4.1. Introduction

Manganese is an essential trace nutrient in all forms of life. Manganese and its compounds find very historical importance in medicine and also have some biological importance. The classes of enzymes that have manganese cofactors are very broad and include such classes as oxidoreductases, transferases, hydrolases, lyases, isomerases, ligases, lectins and integrins. The reverse transcriptases of many retroviruses (though not lentiviruses such as HIV) contain manganese. The best known manganese-containing polypeptides may be arginase, the diphtheria toxin, and Mn-containing superoxide dismutase (Mn-SOD). There has been a growing interest in the chemistry and biochemistry of manganese because of its implication in many biological redox processes [1].

The manganese complexes are used as mimics of Mn-SOD and are more suitable than Cu2Zn2SOD because manganese has a lower toxicity in mammalian systems [2]. Recently, various mononuclear manganese complexes have been selected for pharmaceutical uses [3] such as manganese complexes with Schiff-base ligands [4].
Complexes of manganese play important roles ranging from bioinorganic chemistry to solid state physics [5,6]. They take part in catalytic reactions and also in many biological redox processes, including photosynthetic oxygen evolution in chloroplasts in plants. The most important and primordial example, yet recognized, of manganese involvement in biological milieu is its unique role in the light-induced oxidation of water to molecular oxygen in photosystem II (PS II) of green plants [7,8].

Manganese(II) complexes are well known for their excellent catalytic activity towards the disproportionation of hydrogen peroxide and a number of them have been shown to catalyze the low temperature peroxide bleaching of fabrics [9,10]. They are also interesting due to their catalytic antioxidant activity. Manganese plays a significant role in enzyme activation. Citrate cyclase catalyzes the cleavage of citrate to oxaloacetate and acetate in the presence of manganese(II) or magnesium(II) [11]. In addition, Mn$^{2+}$ has been often used as a substitute for Mg$^{2+}$, which does not have a unique spectroscopic signature [12].

Studies of synthetic mono- and oligomeric manganese model complexes provide important insights into the structure and function of the more complex biological systems. It is thus not surprising that, in the past few years, there has been a tremendous surge in research on the synthesis of various manganese complexes [13-16] and the strategy in the synthesis of the manganese complexes has been to incorporate the nitrogen and oxygen ligands to mimic the functional groups characteristic of the biological milieu. In this context, Schiff bases represent suitable and appropriate biomimetic ligands.

The coordination chemistry of manganese has received a great deal of attention because of the variable structures of manganese complexes and the possibility of magnetic coupling interaction [17-21]. The chemistry of manganese, in various oxidation states of the metal and in various combinations of nitrogen and oxygen donor environment, is presently witnessing intense activity. Manganese in biological systems adopts a range of coordination environments and may have oxidation states of +2, +3, +4 and possibly +5.
This chapter focuses on the syntheses and spectral characterization of manganese(II) complexes of the acylhydrazones.

4.2. Experimental
4.2.1. Materials

All the chemicals and solvents used for the syntheses were of analytical grade. Quinoline-2-carbaldehyde (Aldrich), benzhydrazide (Aldrich), nicotinic hydrazide (Aldrich), manganese(II) acetate tetrahydrate (Merck) and manganese(II) chloride tetrahydrate (Merck) were used as received. Solvents were purified by standard procedures before use.

4.2.2. Syntheses of ligands

Preparation of the ligands HQb and HQn were done as described previously in Chapter 2.

4.2.3. Syntheses of manganese(II) complexes

4.2.3a. Synthesis of $[\text{Mn(HQb)Cl}_2]$ (3)

To a solution of HQb·1.5H$_2$O (0.303 g, 1 mmol) in methanol (20 ml), manganese(II) chloride tetrahydrate (0.198 g, 1 mmol) in methanol (20 ml) was added. The resulting solution was refluxed for 4 h. and then kept at room temperature. The pale yellow precipitate of 3 that separated out was filtered, washed with ether and then dried over P$_4$O$_{10}$ in vacuo. Yield: 52%. $\lambda_m$ (DMF): 15 ohm$^{-1}$ cm$^2$ mol$^{-1}$. $\mu$ (B.M.): 6.13. Elemental Anal. Found (Calcd) %: C, 50.24 (50.90); H, 3.41 (3.27); N, 10.53 (10.47) for [Mn(HQb)Cl$_2$].

