CHAPTER IV

ELECTRONIC SPECTRAL STUDIES ON IRON(III) COMPLEXES
WITH 2-THIOURYL-6-BENZO-THIAZOLE ACETIC ACID
AND ITS DERIVATIVES:

INTRODUCTION:

Nucleic acid bases with sulphur atom have been detected in natural 1-RNA and therefore have attracted considerable interest during last decade\(^1\). 2-Thiouracil and its derivatives have been found to induce modifications in thyroid gland and are claimed as an antithyroid drugs\(^2\)\(^-\)\(^3\). Two well known thiouracil antithyroid drugs, 6-propyl-2-thiouracil and 6-methyl-2-thiouracil, have also been shown to be competitive inhibitors of neuronal nitric oxide synthase\(^4\). 2-Thiouracil and its derivatives have also been used as antitumour agents\(^5\)\(^-\)\(^8\).

The synthesis of thiolato compounds from the activation of thiols on transition metals has been the subject of numerous studies because of the relevance of transition metal thiolates to industrially important catalytic processes and to metallo protein chemistry\(^7\)\(^-\)\(^12\). Trimetallic clusters containing bridging sulfide ligands are often used to facilitate the synthesis of high nuclearity clusters\(^13\).

Synthetic and structural characterization of molecules in which coordinated metal ions are key structure determining units is an area of active research\(^14\)\(^-\)\(^19\). The use of mononuclear coordination centres especially with transition metal ions as the geometry setting metallic component is found in literature\(^18\). Lawrence et al\(^19\) observed that a process which plays an important role in biological systems should offer some advantages relative to the alternative approach of synthesizing molecules and macromolecules having predominately covalent character. However the nature of non covalent interactions like hydrogen bonding has currently been the centre of intense activities among organic and inorganic
chemists\(^{20,21}\) due to their ability to assemble with the species bearing complementary functions.

Currently Sherrington and Takiness\(^{22}\) reviewed the process of self assembly in the synthetic macromolecules via multiple hydrogen bonding interactions. In this accomplishment, metal ions have also been exploited as a template for the construction of a rigid frame of remote hydrogen bonding site showing that it is one of the major forces behind the organization of crystal structure of molecular conductors.\(^{23}\)

The present chapter we have studied analytical, magnetic, mssbauer, infrared and electronic spectral properties of Fe(III) complexes with 2-thiouryl-6 Benzo thiazole acetic acid (TBT) and its 4-methyl benzaldehyde, 4-hydroxy 3 aldehyde diphenyl, 2-acetyl thiophene, 2-acetyl pyridine, 2-acetyl furan and 2-formyl benzofuran derivatives abbreviated as MB-TBT, HO-DP-TBT, AF-TBT, AT-TBT, AP-TBT and DF-TBT) respectively.

**EXPERIMENTAL:**

**Preparation and Isolation of Iron(III) Complexes:**

(i) **Dichloro-bis (2-Thiouryl-6-Benzothiazole acetic acid) Iron(III) chloride** \([Fe(C_{10}H_9O_2N_3S_2)_2Cl_2]Cl\)

The ligand 2-thiouryl-6-benzo thiazole acetic acid (2.67 gm; 0.01 M) and FeCl\(_3\).6H\(_2\)O (0.80 gm; 0.005 M) were dissolved separately in hot methanol (15 ml) and mixed immediately. A violet coloured solution formed. The reaction mixture was heated for one hour on a steam bath to ensure the completion of the reaction and then allowed to cool down. After one hour, the violet solid product \([Fe(C_{10}H_9O_2N_3S_2)_2Cl_2]Cl\) was filtered off, washed with methanol followed by diethyl ether and dried in vacuo.

(ii) **Di-ammonia-Bis (2-Thiouryl-6-Benzothiazole acetic acid) Iron(III) chloride** \([Fe(C_{10}H_9O_2N_3S_2)_2(NH_3)_2]Cl\)
The deep blue filtrate obtained above in (1) complex was concentrated on steam bath followed by its adjustment of pH 6-6.5 with dilute solution of alcoholic ammonia, resulting in the formation of blue violet product. \([\text{Fe}(\text{C}_{16}\text{H}_{15}\text{O}_{2}\text{N}_{3}\text{S}_{2})]_{2}\text{Cl}_{2}\text{(NH}_{3}\text{)}_{2}]\text{Cl}\) was filtered off, washed with isopropanol followed by diethyl ether and dried in vacuo.

(iii) **Diammonia bis (4- methyl- benzylidene -2-Thiouryl-6- Benzo thiazolyl acetic acid) iron(III) chloride:**

\([\text{Fe}(\text{C}_{16}\text{H}_{15}\text{O}_{2}\text{N}_{3}\text{S}_{2})_{2}\text{(NH}_{3}\text{)}_{2}]\text{Cl}\) - The ligand 4- methyl benzylidene-2 -thiouryl - 6-benzo thiazolyl acetic acid (3.69 gm; 0.01 M) and anhydrous ferric chloride (0.805 g; 0.005 M) were dissolved separately in hot methanol (20 ml) and mixed. The reaction mixture was heated on a steam bath for 45-minute, after adjusting the pH 6-6.5 with dilute alcoholic solution of ammonium hydroxide, when a bright red product started to separate. After allowing it to stand at room temperature for one hour, the red product \([\text{Fe}(\text{C}_{16}\text{H}_{15}\text{O}_{2}\text{N}_{3}\text{S}_{2})_{2}\text{(NH}_{3}\text{)}_{2}]\text{Cl}\) was filtered off, washed with ethanol followed by diethyl ether and then dried in vacuo.

