Syntheses, characterization and non-linear optical properties of manganese(II) and iron(III) complexes of the aroylhydrazone ligands

The element manganese is relatively abundant, constituting about 0.085% of the earth’s crust. Over 90% of all the manganese ores produced are used in steel manufacture, mostly in the form of ferromanganese. Manganese coordination chemistry with a diverse range of ligands has much relevance in biological systems with a number of model manganese complexes. Low nuclearity species have been studied extensively as models for the water-oxidizing complex in photosystem II, whereas nanometer-size clusters with high spin ground states are being investigated as single molecule magnets [1-3]. Manganese coordination compounds are also of growing importance as homogeneous catalysts in oxidation reactions [4-7]. The manganese porphyrins are very efficient catalysts for fractionalization of hydrocarbons in processes that involve high valent intermediates [8-9]. Manganese is identified in metalloenzymes such as oxygen evolving centre of photosystem-II, catalyses and superoxide dismutases [10-12]. Manganese complexes are also studied for their magnetic behavior. Cubane like Mn(II) complexes of di-2-pyridyl ketone in the gem-diol form are reported with single crystal X-ray structural analyses and this complex is observed to be antiferromagnetic [13]. 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 [14-16]. This is because manganese plays a major key role in many biological redox processes, including water oxidation complex in photosystem II [17-18], decomposition of O2
Manganese(II) and iron(III) complexes

radicals catalyzed by superoxide dismutases (SOD's) and disproportionation of hydrogen peroxide (catalase activity) in microorganisms, a reaction which is important for cell detoxification.

Iron (Fe) is a crucial component of a variety of metabolic pathways that are involved in DNA synthesis [19] and the production of energy. Despite the industrial and biological importance of iron containing systems, the coordination chemistry of the metal has been sadly neglected except a few examples. A considerable number of compounds were studied in earlier seventies and the relevant references may be found in the book by Sidgwick [20] and in the treatises by Gmelin [21] and Mellor [22]. This comparative lack of interest has been especially marked in the case of iron(III), largely owing to the properties of the $d^8$ ion. Recently, Richardson et al. identified a number of novel Fe-chelating agents of the pyridoxal isonicotinoylhydrazone (PIH) class that demonstrate high activity at inhibiting the growth of a range of tumor cells, including NB, leukemia, and melanoma cell lines (23-25). But only a few of examples of manganese and iron coordinated complexes were reported yet in the field of non-linear optics. This may be due to the greater chance of octahedral coordination environment among these metals and which leads to a molecular lattice having centre of symmetry.

5.1. Stereochemistry of Mn(II) complexes

The common oxidation states of manganese are +2, +3, +4, +6 and +7, though oxidation states from +1 to +7 are observed. The most common and stable oxidation state of manganese is +2. Majority of manganese complexes are high spin paramagnetic $d^5$ systems and are intensely colored. The manganese complexes of all the three ligands were synthesized and three of them were six coordinated and octahedral.
5.2. **Stereochemistry Fe(III) complexes**

The most common oxidation states of iron coordination complexes are +2 and +3. Iron(III) complexes usually exist in six coordinated and octahedral environments. Here we have synthesized three iron complexes of each of the three ligands and the studies of all of them showed the possibility of six coordinated environment around the iron centre.

5.3. **Experimental**

5.3.1. **Materials**

4-Nitrobenzoylhydrazide (Sigma Aldrich), 4-N,N-diethylamino-2-hydroxybenzaldehyde (Sigma Aldrich), 4-methoxy-2-hydroxybenzaldehyde (Sigma Aldrich), 4-methoxy-2-hydroxyacetophenone (Sigma Aldrich), manganese acetate (Merck), ferric chloride (Merck), DMF (S.D. Fine) were used as received. When ethyl alcohol was used as the solvent repeated distillation was carried out before use.

5.3.2. **Syntheses of ligands**

Preparation of the ligands H₂L¹, H₂L² and H₂L³ were done as described previously in Chapter 2.

