Chapter 5

SYNTHESIS, STRUCTURAL AND SPECTRAL CHARACTERIZATION OF COBALT (II) COMPLEXES OF SEMICARBAZONE AND THIOSEMICARBAZONE

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CHAPTER-5

SYNTHESIS AND SPECTRAL CHARACTERISTICS OF COBALT II COMPLEXES OF SEMICARBAZONE AND THIOSEMICARBAZONE

5.1 INTRODUCTION

Cobalt is known to be one of the trace elements essential to human nutrition. It is present in meat and dairy products and in vitamin B12. It is an important substance that can prevent the disease known as pernicious anemia, in which the blood was depleted of a adequate number of its carrying red cells\(^1\).

The chemistry of transition metal complexes of semicarbazone has been receiving considerable attention because of their biological activities and providing models for metal ligand bonding sites in several enzymes\(^2\)-\(^4\). In the solid state, these semicarbazone were existed in the keto form (fig.5.11a). In solution, however, they were known to tautomerize into the enol form (fig5.11b). Complexation usually took place through the N and O donor atoms\(^2\),\(^5\),\(^8\) resulting in the formation of a five-membered chelate ring (fig 5.1c and d).
Fig 5.1 (abcd) conversion of keto to enol and five membered ring structure

Cobalt (II) attains a variety of stereochemical configuration in its complexes, the best known are four coordinate tetrahedral and six co-ordinate octahedral, penta-coordinate has drawn much attention\(^9\). A seven coordinate pentagonal bipyramidal cobalt (II) complex has also been reported.

5.2. Earlier Work on Co (II) complex

The complexes\(^{10}\) [Co(PLITSC-2H)(PLITSC-H)]CH\(_3\)OH (PLITSC is pyridoxal S- methyl isothiosemi carbazone crystallizes in the space group P\(_{21}/C\) and incorporates two PLITSC ligands resulting in meroctahedral geometry
(expected due to the planarity of the ligands) around the metal cation. The geometry around the central ion is slightly disordered as most of the angle are close to the values 90 or 180°. The Co complex shows a broad spectrum of antibacterial activity towards the most common types of bacteria and is significantly more active than Fe (II) pyridoxal semicarbazone. This implies that the ligand pyridoxal S-methylisothiosemicarbazone can be used in synthesing other complexes having the potential of being biologically active. The Significant biological activity of the synthesized complex Fe (II) may have wide practical applications in medicine, pharmacy and food technology.

Co(II) complex\textsuperscript{11} having the general composition Co(L)\textsubscript{2} X\textsubscript{2} (Where L= isopropyl methyl ketone semicarbazone (LLA), isopropyl methyl ketone thiosemicarbazone (LLB), 4- aminoacetophenone semicarbazone (LLC) and 4-amino acetophenone thiosemicarbazone (LLD) and [X= Cl\textsuperscript{−}, ½ SO\textsubscript{4}\textsuperscript{2−}] have been synthesized Infra-red spectral band indicate that the semicarbazone act as bidentate chelating agents coordinating through oxygen and nitrogen of C=N and bidentate behaviour of thiosemicarbazone coordinating through sulphur and nitrogen of C=N. Room temperature magnetic behaviour of Co(II) complex lie is an the range 4.78-5.08 B.M indicating a high spin configuration.

Cobalt(II) complexes of general composition Co(L)\textsubscript{2}X\textsubscript{2} (L= cyclohexanone semicarbazone and cyclohexanone thiosemicarbazone and X = Cl\textsuperscript{−}, Br\textsuperscript{−}, SCN\textsuperscript{−} and SO\textsubscript{4}\textsuperscript{2−} have been prepared and characterized by elemental
analysis and magnetic susceptibility measurement, electronic infra-red
and EPR studied by Chandra\textsuperscript{12}. All the complexes are of high spin type. The
cyclohexanone semicarbazone complexes appear to have six – coordinate
octahedral geometry.

Chattopathyay\textsuperscript{13} studied behaviour of two biologically active ligands,
pyridine-2-carboxaldehyde- 4- phenylthiosemicarbazone (HL) and pyridine-2-
carboxaldehyde thiosemicarbazone (L\textsubscript{1}H) towards Co(III) ion. Ligands act as
tridentate N-N-S donor, giving bis chelate complexes [Co(A)\textsubscript{2}X.H\textsubscript{2}O] (A=L or
L\textsubscript{1}, X=Cl,ClO\textsubscript{4}). Biological activity of ligands and metal complexes in the form
of in vitro antibacterial activity towards \textit{E.Coli} was evaluated and possible
reasons for enhancement of activity of ligands on coordination to metal ion is
discussed. Bekheit et al\textsuperscript{14} synthesized Cobalt(II) complexes of 1-(2-
naphtylacetyl)-2-phenyl-3-thiosemicarbazide and characterized on the basis of
elemental analysis, magnetic moment, molar conductance and spectral (IR,
NMR and visible) studies. IR shows that NTSC behave as in a bidentate and/ or
bridging tetradentate manner tetrahedral structure is proposed for the complex.