(iv) **Tetrachloro-bis (4L-hydroxy -3L- aldehyde diphenylidene -2-Thiouryl -6- Benzo thiazole acetic acid)- di iron(III)]**

\([\text{Fe}_{2}(\text{C}_{2}\text{H}_{14}\text{O}_{2}\text{N}_{3}\text{S}_{2})_{2}\text{Cl}_{4}]\text{Cl}\) :

The ligand 4L-hydroxy-3L-aldehyde diphenylidene (0.45 g; 1.0 mmol) was added to a solution of equivalent amount of anhydrous ferric chloride hexa hydrate in methanol (50 ml) and mixed. An intense red colour developed on heating for 5-minute. The reaction mixture was refluxed for one hour on a steam bath to ensure the completion of the reaction and then allowed to cool down. After one hour the solid product was filtered off, washed with methanol followed by diethyl ether and dried in vacuo.

(v) **Tetrachloro-bis (2-acetyl furan-2-Thiouryl-6-Benzo Thiazole acetic acid) di iron(III) chloride [Fe_{2}(C_{16}H_{15}O_{2}N_{3}S_{2})_{2}Cl_{4}]Cl_{2}**
An ethanolic solution (20 ml) of ligand and the anhydrous ferric chloride solution in equivalent amount were mixed and refluxed for two hours on steam bath. The solid product obtained was filtered and washed with ethanol and dried as usual.

(vi) Tetrachloro bis (2'-Acetyl thiophene 2-Thiouryl-5-Benzo thiazole acetic acid) di Iron(III) chloride di hydrate

\[ \text{Fe}_2\left(\text{C}_{18}\text{H}_{11}\text{O}_2\text{N}_2\text{S}_2\right)_2\text{Cl}_4\text{Cl}_2\cdot 2\text{H}_2\text{O} \]

An ethanolic solution of ligand (1.88 g; 0.005 M) was added to ferric chloride solution (1.73 g; 0.005 M) in 20 ml and refluxed for one hour on water bath. After cooling coloured precipitate separated out. It was filtered, washed with water and ethanol and dried under vacuum.

(vii) Tetrachloro bis (2'-Acetyl pyridine 2-Thiouryl-5-Benzo thiazole acetic acid) di Iron(II) chloride di hydrate

\[ \text{Fe}_2\left(\text{C}_{19}\text{H}_{14}\text{O}_2\text{N}_2\text{S}_2\right)_2\text{Cl}_4\text{Cl}_2\cdot 2\text{H}_2\text{O} \]

To a solution of ligand (1.85 g, 0.005 M) was added ferric chloride (0.805 g, 0.005 M) in equal ratio in 20 ml acetone. The reaction mixture was then boiled to reflux for two hour. A coloured precipitate was filtered, washed thoroughly with ether and dried in vacuo.

(viii) Tetrachloro bis (2'-Aldehyde benzofuranedene 2- Thiouryl -5- Benzo thiazole acetic acid) di Iron(III) chloride

\[ \text{Fe}_2\left(\text{C}_{19}\text{H}_{13}\text{N}_3\text{O}_2\text{S}_2\right)_2\text{Cl}_4\text{Cl}_2 \]

To a solution of \((\text{C}_{19}\text{H}_{13}\text{N}_3\text{O}_2\text{S}_2)\times 1.98 \text{ g}, 0.005 \text{ M}) in methanol was added anhydrous ferric chloride hexa hydrate (0.805 g, 0.005 M) in 1:1 molar ratio. The reaction mixture was boiled to reflux for two hour and a brown precipitate was obtained, was thoroughly washed with alcohol and dried in vacuo.

Results and Discussion: Metal complexes were analysed gravimetrically for their metal content using standard procedure after decomposing them in aquo regia. The micro analysis was done on Carlo Erba analyzer.
**Magnetic Studies:** Iron(III) complexes under study have moment value in the range 15.70 – 5.98 B.M. ascertaining high spin outer orbital octahedral stereochemistry, having no orbital angular moment.

**Mossbauer or Recoilless Resonance Gamma Fluorescence Studies:** Mossbauer spectral studies of the isolated iron(II) complexes were recorded at two different temperature, 300°K and 78°K to correlate the magnetic moment and stereochemistry around the metal ion.

Normally high spin iron(III) complexes exhibits isomer shift $\delta^{l5}$ in the range 0.40–0.70 mm/sec. the quadrupole splitting value is connected with distribution of d and p– electrons around the Mossbauer nucleus and makes a very good basis of choice among several stereochemical possibilities. From Mossbauer spectra of the present iron(III) complexes derived from present 2-thiouryl-6-benzo-thiazole acetic acid and its various aldehydeic derivatives, the isomer shift ($\delta^{l5}$) and quadrupole splitting ($\Delta E_{q}$) were found in the range 0.16–0.22 & 0.23–0.37 mm/sec and 1.31–2.02 & 2.24–2.73 mm/sec at the temp. of studies viz. 300°K & 78°K respectively. These datas clearly ascertain$^{[24,25]}$ to iron(III) having high spin or weak ligand field outer octahedral microsymmetry of ligands around the Mossbauer and these observations are also in agreement to Ablow et.al.$^{[25,26]}$ observations.

The values of magnetic moment observed for the present complexes 5.70–5.98 B.M. are also in agreement with the observations of Gerlsh–Lewis$^{[26]}$ et.al. and suggested that the environment of the Mossbauer atom is high spin octahedral. A decrease in isomer shift may be presumed$^{[30]}$ due to slight increase in the electron density on the N–, S– and O– donor atoms, which in turn should result into greater $\sigma$ overlap and hence increased $s$–electron density on the iron nucleus. In other words the lower values of $\delta^{l5}$ in the present high spin iron(III) octahedral complexes, may also be attributed to a decrease in $4s$–electron density on the iron
nucleus due to the decreased covalency of donor-metal bonds. Ablov (Loc. Cit) reported that Fe-N bond is more covalent than Fe-S bond. In our complex No. 4 and 5 (Table 4 4), there are four Fe-S bonds and two Fe-N bonds. So our results with lower $\delta^{15}$ and $\Delta E_{eq}$ values are quite in agreement to the earlier reports. Relatively small values of $\delta^{15}$ and $\Delta E_{eq}$ obtained in our chelates at both the temperature of study 298°K and 78°K revealed considerable symmetry or environment around the Mossbauer close to the spherical one.

