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## Synthesis and characterization of complexes of a salicylaldehyde Schiff base derivative with Mn(II), Co(II), Ni(II) and Pb(II)

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### ABSTRACT

A new series of metal complexes with a Schiff base ligand derived from condensation of 1,6-hexamethylene diamine and salicylaldehyde have been synthesized and characterized by elemental analysis, conductivity, thermogravimetric analysis, IR and electronic spectra. These complexes have the formula  $ML$  or  $ML(CH_3OH)_2$  where  $L$  is the Schiff base tetradentate ligand  $N,N'$ -disalicylidenehexamethylenediamine ( $salhmnH_2$ ) that coordinates through  $N_2O_2$ . The studies reveal formation of square or octahedral complexes. These complexes are potentially useful in devising metal probes, catalysis, and as models for some metalloenzymes. © 2008 Trade Science Inc. - INDIA

### INTRODUCTION

Schiff base ligands are considered “privileged ligands”<sup>[1]</sup> because they are easily prepared by condensation between aldehydes and primary amines. These ligands are able to coordinate many different metals and to stabilize them in various oxidation states<sup>[2]</sup>. The Schiff base metal complexes show a large variety of catalytic<sup>[3,4]</sup> and biological activities such as antibacterial<sup>5</sup> and antifungal<sup>[6]</sup>. Furthermore, Schiff bases are utilized as starting material in the synthesis of industrial<sup>[7]</sup> and biological compounds such as  $\beta$ -lactams<sup>[8]</sup>. These compounds have been recently used in construction of poly vinyl chloride powder (PVC)- based membrane selective sensors<sup>[9]</sup>.

For a long time tetradentate Schiff base complexes of transition metal ions have attracted many researchers interest in the field of coordination chemistry<sup>[10-12]</sup>. During exploration of the chemistry of  $salhmnH_2$  we have found that some complexes of  $salhmn$  and  $salophen$  have utilizable properties<sup>[13,14]</sup>. A report on the crystal structure of this ligand appeared during preparation of

this manuscript<sup>[15]</sup>.

The present study deals with the preparation and characterization of complexes of  $salhmn$  with some divalent metal ions, namely Mn(II), Co(II), Ni(II) and Pb(II) due to their potentially useful properties. The solid complexes have been synthesized and studied by elemental analysis, conductivity, thermogravimetric analysis (TG), IR and electronic spectra.

### EXPERIMENTAL

#### 1. Reagents

Salicylaldehyde, hexamethylenediamine, and lead nitrate were obtained from Riedel-de Haen. Reagent grade pure chlorides, nitrates, sulphates, acetates of all cations were purchased from Aldrich and used as received. Commercially available solvents were used as received.

#### 2. Apparatus

The infrared spectra for the materials were recorded on a Perkin-Elmer FT-IR spectrometer using KBr disc

TABLE 1: Physical and chemical data of the complexes made in this study

Sample	C		H		N		M		% yield	m.p.
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	found		
MnL(CH <sub>3</sub> OH) <sub>2</sub>	59.85	59.91	6.84	6.95	6.35	6.30	12.45	12.10	70%	dec..>300°C
CoL	62.99	62.57	5.82	5.90	7.35	7.28	15.45	15.20	55%	dec..> 300°C
NiL(CH <sub>3</sub> OH) <sub>2</sub>	59.35	59.22	6.78	6.87	6.29	6.21	13.18	12.78	40%	dec..> 300°C
PbL	45.36	44.98	4.19	4.28	5.29	5.20	39.12	38.91	85%	dec.at 300°C

TABLE 2 : Infrared and uv-visible spectra of the ligand and the complexes studied

Sample	Infrared (cm <sup>-1</sup> , KBr)				Uv-vis (nm) observed peaks
	v(C=N)	v(M-N)	v(M-O)	v(OH)	
Salhmn	1625	-	-	3430	yellow
Mn complex	1610	445	519	3400	Brown 392, 314, 280
Co complex	1600	437	517	-	green 600(w), 395.4(s), 380(s)
Ni complex	1595	448	514	3410	Pale green 400
Pb complex	1590	448	511	-	Yellow 400

in the range of 4000 to 400cm<sup>-1</sup>.

Uv-vis spectra of methanolic solutions of the complexes were recorded on a Lambda 20 Perkin Elmer spectrophotometer.

Conductivity measurements were made on a PHYWE conductivity meter.

The metal content of the complexes was determined using a Perkin Elmer AAnalyst-100. The complexes were decomposed and digested in conc. sulfuric and/ or nitric acid before determination of the metal ions in their aqueous solutions. Manganese was determined volumetrically by complexometric titration vs. EDTA.

