CHAPTER - III

SYNTHESIS AND CHARACTERISATION OF COBALT(II) COMPLEXES
WITH SEMICARBAZONE/THIOSEMICARBAZONE

INTRODUCTION:

Investigations of novel transition metal complexes to probe nucleic acids are the focus of current research\(^{(1-5)}\). Thiosemicarbazones are biologically active pharmacophores besides having good complexing ability and their activity enhances on complexation with metal ions\(^{(6-9)}\). Although oximes and their transition metal complexes have been investigated as chemical nucleases\(^{(10)}\). Metal complexes of ligands containing both oximes and thiosemicarbazones are pharmacophores much less investigated. Metal compounds of diacetyl monoxime thiosemicarbazone have been characterized but their nuclease activity has not been investigated.\(^{(11-13)}\) Recently nuclease activity of copper complexes of ortho substituted heteroaromatic thiosemicarbazones and semicarbazones have been reported.\(^{(14-16)}\)

Cobalt(II) attains a variety of stereochemical configurations in its complexes, the best known are 4-coordinate tetrahedral and six-coordinated octahedral, penta coordination has drawn much attention.\(^{(15)}\) A seven coordinate pentagonal bipyramidal cobalt(II) complex has also been reported.\(^{(16)}\) The coordination sphere of the ion is liable and equilibrium between stereochemistries in solution\(^{(17-21)}\) is quite common. However the factors which determine obtaining of a particular stereochemistry are not fully understood.\(^{(22-26)}\) The occurrence of equilibrium between high spin and low spin states of octahedral configuration of cobalt(II) has also been frequently reported.\(^{(27-30)}\)

Akhmedli et al\(^{(31)}\) have synthesized a pale-violet coloured cobalt(II) complex \([\text{Co(TSe)}_3](\text{NO}_3)_2\) by reaction of \(\text{Co(NO}_3)_2\) with thiosemicarbazide in the presence
of concentrated HNO₃ or salt solution of sodium nitrate. Coordination compounds of cobalt(II) with S−methylated thiosemicarbazide and S−methylated acetone thiosemicarbazone have been reported[2]. The proposed NN coordination of the ligand as against NS coordination of the thiosemicarbazide is a significant. The red-brown coloured [CoL₃]I₃ is diamagnetic. With acetone, S−methylated thiosemicarbazone a cobalt(II) complex, [CoL₂(CH₃COO)] is obtained, which is of high spin type (4.45 B.M.).

With 2−methylthiosemicarbazide (NH₂NMeCSNH₂) and its Schiff’s bases PhCH:NNMe (CS) NH₂ (L), Malik et al[3] have isolated cobalt(II) complexes of composition CoLX₂ (X = Cl⁻, Br⁻) which show electronic spectral bands and magnetic moment data corresponding to tetrahedral structures. With acetone Schiff’s base five coordinate complexes [Co(L)₂Cl]−Cl.H₂O and [Co(L)₂Br] Br.5ETOH are formed.

Malik et al[4] have also reported cobalt(II) complexes of the type CoL₂X₂ (X= Cl⁻, Br⁻, NO₃⁻) with thiosemicarbazone of acetone, diethyl ketone and cyclopentanone. The complexes have been shown to have trigonal−bipyramidal geometry [Co(TSc)₂X] except [Co(TSc)₂NO₃]NO₃, which shows six coordinate octahedral geometry with bidentate nitrate group.

Bellitto et al[5] have carried out detailed investigations on cobalt(II) complexes, CoL₂X₂ (X = Cl⁻, Br⁻, I⁻ and L = NH₂ C(S) NHN: CR₁ R₂, R₁ = R₂ =Me R₁ = Me, R₂ = Ph, R₁ = R₂ = cyclohexanone, R₁ = H, R₂ = Ph). From the electronic spectral data it is concluded that when R₁ and R₂ is an aryl group, the structure in solid state is tetrahedral having chromophore CoS₂X₂ where R₁ = R₂ = Me or cyclohexanone, however, the solid state structure is trigonal bipyramidal (CoN₂S₂X). These findings are in conformation to the results of earlier crystal
structure studies on iodo–bis (acetophenone thiosemicarbazone)\(^{36}\) cobalt(II) and chloro bis (acetone thiosemicarbazone) cobalt complexes\(^{37}\). The aryl derivatives on the other hand give different electronic spectra in solution probably due to change in geometry.

Ablov et al\(^ {38}\) have synthesized cobalt(II) complexes \(\text{CoL}_2X_2\) \((X = \text{Cl}^-, \text{Br}^-\) and \(\text{ClO}_4^-\)\) with thiosemicarbazones of a number of aliphatic and aromatic ketones and have reported X–ray diffractograms of these complexes. Campbell\(^ {39}\) have also reinvestigated these complexes and have shown that they have \((\text{CoN}_2\text{S}_2\text{X})\) chromophores.

Vedyanu et al\(^ {40}\) have reported cobalt(II) thiocyanato complexes \([\text{CoL}_2(\text{NCS})_2]\) with acetone thiosemicarbazone and methyl isobutylketone thiosemicarbazone. All the complexes are high spin six–coordinated octahedral.

With thiosemicarbazones of acetone, ethyl methyl ketone, diethylketone and methyl–n–propyl ketone, Khariton et al\(^ {41}\) have synthesized cobalt(II) complexes of composition \(\text{Co(Ligand}–\text{H})_2\). All the complexes show magnetic moments of 4.50 B.M. at room temperature. Thermal studies of these complexes reveal two exothermic effects at 175\(^\circ\) and 187\(^\circ\)C.

The present work describes the synthesis and structural elucidation of some cobalt thioschiff base (2–Acetyl–6–Methyl Naphthalene semicabrazone/thiosemicarbazone complexes in which the participation of the sulphur atom in coordination is studied along with nitrogen and oxygen.

**EXPERIMENTAL:**

**Preparation of Complexes:** All the complexes were isolated by in situ method. The ligands 2–Acetyl–6–Methyl–Naphthalene semicarbazone and 2–Acetyl–6–Methyl–Naphthalene Thiosemicarbazone were also used for the preparation of
complexes and were found to produce identical complexes compared to in situ preparation. The preparation is summarized below.

