

## Short Communication

# Synthesis, Characterization and Antimicrobial Studies of Some Transition Metal Complexes of Schiff Bases

Gupta Y.K.<sup>1\*</sup>, Agarwal S.C.<sup>2</sup>, Madnawat S.P.<sup>3</sup> and Ram Narain<sup>2</sup><sup>1</sup>Department of Chemistry, B.K. Birla Institute of Engineering and Technology, Pilani, Rajasthan, INDIA<sup>2</sup>Department of Chemistry, Agra College, Agra, UP, INDIA<sup>3</sup>Department of Chemistry, R.B.S. College, Agra, UP, INDIAAvailable online at: [www.isca.in](http://www.isca.in)(Received 9<sup>th</sup> February 2012, revised 16<sup>th</sup> February 2012, accepted 18<sup>th</sup> February 2012)

## Abstract

A series of transition metal complexes of Cu(II), Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) with a bi dentate ligand, bis (2-Pyridyl Carboxyl aldehyde) ethylene diamine prepared by the condensation of 2-Pyridyl carboxyl aldehyde and ethylene diamine. The metal complexes has been characterized on the basis of elemental analysis, conductance and magnetic data, infrared, <sup>1</sup>H NMR data. From elemental analysis, the complexes has been found to be 1:2 (metal: ligand). According to this data, we propose an octahedral geometry for metal (II) complexes. The ligand and metal complexes were screened for their physiological activities against *E.coli*, *Staphylococcus aureus*, *Bacillus subtilis* and *Salmonella typhi*.

**Keywords:** Schiff base, metal complexes, antibacterial activity.

## Introduction

The Schiff bases and their metal complexes have more importance recently<sup>1-5</sup> because of their application as biological, biochemical, analytical, antimicrobial, anticancer, antibacterial, antifungal and anti tumor activity. They have been studied as a class of ligands<sup>6-8</sup> and are known to coordinate with metal ions through the azomethine nitrogen atom. The synthesis of transition metal complexes with Schiff base ligands are studied due to sensitivity, selectivity and synthetic flexibility towards metal atoms<sup>9</sup>. They used as catalyst, in medicine like antibiotics and anti-inflammatory agents and in the industry as anticorrosion<sup>10-16</sup>. The work is abundant on physico-chemical properties of various Symmetrical Schiff bases and chelates with their Pyridine, 2, 2'-bipyridine and 1, 10-phenanthroline adducts<sup>17-21</sup>, while comparatively little is known on asymmetric Schiff base transition metal complexes. In this paper we describe the behavior of the bidentate aromatic Schiff base ligands with various transition metal (II) ions.

The spectral properties of the ligand and their complexes have been measured and the results are discussed in order to obtain information on the stereochemistry of the compounds in the solid state. All these compounds with the ligands (figure-1) are new, being reported for the first time and the Schematic representation of metal complexes is shown in (figure-2). The structures of all these complexes have been investigated by using elemental analysis, FTIR, <sup>1</sup>H NMR, UV-VIS, Magnetic susceptibility and conductivity measurements. Antibacterial activities were determined as MICs values using the micro dilution broth method against gram-positive bacteria; staphylococcus aureus and Bacillus subtilis and gram-negative bacteria Salmonella typhi and Escherichia coli.

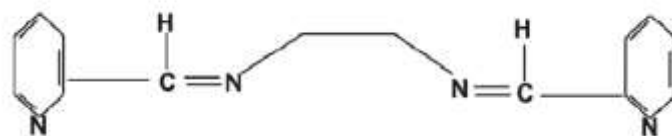


Figure-1  
Bis(2-Pyridyl carboxyl aldehyde) ethylene diamine

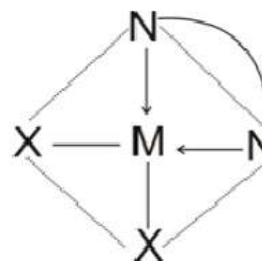


Figure-2  
Schematic representation of metal complex

## Material and Methods

**Physical measurements:** All reagents were used without purification and supplied by Merck. Melting points were determined in a Electro thermal 9200. <sup>1</sup>H NMR spectra in CDCl<sub>3</sub> and DMSO were recorded on NMR spectrophotometer. The IR spectra (Nujol/KBr) were recorded in the range 400- 4000 cm<sup>-1</sup> by KBr pellet using Perkin-Elmer 457 spectrophotometer. Conductance was measured in DMF at room temperature using a Digital conductivity bridge. The UV Visible spectra in CH<sub>3</sub>OH were recorded on a shimadzu UV 1800 spectrophotometer. The metal contents were determined gravimetrically.

