

## PREPARATIVE AND STRUCTURAL STUDIES ON COMPLEXES OF Cu(II), Co(II), Zn(II) AND Mn(II) WITH TRIDENTATE LIGAND

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Solid metal complexes with 2-hydroxy-1-naphthaldehyde-tris (OHNAT) have been prepared and characterized using elemental analysis, conductivity measurements, IR studies, magnetic susceptibility measurements and thermal studies. Cu(II) forms square planar complex, Co(II) and Mn(II) exhibit octahedral geometry and Zn(II) gives tetrahedral symmetry. All these metal ions form 1:1 complexes.

**Key Words:** Structural Studies; Cu(II), Co(II), Zn(II) and Mn(II) Complexes; Tridentate Ligand

### Introduction

Schiff bases are very good complexing agents. A perusal of literature survey reveals that the field of Schiff base metal complexes is vast and fast developing on account of numerous applications in various important fields and the wide variety of structures possible for the ligands depending upon the aldehydes and amines. Reactions of tris(hydroxy-methyl)methylamine (Tris) with some aldehydes were carried out by several authors<sup>1-4</sup>. Recently, new Schiff bases of tris with ketones have also been reported<sup>5,6</sup>. The present investigation describes the isolation of complexes of 2-hydroxy-1-naphthaldehyde-tris (OHNAT) with Cu(II), Co(II), Zn(II) and Mn(II) and their structural elucidation on the basis of elemental analysis, conductivity, infrared, magnetic and thermal studies.

### Experimental

All chemicals used were of AnalaR grade. Metal acetates were used in the preparation of Cu(II), Co(II) and Zn(II) chelates. Manganese sulphate was used to prepare Mn(II) complex.

#### *Preparation of the Ligand*

Equimolar concentrations (0.1 mole) of Tris (Loba-Chemie, GR Grade) and pure 2-hydroxy-1-naphthaldehyde (Fluka, AG) dissolved in methanol and the mixture was refluxed for 30 minutes on a water bath. On cooling yellow needles were separated out. The compound was washed with ether and then dried. The compound was recrystallised from methanol. The percentage yield was 80 mp of the compound was 169-70 °C.

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### Synthesis of Metal Chelates

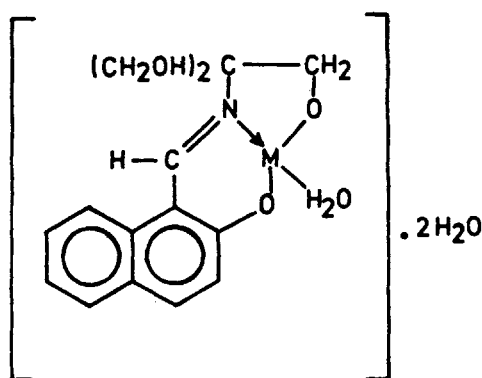
Metal complexes were prepared by adding a requisite amount of Schiff base in methanol to the metal ion in water in presence of sodium acetate and refluxed the mixture for one hour on a water bath. The reaction mixture was poured in excess of cold water. Coloured precipitates of metal chelates were obtained with good yield. The coloured metal complexes were washed several times with water and cold methanol to free them from unreacted metal salts and ligand respectively and finally with ether and dried in a vacuum dessicator.

Carbon and hydrogen were analysed on a Coleman Carbon-Hydrogen Analyzer Model 33 and nitrogen was estimated by Kjeldahl's method. Analysis for the metal content was carried out by complexometric titration after decomposing a known weight of the complex with a mixture of Conc.  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  and also by gravimetric oxide method.

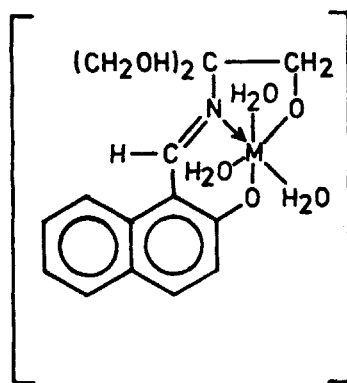
The molar conductivities of the complexes in DMF were measured using Toshniwal conductivity bridge. The infrared spectra of the ligand and the complexes were recorded in nujol-mull on a Perkin-Elmer infrared spectrophotometer. Magnetic susceptibilities were on standard Guoy's balance using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as the calibrant. A Stanton thermobalance was employed to record the thermograms.

