

## Synthesis and Characterization of Some Schiff Base Metal Complexes

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The new Schiff bases of tris-4-methoxy-3-hydroxy-5-bromobenzilidene-4-anisidine with  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  have been synthesized and characterized on the basis of elemental analysis, infrared spectra, electronic spectra, molar conductance, magnetic measurement, thermal analysis and X-ray powder diffraction. The magnetic moment of complexes  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  are paramagnetic, whereas  $\text{Zn}^{2+}$  is diamagnetic. The  $\beta$  values show considerable orbital overlaps between metal-ligand bonds.

**Key Words:** Synthesis, Metal complexes, Schiff base.

### INTRODUCTION

Recently Schiff base derivatives have been used in various diseases<sup>1-5</sup>. Some of them are fungicides used to protect cereal crops and also used in treatment of various infections<sup>6, 7</sup>. In this paper, we report the synthesis and characterization of tris-4-methoxy-3-hydroxy-5-bromobenzilidene-4-anisidine with their metal ion complexes ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ) and general formula of the complex is  $[\text{ML}_2 \cdot 2\text{H}_2\text{O}]$  where  $\text{M} = \text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{L} = \text{tris-4-methoxy-3-hydroxy-5-bromobenzilidene-4-anisidine}$ .

### EXPERIMENTAL

Bromo-vanilline and *p*-anisidine was obtained from Merck Laboratories, Mumbai and Metal chlorides from BDH. Infrared spectra were recorded on Perkin-Elmer Paragon-500 spectrophotometer using KBr pellets. Electronic spectra on recorded on Cintra-5 GBC UV-Visible spectrophotometer at University Department of Chemical Technology, Mumbai. Magnetic susceptibility measurements were carried out using  $[\text{HgCO}(\text{CNS})_4]$  as a calibrate at Dr. Babasaheb Ambedkar Marathwada University, Aurangabad. X-ray powder diffraction was recorded on Jeol-8030 double goniometer X-ray powder diffractometer at Tata Institute of Fundamental Research, Mumbai. The densities of the complexes were calculated using specific density bottle in toluene solvent. TGA, DTA were

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recorded on Mettler Toledo star<sup>c</sup> system at Indian Institute of Chemical Technology, Hyderabad, in the range 25–1000°C in atmospheric nitrogen. The conductivity measurements were made on an Ilico conductivity bridge.

**Preparation of Metal Complexes:** The ligand tris-4-methoxy-3-hydroxy-5-bromobenzilidene-4-anisidine (L) was prepared by literature method<sup>8</sup>. The equimolar alcoholic solution of metal chlorides and ligand (0.05 m) were taken in a round-bottom flask. This reaction mixture was refluxed for *ca.* 3 h using water condenser. After *ca.* 3 h a slight precipitate appeared; when the pH of resulting mixture was adjusted in between 5.5 to 6.0, more precipitate was obtained. This precipitate was filtered and washed with double distilled ethanol and dried at 60°C.

## RESULTS AND DISCUSSION

The analytical data and physical data of complexes are listed in Table-1. The molar conductance of 10<sup>-3</sup> molar solution of complexes was measured in DMSO. The molar conductivity of complexes indicates that these complexes are non-electrolytic in nature<sup>9</sup>. The complexes decomposed in the range 165–210°C. The melting point and decomposition point was reported in open capillary and are uncorrected. The metal content was estimated by EDTA using xylenol orange as an indicator<sup>10</sup>. The metal-ligand ratio of the complexes is 1 : 2. These complexes are insoluble in organic solvents like benzene, acetone, ether, chloroform and acetonitrile, but these complexes are soluble in dimethyl formamide and dimethyl sulfoxide.

TABLE-1  
ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

Complexes	Colour (yield, %)	m.p. (°C)	% Elemental analysis: Found (Calcd.)				$\mu_{\text{eff}}$ (B.M.)
			C	H	N	M	
CoL <sub>2</sub> ·2H <sub>2</sub> O	Green (68)	204	41.52 (41.38)	3.22 (3.08)	1.61 (1.52)	6.80 (6.71)	3.85
NiL <sub>2</sub> ·2H <sub>2</sub> O	Brick red (64)	175	41.53 (41.42)	3.23 (3.11)	1.61 (1.47)	6.77 (6.67)	2.88
CuL <sub>2</sub> ·2H <sub>2</sub> O	Brown (63)	200	41.30 (41.19)	3.21 (3.15)	1.59 (1.48)	7.28 (7.10)	1.81
ZnL <sub>2</sub> ·2H <sub>2</sub> O	Black (66)	186	41.21 (41.10)	3.20 (3.11)	1.58 (1.45)	7.48 (7.36)	0