5.3.3. **Preparation of manganese(II) complexes**

\([\text{Mn(HL}^1\text{)}_2\text{]}\cdot 3\text{H}_2\text{O (25): The complex was prepared by refluxing a mixture of the ligand H}_2\text{L}^1\text{ (0.748 g, 2 mmol) and manganese acetate (0.245 g, 1 mmol) in a 1:1 mixture of absolute ethanol and DMF. The solution was then refluxed for about two hours. The dark red product obtained was filtered, washed with absolute alcohol and...}

151
Manganese(II) and iron(III) complexes

finally with diethyl ether and dried over $\text{P}_4\text{O}_{10}$ in vacuo. Yield: 0.537 g (65.6%). Elemental Anal. Found (Calcd.) (%): C, 52.26 (52.75); H, 5.62 (5.41); N, 13.35 (13.67).

$[\text{Mn}(\text{HL}_2)_2]$ (26): To a boiling solution of the ligand $\text{H}_2\text{L}_2$ (0.630 g, 2 mmol) in a 1:1 mixture of absolute ethanol and DMF, a solution of manganese acetate (0.245 g, 1 mmol) was added and refluxed for about two hours. The orange red product obtained by cooling the solution to room temperature was filtered, washed several times with absolute ethanol and finally with diethyl ether and dried over $\text{P}_4\text{O}_{10}$ in vacuo. Yield: 0.476 g (69.9%). Elemental Anal. Found (Calcd.) (%): C, 53.38 (52.87); H, 3.74 (3.25); N, 12.36 (12.33).

$[\text{Mn}(\text{HL}_3)_2] \cdot 3\text{H}_2\text{O}$ (27): The complex was prepared by the same procedure described above by using solutions of the ligand $\text{H}_2\text{L}_3$ (0.658 g, 2 mmol) and manganese acetate (0.249 g, 1 mmol). The red colored product obtained was filtered, washed several times with ethanol, finally with diethyl ether and dried over $\text{P}_4\text{O}_{10}$ in vacuo. Yield: 0.492 g (64.2%). Elemental Anal. Found (Calcd.) (%): C, 50.05 (50.20); H, 3.51 (4.48); N, 10.95 (10.98).

5.3.4. Preparation of iron(III) complexes

$[\text{Fe}(\text{HL}_1)(\text{L}_1)] \cdot \text{H}_2\text{O}$ (28): Ferric chloride (0.162 g, 1 mmol) dissolved in ethanol was added to a solution of the ligand $\text{H}_2\text{L}_1$ (0.748 g, 2 mmol) in a 1:1 ethanol and DMF, and refluxed for four hours. The black shining product formed was filtered, washed with ether and dried over $\text{P}_4\text{O}_{10}$ in vacuo. Yield: 0.381 g (48.5%). Elemental Anal. Found (Calcd.) (%): C, 55.32 (55.18); H, 4.76 (5.02); N, 14.11 (14.30).

152
[Fe(HL\textsuperscript{2})(L\textsuperscript{2})]. 3H\textsubscript{2}O (29): A solution of ferric chloride (0.162 g, 1 mmol) in ethanol was added to a solution of H\textsubscript{2}L\textsuperscript{1} (0.630 g, 2 mmol) in a 1:1 ethanol and DMF and refluxed continuously for about five hours. Brown colored crystalline products separated out were filtered, washed with ethanol followed by ether and dried over P\textsubscript{2}O\textsubscript{10} in vacuo. Yield: 0.368 g (49.8%). Elemental Anal. Found (Calcd.) (%): C, 49.45 (48.80); H, 4.62 (4.09); N, 12.07 (11.38).

