

## Synthesis and Characterisation of Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) Complexes of Bidentate Ligand of Schiff Base

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A few metallic complexes of Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) metals with bidentate Schiff base have been prepared and characterized. The complexes were coloured, amorphous in nature and are soluble in DMSO and DMF. The conductance measurement shows the complexes are non-electrolytes in DMF. Elemental analysis confirmed to the 1 : 2 stoichiometry. Magnetic, electronic, IR and NMR spectral information suggest the squareplanar structure for Co(II), Ni(II) and Cu(II) complexes while tetrahedral geometry to Zn(II) and Hg(II) complexes.

**Key Words:** Schiff Base, NMR, IR, Square-planar, Tetrahedral.

### INTRODUCTION

Schiff bases and related complexes have been extensively studied because of their applications in analytical<sup>1</sup>, clinical<sup>2</sup> and biological<sup>3</sup> systems. Literature survey reveals that although metal complexes of Schiff bases derived from various amines have been studied extensively<sup>4</sup>, no report is there on the complexes of Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) with *o*-hydroxy benzylamine and *p*-methoxy aniline. In this paper I report the synthesis of a new type of bidentate ligand formed by the condensation of *o*-hydroxy benzylamine with *p*-methoxy aniline. This ligand system has both nitrogen and oxygen donor sites. It coordinates with the metal ion in a bidentate manner through the carbonyl and nitrogen group of the *o*-hydroxybenzylamine moiety.

### EXPERIMENTAL

<sup>1</sup>H NMR spectra of the compounds were recorded on the Bruker's AMX-400 spectrometer at the Sophisticated Instruments Facility, Indian Institute of Science, Bangalore. Electronic spectra of the complexes were recorded on a Shimadzu UV-160 spectrophotometer. IR spectra of the samples were recorded on a Perkin-Elmer 783 spectrophotometer as KBr discs. Magnetic susceptibility measurements

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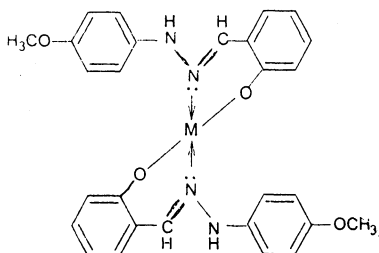
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of the complexes were determined using a Gouy balance at room temperature by using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as a calibrant. Molar conductance of the complexes was measured in ethanol-water at room temperature using a Systronics conductivity bridge type 305.

All the chemicals used were of AR grade.

**Synthesis of ligands:** The mixture of *o*-hydroxybenzylamine (0.01 mol) and *p*-methoxy aniline (0.01 mol) in ethanol was refluxed for 7.0 h. in a water bath. The reaction mixture was cooled and treated with cold water. The pale yellow mass, thus separated, was washed with slightly acidic water to remove unreacted amine. It was crystallized from ethanol, m.p.  $> 30^\circ\text{C}$ ; yield 61.35%.

**Synthesis of complexes:** An ethanolic solution of Schiff base (0.02 mol) was refluxed with  $\text{MCl}_2$  (0.01 mol) for about 4 h and then was added 2 g of sodium acetate. Again the reaction mixture was poured into distilled water and dried in vacuum over fused  $\text{CaCl}_2$ .



$\text{M} = \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II}), \text{Zn}(\text{II}), \text{Hg}(\text{II})$

## RESULTS AND DISCUSSION

Micro-analytical and magnetic susceptibility data of the complexes are given in Table-1. The analytical data of all the complexes correspond to the general formula  $\text{ML}_2$ . Magnetic susceptibility values of  $\text{Co}(\text{II})$ ,  $\text{Ni}(\text{II})$  and  $\text{Cu}(\text{II})$  complexes at room temperature are consistent with square-planar geometry around the central metal ion and  $\text{Zn}(\text{II})$  and  $\text{Hg}(\text{II})$  exhibit tetrahedral geometry. The chelates show no appreciable conductance and this supports their neutral nature.

### $^1\text{H}$ NMR spectra

The spectra for the ligand exhibit four characteristic resonance signals at 13.2 and 9.1 ppm attributed to *o*-hydroxy and azomethine protons respectively. Sharp multiplets observed at 7.0 to 8.2 ppm are attributed to the phenyl protons. Methoxy protons are observed at 1.2–1.6 ppm, while methylene proton is observed around 2.5–3.1 ppm.

In the  $^1\text{H}$  spectra of  $\text{Ni}(\text{II})$ ,  $\text{Zn}(\text{II})$  and  $\text{Hg}(\text{II})$  complexes the following changes were observed:

The azomethine proton signal appears around 8.8 ppm. The downfield shift due to deshielding of azomethine protons suggests the coordination of  $\text{CH}=\text{N}$  group through nitrogen.

The signals due to  $-\text{OH}$  protons disappear in all the complexes indicating that  $-\text{OH}$  group reacts to  $\text{M}(\text{II})$  moiety *via* deprotonation. No appreciable change in the signals due to phenyl protons was observed in the complexes.

