CHAPTER-IV

SOLID COMPLEX PREPARATION

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   b) Mechanochemical method

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CHAPTER -IV

SOLID COMPLEX PREPARATION

1. Introduction

On the basis of literature\textsuperscript{1-6} survey, it is revealed that hydroxytriazenes form complexes with number of transition metals as well as some of the non transition metals. In chapter-III complex formation of iron (III) with hydroxytriazenes in acidic medium (pH = 2.2-6.4) has been described. The colour of complex is dark blue or black. The composition of binary complexes of iron(III), hydroxytriazenes has been established by mole ratio method. The composition of iron(III) complexes has been found to be 1:2 [iron(III):R] in all the five cases. In order to confirm the results of solution studies an attempt has been made to isolate solid complexes of iron(III) with hydroxytriazene which have been used in its spectrophotometric determination. All the five hydroxytriazenes which have been used in spectrophotometric determination of iron(III) as described in chapter-III have been used for isolation of binary complex.

1.1. General method:-

For preparation of metal complex two methods has been used.

1.1.a. Conventional method

1.1.b. Mechanochemical method

As mentioned in chapter III composition of iron (III) complexes with hydroxytriazenes has been established by mole ratio method which is found to be 1: 2 [M:L] in all the five cases. The pH for complex formation has been found to be in the range of 2.2 – 6.4.

2. Experimental :

A general conventional method for preparation of iron(III) complexes has been described below.
2. Conventional method

2.a. Schematic presentation of conventional synthesis of Fe(III)-ASPT-1 Complex

| Requisite quantities of hydroxytriazenes (0.0002 Mole) dissolved in ethanol/methanol |
| Requisite quantity of A.R. grade ferric nitrate nonhydrate (0.00012 Mole) dissolved in double distilled water |
| Addition of solution of metal in Hydroxytriazene solution by maintaining pH by using 1% Tris-Buffer or perchloric acid |
| Reaction mixture was kept in ice bath after complete addition of metal solution |
| Complex formed was filtered and washed with double distilled water and ethanol/methanol |
| Crystallized with ethanol/methanol |

2.b. Mechanochemical method

On the basis of solution study the composition of Fe-hydroxytriazene complex has been found to be 1:2 (M:L). To prepare solvent free metal complexes mechanochemically the respective quantities of Fe(NO$_3$)$_3$.9H$_2$O and ASPT-1 were taken in their requisite quantities. [M: L:: 0.0002:0.00012].

Mechanochemistry deals with either liquid assisted grinding (LAG) or ball milling using SPEX 8000M High Energy Ball Mill. However the complex was prepared using ball milling method.
2.b. Schematic presentation of mechanochemical synthesis of Fe(III)-ASPT-1 Complex

<table>
<thead>
<tr>
<th>Requisite quantities of hydroxytriazenes (0.0002 Mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Requisite quantity of A.R. grade ferric nitrate nonhydrate (0.00012 Mole)</td>
</tr>
</tbody>
</table>

Grinding in the mortar pestle initially

Transferring the sample to stainless steel vial and grinding for different time

Collecting the sample & characterizing the sample

Five complexes were prepared by conventional method and one complex of ASPT-1 with Fe(III) was prepared by mechanochemical method.

Following hydroxytriazenes were used for preparation of complex by conventional method.

(i). 3-hydroxy-3-phenyl-1-(4-acetylsulfonyl)phenyltriazene (ASPT-1)
(ii). 3-hydroxy-3-(3-methylphenyl)-1-(4-acetylsulfonyl)phenyltriazene (ASPT-3)
(iii). 3-hydroxy-3-methyl-1-(4-acetylsulfonyl)phenyltriazene (ASPT-8)
(iv). 3-hydroxy-3-ethyl-1-(4-acetylsulfonyl)phenyltriazene (ASPT-9)
(v). 3-hydroxy-3-(1-methylethyl)-1-(4-acetylsulfonyl)phenyltriazene (ASPT-10)

The quantities of ferric nitrate and hydroxytriazene taken, pH, percentage yield of each complex are given in Table No.IV-1 and for preparation of metal complex by mechanochemical method ASPT-1 has been taken.
### Table No.- IV-1