### 3. Synthesis of the Schiff base ligand,

N,N'-disalicylidenehexamethylenediamine (salhmnH<sub>2</sub>)

1,6-hexamethylenediamine 1.16g(10mmol) was dissolved in 30ml of ethanol and added dropwise to a hot solution of 2.44g(20mmol) of salicylaldehyde in 30ml ethanol. The stirred mixture was refluxed for about 1 hour, and left to stand overnight at room temperature. The solid mass was filtered and the product N,N'-disalicylidenehexamethylenediamine (salhmnH<sub>2</sub>) was recrystallized from ethanol and air dried, m.p. 78°C, yield 80%. Anal. calcd. for C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>: C, 74.05; H, 7.46; N,8.63. Found: C, 73.86; H, 7.52; N, 8.71. IR(v, cm<sup>-1</sup>): 3430(OH), 1625(C=N).

### 4. Synthesis of N,N'-disalicylidenehexamethylenediamine metal complexes

To a hot solution of 0.324(1mmol) of salhmnH<sub>2</sub> in

20ml of methanol was added a solution of (1m mol) of the metal salt(chloride or acetate or nitrate) in methanol and the hot mixture was stirred for 2 hours and left to cool. The precipitate that formed was filtered, washed with methanol and left to dry. Elemental analyses of C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>M is given in TABLE 1. The solutions of the complexes in methanol were nonconductive. A partial list of the spectral data of the Schiff-base and the complexes is given in TABLE 2.

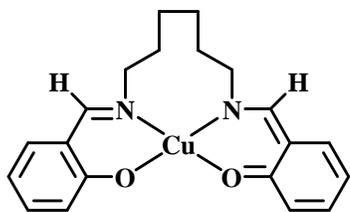
## RESULTS AND DISCUSSION

### 1. Synthesis and characterization

The ligand was prepared recently<sup>[13]</sup> and was found to have strong coordination with Cu(II). The complex Cusalhmn was utilized in devising an ion-selective electrode for copper ions. Synthesis of the metal complexes was essentially the same and involved heating and stirring of stoichiometric amounts of salhmnH<sub>2</sub> and metal salt (chloride, acetate or nitrate) in methanol.

The elemental composition (C, H, N and M) of the complexes, presented in TABLE 1, are relatively close to those calculated based on molecular formulae proposed, which indicates the correctness of these formulae. Elemental analyses indicate that all of the complexes are formed by coordination of 1mol of the metal ion and 1 mol of salhmn. All of the metal chelates in this study are insoluble in water. However, they dissolve to various degrees in methanol and chloroform. Electrical conductivity measurements of the complexes give  $\Lambda_M$  values of 10-20 $\Omega^{-1}\text{cm}^{-1}\text{mol}^{-1}$  and confirm they are non-electrolytes.

The metal content of the complexes was estimated by dissolving and digesting accurately weighted amounts of the complexes in conc. H<sub>2</sub>SO<sub>4</sub> and/ or conc. HNO<sub>3</sub> and properly diluting these solutions to measure their transition metal content by atomic absorption spectrometer. The chemical composition (TABLE 1) confirmed the purity and stoichiometry of the complexes.



**Figure 1:** Structural representation of the compound of N,N'-disalicylidenehexamethylenediamine copper(II) [Cu(salhm)]

A partial list of the IR spectral data of the ligand and the complexes is presented in TABLE 2. Significant changes in some important bands from the ligand were noticed. For example, the ligand exhibits  $\nu(\text{C}=\text{N})$  at  $1625\text{cm}^{-1}$  but in complexes, this band shifts to lower frequency and appears at  $1590\text{--}1610\text{cm}^{-1}$  indicating coordination of azomethine to the metal. Appearance of two to three bands in the low frequency region (between  $410$  and  $527\text{cm}^{-1}$ ) indicates the coordination of phenolic oxygen in addition to azomethine nitrogen. Upon complexation, the broad  $\nu(\text{O}-\text{H})$  band disappears indicating the occurrence of coordination of phenolic oxygen to the metal.

Manganese complex dissolves in methanol but lead complex dissolves slightly. Cobalt complex dissolves slightly in chloroform but nickel complex to a much smaller extent.

Electronic spectral data for the complexes measured in chloroform indicate square planar geometry of the complexes  $\text{Msalhm}$  where  $\text{M} = \text{Co}$  and  $\text{Pb}$ . This is indicated by the similarities in the visible spectra of these chelates with known square-planar complexes containing oxygen-nitrogen donor atoms<sup>3</sup>. The peaks at about  $380\text{--}400\text{nm}$  is probably due to symmetry forbidden ligand to metal charge transfer transition similar to that observed for copper acetate<sup>[16]</sup> at  $370\text{nm}$ .

A very weak and broad absorption near  $600\text{nm}$  is observed when concentrated sample was used to record the spectrum which is due to d-d transition in the complex<sup>[3]</sup>.

The above discussion shows that these complexes involve binding of the metal and the ligand salhm in the ratio 1:1 similar to that observed for  $\text{salhmCu}^{\text{II}}$  which has the structure given in Fig 1. However, manganese and nickel adopt the octahedral structure as supported by elemental analysis and IR spectra.

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