



# Synthesis and characterization of complexes of Co (II), Ni (II), Cu (II) and Zn (II) with ligand of Thiosemicarbazide derivative of “Ortho-Benzoyl p-Cumenol”.

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**Abstract :** Some new Co (II), Ni (II), Cu (II), and Zn (II) complexes of the Schiff base ligand, the condensation product of thiosemicarbazide with Ortho-benzoyl p-cumenol, was synthesized in a methanolic medium and the change in colour of metal salt indicated the formation of complexes. Elemental analysis, IR- spectra, molar conductance measurements, and melting points were used to characterize the Schiff base and its metal complexes. From the elemental analysis data, the metal complexes formed had the general formulae  $[M(L)_2(H_2O)_2]$ , where L = Schiff base ligand and M = Co, Ni, Cu, and Zn. The bonding of the ligand with central metal ions was confirmed by the IR-Spectra of the ligand. The IR- frequency of OH and HNN reduced after complexation. It indicated that the coordination bond was formed with the “N” and “O” donor atoms of the Schiff base ligand, and thus, a six coordinated octahedral geometry was proposed for all the prepared complexes.

**Keywords-** Ambidentate ligand, IR-spectra, Paramagnetism, Schiff base, Thiosemicarbazide.

## Introduction:

Hugo Schiff gave the term "Schiff base" to molecules having functional groups that contain carbon nitrogen double bonds in which the nitrogen atom is connected to aryl or an alkyl group rather than to hydrogen<sup>[1]</sup>. The metal complexes with Schiff base ligand having oxygen and nitrogen as donor atoms attracting the attention of researchers because of its vast biological activity with the main aim being the discover of safe and effective therapeutic agents for the treatment of various Human dieases<sup>[2]</sup>.

A lot of complexes of Co (II), Ni (II), Cu (II) and Zn (II) have been reported in their divalent states respectively with organic bidentate Schiff base ligands coordinating with oxygen and nitrogen as donor atoms.

In this present paper, we have focused on the synthesis of a novel Schiff base ligand, by the condensation of thiosemicarbazide<sup>[3]</sup> with Ortho-Benzoyl p-Cumenol and its metal complexes with Co (II), Ni (II), Cu (II) and Zn (II) salts. The coordination behaviour of the ligands towards transition metal ions was fully investigated by various spectral, elemental techniques.

The study of complexes containing nitrogen and oxygen as donor atoms of ligands is an active area of research because of their extensive biological activities<sup>[4]</sup>

**A condensation product of Thiosemicarbazide with 2-Benzoyl p-cumenol (L):** Equal volume of p-cumenol and benzoyl chloride were mixed in a round bottom flask in dry carbon tetrachloride, adjusted the apparatus connecting with an air condenser and reflux upto 110° Celcius. Again this reaction mixture was cooled and then anhydrous AlCl<sub>3</sub> about 2-3gm was added into the reaction mixture. After mixing the anhydrous AlCl<sub>3</sub>, the whole mixture was heated upto 172° Celcius for half an hour. The mixture was dissolved in ethanol and crystallized. After that, this crystal was mixed with thiosemicarbazide, added dilute Acetic acid, and methanol and the whole mixture was refluxed upto 2 hours. A sandy crystal was found which was crystallized with ethanol. After that, the m.p of the formed compound was measured. It was 352°C.

After that, the alcoholic solution of this ligand was mixed with 0.01 molar solution of Co (II), Ni (II), Cu (II), and Zn (II) separately and refluxing the content for 6-7 hours, the change in colour of the reaction mixture indicated the formation of complex compounds.

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In the case of Co (II) brown colour complex was obtained, which was washed thoroughly with water and then a small portion of ethanol. After that, the complex was dried over CaCl<sub>2</sub> in a desiccator. The process of the synthesis of all complexes was similar. In all the cases chloride of transition metals was taken in (0.01M) solution, and the change in colour of the reaction mixture indicated the formation of the complexes. The colour of the Ni (II) complexes was reddish brown, Cu (II) has brown and Zn (II) has pale yellow colour.

**Elemental analysis of ligand:** Required: C, 65.17%, H, 6.07%, N, 13.41%, and O, 5.11%, S, 10.22%, Found: C, 65.13%, H, 5.89%, N, 13.11%, and O, 5.09%, S, 10.20%.