**Formation of Solid Complexes of Iron (III) with hydroxytriazenes**

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Binary complex of Fe(III) with Hydroxytriazene</th>
<th>pH</th>
<th>Fe(NO₃)₃.9H₂O Taken (in gm)</th>
<th>Ligand taken (in gm)</th>
<th>% yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>3-hydroxy-3-phenyl-1-(4-acetylsulfonyl)phenyltriazene</td>
<td>5.5-6.4</td>
<td>0.04848</td>
<td>0.0668</td>
<td>54</td>
</tr>
<tr>
<td>(ii)</td>
<td>3-hydroxy-3-(3-methylphenyl)-1-(4-acetylsulfonyl)phenyltriazene</td>
<td>2.2-2.9</td>
<td>0.04848</td>
<td>0.0696</td>
<td>52</td>
</tr>
<tr>
<td>(iii)</td>
<td>3-hydroxy-3-methyl-1-(4-acetylsulfonyl)phenyltriazene</td>
<td>4.5-5.3</td>
<td>0.04848</td>
<td>0.0544</td>
<td>58</td>
</tr>
<tr>
<td>(iv)</td>
<td>3-hydroxy-3-ethyl-1-(4-acetylsulfonyl)phenyltriazene</td>
<td>4.9-5.8</td>
<td>0.04848</td>
<td>0.0572</td>
<td>46</td>
</tr>
<tr>
<td>(v)</td>
<td>3-hydroxy-3-(1-methylethyl)-1-(4-acetylsulfonyl)phenyltriazene</td>
<td>4.6-5.3</td>
<td>0.04848</td>
<td>0.0600</td>
<td>61</td>
</tr>
</tbody>
</table>

### 3. Characterization of Binary complexes of Iron (III)-Hydroxytriazene:

#### 3.1. Physical characteristics

All the five binary solid complexes were found to be insoluble in water but soluble in ethanol/ methanol. Colour, shape of crystal and molecular formulae of these solid complexes have been given in Table No.IV-2.
TABLE NO: - IV-2: PHYSICAL CHARACTERISTICS OF SOLID COMPLEXES OF IRON (III)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour and Crystal shape</th>
<th>Molecular Formula</th>
<th>M.W.</th>
<th>m.p</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(ASPT-1)₂(H₂O)₂]</td>
<td>Shiny bluish black powder</td>
<td>C$<em>{28}$H$</em>{32}$FeN$<em>8$O$</em>{10}$S$_2$</td>
<td>760.5767 [1:2:2H$_2$O]</td>
<td>114-118°C</td>
</tr>
<tr>
<td>[Fe(ASPT-3)₂(H₂O)₂]</td>
<td>Bluish black powder</td>
<td>C$<em>{30}$H$</em>{34}$FeN$<em>8$O$</em>{10}$S$_2$</td>
<td>788.7191 [1:2:2H$_2$O]</td>
<td>165-170°C</td>
</tr>
<tr>
<td>[Fe(ASPT-8)₂(H₂O)₂]</td>
<td>Greenish powder</td>
<td>C$<em>{18}$H$</em>{28}$FeN$<em>8$O$</em>{10}$S$_2$</td>
<td>636.4373 [1:2:2H$_2$O]</td>
<td>172-180°C</td>
</tr>
<tr>
<td>[Fe(ASPT-9)₂(H₂O)₂]</td>
<td>Black powder</td>
<td>C$<em>{20}$H$</em>{32}$FeN$<em>8$O$</em>{10}$S$_2$</td>
<td>664.5803 [1:2:2H$_2$O]</td>
<td>180-184°C</td>
</tr>
<tr>
<td>[Fe(ASPT-10)₂(H₂O)₂]</td>
<td>Black powder</td>
<td>C$<em>{22}$H$</em>{36}$FeN$<em>8$O$</em>{10}$S$_2$</td>
<td>692.6335 [1:2:2H$_2$O]</td>
<td>210-220°C</td>
</tr>
</tbody>
</table>

Binary complex formation in solution has been described in chapter-III. The composition of complex formed in solution has been determined by mole ratio method of Yoe and Jones\(^7\). It has been found that by this method iron (III) is shown to form binary complex with hydroxytriazene in the molar ratio 1:2.

In this chapter attempt has been made to prepare and isolate binary complexes in solid state. For the preparation of binary complexes quantities of iron (III) hydroxytriazene were taken in same molar ratio i.e. 1:2. Thus, it was assumed that complex isolated in solid state has same molar composition i.e. 1:2 [Fe (III): R] All iron complexes with hydroxytriazenes have been characterized by following spectroscopic techniques.

