

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

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Abstract : A new series of Co(II), Ni(II), Cu(II), and Zn(II) complexes was synthesized using a Schiff base ligand derived from phenyl hydrazine and Ortho-benzoyl p-cumenol. Elemental analysis, IR spectroscopy, molar conductance measurements, and melting point determination characterized the Schiff base and its metal complexes. IR spectra confirmed coordination bonding with “N” and “O” donor atoms, suggesting a six-coordinated octahedral geometry for all complexes.

(Keywords : Ambidentate ligand, Hydrazine, IR-spectra, Paramagnetism, Schiff base)

Introduction

The chemistry of metal complexes with Schiff base ligands, characterized by oxygen and nitrogen as donor atoms, continues to be a focal point for researchers. These ligands demonstrate diverse coordination behavior towards metal atoms under varying reaction conditions, typically synthesized through the condensation reaction of aldehydes and primary amines¹. 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 atoms².

Schiff base metal complexes exhibit a wide range of biological and pharmaceutical activities. Notably, transition metal complexes of Schiff base ligands featuring “O” and “N” donor

atoms possess significant biological properties, including antibacterial, antifungal, anti-inflammatory, analgesic, anticonvulsant, antitubercular, antioxidant, and anthelmintic activities. Moreover, these complexes serve as valuable biological models for elucidating biomolecular structures and processes³.

Cobalt, nickel, copper, and zinc are essential metallic elements vital for life processes. Their association with specific metal protein complexes enhances their biological activity, facilitating oxygen transport, electronic transfer reactions, and ion storage⁴. Consequently, the study of systems involving these metals has garnered considerable attention in scientific research.

In this present paper, we have focused on the synthesis of a novel Schiff base⁵ ligand, by the condensation of phenyl hydrazine⁶ 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.

Methodology:

A condensation product of Phenyl hydrazine 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_3 of about 2-3gm was added to the reaction mixture. After mixing the anhydrous AlCl_3 , the whole mixture was heated upto 155° Celcius for half an hour. The mixture was dissolved in ethanol and crystallized. After that, this crystal was mixed with phenyl hydrazine, added dilute Acetic acid, and methanol and the whole mixture was refluxed for upto 2 hours. A brownish crystal was found which was crystallized with ethanol. After that, the m.p of the formed compound was measured. It was 255!.

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.

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_2 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, 79.75%, H, 6.66%, N, 8.48%, and O, 4.84%, Found: C, 79.54%, H, 6.01%, N, 8.23%, and O, 4.22%.

Elemental analysis of metal complexes having ligand (L) :

Cobalt (II) complexes, C_1 . Elemental analysis data for $[\text{Co L}_2(\text{H}_2\text{O})_2]$, Required: C, 70.12%; H, 6.10%; N, 7.43%, O, 8.50%, Co, 7.82% found: C, 69.89%; H, 6.06%; N, 7.32%,

O, 8.45%, Co, 7.78%. Nickel (II) complexes, C_2 . Elemental analysis data for $[\text{Ni L}_2(\text{H}_2\text{O})_2]$, Required: C, 70.14%; H, 6.11%; N, 7.43%, O, 8.51%, Ni, 7.82% found: C, 69.87%; H, 6.04%; N, 7.32%, O, 8.45%, Ni, 7.77%. Copper (II) complexes, C_3 . Elemental analysis data for $[\text{Cu L}_2(\text{H}_2\text{O})_2]$, Required: C, 69.97%; H, 6.09%; N, 7.42%, O, 8.48%, Cu, 8.42% found: C, 69.77%; H, 6.03%; N, 7.29%, O, 8.45%, Cu, 8.41%. Zinc (II) complexes, C_4 . Elemental analysis data for $[\text{Zn L}_2(\text{H}_2\text{O})_2]$, Required: C, 69.52%; H, 6.05%; N, 7.34%, O, 8.42%, Zn, 8.61% found: C, 69.49%; H, 6.01%; N, 7.31%, O, 8.48%, Zn, 8.56%.

