



## SYNTHESIS AND CHARACTERIZATION OF $L_N/L_2$ -BIS (BENZIMIDAZOLE) COBALT (II) COMPLEXES EMPLOYING NON-CARCINOGENIC MEDIUM

M.Chandrakala<sup>1\*</sup>, M.N.Manjunatha<sup>2</sup>, Hemanth Kumar. C.M<sup>3</sup>

### Abstract

Chloride reacts with benzimidazole (BzlH) in the molar ratio 1:2 or 1:3 in ethanol at room temperature to produce  $CoCl_2L_2$  (L = BzlH) and  $Co(L-H)_2$  (L-H = Bzl) As dark blue and purple solids respectively. The former complex is soluble in ethanol or acetone whereas the latter is insoluble in these solvents. The above reaction under refluxing condition yields exclusively  $Co(L-H)_2$ . Neutral or basic condition seems to favor the reaction as acidic medium does not give any complex.  $Co(L-H)_2$  reacts with acetic acid to form  $Co(CH_3COO)_2L_2$  as pink crystals and this complex can also be obtained by reacting cobalt acetate with stoichiometric quantities of BzlH in ethanol at RT, and the latter at refluxing temperature produces  $Co(L-H)_2$ . The complexes have been further characterized by elemental analysis, IR, UV-Visible spectroscopy, conductivity and magnetic susceptibility measurements.  $CoCl_2L_2$  and  $Co(CH_3COO)_2L_2$  complexes are mononuclear and are proposed to have tetrahedral and octahedral structure respectively.  $Co(L-H)_2$  is polymeric with bridging benzimidazole (BzlH) and is assigned a tetrahedral geometry around each metal ion.

**Keywords:** Benzimidazole (BzlH), magnetic susceptibility, Bidentate Acetate complex.

<sup>1</sup>\*PG Department of Chemistry, Visveswarapura College of Science, K R Road, Bengaluru-560 004, Karnataka, India.

<sup>2</sup>M.S.Ramaiah Institute of Technology, M.S. Ramaiah Nagar, Bengaluru-560054, Karnataka, India.

<sup>3</sup>Chemistry Research center, Bangalore Institute of Technology, K R Road, Bengaluru-560 004, Karnataka, India.

**\*Corresponding author:-** M.Chandrakala

\*PG Department of Chemistry, Visveswarapura College of Science, K R Road, Bengaluru-560 004, Karnataka, India. Tel.: +91 9538213845 Email address :mchandrakala.kum@gmail.com

**DOI:** 10.53555/ecb/2024.13.01.24

## 1. Introduction

Considerable attention is being paid to the study of transition metal complexes of benzimidazole and its derivatives because of their biological, herbicidal and antiviral properties<sup>1,2</sup>. Further the study of these complexes is also of interest in view of their spectral and magnetic properties<sup>3-7</sup>. Benzimidazole is an amphoteric and moderately strong organic base, it can behave as a base by accepting a proton at tertiary nitrogen or as weak acid by losing the imine proton. The coordinating ability of benzimidazole and its methyl derivatives towards several metal ions have been investigated by Goodgame et.al and a few others<sup>8-11</sup>. Present study is focused on investigating reactions of Co(II) salts with benzimidazole in ethanolic medium under acidic, neutral and basic conditions at varied temperature has produced some interesting results.

## 2. Experimental

Benzimidazole was prepared according to the literature method<sup>12</sup> and its purity was established by CHN analysis, Cobalt salts are qualigens make and the elemental analysis were carried out at central drug research institute, lucknow. Conductivity measurements were made on Elico-180 digital conductivity meter at RT. The infrared spectra of the complexes in KBR pellets were recorded on nicolet FT-IR spectrometer. The UV-Visible reflectance spectra of complexes and that of the ligand in nujol have been recorded on shimadzu UV-Visible NIR scanning spectrometer. Magnetic susceptibility measurements have been made at RT using Gouy balance. Metal and halogen estimation have been carried out according to literature methods<sup>13</sup>.

### 2.1. Preparation of complexes:

#### 2.1.1. Synthesis of Bis(benzimidazolato) Cobalt(II) complex $[Co(Bzl)_2]n$ : (Bzl-H = Bzl)

An ethanolic solution (10 ml) of cobalt chloride and benzimidazole in 1:2 or 1:3 mole ratio in presence of one drop of 1N sodium hydroxide on refluxing for 3 hours produced purple coloured crystals. The crystals were washed with ethanol followed by water and dried in vacuo. The crystals are insoluble in common organic solvents but soluble in 1:4 acetic acid giving a pink colour solution.

