



## **SYNTHESIS AND CHARACTERIZATION OF SOME TETRADENTATE SCHIFF BASE COMPLEXES**

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### **ABSTRACT**

A study on some complexes of Schiff base (MSSB) prepared from salicylaldehyde and mesalamine (5-amino-salicylic acid) is presented here. The metal ions used for the complexation are Co (II), Ni (II), Cu (II), Mn (II), Zn (II) and Cd (II). The characterization of these complexes is attempted using various traditional tools like physical properties, elemental analysis, metal estimation and percentage yield. The modern techniques like magnetic measurements, infrared spectroscopy, UV and visible spectroscopy and thermogravimetric analysis have also been applied to deduce the structure and bonding in these complexes. Using all the above data, an octahedral geometry for the complexes is proposed. While the tetradentate ligand uses its four coordinating atoms (3O's and 1 N) for bonding, the remaining two positions are occupied by aquo ligands.

**Keywords :** Schiff Base, Mesalamine, Thermogravimetric analysis.

### **INTRODUCTION**

The Schiff bases are found to be very important class of ligands due to their wide applications<sup>1, 2</sup>. Because of this, the inorganic chemists try a variety of aldehydes and amines to obtain new Schiff bases<sup>3-5</sup>. The complexes of Schiff bases have remained an all-time delight for the researchers in coordination chemistry. This interest is attributed to their excellent biocidal activity and potential application in medicines and as model systems in biology. Hence, it was thought appropriate to synthesize and characterize metal complexes with a novel Schiff base ligand (MSSB) prepared from salicylaldehyde and mesalamine (5-amino-salicylic acid). The metal ions used for the complexation were Co (II), Ni (II), Cu (II), Mn (II), Zn (II) and Cd (II). The characterization of these complexes using various traditional tools like physical properties, elemental analysis, metal estimation and

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percentage yield coupled with the modern techniques like magnetic measurements, infrared spectroscopy, UV and visible spectroscopy and thermogravimetric analysis has provided significant insight in the structure and bonding in these complexes.

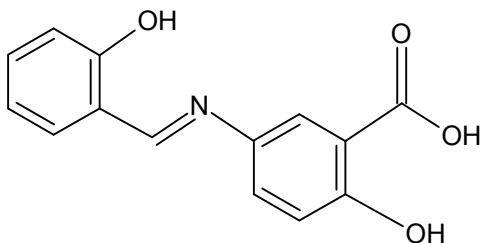
## EXPERIMENTAL

### Materials

The reagents used were of AR grade. The solvents used were purified using standard methods<sup>6</sup>. Laboratory reagent grade salicylaldehyde and mesalamine were purified by standard methods before use.

### Synthesis of Schiff base (MSSB)

An ethanolic solution of mesalamine was mixed with salicylaldehyde in 1 : 1 molar ratio. Salicylaldehyde solution was added to the mesalamine slowly with constant stirring. The reaction was catalyzed by addition of a few drops of acetic acid to the salicylaldehyde solution. Refluxing was carried out in a water bath for an hour and the reaction mixture was cooled to room temperature. The crystals obtained were filtered, washed several times with rectified spirit to remove any unreacted material and finally dried in air. The Schiff base shown (Fig. 1) was soluble in alcohol but freely soluble in dimethylformamide.

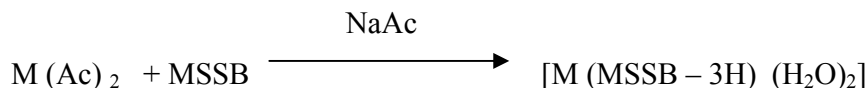


(E)-2-Hydroxy-5-(2-hydroxybenzylideneamino)benzoic acid

**Fig. 1 : Schiff base MSSB**

### Synthesis of metal complexes

All the metal complexes were prepared in a similar way as shown below:



Where M = Co (II), Ni (II), Cu (II), Mn (II), Zn (II) and Cd (II)