To an ethanolic solution (30 cm$^3$) of 2-Acetyl-6-Methyl naphthalene semicarbazone (0.001 mol) or 2-Acetyl-6-Methyl naphthalene Thiosemicarbazone prepared in situ by the condensation of 2-Acetyl-6-Methyl naphthalene and Thiosemicarbazone (0.001 mol) in ethanol] was added the metal salt solution (0.001 mol) in ethanol (20 cm$^3$) and the mixture heated under reflux at pH ~9 (15% NH$_4$OH) for 2–hour on water bath. On cooling the contents the complex separated out. It was filtered washed with 50% ethanol and dried in an electric oven at ~50°C.

**Results and Discussion:**

(i) **Magnetic Measurements:** The results of elemental analysis and metal content estimation are in good agreement with those required by the formulae in all the cases where 1:2 (M:L) Co(semicarbazone)$_2$X$_2$–where X = Br$^-$, NCS$^-$, 1/2SO$_4$$^{2-}$ and CH$_3$COO$^-$ solid chelates were isolated. Since semicarbazones behave as bidentate coordinating through $>$C=O and –CH=N groups, the isolated complexes may be four, five or six-coordinate depending upon the number of anions taking part in coordination. Magnetic moments and the electronic spectra of the complexes suggest six coordinate octahedral geometry for all the complexes except Co(semicarbazone)$_2$SO$_4$, which is tetrahedral in nature. The room temperature magnetic moment lie in the range (4.45 to 5.20 B.M.) indicating a spin quartet ground state, which is obtained for four coordinate tetrahedral, five coordinate square pyramidal or trigonal bipyramidal and six coordinate octahedral cobalt(II) complexes. On the basis of electronic spectra and virbational spectra of all the complexes, can be ascertain the possible stereochemistry of the individual complex.
(ii) **Electronic Spectral Studies:** Gaseous cobalt(II) metal ion has ground state \(4F\), and the higher state having the same spin multiplicity is \(4P\), the splitting of these in weak octahedral and tetrahedral crystal fields occurs. Thus in octahedral complexes three bands corresponding to the following transition should be expected

\[ ^4T_{1g}(F) \rightarrow ^4T_{2g}(F); \quad ^4T_{1g}(F) \rightarrow ^4A_{2g}(F); \quad ^4T_{1g}(F) \rightarrow ^4T_{1g}(P) \]

These occur around 8000–17000 and 20000–22000 cm\(^{-1}\) respectively. These are laproate forbidden transitions and the extinction coefficients lie between 1–201 mole\(^{-1}\) cm\(^{-1}\). In tetrahedral Co(II) complexes also, three bands corresponding to the following spin allowed transitions are expected.

\[ ^4A_2 \rightarrow ^4T_{2g}(F); \quad ^4A_2 \rightarrow ^4T_{1}(F); \quad ^4A_2 \rightarrow ^4T_{1}(P) \]

The bands are generally found around 5000, 8000 and 19000 cm\(^{-1}\) respectively. Thus, in both the tetrahedral and octahedral fields, cobalt(II) will absorb around 8000 and 17000 cm\(^{-1}\) regions and so these two geometries may not be differentiated by these absorptions. However, in tetrahedral case, a third band is expected to appear in the near infrared region (5000 cm\(^{-1}\)) which could not be present in octahedral complexes. So the appearance of this band could be used to distinguish between tetrahedral and octahedral complexes.

**Co(C_{14}H_{15}N_3O)_2(NCS)_2**

Infrared spectrum of Co(C_{14}H_{15}N_3O)_2(NCS)_2 exhibits two \(\nu\)C=N bands, one corresponding to coordinated and other due to uncoordinated NCS. A five coordinate structure (distorted trigonal bipyramidal or square pyramidal) for the complex may be suggested. Further a five coordinate geometry has been confirmed on the basis of electronic spectrum of the complexes as discussed below.

The electronic spectrum of the complex displays four well defined bands at 4950, 5800, 13100 and 17400 cm\(^{-1}\). Similar spectra have been reported for high
spin five coordinate cobalt(II) complexes and the bands are assigned to the following transition for high-spin five-coordinate cobalt(II)

\[ 4A_2^1 \rightarrow 4A_2^{11}, \quad 4A_2^1 \rightarrow 4A_2^{11}, \quad 4A_2^1 \rightarrow 4E(F) \text{ and } 4A_2^1 \rightarrow 4A_2^{11}(P) \]

\([\text{Co(C}_{14}\text{H}_{15}\text{N}_{3}\text{O})_{2}X_{2} (X = \text{Cl}^-, \text{Br}^-, \text{NO}_3^-, \text{CH}_3\text{COO}^- \text{ and CNS}^-)]:\) The electronic spectra of Co(II) complexes show two bands in the ranges 7800–8500 cm\(^{-1}\) and 18500–20000 cm\(^{-1}\) which may be assigned to the transitions \(4T_{2g}(F) \leftrightarrow 4T_{1g}(F)(v_1)\) and \(4T_{1g}(P) \leftrightarrow 4T_{1g}(F)(v_3)\) respectively. These transitions indicate octahedral structure for the Co(II) complexes. The \(v_2\)-band which involves a two electron transition is not observed in the spectra but is calculated from konig equation\(^{42-44}\). The ligand field parameters calculated for the Co(II) complexes are \(Dq = 885–966\text{cm}^{-1}\), \(B^1 = 784–844\text{ cm}^{-1}\), \(\beta = 0.807–0.868\), \(v_2 = 16635–18000\text{ cm}^{-1}\) and \(\text{LFSE} = 85.1–92.7\text{ KJ mol}^{-1}\). This structure is further supported by the ratio \(v_2/v_1 = 1.44\) which is close to the value expected for octahedral structure. The ligand field parameters viz. \(B^-\) and \(\beta\)–suggest appreciable amount of the covalence character in the metal–ligand bonds.\(^{45}\)

