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SYNTHESIS AND CHARACTERIZATION OF MIXED LIGAND COMPLEXES OF 1-[(1*E*)-*N*-(4-BROMO-3-ETHOXYPHENYL) ETHANIMIDOYL]NAPHTHALEN-2-OL AND 4-BROMO-2-{(*E*)-[(2-METHYL-5-NITROPHENYL)IMINO]METHYL}PHENOL TRANSITION METAL(II) IONS.

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ABSTRACT

The mixed ligand complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Schiff bases 1-[(1*E*)-*N*-(4-bromo-3-ethoxyphenyl)ethanimidoyl] naphthalen-2-ol(L^1H) and 4-bromo-2-{(*E*)-[(2-methyl-5-nitrophenyl) 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 thestoichiometry 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.

INTRODUCTION

In the field of coordination chemistry, Schiff base metal complexes have a curious history.[1,2] The present work is the study of mixed ligand complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Schiff bases 1-[(1*E*)-*N*-(4-bromo-3-ethoxyphenyl)ethanimidoyl]naphthalen-2-ol (L^1H)

and 4-bromo-2-{(E)-[(2-methyl-5-nitrophenyl)imino]methyl}phenol (L^2H) shown Figure 1 and 2 respectively.

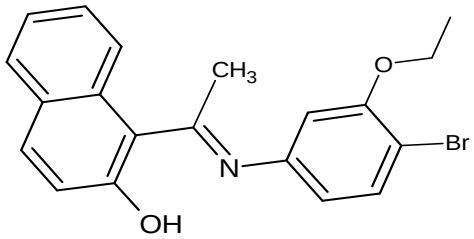


Figure 1: 1-[(1*E*)-*N*-(4-bromo-3-ethoxyphenyl)ethanimidoyl]naphthalen-2-ol (L^1H).

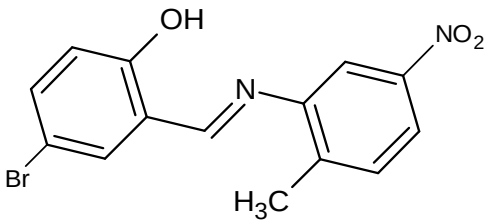


Figure 2: 4-bromo-2-{(*E*)-[(2-methyl-5-nitrophenyl)imino]methyl}phenol (L^2H).

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.[3]

Preparation of complexes

The mixed ligand metal complexes were prepared by precipitation method.[4]

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 are0.014, 0.016, 0.018 and 0.021ohm^{-1} mol^{-1} cm^2 respectivelyof 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 absorptionspectrum of theCo(II) complex showsbands at ~10014 cm^{-1} (ε ~ 15)

and ~ 19604cm^{-1} (ε ~ 45) attributed to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions respectively in an octahedral field[4]. The Co(II) complex has magnetic moment 5.15 BM also suggest an octahedral geometry. Ni(II) complex exhibits two electronic spectral bands at ~ 10616 cm^{-1} (ε ~ 20)and ~ 16564 cm^{-1} (ε ~ 62) which can be assigned to$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1) and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) transitions in an octahedral field.[5] The Ni(II) complex has magnetic moment 3.45 BM also suggest an octahedral geometry. The Cu(II) complex exhibit broadband centered at ~ 14708 cm^{-1} (ε ~ 78) mainly due to $^2E_g \rightarrow {}^2T_{2g}$ transition suggesting the distorted octahedral geometry.[6] The observed magnetic moment value for Cu(II) complex is 1.80 BM suggestive of distorted octahedral nature for the complex.[4,5] Zn(II) complex does not exhibit any characteristic d-d transitions and is also found to be diamagnetic in nature.

Infrared spectra

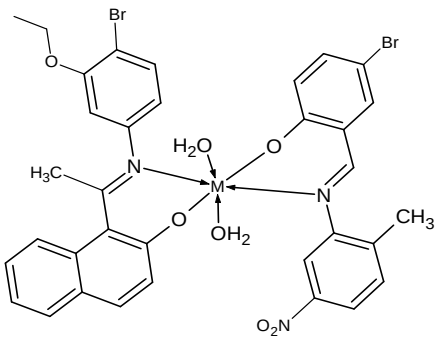
The important infrared frequencies exhibited by the ligands L^1H and L^2H and their mixed ligand complexes are given in the Table 1. Infrared spectra of the schiff bases L^1H and L^2H show a broad band centered at around 3450 and 3447 cm^{-1} due to the phenolic hydroxyl group respectively in free ligands, 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 ν(C-O) group of is shifted to higher region indicating the coordination through the phenolic oxygen atoms.[2] The IR spectra of the schiff bases L^1H and L^2H exhibit a strong band at 1618 and 1616 cm^{-1} due to ν(C=N) (azomethine) which has beenshifted towards lower region in the spectra of complexes indicating the participation of the azomethine groups in the complex formation.[3] 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 weekintensity bands at825-831 cm^{-1} due to ν(OH), δ(OH) and ρ_r(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.[5]

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)	$\nu_{C=N}$	δ_{OH} (H_2O)	ν_{C-O} (phenolic)	ρ_{rOH} (H_2O)	ν_{M-O}	ν_{M-N}
L^1H	3450	-	1618	-	1327	-	-	-
L^2H	3447	-	1616	-	1279	-	-	-
$[Co(L^1)(L^2)(H_2O)_2]$	-	3150 – 3650	1612, 1609	1535	1387, 1361	828	556, 501	464, 417
$[Ni(L^1)(L^2)(H_2O)_2]$	-	3200 – 3650	1611, 1608	1533	1384, 1362	826	547, 502	462, 416
$[Cu(L^1)(L^2)(H_2O)_2]$	-	3150 – 3650	1613, 1607	1534	1385, 1363	825	548, 496	461, 420
$[Zn(L^1)(L^2)(H_2O)_2]$	-	3100 – 3650	1612, 1608	1538	1392, 1364	831	547, 505	464, 419

Thermogravimetric analysis

The Co(II), Ni(II), Cu(II) and Zn(II) complexes lose their weight in the temperature range ~ 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.[5]



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

Figure 3: Proposed structure for the complexes.

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.

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