0.01 mole of MSSB was dissolved in about 100 mL of absolute ethanol. A solution containing 0.01 mole of acetate of cobalt (II), nickel (II), copper (II), manganese (II), zinc (II) and cadmium (II) in 1 : 1 ethanol- water was added slowly to the ligand solution, which was kept on stirring with a magnetic stirrer for about 1 hour. Sodium acetate was added to maintain pH around 8-9. The complex gradually separated out after 1.5 hours stirring. The product was filtered and washed with ethanol followed by water and dried under vacuum over conc. H<sub>2</sub>SO<sub>4</sub> for 48 hours. All the complexes were insoluble in water, alcohol, carbon tetrachloride, chloroform, benzene and other common organic solvents.

### Measurements

The FT-IR spectra were recorded on Perkin Elmer – Spectrum GXFT-IR spectrophotometer employing KBr pellets of the compounds. The UV visible spectra were recorded on Shimadzu UV visible recording spectrophotometer model UV-160 A. Thermograms were recorded on Perkin Elmer thermogravimetric analyser- TGA-1. The carbon, hydrogen and nitrogen were analyzed with Perkin-Elmer C H N S - O analyzer Model 2400 Series II. The magnetic susceptibility was obtained using Guoy balance.

### Metal Estimation

The metal estimation was done by EDTA titration<sup>7</sup> after decomposing the chelates (~ 0.2 gram) with a mixture of conc. H<sub>2</sub>SO<sub>4</sub> (~2 mL), HNO<sub>3</sub> (~6 mL) and HClO<sub>4</sub> (~6 mL). The results suggest the 1 : 1 mole ratio of metal to ligand.

## RESULTS AND DISCUSSION

### Elemental analysis and metal estimation

The analytical data for the MSSB and its complexes are shown in Table 1.

**Table 1. Analytical data of Schiff base and it's complexes**

System	Formula weight (g)	Colour	Found ( Calc. )				% Yield
			% C	% H	% N	% M	
MSSB	257	Yellow	65.31 (65.36)	4.23 (4.28)	5.41 (5.44)	-	82.97

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System	Formula weight (g)	Colour	Found ( Calc. )				% Yield
			% C	% H	% N	% M	
[Co(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	348.93	Brown	48.02 (48.15)	3.23 (3.44)	3.87 (3.95)	16.79 (16.88)	84.37
[Ni(II) MSSB(H <sub>2</sub> O) <sub>2</sub> ]	348.69	Green	48.05 (48.18)	3.31 (3.44)	3.97 (4.01)	16.75 (16.83)	52.57
[Cu(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	353.55	Brown	47.13 (47.51)	(3.31) (3.35)	3.90 (3.95)	17.89 (17.97)	82.7
[Mn(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	344.93	Yellow	48.55 (48.70)	3.35 (3.49)	4.01 (4.05)	15.88 (15.92)	74.87
[Zn(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	355.38	Yellow	47.11 (47.27)	3.29 (3.37)	3.89 (3.94)	18.34 (18.39)	78.35
[Cd(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	402.4	Yellow	41.62 (41.75)	2.87 (2.98)	3.39 (3.48)	27.81 (27.9)	76.2

The experimental C, H, N percentages are in close agreement with those obtained theoretically. The percentage metal calculated using the predicted structure are also same as those obtained practically using titrimetric methods<sup>7</sup>.