In our present high spin weak field outer octahedral iron(III) complexes inclusion of spin orbit coupling and covalency effect may also lead to the decrease in the $\Delta E_{eq}$ and $\delta^{15}$ values. These decreased values are also correlated to "Least Axial Perturbation." So it may be concluded that quadrupole splitting ($\Delta E_{eq}$) is connected with the distribution of d- and p- electron around the Mossbauer atoms.
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<th>S.No.</th>
<th>Compound (Colour)</th>
<th>MP/DT $^\circ$C</th>
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<th>Magnetic data at $301 \pm 1^\circ$K</th>
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| 1.    | [Fe(C$_{10}$H$_{12}$O$_2$N$_5$S$_2$)$_2$Cl$_2$]Cl  
(Reddish Brown) | 182°C             | 34.46 | 2.58 | 12.08 | 13.38 | 15.29 | 7.96 | 14560 | 5.88 | H.S.O.* |
| 2.    | [Fe(C$_{10}$H$_{12}$O$_2$N$_5$S$_2$)(NH$_3$)$_2$]Cl  
(Light Brown) | 262°C             | 36.38 | 3.63 | 16.87 | 19.40 | 5.35 | 8.46 | 13531 | 5.70 | H.S.O.* |
| 3.    | [Fe(C$_{10}$H$_{14}$O$_3$N$_5$S$_2$)$_2$(NH$_3$)$_2$]Cl  
(Dark Brown) | 214°C             | 50.02 | 4.16 | 12.66 | 14.82 | 4.11 | 6.46 | 14560 | 5.89 | H.S.O.* |
| 4.    | Fe$_2$(C$_{10}$H$_{14}$O$_3$N$_5$S$_2$)$_2$Cl$_2$  
(Light Brown) | 190°C             | 48.07 | 2.96 | 7.31 | 11.14 | 12.36 | 9.72 | 14323 | 5.84 | H.S.O.* |
| 5.    | Fe$_2$(C$_{10}$H$_{14}$O$_3$N$_5$S$_2$)$_2$Cl$_2$  
(Dark Brown) | 135°C$^\ddagger$ | 36.82 | 2.49 | 8.05 | 12.27 | 20.42 | 10.71 | 14766 | 5.96 | H.S.O.* |
| 6.    | Fe$_2$(C$_{10}$H$_{14}$O$_3$N$_5$S$_2$)$_2$Cl$_2$(H$_2$O)  
(Dark Brown) | 120°C             | 34.56 | 2.70 | 7.56 | 17.28 | 19.17 | 10.05 | 14394 | 5.88 | H.S.O.* |
| 7.    | Fe$_2$(C$_{10}$H$_{14}$O$_3$N$_5$S$_2$)$_2$Cl$_2$(H$_2$O)  
(Dark red Brown) | 150°C             | 37.06 | 2.90 | 10.17 | 11.62 | 18.35 | 10.14 | 14654 | 5.82 | H.S.O.* |
| 8.    | Fe$_2$(C$_{10}$H$_{14}$O$_3$N$_5$S$_2$)$_2$Cl$_2$  
(Buff Brown) | 210°C$^\ddagger$ | 40.90 | 2.33 | 7.53 | 11.48 | 19.10 | 10.01 | 14177 | 5.85 | H.S.O.* |

* H.S.O. = High Spin Octahedral
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<th>Assignments</th>
<th>10Dq cm(^{-1})</th>
<th>B cm(^{-1})</th>
<th>C cm(^{-1})</th>
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TBT—(C₁₀H₁₅O₂N₂S₂); MB—TBT—(C₁₆H₁₆O₂N₂S₂); HO—DP—TBT—(C₂₃H₁₇O₃N₃S₂); AF—TBT—(C₁₆H₁₇O₃N₃S₂); AT—TBT—(C₁₈H₁₇O₃N₃S₂); AP—TBT—(C₁₇H₁₄O₂N₄S₂); BF—TBT—(C₁₉H₁₉N₂O₃S₂)
Fig. I: Mössbauer curves from 
\[ \text{Fe(C}_{10}\text{H}_{10}\text{O}_{3}\text{N}_{3}\text{S}_{2})\text{Cl}_{2}]\text{Cl} \]

at 300 K ---
78 K -----

Compound no. 1 (Table IV)

---

Fig. II: Mössbauer curves from 
\[ \text{Fe(C}_{10}\text{H}_{10}\text{O}_{3}\text{N}_{3}\text{S}_{2})\text{Cl}_{2}]\text{Cl} \]

at 300 K ---
78 K -----

Compound no. 2 (Table IV)
### TABLE 4.4: MOSSBAUER ($\gamma$ RESONANCE) SPECTRA FOR IRON(III) COMPLEXES