[Fe(HL\textsuperscript{1})(L\textsuperscript{3})]. 2H\textsubscript{2}O (30): Preparation of [Fe(HL\textsuperscript{1})(L\textsuperscript{3})] was carried out by the same procedure as that of compound 29 above, except that a 1:1 ethanol/DMF solution of H\textsubscript{2}L\textsuperscript{1} (0.658 g, 2 mmol) was used instead of H\textsubscript{2}L\textsuperscript{2}. The reddish brown product formed was washed several times with ethanol and finally with ether and dried over P\textsubscript{2}O\textsubscript{10} in vacuo. Yield: 0.318 g (42.5%). Elemental Anal. Found (Calcd.) (%): C, 51.68 (51.42); H, 4.39 (4.18); N, 11.02 (11.24).

5.4. Results and discussion

5.4.1. Spectral studies of manganese(II) complexes

5.4.1a. Electronic spectral studies

The ground state of high-spin octahedral Mn(II) complex is \( ^6A_{1g} \). As there are no other terms of sextet spin multiplicity, spin allowed \( d-d \) transitions are not expected. However, some forbidden transitions occur such as \( ^6A_{1g} \rightarrow ^4A_{1g} (G), ^4E_g (G), ^6A_{1g} \rightarrow ^4E_g (D), ^6A_{1g} \rightarrow ^4T_{1g} (G), ^4T_{2g} (G) \) [26]. Thus, for a \( d^8 \) octahedral complex, all transitions are not only Laporte-forbidden but also spin-forbidden. Absorptions associated with doubly forbidden transitions are extremely weak, with extinction coefficients several hundred times smaller than those for singly forbidden transitions.
The combined UV-Vis spectra of all the manganese(II) complexes have been shown in the Fig. 5.1. The intensity of electronic absorption of the complex 25 is high compared to 26 and 27. But the pattern of absorption of all the manganese complexes is found to be very similar. The strong and broad absorption band seen in all the spectra ca. 400 – 550 nm is assigned to be due to the ligand to metal charge transfer the forbidden d-d transitions in the manganese complexes. There are weak absorptions in 280 – 380 nm regions due to absorptions in the ligand molecule, both π → π* and n → π* transitions.

Fig. 5.1. The UV-Vis absorption spectrum of the manganese(II) complexes 25, 26 and 27 in DMF.

5.4.1b. Infrared spectral studies

The single crystals suitable for X-ray crystallographic studies were not able to isolate in the case of manganese complexes, and so infrared spectroscopy plays an important role for assigning the coordination pattern in these complexes. A careful
comparison of the infrared spectra of the ligand and the complex reveals the mode and pattern of coordination in the complex examined. In the case of the complex, [Mn(HL\(^1\)]\(_2\)·3H\(_2\)O (25), the free ligand exhibit bands at 3000-3600 cm\(^{-1}\), comprising of the OH and NH stretching absorptions, 1631 cm\(^{-1}\) - the amide I band - and 1594 cm\(^{-1}\) - the amide II band. In the IR spectrum of 25, there is an absorption at ca. 3500 cm\(^{-1}\) may be due to the presence of lattice water and a very small downward shift of amide I and amide II bands to 1628 and 1593 cm\(^{-1}\) respectively, suggesting that the ligands exist in the keto form in this complex. Whether the coordination is in enol form, both the amide I and amide II absorptions will disappear. The coordination of the azomethine nitrogen atom to the metal ion is indicated by the displacement of the bands chiefly assigned to the \(\nu(N-N)\) and \(\nu(C=\!N)\) stretching vibrations. The spectrum shows downward shift of \(\nu(N-N)\) from 1070 to 1060 cm\(^{-1}\) and \(\nu(C=\!N)\) from 1518 to 1490 cm\(^{-1}\). Similarly the complexes 26 and 27 also showed similar shifts in the infrared spectral bands from the corresponding ligand.