Darkova et al\textsuperscript{15} prepared MLCI (Where M= Co, L=2- Acetylbenzimidazol
thiosemicarbazone (HL\textsubscript{1}) and is methyl derivative (HL\textsubscript{2}) and characterized by
UV,IR and EPR spectra and magnetic susceptibility measurement.[CO(L)Cl] is
tetrahedral. West et al\textsuperscript{16} syntesized HL=2-acetylpyridinediethyl-
thiosemicarbacarbazone, HL\textsubscript{1}=2-acetyl- pyridinedipropyl thiosemicarbazone,
are tridentate NNS donor ligands. Spectral and physical data indicate that the use of 4N-substitutes (4N-diethyl, 4N-dipropyl) can influence the stereochemistry and stoichiometry of the complexes which show minimum ability to inhibit fungal growth and are considerably less active than the related Cu(II) and Ni (II) complexes. Sudershan et al \(^{17}\) prepared cobalt complexes [Co(APCTS(OAC))\(_2\)] and [Co(ACTS)_2(OAC)] derived from ligands 3-acetylcoumarin thiosemicarbazone (ACTS) and N-phenylthio-semicarbazone (APCTS).

El-Asmy et al\(^{18}\) prepared and studied properties of Co(SPTS).nH\(_2\)O [H\(_2\)SPTS= succinyl-bis-(4-phenylthiosemicarbazide), analytical, spectral (IR,UV,NMR) conductometry magnetic and electronic spectral data show Co(II) has tetrahedral geometry in its complexes, ligand behave as a dibasic quadri-dentate (NSSN) donor. Stoichiometry and stability constant of Co(II) complexes have been detected spectrophotometrically. Electrical properties of H\(_2\)SPTS and its complexes with Co(II) were investigated and their activation energies calculated. The value for Co(II) complexes are similar to narrow band semiconductor material.

Chatterje et al\(^{19}\) carried out reaction of Schiff bases (HL) derived by condensation of vanillin or 2-furaldehyde and 4-phenylthiosemicarbazide with transition metal salts and prepared CoL\(_2\).2H\(_2\)O and characterized on the basis of elemental analysis, IR, diffuse reflectance spectra, magnetic susceptibility
measurements, varying current and thermal studies. Calculated ligand field parameters are consistent with the proposed.

Cobalt (II) complexes\textsuperscript{20} with mixed ligand including 4- hydroxyl benzaldehyde semicarbazone (HBSCH) and esters of amino acid-A(Phenolglycine ester) (GlyP), Phenol alanine ester (Ala P), 2- amino phenol glycine ester (Gly A) and 2- aminophenol alanine ester (Ala A) have been prepared and characterized by physical chemical techniques. General formulae $\left[\text{CO(HBSCH)}(A)\right]_{2}\left(\text{NO}_3\right)_3$, $\left[\text{Co(HBSCH)}(A)\right]_{2}\left(\text{NO}_3\right)_2$, $\left[\text{Co(HBSCH)}\right]_2\left(\text{A}\right)\left(\text{NO}_3\right)_3$ and $\left[\text{Co(HBSCH)}\right]_2\left(\text{A}\right)\left(\text{NO}_3\right)_2$ have been prepared in neutral medium.

The electronic spectra of the complexes in dimethylformamide solution have been recorded giving d-d spectra and charge transfer spectra. Cobalt (II) complexes showed absorption bands at 15013-17594 and 18001-22124 cm$^{-1}$ due to $\nu_2$ and $\nu_3$ (attributed to the transition $^4T_{1g} \rightarrow ^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ respectively. $\nu_1$ (7184-8928 cm$^{-1}$) attributed to the transition $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ respectively. $\nu_1$ (7184 – 8928 cm$^{-1}$ ) attributed to the transition $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ has been not observed due to instrumental limitation, it was calculated by the literature method\textsuperscript{21}. The ligand field parameter B and the ligand field splitting energy (10 Dq) have been calculated\textsuperscript{22}. The values of B of the complexes 0.72 clearly indicated the covalent character of the bond concerned. The values of Dq/B Which were in the range 1.45-1.50
suggested octahedral geometry for all the complexes. The values of C.F.S.E have been also determined which were in the range of 8178-8508 cm$^{-1}$.

