CHAPTER –V

Mossbauer Study of Some Iron Complexes *

5.1 Introduction

The biological complexes are well studied through various techniques and it is an established fact that their properties are due to varied geometrical arrangement of ligands surrounding the metal ion [1-4]. Many biological molecules contain iron. The Mossbauer effect provides a powerful probe to chemical state and the environment of iron atoms [5].

The complexes chosen for these investigations are newly synthesized species with different ligands attached to iron metal which is a Mossbauer probe. The ligands used are of Schiff bases and they are important from the point of view of their wide applicability. These complexes are used as drug derivatives, occurring like industrially, biologically, etc. They are also useful metal binding sites in substantial array of metalloproteins in biological systems [6-8]. Thus, these macrocyclic complexes are thought to be interesting for the Mossbauer investigations [5] as the determination of hyperfine field parameters will reflect several important chemical aspects at the microscopic level.

From the investigations of the complexes, the line width, area of the line, the isomer shift, the s-electron density, quadrupole coupling constant (q.c.c.) and electric field gradient are found to be positive. The knowledge of q.c.c. gives

* This work has been communicated for publication.
information about co-ordination number of the complexes [9]. It is a fact that as the co-ordination number increases, the s-electron charge distribution surrounding the metal ion tends to spherical symmetry and, therefore, decreases quadrupole coupling constant.

5.2 Preparation of Complexes

All the absorbers used here are prepared from the chemicals of reagent grade in the laboratory of Department of Chemistry, Aligarh Muslim University, Aligarh, India. They are prepared as following:

5.2.1 $\text{C}_{48}\text{H}_{50}\text{N}_{10}\text{Fe}_{2}\text{Cl}_{6}\text{O}_{8}$

Using template effect method [10], the methanolic solution (20 ml) of anhydrous FeCl$_3$ (0.33 g, 1.88 m mol) is added dropwise to the ligand (1.0g, 1.03 m mol) over one hour in 1,4-Dioxane (30 ml) at room temperature. The whole reaction mixture is stirred for 48 hours which gives brown coloured precipitate. It is filtered and washed with 1,4-Dioxane followed by methanol. The compound obtained is dried in vacuo. It is dark brown coloured solid. Now the complex $\text{C}_{48}\text{H}_{50}\text{N}_{10}\text{Fe}_{2}\text{Cl}_{6}\text{O}_{8}$ prepared. The complex has two metallic ions in cavity. The melting point of the complex is 240°C (decomposed) and yield is found 0.21 g, 35%.

5.2.2 $\text{C}_{42}\text{H}_{56}\text{N}_{12}\text{Fe}_{2}\text{Cl}_{4}\text{O}_{8}$

Using template effect method [10], the methanolic solution (20 ml) of anhydrous FeCl$_3$ (0.347 g, 2.14 m mol) is added dropwise to the ligand solution (1.0 g, 1.07 m mol) over one hour in 1,4-Dioxane (30 ml) at room temperature.
The whole reaction mixture is stirred for 48 hours, which gives blackish-brown precipitate. It is filtered and washed with 1-4-Dioxane followed by methanol. The compound obtained is dried in vacuo and blackish-brown coloured solid is obtained. Now the complex, $C_{42}H_{56}N_{12}Fe_{2}Cl_{4}O_{8}$ is prepared. The complex has two metallic ions in cavity. The melting point of the complex is 310°C (decomposed) and yield is found 0.425g, 33%.

5.2.3 Iron (III) Encapsulation of Hexaazamacrocycle

Using the method of condensation reaction, the ligand (0.82 g, 2 m mol) is dissolved in warm dimethyl formamide (DMF) (20 ml) to which a methanolic solution of FeCl$_3$ (0.33g, 2 m mol) is added dropwise with continuous stirring [11]. The reaction mixture is stirred for 48 hours at room temperature (RT). It is concentrated to ~ 5ml on steam bath. It is then poured in methanol ether (15 ml; 20 ml) mixture producing brown coloured solid which is separated by filtration, washed with methanol and ether dried in vacuo. Now, the complex iron (III) encapsulation of hexaazamacrocycle [$C_{18}H_{14}N_{6}O_{6}FeCl_{3}$] is prepared. The complex has one metallic ion in cavity. The melting point of the complex is 254-256°C and yield is found 54%.