#### 2.1.2. Synthesis of Diacetobis(benzimidazole) Cobalt(II) semi hydrate- $[Co(OAC)_2(BzlH)_2 \cdot 0.5H_2O]$

An ethanolic solution (10 ml) of cobalt acetate and benzimidazole in 1:1.8 mole ratio on stirring at RT

for 10 min and evaporation of the solvent under reduced pressure yielded pink coloured crystals, the crystals were washed with dilute aqueous acetic acid (1:4) and dried in vacuo (the crystals are sensitive and turn into blue if washed with water).

#### 2.1.3. Synthesis of Dichlorobis (benzimidazole) Cobalt(II) complex- $[CoCl_2(BzlH)_2]$

An ethanolic solution (10 ml) of cobalt chloride and benzimidazole in the mole ratio 1:2 on stirring at RT for 5 minutes and on slow evaporation of solvent (at RT) gave a mixture of dark blue and purple coloured crystals. The major constituent is dark blue chloro complex along with a purple polymeric minor constituent. This complex mixture was washed in hot water to remove unreacted reactants, and insoluble polymeric compound was separated from the mixture with acetone. The filtrate on evaporation gave chloro complex which is soluble in both ethanol and acetone.

#### 2.1.4. Synthesis of Di(isothiocyanato) bis (benzimidazole) Cobalt(II) Complex- $[Co(NCS)_2(BzlH)_2]$

$[CoCl_2(BzlH)_2]$  and KSCN in ethanol / acetone (10 ml) in a mole ratio 1:2 on stirring for 10 minutes at room temperature and subsequent removal of the solvent by evaporation at room temperature produced blue coloured crystals. These crystals were washed with water, recrystallised from acetone and dried in vacuo.

## 3. Results and Discussion

Cobalt chloride reacts with benzimidazole (BzlH) in the mole ratio 1: 2/1: 3 in ethanol at room temperature to give dark blue and purple coloured solids of empirical formulae  $[CoCl_2L_2]$  (L = BzlH) and  $[Co(L-H)_2]$  (L-H = Bzl) respectively. The latter complex on treatment with acetic acid produces pink crystals of composition  $[Co(CH_3COO)_2L_2]$ . The acetato complex can also be obtained by the reaction of cobalt acetate with benzimidazole in stoichiometric quantities using ethanol at room temperature. In case of increased metal ligand ratio from 1: 2 to 1: 5 a mixture of purple and pink crystals is obtained where the former crystals correspond to  $[Co(L-H)_2]$  and these on treatment with acetic acid turn into pink crystals. The pink crystals are sensitive to water and change over to purple coloured crystals. Further, the pink crystals are insoluble in ethanol at room temperature but gradually turn into purple colour on warming. At refluxing temperature  $[Co(CH_3COO)_2L_2]$  in ethanol reverts back to  $[Co(L-H)_2]$ . Both  $[CoCl_2L_2]$ ,  $[Co(L-H)_2]$

complexes have been synthesized earlier by Goodgame and Cotton<sup>14</sup> by slightly different procedures. They have prepared dichloro complex using absolute ethanol and benzene. In the present investigation the use of carcinogenic benzene has been avoided. The dichloro complex on treatment with potassium thiocyanate in ethanol undergoes metathesis reaction to produce  $[\text{Co}(\text{NCS})_2\text{L}_2]$ . Physical properties and analytical data of the synthesized complexes are given in **Table-1**.

Formation of purple coloured complex seems to be dependent on pH of the reaction medium it has been observed that this complex is not formed when the reaction medium is acidic. As the medium changes to neutral or basic the reaction progresses to produce the desired product. Preliminary investigations have revealed that the formation of  $[\text{Co}(\text{L-H})_2]$  is catalyzed by hydroxyl ions. In the absence of hydroxyl ions, complex formation is achieved at longer durations.

