

SYNTHESIS AND CHARACTERIZATION OF MIXED LIGAND COMPLEXES OF 1-{(E)-[(4-METHYL-2 NITROPHENYL) IMINO]METHYL} NAPHTHALEN-2-OL AND 2-{(E)-[(2,3-DIMETHYLPHENYL) IMINO]METHYL}PHENOL WITH CO(II), NI(II), CU(II) AND ZN(II) IONS.

Atmaram K. Mapari^{*1}

^{*1}Department Of Chemistry, Ramnarain Ruia Autonomous College, Matunga (E), Mumbai, Maharashtra, India.

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ABSTRACT

The mixed ligand complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Schiff bases 1-{(E)-[(4-methyl-2-nitrophenyl)imino]methyl}naphthalen-2-ol (L^1H) and 2-{(E)-[(2,3-dimethylphenyl)imino]methyl}phenol (L^2H) have been synthesized and characterized. The resulting complexes were characterized by thermogravimetric analysis, magnetic moment measurements, conductivity measurements, IR, UV-visible spectral studies. The Schiff bases acts as bidentate monobasic ligands, coordinating through deprotonated phenolic oxygen and azomethine nitrogen atoms. The complexes are non-electrolytic in DMSO. The presence of the two coordinated water molecules in these complexes was indicated by IR spectra and thermogravimetric analysis of the complexes. From the analytical and spectral data the stoichiometry of these complexes have been found to be $[M(L^1)(L^2)(H_2O)_2]$ {where $M = Co(II)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$ }. It is found that Co(II), Ni(II), Cu(II) and Zn(II) complexes exhibited octahedral geometry.

Keywords: Schiff Bases, Mixed Ligand, Metal Complexes.

1. INTRODUCTION

In the field of coordination chemistry, Schiff base metal complexes have a curious history [1]. The present work is the study of mixed ligand complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Schiff bases 1-{(E)-[(4-methyl-2-nitrophenyl)imino]methyl}naphthalen-2-ol (L^1H) and 2-{(E)-[(2,3-dimethylphenyl)imino]methyl}phenol (L^2H). The structure of ligands L^1H and L^2H are shown in figure 1 and 2 respectively.

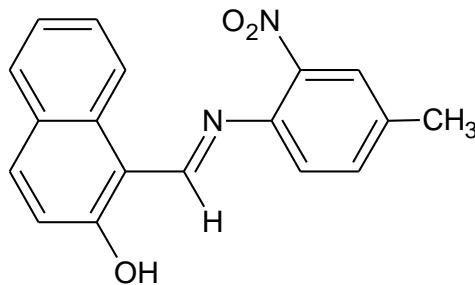


Figure 1: 1-{(E)-[(4-methyl-2-nitrophenyl)imino]methyl}naphthalen-2-ol (L^1H)

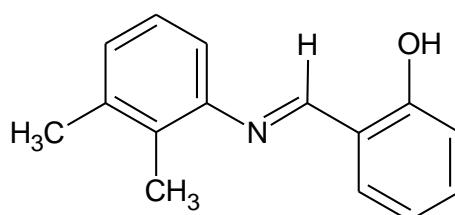


Figure 2: 2-{(E)-[(2,3-dimethylphenyl)imino]methyl}phenol (L^2H)

2. MATERIALS AND METHODS

Synthesis of ligands

The ligands (L^1H and L^2H) were prepared by the condensation of the corresponding aldehyde and amine in 1:1 molar ratio by refluxing in ethanol [2].

Preparation of complexes

The mixed ligand metal complexes were prepared by precipitation method [3].

3. RESULTS AND DISCUSSIONS

The resulting complexes were characterized by thermogravimetric analysis, magnetic moment measurements, IR and UV-visible studies.

Conductivity Measurements

The molar conductance values of Co(II), Ni(II), Cu(II) and Zn(II) complexes are 0.013, 0.018, 0.015 and 0.021 $\text{ohm}^{-1} \text{mol}^{-1} \text{cm}^2$ respectively of 10^{-3} M solution in DMSO indicate that the metal complexes are non-electrolytic in nature.

Electronic spectra and Magnetic moment

The electronic spectral studies of Mixed Ligand metal Complexes carried out in DMSO solution. The absorption spectrum of the Co(II) complex shows bands at $\sim 10013 \text{ cm}^{-1}$ ($\epsilon \sim 15$) and $\sim 19604 \text{ cm}^{-1}$ ($\epsilon \sim 45$) attributed to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ (ν_1) and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ (ν_3) transitions respectively in an octahedral field. The Co(II) complex has magnetic moment 5.14 BM also suggest an octahedral geometry [3], [4].. Ni(II) complex exhibits two electronic spectral bands at $\sim 10613 \text{ cm}^{-1}$ ($\epsilon \sim 20$) and $\sim 16564 \text{ cm}^{-1}$ ($\epsilon \sim 61$) which can be assigned to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ (ν_1) and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ (ν_2) transitions in an octahedral field⁵. The Ni(II) complex has magnetic moment 3.42 BM also suggest an octahedral geometry [3], [4]. The Cu(II) complex exhibit broad band centered at $\sim 14704 \text{ cm}^{-1}$ ($\epsilon \sim 77$) mainly due to ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition suggesting the distorted octahedral geometry. The observed magnetic moment value for Cu(II) complex is 1.82 BM suggestive of distorted octahedral nature for the complex [3], [4]. Zn(II) complex does not exhibit any characteristic d-d transitions and is also found to be diamagnetic in nature [5].