TABLE-1  
ANALYTICAL AND MAGNETIC SUSCEPTIBILITY DATA OF THE COMPLEXES

Compound	% Analysis, found (calcd.)				$\mu_{\text{eff}}$ (B.M.)
	M	C	H	N	
L	—	56.77 (57.14)	4.77 (4.79)	6.02 (6.07)	—
CoL	6.78 (6.68)	57.13 (57.31)	4.85 (4.90)	6.18 (6.21)	2.5
NiL	6.25 (6.71)	57.23 (57.53)	5.41 (5.46)	5.85 (5.61)	Diamagnetic
CuL	6.57 (6.75)	58.25 (58.01)	5.31 (5.29)	5.87 (5.82)	1.82
ZnL	6.18 (6.69)	56.83 (56.28)	4.91 (4.85)	5.49 (5.47)	Diamagnetic
HgL	6.34 (6.84)	59.63 (60.27)	5.37 (5.42)	5.99 (5.97)	Diamagnetic

### Infrared spectra

The important frequencies are given in Table-2. The IR spectra of the complexes are compared with that of the free ligand to determine the changes that might have taken place during the complexation. The band at *ca.* 1620  $\text{cm}^{-1}$  is characteristic of the azomethine nitrogen atom present in the free ligand. The lowering in this frequency region (1600–1550  $\text{cm}^{-1}$ ), observed in all the complexes, indicates the involvement of the azomethine nitrogen atom in coordination<sup>5</sup>. It has been established that the formation of inter-molecular hydrogen bonding results in weakening and broadening of the band attributable to —OH vibration and also shifts to lower frequency<sup>6</sup>. In view of this, broadband with fine structure observed in the 2700–2650  $\text{cm}^{-1}$  range is attributed to the intramolecular H-bonded —OH stretch<sup>6</sup>. This band is absent in the complexes showing that the ligands have reacted with the metal ions *via* deprotonation. Also the ligand and the complexes show an intense peak at 3260  $\text{cm}^{-1}$ , which is characteristic of —NH stretching, indicating the existence of a free —NH group.

TABLE-2  
THE IR ( $\text{cm}^{-1}$ ) FREQUENCIES OF THE SCHIFF BASES AND THEIR COMPLEXES

Assignments	L	CoL	NiL	CuL	ZnL	HgL
$\nu(\text{C}=\text{N})$	1650	1598	1591	1587	1582	1581
$\nu(\text{C}—\text{O})$	1280	1372	1371	1370	1367	1369

The band due to phenolic  $\nu(\text{C}—\text{O})$ <sup>8</sup> around 1280  $\text{cm}^{-1}$  in ligands shows considerably high frequency shift and observed in the complexes around 1370  $\text{cm}^{-1}$ . This suggests that oxygen atom of the phenolic —OH group has participated in coordination. The  $\text{C}=\text{N}$  stretch<sup>8</sup> for the ligands observed in the region 1625–1610  $\text{cm}^{-1}$  which appeared at 1600–1550  $\text{cm}^{-1}$  in the complexes suggesting the coordination between nitrogen of the azomethine group and metal ion.

### Electronic spectra

The electronic spectra and magnetic data of the complexes are given in Table-2.

In the electronic spectrum of  $[\text{CoL}_2]$  complex, two new absorption bands are observed at  $16500\text{ cm}^{-1}$  and  $13888\text{ cm}^{-1}$ . These bands are assigned to  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{P})$  and  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$  transitions respectively<sup>9</sup>. The bands corresponding to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions are observed at  $24569\text{ cm}^{-1}$  and  $20081\text{ cm}^{-1}$  respectively. These transitions indicate a square-planar geometry of the complex combination. The observed magnetic moment  $2.5\text{ BM}^{10}$  is in agreement with this structure.

The electronic spectrum of  $[\text{NiL}_2]$  complex shows two new bands at  $16393\text{ cm}^{-1}$  and  $10204\text{ cm}^{-1}$  which are attributed to  ${}^4\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$  and  ${}^4\text{A}_{1g} \rightarrow {}^1\text{B}_{2g}$  transitions respectively. The bands at  $26889\text{ cm}^{-1}$  and  $20281\text{ cm}^{-1}$  are assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions. These transitions<sup>9</sup> and the magnetic moments ( $\mu_{\text{eff}} = 0$ ) suggest a square-planar geometry.

In the electronic spectrum of  $[\text{CuL}_2]$  complex, the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions are observed at  $27473\text{ cm}^{-1}$  and  $21140\text{ cm}^{-1}$  along with two new bands at  $17006\text{ cm}^{-1}$  and  $13210\text{ cm}^{-1}$ , which are assigned to the  $d_{xz} \rightarrow d_{xz}$  and  $d_{xy} \rightarrow d_z^2$  transitions<sup>9</sup>. These transitions, as well as the measured value of the magnetic moment ( $1.82\text{ BM}$ ) suggests a square-planar structure of compound.

Electronic spectrum of  $\text{Zn(II)}$  and  $\text{Hg(II)}$  shows two bands which can be ascribed to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions. One band is assigned to charge transfer transition. The magnetic moment ( $\mu_{\text{eff}} = 0$ ) suggests tetrahedral geometry<sup>9</sup>.

In conclusion, the  ${}^1\text{H}$  NMR, IR, magnetic moment and analytical data suggest that coordination has taken place through azomethine nitrogen as well as phenolic oxygen. All these observations project the following probable structure of these complexes.

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