Results and Discussion:

The complexes were synthesized by reacting ligand with the metal ions in 1:2 molar ratio in the methanolic medium. Complexes were insoluble in common organic solvents such as methanol, dichloromethane, ethanol, and acetone but soluble in DMSO and DMF.

Molar conductance: Molar conductance values of the synthesized compounds were below $40 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, indicating their nonelectrolytic nature¹⁷. This suggested that there were no anions present outside the coordination sphere of the complexes.

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 nature⁸. 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 contribution⁹ 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 ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$, favours an octahedral geometry^{[6][10]}. The Magnetic susceptibility of nickel(II) lies in the range 2.80-3.50 B.M.

The copper (II) complexes exhibit three spectral bands assigned to the transition occurred from ${}^2B_{1g}$, ${}^2A_{1g}$, ${}^2B_{2g}$ or the ${}^2E_g$. This occurred because slight jahn- teller splitting¹¹ of ${}^2E_g$ and

${}^2T_{2g}$ as unsymmetrically filled 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)¹² and octahedral geometry is proposed which was further supported by its diamagnetic nature and absence of d-d band, due to completely filled d^{10} orbital¹³. *Spectral analysis:* IR- spectra¹⁴ of ligand (L), C=N stretching “1630 cm^{-1} ”, N”H stretching “3101 cm^{-1} ”, C=C aromatic stretching”1643 cm^{-1} ”, N”H bending “1661 cm^{-1} ”, O”H stretching “3170 cm^{-1} ”, substituted benzene “740 cm^{-1} ”.

TABLE - 1

Complexes	t(N-H) str cm^{-1}	t(C=N)str cm^{-1}	t(C=C) aromatic cm^{-1}	t(M”N)str cm^{-1}	t(M”O)str cm^{-1}
[CoL ₂ (H ₂ O) ₂]	3101 cm^{-1}	1622 cm^{-1}	1643 cm^{-1}	526 cm^{-1}	486 cm^{-1}
[NiL ₂ (H ₂ O) ₂]	3106 cm^{-1}	1628 cm^{-1}	1646 cm^{-1}	523 cm^{-1}	482 cm^{-1}
[CuL ₂ (H ₂ O) ₂]	3111 cm^{-1}	1625 cm^{-1}	1642 cm^{-1}	525 cm^{-1}	487 cm^{-1}
[ZnL ₂ (H ₂ O) ₂]	3108 cm^{-1}	1621 cm^{-1}	1643 cm^{-1}	522 cm^{-1}	488 cm^{-1}

The peak observed at approximately 3200-3300 cm^{-1} suggests the non-participation of the N-H group in the process of complexation. In the context of a mixed ligand complex, a reduction in the stretching frequency of the >C=O bond signifies its involvement in the coordination process. Furthermore, the disappearance of a broad band centered at approximately 3170 cm^{-1} , which is attributed to the phenolic O-H group, upon formation of the complex indicates the abstraction of the hydroxyl proton during complexation. Additionally, a distinct band detected within the range of 1600-1650 cm^{-1} , corresponding to the C=N stretching frequency^[15], exhibits a notable decrease in intensity upon complex formation, indicative of coordination by the azomethine group.

The observed spectral changes are consistent with the coordination of the ligand

within the complex structure, with specific functional groups undergoing alterations in vibrational frequencies as a result of their involvement in coordination bonding. These findings align with established principles of coordination chemistry, elucidating the structural changes occurring during the formation of the complex.

Conclusion

The ligand was bidentate, forming a six-membered ring in the discussed complexes, which experiences less strain and is considered more stable. Consequently, it was confirmed that the formation of complexes by metals and Schiff base ligand L occurred through coordination with the phenolic oxygen and azomethine nitrogen of the ligands. However, there is still a need to explore the biological properties of these already synthesized transition metal complexes.

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