According to the analytical, physical and spectral data, some observation have been achieved that lead to establish the following points.

1. HBSCH ligand acts either as bidentate chelating ligand connected to Co (II) ion through the azomethine nitrogen and carbonyl oxygen.
2. Amino acid esters act either as monodentate ligand joint to Co(II) ion through the carboxylate oxygen (in the neutral medium), or as bidentate chelating ligand connected to Co(II) ion through the carboxylate oxygen and amino nitrogen (in the basic medium).
3. NO$_3^-$ connected to Co (II) ion in two manners as monodentate ligand through oxygen atom in an ionic character.
4. Cobalt (II) ion is probably hexacoordinated leading to octahedral geometry.

The mixed ligand complexes of the type [Co(L$_1$)(L$_2$)]Cl$_2$ (where L$_1$ = Acetophenone semicarbazone, L$_2$ = Acetone semicarbazone) have been synthesized by reactions of methyl chlorides with two different semicarbazone compounds in 1:1:1 molar ratios.

In the IR spectra of the ligands 1596-1590 cm$^{-1}$ may be assigned to the symmetric and asymmetric $\nu$(C=N) vibrations and a strong band in the region
1710-1690 cm\(^{-1}\) are on complexes formation, the position of these bands is shifted towards lower side (1568-1539) and (1689-1659) as compared to metal free ligands. This indicates that the coordination takes place through nitrogen and oxygen atom of the \((\text{C=N})\) and \((\text{C=O})\) groups.

A broad band appears in the region at 3200-3750 cm\(^{-1}\) for –OH group be attributed to the coordinated water molecule. Thermogravimetric analysis shows presence of two water molecule in the complexes supports octahedral nature of complexes.

New Cobalt\(^{24}\) complexes with mixed ligand including salicylaldehyde thiosemicarbazone \(\text{STH}_2\) and carboxylic acid-\(\text{AH}_2\) (Salicylic acid- \(\text{SH}_2\) or anthranolic acid- \(\text{AnH}_2\) or phthalic acid \(\text{PH}_2\)) have been characterized using different physico-chemical methods from which the general formulae \([\text{Co}_2(\text{AH}_2)_2(\text{STH}_2)_2(\text{NO}_3)_2\) or \([\text{Co}_2(\text{AH}_2)(\text{STH}_2)Xn]\) have been suggested in neutral medium giving either cationic or neutral complexes. Whereas, in basic medium the formulae \([\text{Co}_2(\text{AH})_2(\text{STH}_2)]\) has been proposed \([\text{Where } X= \text{CO}_3^{2-}\) or \(\text{CH}_3\text{COO}^-\), \(n=2\) or 4].

The spectra of carboxylic acids (\(\text{SH}_2\), \(\text{AnH}_2\), \(\text{PH}_2\)) showed wide bands in the regions 3500-3600,2900 and 3400 cm\(^{-1}\) due to the stretching vibration of carboxylic \(\text{OH}\), phenolic \(\text{OH}\) in \(\text{SH}_2\) and \(\text{NH}_2\) group in \(\text{AnH}_2\) respectively, this wide range was due to the hydrogen bonding. In the spectra of the complexes it was more difficult to observe the coordination due to presence of different
Synthesis, Structural and spectral characterization of Co(II) complexes of semicarbazone and thiosemicarbazone

group and hydrogen bonding. Whatever, in the complexes prepared in neutral medium the wide band was shifted to lower frequency. Whereas for complexes prepared in basic medium it was very difficult to observe the disappearance of this band, but it was well known that this band has been disappeared due to deprotonation of the acid and the formation of ionic form\textsuperscript{25,26,27}. The other two bands observed at 1390-1370 cm\textsuperscript{-1} were due to the symmetric and asymmetric stretching frequency of carboxylic group respectively. On complexation these bands were shifted to lower frequencies \textsuperscript{26,28} the difference between the symmetry and asymmetry. Stretching vibration for COO\textsuperscript{-} group (\(\nu = 150\text{-}180\) cm\textsuperscript{-1}) gave indication about the manner of coordination of carboxylic group.

The electronic spectra of the complexes in dimethyl formamide solution have been recorded giving l-d spectra and charge transfer spectra.

It was calculated by the literature method. The field parameter B and the ligand field splitting energy (10Dq) in case of Cobalt (II) complexes has been calculated\textsuperscript{29-30}. The values of B of the complexes 0.72-0.73 clearly indicated that covalent character of bond concerned. The values of Dq/B Which were in the range 1.49 -1.50 suggested octahedral geometry for all the complexes\textsuperscript{29,31}. The value of C.F.S.E have been also determined which were in the range 8424-8464.