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound</th>
<th>Temp. °K</th>
<th>Mossbauer Parameter</th>
<th>Mass. at 300±1°K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\delta$&lt;sub&gt;IS&lt;/sub&gt; (mm sec&lt;sup&gt;-1&lt;/sup&gt;)&lt;br&gt;(± 0.04 mms&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>$\Delta E_q$ (mm sec&lt;sup&gt;-1&lt;/sup&gt;)&lt;br&gt;(± 0.04 mms&lt;sup&gt;-1&lt;/sup&gt;)</td>
</tr>
<tr>
<td>1.</td>
<td>[Fe(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;N&lt;sub&gt;3&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;):Cl&lt;sub&gt;2&lt;/sub&gt;]Cl</td>
<td>300</td>
<td>0.16</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>78</td>
<td>0.24</td>
<td>2.26</td>
</tr>
<tr>
<td>2.</td>
<td>[Fe(C&lt;sub&gt;16&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;N&lt;sub&gt;5&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;):(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Cl]</td>
<td>300</td>
<td>0.17</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>78</td>
<td>0.23</td>
<td>2.32</td>
</tr>
<tr>
<td>3.</td>
<td>[Fe(C&lt;sub&gt;8&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;N&lt;sub&gt;3&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;):(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Cl]</td>
<td>300</td>
<td>0.22</td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td>78</td>
<td>0.32</td>
<td>2.26</td>
</tr>
<tr>
<td>4.</td>
<td>[Fe&lt;sub&gt;2&lt;/sub&gt;(C&lt;sub&gt;23&lt;/sub&gt;H&lt;sub&gt;37&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;N&lt;sub&gt;5&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;):Cl&lt;sub&gt;4&lt;/sub&gt;]Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>300</td>
<td>0.20</td>
<td>1.78</td>
</tr>
<tr>
<td></td>
<td></td>
<td>78</td>
<td>0.30</td>
<td>2.46</td>
</tr>
<tr>
<td>5.</td>
<td>[Fe&lt;sub&gt;2&lt;/sub&gt;(C&lt;sub&gt;16&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;3&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;):Cl&lt;sub&gt;4&lt;/sub&gt;]Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>300</td>
<td>0.21</td>
<td>2.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>78</td>
<td>0.36</td>
<td>2.74</td>
</tr>
</tbody>
</table>

Following the convention $\delta$<sub>IS</sub> is taken as positive when the source is moved towards the absorber. A computer fit of the spectras has also been attempted and the values with least difference between experimental and theoretical data, are considered.
Fig. III: Mössbauer curves from
\[
\text{Fe(C}_{18}\text{H}_{15}\text{O}_{2}\text{N}_{3}\text{S}_{2})_{2}(\text{NH}_{3})_{2}\text{Cl}
\]
at 300 K

78 K

Compound no. 3 (Table IV)

Fig. IV: Mössbauer curves from
\[
\text{Fe}_{2}(\text{C}_{28}\text{H}_{17}\text{O}_{3}\text{N}_{3}\text{S}_{2})\text{Cl}_{6}
\]
at 300 K

78 K

Compound no. 4 (Table IV)
**TABLE 4.5: TENTATIVE ASSIGNMENTS OF THE FREQUENCIES (cm\(^{-1}\)) IN THE IR SPECTRA OF IRON(III) COMPLEXES WITH TBT, MB - TBT, HO - DP - TBT, AF - TBT, AT - TBT, AP - TBT AND BF - TBT**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound</th>
<th>(\nu(NH)) and (\nu(OH)^*)</th>
<th>(\nu(CN)) of immine N and NH bending</th>
<th>Sy. &amp; Assy. (\nu(C=C)+\nu(CN)+\nu(CN)) of Thiazo. ring</th>
<th>(\nu(CS)) + (\nu(CS)) + (\nu(CN))</th>
<th>(\nu(NCS)) + (\nu(CS)) Bend modes</th>
<th>Thiazolene Ring deform. &amp; its (\nu(CN))</th>
<th>Thiazolene Ring deform. &amp; its (\nu(CN))</th>
<th>Vibration due to benz./ Furan./ Thiop./ Pyri. Moiety</th>
<th>(M-donor)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>((C_{12}H_{12}O_{2}N_{2}S_{2}))</td>
<td>3350 vs 3260 s 2920 m(^*)</td>
<td>-</td>
<td>1555 vs 1350 s 1300 vs 1140 vs 1150 ma 1050 s</td>
<td>930 m 895 s* 850 vs 750 ms</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1. (\nu(M\text{- immineN}))</td>
<td>2. (\nu(M\text{- Thio-ketoS}))</td>
</tr>
<tr>
<td>2</td>
<td>([Fe(C_{12}H_{12}O_{2}N_{2}S_{2})<em>{2}(NH</em>{3})Cl])</td>
<td>3325 s 3220 s 2910 m(^*)</td>
<td>-</td>
<td>1588 vs 1280 m 1220 ms 1170 m 1110 s 1021 s</td>
<td>910 m 884 m* 725 s</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1. 467 m</td>
<td>2. -</td>
</tr>
<tr>
<td>3</td>
<td>([Fe(C_{12}H_{12}O_{2}N_{2}S_{2})<em>{2}(NH</em>{3})Cl])</td>
<td>3330 s 3220 s 3205 ms 3140 m 2900 m(^*)</td>
<td>-</td>
<td>1588 vs 1275 m 1224 m 1175 m 1025 s</td>
<td>900 ms 884 s* 720 s 715 ms</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1. 465 m</td>
<td>2. -</td>
</tr>
<tr>
<td>4</td>
<td>((C_{12}H_{12}O_{2}N_{2}S_{2}))</td>
<td>3350 vs 3200 vs 2950 m(^*)</td>
<td>1630 vs 1550 s 1370 vs 1350 s 1300 vs 1135 vs 1050 s</td>
<td>930 m 900 s* 905 m 875 m* 805 s 750 ms</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>([Fe(C_{12}H_{12}O_{2}N_{2}S_{2})<em>{2}(NH</em>{3})Cl])</td>
<td>3300 s 3160 s 2900 m(^*)</td>
<td>1635 vs 1575 s 1316 s 1280 m 1105 ms 1030 s</td>
<td>905 m 875 m* 720 s 710 ms</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1. 460 ms</td>
<td>2. -</td>
</tr>
</tbody>
</table>