### Infrared spectral data

The sites of bonding of the metal complexes have primarily been obtained from the IR data (Table 2). Both, the Schiff base and complexes show an absorption at 3400 cm<sup>-1</sup> indicating the presence of hydroxyl group or a coordinated water molecule<sup>8,9</sup>. An absorption in the vicinity of 1675 cm<sup>-1</sup> is observed in both ligand as well as complexes, this band is attributed to the C=O stretching vibration<sup>9</sup>. A strong absorption around 1660 cm<sup>-1</sup> indicates the presence of C=N group<sup>3-5</sup>. As expected, these Schiff bases show absorption in the region 1500-1600 cm<sup>-1</sup>, which may be assigned to aromatic ring vibrations<sup>3, 4</sup>. The C-O(H) bending frequency is assigned to the absorption around 1300 cm<sup>-1</sup><sup>10</sup>. The C-H stretching frequency of the aromatic ring is observed around 3050 cm<sup>-1</sup><sup>8,11</sup> while the same for the azomethine linkage is assigned to a vibration of 2950 cm<sup>-1</sup>. The polychelates do have a broad absorption around 3400 cm<sup>-1</sup> as there are water molecules in the chelates. Band around 1300 cm<sup>-1</sup>, which was assigned to C-O(H) bending in ligands, disappears after chelation suggesting a bond formation of metal with phenolic oxygen of the ligand. The >C=N vibration assigned around 1660 cm<sup>-1</sup> shifts to lower wave

number in each chelates, indicating metal – nitrogen bond formation<sup>3-5</sup>. A band around 1580 cm<sup>-1</sup> in all of these chelates may be assigned to bending of coordinated water<sup>8</sup>. In all the metal complexes, medium to strong absorption appears in the range 860 – 870 cm<sup>-1</sup>, which may be assigned to rocking of coordinated water<sup>10</sup>. The wagging mode of coordinated water around 640 – 650 cm<sup>-1</sup> is difficult to assign, as the free ligands also have weak shoulder around 640 – 660 cm<sup>-1</sup>. However in the complexes, the intensity of the peak in the said range increases.

**Table 2. Important IR bands (cm<sup>-1</sup>) of Schiff base and it's complexes**

System	$\nu_{OH}$	$\nu_{C=N}$	$\nu_{C=O}$	$\delta_{C-O(H)}$	$\nu_{Ar-H}$	$\delta_{H_2O}$ (Co-ordinated)
MSSB	3401	1660	1675	1310	3050	-
[Co(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	3405	1632	1678	-	3050	1580
[Ni(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	3402	1635	1671	-	3050	1580
[Cu(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	3404	1634	1673	-	3050	1580
[Mn(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	3403	1631	1677	-	3050	1580
[Zn(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	3405	1633	1672	-	3050	1580
[Cd(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	3402	1662	1679	-	3050	1850

$\nu$  = stretching,  $\delta$  = bending

During complexation, Schiff base loses 3 H atoms.

### Electronic transitions

The d-d transitions in transition metal complexes are of paramount importance to elucidate the geometry around the transition metal ions in their complexes. The d-d transitions for the complexes investigated in this study are shown in Table 3.

In the complex of Co (II), the first transition observed at 9500 cm<sup>-1</sup> may be assigned to (<sup>4</sup>T<sub>1g</sub> (F) → <sup>4</sup>T<sub>2g</sub>) ( $\nu_1$ ). Second transition (<sup>4</sup>T<sub>1g</sub> (F) → <sup>4</sup>A<sub>2g</sub> (P)) ( $\nu_2$ ) is assigned to the absorption observed at 19052 cm<sup>-1</sup>. The third transition is observed at 22210 cm<sup>-1</sup> is assigned to (<sup>4</sup>T<sub>1g</sub> (F) → <sup>4</sup>T<sub>1g</sub> (P)) ( $\nu_3$ ). These transitions indicate octahedral geometry around Co (II) in these complexes<sup>4,5,12</sup>.

The Ni (II) chelate studied in this investigation show three bands at 10500 cm<sup>-1</sup>

( ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ),  $17567\text{ cm}^{-1}$  ( ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ) and  $24596\text{ cm}^{-1}$  ( ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(P)$ ). On the basis of the spectral data, the Ni(II) chelate is proposed to have octahedral geometry<sup>4,5</sup>.