**Elemental analysis of metal complexes having ligand (L) :**

Cobalt (II) complexes, C<sub>1</sub>. Elemental analysis data for [Co L<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>], Required: C, 56.75%; H, 5.56%; N, 11.68%, O, 8.90%, S, 8.90%, Co, 8.19% found: C, 56.71%; H, 5.51%; N, 11.55%, O, 8.71%, S, 8.78%, Co, 8.12%. Nickel (II) complexes, C<sub>2</sub>. Elemental analysis data for [Ni L<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>], Required: C, 56.71%; H, 5.55%; N, 11.66%, O, 8.91%, S, 8.91% Ni, 8.15% found: C, 56.69%; H, 5.48%; N, 11.61%, O, 8.87%, S, 8.88%, Ni, 8.11%. Copper (II) complexes, C<sub>3</sub>. Elemental analysis data for [Cu L<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>], Required: C, 56.39%; H, 5.52%; N, 11.61%, O, 8.84%, S, 8.84%, Cu, 8.77% found: C, 56.31%; H, 5.51%; N, 11.58%, O, 8.81%, S, 8.83% Cu, 8.72%. Zinc (II) complexes, C<sub>4</sub>. Elemental analysis data for [Zn L<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>], Required: C, 56.25%; H, 5.51%; N, 11.58%, O, 8.82%, S, 8.82%, Zn, 9.01% found: C, 56.19%; H, 5.50%; N, 11.53%, O, 8.77%, S, 8.77%, Zn, 8.98%.

**Results and Discussion:**

Spectral analysis: IR- Spectra<sup>[5]</sup> For ligand (L), C=N stretching  $-1645\text{ cm}^{-1}$ , N-H stretching  $-3300\text{ cm}^{-1}$ , C=C aromatic stretching  $-1650\text{ cm}^{-1}$ , N-H bending  $-1668\text{ cm}^{-1}$ , O-H stretching  $-3275\text{ cm}^{-1}$ , substituted benzene  $-740\text{ cm}^{-1}$ , C=S str  $-1535\text{ cm}^{-1}$ .

Complexes	V(N-H) str cm-1	V(C=N) str cm-1	V(C=C) aromatic cm-1	V(M-N)st r cm-1	V(M-O)st r cm-1	V(C=S) str cm-1
[CoL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3300	1596	1650	531	496	1530
[NiL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3321	1597	1645	533	496	1531
[CuL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3323	1596	1653	536	493	5137
[ZnL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3328	1598	1651	531	499	1531

The peak around 3200-3300  $\text{cm}^{-1}$  indicated the non-involvement of the N-H group in complexation. In a mixed ligand complex, the decrease in  $>\text{C}=\text{O}$  stretching frequency indicates its involvement. A broad band at around  $3275\text{ cm}^{-1}$  exhibited by the ligand and assigned to the phenolic O-H group disappeared in the complex indicating the removal of hydroxyl proton through complexation. A sharp band observed at around  $1600\text{--}1650\text{ cm}^{-1}$  assigned to C=N stretching frequency, this band lowers appreciably in complex indicating coordination by the azomethine group.

*Magnetic susceptibility of metal complexes* – The magnetic moment value of formed complexes for the ligand (L). The complexes of Co (II), Ni (II), and Cu (II) were paramagnetic having 3, 2 and 1 number of unpaired electrons whereas Zn (II) complexes were diamagnetic in nature <sup>[6]</sup>. The cobalt (II) complexes exhibit two spectral bands assigned to the transition,  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  and  ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$  proposing octahedral geometry. The proposed geometry of Cobalt (II) complexes is further supported by the high magnetic susceptibility value in the range of 4.30 – 5.20 B.M. The Co (II) complexes were high spin complexes having electronic configuration  $\text{Co}^{+2} - t_{2g}^5 e_g^2$ . Cobalt being unsymmetrically filled  $t_{2g}$  orbital has orbital contribution<sup>[7]</sup> to the magnetic moment value and it was confirmed by the magnetic susceptibility value.

The nickel (II) complexes for both ligands display three spectral bands assigned to transitions  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ ,  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ , and  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ , favours an octahedral geometry<sup>[8]</sup>. The Magnetic susceptibility of nickel(II) lies in the range of 2.80-3.50 B.M.

The copper (II) complexes exhibit three spectral bands assigned to the transition occurred from  ${}^2\text{B}_{1g}$ ,  ${}^2\text{A}_{1g}$ ,  ${}^2\text{B}_{2g}$  or the  ${}^2\text{E}_g$ . This occurred because slight jahn-teller splitting<sup>[9]</sup> of  ${}^2\text{E}_g$  and  ${}^2\text{T}_{2g}$ , as unsymmetrically filled  $\text{E}_g$  orbital showed orbital contribution to magnetic moment value as well as jahn-teller distortion. This transition favours octahedral geometry around Cu (II) ions.

Zn (II) complexes showed absorption band due to intraligand transition and metal to ligand charge transfer (MLCT)<sup>[10]</sup> and octahedral geometry is proposed which was further supported by its diamagnetic nature and absence of d-d band, due to completely filled d<sup>10</sup> orbital<sup>[11]</sup>.

*Molar conductance:* Molar conductance values of the synthesized compounds were below 26 Ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, indicating their non electrolytic nature <sup>[12]</sup>. This suggested that there were no anions present outside the coordination sphere of the complexes.

**Conclusion:** It is evident from the above discussed results that the ligand was bidentate, and the ring formed by the complexes was six-membered and hence has less strain and is considered more stable. Thus it was confirmed that the complexes formed by metals and Schiff base ligands L took place through phenolic oxygen and azomethine nitrogen of ligands. But still, there is a need to explore the biological properties of these already synthesized transition metal complexes.

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