76
Fig. 7: Mössbauer curves from $[\text{Fe}_2(\text{C}_6\text{H}_3\text{O}_{3}\text{N}_3\text{S}_2)_2\text{Cl}_4]\text{Cl}_2$

at 300°K ———, 78°K ———

Compound no. 5 (Table IV)
TABLE 4.5 Contd.: TENTATIVE ASSIGNMENTS OF THE FREQUENCIES (cm⁻¹) IN THE IR SPECTRA OF IRON(III) COMPLEXES WITH TBT, MB-TBT, HO-DP-TBT, AF-TBT, AT-TBT, AP-TBT AND BF-TBT

<table>
<thead>
<tr>
<th>S No.</th>
<th>Compound</th>
<th>ν(NH) and ν(OH)*</th>
<th>ν(CN) of immines and NH bending</th>
<th>ν(C≡C)+ ν(C≡S) + ν(CN) of Thiacyclo ring</th>
<th>ν(C≡S)</th>
<th>ν(NCS) + ν(CS) + ν(CN)</th>
<th>ν(CS) of Thiocarbonyl groups and other ν(CN)</th>
<th>Vibration due to benzyl Furan/Thiophene furyl Pyridine Moiety</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>(C₂₃H₁₄O₂N₃S₂)</td>
<td>3360m, 3200s, 2940m*</td>
<td>1635s, 1560s, 1540ms</td>
<td>1370s, 1145svs, 1020ms</td>
<td>925ssh, 890ms*</td>
<td>815s</td>
<td>–</td>
<td>1.52</td>
</tr>
<tr>
<td>7</td>
<td>[Fe₂(C₂₃H₁₆O₂N₃S₂)₂Cl₂]</td>
<td>3220m, 3160s, 2915m*</td>
<td>1610s, 1590s, 1225m</td>
<td>1310m, 1120s, 1000ms</td>
<td>917ssh, 755s</td>
<td>–</td>
<td>–</td>
<td>4.2</td>
</tr>
<tr>
<td>8</td>
<td>(C₁₆H₁₃O₂N₃S₂)</td>
<td>3400, 3300mb, 2920s*</td>
<td>1620s, 1595s, 1285m</td>
<td>1350vs, 1180s, 1170ms</td>
<td>1100s, 1010ms</td>
<td>935m, 900s*, 810vs, 730vs, 670s</td>
<td>–</td>
<td>1.51</td>
</tr>
<tr>
<td>9</td>
<td>[Fe₂(C₁₆H₁₃O₂N₃S₂)₂Cl₂]Cl₂</td>
<td>3375s, 3285m, 2910s*</td>
<td>1605s, 1575s, 1265m</td>
<td>1310s, 1174s, 1064s</td>
<td>915m, 890s*, 760vs, 725ssh, 670s, 605m</td>
<td>–</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>(C₁₆H₁₃O₂N₃S₂)</td>
<td>3360s, 3200mb, 2940m*</td>
<td>1640s, 1560ms, 1360ms, 1180s, 11100s</td>
<td>1050s, 940s, 905s*, 810s, 670s, 645m</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>4.2</td>
</tr>
<tr>
<td>11</td>
<td>[Fe₂(C₁₆H₁₃O₂N₃S₂)₂Cl₂]Cl₂ - 2H₂O</td>
<td>3340s, 1610m, 1585m, 1340m, 1160s, 1025s, 915m, 755s</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>4.25</td>
</tr>
</tbody>
</table>
FIG (4.1) IR SPECTRA OF Fe(III) COMPLEXES
(I) [Fe(C_{10}H_{9}O_{2}N_{3}S_{2})Cl_{2}]Cl (II) [Fe(C_{10}H_{9}O_{2}N_{3}S_{2})(NH_{3})_{2}]Cl (III) [Fe(C_{18}H_{13}O_{2}N_{3}S_{2})(NH_{3})_{2}]Cl
<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound</th>
<th>ν(NH) and ν(OH)*</th>
<th>ν(CN) of Immine N and NH bending</th>
<th>ν(C≡C) + ν(C≡N) + ν(CS) + ν(CN) Bend modes</th>
<th>ν(NCS) + ν(CS) Ring breath. Modes</th>
<th>Thiazolene Ring deform. &amp; its ν(CN)</th>
<th>Thiazolene (OCS) of Thiourea and Thiazolene</th>
<th>Vibration due to benz./ furan./ thio./ pyr./ mole.</th>
<th>(M-dio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>(C₁₀H₁₅O₂N₄S₂)</td>
<td>3400ms</td>
<td>1610s</td>
<td>1575s</td>
<td>1340m</td>
<td>1190s</td>
<td>1020m</td>
<td>930m</td>
<td>810s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3280m</td>
<td>1530ms</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>900m</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2925m*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>[Fe₂(C₁₀H₁₅O₂N₄S₂)₂Cl₄]Cl₂</td>
<td>3350m</td>
<td>1585m</td>
<td>1565s</td>
<td>1305mw</td>
<td>1166m</td>
<td>1010m</td>
<td>910m</td>
<td>750s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3245m</td>
<td>1100m</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>864m*</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2905m*</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>(C₁₀H₁₅N₃O₃S₂)</td>
<td>3350vs</td>
<td>1635s</td>
<td>1560s</td>
<td>1360vs</td>
<td>1145s</td>
<td>1020ms</td>
<td>940m</td>
<td>815s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3260ms</td>
<td>1300s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>890ms*</td>
<td>760ms</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2850m*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>585m</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>[Fe₂(C₁₀H₁₅N₃O₃S₂)₂Cl₄]Cl₂</td>
<td>3280s</td>
<td>1590m</td>
<td>1580s</td>
<td>1320ms</td>
<td>1125m</td>
<td>1010m</td>
<td>905m</td>
<td>615m</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3210ms</td>
<td>1290s</td>
<td></td>
<td></td>
<td></td>
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<td>2845m*</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
The differences in the isomer shifts and quadrupole splitting observed in the present iron(III) complexes are not so significant and are comparable to experimental errors. The magnitudes of $\Delta$Eq are unlikely to prove of much help in determining symmetry, since the presence of a low symmetry component in the crystal field readily gives an orbital singlet ground state even in those cases where the approximate symmetry is much higher. But at the same time in the absence of complete x-ray structural studies, Mossbauer appears to be most convenient techniques for establishing the stereo-chemical behaviour of the present ligands around iron(III) ion or mossbauer atom.