(iii) **Infrared Spectral Studies:** The infra red spectra of ligand show a broad band around 3445–3420 cm\(^{-1}\) due to the intramolecular hydrogen bonded \(-\text{OH}\). The ligand show bands in the region 3240–3200 and 1705–1685 cm\(^{-1}\) assigned to \(v(\text{N-H})\) and \(v(\text{C=O})\) respectively. The bands due to \(v(\text{C=N})\) are located in the regions 1654–1648 cm\(^{-1}\). The band due to \(v(\text{N-H})\) remains unaltered. Non shifting of \(v(\text{N-H})\) clearly suggests coordination of the ligand in keto form. The band due to \(v(\text{C=O})\) shifts to lower frequency by 12–18 cm\(^{-1}\) indicating the involvement of coordination of carbonyl oxygen to the metal ion. The band due to \(v(\text{C=N})\) also suffers a negative shift by 15–20 cm\(^{-1}\) indicating the involvement of azomethine nitrogen in the coordination\(^{46}\).
<table>
<thead>
<tr>
<th>S.No.</th>
<th>Complexes</th>
<th>Transition (λ.max cm⁻¹)</th>
<th>Dq cm⁻¹</th>
<th>B cm⁻¹</th>
<th>β</th>
<th>L.F.S.E. KJ mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>[Co(C₁₄H₁₅N₃O)₂Br₂]</td>
<td>7800 16635 18500</td>
<td>885</td>
<td>784</td>
<td>0.807</td>
<td>85.1</td>
</tr>
<tr>
<td>2.</td>
<td>[Co(C₁₄H₁₅N₃O)₂(NO₃)₂]</td>
<td>8000 16200 18200</td>
<td>961</td>
<td>844</td>
<td>0.822</td>
<td>92.7</td>
</tr>
<tr>
<td>3.</td>
<td>[Co(C₁₄H₁₅N₃O)₂(CH₃COO)₂]</td>
<td>8500 16400 19500</td>
<td>966</td>
<td>830</td>
<td>0.831</td>
<td>92.4</td>
</tr>
<tr>
<td>4.</td>
<td>[Co(C₁₄H₁₅N₃O)₂SO₄]</td>
<td>5700 8335 17045</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td><a href="NCS">Co(C₁₄H₁₅N₃O)₂(NCS)</a></td>
<td>4970 5816 13112</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>[Co(C₁₄H₁₅N₃O)₂Cl₂]</td>
<td>8463 18000 17384</td>
<td>897</td>
<td>816</td>
<td>0.845</td>
<td>92.0</td>
</tr>
</tbody>
</table>

Table 3.1
Electronic Spectral bands of Semicarbazone complexes
The non-ligand bands of the present complexes can be carefully picked up for assignments. In general the \( \nu(M-N) \) band is usually sharp and strong and the \( \nu(M-O) \) band is broad and strong since a large dipole moment change is involved in the vibration of the \((M-O)\) bond in comparison to that of the \((M-N)\) bond. Hence it is expected that the \( \nu(M-O) \) band shall appear at a higher energy in comparison to that of the \( \nu(M-N) \) band. The \((M-O)\) bond length is usually shorter than the \( \nu(M-N) \) bond length and this also supports the occurrence of the \( \nu(M-O) \) band at a higher energy in comparison to that of the \( \nu(M-N) \) band. Thus in the present complexes the non-ligand bands appearing in the regions 570–550 and 480–450 cm\(^{-1}\) are assigned to \( \nu(M-O) \) 480–450 cm\(^{-1}\) and \( \nu(M-N) \) modes respectively.\(^{47,48}\)

The infrared spectra of the nitrato complex show bands corresponding to both coordinated and uncoordinated nitrate groups.\(^{49}\) The coordinated nitrate group should show absorption at 1505–1475 cm\(^{-1}\) \( (\nu_1) \); 1325–1275 cm\(^{-1}\) \( (\nu_5) \); 1045–1020 cm\(^{-1}\) \( (\nu_2) \) and 808–8703 cm\(^{-1}\) \( (\nu_6) \). The complex under study shows IR band at 1475 cm\(^{-1}\) \( (\nu_1) \), 1390 cm\(^{-1}\) \( (\nu_3) \); 1275 cm\(^{-1}\) \( (\nu_5) \), 1020 cm\(^{-1}\) \( (\nu_2) \); and 820 cm\(^{-1}\) \( (\nu_6) \). The separation of \(-200\) cm\(^{-1}\) between \( \nu_1 \) and \( \nu_3 \) indicates the bidentate nature of the nitrate group. The broad absorption at 1390 cm\(^{-1}\) is assigned to \( \nu_3 \) of the uncoordinated nitrate.\(^{50-52}\)

Extensive IR-spectral studies have been made on metal complexes of carboxylic acids. The acetate ion may coordinate to a metal ion in one of the following modes.

\[
\begin{align*}
\text{(A)} & \quad \begin{array}{c}
\text{M} \\
\text{O} \\
\text{C} - \text{CH}_3
\end{array} \\
\text{(B)} & \quad \begin{array}{c}
\text{M} \\
\text{O} \\
\text{O} \quad \text{C} - \text{CH}_3
\end{array} \\
\text{(C)} & \quad \begin{array}{c}
\text{M} \\
\text{O} \\
\text{O} \quad \text{C} - \text{CH}_3
\end{array}
\end{align*}
\]
The $\nu_{as}(COO^{-})$ and $\nu_{s}(COO^{-})$ of free acetate ions are of ~1560 cm$^{-1}$ and 1416 cm$^{-1}$ respectively. In the unidentate complex (St–A) $\nu(C=O)$ is higher than $\nu_{as}(COO^{-})$ and $\nu(C-O)$ is lower than $\nu_s(COO^{-})$. As a result the separation between the two $\nu(CO)$ is much larger in unidentate complexes than free ion. The opposite trend is observed in the bidentate complex (St–B) the separation between the $\nu(CO)$ is smaller than that of free ion in this case. In the bridging complexes (St–C) however two $\nu(CO)$ are close to the free ion values. The present complexes show infrared frequency bands corresponding to $\nu_{as}(COO^{-})$ and $\nu_{s}(COO^{-})$ at 1608 and 1370 cm$^{-1}$ respectively. This observation indicates that both the acetate group are unidentate.