The complex  $[\text{Co}(\text{L-H})_2]$  has very high M.P and is insoluble in common organic solvents but dissolves in acidic acid and solution turns to pink colour. This compound has been proposed to have polymeric structure,  $[\text{Co}(\text{L-H})_2]_n$  (**Str. I**). The compound showed a magnetic moment of 4.41 BM at room temperature corresponding to three unpaired electrons<sup>15</sup>. Its IR spectrum (**Fig1**) does not show any band assignable to  $\gamma_{\text{NH}}$  indicating the deprotonation of the imine proton. However the spectrum has a number of peaks and the once at 1774 and 1604 $\text{cm}^{-1}$  are ascribed to  $\gamma_{\text{C=C}}$  and  $\gamma_{\text{C=N}}$  respectively (**Table-2**). The band around 3050 $\text{cm}^{-1}$  is assigned to  $\gamma_{\text{CH}}$  of the  $\text{C}_6\text{H}_4$  ring of benzimidazole.

The chloro, acetato and isothiocyanato complexes exhibit broad absorption bands around 3300 $\text{cm}^{-1}$  assignable to  $\gamma_{\text{NH}}$ . The  $\gamma_{\text{C=C}}$  and  $\gamma_{\text{C=N}}$  bands are observed around 1760 and 1600 $\text{cm}^{-1}$ . The isothiocyanato complex shows a very intense band at 2075  $\text{cm}^{-1}$  in its IR Spectrum (**Fig-2**) due to  $\gamma_{\text{CNof}}$  NCS group. The value is characteristic of NCS group binding through hard nitrogen rather than soft sulphur to the metal ion. The acetato complex shows  $\gamma_{\text{aCOO}}$  at 1605 $\text{cm}^{-1}$  and  $\gamma_{\text{sCOO}}$  at 1543 $\text{cm}^{-1}$ . The difference between these two values corresponds to 62 $\text{cm}^{-1}$  and this suggest bidentate nature of acetato group binding to the metal ion<sup>16</sup>. The nujol mull reflectance UV-Vis spectrum (**Fig-3**) of BzlH exhibits a prominent band at 270nm(**Table-3**) and this may be assigned to  $\rightarrow \pi\pi^*$  transition. This band has shifted to lower wave number region in the spectra of all cobalt complexes except in the case of  $\text{Co}(\text{NCS})_2\text{L}_2$  for which it has shifted to higher wave number region. In addition to the ligand band the complexes also exhibit bands in the range 16000 – 18000 $\text{cm}^{-1}$  for  $\text{CoX}_2\text{L}_2(\text{X}=\text{Cl})$  and 18800 – 21000 $\text{cm}^{-1}$  for  $\text{Co}(\text{CH}_3\text{COO})_2\text{L}_2$  complexes. These bands are of lower intensity as compared to that of the ligand band and hence are assigned to  $d \rightarrow d$  transitions. In the case of polymeric complex, the spectrum exhibits bands at 5025, 8850(9560 sh), 17060(18730 sh) $\text{cm}^{-1}$  and these may be ascribed to  $^4\text{A}_2 \rightarrow ^4\text{T}_2$ ,  $^4\text{A}_2 \rightarrow ^4\text{T}_1$  and  $^4\text{A}_2 \rightarrow ^4\text{T}_1(\text{P})$  transitions respectively(**Fig-4**)<sup>17</sup>.

**TABLE-1** Physical, Magnetic and Analytical data of Cobalt complexes

Compound (Colour) L = BzlH; $\text{C}_7\text{N}_2\text{H}_6$	M.P (°C)	$\mu_{\text{eff}}$ BM (at 298 K)	Analytical data(%) (Calculated values are in parenthesis) C H N Cl/NCSCo				
$[\text{Co}(\text{L-H})_2]$ (Purple) Bzl= $\text{C}_7\text{N}_2\text{H}_5$	>250	4.041	56.42 (55.64)	3.61 (3.64)	18.30 (18.54)	-- (--)	19.20 (19.50)
$[\text{Co}(\text{CH}_3\text{COO})_2\text{L}_2]$ 0.5 $\text{H}_2\text{O}$ (Pink)	152-154	5.03	51.09 (51.19)	4.46 (4.50)	12.95 (13.27)	-- (--)	13.96 (14.33)
$\text{CoCl}_2\text{L}_2$ (Dark Blue)	200	4.56	46.37 (45.92)	3.13 (3.287)	15.18 (15.30)	18.95 (19.38)	16.42 (16.10)
$\text{Co}(\text{NCS})_2\text{L}_2$ (Blue)	142-144	4.32	46.02 (46.82)	2.52 (2.92)	20.21 (20.48)	27.47 (28.23)	14.57 (14.33)