<table>
<thead>
<tr>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. Elemental analysis</td>
</tr>
<tr>
<td>b. IR Spectroscopic analysis</td>
</tr>
<tr>
<td>c. Thermo gravimetric analysis</td>
</tr>
<tr>
<td>d. Differential Thermal analysis</td>
</tr>
<tr>
<td>e. Magnetic Property measurement by VSM</td>
</tr>
<tr>
<td>f. Powder X-Ray Diffraction</td>
</tr>
</tbody>
</table>
a. Elemental Analysis

To ascertain percentage of CHN by micro-analytical method all the Fe(III) complexes with hydroxytriazenes synthesized were subjected to elemental analysis. The elemental analysis of all iron complexes were done on Vario EL-III Elemental analyzer form Sophisticated Analytical Instrument, Facility, (SAIF) Central Drug Research Institute, Lucknow.

b. IR spectroscopic characterization

IR spectra were recorded from 4000-450 cm\(^{-1}\) on a Perkin-Elmer RX1 IR spectrometer from Sophisticated Analytical Instrument Facility, (SAIF) Central Drug Research Institute, Lucknow, and Perkin Elmer FTIR spectrometer with ATR from Delhi University.

c. Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA) provides authentic information regarding the presence and absence of water molecules inside or outside of the coordination sphere of the complex. TGA was carried out on a Perkin–Elmer, Pyris diamond TGA/DTA instrument from university of Delhi, Delhi.

d. Differential Thermal Analysis (DTA)

This technique involves the measurement of the temperature difference between the sample and a thermally inert reference material when both are subjected to identical thermal regime heated or cooled at a constant rate. It deals with enthalpy changes for almost all reactions irrespective of whether they are accompanied by mass change or not.

DTA curve is a plot of the differential temperature (Tsamp.- Tref) against time or temperature. In the absence of any reaction in the sample, (Tsamp. - Tref) = ΔT = 0 constitutes the baseline signal. During an endothermic reaction, the sample absorbs heat from the surroundings so the differential temperature (DT) becomes negative whereas heating of the sample and a positive (upward) peak is observed than reaction is exothermic in nature.
A typical DTA Curve representing nature of reaction is as follows-

![Fig. 4.3.d. Typical DTA Curve](image)

**e. Magnetic Nature of Complex by Vibrating Sample Magnetometer (VSM):**

Vibrating Sample Magnetometer (VSM) systems are used to measure the magnetic properties of materials as a function of magnetic field, temperature, and time. This is commonly employed for measuring the magnetic properties of permanent magnet materials, because measurements can be performed on solids, powders, single crystals, thin films, nanostructures and liquids and also regularly employed because measurements can be performed over a broad range of temperatures (4 K to 1,273 K). In a VSM, a sample is placed within suitably placed sensing coils, and is made to undergo sinusoidal motion, i.e., mechanically vibrated. The resulting magnetic flux changes induce a voltage in the sensing coils that is proportional to the magnetic moment of the sample.

![Fig.4.3.e. Typical Hysteresis loop of a ferromagnetic material](image)
With a VSM, the magnetic moment of a sample as a function of the external magnetic field strength can be measured. Increasing and decreasing the external field from the demagnetized state to positive saturation to negative saturation and back gives a ferromagnetic hysteresis loop as shown in Fig. 4.3.e.

VSM measurement have done on Lakeshore make Model 7403, equipped with low temperature CCR and high temperature oven for measurement in the range of 10K-1000K.

f. Powder X-Ray Diffraction:
X-Ray Powder Diffraction Technique is an indispensable method of material investigation, characterization and quality control. The scattering of X-rays from atoms produce a diffraction pattern which gives information about the atomic arrangement in crystal. Amorphous materials do not produce any significant peak in diffraction pattern like glass which do not have periodic array with long-range order $10^{-12}$. A diffraction pattern plots intensity against the angle of the detector, 2$\theta$. The result obtained is called diffractogram.

![Typical diffractogram of crystalline compound](image)

Fig. 4.3.f. Typical diffractogram of crystalline compound
Fig. 4.3.f. Typical diffractogram of Semicrystalline and amorphous compound

PXRD measurement have done on Rigaku Model X-Ray Powder diffractometer, from department of physics, MLSU. In present study by PXRD, Complex phase is crystalline or amorphous have determined.