The complexes exhibited a strong band at 1650 and a weak band at 1330 cm$^{-1}$ due to $\nu_{as}(COO^{-})$ and $\nu_{s}(COO^{-})$ vibrations respectively of acetate ion. A negative shift of 70 cm$^{-1}$ in $\nu_{s}(COO^{-})$ and no change in $\nu_{as}(COO^{-})$ frequency confirms the coordination of acetate ion as a monodentate ligand.$^{(53)}$ Further bands around 1510, 1440, and 1340 cm$^{-1}$ which can be assigned to $\nu_{as}(COO)$, $\nu_{s}(COO)$ and $\delta CH_3$, vibration indicating the presence of acetate ion in the coordination sphere.$^{(54)}$ 

**Co(C$_{14}$H$_{12}$N$_{3}$O)$_{2}$SO$_{4}$**: The ligand show a sharp band around 3200 cm$^{-1}$ which may be assigned to stretching vibration of the $\nu(N-H)$ group. This band do not shift in the complex showing its non participation in coordination. $\nu(C=O)$ vibration which appears in the region 1640–1680 cm$^{-1}$ in the ligand is shifted by 20–40 cm$^{-1}$ towards lower wave number region in the complex. This indicate that the carbonyl oxygen also coordinates. A band of 1600 cm$^{-1}$ in the ligand is ascribed to $\nu(C=N)$ azomethine. On complexation shifting of the $\nu(C=N)$ to lower frequency region (~1570 cm$^{-1}$) suggest the bonding of azomethine nitrogen to metal ion. The participation of nitrogen of azomethine group and oxygen of $\nu(C=O)$ group in
The $v_{as}(\text{COO}^-)$ and $v_{s}(\text{COO}^-)$ of free acetate ions are of ~1560 cm$^{-1}$ and 1416 cm$^{-1}$ respectively. In the unidentate complex (St–A) $v(\text{C}=\text{O})$ is higher than $v_{as}(\text{COO}^-)$ and $v(\text{C}=\text{O})$ is lower than $v_{s}(\text{COO}^-)$. As a result the separation between the two $v(\text{CO})$ is much larger in unidentate complexes than free ion. The opposite trend is observed in the bidentate complex (St–B) the separation between the $v(\text{CO})$ is smaller than that of free ion in this case. In the bridging complexes (St–C) however two $v(\text{CO})$ are close to the free ion values. The present complexes show infrared frequency bands corresponding to $v_{as}(\text{COO}^-)$ and $v_{s}(\text{COO}^-)$ at 1608 and 1370 cm$^{-1}$ respectively. This observation indicates that both the acetate group are unidentate.

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$\text{Co(C}_{14}\text{H}_{12}\text{N}_{2}\text{O})_2\text{SO}_4$: The ligand show a sharp band around 3200 cm$^{-1}$ which may be assigned to stretching vibration of the $v(\text{N}=\text{H})$ group. This band do not shift in the complex showing its non participation in coordination. $v(\text{C}=\text{O})$ vibration which appears in the region 1640–1680 cm$^{-1}$ in the ligand is shifted by 20–40 cm$^{-1}$ towards lower wave number region in the complex. This indicate that the carbonyl oxygen also coordinates. A band of 1600 cm$^{-1}$ in the ligand is ascribed to $v(\text{C}=\text{N})$ azomethine. On complexation shifting of the $v(\text{C}=\text{N})$ to lower frequency region (~1570 cm$^{-1}$) suggest the bonding of azomethine nitrogen to metal ion. The participation of nitrogen of azomethine group and oxygen of $v(\text{C}=\text{O})$ group in
Fig - 3.1: IR-Spectra of Co(II) Complexes
(I) Co(C_{14}H_{15}N_3O)_2Cl_2  (II) Co(C_{14}H_{15}N_3O)_2Br_2  (III) Co(C_{14}H_{15}N_3O)_2(NO_3)_2
The important vibrational bands of metal complexes are included in table. The absence of SH–band at 2570 cm⁻¹ and presence of NH–band at 3233 cm⁻¹ in the IR–spectrum of ligand suggest that the ligand remain in thione form at least in solid state. A strong band appearing at 1200 cm⁻¹ in the spectra of ligand and shifted to lower frequency indicating the involvement of thioketosulphur in coordination. The >C=N (imine band) is observed at 1610 cm⁻¹ in the IR–spectra of ligand. This band is shifted to lower wave numbers in the spectra of complexes suggesting the participation of imine nitrogen atom in coordination. Additional bands are observed in the far IR–spectra of metal complexes in 500–480 and 365–315 cm⁻¹ regions due to ν(M–N) and ν(M–S) modes respectively.

Infrared Spectral Studies: The IR–spectrum of the thiocyanate complex show two ν(C≡N) absorptions at 2085 and 2055 cm⁻¹ indicating two types of thiocyanate linkage. It is not certain whether the two ν(C≡N) frequency arises from the presence of (i) one terminal N–bonded and one ionic thiocyanato group or (ii) one bridging and one terminal N–bonded thiocyanato group. The free thiocyanate ion shows three IR–bands due to ν(CN), δ(SCN) and ν(CS) modes. The first and the last bands occur at 2050 and 748 cm⁻¹ respectively in the present complex. The positions of these when compared to those in KSCN show change hence the ion is coordinated. The electronic spectrum indicate that in solid states the complex has penta-coordinated geometry arising due to bidentate behavior of thiosemicarbazone.

Coordination of one thiocyanato group and the ionic nature of the other thiocyanato group indicated.