**TABLE-2** Infrared data(KBR Pellet:  $\text{cm}^{-1}$ ) of Cobalt(II) Complexes

Entry	Complex	$\gamma_{\text{NH}}$	$\gamma_{\text{CH}(\text{C}_6\text{H}_4)}$	$\gamma_{\text{C=C}}$	$\gamma_{\text{C=N}}$	$\gamma_{\text{aCOO}}$	$\gamma_{\text{sCOO}}$
1	$[\text{Co}(\text{Bzl-H})_2]$	---	3074, 3028, 2905( $\gamma_{\text{CHof}}$ imidazole)	1774	1604	---	---
2	$[\text{Co}(\text{CH}_3\text{COO})_2\text{BzlH}_2]$ 0.5 $\text{H}_2\text{O}$	3213	3075, 2975, 2905, 2835( $\gamma_{\text{CHof}}$ acetate and imidazole)	1762	---	1605	1543
3	$\text{CoCl}_2\text{BzlH}_2$	3320	3124, 3062, 2977, 2901, 2816( $\gamma_{\text{CHof}}$ imidazole)	1761	1619, 1594	---	---
4	$\text{Co}(\text{NCS})_2\text{BzlH}_2$	3289	3116, 2916, 2805( $\gamma_{\text{CHof}}$ imidazole)	1765	1621, 1598	2075( $\gamma_{\text{CHof}}$ NCS)	---

TABLE-3 Electronic spectral data (nujol mull)

Entry	Complex	$\lambda$ (nm)	$\gamma$ ( $\text{cm}^{-1}$ )	Assignment
1	BzlH(L)	270	37,040	$\pi \rightarrow \pi^*$
2	[Co(Bzl-H) <sub>2</sub> ] Td	274, 534, 586 1046, 1130, 1990	36,476 17,060(18,730 sh) 8,850(9,560 sh) 5,025	$\pi \rightarrow \pi^*$ (L) ${}^4A_2 \rightarrow {}^4E_1$ (P) ${}^4A_2 \rightarrow {}^4E_1$ ${}^4A_2 \rightarrow {}^4E_2$
3	[Co(CH <sub>3</sub> COO) <sub>2</sub> BzlH <sub>2</sub> ] 0.5H <sub>2</sub> O; Oh	276 481.5 521.0	36,230 20,770 18,830	$\pi \rightarrow \pi^*$ (L) d $\rightarrow$ d d $\rightarrow$ d
4	CoCl <sub>2</sub> BzlH <sub>2</sub> Td	271 580.5 625	36,900 17,230 16,000	$\pi \rightarrow \pi^*$ (L) d $\rightarrow$ d d $\rightarrow$ d
5	Co(NCS) <sub>2</sub> BzlH <sub>2</sub> Td	265.5 328 560599	37,740 34,490 17,860 16,700	$\pi \rightarrow \pi^*$ (L) $\pi \rightarrow \pi^*$ (L) d $\rightarrow$ d d $\rightarrow$ d

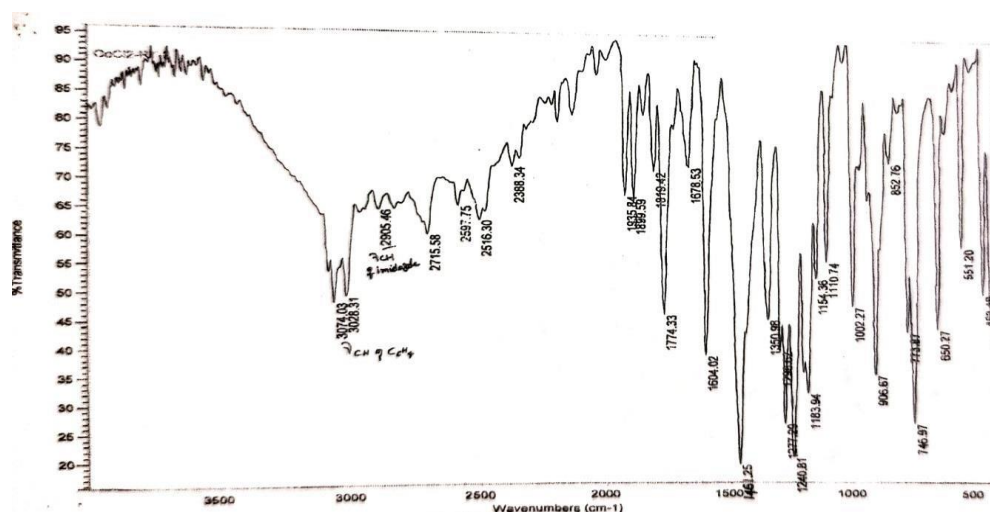


Fig-1 : IR spectrum of [Co(Bzl-H)<sub>2</sub>]