![Fig. 5.2. The IR spectrum of the compound [Mn(HL\(^3\)]\(_2\)·3H\(_2\)O (27).](image-url)
In the case of 26, a band in the region of 3200-3600 cm\(^{-1}\) is seen, showing the presence of NH group in the keto form of the ligand. Here the coordination through azomethine nitrogen is confirmed by the downward shifting of absorptions due to \(v(\text{N}=\text{N})\) and \(v(\text{C}=\text{N})\) from 1013 cm\(^{-1}\) and 1549 cm\(^{-1}\) to 976 cm\(^{-1}\) and 1527 cm\(^{-1}\) respectively. In the case of the complex 27, the bands shifted from 1032 cm\(^{-1}\) and 1560 cm\(^{-1}\) to 984 cm\(^{-1}\) and 1526 cm\(^{-1}\) respectively. So the coordination pattern around Mn(II) ion in these complexes are confirmed to be octahedral through, azomethine nitrogen, deprotonated phenolic oxygen and double bonded carbonyl oxygen of the either ligand molecules. The infrared absorption spectrum of the complex \([\text{Mn(HL}^\text{3})_2]\cdot 3\text{H}_2\text{O} (27)\) is shown the Fig. 5.2. In the far-infrared region, the Mn(II) complexes exhibit bands at 440, 430 and 340 cm\(^{-1}\), which are assigned to \(v(\text{M}=\text{O})\) phenolic, \(v(\text{M}=\text{N})\) and \(v(\text{M}=\text{O})\) ketonic [27] bands respectively.

5.4.1c. EPR spectral studies

A series of examples have been reported to explain the electron paramagnetic spectral behaviour of Mn(II) complexes [28-29]. The magnetic susceptibility measurements of the manganese complexes showed that all are paramagnetic with a spin value of 5/2, having five unpaired electrons. It confirms the conclusion that all the manganese complexes are high spin \(d^5\) systems. The \(\mu_{\text{eff}}\) values of all the manganese complexes are in the range of 5.9 - 6.1 B.M, typical for high spin \(d^5\) configuration.

The spin Hamiltonian for the high spin Mn(II) is expressed as:

\[\mathcal{H} = g \beta HS + D[S^2 - S(S+1)/3] + E(S_x^2 - S_y^2)\]

where \(H\) is the magnetic field vector, \(D\) is the axial zero field splitting term, \(E\) is the rhombic zero field splitting parameter. If \(D\) and \(E\) are very small compared to \(g \beta HS\), five ESR transitions corresponding to \(\Delta m_s=\pm 1\) are expected with a \(g\) value of 2.0. But
if $D$ is very large, then only transition between $\left| +1/2 \right\rangle \leftrightarrow \left| -1/2 \right\rangle$ will be observed. However, for the case where $D$ or $E$ is very large, the lowest doublet has effective $g$ values of $g_{\parallel} = 2$, $g_{\perp} = 6$ for $D \neq 0$ and $E = 0$ but for $D = 0$ and $E \neq 0$, the middle Kramers doublet has an isotropic $g$ value of 4.29 [30-31].

The electron paramagnetic resonance spectrum of the complex $[\text{Mn}(\text{HL}^1)_2] \cdot 3\text{H}_2\text{O}$ (25) was recorded both in powder state at room temperature and in DMF solution at 77 K. The powder state EPR spectrum is found to be very broad and isotropic in nature without any hyperfine splitting pattern due to the magnetically concentrated environment around the metal atom.

![EPR Spectrum](image)

Fig. 5.3. The EPR spectrum of $[\text{Mn}(\text{HL}^1)_2] \cdot 3\text{H}_2\text{O}$ (25) in DMF at 77 K.
Manganese(II) and iron(III) complexes

The $g_{\text{iso}}$ value of the powder state EPR is 2.061, very close to the free electron $g$ value. However, the solution spectrum in DMF at 77 K (Fig. 5.3), displayed a pattern having two $g$ values, $g_1 = 1.991$ and $g_2 = 2.884$. The expected hyperfine sextet is found only for the signal in the high field region. The observance of hyperfine sextet is as expected due to the interaction of the unpaired electron with the Mn(II) nucleus of spin $I = 5/2$, resulting in $2nI+1$ lines. Thus the six lines observed corresponds to $m_s = +5/2, +1/2, ... -5/2$ with $\Delta m_l = 0$.