**Co(C_{14}H_{15}N_{3}S)_{3}(NO_{3})_{2}:** The molar conductance of the compound was recorded in methanol and found in the range 118–140 ohm⁻¹ cm² mol⁻¹ which confirmed the (1:2) electrolytic nature of the compound.
Fig - 3.2 : IR-Spectra of Co(II) Complexes
(I) Co(C_{14}H_{15}N_{3}O)(CH_{3}COO)_{2} (II) Co(C_{14}H_{15}N_{3}O)_{2}SO_{4} (III) Co(C_{14}H_{15}N_{3}O)_{2}(SCN)_{2}
Important IR absorption bands are summarized in table. The possibility of thione-thiol tautomerism (H-N-C=S $\rightleftharpoons$ C=N-SH) in the ligand has been ruled out, since there is no band around 2500–2600 cm$^{-1}$ which is characteristic of thiol group. Coupled vibration among the components of thioamide bands–I $\beta$(NH)+$\nu$(CN), II $\nu$(CN) + $\beta$(NH), III and IV are distributed around 1540, 1450, 1330 and 930 cm$^{-1}$. Thioamide bands III and IV which have major contribution of $\nu$(C=S) have gone considerable reduction in intensity in the complex due to thioenolisation and subsequent coordination to metal which is supported by the appearance of a weak band around 610 cm$^{-1}$ due to $\nu$(C=S). The band due to $\nu$(NH) persists in complex. The band around 1595–1603 cm$^{-1}$ which is assigned to $\nu$(C=N) has shifted to higher energy by 3–10 cm$^{-1}$ supporting the coordination of azomethine nitrogen. Coordination of azomethine nitrogen has been proposed for the majority of thiosemicarbazone complexes with evidence based on shifting of $\nu$(C=N). Interestingly the shifting has been reported both to higher and lower energies.

The shift of these bands depends on bond order to $\nu$(C=N) on coordination which in turn depends on group attached to azomethine group. The low frequency bands in the 500–470 and 370–292 cm$^{-1}$ regions are assigned to $\nu$(M–N) and $\nu$(M–S) respectively. The infrared spectrum of the complex show the band (NO$_2$–asymmetric stretch) of ionic nitrate at 1388 cm$^{-1}$ but do not show bands which could be attributed the $v_4$, $v_1$ and $v_2$ bands of the coordinated nitrato group in the region 1530–1580, 1290–1250 and 1035–970 cm$^{-1}$. This confirms that the nitrate groups are ionic in solid state also. Two bidentate ligand molecules around cobalt(II) should give rise to four coordinate tetrahedral structure.
Fig - 3.3 : IR-Spectra of Co(II) Complexes
(I) Co(C_{14}H_{15}N_{3}S)_{2}Cl_{2}  (II) Co(C_{14}H_{15}N_{3}S)_{2}Br_{2}  (III) Co(C_{14}H_{15}N_{3}S)_{2}I_{2}
The solid state electronic spectrum of \([\text{Co} (\text{C}_{14} \text{H}_{15} \text{N}_3 \text{S})_2] (\text{NO}_3)_2\) shows bands at 8333 and 15380 cm\(^{-1}\) with a shoulder at 16670 cm\(^{-1}\) attributable to characteristic tetrahedral transitions \(4A_2 \rightarrow 4T_1(F)(v_2)\) and \(4A_2 \rightarrow 4T_1(P)(v_3)\) respectively. The intense band observed around 28000 cm\(^{-1}\) may be a charge transfer band considering the energy of \(v_3\)-transition as the average of the bands at 15380 and 16670 cm\(^{-1}\), the various ligand field parameters have been evaluated\(^{(63)}\) \([\text{Dq}=495 \text{ cm}^{-1}; \text{B}=633 \text{ cm}^{-1}; \beta = 0.65; \beta^\circ = 34-53\%; \nu_2/\nu_1 = 1.68 \text{ and LFSE} = 16.97 \text{ Kcal/mol}]\).

The light green coloured solid \([\text{Co} (\text{C}_{14} \text{H}_{15} \text{N}_3 \text{S})_2] (\text{NCS})_2\) dissolves in DMF exhibiting an absorption band at 15150 cm\(^{-1}\) (\(\varepsilon = 210\)) with a shoulder at 16670 cm\(^{-1}\) (\(\varepsilon = 185\)) which may be due to \(v_3\)-transition\(^{(64)}\). The \(v_2\)-band could not be located. The complex on dissolution in a strong coordinating base like pyridine shows a characteristic band around 19300 cm\(^{-1}\) which may be probably due to coordination of two pyridine molecules resulting in an octahedral geometry around\(^{(65)}\) the Co(II) ion. An appreciable reduction in \(B'\) (633 cm\(^{-1}\)) and a spin–orbit coupling constant \(\lambda'(-133)\) suggests a considerable covalent character of metal–ligand bond [Free ion values \(\lambda' = -178\) and \(B' = 967\) cm\(^{-1}\) for Co(II) ion]\(^{(66)}\).

**[Co(C\(_{14}\)H\(_{15}\)N\(_3\)S\(_2\))SO\(_4\)]**: The analytical data of the complex reveal that the Co(II) complex is of (1:2) metal to ligand stoichiometry and can be represented by the formula \([\text{Co} (\text{C}_{14} \text{H}_{15} \text{N}_3 \text{S})_2] \text{SO}_4\). The complex is insoluble in water, ethanol and methanol but soluble in coordinating solvents like DMF and DMSO. The molar conductance value of the complex at \(10^{-3}\) M in DMF fall in the range 10–16 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\), indicating the non electrolytic nature of the complex.

The free ligand show a very strong absorption in the range 1605–1602 cm\(^{-1}\) in their IR spectra which is characteristic of the azomethine group. In the IR-spectra of the complex this band is shifted to lower region 1600–1575 cm\(^{-1}\)
Fig. 3.4: IR-Spectra of Co(II) Complexes
(I) Co(C_14H_15N_3)S_2(NO_3)_2, (II) Co(C_14H_15N_3)S_2(CH_3COO)_2, (III) Co(C_14H_15N_3)S_2SO_4, (IV) Co(C_14H_15N_3)S_2(SCN)_2.
indicating the coordination of nitrogen atom of the ligand to metal ion. ν(C=S) stretching frequency is observed around 2600 cm⁻¹ in the ligand get reduce in complex indicate that sulphur is coordinated to metal ion.⁶⁷

The infrared spectrum of the complex show the band⁶⁸ (NO₂–asymmetric stretch) of ionic nitrate at 1388 cm⁻¹ but do not show bands which could be attributed to the ν₁−, ν₂− and ν₃− bands of the coordinated⁶⁹ nitrato group in the region 1530–1580, 1290–1250 and 1035–930 cm⁻¹. This confirms that the nitrato groups are ionic in solid state also two bidentate ligand molecules around cobalt(II) should give rise to four coordinate tetrahedral structure.