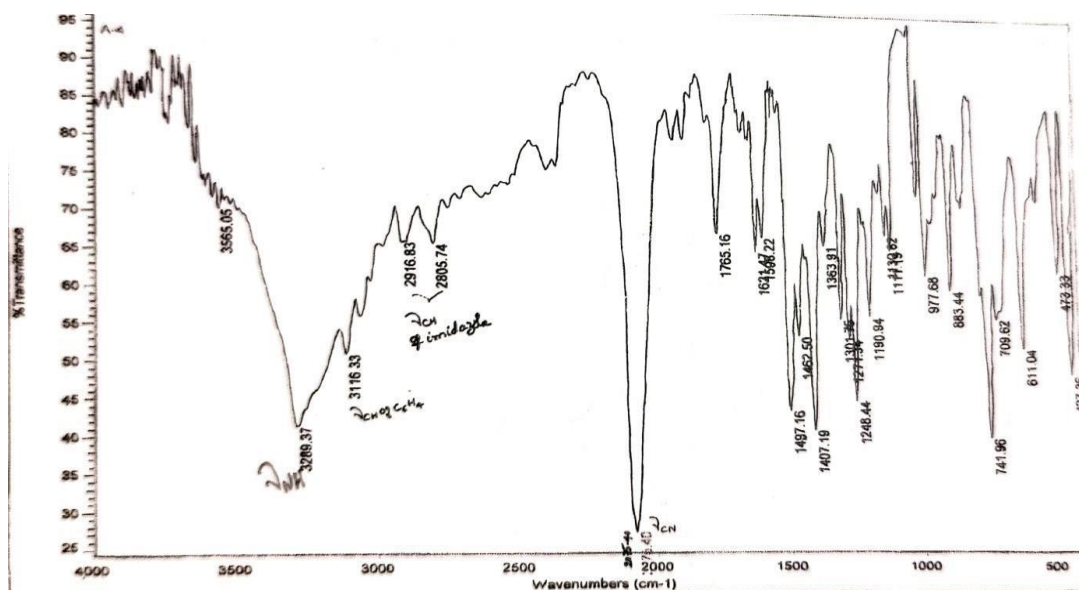


Fig-2 : IR spectrum of Co(NCS)<sub>2</sub>BzlH<sub>2</sub>

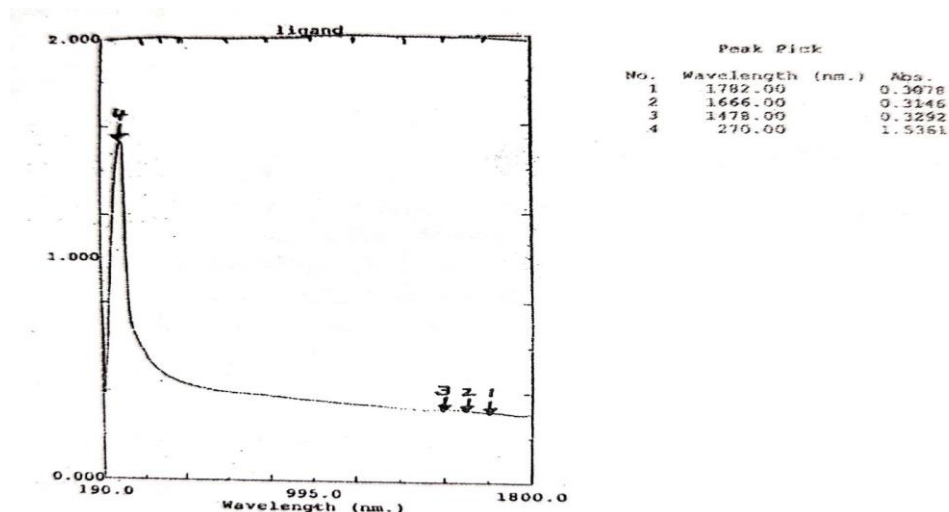


Fig-3 : UV-Visible spectrum of BzlH

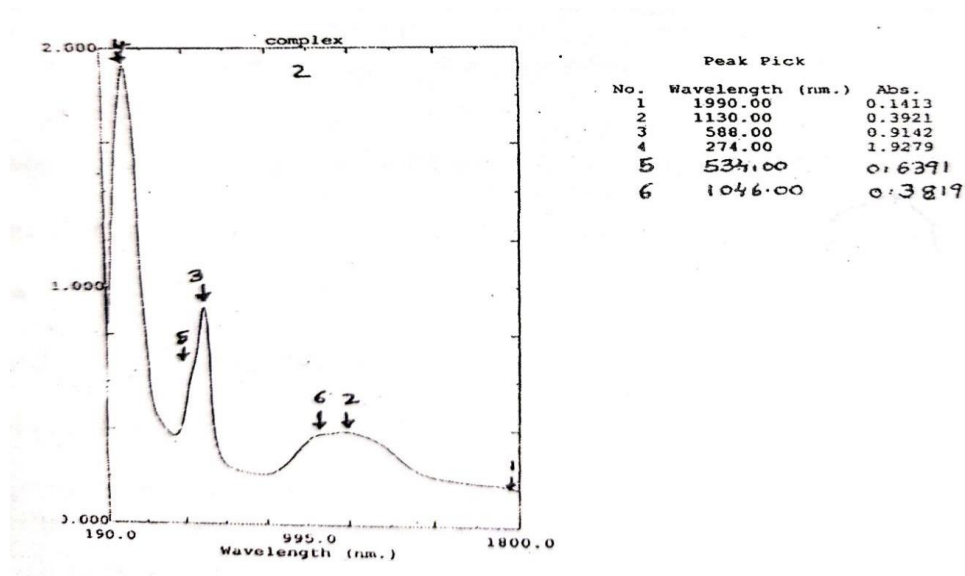