Mossbauer spectra of complexes shows isomer shift values with respect to natural iron as is typically observed for other high spin iron(III) complexes having substantial covalency in Fe(III) ligand bond. It has been shown that quadrupole splitting decreases with increase in the symmetry of the central iron atom i.e. larger is the quadrupole splitting more unsymmetrical is the central iron atom. Complexes show quite a large quadrupole splitting value, suggesting more distorted complexes. Similar values are obtained for structurally characterized rhombically distorted iron(III) complexes as well as in certain iron tyrosinate proteins.

**Electronic Spectral Studies**: All the complexes show UV-spectral bands (in DMF) characteristic of thiazolyl group. Fe(III) complexes show a charge transfer band in the region of 300–330 nm which is ascribed to thiazolyl $\pi$(N)→d$\sigma$ Fe(III). Such a charge transfer band has been observed for other Fe(III) complexes. For the
chloride bound complex a band at 365 nm may be ascribed to \( \pi(\text{O}) \rightarrow \text{Fe(III)} \) charge transfer.

Fe(III) complexes also show a band in the region a band in the region of 450–480 nm which may be assigned as low energy L \( \rightarrow \) iron(III) charge transfer band and these may also include contribution from \( ^6A_{1g}(\text{6S}) \rightarrow ^4T_{2g} \) (4G) transition. This confirms the binding of chloride to Fe(III) center.\(^{41}\)

In the present iron(III) complexes the bands observed in the region 12800–14300 cm\(^{-1}\), 16000–19400 cm\(^{-1}\), 23000–25400 cm\(^{-1}\), 27000–31600 cm\(^{-1}\) and 36000–41700 cm\(^{-1}\) are tentatively assigned to \( ^6A_{1g} \rightarrow ^4T_{1g} \) (G) (d–d transition), \( ^6A_{1g} \rightarrow ^4T_{2g} \) (G) (d–d transition), \( t_2g \rightarrow \pi^* \) (charge transfer transition), \( \pi \rightarrow e_g \) (Charge transfer transition and \( \pi \rightarrow \pi^* \) respectively.

The assignments to different transitions observed in the absorption spectra of the present ferric complex have been made by getting the best fit in the Tanabe–Sugano diagram for d\(^6\) configuration.

\[
\frac{^6A_{1g} \rightarrow ^4T_{1g}}{B} = 110 \quad \text{or} \quad \frac{D_{2g}}{B} = 11.0
\]

The transition \( ^6A_{1g} \rightarrow ^4T_{1g} \) gives directly the values\(^{42}\) of 10D\(_q\) and B. The calculated values of 10D\(_q\), B, C and \( \beta_{35} \) from present iron(III) complexes tabulated in Table II.

From absorption spectra of present iron(III) complexes (\( \pi \rightarrow t_{2g} \)) and (\( e_g \rightarrow \pi^* \)) are evaluated from charge transfer bands by using the following relations:

\[
(\pi \rightarrow e_g) - \lambda = (\pi \rightarrow t_{2g}) \text{ in K.K.}
\]
\((t_{2g} \rightarrow \pi^*) - \Delta = (e_{g} \rightarrow \pi^*)\) in K.K. \hspace{1cm} (2)

\((\pi \rightarrow t_{2g}) + (t_{2g} \rightarrow e_{g}) + (e_{g} \rightarrow \pi^*) = (\pi \rightarrow \pi^*)\) \hspace{1cm} (3)

According to Miller et al.\(^{44}\) for simple one electron molecular orbital treatment the sum of \((\pi \rightarrow t_{2g})\), \((t_{2g} \rightarrow e_{g})\) and \((e_{g} \rightarrow \pi^*)\) in K.K should be equal to the energy of the \((\pi \rightarrow \pi^*)\) transition. The value of \((t_{2g} \rightarrow e_{g})\) is commonly known as 10Dq and can also be evaluated by Figgis equation\(^{44}\)

\[ \frac{\lambda_{e}}{B} = 24 \]

The observed and calculated values for the transition \((\pi \rightarrow \pi^*)\) are in the range 36.2–41.6 K.K. and 38.80–42.50 K.K. respectively. Thus the calculated and observed \((\pi \rightarrow \pi^*)\) energies are in good agreement.

The values of spin orbit coupling constant \((\lambda_{e})\) and Lande’s splitting factor \((g)\) for the present iron(III) complexes are calculated by using the following relations and their values are tabulated in Table (4.3)

\[ \mu = \mu_{o} \left(1 - \frac{\alpha d}{10Dq}\right) \]

\[ g = \left[2 - \frac{8.4}{10Dq}\right] \]

Where, \(\mu\) = observed magnetic moment in B.M.

\(\mu_{o}\) = spin only value 5.92 B.M.

\(\alpha\) = A constant depending on metal ion stereochemistry.