5.2.4 $C_{11}H_{24}N_{5}S_{2}FeCl_{2}$

Using the simple addition reaction method, the FeCl$_2$2H$_2$O (0.3 m mol) solution and tris 2-amino ethylamine (tren) (0.3 m mol) are mixed in a three neck round bottom flask at room temperature and is stirred for 3-4 hours. A brown colour mixture is obtained. Now, it is added in sodium diethyl dithiocarbamate
(0.3 m mol) and is stirred for 4 hours. A reddish dark brown precipitate is obtained. This precipitate is separated by suction pump through a filtration for half an hour. The obtained solid is dried in desiccator. Now, a reddish dark brown complex \( \text{C}_{11}\text{H}_{24}\text{N}_5\text{S}_2\text{FeCl}_2 \) is prepared. It is found that the complex is soluble in dimethyle sulfoxide (DMSO) and the melting point is greater than 300°C (decomposed). The yield is found 53%.

5.2.5 \( \text{C}_{11}\text{H}_{24}\text{N}_3\text{S}_2\text{Fe(NO}_3)_3 \)

Using the simple addition reaction the Fe (NO\(_3\))\(_3\) \(9\text{H}_2\text{O}\) solution (0.3 m mol) and tris 2-amino ethylamine (tern) (0.3 m mol) are mixed in a three neck round bottom flask at room temperature and is stirred for 3-4 hours. A brown colour mixture is obtained. Now, it is added in sodium diethyl dithiocarbamate (0.3 m mol) and is stirred for 4 hours. A dark brown precipitate is obtained. This precipitate is separated by suction pump through a filtration for half an hour. The obtained solid is dried in desiccator. Now a dark brown complex \( \text{C}_{11}\text{H}_{24}\text{N}_3\text{S}_2\text{Fe(NO}_3)_3 \) is prepared. It is found that the complex is soluble in dimethyl sulphoxide (DMSO). The melting point of the complex is greater than 300°C (decomposed). The yield is found 55%.

5.3 Experimental Details

All the samples were examined in the powder form. The Mossbauer data were taken with \(^{57}\text{Co}\) (50 mCi, metal matrix Ph, thinness 8µm, active dimension 1×3 mm, from Moscow, Russia) diffused into a copper matrix supplied by the Inter University Consortium for the Department of Atomic Energy Facilities (DAEF) Indore (M.P.), India. The experiment was performed at room temperature about 300 K. The absorber kept stationary and source was moving with velocity ranging from 0 to ±10 mm/s. The data collection procedure is described in
Chapter-IV. A series of up-down counters are used to count-up the channel address advance pulses for the 1\textsuperscript{st} half and to count them for the 2\textsuperscript{nd} half. Thus, the data stored (512) is required with twice the number of channels (256) which is taken care of by folding the data, which is turned serve to eliminate the background curvature due to variation of source detector distance. The calibration (comparative study) is made by an $\alpha$-iron foil (natural iron) standard. It was purchased from Obnisk, Russia. The spectrum was fitted with NORMOS programs, 1990, i.e. R.A. Brand, Laboratorium fuer Angewande Physik Universitaet Duisburg. Lotharstr 1, D-41000 Duisburg 1. All the spectra were taken without an applied magnetic field and it is found quadrupole doublet. The quadrupole splitting and isomer shift both are found positive in each case. The experimental results (line width, area of the line, quadrupole splitting and isomer shift) are shown in table 5.1. The complexes were examined for crystalline amorphous nature through XRD discussed in chapter-IV. It is found that except complex No. 3, all other complexes are found to be amorphous.