The Cu (II) chelate investigated here show a broad band at  $15001\text{ cm}^{-1}$  ( ${}^2E_g \rightarrow {}^2T_{2g}$ ) and a strong and at  $26666\text{ cm}^{-1}$ , which may be due to charge transfer transition. Considering the composition and magnetic data the Cu (II) complex may be taken to possess octahedral/distorted octahedral structures<sup>4,5,19</sup>.

**Table 3. Magnetic moment and electronic spectral data of MSSB and its complexes**

System	$\mu_{\text{eff}}$ (B. M)	Observed band and transitions ( $\text{cm}^{-1}$ )		
		$\nu_1$	$\nu_2$	$\nu_3$
MSSB		11927	14297	-
[Co(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	4.7	9500 ( ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$ )	19052 ( ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ )	22210 ( ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ )
[Ni(II) MSSB(H <sub>2</sub> O) <sub>2</sub> ]	3.02	10500 ( ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ )	17576 ( ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ )	24596 ( ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(P)$ )
[Cu(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	1.59	15001 ( ${}^2E_g \rightarrow {}^2T_{2g}$ )	26666 CT Band	-
[Mn(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	6.1	14132 ( ${}^6A_{1g} \rightarrow {}^4T_{1g}(4G)$ )	19515 ( ${}^6A_{1g} \rightarrow {}^4T_{2g}(4G)$ )	26451 ( ${}^6A_{1g} \rightarrow {}^4A_{1g}$ , ${}^4E_g(4G)$ )
[Zn(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	-	25641 (Ligand transition band) ( $n \rightarrow \pi^*$ )	33225 (Ligand transition band) ( $n \rightarrow \pi^*$ )	44000 (Ligand transition band) ( $n \rightarrow \pi^*$ )
[Cd(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	-	10573 (Ligand transition band) ( $n \rightarrow \pi^*$ )	12971 (Ligand transition band) ( $n \rightarrow \pi^*$ )	14923 (Ligand transition band) ( $n \rightarrow \pi^*$ )

The Mn (II) chelate investigated in the present study show three bands at  $14132\text{ cm}^{-1}$  ( ${}^6A_{1g} \rightarrow {}^4T_{1g}(4G)$ ),  $19515\text{ cm}^{-1}$  ( ${}^6A_{1g} \rightarrow {}^4T_{2g}(4G)$ ) and  $26451\text{ cm}^{-1}$  ( ${}^6A_{1g} \rightarrow {}^4A_{1g}$ ,  ${}^4E_g(4G)$ ). On the basis of these spectral data, the Mn(II) chelate is proposed to have octahedral geometry<sup>13</sup>.

The Zn (II) chelate investigated here show three bands at  $25641\text{ cm}^{-1}$ ,  $33225\text{ cm}^{-1}$

and  $44000\text{ cm}^{-1}$  while the Cd (II) chelate shows three bands at  $10573\text{ cm}^{-1}$ ,  $12971\text{ cm}^{-1}$  and  $14923\text{ cm}^{-1}$ . All these bands for Zn (II) and Cd (II) chelates are assigned to ( $n \rightarrow \pi^*$ ) transitions. On the basis of these spectral data, the Zn (II) and Cd (II) chelate are also proposed to have octahedral geometry<sup>10</sup>.

### Magnetic measurements

Table 3 shows the effective magnetic moment values for all the complexes under investigation. The compounds of Co (II), Ni (II), Cu (II) and Mn (II) are found to be paramagnetic. The magnetic moment of the complex of Ni (II) investigated here is 3.02 B. M. indicating octahedral Ni (II) chelate<sup>4, 14</sup>. The magnetic moment value of the Co (II) chelate is 4.70 B. M., which makes it difficult to assign the geometry conclusively from magnetic data only, as many times for tetrahedral and octahedral Co (II) complexes<sup>5, 15</sup>, the value of magnetic moment lies in overlapping region. The magnetic moment of Cu (II) complexes is 1.59 B. M. and Mn (II) complexes is 6.10 B. M. These values are consistent with an octahedral geometry<sup>14, 15</sup>. As expected, the Zn (II) and Cd (II) compounds are diamagnetic.