### Results and Discussion

The colour and analytical data of the ligand and its metal chelates are given in Table I. The results of elemental analysis of the complexes show that one molecule of the Schiff base is attached per molecule of the metal(II) ion along with three water molecules. The presence of coordinated water is confirmed by TGA data where loss in weight corresponding to one water molecule for  $\text{Cu}(\text{II})$  and  $\text{Zn}(\text{II})$  and three water molecules for  $\text{Co}(\text{II})$  and  $\text{Mn}(\text{II})$  at more than  $170^\circ\text{C}$ .



Where  $\text{M} = \text{Cu}(\text{II})$  and  $\text{Zn}(\text{II})$



Where  $\text{M} = \text{Co}(\text{II})$  and  $\text{Mn}(\text{II})$

Table I Analytical, infrared, conductance and magnetic data of the ligand and its solid metal complexes

Sl. No.	Molecular formula [ $L=C_{13}H_{17}NO_4$ and $X=H_2O$ ]	Molecular weight	Colour	Melting point/ Decomposition position temp. °C	Elemental Analysis						C=N in $cm^{-1}$	Molar conductance*	$\mu_{eff}$ in B.M. Theo. Obs		
					Carbon %		Hydrogen %		Nitrogen %					Metal %	
					Calc.	Found	Calc.	Found	Calc.	Found					Calc.
1	$C_{13}H_{17}NO_4$	275.00	Bright yellow	169-70	65.45	65.41	6.18	6.17	5.09	5.08	—	—	1635	—	—
2	$[Cu.L.X]2X$	390.54	Dark green	270	46.09	46.06	5.37	5.34	5.58	5.56	16.27	16.26	1610	1.917	1.73
3	$[Co.L.X_3]$	385.94	Dark red	362-65	46.64	46.61	5.44	5.41	3.63	3.61	15.20	15.30	1625	4.526	3.88
4	$[Mn.L.X_3]$	381.94	Bright yellow	145-47	47.12	47.10	5.50	5.49	3.66	3.66	14.40	14.41	1625	1.864	5.92
5	$[Zn.L.X]2X$	392.38	Bright yellow	280	45.87	45.85	5.35	5.34	3.57	3.54	16.66	16.66	1610	2.343	Diamagnetic

\*ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>

### Conductivity Measurements

The molar conductances of complexes are in the range of 1.86 to 4.52 ohm  $m^{-1} cm^2 mol^{-1}$ , suggesting non-ionic behaviour of the complexes, i.e., the overall charge on the complex is zero. The elemental analysis and the determination of metal ion content reveal that 1:1 complexes have been formed. Hence, the ligand besides being coordinated to the metal(II) ion, also neutralises its charge. It is possible only when the ligand loses two protons from it. One proton is from phenolic  $-OH$  and other from one of the alcoholic  $-OH$  of  $(-CH_2OH)_3$ . The participation of one of the alcoholic  $OH$ 's of tris in chelation has been reported by Kyusun<sup>7</sup> and Kemula<sup>8,9</sup>. The conductivity measurements thus help in confirming 1:1 complex formation and behaviour of the ligand as tridentate.

### Infrared Studies

Infrared studies help immensely in deciding the nature of bonding in metal complexes. The peaks observed in the ligand at  $3190cm^{-1}$  (phenolic  $-CH$ ) and  $3320cm^{-1}$  ( $O-H$  stretching) disappear in all the metal complexes indicating the deprotonation of metal ions<sup>10</sup>. Peak at  $1280cm^{-1}$  in the ligand is shifted to higher frequencies of  $1510cm^{-1}$  in the complex shows the chelation of the ligand to the metal ion through phenolic oxygen atom<sup>10-12</sup>. Broad peaks around  $2920-2845cm^{-1}$  is attributed to a combination of  $\gamma-OH$  (phenolic),  $\gamma N-H$  and  $\gamma > C-H$  modes.

Sharp peak at  $1635cm^{-1}$  in the ligand shifted to lower frequency around  $1610cm^{-1}$  indicates  $>C=N$  azomethine in ring<sup>11,13</sup>. Peaks at  $1455$  and  $1490cm^{-1}$  show aromatic  $\gamma > C=C$  stretching<sup>1,14</sup>. Peaks at  $1210$  and  $1300cm^{-1}$  indicate  $\gamma > C-C$  stretching coupled with phenolic  $-OH$  deformation, and peaks at  $1580$ ,  $1500$  and  $1450cm^{-1}$  show aromatic  $\gamma > C=C$  stretching vibrations. Very weak peak at  $1080cm^{-1}$  is for  $\gamma > C-O$  stretching coupled with aliphatic  $-OH$  deformation.