4.2.3b. Synthesis of $[\text{Mn(Qb)}_2]$ (4)

Manganese (II) acetate tetrahydrate (0.245 g, 1 mmol) in methanol (20 ml) was added to a solution of HQb·1.5H$_2$O (0.606 g, 2 mmol) in methanol (20 ml). The reaction mixture was refluxed for 3 h, cooled and filtered. The dark blue precipitate obtained was washed with methanol followed by ether and then dried over P$_4$O$_{10}$ in vacuo. Yield: 58%. $\lambda_m$ (DMF): 8 ohm$^{-1}$ cm$^2$ mol$^{-1}$. $\mu$ (B.M.): 5.70.
Elemental Anal. Found (Calcd) %: C, 67.60 (67.66); H, 4.41 (4.01); N, 13.78 (13.92) for [Mn(Qb)₂].

4.2.3c. Synthesis of [Mn(HQn)Cl₂·2H₂O (5)]

HQn·1.5H₂O (0.303 g, 1 mmol) in methanol (20 ml) and manganese(II) chloride tetrahydrate (0.198 g, 1 mmol) in methanol (20 ml) were mixed and refluxed for 4 h. Pale yellow precipitate was obtained. The reaction mixture was cooled and filtered. Then the precipitate was washed with methanol followed by ether and then dried over P₄O₁₀ in vacuo. Yield: 49%. λₘ (DMF): 20 ohm⁻¹ cm² mol⁻¹. μ (B.M.): 5.67. Elemental Anal. Found (Calcd) %: C, 44.27 (43.86); H, 3.59 (3.68); N, 12.93 (12.79) for [Mn(HQn)Cl₂·2H₂O].

4.2.3d. Synthesis of [Mn(Qn)₂] (6)

Manganese acetate tetrahydrate (0.245 g, 1 mmol) in methanol was added to the methanolic solution of HQn·1.5H₂O (0.606 g, 2 mmol). The reaction mixture was refluxed for 2 hours, cooled and filtered. The dark blue precipitate obtained was washed with methanol followed by ether and then dried over P₄O₁₀ in vacuo. Yield: 54%. λₘ (DMF): 10 ohm⁻¹ cm² mol⁻¹. μ (B.M.): 5.91. Elemental Anal. Found (Calcd.) (%): C, 63.57 (63.47); H, 3.26 (3.66); N, 18.30 (18.51) for [Mn(Qn)₂].

4.3. Results and discussion

The common oxidation states of manganese are +2, +3, +4, +6 and +7, though oxidation states from -3 to +7 are observed. It is reported that manganese (II) is the most common among these different oxidation states, which is the state used in living organisms for essential functions. Mn²⁺ often competes with Mg²⁺ in biological systems. Exchange energy favors the high spin configuration. Due to the absence of LFSE of d⁵ configuration, the formation constants of manganese(II) complexes are smaller than those of other first row transition metals.

Here, the reaction of equimolar ratio of the tridentate ligand and the metal salt yielded complexes 3 and 5, whereas reaction of the ligand and metal salt in
ratio 2:1 resulted in metal complexes 4 and 6. Based on the elemental analyses, conductivity measurements and spectral investigations, the complexes were formulated.

The manganese(II) complexes were found to be pale yellow or dark blue in color. Here, the acylhydrazones act as NNO - donor ligands and they can coordinate to the metal in neutral keto form or in anionic enolate form. Analytical data show that in complexes 3 and 5, ligand moiety is in keto form whereas in complexes 4 and 6, enolization of the ligand has taken place.