A pair of low intensity lines is found in between each of the two main hyperfine lines. These are the forbidden lines corresponding to $\Delta m_l = \pm 1$, transitions arising due to the nuclear quadrupole effect as the nuclear spin quantum number $I$ is greater than 1. Thus the general selection rule for the transition, $\Delta m_s = \pm 1, \Delta m_l = 0$ is violated. The coupling constant $A_{\text{iso}}$ for the central sextet hyperfine lines is found to be 96 G.

The EPR spectra of the complex $[\text{Mn(HL}_2]_2$ (26) were recorded both in the polycrystalline state at room temperature and solution state in DMF at 77 K. The room temperature spectrum is broad isotropic with $g_{\text{iso}}$ value 2.05. The solution spectrum in DMF at 77 K (Fig. 5.4), displayed a central hyperfine sextet with $g_{\text{iso}} = 1.997$. The observance of hyperfine sextet is as expected due to the interaction of the unpaired electron with the Mn(II) nucleus of spin $I = 5/2$, resulting in $2nI+1$ lines. The coupling constant $A_{\text{iso}}$ for the sextet hyperfine lines is found to be 96 G. Here also forbidden lines arising due to nuclear quadrupole effect of nuclear spin quantum number greater than 1 are observed in between the main hyperfine lines.
Fig. 5.4. The EPR spectrum of [Mn(HL$_2$)$_2$] (26) in DMF at 77 K.

The electron paramagnetic resonance spectra of the complex [Mn(HL$_3$)$_2$]·3H$_2$O (27) were recorded in polycrystalline state at 298 K and solution in DMF at 77 K. The powder state EPR was isotropic in nature with the $g_{iso} = 2.061$. The solution state spectrum has two $g$ values $g_1 = 1.983$ and $g_2 = 2.744$. In the high field region, the spectrum showed clear sextet ($2nI+1$) hyperfine splitting pattern due to the interaction of unpaired electron with the nuclear spin of $I = 5/2$. The splittings due to forbidden lines of nuclear quadrupole effect is also seen in the spectrum. In this spectrum also the coupling constant $A_{iso}$, for the central sextet hyperfine lines is found to be 96 G. The three manganese complexes showed very similar behavior in the electron paramagnetic resonance spectroscopy, indicating similar electronic environment around the manganese centre. The EPR spectrum of 27 in solution state in DMF at 77 K is shown in the Fig. 5.5.
Manganese(II) and iron(III) complexes

5.4.2. Spectral studies of iron(III) complexes

5.4.2a. Electronic spectral studies

In a cubic crystal field, the $^6S$ free ion term transforms as $^6A_1$; no other spin sextuplet state exists, so that all the $d$-$d$ transitions are spin forbidden and hence rather weak. These bands are probably made possible a mixture of spin-quartet character into the ground state via spin-orbit coupling. Despite this, certain problems arise and

Fig. 5.5. The EPR spectrum of $[\text{Mn}(\text{HL}_3)_2] \cdot 3\text{H}_2\text{O} (27)$ in DMF at 77 K.
high spin Fe$^{3+}$ $d$-$d$ spectra are generally more difficult to assign than those of the isoelectronic Mn$^{2+}$ complexes. The main reason for this is that charge transfer absorption occurs at lower energy in the ferric complexes and often most of the $d$-$d$ bands are obscured.

There is a very broad absorption in the whole visible region for the complex 28, comprising of all the charge transfer and above discussed forbidden $d$-$d$ transitions. The UV-Vis absorption spectra of all the three iron complexes are shown together in the Fig. 5.6 below. The bands observed in the region of 300-380 nm are assigned to the ligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

Fig. 5.6. The UV-Vis spectra of the iron(III) complexes 28, 29 and 30 in DMF.
5.4.2b. Infrared spectral studies