Condon-Shortley Ligand field repulsion parameters \(F_{2}\) and \(F_{4}\) are also calculated by using the mathematical formulations given by Low and Rosengarten.\(^{45}\)
\[ C = \frac{35F_1}{442} \quad \text{and} \quad B = \begin{bmatrix} 54 \; 51 \, \frac{51}{441} \end{bmatrix} \]

The free ion value \( F_2 \) and \( F_4 \) for iron(III) complexes are 80.93 K.K. and 50.27 K.K. respectively, while the corresponding values for complexed iron(III) ion are found in the range 90.09-98.35 K.K. and 58.97-65.06 K.K. respectively. The phenomenal increase in \( F_2 \) and \( F_4 \) values during complexation may be due to expanded radial functions of the d-electrons.\(^{48}\)

As reported by Carlo-Tosi\(^{47}\) very weak spin forbidden transition in high spin outer octahedral iron(III) complexes observed in the region 28170-29150 cm\(^{-1}\) and 37600-38750 are further splitted as well as expected to overlap. In our present iron(III) complexes the bands observed in the region 27300-31500 cm\(^{-1}\) and 36200-41600 cm\(^{-1}\) are also splitted as below:

\[ \begin{align*}
27300 & \quad 31500 \text{ cm}^{-1} : (d_1 \rightarrow \pi_4) \\
& \quad \rightarrow \pi_4 (a_1) (\nu\alpha) \\
36200 & \quad 41600 \text{ cm}^{-1} : (\pi_3 \rightarrow \pi_4) \\
& \quad \rightarrow \pi_4 (e) (\nu\beta) \\
& \quad \rightarrow \pi_4 (a_1) (\nu\beta') \\
& \quad \rightarrow \pi_4 (a_1) (\nu\beta')
\end{align*} \]

These splitted band (\( \nu\alpha \) & \( \nu\beta \)) and (\( \nu\alpha' \) & \( \nu\beta' \)) have about the same energy and are expected\(^{49}\) to overlap.

**INFRARED STUDIES:**

A study and comparison of the infrared species of the free ligands TBT, MB TBT, HODP–TBT, AF–TBT, AT–TBT, AP–TBT and BF–TBT and their iron(III) complexes imply that possible donor sites are hetero–S & thioketo S (TBT & MB–TBT) while other ligands have
FIG (4.2) IR SPECTRA OF Fe(III) COMPLEXES
(I) \([\text{Fe}_2(C_{23}H_{17}O_3N_3S_2)_2Cl_4]\)  (II) \([\text{Fe}_2(C_{16}H_{13}O_2N_3S_2)_2\text{Cl}_4]\)Cl_2  (III) \([\text{Fe}_2(C_{16}H_{13}O_2N_3S_2)_2\text{Cl}_4]\)Cl_2·2H_2O
two more donor sites viz. azomethine N and hetero-donor, characterizing TBT and MB-TBT as bidentate and HODP-TBT, AF-TBT, AT-TBT, AP-TBT and BF-TBT as tetradentate.

(A) Vibrations due to benzothiazole group:

A strong and sharp band is observed in the spectra of ligands around 1590-1520 cm\(^{-1}\) which is assigned to symmetrical and asymmetrical\(^{(48,49)}\) \([\nu(C=C) + \nu(C=N) + \nu(C=S)]\) of thiazolene ring. On complexation this shifted to higher range showing the involvement of S-atom in chelation.

A sharp absorption band observed in the range 1695-1680 cm\(^{-1}\) is due to acetate group.

Thiazole ring breathing modes and ring deformations observed in the region 1100-1010 cm\(^{-1}\) and 940-930 cm\(^{-1}\) respectively in the free ligands show no apparent change in intensity and the blue/red shifts (10-30 cm\(^{-1}\)) on chelation.\(^{(50,51)}\)

(B) Vibrations due to Thiourea moiety:

The \(\nu(NH)_2\), \(\nu(C-S)\) and thioamide(IV) mainly due to \(\nu(C=S)\) bands found in the ligands at 3400, 1730 and \(-810\) cm\(^{-1}\) respectively, disappear in the spectra of their complexes indicating destruction of these group through deprotonation thienolisation and enolisation. The appearance of a new band in the region 710-720 cm\(^{-1}\) due to \(\nu(C-S)\) in the spectra of all the complexes and \(\nu(NCS)\) in the region (1560-1600)cm\(^{-1}\) in the spectra of complexes are in accord with the above findings.\(^{(52,53)}\)

The bands occurring in the regions 1440-1460, 1300 and 1050-1090 cm\(^{-1}\) in the ligands due to thioamide-I (\(\beta NH + \nu CN\)), II
FIG (4.3) IR SPECTRA OF Fe(III) COMPLEXES
(I) \([\text{Fe}_2(\text{C}_{17}\text{H}_{14}\text{O}_3\text{N}_4\text{S}_2)_2\text{Cl}_4]\)\(_2\text{H}_2\text{O}\) (II) \([\text{Fe}_2(\text{C}_{15}\text{H}_{13}\text{O}_3\text{N}_3\text{S}_2)_2\text{Cl}_4]\)\(_2\)
\( \nu(CN + \beta NH) \) bands respectively, show positive shifts respectively in complexes supporting bonding through thiolo sulphur\(^{54}\).

The strong bonds observed in the region 1370–1340 cm\(^{-1}\), 1190–1050 cm\(^{-1}\), and 815–730 cm\(^{-1}\) are assigned to \( [\nu(CS) + \nu(CN)] \) vs-a-vis \( [\nu(CS) + \nu(CN)] \), \( [\nu(NCS) + \nu(CS)] \) bending modes and \( \nu(C=S) \) of thiourea respectively show down ward shift with nearly (30–60 cm\(^{-1}\)), while \( \nu(C=S) \) are highly reduced in intensity as well as in frequency approximately (40–80 cm\(^{-1}\)) showing the involvement of \( \beta C=S \) in bonding with metal ion.

(C) Vibrations due to imine nitrogen:

The IR-spectrum of ligand shows band at 3180 cm\(^{-1}\) due to \( \nu(NH) \) stretch. The IR-spectrum of the ligand does not display the \( \nu(SH) \) band in the 2450–2600 cm\(^{-1}\) region suggesting that in solid state Schiff base remains in the thiokeeto form, but in solution it may remain as an equilibrium mixture of both the thiokeeto and thiol tautomeric forms. A sharp band at 1060 cm\(^{-1}\) in the IR-spectrum of Schiff base is a characteristic of \( =NH-C=S \) (thioamide) group. This bond reduces in frequency in the complexes suggesting coordination through \( \beta C=S \) sulphur atom.