5.4 Experimental Results and Discussion

The Mossbauer spectra of all the complexes were taken at room temperature near about 300K as shown in Figs. 5.1-5.5. The Mossbauer parameters are summerised in Table 5.1 [9, 12]. The isomer shift is found to be maximum in the complexes No.1 (0.361410 mm/s) and minimum in the complex No.3 (0.211569 mm/s). The magnitude of isomer shift is comparable to that reported data at room temperature for various Fe (iii) and Fe (ii) complexes having hexa co-ordination around metal ion [13,14].
Table The line width, isomer shift, quadrupole splitting, electric field gradient, quadrupole coupling constant and s-electron density are obtained through the computer analysis at room temperature of the iron complexes.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Complex</th>
<th>Line width (mm/s)</th>
<th>Line width x10^-8 (eV)</th>
<th>Area of line (mm/s)</th>
<th>Area of the line x10^-8(eV)</th>
<th>Isomer shift (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>C₄₈H₅₀N₁₀Fe₂Cl₆O₈</td>
<td>0.551618 ±0.014921</td>
<td>2.651958 ±0.071735</td>
<td>0.037991 ±0.000695</td>
<td>0.182648 ±0.003341</td>
<td>0.361410 ±0.009775</td>
</tr>
<tr>
<td>2.</td>
<td>C₄₂H₅₀N₁₂Fe₂Cl₄O₈</td>
<td>0.820244 ±0.114853</td>
<td>3.943454 ±0.552174</td>
<td>0.004902 ±0.000318</td>
<td>0.023692 ±0.001529</td>
<td>0.294404 ±0.037944</td>
</tr>
<tr>
<td>3.</td>
<td>C₁₈H₁₄N₆FeCl₃O₆</td>
<td>0.649979 ±0.082330</td>
<td>3.124878 ±0.395815</td>
<td>0.004902 ±0.000358</td>
<td>0.023692 ±0.001721</td>
<td>0.211569 ±0.028979</td>
</tr>
<tr>
<td>4.</td>
<td>C₁₁H₂₄N₅S₂FeCl₂</td>
<td>0.694625 ±0.014127</td>
<td>3.339521 ±0.067918</td>
<td>0.177948 ±0.001910</td>
<td>0.855513 ±0.009183</td>
<td>0.341426 ±0.004950</td>
</tr>
<tr>
<td>5.</td>
<td>C₁₁H₂₄N₃S₂Fe(NO₃)₃</td>
<td>0.640725 ±0.005108</td>
<td>3.080388 ±0.024557</td>
<td>0.171979 ±0.000934</td>
<td>0.826816 ±0.004490</td>
<td>0.339974 ±0.003457</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>S.N</th>
<th>Isomer shift x10^-8 (eV)</th>
<th>Quadrupole splitting (mm/s)</th>
<th>Quadrupole splitting x10^-8(eV)</th>
<th>Electric field gradient x10^21V/m²</th>
<th>Quadrupole coupling constant x10^-8 (eV)</th>
<th>s-electron density x10^21</th>
<th>Grain size Å</th>
<th>Colour of compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>1.737536 ±0.046995</td>
<td>0.667494 ±0.013428</td>
<td>3.209084 ±0.064157</td>
<td>3.209084 ±0.064157</td>
<td>0.534847 ±0.010759</td>
<td>10.858623 ±0.293692</td>
<td>Amorphous</td>
<td>Dark-brown</td>
</tr>
<tr>
<td>2.</td>
<td>1.415394 ±0.182422</td>
<td>0.483642 ±0.070945</td>
<td>2.325186 ±0.341079</td>
<td>2.325186 ±0.341079</td>
<td>0.387531 ±0.0568465</td>
<td>8.845414 ±1.140031</td>
<td>Amorphous</td>
<td>Blackish brown</td>
</tr>
<tr>
<td>3.</td>
<td>1.017152 ±0.139321</td>
<td>0.436145 ±0.052928</td>
<td>2.096837 ±0.254460</td>
<td>2.096837 ±0.254460</td>
<td>0.349473 ±0.042408</td>
<td>6.356621 ±0.870601</td>
<td>10.162859 Å</td>
<td>Brown</td>
</tr>
<tr>
<td>4.</td>
<td>1.641460 ±0.023798</td>
<td>0.725709 ±0.008936</td>
<td>3.488962 ±0.042961</td>
<td>3.488962 ±0.042961</td>
<td>0.581494 ±0.007160</td>
<td>10.25820 ±0.148720</td>
<td>Amorphous</td>
<td>Reddish-dark brown</td>
</tr>
<tr>
<td>5.</td>
<td>1.634479 ±0.016620</td>
<td>0.694689 ±0.003744</td>
<td>3.339828 ±0.017999</td>
<td>3.339828 ±0.017999</td>
<td>0.556631 ±0.003000</td>
<td>10.21457 ±0.103860</td>
<td>Amorphous</td>
<td>Dark-brown</td>
</tr>
</tbody>
</table>
Fig. 5.1 (a) The Mossbauer spectrum of complex $C_{48}H_{50}N_{10}Fe_2Cl_6O_8$ at room temperature. The solid circles are experimental data points and the solid line is fitted to them. (b) X-ray diffraction pattern of complex $C_{48}H_{50}N_{10}Fe_2Cl_6O_8$. 
Fig. 5.2 (a) The Mossbauer spectrum of complex $\text{C}_{42}\text{H}_{56}\text{N}_{12}\text{Fe}_{2}\text{Cl}_{4}\text{O}_{8}$ at room temperature. The solid circles are experimental data points and the solid line is fitted to them. (b) X-ray diffraction pattern of complex $\text{C}_{42}\text{H}_{56}\text{N}_{12}\text{Fe}_{2}\text{Cl}_{4}\text{O}_{8}$. 
Fig. 5.3 (a) The Mossbauer spectrum of complex $\text{C}_{18}\text{H}_{14}\text{N}_{6}\text{FeCl}_{3}\text{O}_{6}$ at room temperature. The solid circles are experimental data points and the solid line is fitted to them. (b) X-ray diffraction pattern of complex $\text{C}_{18}\text{H}_{14}\text{N}_{6}\text{FeCl}_{3}\text{O}_{6}$. 
Fig. 5.4 (a) The Mossbauer spectrum of complex C₁₁H₂₄N₅S₂FeCl₂ at room temperature. The solid circles are experimental data points and the solid line is fitted to them. (b) X-ray diffraction pattern of complex C₁₁H₂₄N₅S₂FeCl₂.
Fig. 5.5 (a) The Mössbauer spectrum of complex $\text{C}_{11}\text{H}_{24}\text{N}_{3}\text{S}_{2}\text{Fe(NO}_{3}\text{)}_{3}$ at room temperature. The solid circles are experimental data points and the solid line is fitted to them. (b) X-ray diffraction pattern of complex $\text{C}_{11}\text{H}_{24}\text{N}_{3}\text{S}_{2}\text{Fe(NO}_{3}\text{)}_{3}$.
The positive isomer shift shows that the s-electron density is higher in the complexes than that in the source.