4. Results

(i). Analysis results of [Fe(ASPT-1)2(H2O)2]

a. Elemental Analysis of [Fe(ASPT-1)2(H2O)2]

<table>
<thead>
<tr>
<th>Binary complex of Fe (III) and hydroxytriazene</th>
<th>%C Theo.</th>
<th>%C Exp.</th>
<th>%H Theo.</th>
<th>%H Exp.</th>
<th>%N Theo.</th>
<th>%N Exp.</th>
<th>Molecular Formulae</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(ASPT-1)2 (H2O)2]</td>
<td>48.97</td>
<td>48.90</td>
<td>4.40</td>
<td>4.48</td>
<td>16.32</td>
<td>15.98</td>
<td>C28H32FeN8O10S2</td>
</tr>
</tbody>
</table>
b. IR Analysis of [Fe(ASPT-1)₂(H₂O)₂]

Fig. 4.4.(i).b. IR Graph of [Fe(ASPT-1)₂(H₂O)₂] (Conventional)

Fig. 4.4.(i).b. IR Graph of [Fe(ASPT-1)₂(H₂O)₂] (Mechanochemical)
c. TGA Analysis of $[\text{Fe(ASPT-1)}_2(\text{H}_2\text{O})_2]$  

Fig. 4.4.(i).c. TGA Graph of $[\text{Fe(ASPT-1)}_2(\text{H}_2\text{O})_2]$ (Conventional)

Fig. 4.4.(i).c. TGA Graph of $[\text{Fe(ASPT-1)}_2(\text{H}_2\text{O})_2]$ (Mechanochemical)
d. DTA Analysis of $[\text{Fe(ASPT-1)}_2(\text{H}_2\text{O})_2]$ 

Fig. 4.4.(i).d. DTA Graph of $[\text{Fe(ASPT-1)}_2(\text{H}_2\text{O})_2]$ (Conventional)

Fig. 4.4.(i).d. DTA Graph of $[\text{Fe(ASPT-1)}_2(\text{H}_2\text{O})_2]$ (Mechanochemical)
e. VSM measurement of $[\text{Fe(ASPT-1)}_2(\text{H}_2\text{O})_2]$  
Fig. 4.4.(i).e. VSM Graph of $[\text{Fe(ASPT-1)}_2(\text{H}_2\text{O})_2]$  

f. PXRD pattern of $[\text{Fe(ASPT-1)}_2(\text{H}_2\text{O})_2]$  
Fig. 4.4.(i).f. PXRD pattern of $[\text{Fe(ASPT-1)}_2(\text{H}_2\text{O})_2]$ (Conventional)
Fig. 4.4.(i).f. PXRD pattern of $[\text{Fe(ASPT-1)}]_2(\text{H}_2\text{O})_2$ (Mechanochemical)
(ii). Analysis results of \([\text{Fe(ASPT-3)}_2(\text{H}_2\text{O})_2]\)

A. ELEMENTAL ANALYSIS OF \([\text{Fe(ASPT-3)}_2(\text{H}_2\text{O})_2]\)

<table>
<thead>
<tr>
<th>Binary complex of Fe (III) and hydroxytriazenes</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>Molecular Formulae</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Fe(ASPT-3)}_2(\text{H}_2\text{O})_2])</td>
<td>50.41</td>
<td>51.42</td>
<td>4.79</td>
<td>C\text{30}H\text{36}Fe\text{N}<em>8O</em>{\text{10}S_2}</td>
</tr>
</tbody>
</table>

b. IR Analysis of \([\text{Fe(ASPT-3)}_2(\text{H}_2\text{O})_2]\)

Fig. 4.4.(ii).b. IR Graph of \([\text{Fe(ASPT-3)}_2(\text{H}_2\text{O})_2]\)
c. TGA Analysis of $[\text{Fe(ASPT-3)}_2(\text{H}_2\text{O})_2]$  
Fig. 4.4.(ii).c. TGA Graph of $[\text{Fe(ASPT-3)}_2(\text{H}_2\text{O})_2]$  

![TGA Graph](image)

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d. DTA Analysis of $[\text{Fe(ASPT-3)}_2(\text{H}_2\text{O})_2]$  
Fig. 4.4.(ii).d. DTA Graph of $[\text{Fe(ASPT-3)}_2(\text{H}_2\text{O})_2]$  

![DTA Graph](image)
e. VSM Measurement of [Fe(ASPT-3)$_2$(H$_2$O)$_2$]

Fig. 4.4.(ii).e. VSM Graph of [Fe(ASPT-3)$_2$(H$_2$O)$_2$]

