



## Synthesis, Characterization and Microbiological evaluation of Co(II), Cu(II), Zn(II) Cr(III) and Fe(III) complexes of 2,4-dimethylaniline salicylaldimine

S.R. KELODE and P. R. MANDLIK

P. G. Department of Chemistry, Shri Shivaji Science College, Amravati (India).

\*Corresponding author: E-mail: sandeep\_kelode@yahoo.co.in

(Received: December 25, 2011; Accepted: February 11, 2012)

### ABSTRACT

Solid complexes involving Co(II), Cu(II), Zn(II) Cr(III) and Fe(III) ions and Schiff base derived from salicylaldehyde and 2,4-dimethylaniline have been synthesized by conventional method. All the complexes have been characterized by elemental analyses, magnetic moment, electronic and infrared spectra and thermogravimetric analysis. An analysis of TG curves of LH and its metal complexes show that the ligand decomposed in two stages while all the complexes decomposed in three stages. Thermal stability order of the complexes was obtained on the basis of their half decomposition temperature. All the compounds have been assessed by screening the compounds against *E. coli*, *S. abong*, *S. aureus*, *P. argineosa*, *B. subtilis*, *A. niger* and *C. albicans*.

### INTRODUCTION

Schiff base derived from salicylaldehyde and aromatic amines containing nitrogen and oxygen donor atoms are structural models of complicated biological systems<sup>1,2</sup>, and their metal complexes have wide applications such as biochemical, analytical, industrial, antimicrobial agents<sup>3,4</sup> and catalysis<sup>5</sup>. Hence, it was thought of interest to carry out systematic investigation on bidentate NO donor Schiff base ligand which can form complexes with metal ions. In the present investigation the Schiff base ligand has been synthesized from salicylaldehyde and 2,4-dimethylaniline. The complexes Co(II), Cu(II), Zn(II) Cr(III) and Fe(III) have been synthesized and characterized by various physicochemical methods

### EXPERIMENTAL

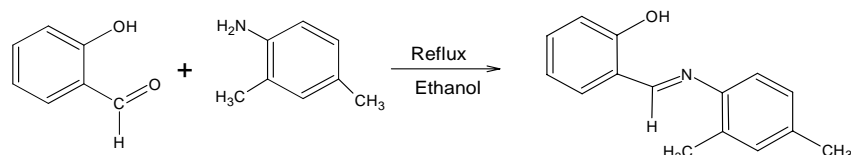
All the chemicals used for the synthesis of the ligands & their metal complexes were chemically pure. Solvents were purified & dried before use by literature method<sup>6</sup>. The ligand used in the present work was not commercially available hence it was synthesized in our laboratory by conventional method. All the metal salts were obtained from SD's fine chemicals.

#### Synthesis 2,4-dimethylanilinesalicylaldimine(LH)

A hot ethanolic solution of salicylaldehyde (0.01 mol in 20 ml ethanol) was added to a hot ethanolic solution of 2,4-dimethyl aniline (0.01 mol in 20 ml ethanol) and the reaction mixture was

refluxed on a water-bath for about 5-6h. On cooling two layers were formed in the solutions which were separated by separating funnel. After two or three days yellow coloured crystals were appeared. The product was filtered under suction and re-crystallized from 50% ethanol.

The ligand was obtained as yellow coloured crystalline solids which were filtered, washed with ethanol, dried at room temperature



washed thoroughly with ethanol and finally with petroether and dried at room temperature. Yield ~ 65 %.

The metal and chloride content of complexes were analyzed by standard methods.<sup>6</sup> The <sup>1</sup>H

NMR spectra of ligand was recorded and obtained from RSIC Chandigarh. IR spectra of the compounds were recorded on Perkin Elmer 842 spectrophotometer in the region 400-4000cm<sup>-1</sup>, Carbon, Hydrogen and Nitrogen analysis were carried out at RSIC, Punjab University, Chandigarh. The molar conductance of the complexes at 10<sup>-3</sup> M

and finally recrystallized from hot ethanol (yield; 70 %, m. p. 170°C).