The molar conductivities of the complexes in DMF (10^-3 M) solution were measured at 298 K with a Systronic model 303 direct-reading conductivity bridge, which show the non-electrolytic nature of the complexes in solution [22]. The magnetic moments of the complexes were calculated from the magnetic susceptibility measurements and the values are found to be in the range 5.6 – 6.2 B.M., which are indicative of a high spin d^5 system. The complexes are found to be EPR active.

4.3.1. Infrared spectra

The IR spectra of the manganese complexes were analyzed in comparison with that of their respective free ligands in the region 4000-100 cm^{-1}.

A comparison of the IR spectra of the ligands and the complexes revealed significant variations in the characteristic bands due to coordination with the central metal ion. It was found that the absorption bands attributed to v(C=O) and v(N–H) in the free ligands, disappeared in the complexes 4 and 6, due to coordination through enolate oxygen. But the presence of these bands in the other two complexes revealed the existence of the ligand in keto form in these complexes [23].

In the IR spectrum of complex 3, the bands due to v(C=O) and v(N–H) are observed at 1630 and 3176 cm\(^{-1}\). The azomethine band is shifted to 1546 cm\(^{-1}\) due to binding with the metal ion. The shifting of the azomethine (C=N) band to a
lower frequency is attributed to the conjugation of the \( p \)-orbital on the double bond with the \( d \)-orbital on the metal ion with reduction of the force constant. The sharp bands at 1492 and 1438 cm\(^{-1}\) are due to the aromatic ring vibrations (Fig. 4.1).

![IR spectrum of \([Mn(Qb)Cl_2]\) (3).](image)

The ligand coordination to the metal centre is substantiated by the bands appearing at 485, 403 and 323 cm\(^{-1}\) which are respectively attributed to \( \nu(Mn–N) \) for azomethine nitrogen, \( \nu(Mn–O) \) for amide oxygen and \( \nu(Mn–N) \) for quinoline nitrogen. In the far IR spectrum of the complex \([Mn(HQb)Cl_2]\) (3), a peak is observed at 303 cm\(^{-1}\), indicating the terminal nature of chlorine atom [24,25].

The band, observed at 1590 cm\(^{-1}\) in the IR spectrum of \([Mn(Qb)_2]\), is assigned to the new \( –C=\text{N}– \) moiety, formed as a result of enolization of the ligand on coordination. The azomethine band experienced a negative shift and is observed at 1547 cm\(^{-1}\). The new band at 1368 cm\(^{-1}\) is assigned to the \( \nu(C–O) \) stretch (Fig. 4.2).
The broad band observed at 3462 cm\(^{-1}\) evidences the presence of lattice water in compound [Mn(HQn)Cl\(_2\)]\(\cdot\)2H\(_2\)O. The bands observed at 1665 and 3203 cm\(^{-1}\) are attributed to \(\nu(C=O)\) and \(\nu(N–H)\) modes. The \(\nu(C=N)\) band is observed at 1562 cm\(^{-1}\) and the aromatic ring vibrations at 1492 and 1438 cm\(^{-1}\) (Fig. 4.3).

In the far IR spectrum of the complex, the bands due to \(\nu(Mn–N)\) for azomethine nitrogen, \(\nu(Mn–O)\) for amide oxygen and \(\nu(Mn–N)\) for quinoline nitrogen appear at 489, 410 and 321 cm\(^{-1}\), respectively. The band observed at 305 cm\(^{-1}\) indicates the presence of terminal Mn–Cl stretching frequency.

In the IR spectrum of [Mn(Qn)_2], the bands due to \(\nu(C=O)\) and \(\nu(N–H)\) are absent and the azomethine band due to coordination with Mn(II) is shifted to 1548 cm\(^{-1}\). The \(\nu(C–O)\) band is observed at 1352 cm\(^{-1}\) and the band due to the newly formed \(-C=N-\)group is found at 1585 cm\(^{-1}\). The characteristic ring vibrations were seen in the usual region (Fig. 4.4). The selected IR bands of the hydrazones and complexes are represented in Table 4.1.
Fig. 4.3. IR spectrum of [Mn(HQn)Cl₂]·2H₂O (5).