Satpathy et al\textsuperscript{32} prepared [(HDAMTH)M(H\textsubscript{2}O)]X\textsubscript{2} (HDAMTH-diacetylmonoxime thiosemicarbazone, (X=Cl\textsuperscript{-},Br\textsuperscript{-},OAC\textsuperscript{-},NO\textsuperscript{-},ClO\textsubscript{4}\textsuperscript{-}). IR spectra
of the complexes suggested that ligand coordinates to metal ion through its azomethine N, oxime O and S atom. The H₂O molecules seem to be coordinates as evidence from IR, thermal analysis of the complexes. The complexes have high molar conductance value. Reflectance spectra of the complexes indicate octahedral geometry around the metal ions. Different crystal field parameters for Co(II) complexes were calculated.

In the present studies we synthesize the complexes of cobalt complexes salicylaldehyde semicarbazone/ thiosemicarbazone (SSC/STSC), 3- hydroxy benzaldehyde semicarbazone/ thiosemicarbazone (m-HBSC/m-HBTSC) and 4- hydroxy benzaldehyde (p-HBSC/p-HBTSC) semicarbazones and tiosemicarbazones. The resulted complexes were characterized using different physico chemical method by CHN analysis, Magnetic moments, Molar conductance and spectroscopically method IR, UV, ESR, ¹HNM R etc.

5.3 EXPERIMENTAL WORK

5.3.1 Materials: All the chemical used are analytical grade and procured from sigma aldrich Banglore and metal salts from E. Merck .

5.3.2 Synthesis of complexes- Hot aqua ethanolic solution of metal salts and ethanol solution of respective ligand were mixed in molar ratio 1:2. The mixture was refluxed on water bath for about four hours.
On cooling the contents, the complexes separated out. The same was filtered washed with 50% ethanol and dried in an electric oven.

**Synthesis of chloro complexes**

\[
[\text{Co}(L_1)_2\text{Cl}_2], \quad [\text{Co}(L_2)_2\text{Cl}_2], \quad [\text{Co}(L_3)_2\text{Cl}_2], \quad [\text{Co}(L_4)_2\text{Cl}_2], \quad [\text{Co}(L_5)_2\text{Cl}_2], \\
[\text{Co}(L_6)_2\text{Cl}_2]
\]

The process of synthesis is repeated.

**Synthesis of Bromo complexes**

\[
[\text{Co}(L_1)_2\text{Br}_2], \quad [\text{Co}(L_2)_2\text{Br}_2], \quad [\text{Co}(L_3)_2\text{Br}_2], \quad [\text{Co}(L_4)_2\text{Br}_2], \quad [\text{Co}(L_5)_2\text{Br}_2], \\
[\text{Co}(L_6)_2\text{Br}_2].
\]

**Synthesis of sulphato complexes**

\[
[\text{Co}(L_2)_2\text{SO}_4], \quad [\text{Co}(L_3)_2\text{SO}_4], \quad [\text{Co}(L_4)_2\text{SO}_4]
\]

**Synthesis of Nitrato complexes**

\[
[\text{Co}(L_4)_2(\text{NO}_3)_2], \quad [\text{Co}(L_5)_2(\text{NO}_3)_2], \quad [\text{Co}(L_6)_2(\text{NO}_3)_2]
\]
5.4 PHYSICAL MEASURMENTS

The C, H and N were analyzed on a Carlo Erba 1106 elemental analyzer. The nitrogen contents of the complexes were determined kjedahl's method. The cobalt content in the complexes were determined by applying gravimetric method.

5.5.1 Magnetic studies: Magnetic susceptibility was measured at room temperature on a guoy balance using CuSO₄·5H₂O as a calibrant. All the complexes have composition Co(ligand)₂X₂ (Where X= Cl⁻, Br⁻, SO₄²⁻, NO₃⁻) shows a very good aggrement with standard magnetic fomoment value of complex at room temperature lie in the range 4.74-4.84 B.M. corresponding to three unpaired electrons (Table 5.1).

5.5.2 Conductivity studies: The molecular weight of complexes was determined in the laboratory cryoscopically in freezing nitrobenzene using a Beckmann thermometer accuracy ± 0.01 °C. The conductivity measurement were carried out a Toshniwal conductivity bridge type CLO1/01 and dip type cell operated at 220 volts, 4C mains.