**Synthesis of Schiff base ligands:** The Schiff base ligand was prepared by equimolar mixture of aldehyde derivatives (2mmol) and diamine (1mmol) in methanol for 3 hr. TLC Examination suggested the complete conversion of the starting materials to the Schiff base. On cooling, the obtained crystalline precipitates were filtered, washed with ethanol and recrystallized from absolute ethanol and dried. They are colorless, and light yellow crystalline solids, stable at normal condition and soluble in DMSO, DMF; partially soluble in benzene and water.

**Synthesis of transition metal (II) complexes:** All metal complexes were prepared by the following method. A hot methanoic solution of the corresponding metal (II) salt was mixed with a hot methanoic solution. The reaction mixture was refluxed on a water bath for ~ 2 hours. On cooling the reaction mixture at room temperature the colored complexes precipitated out. The complexes were filtered and recrystallized, washed with methanol and dried over P<sub>4</sub>O<sub>10</sub> under vacuum.

**Procedure for antibacterial activity:** The antibacterial activity of the free ligands and their complexes were tested against the gram positive bacteria: *S. aureus*, and *Bacillus subtilis* and gram negative bacteria *E. coli* and *Salmonella typhi*. Minimum inhibitory concentrations (MICs) were determined by the micro dilution broth method following the procedures recommended by the National committee for clinical laboratory standards<sup>22-23</sup>. MICs were defined as the lowest concentrations of compounds which inhibit the growth of micro organisms. All tests were performed in nutrient broth (NB) dissolved in DMSO which lacked anti bacterial activity against any of the test bacteria. The micro plates were incubated at 37° C and read visually after 24 hr for MICs<sup>24</sup>. The results were recorded according to the presence and absence of growth.

## Results and Discussion

The transition metal (II) complexes with bidentate aromatic Schiff base ligands were prepared by stirring stoichiometric en atom of the free ligands<sup>25</sup>.

amounts of metal (II) chloride and bidentate aromatic Schiff base ligand. Analytical data and some Physical properties of the Bidentate Schiff base ligands and their metal complexes are listed in table-1.

The complexes were characterized by the usual methods: elemental analysis, FTIR, H<sup>1</sup>NMR. The complexes are stable in air and light and are soluble in organic solvents such as DMF and DMSO. Elemental analysis ( $\pm 0.5\%$  for C, H, and N) and molar conductance data (Less than  $60 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  in acetone) suggest the complexes to be non-electrolyte with composition of MX<sub>2</sub>-SB<sup>26</sup>.

**Structural Interpretation: Infrared spectra:** The infrared spectra of the complexes taken in the region 400-4000 cm<sup>-1</sup> were compared with those of the free ligands. There are some significant changes between the metal (II) complexes and their free ligands for chelation as expected. The IR bands observed at 1610-1660 cm<sup>-1</sup> of all the ligands and the complexes are assigned to  $\nu$  C=N vibration<sup>27</sup>. The ligand bands around 1610 cm<sup>-1</sup> (C=N) shifted to 1635-1660 cm<sup>-1</sup> in the complexes due to an increase of bond order on co-ordination<sup>28</sup>. The bands at 420-390 and 344-210 cm<sup>-1</sup> in the complexes may be assigned to  $\nu$  M-N and  $\nu$  M-Cl modes<sup>29</sup> respectively. The IR spectra of [ML<sub>2</sub>]Cl<sub>2</sub> complexes, the ligands act as a neutral bidentate through the azomethine and carbonyl groups<sup>30</sup>.

The azomethine band is shifted to lower frequency in all metal complexes, suggesting that this group takes part in coordination. The co-ordination of nitrogen to the metal atom would be expected to reduce the electron density on the azomethine link and thus cause a shift in the C=N band. Moreover, in the spectra of the complexes, a considerable negative shift in  $\nu$  (C=O) are observed indicating a decrease in the stretching force constant of C=O as a consequence of co-ordination through the carbonyl oxyg.

**Table-1**  
**The Physical and analytical data of the ligand and complexes**

Compounds	Color/yield (%)	m.p. (°C)	Calculation (found %)				$\Lambda_m^*$ ( $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ )	$\mu_{\text{eff}}(\text{BM})$
			C	H	N	M		
Schiff base[L]	Yellow/(75)	210°C	32.4 (32.7)	3.2 (3.5)	10.8 (10.9)	-	-	-
[CoL <sub>2</sub> Cl <sub>2</sub> ]	Brown/(72)	230°C	38.2 (38.4)	3.0 (3.2)	9.6 (9.9)	9.03 (9.00)	22	3.88
[NiL <sub>2</sub> Cl <sub>2</sub> ]	Green/(60)	160°C	29.4 (29.6)	2.6 (2.8)	11.4 (11.5)	8.9 (8.8)	24	3.10
[CuL <sub>2</sub> Cl <sub>2</sub> ]	Brown/ (78)	200°C	35.4 (35.9)	2.2 (2.6)	10.4 (10.4)	9.57 (9.55)	28	1.88
[ZnL <sub>2</sub> ]Cl <sub>2</sub>	Yellow/ (80)	180°C	29.4 (29.5)	3.0 (3.1)	14.4 (14.2)	8.5 (8.6)	34	-
[CdL <sub>2</sub> ]Cl <sub>2</sub>	Yellow/ (75)	170°C	32.4 (32.9)	2.2 (2.5)	10.2 (14.4)	15.82 (15.81)	32	-
[HgL <sub>2</sub> ]Cl <sub>2</sub>	White/ (70)	220°C	38.6 (38.7)	2.2 (2.5)	14.8 (14.4)	37.2 (37.5)	36	-