Fig. 4.4. IR spectrum of [Mn(Qn)₂] (6).
Table 4.1. Infrared spectral data of the hydrazones and their manganese(II) complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$v$(C=O) cm$^{-1}$</th>
<th>$v$(N–H) cm$^{-1}$</th>
<th>$v$(C=N) cm$^{-1}$</th>
<th>$v$(C=N)$^a$ cm$^{-1}$</th>
<th>$v$(C–O) cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HQb·1.5H$_2$O</td>
<td>1655</td>
<td>3193</td>
<td>1593</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>[Mn(HQb)Cl$_2$] (3)</td>
<td>1630</td>
<td>3176</td>
<td>1546</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>[Mn(Qb)$_2$] (4)</td>
<td>----</td>
<td>----</td>
<td>1547</td>
<td>1590</td>
<td>1347</td>
</tr>
<tr>
<td>HQn·1.5H$_2$O</td>
<td>1656</td>
<td>3173</td>
<td>1591</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>[Mn(HQn)Cl$_2$·2H$_2$O (5)</td>
<td>1665</td>
<td>3203</td>
<td>1562</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>[Mn(Qn)$_2$] (6)</td>
<td>----</td>
<td>----</td>
<td>1548</td>
<td>1585</td>
<td>1352</td>
</tr>
</tbody>
</table>

$^a$ Newly formed C=N.

4.3.2. Electronic spectra

The Mn(II) complexes belong to the $d^5$ system. The Tanabe-Sugano diagram shows that the Russell-Saunders term for such a system in high spin state is $^6S$ and the ground state of high-spin octahedral Mn(II) complex is $^6A_{1g}$. The $d^5$ configuration gives rise to the $^4G$, $^4D$ and $^4P$ excited states.

As there are no excited terms of sextet spin multiplicity, spin allowed $d$-$d$ transitions are not expected. Also for octahedral complexes, these transitions are Laporte forbidden. So the $d$-$d$ transitions in a high spin octahedral Mn(II) complexes are doubly forbidden; Laporte forbidden and spin forbidden [26-28]. However, some forbidden transitions occur and consequently, these transitions have an extremely low molar extinction coefficient value.

The electronic spectra of the Mn(II) complexes were recorded both in acetonitrile and DMF, in the region 50000-11000 cm$^{-1}$. The spectra, within the range 45000-20000 cm$^{-1}$ recorded in acetonitrile, are shown in Figs. 4.5 and 4.6.
**Fig. 4.5.** Electronic spectra of manganese(II) complexes of HQb·1.5H₂O.

**Fig. 4.6.** Electronic spectra of manganese(II) complexes of HQn·1.5H₂O.
The high intense intraligand transitions and charge transfer transitions, tailing into the visible region, obscure the very weak d-d transitions of the manganese(II) complexes. In all the complexes, a high intense transition is observed at ca. 24000 cm⁻¹ which is assumed to be due to the ligand to metal charge transfer (LMCT) transition.

For octahedral Mn(II) complexes, electronic spectra show two bands at ca. 18000 and 20000 cm⁻¹, which are assigned to $^{4}T_{1g} (G) \leftarrow ^{6}A_{1g}$ and $^{4}T_{2g} (G) \leftarrow ^{6}A_{1g}$ respectively. These assignments are obtained by fitting the observed spectrum to the Tanabe Sugano diagram and for $d^{5}$ octahedral complex, 

$$\frac{Dq}{B} = 1.1.$$  

At this $\frac{Dq}{B}$, the ratio of the first transition energy and B (ie, $\frac{E}{B}$) is found to be 24.0. The electronic repulsion parameter (Racah parameter), B, is a function of the ligand and the metal ion and is a built in feature of these Tanabe Sugano diagrams [29].