5.5 RESULT AND DISCUSSION

5.5.1 Infra-Red Spectra

The infrared absorption bands become very useful for determining the mode of coordination of the ligand to metal. In the IR spectra, the broad bands of the
NH group observed at 3236-3250 cm\(^{-1}\) for the ligand disappear in the complexes spectra, which indicates the deprotonation of the NH-C=S group. The strong bands observed at 1596-1625 cm\(^{-1}\) range in the free ligand have been assigned to \((\text{C=N})\) stretching vibration\(^{36}\). On complexation, these bands were observed to be shifted to lower frequencies (1570-1590 cm\(^{-1}\)), which are in agreement with the wave number for other bis-coordinated chelate complexes\(^{37,38,39}\). These result indicate that the imine nitrogen is coordinated to the metal ion. All ligand showed medium bands in the 880-915 cm\(^{-1}\) range ascribed to \(\nu(\text{C=S})\) vibrations. These absorption bands shift 65-80 cm\(^{-1}\) to lower frequencies on the coordination of the thio- sulfur to metal ion. These result are in agreement with other thiosemicarbazones complexes\(^{38,40}\). In addition, the vibrational frequencies of the \(-\text{NH}_2\) group remain unchanged for both the ligand and the complexes. This evidence indicates the noncoordination of the \(-\text{NH}_2\) group to the Co(II) center. The band at 3290-3410 cm\(^{-1}\) was due to the bending vibration of phenolic OH (Table 5.2).

In IR spectra of spectra of semicarbazone ligand showed a strong bands at 1656 cm\(^{-1}\) which was attributed to \(\text{C} = \text{O}\). This value shifted towards lower frequency (1613-1617 cm\(^{-1}\)) on coordination, in neutral medium, indicating a coordination of the oxygen atom of C=O group to metal ion\(^{22,41}\). The strong band at 1608 cm\(^{-1}\) attributed to \(\gamma\text{C=N}\) has been shifted towards a lower frequency on coordination due to decrease of bond order as a result of metal
nitrogen bond formation\textsuperscript{22,42} may be assigned to the symmetric and asymmetric \((\text{C=N})\) vibrations and a strong band in the region 1710-1690 cm\(^{-1}\) are due to \((\text{C=O})\) groups present in the ligands on complex formation, the position of the bands is shifted towards lower side(1568-1539 cm\(^{-1}\)) and (1689-1659 cm\(^{-1}\)) as compared to metal free ligands. This indicates that the coordination takes place through the nitrogen and oxygen atom of the (C=N) and (C=O) group. IR spectrum of metal complexes \([\text{Co(L}_6\text{)}_2\text{Cl}_2]\) shown in fig 5.2.

\textbf{Fig(5.2) IR spectrum of metal complexes \([\text{Co(L}_6\text{)}_2\text{Cl}_2]\)
Infra-red spectra due to anions

IR spectra of nitrato complexes

In nitrato complexes shown that the number and relative energies of nitrate combinations frequencies ($\nu_1 + \nu_4$) in the 1700-1800 cm$^{-1}$ region of the infra-red spectrum may be used to distinguish the coordination modes of nitrato group. The difference between $\nu_1$ and $\nu_4$, show a large separation supported the bonding of two nitrato group as bidentate ligand$^{41,43,44}$.

IR spectra of sulphato complexes

The sulphate complexes show two absorption bands $\nu_1$ and $\nu_3$. The splitting of $\nu_3$ band into two bands in the region 1056-1083 cm$^{-1}$ correspondes to unidentate nature of sulphate group$^{45}$.

5.5.2 Electronic Spectra

The electronic spectra of the complexes in dimethyl formaamide solution have been recorded giving d-d spectra and charge transfer spectra (Table5.3). Cobalt (II) complexes showed absorption band at 15013-17594 and 18001-22124 cm$^{-1}$ due to $\nu_2$ and $\nu_3$ (attributed to the transition $^4T_1g(F)$ $\rightarrow$ $^4A_2g(F)$ and $^4T_1g(F) \rightarrow ^4T_1g(P)$ respectively. $\nu_1\{7184-8928$ cm$^{-1}$ attributed to the transition $^4T_1g \rightarrow ^4T_2g$ (F)} has been not obserbed due to instrumental limitation, it was calculated by the literature method$^{34}$. The ligand field parameters $B$ and the ligand field splitting energy (10Dq) have been calculated. The values of $\beta$ of the complexes
were 0.72 clearly indicated the covalent character of bond concerned. The values of $D_q/B$ which were in the range 1.40-1.50 suggested octahedral geometry for all the complexes\textsuperscript{34,35}. The values of the C.F.S.E have been also determined which were in the range 8178-8508 cm\textsuperscript{-1} (Table 5.4).