**Co(C₁₂H₁₅N₃S)₂SO₄:** The elemental analysis compiles with (1:2) (M:L) stoichiometry of the adducts. In the IR-spectra of ligand strong bands observed between 3400–3500 cm⁻¹ are assigned to symmetric and asymmetric stretching modes to NH₂ group. These bands remain unaltered in the spectra of adducts indicating non participation of NH₂ group in the bonding. The bands observed in the region 2900–3350 cm⁻¹ are due to ν(NH) and ν(CH) stretching of the ligand. In the complex the position of this band is not much changed indicating that the NH–group is not deprotonated. The bands observed at ~1620 and ~1060 cm⁻¹ in the spectra of complex are assigned to ν(C≡N) and ν(C=S) respectively. These bands get shifted to lower wave number compared to ligand. These observations are consistent with ligand coordination through sulphur and azomethine nitrogen.⁷⁰ The spectra in the region 600–200 cm⁻¹ are complicated and changes in the spectra of complexes could not be unambiguously assigned. However new bands in the spectra of complexes at ~455 and ~290 cm⁻¹ may be assigned to ν(M–S) and ν(M–N).
The infrared spectrum\(^{(71)}\) of the complex shows bands corresponding to unidentate sulphate group. The free sulphate ions\(^{(72)}\) belongs to high symmetry point Td, of the four fundamentals only \(v_3\) and \(v_4\) are infrared active absorbing at 1104 cm\(^{-1}\) and 615 cm\(^{-1}\), if the ion is coordinated to a metal, the symmetry is lowered and splitting of the degenerate modes occur together with the appearance of new bands in the infrared spectrum corresponding to raman active band in the free ion. The lowering of symmetry caused by coordination is different for the unidentate and bidentate complexes as shown by the accompanying structures\(^{(73)}\). (Fig. 3.1)

![Diagrams](image)

**Fig. 3.1**

For unidentate SO\(_4\), the symmetry is lowered to C3v. Both \(v_1\) and \(v_2\) appear with medium intensity. Moreover, \(v_1\) and \(v_4\) each split into two bands. For bidentate SO\(_4\) ions, the symmetry is lowered to C\(_{2v}\) and \(v_3\), \(v_4\) each split into three bands. Electronic spectrum of this complex also indicates five-coordinate geometry.

(iv) **ESR–Studies:** The 4F state of d\(^7\) in an octahedral crystal field is split into three states with three orbital state lowest in energy. Since these states are connected by the spin–orbit coupling, the spin–lattice–relaxation times are short, making ESR measurements possible only at very low temperatures. In octahedral or near octahedral symmetry the spin–orbit coupling splits the twelve low-lying spin states, leaving a doublet state lowest in energy. This Kramer’s doublet is split by the magnetic field, and the only transitions observed in ESR are between these two states, since they are the only ones populated each line temperatures required to
observed the ESR. Transitions in this Kramer’s doublet can be represented by spin Hamiltonian solved for.

\[ H = \beta e \left[ g_x H_x S_x + g_y H_y S_y + g_z H_z S_z \right] + A_x S_x I_x + A_y S_y I_y + A_z S_z I_z \]

\( S = \frac{1}{2} \) and all results of \( d^7 \) in near-octahedral fields have been interpreted with this Hamiltonian.

Olle has considered the case of \( d^7 \) in an octahedral field. The spin–orbit coupling splits the twelve spin states of the three orbital ground states into two states of energy, \((15/4)\ A\) four states of energy \(3/2\) and six states of energy, \((9/4)\). For \( d^7 \) is negative, so that doublet state is the ground state. The \( g \) and \( A \) parameters may be given by following expression.

\[ g = 1 + \frac{5}{3} (2.0023) = 4.3372 \]

\[ A = p \left[ -\frac{5}{3} k + 1 + \frac{2}{63} \right] \]

Inclusion of covalent bonding and configuration interaction with the \( ^4p \) states of \( d^7 \) tend to reduce both \( g \) and \( A \) in magnitude, whereas inclusion of second-order terms involving the \( ^4T_{2g} \) state of \( ^4F \) tends to increase \( g \) and \( A \). Low and Rubin estimate the reduction in the orbital contribution to \( g \) from covalent effects to be 0.89 for \( Co^{2+} \) in the orbital contribution to go from covalent effects to be 0.89 for \( Co^{2+} \) in both MgO and CaO.

Zhu et al have discussed the Theory of \( d^7 \) in an octahedral field with small tetragonal and trigonal distortions. They found that the values of \( g \) for transition between the two states of Kramer’s doublet may be very sensitive to distortions in the crystal field and were able to account for observed values readily in terms of the theory.

In strong crystalline fields or highly distorted fields a doublet \( S=1/2 \) state becomes lowest in energy. In this situation there are generally no nearly states. So that of factors are close to 2.0023 and the ESR is observed at higher temperatures.
ESR results can be fitted into above spin Hamiltonian and observed values are given in Table 3.1.

In tetrahedral and cubic symmetry, the crystal field levels are inverted, giving a single orbital state lowest. For $d^3$ in an octahedral field, the $^4F$ state also has the single orbital state lowest, so we would expect that $d^7$ configuration in a tetrahedral or cubic field to behave in a similar fashion and fit the spin Hamiltonian, solved for

$$H = g_{11} \vec{\beta}_c H_z S_z + g_1 \vec{\beta}_c [H_x S_x + H_y S_y] + D [S_x^2 - S_y^2] + E [S_x S_y - S_y S_x] + A S_z I_z + B [S_x I_x + S_y I_y]$$

$S = 3/2$. For most examples, listed in Table 3.1 the tetrahedral symmetry is not distorted so that $D = E = 0$ and no five structure is reported. The $S = 3/2$ character of spin state is revealed in these cases by the fact that equation $(S_x^2 H, S_y^2 H - 1/5 [35 (S+1)] SH)$. Must be added to the spin Hamiltonian to explain ESR results on $d^7$ in tetrahedral and cubic field\(^{(76)}\). For Co\(^{2+}\) in Cs\(_3\)CoI\(_5\), $D = -4.5 \text{ cm}^{-1}$ and in CdS $D = 2 \text{ cm}^{-1}\(^{(77)}\).