**Infrared spectra:** The bands are observed in ligand for hydroxy group at 3450 cm<sup>-1</sup>, for tertiary nitrogen at 1550 cm<sup>-1</sup> and for benzene ring at 3016–2969 cm<sup>-1</sup>, but in the complexes the hydroxy group change their position<sup>11, 12</sup> from 3390 to 3440 cm<sup>-1</sup> and the tertiary nitrogen changes its position from 1520 to 1510 cm<sup>-1</sup>. Hence the bonding between hydroxy of benzene ring and tertiary nitrogen of the Schiff base with metal ions. There is no change in other bands in ligand and complexes, but two new bands were observed at 3510–3480 cm<sup>-1</sup> and 3475–3430 cm<sup>-1</sup> for involvement of two water molecules in the coordination

sphere. The new bands for M—N and M—O are at 490–470  $\text{cm}^{-1}$  and 450–430  $\text{cm}^{-1}$  respectively<sup>13, 14</sup>. **Electronic spectra and magnetic moment:** The electronic spectra of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  were recorded and their parameters  $\beta$ ,  $\delta\%$  and  $b^{1/2}$  are<sup>15–17</sup> given in Table-2.

TABLE-2  
ELECTRONIC SPECTRA AND THEIR ASSIGNMENT

Complexes	$\beta$	$\delta\%$	$b^{1/2}$
$\text{CoL}_2 \cdot 2\text{H}_2\text{O}$	0.9880	1.210	0.0774
$\text{NiL}_2 \cdot 2\text{H}_2\text{O}$	0.9893	1.080	0.0731
$\text{CuL}_2 \cdot 2\text{H}_2\text{O}$	0.9902	0.9896	0.0700

The magnetic moment of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  recorded at room Temperature are found to be close<sup>18</sup>. The complexes  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  are paramagnetic while  $\text{Zn}^{2+}$  is diamagnetic.

**Thermal analysis:** TGA and DTA of  $\text{Co}^{2+}$  complex were studied (Table-3). These complexes are thermally stable at room temperature. The complexes start decomposing above 100°C. The complexes decompose in five steps and finely get converted into metal oxide<sup>19, 20</sup>. The detail decomposition of complex is given in Table-3

TABLE-3  
THERMAL ANALYSIS OF  $\text{Co}^{2+}$  COMPLEX

Complex	Peak range (°C)	Theoretical (% loss)	Experimental (% loss)	Possible leaving group
$\text{CoL}_2 \cdot 2\text{H}_2\text{O}$	110–240	16.95 b	17.18	$2\text{H}_2\text{O}$ , $\text{OCH}_3$ , Br
	260–330	40.94 b	41.12	$\text{OCH}_3$ , $2\text{C}_6\text{H}_6$ , CHN
	380–450	62.28 a	63.01	$\text{OCH}_3$ , Br, $\text{C}_6\text{H}_6$
	480–560	70.58 a	71.23	$\text{C}_6\text{H}_6$ , CHN
	600–850	81.66 b	82.22	CoO

a = exothermic, b = endothermic.

**X-ray powder diffraction:** X-ray powder diffraction measurements were carried out in order to estimate an external powder form of the complexes. The diffractogram analysis suggests they are poly-crystalline compound with low symmetry. The major reflexes were used to calculate crystal lattice parameters using back-cal programmer on computer by Ito's method<sup>21–22</sup>. The complexes are hexagonal, space group is P 6/m, Formula factor Z = 8. The density value of  $\text{Cu}^{2+}$  complex is 1.7323  $\text{g}/\text{cm}^3$  and calculated 1.7516  $\text{g}/\text{cm}^3$  respectively<sup>23, 24</sup>. The parameters are given in Table-4.

TABLE-4  
CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR [CoL<sub>2</sub>·2H<sub>2</sub>O] COMPLEX

a (Å) = 15.3095	D <sub>cal</sub> (g/cm <sup>3</sup> ) = 1.7516
c (Å) = 23.7584	D <sub>obs</sub> (g/cm <sup>3</sup> ) = 1.7323
c/a (Å) = 1.5519	Space group = P6/m
Crystal system = Hexagonal	V (Å) <sup>3</sup> = 4822.69
Z = 8	

D <sub>obs</sub>	D <sub>cal</sub>	h	k	l	I/I <sub>0</sub>	2θ
8.8451	8.8474	1	0	2	81	10.0
7.6547	7.6547	1	1	0	68	11.56
5.8060	5.7888	2	0	2	49	15.26
5.5050	5.5039	1	1	3	77	16.10
4.2382	4.2346	2	1	3	55	20.96
3.8700	3.8620	2	0	5	74	22.98
3.5120	3.5128	3	1	2	72	25.36
3.2856	3.2880	1	0	7	37	27.14
3.2181	3.2173	2	2	4	100	27.72
3.1275	3.1265	3	1	4	82	28.54
3.0460	3.0417	3	2	0	44	29.32
2.7698	2.7687	1	1	8	29	32.32
2.4656	2.4650	3	0	8	41	36.44
2.4107	2.4122	3	2	6	35	37.30
2.2368	2.2365	2	0	10	42	40.32
2.2126	2.2119	4	0	8	42	40.78

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