theta - 1)$$

$$\Delta m_s = \pm 3/2 \leftrightarrow 1/2; H = H_0 = D(3 \cos^2 \theta - 1)$$

$$\Delta m_s = \pm 1/2 \leftrightarrow -1/2; H = H_0$$

where $H_0 = h\nu / g\beta$ and θ is the angle between the applied magnetic field and the direction of the axial distortion. When the complex is very nearly octahedral only the central $\Delta m_s = -1/2 \leftrightarrow +1/2$ transition will be observed since it

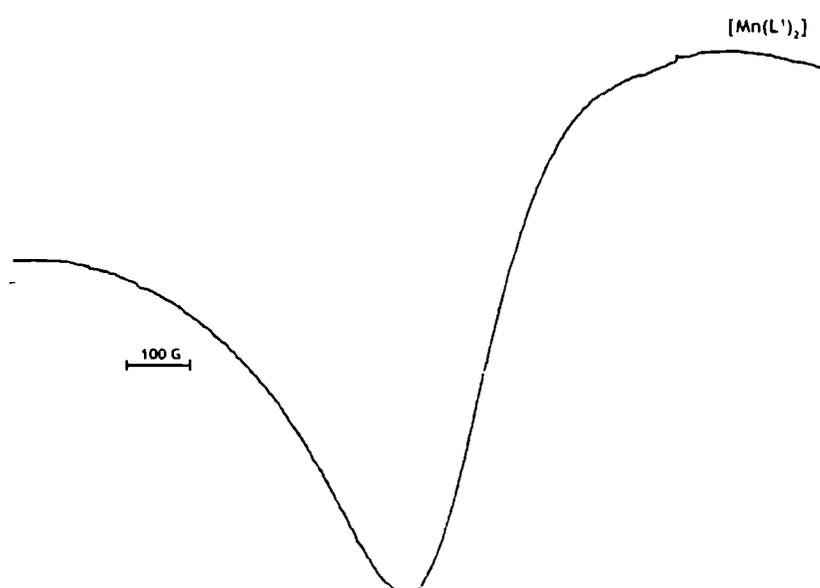


Fig.6.5. EPR spectrum of compound 17 in the polycrystalline state at 298 K

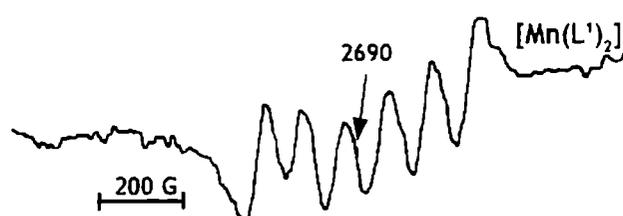


Fig. 6.6. EPR spectrum of compound 17 in DMF at 298 K

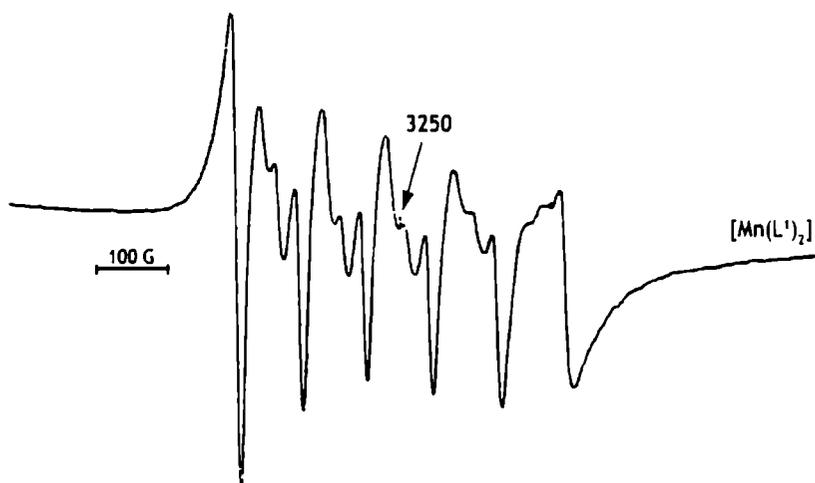


Fig.6.7. EPR spectrum of compound 17 in DMF at 77K

has only a second order dependence on D . This central line will of course be split into a sextet due to electron spin – nuclear spin hyperfine coupling (^{55}Mn , $I=5/2$). In addition to these allowed transitions the frozen solution spectra give low intensity pair of forbidden lines between each pair of hyperfine lines. These lines are due to the simultaneous change of both the electron and nuclear spin by ± 1 . The electron spin- nuclear spin hyperfine coupling constant A has been calculated by taking the average of all the observed lines [13].

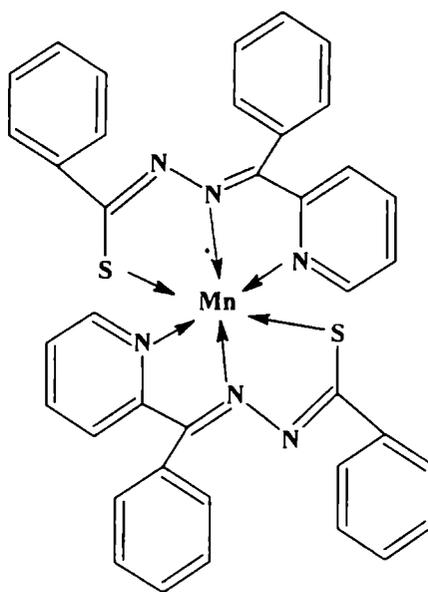
In the EPR spectra of the polycrystalline samples of two Mn(II) complexes at room temperature, a broad signal is observed with g value ~ 2.19 . In polycrystalline samples, at room temperature, Mn(II) complexes give very broad signals, which are due to dipolar interactions and enhanced spin lattice relaxation [14].

The EPR spectra of the two compounds in DMF solution at RT are almost similar exhibiting a six line manganese hyperfine pattern centered at $g = 1.993$ and 2.008 with hyperfine coupling constant $A = 90$ and 88 G respectively. A sextet is

observed in the spectra of the compound **17** in DMF solution at room temperature due to electron spin nuclear spin coupling. This hyperfine spectrum of six lines corresponds to $m_I = \pm 5/2, \pm 3/2, \pm 1/2$, resulting from allowed transitions ($\Delta m_S = \pm 1, \Delta m_I = 0$). This hyperfine lines are not clearly resolved in the spectrum of compound **18**. due to poor glass formation.

In addition to this axial field spectrum a pair of low intensity forbidden lines lying between each of the two main hyperfine lines is observed in the solution spectra of the complex **17** in DMF at 77 K, which is shown in figure 6.7. The forbidden lines in the spectrum arise due to the mixing of the nuclear hyperfine levels by the zero- field splitting factor of the Hamiltonian [15,16]. The g value is 2.005 and the A_{iso} value $84.13 \times 10^{-4} \text{ cm}^{-1}$. The average separation of the forbidden hyperfine lines in the spectrum is $23.36 \times 10^{-4} \text{ cm}^{-1}$.

The observed g values are very close to the free electron spin value of 2.0023 indicating the absence of spin-orbit coupling in the ground state, 6A_1 . It is seen that the A values are somewhat lower than those of the pure ionic compounds. The A_{iso} values are consistent with the octahedral coordination [13] since A_{iso} in tetrahedral sites is 20-25% lower than those in octahedral sites. Based on the spectral studies an octahedral structure can be assigned to the Mn(II) complex as shown in Fig 6.8.

Fig.6.8. Tentative structure for $[Mn(L^2)_2]$

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