### Synthesis of the Complexes

A hot ethanolic solution (10 ml) of corresponding metal salt [Co(OAc)<sub>2</sub>.4H<sub>2</sub>O; Cu(OAc)<sub>2</sub>.H<sub>2</sub>O; ZnCl<sub>2</sub>; CrCl<sub>3</sub>.6H<sub>2</sub>O and anhydrous FeCl<sub>3</sub>] was added to a warm ethanolic (10 ml) solution of ligand LH. The reaction mixture was heated under reflux with stirring for about 4-5 h. The isolated coloured solid obtained was filtered, and

dilution in DMF were determined using equipronic digital conductivity meter EQ-660 with a cell constant 1.00 cm<sup>-1</sup> at room temperature. The magnetic moment measurement were made on a Gouy balance at room temperature using [HgCo(SCN)<sub>4</sub>] as the calibrant.

Antimicrobial and antifungal activities of ligands and there complexes were carried out against the bacteria *E. coli*, *S. abong*, *P. aeruginosa*, *S. aureus* and *B. subtilis* and the fungi *A. niger* and *C. albicans* by disc diffusion method.

**Table1: Analytical data, magnetic moment and molar conductance of the compound**

Compounds	Colour	Mol.wt.	Analysis %Found(calc.)				$\mu_{\text{eff}}^{\text{Cl}}$	$\Lambda_{\text{M}}(\Omega^{-1}\text{cm}^2)$	
			M	C	H	N		B.M	mol <sup>-1</sup>
C <sub>15</sub> H <sub>15</sub> NO (LH)	Yellow Crystalline	225	— (80.00)	80.34 (06.66)	06.87 (06.22)	06.41	—	—	—
[CoL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	Pale Yellow	560.93	9.01 (9.18)	64.12 (64.25)	5.25 (5.34)	4.83 (4.99)	—	4.58	12.8
[CuL <sub>2</sub> ] <sub>2</sub> H <sub>2</sub> O	Black	547.54	11.48 (11.60)	65.69 (65.80)	5.35 (5.47)	5.09 (5.15)	—	1.85	6.28
[ZnL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Yellow	549.37	11.74 (11.89)	65.49 (65.52)	5.30 (5.46)	5.00 (5.09)	4.52 (4.61)	—	15.2
[CrL <sub>2</sub> (H <sub>2</sub> O)Cl] H <sub>2</sub> O	Terracota <sup>571.49</sup>	9.02	62.85 (9.09)	5.15 (62.99)	4.75 (5.24)	6.14 (4.89)	3.45 (6.21)	12.7	—
[FeL <sub>2</sub> (H <sub>2</sub> O)Cl] H <sub>2</sub> O	Black	575.35	9.67 (9.70)	62.54 (62.62)	5.10 (5.21)	4.72 (4.86)	6.11 (6.17)	5.46	8.5

## RESULTS AND DISCUSSION

The complexes prepared are coloured solids and air stable and are non-hygroscopic. The elemental analyses of the complexes suggest 1:2 (metal : ligand) stoichiometry.

### **<sup>1</sup>H NMR Spectral data of the ligand**

The coordinating modes of the ligand were confirmed by <sup>1</sup>H NMR spectra (CDCl<sub>3</sub> + DMSO). The observed signals (δ in ppm) are 10.95 (1H, s, phenolic OH); 9.11 (1H, s, benzylidenimin); 7.95, 7.55, 7.35 7.10 (4H, m, phenyl) 7.00, 6.85(3H, m phenyl) and 2.44 ppm (6H, S, Ar-methyl).<sup>7,8</sup>

### **Infrared Spectra of the compounds**

The coordination sites participating in bonding with metal ion have been determined by comparing the infrared spectra of complexes to that with the free ligands. The IR spectra of complexes show peculiar changes as compared to the free ligand.