The extent of covalence in metal-ligand bond may be evaluated from the electronic spectrum by estimating the nephelauxetic ratio ($\beta = \frac{B}{B_o}$). The free ion value of $B_o$ for octahedral Mn²⁺ is 860 cm⁻¹. The value of $\beta$ decreases with increase in delocalization [26].

The electronic spectra of the manganese(II) complexes [Mn(HQb)Cl₂] (3) and [Mn(HQn)Cl₂]·2H₂O (5) exhibit weak-intensity absorption bands at ca. 18000, 22000 and 27000 cm⁻¹, which may be assigned to the transitions: $^{4}T_{1g} (G) \leftarrow ^{6}A_{1g}$, $^{4}A_{1g} (G), ^{4}E_{g} (G) \leftarrow ^{6}A_{1g} (10B+5C), ^{4}E_{g} (D) \leftarrow ^{6}A_{1g} (17B+5C)$.

The ligand field parameter B and C values have been calculated by using the second and third transition energies. This is due to the fact that the energies of these two transitions are independent from the crystal field splitting energy and
depends only on the parameters $B$ and $C$ \cite{30,31}. Electronic spectral data for the hydrazones and their manganese(II) complexes are given in Table 4.2.

### Table 4.2. Electronic spectral data for the hydrazones and their manganese(II) complexes, recorded in acetonitrile and in DMF.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorbance $\lambda_{\text{max}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HQb·1.5H$_2$O</td>
<td>43790, 41640, 35860, 32580, 31690, 30430, 29130</td>
</tr>
<tr>
<td>[Mn(HQb)Cl$_2$] (3)</td>
<td>35660, 34770, 31540, 30150, 28960, 26750, 24580, 21550, 17360.</td>
</tr>
<tr>
<td>[Mn(Qb)$_2$] (4)</td>
<td>42250, 40600, 37310, 33510, 31080, 29800, 24530, 20170, 17100,</td>
</tr>
<tr>
<td>HQn·1.5H$_2$O</td>
<td>43920, 41490, 35840, 32580, 31750, 30440, 29150</td>
</tr>
<tr>
<td>[Mn(HQn)Cl$_2$]·2H$_2$O (5)</td>
<td>43860, 42700, 36520, 32900, 32240, 30960, 29680, 27190, 25230, 22410, 18990</td>
</tr>
<tr>
<td>[Mn(Qn)$_2$] (6)</td>
<td>42410, 41630, 40640, 39530, 37510, 33350, 31000, 29720, 25600, 20500, 19100.</td>
</tr>
</tbody>
</table>

The $Dq$ value has been evaluated with the help of curve, transition energies vs. $Dq$, by Orgel \cite{32} using the energy due to the transition $^{4}T_{1g} \leftarrow ^{6}A_{1g}$.

Parameters $B$ and $C$ are linear combination of certain Coulomb and exchange integrals and are generally treated as empirical parameters obtained from the spectra of the free ions. Slater Condon–Shortly parameters $F_2$ and $F_4$ are related to the Racah inter-electronic repulsion parameters $B$ and $C$, as follows: $B = F_2 - 5F_4$ and $C = 35F_4$ \cite{33}.

The ligand field parameters of the complexes are given in Table 4.3.

### Table 4.3. Ligand field parameters of manganese(II) complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$B$</th>
<th>$C$</th>
<th>$F_2$</th>
<th>$F_4$</th>
<th>$10Dq$ (A)</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mn(HQb)Cl$_2$] (3)</td>
<td>742.8</td>
<td>2824.4</td>
<td>1146.3</td>
<td>80.7</td>
<td>-----</td>
<td>0.95</td>
</tr>
<tr>
<td>[Mn(Qb)$_2$] (4)</td>
<td>712.5</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>7837.5</td>
<td>0.83</td>
</tr>
<tr>
<td>[Mn(HQn)Cl$_2$]·2H$_2$O (5)</td>
<td>682.9</td>
<td>3116.2</td>
<td>1127.9</td>
<td>89.0</td>
<td>-----</td>
<td>0.87</td>
</tr>
<tr>
<td>[Mn(Qn)$_2$] (6)</td>
<td>795.8</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>8754.2</td>
<td>0.92</td>
</tr>
</tbody>
</table>
4.3.3. Electron paramagnetic resonance spectroscopy

The electron spin properties of manganese have long been of interest as a spectroscopic probe of manganese centers in manganese proteins. The Mn(II) system possesses Kramer’s ground-state doublets and exhibits characteristic spin transitions in the normal mode X-band regime.