![VSM Graph of [Fe(ASPT-3)$_2$(H$_2$O)$_2$]](image)

f. PXRD Pattern of [Fe(ASPT-3)$_2$(H$_2$O)$_2$]

Fig. 4.4.(ii).f. PXRD Pattern of [Fe(ASPT-3)$_2$(H$_2$O)$_2$]

![PXRD Pattern of [Fe(ASPT-3)$_2$(H$_2$O)$_2$]](image)
(iii). Analysis results of $[\text{Fe(ASPT-8)}_2(\text{H}_2\text{O})_2]$  

A. ELEMENTAL ANALYSIS OF $[\text{Fe(ASPT-8)}_2(\text{H}_2\text{O})_2]$  

<table>
<thead>
<tr>
<th>Binary complex of Fe (III) and hydroxytriazene</th>
<th>%C Theo.</th>
<th>%H Theo.</th>
<th>%N Theo.</th>
<th>Molecular Formulae</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Fe(ASPT-8)}_2(\text{H}_2\text{O})_2]$</td>
<td>38.43</td>
<td>4.66</td>
<td>19.92</td>
<td>$\text{C}<em>{18}\text{H}</em>{28}\text{FeN}<em>8\text{O}</em>{10}\text{S}_2$</td>
</tr>
</tbody>
</table>

b. IR Analysis of $[\text{Fe(ASPT-8)}_2(\text{H}_2\text{O})_2]$  

Fig. 4.4.(iii).b. IR Graph of $[\text{Fe(ASPT-8)}_2(\text{H}_2\text{O})_2]$
e. VSM Measurement of \([\text{Fe(ASPT-8)}_2(\text{H}_2\text{O})_2]\)

Fig. 4.4.(iii).e. VSM Graph of \([\text{Fe(ASPT-8)}_2(\text{H}_2\text{O})_2]\)

\[
\text{Fe(III)-ASPT-8}
\]

\[
\begin{array}{c}
\text{Moment (emu)} \\
\text{Magnetic Field (Oe)}
\end{array}
\]

f. PXRD Pattern of \([\text{Fe(ASPT-8)}_2(\text{H}_2\text{O})_2]\)

Fig. 4.4.(iii).f. PXRD Pattern of \([\text{Fe(ASPT-8)}_2(\text{H}_2\text{O})_2]\)

\[
\text{[Fe(ASPT-8)](H}_2\text{O)}_2]
\]

\[
\begin{array}{c}
\text{Intensity (a.u.)} \\
\text{2 Theta (degree)}
\end{array}
\]
(iv). Analysis results of [Fe(ASPT-9)$_2$(H$_2$O)$_2$]

A. ELEMENTAL ANALYSIS OF [Fe(ASPT-9)$_2$(H$_2$O)$_2$]

<table>
<thead>
<tr>
<th>Binary complex of Fe (III) and hydroxytriazene</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>Molecular Formulae</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(ASPT-9)$_2$(H$_2$O)$_2$]</td>
<td>40.67</td>
<td>5.12</td>
<td>18.97</td>
<td>C$<em>{20}$H$</em>{32}$FeN$<em>8$O$</em>{10}$S$_2$</td>
</tr>
</tbody>
</table>

b. IR Analysis of [Fe(ASPT-9)$_2$(H$_2$O)$_2$]

Fig. 4.4.(iv).b. IR Graph of [Fe(ASPT-9)$_2$(H$_2$O)$_2$]

e. VSM Measurement of [Fe(ASPT-9)$_2$(H$_2$O)$_2$]

Fig. 4.4.(iv).e. VSM Graph of [Fe(ASPT-9)$_2$(H$_2$O)$_2$]
f. PXRD Pattern of [Fe(ASPT-9)$_2$(H$_2$O)$_2$]

Fig. 4.4.(iv).f. PXRD Pattern of [Fe(ASPT-9)$_2$(H$_2$O)$_2$]

![Graph of PXRD Pattern](image)

Fig. 4.3.IV.f. PXRD Graph of [Fe(ASPT-9)$_2$(H$_2$O)$_2$]
V. Analysis results of [Fe(ASPT-10)₂(H₂O)₂]