### Thermogravimetric analysis

The thermograms of the ligand and the complexes were recorded at a constant heating rate of  $10^\circ\text{C}/\text{minute}$ . In all the complexes, temperature range for significant decomposition was  $100\text{-}650^\circ\text{C}$ . Each of the complexes exhibited 50 % weight loss in the vicinity of  $600^\circ\text{C}$ . Oxides of the corresponding metals are expected to be the final products of these experiments<sup>5</sup>. While, the ligand lost about 3.5 % weight at  $150^\circ\text{C}$ , the complexes lost almost 13% until the same temperature. This may be attributed to the presence of two coordinated water molecules in the complexes<sup>5</sup>. The theoretical %  $\text{H}_2\text{O}$  in complexes is about 10%. Thus the thermograms of the complexes and the ligand also reaffirm the proposed bonding and structure for the complexes under investigation.

**Table 4. Thermal and kinetic parameters for metal complexes evaluated from TGA.**

System	150 <sup>a</sup>	Decomposition temperature range ( $^\circ\text{C}$ )	T <sub>max</sub> <sup>b</sup>	T <sub>50</sub> <sup>c</sup>
MSSB	3.4	100-650	250	280
[Co(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	13.0	100-550	260	590

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System	150 <sup>a</sup>	Decomposition temperature range (°C)	T <sub>max</sub> <sup>b</sup>	T <sub>50</sub> <sup>c</sup>
[Ni(II) MSSB(H <sub>2</sub> O) <sub>2</sub> ]	12.2	100-700	240	560
[Cu(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	12.1	100-650	244	565
[Mn(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	13.4	100-650	255	555
[Zn(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	12.4	100-600	249	570
[Cd(II)MSSB(H <sub>2</sub> O) <sub>2</sub> ]	13.3	100-600	253	580

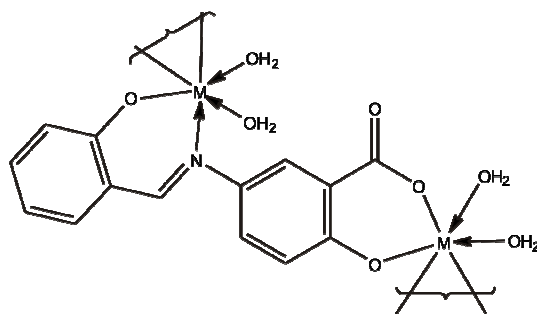
<sup>a</sup> % Weight loss upto 150°C

<sup>b</sup> Temperature for maximum rate of decomposition from TGA.

<sup>c</sup> Temperature for 50% weight loss.

### Geometry and bonding in complexes

The Schiff base (MSSB) has two phenolic OH groups, one carboxylic group and one azomethine nitrogen available for coordination. These account for four positions around the metal. The remaining two positions of an octahedron are expected to be occupied by water molecules. IR spectra also indicate presence of water in complexes. The presence of the coordinated water molecules is reaffirmed from the thermograms of the complexes. The visible spectra (d – d transitions) and magnetic moment values of the complexes indicate octahedral geometry around each metal ion in the complexes. Since the elemental analyses and metal estimation indicate 1 : 1 metal to ligand ratio, the following structure (Fig. 2) may be proposed to satisfy six coordination around each metal ion.



**Fig. 2 : Structure for complexes**

In MSSB, one of the phenolic OH group and carboxylic group are closer to each other while the other phenolic OH group and azomethine nitrogen are closer to each other.



Hence, it is evident that one MSSB may not be able to use all the four coordinating atoms with the same metal ion for the complex formation. Instead of this, dimeric structure appears to be energetically more favourable. Probably, Laser Raman spectra coupled with electron spin resonance spectra will help to assign the structure correctly. The molecular mechanical computations may also provide an insight in deciding the conformations of complexes.

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