The spin Hamiltonian,

\[ \hat{H} = g\beta BS + D \left( S^2 - \frac{S(S+1)}{3} \right) + E \left( S^x - S^y \right) \]

may be used to describe the EPR spectra of Mn(II) complexes. In the expression, \( B \) is the magnetic field vector, \( g \) is the spectroscopic splitting factor, \( \beta \) is the Bohr magneton, \( D \) is the axial zero field splitting parameter, \( E \) is rhombic zero field splitting parameter and \( S \) is the electron spin vector [34].

If \( D \) and \( E \) are both zero, then the only contributor to the spectrum is the first-order Zeeman term and the result for Mn\(^{2+}\) is an isotropic spectrum, with a single six-line signal with \( g_{\text{eff}} \) near 2.0. In weak ligand fields, Mn(II) centers give a single transition at \( g = 2 \), which splits into six hyperfine lines by the \(^{55}\)Mn nucleus (\( I = 5/2 \)). However, simple spectra of this type are indicative of a cubic ligand field where the zero-field splitting parameter \( D \) is negligible and all of the \( \Delta M_s = \pm 1 \) transitions are degenerate, as a result. For a small but finite value for \( D \) and \( E \), the degeneracy is removed and the spectrum exhibits 5-fold fine structure with a \( g \) value of 2.0.

If \( D \) is very large, only one transition is expected. However, for the case where \( D \) or \( E \) is very large, the lowest doublet has effective \( g \) values of \( g_\| = 2 \) and \( g_\perp = 6 \) for \( D \neq 0 \) and \( E = 0 \) but for \( D = 0 \) and \( E \neq 0 \), the middle Kramer’s doublet has an isotropic \( g \) value of 4.29.

In more strongly axial systems where \( D \) is comparable to \( \hbar \nu \), high-spin \( d^5 \) ions such as Mn\(^{2+}\) often exhibit tetragonal spectra with \( g_\perp \approx 6 \) and \( g_\| = 2 \), a situation observed for many porphyrin, phthalocyanin and related complexes of Mn\(^{2+}\).
Depending on the values of $D$ and $A$, the number of lines observable in the spectra will be 30, 24 or 6. As delocalization increases, $A$ value decreases. When $2D > 5A$, 30 lines will be obtained; when $2D = 5A$, overlapping occurs and we get only 24 lines. When $2D < 5A$, the number of lines still decreases and when $D = 0$, we will see only six lines [35,36].

Ligand fields of lower symmetry are often characterized by a rhombic signal at $g = 4.3$, but this is typically observed for relatively strong field ligands.

The X-band EPR spectra of the manganese complexes were recorded in polycrystalline state at 298 K and in frozen DMF at 77 K. The EPR spectrum of the compound [Mn(HQb)Cl$_2$] (3) at 298 K in polycrystalline state exhibited two $g$ values at $g_1 = 1.984$ and $g_2 = 3.120$, with no hyperfine splitting (Fig. 4.7). The spectrum is very broad due to dipolar interactions and enhanced spin lattice relaxation.