The coordinated water molecule is confirmed<sup>10,15</sup> by the appearance of rocking mode of medium intensity at  $840cm^{-1}$ . Finally peak at  $740cm^{-1}$  indicates the presence of more methylene groups in the complex.

From the above critical IR analysis for the metal complexes, it is understood that the phenolic-oxygen atom,  $-N$  atom of the azomethine  $>C=N$  group and aliphatic oxygen atom of  $-CH_2OH$  contribute to form metal chelate ring. All the points clearly substantiate that the ligand behaves like a tridentate ligand satisfying three coordinate sites of the metal atom. It is also seen from the IR studies that water is coordinated in majority of the metal complexes studied.

### Magnetic Susceptibility Measurements

The magnetic moment values calculated from magnetic susceptibility measurements reveal that  $Cu(II)$ ,  $Co(II)$  and  $Mn(II)$  complexes behave as paramagnetic substances with 1, 3 and 5 unpaired electrons respectively whereas  $Zn(II)$  shows diamagnetic nature.

Table II Mode of decomposition of metal chelates

Sl. No.	Complex [ $L=C_{15}H_{17}NO_4$ ; $X=H_2O$ ]	Molecular weight	Weight of the complex taken in mgs	Temperature range during weight loss °C	Per cent of fraction weight		Probable assignment
					Calc.	Found	
1	[Cu.L.X]2X	390.54	2.06	0-190	13.83	14.99	Loss of three water molecules
				190-405	69.90	69.99	Loss of one ligand molecule
				405-575	20.36	15.08	Remaining residue corresponds to CuO
2	[Co.L.X <sub>3</sub> ]	385.94	5.99	0-170	13.99	13.99	Loss of three water molecules
				170-475	70.74	70.50	Loss of one ligand molecule
				475-590	19.15	15.50	Remaining residue corresponds to CoO
3	[Mn.L.X <sub>3</sub> ]	381.94	2.25	0-170	14.13	14.22	Loss of three water molecules
				170-470	71.47	71.50	Loss of one ligand molecule
				470-590	22.79	18.31	Remaining residue corresponds to MnO
4	[Zn.L.X]2X	392.38	2.28	0-170	13.78	13.99	Loss of three water molecules
				170-560	69.64	69.499	Loss of one ligand molecule
				560-660	20.64	15.99	Remaining residue corresponds to ZnO

### Cu(II) Complex

The magnetic moment of planar chelates are generally lower than that of octahedral complexes. The  $\mu_{\text{eff}}$  value of Cu(II) complex is very much in agreement with theoretical value suggesting no metal to metal interactions. In view of the above facts on copper Schiff base complexes, square planar geometry is assigned.

### Mn(II) Complex

A little lower value (5.87 B.M.) of the magnetic moment of Mn(II) complex than the theoretical value of 5.92 B.M for tetrahedral and octahedral Mn(II) complexes<sup>17</sup> may be due to spin exchange in the solid state or due to the presence of a little Mn(III) species which may have been found due to aerial oxidation<sup>16,18</sup>. Hence, octahedral geometry is suggested for Mn(II) complex.

*Co(II) Complex*

From molecular structure and number of unpaired electrons ( $\mu_{\text{eff}} = 3.89$  B.M) octahedral structure is assigned for Co (II) complex.

*Zn(II) Complex*

It is diamagnetic in nature and from its molecular structure tetrahedral geometry is proposed.

*Thermal Decomposition*

The TGA curves of all the complexes reveal that a plateau corresponding to loss of water molecules is observed between 60-190°C. The loss of water molecules at higher temperatures clearly indicates that water molecules are also involved in coordination. On further heating weight loss is observed approximately between 170-500°C which corresponds to loss of one molecule of the Schiff base. The final product is the respective oxide of the metal formed after 560°C. Mode of decomposition of metal complexes has been given (Table II).

The following structures (inserted on separate sheet) have been assigned for 1:1 metal complexes on the basis of the experimental results obtained from the above studies.

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