Examples of regular and distorted tetrahedral and high spin octahedral cobalt(II) complexes along with their spin Hamiltonian parameters $g$ are given in Table 3.1.

ESR spectra of the polycrystalline complexes under study were recorded at liquid nitrogen temperature. Because the rapid spin lattice relaxation of Co\(^{2+}\) broadens the lines at higher temperatures, $g$-values are presented in Table 3.5. The large deviation of the $g$ values from the spin only value ($g = 2.0023$) is due to the large angular momentum contribution, this result accords with the magnetic susceptibilities and electronic spectra as discussed earlier.\(^{(78-85)}\)
<table>
<thead>
<tr>
<th>Ion</th>
<th>Host lattice</th>
<th>$g_z$</th>
<th>$g_x$</th>
<th>$X_{10}^{4}$ cm$^{-1}$</th>
<th>$g_y$</th>
<th>$A_x$</th>
<th>$A_y$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
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<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Octahedral crystal field</td>
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<td></td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>HgO</td>
<td>4.2785</td>
<td></td>
<td>97.79</td>
<td></td>
<td></td>
<td></td>
<td>78,79</td>
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<tr>
<td></td>
<td>CaO</td>
<td>4.372</td>
<td></td>
<td>132.2</td>
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<td></td>
<td></td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>Tetrahedral crystal field</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>CdTe</td>
<td>2.3093</td>
<td></td>
<td>23.4</td>
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<td></td>
<td>81</td>
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<tr>
<td></td>
<td>ZnS</td>
<td>2.248</td>
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<td>1.8</td>
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<td></td>
<td>82</td>
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<tr>
<td></td>
<td>ZnSe</td>
<td>2.270</td>
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<td>17.5</td>
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<td></td>
<td>ZnTe</td>
<td>2.292</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>Cubic crystal field</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>CaF$_2$</td>
<td>2.309</td>
<td></td>
<td></td>
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<td></td>
<td>54</td>
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<tr>
<td></td>
<td>CdF$_2$</td>
<td>2.278</td>
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<td>23</td>
<td></td>
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<td></td>
<td>54</td>
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<tr>
<td></td>
<td>Distorted octahedral crystal field</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>(NH$_4$)$_2$Zn(SO$_4$)$_2$ ·6H$_2$O</td>
<td>6.45</td>
<td>3.06</td>
<td>2.45</td>
<td>20</td>
<td></td>
<td>49</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Rb$_2$ Zn (SO$_4$)$_2$ 6H$_2$O</td>
<td>6.65</td>
<td>2.7</td>
<td>3.44</td>
<td>3.3</td>
<td>2.93</td>
<td>49</td>
<td>50</td>
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<tr>
<td></td>
<td>Zn Si F$_6$·6H$_2$O</td>
<td>5.82</td>
<td>---</td>
<td>3.44</td>
<td>---</td>
<td>1.84</td>
<td>47</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>Zn SO$_4$. 7H$_2$O</td>
<td>6.90</td>
<td>2.30</td>
<td>4.947</td>
<td>---</td>
<td>2.54</td>
<td>28</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$</td>
<td>2.292</td>
<td>---</td>
<td>---</td>
<td></td>
<td>32.4</td>
<td>97.2</td>
<td>51, 52</td>
</tr>
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### Table 3.2 Contd...

**Spin Hamiltonian Parameters for d⁷ ions**

<table>
<thead>
<tr>
<th>Ion</th>
<th>Host lattice</th>
<th>gₓ</th>
<th>gᵧ</th>
<th>Aₓ</th>
<th>Aᵧ</th>
<th>X₁₀⁵ cm⁻¹</th>
<th>Reference</th>
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<tr>
<td>TiO</td>
<td></td>
<td>5.860</td>
<td>2.090</td>
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<td></td>
<td>3.725</td>
<td>140.2839</td>
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<tr>
<td>ZnF₂</td>
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<td>6.05</td>
<td>2.0</td>
<td></td>
<td></td>
<td>4.1</td>
<td>217</td>
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<tr>
<td>CdCl₂</td>
<td></td>
<td>3.04</td>
<td>---</td>
<td></td>
<td></td>
<td>4.95</td>
<td>36</td>
</tr>
<tr>
<td>CdBr₂</td>
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<td>2.71</td>
<td>---</td>
<td></td>
<td></td>
<td>4.99</td>
<td>32</td>
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</table>

**Distorted Tetrahedral**

<table>
<thead>
<tr>
<th>Co²⁺</th>
<th>Ca₃ Co Cl₅</th>
<th></th>
<th></th>
<th>2.32</th>
<th>2.27</th>
<th>4.6</th>
<th>102</th>
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<tr>
<td>CdS</td>
<td></td>
<td>2.69</td>
<td>2.27</td>
<td></td>
<td></td>
<td>12</td>
<td>103</td>
</tr>
</tbody>
</table>