![EPR spectrum](image)

**Fig. 4.7.** EPR spectrum of [Mn(HQb)Cl$_2$] (3) in polycrystalline state at 298 K.
The solution spectrum (Fig. 4.8) of the compound in DMF at 77 K displayed a hyperfine sextet with $g = 2.018$ and hyperfine coupling constant $69.0 \times 10^{-4}$ cm$^{-1}$. The hyperfine structure results from a transition from the $|\frac{-1}{2}, M_I>\text{ to } |\frac{1}{2}, M_I>$ level, where the $-\frac{1}{2}$ and $+\frac{1}{2}$ denote the electron spin magnetic quantum numbers and $M_I$, the nuclear spin quantum number. The hyperfine spectrum of the compound consists of six allowed lines corresponding to $M_s = +5/2, +3/2, +1/2, -1/2, -3/2, -5/2$ with $\Delta M_I = 0$ in the transition. The observed $g$ value is very close to the free electron spin value of 2.0023, which is consistent with the typical manganese(II) system and also suggestive of the absence of spin orbit coupling in the ground state $^6A_{1g}$ without another sextet term of higher energy.

Fig. 4.8. Simulated and experimental best fits of the EPR spectrum of [Mn(HQb)Cl$_2$] (3) in DMF at 77 K.
EPR spectrum of [Mn(Qb)$_2$] (4) in polycrystalline state at 298 K exhibits three $g$ values; $g_1 = 1.802$, $g_2 = 2.386$, $g_3 = 3.565$ (Fig. 4.9). The three $g$ values imply that the molecule is rhombically distorted. The signals are comparatively broad with no hyperfine splitting. The broadness of the peaks is a characteristic feature of Mn(II) complex in the polycrystalline state, which arises due to dipolar interactions and enhanced spin lattice relaxation [36].

The compound [Mn(Qb)$_2$] in DMF at 77 K displays three $g$ values at $g_1 = 1.803$, $g_2 = 2.368$ and $g_3 = 3.310$.

A broad isotropic signal with $g_{iso} = 2.053$ was found for the compound [Mn(HQn)Cl$_2$]·2H$_2$O (5) in polycrystalline state at 298 K and the hyperfine structure is not observed in the spectrum (Fig. 4.10).

![EPR spectrum of [Mn(Qb)$_2$] in polycrystalline state at 298 K.](image)

Fig. 4.9. EPR spectrum of [Mn(Qb)$_2$] (4) in polycrystalline state at 298 K.
In DMF at 77 K, the EPR spectrum of \([\text{Mn(HQn)Cl}_2\cdot 2\text{H}_2\text{O}}\) is isotropic with \(g_{\text{iso}} = 1.996\). The spectrum exhibits sixfold well-resolved hyperfine splitting pattern with the coupling constant \(A_{\text{iso}} = 96 \times 10^{-4} \text{ cm}^{-1}\) (Fig. 4.11).

Due to the interaction of the unpaired electron with the \(\text{Mn(II)}\) nucleus \((I = 5/2)\), a hyperfine sextet \((2nI+1\text{ lines})\) observed corresponds to \(\Delta M_s = \pm 1\) and \(\Delta M_I = 0\). But due to the nuclear quadrupole effect, the forbidden lines corresponding to \(\Delta M_I = \pm 1\) transitions may arise. This is observed in the EPR spectrum of \([\text{Mn(HQn)Cl}_2\cdot 2\text{H}_2\text{O}}\) in DMF at 77 K as a pair of low intensity lines in between each of the two main hyperfine lines. According to Bleaney and Low, such forbidden transitions are brought about by the mixing of the nuclear hyperfine levels by the zero field splitting parameter \(D\) [37-40].
Fig. 4.11. Simulated and experimental best fits of the EPR spectrum of [Mn(HQn)Cl₂]·2H₂O (5) in DMF at 77 K.

The EPR spectrum of [Mn(Qn)₂] (6) in polycrystalline state at 298 K gave two g values; g₁ = 1.991 and g₂ = 2.773. The spectrum is broad with no hyperfine splitting (Fig. 4.12).

Fig. 4.12. EPR spectrum of [Mn(Qn)₂] (6) in polycrystalline state at 298 K.
The compound [Mn(Qn)2] (6) displayed four g values viz. 2.034, 2.421, 3.181 and 4.920 for the frozen solution spectrum in DMF at 77 K. The hyperfine splitting constant, $A$, calculated for the hyperfine sextet in the high field region is $117.7 \times 10^{-4}$ cm$^{-1}$.