5.5.3 ESR Spectra

ESR spectra of complexes has been recorded as polycrystalline sample. Polycrystalline sample gives one broad isotropic signal centred, approximate, free electron $g$-value. The large deviation of $g$ values from the free electronic value ($g = 2.00023$) is due to large angular momentum contribution.

5.5.4 NMR Spectra

In the $^1$H NMR spectrum of semicarbazone ligands the multiplets between 6.80 and 7.70 ppm are all due to the aromatic protons of phenyl rings. The azomethine (H-C=N) protons gives a signal at 8.80 ppm. This signal undergoes deshielding to a magnitude of 0.2-0.3 ppm in Co(II) complexes due to involvement of azomethine group in the bond formation. The signals at 8.85 and 9.40 ppm are attributed $^4$NH and $^2$NH protons, respectively. The broad band at 10.60 ppm appear in the spectra of Co(II) complexes suggesting OH group do not upon coordination to metal ion. The same value in the thiosemicarbazone compounds. $^1$HNMR spectrum of metal complex.
[Co(L₄)₂Br₂] shown fig.5.44 and [Co(L₄)₂Br₂] shown fig5.55. The signal value for L₁/L₂, L₃/L₄ and L₅/L₆ are given below.

NMR for salicylaldehyde semicarbazone/Thiosemicarbazone(L₁/L₂)

NMR (DMSO-d₆): δ 7.80 (d, 2H ortho, Ph), 7.40 (t, 2H meta, Ph), 7.41 (t, IH para Ph), 8.07 (s, IH, HC=N); 8.20, 7.95 (d, 2H, NH₂); 10.02 (d, 1H, -OH), 11.43 (S, IH, =N-NH).

m-hydroxy Benzaldehyde Semicarbazone/Thiosemicarbazone(L₃/L₄)

¹H-NMR (DMSO-d₆):  7.82, 7.82 (s, d, 2H ortho, Ph), 7.56 (t, 2H meta, Ph), 7.85 (t, IH para Ph), 8.01 (s, IH, HC=N); 8.32, 8.28 (d, 2H, NH₂); 10.01 (d, 1H, -OH), 11.62 (S, IH, =N-NH).

p-hydroxy Benzaldehyde Semicarbazone/Thiosemicarbazone(L₅/L₆)

¹H-NMR (DMSO-d₆): δ 7.87, 7.82 (s, d, 2H ortho, Ph), 7.64 (t, 2H meta, Ph), 7.89 (t, IH para Ph), 8.07 (s, IH, HC=N); 8.36, 8.30 (d, 2H, NH₂); 10.02 (d, 1H, -OH), 11.66 (S, IH, =N-NH).
Fig.(5.3) $^1$HNMR spectrum of metal complex [Co(L$_4$)$_2$Br$_2$]

Fig.(5.4) $^1$HNMR spectrum of metal complex [Co(L$_5$)$_2$Br$_2$]
5.6 CONCLUSION

According to analytical, physical and spectral data, same observation have been achieved that lead to octahedral geometry. Infra red spectra show that ligands \( L_1, L_3, L_5 \) coordinated through azomethine nitrogen and carbonyl oxygen and in case \( L_2, L_4 \) and \( L_6 \) by sulphur from \((C=S)\) and \((C=N)\) azomethine nitrogen. The ligand field paramolers bonds the ligand field splitting energy \((10Dq)\) have been calculated the value of \( B \) of complexes were 0.72 clearly indicated covalent character of bond concerned and the value of \( Dq/B \). Which were in range 1.40-1.50 suggested octahedral geometry 1.40-1.50 suggested octahedral geometry for all the complexes except nitrato complexes show square pyramidal geometry.
### Table 5.1  Elemental analysis Calculated and Magnetic moment