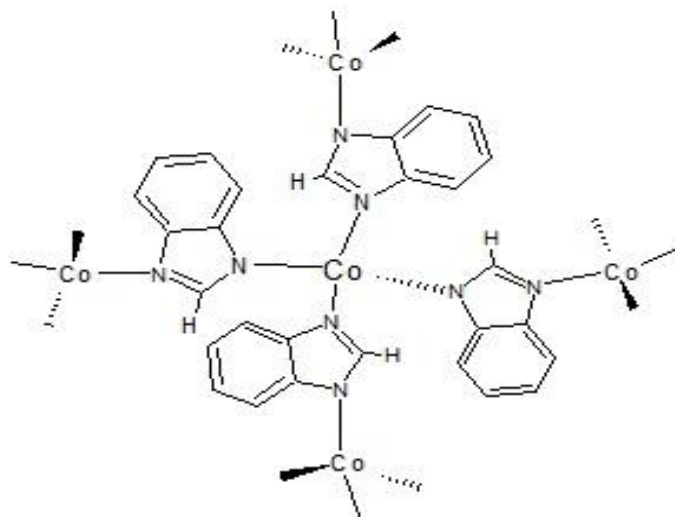
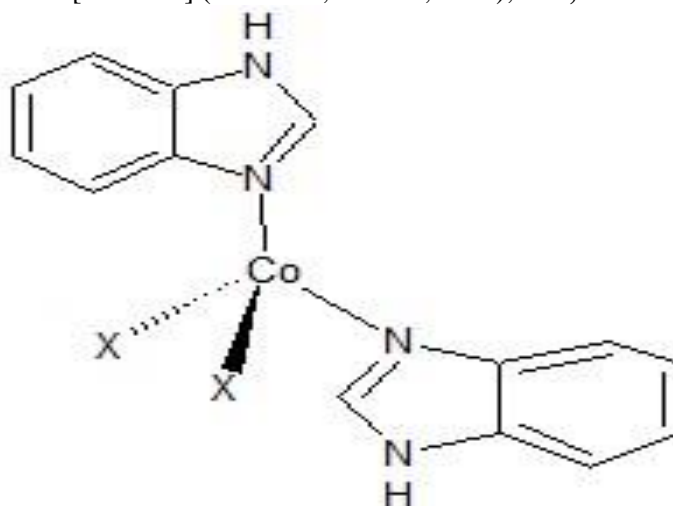
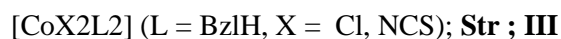
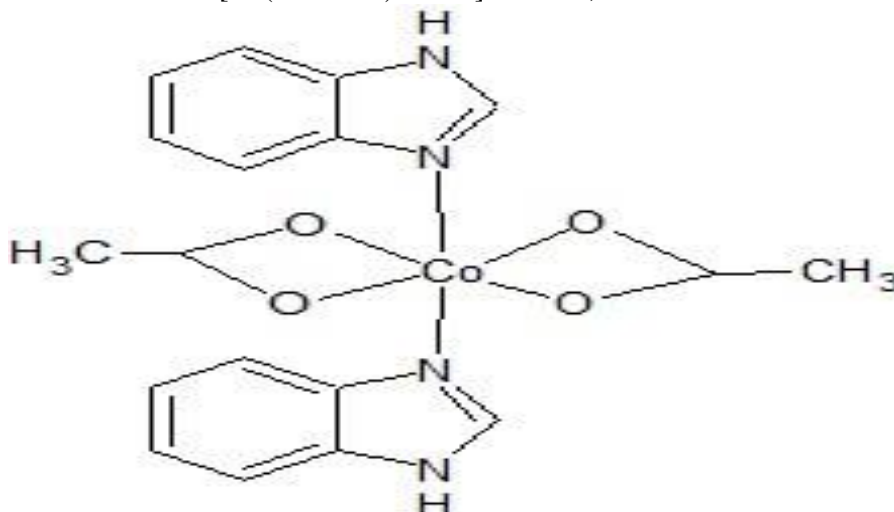
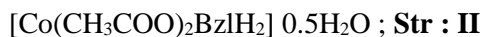