### 4.3.4. Cyclic voltammetry

Cyclic voltammograms were recorded on a CHI II20A electrochemical analyzer with a three electrode compartment consisting of a platinum disc working electrode, platinum wire counter electrode and Ag/Ag$^+$ reference electrode. The solutions of complexes in DMF have been used to study the electrochemical properties using TBAP (tetrabutylammonium phosphate) as the supporting electrolyte. The voltammogram is run between the potentials of +2000 and –2000 mV at a scan speed of 100 mV/s. Cyclic voltammetric data for the hydrazones and their Mn(II) complexes are tabulated in Table 4.4.

**Table 4.4.** Cyclic voltammetric data for the hydrazones and their Mn(II) complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{pc}$ / mV ($I_{pc}$ / µA)</th>
<th>$E_{pa}$ / mV ($I_{pa}$ / µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HQb·1.5H$_2$O</td>
<td>-220 (0.91)</td>
<td>520 (3.48)</td>
</tr>
<tr>
<td>[Mn(HQb)Cl$_2$] (3)</td>
<td>147 (3.32), -499 (5.60)</td>
<td>539 (4.46)</td>
</tr>
<tr>
<td>[Mn(Qb)$_2$] (4)</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>HQn·1.5H$_2$O</td>
<td>-280 (1.83)</td>
<td>830 (13.8)</td>
</tr>
<tr>
<td>[Mn(HQn)Cl$_2$]·2H$_2$O (5)</td>
<td>-134 (0.75), -761 (0.94)</td>
<td>-----</td>
</tr>
<tr>
<td>[Mn(Qn)$_2$] (6)</td>
<td>-98 (0.47), -60 (1.20)</td>
<td>790 (1.71), -60 (1.20)</td>
</tr>
</tbody>
</table>

The complex [Mn(HQb)Cl$_2$]·2H$_2$O (3) displays two reductive responses, viz 147 mV (3.32 µA), -499 mV (5.60 µA). The oxidative peak at 539 mV (4.46 µA), which is very close to the oxidative response of the corresponding ligand, is attributed to the ligand based oxidation reaction. The absence of the metal centered oxidative peak in the complex may be due to the presence of more...
electronegative chlorine atoms attached to the metal ion. Generally, the presence of an electron withdrawing group stabilizes the lower oxidation state and electron donating group favors the higher oxidation state of the metal centre. Electronegative chlorine lowers the electron density on the manganese ion and oxidation of the Mn(II)-Mn(III) becomes more difficult [41].

The cyclic voltammogram of complex [Mn(Qn)2] (4) was of poor quality and cannot be interpreted.

In the cyclic voltammogram of complex [Mn(HQn)Cl2]·2H2O (5), two reductive responses were observed at -134 mV (0.75 µA) and -761 mV (0.94 µA) and oxidative response was absent.

In the cyclic voltammogram of complex [Mn(Qn)2] (6), one reductive response was observed at -98 mV (0.47 µA) and two oxidative responses at 790 mV (1.71 µA) and -60 mV (1.20 µA). The oxidative peak at 790 mV may be due to the ligand based reaction.

Figs. 4.13 - 4.15 illustrate cyclic voltammograms of manganese complexes, [Mn(HQb)Cl2], [Mn(HQn)Cl2]·2H2O (5) and [Mn(Qn)2] (6).

**Fig. 4.13.** Cyclic voltammogram of [Mn(HQb)Cl2] (3) in DMF at 100 mV s⁻¹.
Fig. 4.14. Cyclic voltammogram of [Mn(HQn)Cl2]·2H2O (5) in DMF at 100 mV s⁻¹.

Fig. 4.15. Cyclic voltammogram of [Mn(Qn)2] (6) in DMF at 100 mV s⁻¹.
Chapter -4

References

Syntheses and Spectral Investigations of Manganese(II) Complexes of Acylhydrazone


[40] E. Friedman, W. Low, Phys. Rev. 120 (1960) 408.


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