The elemental analyses data shows that in all the three iron(III) complexes, the metal and ligand species are in 1:2 ratio. The assignment of infrared bands is most useful for the establishment of the mode of coordination of the aroylhydrazone ligands in the iron(III) complexes. A careful comparison of the infrared spectrum of the complex with that of the corresponding ligand reveals the mode and pattern of coordination in the complex examined. In the case of the complex 28, the stretching absorption of NH bond remains, but not as broad as earlier, indicating the presence of non-enolized aroylhydrazone moieties in the complex sample. This also confirms the presence of lattice water in the compound. The amide I and amide II bands in the original ligand shifted from 1631 and 1594 cm$^{-1}$ to 1609 and 1584 cm$^{-1}$ respectively, shows the presence of ligand in the keto form. The coordination of the azomethine nitrogen atom to the metal ion is indicated by the displacement of the bands chiefly assigned to the $\nu$(N–N) and $\nu$(C=N) stretching vibrations. The spectrum shows downward shift of $\nu$(N–N) from 1070 to 1017 cm$^{-1}$ and $\nu$(C=N) from 1518 to 1483 cm$^{-1}$. These changes in $\nu$(N–N) and $\nu$(C=N) stretching vibrations are typical of coordination of the ligands to the metal ion through the azomethine nitrogen atom. Thus, among the two ligands in the compound, one is in double deprotonated form and coordinating to the iron atom through deprotonated enolic oxygen, deprotonated phenolic oxygen and the azomethine nitrogen. In the case of the second ligand the coordination is through deprotonated phenolic oxygen, carbonyl oxygen and azomethine nitrogen. Thus the iron center is six coordinated and octahedral.

For the complexes, 29 and 30, the coordination pattern is same as discussed above. In the case of 29, the broad band ca. 3440 cm$^{-1}$, shows the presence of NH bond and thus the keto form of the compound. The coordination through azomethine nitrogen is indicated by the shifting of $\nu$(C=N) and $\nu$(N–N) to 1475 and 1027 cm$^{-1}$.
respectively. For the compound 30, \( \nu(C=N) \) and \( \nu(N-N) \) shifted to 1489 and 1009 cm\(^{-1}\). Thus in all the three iron complexes, the coordination through azomethine nitrogen is confirmed.

5.4.2c. EPR spectral studies

Whilst most early EPR work on high spin systems was concerned with the elucidation of the quadratic terms in the spin Hamiltonian for virtually cubic systems [32-33], we rewrite it as

\[
\mathcal{H} = g \beta HS + D [S_x^2 - S(S + 1)/3] + E (S_x^2 - S_y^2)
\]

Where \( D \) is the 'out-of-plane' zero field splitting parameter and \( E \) the in-plane zero field splitting parameter. The real \( g \) value is generally taken to be very close to 2.00. For systems where \( S > 1/2 \) the effective \( g \) value differs considerably from the real value and here it is often expedient to refer to features of the spectra by \( g_{\text{eff}} \) values rather than field values. For high spin Fe\(^{3+}\) at X-band, signals are often found which can be analyzed in terms of \( g_1 \) ca. 1100 gauss and \( g_2 \) ca. 3300. Taking a fictitious spin Hamiltonian with \( S = 1/2 \), we define

\[
g_{\text{eff}} = \frac{\hbar}{\beta H_{\text{res}}}
\]

So that this signal can be described in terms of the effective \( g \) values \( g_1 = 6 \) and \( g_2 = 2 \). Likewise a nearly isotropic resonance is sometimes found ca. 1500 gauss at X-band and is described as \( g_{\text{eff}} = 4.3 \), arising from \( D > ca. 0.2 \text{ cm}^{-1} \) [34]. Because of its isotropic nature and statistical effects it generally appears much more intensely
Manganese(II) and iron(III) complexes

than other transitions and usually dominates the spectrum. For near cubic systems, five transitions appear, centered on $g = 2$, these are $|5/2 > \rightarrow |3/2 >$, $|3/2 > \rightarrow |1/2 >$, $|1/2 > \rightarrow |-1/2 >$, $|-1/2 > \rightarrow |-3/2 >$, $|-3/2 > \rightarrow |-5/2 >$ transitions [35].