The spectra of quadrupole splitting at room temperature suggests that the presence of electric field gradient at the metal ion is due to the presence of ligands around the ion. This may also be due to some distortion from the perfect octahedral geometry to an elongated octahedral geometry attained by the complex. It is interesting to note that the quadrupole splitting in complexes No.1, 4 and 5 are much higher than complex No.2 and 3 (table 5.1). This seems plausible in view of the molecular mode examination of the ligands of complexes No.1, 4 and 5, which may provide asymmetric hexa co-ordination to metal ions vis-a-vis to that possible for the ligands of the complexes No1, 4 and 5. It means that the electric field gradient is significant. It also appears from the spectra of complexes No.1-5 that the quadrupole coupling constants (q.c.c.) are positive as the peaks lie to the right of zero velocity. It shows that the transition is taking place from higher energy state to lower energy state $|\pm 3/2\rangle \rightarrow |\pm 1/2\rangle$ as shown in Fig. 5.6. Since the magnetic splitting does not appear in these complexes, therefore, it suggests that the internal magnetic field is absent at the Mossbauer nuclei in each case and the states remain doubly degenerate, showing the Kramer’s degeneracy.

It is seen that the line width of the complexes are found large in comparison to the natural line width $(4.665\times10^{-9} \text{ eV})$ of $^{57}\text{Fe}$. The maximum line width $39.43454\times10^{-9} \text{ eV}$ of the complex No.2 and minimum line width $26.51958\times10^{-9}$
eV of the complex No.1 (Table 5.1). The observation of deviation from the natural line width might be trivial and could be due to Doppler broadening of an improper functioning of Mossbauer apparatus (vibration) or saturation effects in the absorber or in the source. However, there are also a number of inherent physical processes causing line broadening.

5.5 Conclusion

By looking at the Mossbauer spectra, the hyperfine field parameters are found very sensitive and meaningful of each complexe. The line width, isomer shift, quadrupole splitting, electric field gradient and quadrupole coupling constant are found positive. The electric field gradient gives information about the ions surrounding the Mossbauer atom. The charge distribution gives the structure and symmetry of the complex. These complexes of present work are very useful for biological purpose.
Chapter-V

References