Important assignments of the ligand and its metal complexes are given in the Table 3.6. The peak observed at 3250 cm<sup>-1</sup> in the spectrum of ligand may be assigned due to phenolic -O-H stretching frequency.<sup>9</sup> The peak observed at 1630 cm<sup>-1</sup> and 1540 cm<sup>-1</sup> may be assigned due to C=N (azomethine) stretching frequency and phenolic C-O stretching frequency respectively.<sup>10</sup> The peak observed at 3020 cm<sup>-1</sup> may be assigned due to Ar-H stretching vibration. The peaks observed in the range 1500 – 1300 cm<sup>-1</sup> were characteristics of aromatic ring stretching frequency. In the spectra of all the complexes, the n(C=N) (Azomethine) shifts to lower frequency by 10-13 cm<sup>-1</sup> indicating the coordination of azomethine nitrogen atom to the metal ions.<sup>11</sup> The n(C-O) band shifts in the complexes to higher frequency by 15 cm<sup>-1</sup> indicating the coordination of phenolic oxygen atom to the metal ion.<sup>12</sup> This reveals that the ligand coordinated with all the metal ions through nitrogen and phenolic oxygen and behaves as monobasic bidentate. The lower frequency region of the spectra also confirms the participation of the phenolic oxygen & azomethine nitrogen by the appearance of band in the region 580-500 cm<sup>-1</sup> & 490-410 cm<sup>-1</sup> assignable to n(M-O) & n(M-N) respectively.<sup>13,14</sup> The coordination of H<sub>2</sub>O in the Co(II), Zn(II), Cr(III) & Fe(III) is indicated by the appearances of band at

3500-3300, 1640-1610 and 850-830 cm<sup>-1</sup> indicate the presence of coordinated water molecule.<sup>15</sup>

### **Magnetic moment and Electronic Spectra**

The cobalt(II) complexes exhibited ligand field bands at about 8955, 18225, 20800 and 32500 cm<sup>-1</sup>. The transition can be attributed to <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>2g</sub>(F)(n<sub>1</sub>), <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>A<sub>2g</sub>(F)(n<sub>2</sub>) and <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(P)(n<sub>3</sub>), whereas the fourth band may be assigned to CT band. The ligand field parameter like Dq (917.0, 877.5 cm<sup>-1</sup>) B(809.3, 705.1 cm<sup>-1</sup>) n<sub>2</sub>/n<sub>1</sub> (2.02, 2.0) B<sub>15</sub>, (0.83, 0.81) and Q(20.48, 23.45) suggest an octahedral geometry.<sup>16</sup> The electronic spectrum of copper(II) complex shows a broad band at 15307 & 15384 cm<sup>-1</sup> in solution and solid state respectively, which assigned to <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>A<sub>1g</sub>, <sup>2</sup>B<sub>2g</sub> → <sup>2</sup>E<sub>g</sub>, in a square-planar geometry with CuO<sub>2</sub>N<sub>2</sub> chromophore.<sup>17</sup> The electronic spectra of Cr(III) complex shows bands at

16051 cm<sup>-1</sup>(n<sub>1</sub>) corresponds to <sup>4</sup>A<sub>2g</sub>(F) → <sup>4</sup>T<sub>2g</sub>(F) transition, 21276 cm<sup>-1</sup>(v<sub>2</sub>) corresponds to <sup>4</sup>T<sub>2g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(F) transition and 25706 cm<sup>-1</sup>(v<sub>3</sub>) corresponds to <sup>4</sup>A<sub>2g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(P) transition.<sup>18</sup> The electronic spectra of Fe(III) complexes showed three bands at 14930, 25590, and 30150 cm<sup>-1</sup> which may be assigned to <sup>6</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>1g</sub>(G), <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>2g</sub> and charge transfer transition respectively suggesting an octahedral geometry.<sup>19</sup> The Zn(II) complexes are found to be diamagnetic in nature. The octahedral geometry has been suggested on the basis of analytical and IR data.

The magnetic moments of the complexes were measured at room temperature. The magnetic moments of Co(II) complex is 4.58 B.M. suggest the presence of three unpaired electrons. The observed values for the Cu(II) complex is 1.85 B.M. in corresponding to one unpaired electron. The Cr(III) complex has a magnetic moment of 3.45 B.M., indicating the presence of three unpaired electrons, and that of Fe(III) complex, 5.46 B.M. towards the high-spin octahedral configuration of Fe(III) ion. The Zn(II) complex is diamagnetic as expected.