Fig-4 : UV-Visible spectrum of  $[Co(Bzl-H)_2]$  [

$Co(Bzl-H)_2]$  ; Str : I





#### 4. Conclusions

It is evident from the elemental analysis, metal estimation, molar conductance, IR, UV-Visible and Magnetic susceptibility studies that tetrahedral geometries for complexes at entry 2, 4, 5 and octahedral geometry for complex at entry 3 presented in Table-3. Based on the above data, structures I, II and III have been proposed for these complexes.

#### Acknowledgement

I would like to thank RVS and former principal, Visveswarapura college of Science, Sri. Late K.G.Srinivasa Murthy for their support

#### References

1. Isikdag & Noyanalapan N. Doga Bilim Derg Seri C, Chem Abstr, 183; 103:210881j (1985)
2. Isikdag I, Zitouni C & Demirayak S, Doga Bilim Derg Seri C, Chem Astr, 104; 104 25700, 277 (1985)
3. R.J. Sundberg & R.B. Martin, Chem, Rev, 74, 471 (1974)
4. P.N. Preston, Chem, Res, 74, 279 (1974)
5. R.C. Van Landschoot, J.A.M. Van Hss and I. Reedijk, J, Inorg, Nucl. Chem, 38, 185 (1976).
6. L.K. Thompson. B. Ramaswamy and R. D. Dawe, Can, J. Chem, 56, 1311 (1978)
7. G.K.N. Reddy and B.R. Ramesh, Indian J. Chem, Sect, A, 15, 621 (1977).
8. Goodgame DML. Goodgame M & Raynercanham GW, Inorg Chim Acta, 6, 245, (1972)
9. Goodgame M, Holt SD, Piggot B & Williams DJ, Inorg Chim Acta, 49, 107 (1985).
10. Artemenko MV & Slyusarenko KF, Russ J Inorg Chem, 15, 1616, (1970).
11. Garnovski; AD, Skopenko VV. Knyzhanakii, MJ, Osipov OA, Gilyanovskii PV & Artyukhovich TD, zhogshch Khim, Chem Abstr. 78, 21996 42, 2068, (1972)

12. A.I.Vogel, A text book of quantitative organic Analysis, Third edition (ELBS and Longman London), 1975,
13. A.I.Vogel, A text book of quantitative Inorganic Analysis, Third edition(1961)
14. Goodgame&F.A.Cotton JACS, 84, 1543 (1962).
15. Elements of magnatochemistry by: R. L. Dutta and A. Syamal, second edition, P. No. 47 and 157.
16. Spectrometric identification of organic compounds, by: Robert M Silverstein and Francis X Webster, sixth edition, P. No. 96-97.
17. Electronic Absorption Spectroscopy and Related Techniques by: D. N. Sathyanarayana, P. No. 266 and 269.