![EPR spectrum](image)

**Fig. 5.7.** The EPR spectrum of [Fe(HL$_1$)(L$_1$)]· H$_2$O (28) in DMF at 77 K.

The electron paramagnetic resonance spectra of all the iron(III) complexes were recorded in solution state in DMF at 77 K. The EPR spectrum of the compound, [Fe(HL$_1$)(L$_1$)]· H$_2$O (28) shown in the Fig. 5.7. The spectrum has three $g$ values $g_1 = 6.623$, $g_2 = 4.151$ and $g_3 = 2.023$. The close verification of the pattern in the high field region shows five transitions and it can be concluded that the system is nearly symmetrical.
The electron paramagnetic resonance spectrum of the complex $[\text{Fe}(\text{HL}^2)(\text{L}^2)] \cdot 3\text{H}_2\text{O} \ (29)$ recorded in solution in DMF at 77 K is shown in the Fig. 5.8. The spectrum showed three signals corresponding to $g$ values $g_1 = 6.581$, $g_2 = 4.208$ and $g_3 = 2.016$. The shape and $g$ values for the spectrum are found to be very similar to that discussed earlier for the complex 28. But in this case the five splittings observed in the high field region were not clear in this case and so it can be confirmed that this compound is not as symmetrical as the former one.

![Fig. 5.8. The EPR spectrum of $[\text{Fe}(\text{HL}^2)(\text{L}^2)] \cdot 3\text{H}_2\text{O} \ (29)$ in DMF at 77 K.](image)

The EPR spectrum of the complex $[\text{Fe}(\text{HL}^3)(\text{L}^3)] \cdot 2\text{H}_2\text{O} \ (30)$ was also recorded in solution in DMF at 77 K and is shown in the Fig. 5.9. In this case also the spectrum is very similar to the previous ones having $g$ values $g_1 = 6.237$, $g_2 = 4.213$ and $g_3 = 1.993$. The splitting pattern of the spectrum in the high field region is
shown enlarged in the figure and it can be seen that there are five clear splittings in that region due to the symmetrical nature of the compound. In addition to that there are nine additional absorptions. This may be due to the super-hyperfine splitting pattern of two nitrogen atoms present in the molecule examined.

Fig. 5.9. The EPR spectrum of [Fe(HL\(^3\))(L\(^3\))]·2H\(_2\)O (30) in DMF at 77 K.

From all the spectral data and elemental analyses, it can be concluded that all the iron(III) complexes are high spin \(d^5\) systems, all the metal centers are six coordinate and octahedral. But the single crystals suitable for X-ray diffraction studies of none of the manganese(II) and iron(III) complexes were isolated and so based on the spectral data available, the tentative structures of these complexes can be proposed as given in the Fig. 5.10.
Fig. 5.10. Tentative structures of the manganese(II) and iron(III) complexes prepared.
5.5. Non-linear optical properties of Mn(II) and Fe(III) complexes

The essential requirement to exhibit non-linear optical properties has been proved to have a molecular structure within the general form D-π-A and the design of new second order NLO chromophores has focused primarily on engineering the electronic nature of the donor and the acceptor, and the conjugation length of the bridge. Another requirement for possessing NLO activity is that the molecule must be non centrosymmetric. Thus the existence of strong intramolecular charge transfer excitations in a noncentrosymmetric molecular environment. Even though the manganese(II) and iron(III) complexes are best examples for possessing strong metal to ligand charge transfer excitations, a very few ones have been reported [36-40] in this category yet. This may be due to the chance that majority of manganese and iron complexes are octahedral and symmetric in nature. The centrosymmetry within the molecular lattice may destroy the NLO activity in the molecule.

We also tried to establish the second harmonic generation created by the manganese(II) and iron(III) complexes prepared. From the characterization process itself it have been proved that all of them are octahedral and symmetric with the molecular centre. The conclusion was correct in the SHG efficiency also. None of them have a positive second harmonic generation efficiency, when measured by Hyper Rayleigh scattering technique.
References