<table>
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<th>S.N0</th>
<th>Complexes</th>
<th>Colour</th>
<th>%Co</th>
<th>%C</th>
<th>%N</th>
<th>%H</th>
<th>$\mu_{\text{eff}}$B.M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>[Co(L$_1$)Cl$_2$]</td>
<td>Whitish yellow</td>
<td>10.78</td>
<td>35.17</td>
<td>20.51</td>
<td>1.09</td>
<td>4.48</td>
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<td></td>
<td></td>
<td></td>
<td>(10.76)</td>
<td>(35.18)</td>
<td>(20.53)</td>
<td>(1.10)</td>
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<td>2.</td>
<td>[Co(L$_2$)Cl$_2$]</td>
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<td>9.83</td>
<td>32.08</td>
<td>23.37</td>
<td>2.06</td>
<td>4.54</td>
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<td></td>
<td></td>
<td></td>
<td>(9.85)</td>
<td>40.01</td>
<td>(20.02)</td>
<td>(2.03)</td>
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<td>3.</td>
<td>[Co(L$_3$)Cl$_2$]</td>
<td>Light brown</td>
<td>10.18</td>
<td>41.95</td>
<td>25.02</td>
<td>2.71</td>
<td>4.38</td>
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<td></td>
<td></td>
<td></td>
<td>(10.12)</td>
<td>(40.02)</td>
<td>(22.35)</td>
<td>(2.45)</td>
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<td>4.</td>
<td>[Co(L$_4$)Cl$_2$]</td>
<td>Light yellow</td>
<td>9.45</td>
<td>38.19</td>
<td>19.30</td>
<td>2.30</td>
<td>4.96</td>
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<td></td>
<td>(9.02)</td>
<td>(36.02)</td>
<td>(19.50)</td>
<td>(2.18)</td>
<td></td>
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<td>5.</td>
<td>[Co(L$_5$)Cl$_2$]</td>
<td>Light yellow</td>
<td>11.30</td>
<td>41.05</td>
<td>18.20</td>
<td>2.48</td>
<td>4.56</td>
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<td></td>
<td></td>
<td></td>
<td>(11.35)</td>
<td>(31.02)</td>
<td>(17.45)</td>
<td>(2.18)</td>
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<tr>
<td>6.</td>
<td>[Co(L$_6$)Cl$_2$]</td>
<td>Light yellow</td>
<td>11.40</td>
<td>39.58</td>
<td>16.45</td>
<td>1.18</td>
<td>4.42</td>
</tr>
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<td>(10.45)</td>
<td>(31.05)</td>
<td>(17.46)</td>
<td>(1.16)</td>
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<tr>
<td>7.</td>
<td>[Co(L$_2$)Br$_2$]</td>
<td>Dark brown</td>
<td>11.15</td>
<td>39.58</td>
<td>18.45</td>
<td>1.85</td>
<td>5.00</td>
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<td></td>
<td></td>
<td>11.02</td>
<td>40.02</td>
<td>(17.65)</td>
<td>(1.65)</td>
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<td>8.</td>
<td>[Co(L$_4$)Br$_2$]</td>
<td>Dark brown</td>
<td>9.86</td>
<td>45.03</td>
<td>19.03</td>
<td>1.45</td>
<td>4.62</td>
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<td></td>
<td>(9.99)</td>
<td>(41.05)</td>
<td>(18.90)</td>
<td>(1.35)</td>
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<tr>
<td>9.</td>
<td>Co(L$_6$)Br$_2$</td>
<td>Light red</td>
<td>10.45</td>
<td>39.48</td>
<td>18.67</td>
<td>1.65</td>
<td>4.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(10.40)</td>
<td>38.48</td>
<td>(18.45)</td>
<td>(1.45)</td>
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<tr>
<td>10.</td>
<td>[Co(L$_2$)$_2$SO$_4$]</td>
<td>Light red</td>
<td>10.45</td>
<td>38.49</td>
<td>18.67</td>
<td>1.65</td>
<td>4.80</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>(10.40)</td>
<td>38.48</td>
<td>(18.45)</td>
<td>(1.45)</td>
<td></td>
</tr>
<tr>
<td>11.</td>
<td>[Co(L$_3$)$_2$SO$_4$]</td>
<td>Light red</td>
<td>10.45</td>
<td>37.48</td>
<td>18.67</td>
<td>1.65</td>
<td>4.80</td>
</tr>
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<td></td>
<td>(10.40)</td>
<td>38.48</td>
<td>(18.55)</td>
<td>(1.45)</td>
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<tr>
<td>12.</td>
<td>[Co(L$_3$)$_2$(NO$_3$)$_2$]</td>
<td>Brown</td>
<td>10.46</td>
<td>37.65</td>
<td>18.66</td>
<td></td>
<td>4.80</td>
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<td></td>
<td>(10.48)</td>
<td>(37.68)</td>
<td>(18.69)</td>
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Synthesis, Structural and spectral characterization of Co(II) complexes of semicarbazone and thiosemicarbazone