A. ELEMENTAL ANALYSIS OF [Fe(ASPT-10)₂(H₂O)₂]

<table>
<thead>
<tr>
<th>Binary complex of Fe (III) and hydroxytriazene</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>Molecular Formulae</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(ASPT-10)₂(H₂O)₂]</td>
<td>42.71</td>
<td>5.54</td>
<td>18.11</td>
<td>C₂₂H₃₆FeN₆O₁₀S₂</td>
</tr>
</tbody>
</table>

b. IR Analysis of [Fe(ASPT-10)₂(H₂O)₂]

Fig. 4.4.(v).b. IR Graph of [Fe(ASPT-10)₂(H₂O)₂]
e. VSM Measurement of [Fe(ASPT-10)$_2$(H$_2$O)$_2$]

Fig. 4.4.(v).e. VSM Graph of [Fe(ASPT-10)$_2$(H$_2$O)$_2$]

f. PXRD Pattern of [Fe(ASPT-10)$_2$(H$_2$O)$_2$]

Fig. 4.4.(v).f. PXRD Pattern of [Fe(ASPT-10)$_2$(H$_2$O)$_2$]
5. Discussion

4.a. CHN Analysis of complex

Elemental analysis for the complex compounds with C, H, N percentage are presented in table-4(i)a-4(v)a. The experimental values, are mostly in agreement with the theoretical values.

4.b. IR Spectra of complex

IR graphs of all synthesized Fe (III) complexes of hydroxytriazenes are in good agreement with expected range. The hydrated complexes exhibited an IR bands approximately around these bands at 3400, 834 cm\(^{-1}\) and 650–700 cm\(^{-1}\) range due to \(\nu(\text{H}_2\text{O})\), suggestive of water molecules coordinated to the metal in the complexes, some of these bands corresponding to water molecule modes could not be assigned, due to the fact that they overlapped with some other signals\(^{13-14}\). The asymmetric and symmetric (SO\(_2\)) group stretching vibrations in the sulfonamides were observed at 1322-1311 and 1155-1144 cm\(^{-1}\) respectively which indicate no significant shifts. This behavior has been observed in similar sulfonamide complexes that do not coordinate through this group. The \(\nu^{\text{N}=\text{N}}\) and \(\nu^{\text{N}\rightarrow\text{O}}\) bands for the tautomeric triazene-1-oxide [-NH–N=N(\(\rightarrow\text{O}\))\(]\) are of greater intensity in the complexes appearing at 1450±5 and 1330±5, respectively. The strengthening in the bond shows formation of chelate ring by replacing hydrogen atom. The band \(\nu^{\text{C-N}}\) and \(\nu^{\text{N-N}}\) which are present in all hydroxytriazene were merged to one band indicating delocalization of \(\pi\) electrons in chelate rings. The greater value of \(\nu^{\text{N-N}}\) stretching indicates strengthening of N-N bond. New bands which were not present in the spectrum of free hydroxytriazene appeared at 460-440 cm\(^{-1}\) and 520-510 cm\(^{-1}\) may be attributed to \(\nu^{\text{Fe-O}}\) and \(\nu^{\text{Fe-N}}\) vibrations, respectively. The appearance of M-N and M-O vibrations supports the involvement of nitrogen and oxygen atoms in complexation with metal ion.

4.c. Thermogravimetric analysis complex

As shown by TGA curve 4.4.(i).c. and 4.4.(ii).c. a mass loss in between 150-200°C reveals that complex has two coordinated H\(_2\)O molecule has four coordination sites occupied by two bidentate hydroxytriazene and two water
molecules are co-ordinated in addition to two hydroxytriazenes. Thus, the geometry of the complex is octahedral.

4.d. Differential thermal analysis of complex

DTA curve of complex has been shown in Fig. 4.4.(i).d. and 4.4.(ii).d. which represents that decomposition of complex is endothermic in nature.

4.e. VSM analysis of complex

The Hysteresis loop in VSM curve as shown in fig. 4.4.(i).e. - 4.4.(v).e. of complexes gives information that complexes are magnetic in nature. The nature of complex may vary from paramagnetic to ferromagnetic.

4.f. Powder X-Ray Diffraction analysis of complex

Peaks in Powder X-Ray diffraction pattern of complexes show that complexes are semi-crystalline in nature. The diffraction pattern it has been show in fig. 4.4.(i).f. - 4.4.(v).f. under result section.

Conclusively, the results of all characterization data shown that Fe(III) form six co-ordinated complex in all above cases in which four co-ordination sites of the complex are occupied by two bidentate hydroxytriazene and two co-ordination sites are occupied by water molecule is proven by TGA. So the geometry of the complexes is octahedral.
6. References