A strong band at 1630 cm\(^{-1}\) is assigned to the \( \nu(C=N) \) stretch\(^{55}\) and this band undergoes a negative shift (10–15 cm\(^{-1}\)) in the complexes indicating the participation of azomethine nitrogen in coordination.

The strong absorption bands noticed at 1630 cm\(^{-1}\) (MB–TBT); 1635 cm\(^{-1}\) (HO–DP–TBT); 1620 cm\(^{-1}\) (AF–TBT); 1640 cm\(^{-1}\) (AT–TBT); 1610 cm\(^{-1}\) (AP–TBT) and 1630 cm\(^{-1}\) (BF–TBT) are assigned to
**Fig. I**: High-spin octahedral stereochemistry of ligands 'TBT' & 'MB-TBT' around iron (III) ion.

Tentative structure for 
\[ \text{Fe}(\text{L})_2X_2 \] 

Where,
- \( L = \text{TBT} (C_{10}H_{10}O_2N_5S_2) \)
- \( MB-\text{TBT} (C_{18}H_{15}O_2N_5S_2) \)
- \( X = Cl/Br/\text{Hg} \)
- \( X' = Cl \)

**Fig. II**: High-spin octahedral stereochemistry of ligands viz.
- 'HO-DF-TBT' (\( R' = \text{Phenolic ring} \)), 'AF-TBT' (Furanyl ring); 'AT-TBT' (Thiophene ring); 'AP-TBT' (Pyridine ring) and 'BF-TBT' (Benzyl furanyl ring) around iron(III) ion.
- HO-DF-TBT \( (C_{23}H_{17}O_3N_5S_2) \)
- AF-TBT \( (C_{16}H_{15}O_3N_5S_2) \)
- AT-TBT \( (C_{16}H_{13}O_2N_5S_2) \)
- AP-TBT \( (C_{17}H_{14}O_2N_5S_2) \)
- BF-TBT \( (C_{19}H_{13}N_5O_9S_2) \)
\(\nu(C=N)\) vibrations of imine nitrogen, showing downward shift suggesting involvement of azomethine nitrogen in metal ligand bonding.

Medium to strong bands noticed at 690 and 610 cm\(^{-1}\) (AF-TBT) and 600 and 580 cm\(^{-1}\) (BF-TBT) assigned to furan ring deformation modes\(^{(56)}\) show (15–25 cm\(^{-1}\)) blue shift on complexion indicating metal ligand bond through furan oxygen atom. The strong band observed at 650 and 570 cm\(^{-1}\) and medium bands observed at 480 and 460 cm\(^{-1}\) (AT-TBT) are assigned to thiophene (C=C) out of plane bending modes and (C–S–C) bending modes\(^{(57)}\), in thiophene ring are also blue shifted by nearly (10–20 cm\(^{-1}\)) indicating thiophene–sulphur atom involvement in coordination.

The \(\nu(C=C)\) and \(\nu(C=N)\) stretching vibrations and the (CH) deformation vibration of pyridine are observed at 1610–1620 cm\(^{-1}\), 1560–1570 cm\(^{-1}\) and 760–780 cm\(^{-1}\) regions respectively. These bands shifted to lower frequency in complexation suggesting involvement of pyridine nitrogen in chelation\(^{(58)}\).

IR spectrum of the ligand shows a medium band at 2990 cm\(^{-1}\) due to intramolecular hydrogen bonded \(\nu(OH)\) group. This band is absent in the spectra of the complexes, indicating the dissociation of the phenolic proton on complexation. Moreover the strong band at 1250 cm\(^{-1}\) due to \(\nu(C-O)\) phenolic in the ligand has been shifted to the 1270–1290 cm\(^{-1}\) in the spectra of complex (OH–DP–TBT). This shift in wave number towards higher frequency also suggests the formation of (M–O) bond. The mode of coordination through the deprotonated phenolic oxygen\(^{(59)}\) azomethine nitrogen and thione
sulphur atoms is further manifested by the appearance of new bands in the region 550–590, 410–520 and 320–360 cm⁻¹ due to ν(M–O), ν(M–N) and ν(M–S) vibrations respectively.⁶¹,⁶²

The presence of broad band at 3400 cm⁻¹ in the spectra of the complex indicating the presence of water molecule which is further supported by the presence of bands at ~850 and 1530 cm⁻¹ which are ascribed to rocking and bending vibrations of coordinated water.⁶¹,⁶²

The medium bands observed at 3200 and 3140 cm⁻¹ can be assigned symmetrical stretching vibration of NH₃⁻ molecules.⁶³–⁶⁵

**Far infrared spectra**: The non lignad bands occurring in the regions 350–390, 280–310, and 330–350 cm⁻¹ may be tentatively assigned to ν(M–N), ν(M–S) and ν(M–O) modes respectively.⁶⁶,⁶⁷

Thus IR data and valence requirement of the metal ion indicate that the (TBT, MB–TBT) both are bidentate (–C=S; + >C=S); (HO–DP–TBT) (mononegative tetradentate –OH; –CH=N; >C=S; C–S–C) and (AF–TBT); (AP–TBT); (AT–TBT); (BF–TBT) (neutral tetradentate with >C=S, –CH=N; –C=S; –C=S–Cl–C-O–Cl/ C–N–C–coordinating sites.
CHAPTER IV

REFERENCES

MAGNETIC, ELECTRONIC SPECTRAL STUDIES OF CO(II) AND Ni(II) COMPLEXES OF 2–THIOURYL–6– BENZOTHIAZOLYL THIOUREA AND ITS DERIVATIVES