Infrared spectra

The important infrared frequencies exhibited by the ligands L^1H and L^2H and their mixed ligand complexes are given in the Table 1. Infrared spectra of the schiff bases L^1H and L^2H show a broad band centered at around 3453 and 3446 cm^{-1} due to the phenolic hydroxyl group respectively in free ligands, which disappeared in spectra of their complexes indicating probably the coordination through phenolic oxygen moiety. The schiff bases L^1H and L^2H show a medium intensity band at around 1327 and 1279 cm^{-1} due to phenolic $\nu(\text{C}-\text{O})$ group of is shifted to higher region indicating the coordination through the phenolic oxygen atoms [5]. The IR spectra of the schiff bases L^1H and L^2H exhibit a strong band at 1618 and 1614 cm^{-1} due to $\nu(\text{C}=\text{N})$ (azomethine) which has been shifted towards lower region in the spectra of complexes indicating the participation of the azomethine groups in the complex formation [2]. The spectra of the complexes show a broad diffused bands in the region at around 3100-3650 cm^{-1} , strong bands at 1535-1538 cm^{-1} and week intensity bands at 825-831 cm^{-1} due to $\nu(\text{OH})$, $\delta(\text{OH})$ and $\rho_r(\text{OH})$ respectively of the coordinated water molecules [6]. The coordination through nitrogen of azomethine and oxygen of (C-O) group of ligands are further evidenced by the appearance of non-ligand bands in the complexes at around 496-556 cm^{-1} and 420-464 cm^{-1} are due to M-O and M-N bonds respectively [4], [6].

Table 1: Characteristic IR bands of the ligands L^1H and L^2H and their mixed ligand metal complexes.

Schiff base / Complex	IR bands (cm^{-1})							
	ν_{OH} (phenolic)	ν_{OH} (H_2O)	$\nu_{\text{C}=\text{N}}$	δ_{OH} (H_2O)	$\nu_{\text{C}-\text{O}}$ (phenolic)	$\rho_r\text{OH}$ (H_2O)	$\nu_{\text{M}-\text{O}}$	$\nu_{\text{M}-\text{N}}$
L^1H	3455	-	1618	-	1327	-	-	-
L^2H	3447	-	1617	-	1278	-	-	-
$[\text{Co}(\text{L}^1)(\text{L}^2)(\text{H}_2\text{O})_2]$	-	3150 – 3651	1613, 1607	1534	1387, 1363	825	556, 502	464, 417
$[\text{Ni}(\text{L}^1)(\text{L}^2)(\text{H}_2\text{O})_2]$	-	3200 – 3650	1612, 1607	1533	1384, 1365	826	547, 502	462, 416
$[\text{Cu}(\text{L}^1)(\text{L}^2)(\text{H}_2\text{O})_2]$	-	3150 – 3650	1612, 1607	1534	1385, 1363	825	548, 496	461, 420
$[\text{Zn}(\text{L}^1)(\text{L}^2)(\text{H}_2\text{O})_2]$	-	3100 – 3650	1614, 1609	1538	1393, 1365	831	547, 503	464, 417

Thermogravimetric analysis

The Co(II), Ni(II), Cu(II) and Zn(II) complexes lose their weight in the temperature range \sim 130-272 °C, 125-255 °C, 125-263 °C and 130-276 °C respectively corresponding to two coordinated water molecules with an endothermic peak in DTA curve indicates that the two water molecules are coordinated in the metal complexes [4].

4. CONCLUSION

Magnetic susceptibility, Thermogravimetric analysis and spectral observations suggest the octahedral geometry for the Co(II), Ni(II), Cu(II) and Zn(II) complexes and exhibit coordination number six. The general structure of the complexes is shown in figure 3.

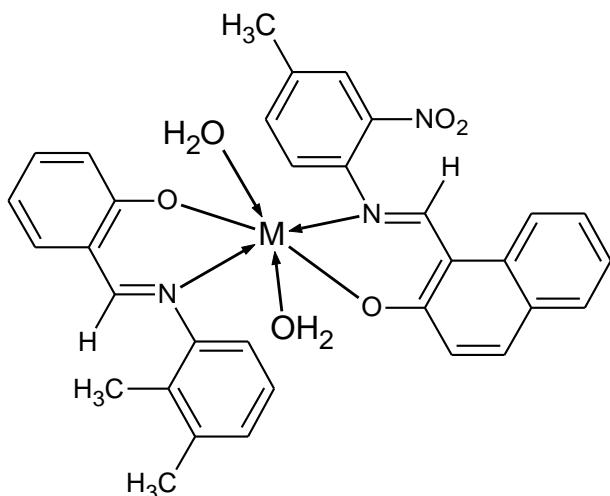


Figure 3: Proposed structure for the complexes.

M = Co(II), Ni(II), Cu(II) and Zn(II).

5. REFERENCES

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