**High spin octahedral**

<p>| Co²⁺    | (Bu₄N₂)Ni(S₂C₂(CN)₂)₂ | 1.977 | 2.798 | 2.025 | 23   | 50        | 28        | 61        |</p>
<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound</th>
<th>Colour</th>
<th>Elemental analysis calcd/Found %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Co</td>
</tr>
<tr>
<td>1.</td>
<td>Co(C₁₄H₁₅N₃O)₂Cl₂</td>
<td>Dark reddish</td>
<td>9.53</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(9.63)</td>
</tr>
<tr>
<td>2.</td>
<td>Co(C₁₄H₁₅N₃O)₂Br₂</td>
<td>Dark Purple</td>
<td>8.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(8.40)</td>
</tr>
<tr>
<td>3.</td>
<td>Co(C₁₄H₁₅N₃O)₂(NO₃)₂</td>
<td>Camel</td>
<td>8.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(8.86)</td>
</tr>
<tr>
<td>4.</td>
<td>Co(C₁₄H₁₅N₃O)₂(CH₃COO)₂</td>
<td>Light Purple</td>
<td>8.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(8.94)</td>
</tr>
<tr>
<td>5.</td>
<td>Co(C₁₄H₁₅N₃O)₂SO₄</td>
<td>Reddish Brown</td>
<td>9.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(9.25)</td>
</tr>
<tr>
<td>6.</td>
<td>Co(C₁₄H₁₅N₃O)₂(SCN)₂</td>
<td>Forest Green</td>
<td>8.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(8.97)</td>
</tr>
<tr>
<td>7.</td>
<td>Co(C₁₄H₁₅N₃S)₂Cl₂</td>
<td>Blackish Green</td>
<td>9.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(9.15)</td>
</tr>
<tr>
<td>8.</td>
<td>Co(C₁₄H₁₅N₃S)₂Br₂</td>
<td>Blackish Green</td>
<td>7.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(8.04)</td>
</tr>
<tr>
<td>9.</td>
<td>Co(C₁₄H₁₅N₃S)₂I₂</td>
<td>Yellowish Green</td>
<td>7.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(8.04)</td>
</tr>
<tr>
<td>10.</td>
<td>Co(C₁₄H₁₅N₃S)₂(NO₃)₂</td>
<td>Dark Maroon</td>
<td>8.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(8.45)</td>
</tr>
<tr>
<td>11.</td>
<td>Co(C₁₄H₁₅N₃S)₂(CH₃COO)₂</td>
<td>Blackish Green</td>
<td>8.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(8.52)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(8.80)</td>
</tr>
<tr>
<td>13.</td>
<td>Co(C₁₄H₁₅N₃S)₂(SCN)₂</td>
<td>Green</td>
<td>8.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(8.55)</td>
</tr>
</tbody>
</table>
### Table 3.4

**Electronic Spectral bands of thiosemicarbazone Complexes**

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$\lambda_{\text{max}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(C$<em>{14}$H$</em>{15}$N$_3$S)$_2$Cl]Cl</td>
<td>5000 5900 13300 17500</td>
</tr>
<tr>
<td>[Co(C$<em>{14}$H$</em>{15}$N$_3$S)$_2$Br]Br</td>
<td>4960 5850 13100 17300</td>
</tr>
<tr>
<td>[Co(C$<em>{14}$H$</em>{15}$N$_3$S)$_2$I]I</td>
<td>4900 5800 13000 17300</td>
</tr>
<tr>
<td>[Co(C$<em>{14}$H$</em>{15}$N$_3$S)$_2$(SCN)]SCN</td>
<td>5200 5950 13000 17800</td>
</tr>
<tr>
<td><a href="NO$_3$">Co(C$<em>{14}$H$</em>{15}$N$_3$S)$_2$(NO$_3$)</a></td>
<td>6000 16100</td>
</tr>
</tbody>
</table>

### Table 3.5

**ESR Data of Co(II) Complexes of Semicarbazones**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Complexes</th>
<th>g$_{11}$</th>
<th>g$_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Co(C$<em>{14}$H$</em>{15}$N$_3$O)$_2$(NO$_3$)$_2$</td>
<td>2.469</td>
<td>1.990</td>
</tr>
<tr>
<td>2.</td>
<td>Co(C$<em>{14}$H$</em>{15}$N$_3$O)$_2$(CH$_3$COO)$_2$</td>
<td>2.458</td>
<td>1.976</td>
</tr>
<tr>
<td>3.</td>
<td>Co(C$<em>{14}$H$</em>{15}$N$_3$O)$_2$SO$_4$</td>
<td>2.476</td>
<td>1.988</td>
</tr>
<tr>
<td>4.</td>
<td>Co(C$<em>{14}$H$</em>{15}$N$_3$O)$_2$(SCN)$_2$</td>
<td>2.440</td>
<td>1.959</td>
</tr>
<tr>
<td>5.</td>
<td>Co(C$<em>{14}$H$</em>{15}$N$_3$S)$_2$(NO$_3$)$_2$</td>
<td>2.374</td>
<td>2.014</td>
</tr>
<tr>
<td>6.</td>
<td>Co(C$<em>{14}$H$</em>{15}$N$_3$S)$_2$(CH$_3$COO)$_2$</td>
<td>2.5060</td>
<td>1.906</td>
</tr>
<tr>
<td>7.</td>
<td>Co(C$<em>{14}$H$</em>{15}$N$_3$S)$_2$SO$_4$</td>
<td>2.423</td>
<td>1.931</td>
</tr>
<tr>
<td>8.</td>
<td>Co(C$<em>{14}$H$</em>{15}$N$_3$S)$_2$(SCN)$_2$</td>
<td>2.4139</td>
<td>1.931</td>
</tr>
</tbody>
</table>
(v) **Thermal Behaviour:** The thermal analysis of the complexes $\text{Co(C}_{14}\text{H}_{15}\text{N}_{3}\text{O})_{2}\text{Cl}_{2}$; $\text{Co(C}_{14}\text{H}_{15}\text{N}_{3}\text{O})_{2}\text{Br}_{2}$; $\text{Co(C}_{14}\text{H}_{15}\text{N}_{3}\text{O})_{2}(\text{NO}_{3})_{2}$ has been undertaken to study their mode of decomposition. The simultaneous DTA–TG curves of the Co(II) complexes show that the complex is stable up to 353 K and starts decomposing gradually, followed by endothermic peaks at temperatures 380, 400 and 477 K characterized by the total weight loss of 70; 61 and 66% corresponding to the loss of two molecules of ligand (calculated weight loss 78.76; 68.85 and 72.59%). A further exothermic reaction takes place at 796K with the loss of the remaining anion and the formation of $\text{CO}_3\text{O}_4$ as an end product. The remaining complexes have also been found to decompose in a manner described above. No stable intermediate species is formed.
CHAPTER-III

REFERENCES

54. K. Nakamoto, Infrared and Raman spectra of inorganic and coordination compounds (Wiley & Sons, New York) 197, 211.