### **Thermogravimetric Analysis**

Thermogravimetric analysis have been carried out to estimate the contribution of the weight losses during ignition and for determination of lattice and coordinated water molecules present in the

complexes and to know their decomposition pattern. The perusal of thermograms of ligand and its metal complexes indicates that the ligand decomposes in two steps while all the complexes in three stages. All the complexes are stable upto 60-70°C. Elimination of one water molecule from Co(II), Cr(III), & Fe(III) complexes up to 120°C and two water molecule from Cu(II) & Zr(IV), complexes up to 140°C

have been observed. The % weight loss (observed /calculated) are depicted in the Table 2.

The Co(II) & Zn(II) Complexes showed further loss in weight upto 220-240°C corresponding to two coordinated molecule and Cr(III) & Fe(III) complexes exhibited further loss in weight in the above temperature range correspondent to one

**Table 2: Percentage weight loss**

Complexes	% Weight loss upto 140°C		% Weight loss upto 220°C	
	Observed	Calculated	Observed	Calculated
Co(II)	3.30	3.20	6.56	3.20
Cu(II)	6.65	6.58	—	—
Zn(II)	—	—	6.60	6.55
Cr(III)	3.20	3.15	3.28	3.15
Fe(III)	3.18	3.13	3.26	3.13

**Table 3: Half decomposition temperature and kinetic parameters of the compound**

Complexes	Half Decomposition Temperature(°C)	Activation energy kJmol <sup>-1</sup>			ZS <sup>-1</sup>	ΔSJK <sup>-1</sup> mol <sup>-1</sup>	ΔFkJ mol <sup>-1</sup>
		FC-Method	HM-Method	Broido-Method			
LH	300	3.88	5.55	4.44	88.85	212.48	118.86
Co(II)	420	6.51	9.30	8.37	167.49	209.35	154.53
Cu(II)	462	11.28	11.28	10.16	203.31	208.54	170.28
Zn(II)	409	6.35	9.07	9.07	181.50	208.58	152.66
Cr(III)	499	11.28	11.28	10.16	203.31	208.54	170.28
Fe(III)	485	8.82	8.82	9.80	196.11	208.26	158.79

**Table 4. Antimicrobial activity<sup>23</sup>**

Ligand and its Complexes	Zone of inhibition (in mm)						
	<i>B. subtilis</i> (mm)	<i>P. vulgaris</i> (mm)	<i>S. aureus</i> (mm)	<i>E. coli</i> (mm)	<i>P. fluorescen</i> (mm)	<i>A. aerogenes</i> (mm)	<i>B. megatherium</i> (mm)
LH	S <sub>15</sub>	S <sub>7</sub>	R	R	R	R	S <sub>11</sub>
Co-LH	S <sub>11</sub>	S <sub>13</sub>	S <sub>10</sub>	R	S <sub>17</sub>	S <sub>16</sub>	R
Cu-LH	R	S <sub>17</sub>	R	R	R	S <sub>11</sub>	R
Zn-LH	S <sub>13</sub>	R	S <sub>11</sub>	S <sub>14</sub>	R	S <sub>12</sub>	R
Cr-LH	S <sub>13</sub>	R	S <sub>15</sub>	S <sub>9</sub>	R	S <sub>8</sub>	S <sub>9</sub>
Fe-LH	R	S <sub>9</sub>	S <sub>14</sub>	R	R	S <sub>13</sub>	R

S-Sensitive (Bacteriocidal)

R-Resistant (Bacteriostatic)

coordinated water molecule. In the second decomposition step an organic moiety decomposes and complete decomposition of the ligand occurs upto 700°C leaving behind the respective metal oxide. The half decomposition temperature and kinetic parameters of the ligand and its metal complexes are listed in Table 3. The Thermal activation energy was calculated by Freeman-Carroll,<sup>20</sup> Horowitz-metzger<sup>21</sup> and Broido<sup>22</sup> method.