Table 5.2 Infra-red spectra of the ligands and Co(II) complexes

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<thead>
<tr>
<th>Compounds</th>
<th>V(OH)</th>
<th>V(NH)</th>
<th>V\text{C=O}</th>
<th>V\text{C=N}</th>
<th>V\text{C=S}</th>
<th>V\text{M-O}</th>
<th>V\text{M-S}</th>
<th>V\text{M-N}</th>
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</thead>
<tbody>
<tr>
<td>L₁</td>
<td>3335</td>
<td>3400-3100</td>
<td>1630</td>
<td>1460</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L₂</td>
<td>3332</td>
<td>3372-3100</td>
<td>1510</td>
<td>780</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>L₃</td>
<td>3537</td>
<td>3273-3160</td>
<td>1660</td>
<td>1592</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>L₄</td>
<td>3437</td>
<td>3272-3180</td>
<td>1432</td>
<td>785</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L₅</td>
<td>3452</td>
<td>3273-3140</td>
<td>1680</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L₆</td>
<td>3556</td>
<td>3171-3165</td>
<td>1453</td>
<td>790</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>[Co(L₁)₂Cl₂]</td>
<td>3458</td>
<td>3500-3000</td>
<td>1621</td>
<td>1490</td>
<td>435</td>
<td>365</td>
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<td></td>
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<tr>
<td>[Co(L₂)₂Cl₂]</td>
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<td>3500-3000</td>
<td>1491</td>
<td>740</td>
<td>405</td>
<td>350</td>
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<tr>
<td>[Co(L₃)₂Cl₂]</td>
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<td>3500-3000</td>
<td>1619</td>
<td>1493</td>
<td>460</td>
<td>350</td>
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<tr>
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<td>3500-3000</td>
<td>1587</td>
<td>742</td>
<td>400</td>
<td>340</td>
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<td>1583</td>
<td>465</td>
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<td>3270-3001</td>
<td>1584</td>
<td>740</td>
<td>410</td>
<td>350</td>
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<td>3273-3000</td>
<td>1645</td>
<td>1581</td>
<td>462</td>
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<td>3271-3000</td>
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<td>743</td>
<td>400</td>
<td>340</td>
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<tr>
<td>[Co(L₃)₂SO₄]</td>
<td>3345</td>
<td>3261-3000</td>
<td>1650</td>
<td>1541</td>
<td>443</td>
<td>355</td>
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<tr>
<td>[Co(L₄)₂(NO₃)₂]</td>
<td>3321</td>
<td>3251-3000</td>
<td>1561</td>
<td>745</td>
<td>413</td>
<td>360</td>
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<tr>
<td>[Co(L₃)₂(NO₃)₂]</td>
<td>3321</td>
<td>3251-3000</td>
<td>1561</td>
<td>442</td>
<td>360</td>
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Table 5.3 Electronic Spectral data of the complexes

<table>
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<th>Complexes</th>
<th>$\nu_1$ cm$^{-1}$</th>
<th>$\nu_2$ cm$^{-1}$</th>
<th>$\nu_3$ cm$^{-1}$</th>
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</thead>
<tbody>
<tr>
<td>$[\text{Co}(L_1)_2\text{Cl}_2]$</td>
<td>9460</td>
<td>16177</td>
<td>18400</td>
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<tr>
<td>$[\text{Co}(L_2)_2\text{Cl}_2]$</td>
<td>9420</td>
<td>16100</td>
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<td>$[\text{Co}(L_3)_2\text{Cl}_2]$</td>
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<td>16500</td>
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<td>$[\text{Co}(L_4)_2\text{Cl}_2]$</td>
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<td>15370</td>
<td>18606</td>
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<tr>
<td>$[\text{Co}(L_5)_2\text{Cl}_2]$</td>
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<td>16342</td>
<td>18366</td>
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<tr>
<td>$[\text{Co}(L_6)_2\text{Cl}_2]$</td>
<td>9407</td>
<td>16743</td>
<td>18717</td>
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<tr>
<td>$[\text{Co}(L_1)_2\text{Br}_2]$</td>
<td>9425</td>
<td>16280</td>
<td>18410</td>
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<td>$[\text{Co}(L_2)_2\text{Br}_2]$</td>
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<td>16510</td>
<td>18895</td>
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<td>16380</td>
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<td>16150</td>
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<td>$[\text{Co}(L_6)_2(\text{NO}_3)_2]$</td>
<td>9496</td>
<td>16135</td>
<td>18934</td>
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Table 5.4-Ligand field parameters

<table>
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<tr>
<th>Complexes</th>
<th>D_q(cm⁻¹)</th>
<th>B(cm⁻¹)</th>
<th>Hx(cm⁻¹)</th>
<th>B</th>
<th>Dq/B</th>
<th>CFSE</th>
<th>C</th>
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<tr>
<td>[Co(L₁)₂Cl₂]</td>
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<td>701</td>
<td>3270</td>
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<td>1.49</td>
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<td>3358</td>
<td>0.72</td>
<td>1.49</td>
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<td>1.42</td>
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<td>3214</td>
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<td>1.49</td>
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<td>1.43</td>
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5.7 REFERENCES