From the half decomposition temperature the relative thermal stability of the compound is to be Cr(III) > Fe(III) > Cu(II) > Co(II) > Zn(II) > LH

#### Antimicrobial activity

The zones of inhibition effect of the Schiff bases ligand and its metal complexes on the growth of various bacteria is summarized in Table 4. The compounds are found to show low bacteriocidal behavior against most of the bacterial culture and are resistance towards the other. In general the

results reveal that the activity of the ligand was found to enhance on complexation with metal.

#### CONCLUSIONS

The Schiff bases ligand and their metal complexes shows more activity towards *A.aerogenes* and least activity towards *P. fluorescen*. The structural changes have marked effect on the sensitivity and sensitivity varies with organisms.

#### ACKNOWLEDGEMENT

The authors wish to thank SAIF Chandigarh, SAIF, IIT Chennai, CDRI Lucknow for recording elemental analyses, IR, NMR and electrical spectral facilities and Microbiology department, Shri Shivaji Science College, Amravati for antimicrobial screening of compounds

#### REFERENCES

1. Neelakantan M A, Jeyakumar T and Muthukumar K, *Spectrochimica Acta Part A*, **71**,628 (2008).
2. Chandra S and Kumar A, *J Saudi Chem. Soc.*, **11**(2), 299 (2007).
3. Nora H and Al-Sha A, *Molecules* **12**, 1080 (2007)
4. Nishant N, Parveen S, Dhyani S and Asma J. *Coord. Chem.*, **62**(7), 1091 (2009)
5. Arun V, Sridevi A, Robinson P P and Yusuff K K M, *Journal of Molecular Catalysis A: Chemical* **304**, 191 (2009).
6. Furniss B.S., Hannaford A. J., Smith P.W. and Tatchell A.R., *Vogel's Textbook of Practical Organic Chem.*, 5th Edition, Longman's London, (1989).
7. Harikumaran M L and Thankamani D, *Indian J Chem.*, **48**(A), 1212 (2009).
8. Temel H and Ilhan S, *Spectrochimica Acta Part A* **69**, 896 (2008).
9. Praveen Kumar A., Reddy P.R. and Reddy V.K., *Indian J.Chem.*, **46A**, 1625 (2007).
10. Warad D.U., Kulkarni V.H., Satish C.D. and Bajgur C.S. *Indian J.Chem.*, **33A**, 320(1994).
11. Chittilappilly P.S and Yusuff K.K.M. *Indian J.Chem.* **47A** , 848(2008).
12. De R.L., Samanta K., Samnta C. and Mukherjee A.K., *Indian J.Chem.*, **38A**, 1010 (1999).
13. Mishra A.P. and Khare M.J. *Indian Chem. Soc.*, **77**, 367 (2000).
14. Jayaramudu M. and Reddy K.H., *Indian J. Chem.*, **38 A**, 1173 (1999).
15. Dey K. Chakraborty K., Bhattacharya P., Bandopadhyay D., Nag S.K.and Bhowmick R., *Indian J. Chem.*, **38A**, 1139 (1999).
16. Mahapatra B.B., Raval M.K., Behera A.K.and Das A.K., *J. Indian Chem. Soc.*, **75**, 84(1998).
17. Dey K. and Chakrabarty K. , *Indian J. Chem.* **39A**, 1140 (2000).
18. Dey Kamalendu and Chakraborty K., *Indian J. Chem.*, **39A**, 1140, (2000).
19. FI- Sonbati A.Z. and Er- Bindary A., *Polish J.Chem.*, **74**, 621(2000).
20. Mallikarjun K., *E. J. Chem.*, **1**(2), 105 (2004).
21. Horowitz H. and Metzger G., *Anal. Chem.*, **35**, 1464 (1963).
22. Broido A., *J. Polym. Sci. Part A2*, 1761 (1964).
23. Baluja S., Solanki A. and Kachhadia N., *Iranian J. Chem. Soc.*, **3**(4), 312 (2006).