\*in 10<sup>-3</sup> M DMF solution at room temperature

**$^1\text{H}$ NMR spectra:** In NMR spectra of metal (II) complexes we observed a shift of electron density from the ligand to the metal.  $^1\text{H}$ NMR spectra of the complexes show all the expected signals. In all the spectra, a singlet corresponding to a single proton is observed in the range  $\delta$  9.2, 11.4 ppm, which is attributed to the azo-methine proton ( $-\text{HC}=\text{N}$ ) in metal (II) complexes respectively. The  $^1\text{H}$ NMR spectra of the  $[\text{ML}_2]\text{Cl}_2$  complexes show a negative shift of the signal due to the NH group. This signal is observed at  $\delta$  8.0, 11.2 ppm in metal complexes, suggesting that the co-ordination proceeds through the carbonyl oxygen or azo-methine nitrogen groups. The downfield shifts of the methyl group signal at 2.4, 2.2 ppm for the metal (II) complexes, support the co-ordination via the azo-methine nitrogen. The multi signals within the range  $\delta$  8-7.1, 8.3-7.6 ppm are assigned to the aromatic protons of ring in metal (II) complexes respectively.

**Antibacterial activity results of the ligands and complexes:**

The antibacterial activity of bidentated aromatic Schiff base ligands and their metal (II) complexes were screened against microorganism. The microorganisms used in the present investigations include bacteria: Staphylococcus aureus, Bacillus subtilis, salmonella typhi and E.coli. Minimum inhibitory concentrations (MICs) method was used to determine the antibacterial activity of the synthesized compounds.

The diffusion method is very simple, it requires commercial disks, the medium used is Mueller-Hinton agar with 2% of glucose and the diameter of inhibition zone is visually read at 24 hr after incubation at 37°C. The antibacterial activity was estimated on the basis of the size of the inhibition zone formed around the paper disks on the seeded agar plates. Streptomycin was used as a standard. The results are presented in table-2.

**Table-2**

**The Antibacterial activity of the ligand and its complexes**

Compound* C*	E. coli	Salmonella typhi	B. subtilis	S. aureus
Schiff base[L]	++	+	+	+
$[\text{CoL}_2\text{Cl}_2]$	++++	+++	+++	++
$[\text{NiL}_2\text{Cl}_2]$	+++	++	++	++
$[\text{CuL}_2\text{Cl}_2]$	++++	++	++	++
$[\text{ZnL}_2]\text{Cl}_2$	+++	++	++	++
$[\text{CdL}_2]\text{Cl}_2$	++	++	++	++
$[\text{HgL}_2]\text{Cl}_2$	++	++	++	++

C\* = 5 mg/L. Inhibition zone diameter mm (% inhibition) “+, 6-10 (27-45 %); ++10-14 (45-64 %); +++ 14-18 (64-82 %); ++++18-22 % (82-100 %)

Percent inhibition values are relative to the inhibition zone (22 mm) of the most active compound with 100% inhibition. The Schiff base and the complexes exhibited varying degrees of inhibitory effects on the growth of the tested bacteria species. The values reveal that the Schiff base become more effective

when coordinated to the metal ions. The biological activity of the complexes follows the order: Co (II) > Ni (II)  $\approx$  Cu (II)  $\approx$  Zn (II) > Cd (II)  $\approx$  Hg (II). Furthermore, the data show that E. coli was inhibited to a greater degree by the Co (II) and Cu (II) complexes. In conclusion the complexes prepared with the new Schiff base could be used for the treatment of some common diseases caused by E.Coli.

**Conclusion**

Cu(II), Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) complexes of the Schiff base derived from 2-pyridyl carboxylaldehyde and ethylenediamine and complexes are non-electrolytes, Schiff base behaves as a neutral Bidentate ligand and is coordinated to the central metal ion through the azomethine. The metal (II) complexes have octahedral geometry. The biological activity of all the complexes is higher than free Schiff base ligand and follows the order: Co (II) > Ni (II)  $\approx$  Cu (II)  $\approx$  Zn (II) > Cd (II)  $\approx$  Hg (II). This means that metal chelation significantly affects the antimicrobial behavior of the organic ligand.

**References**

- Mishra, Lallan and Sinha Ragini, Mononuclear and dinuclear ruthenium(III)( polypyridyl complexes containing 2, 6-bis(2-benzimidazolyl)-pyridine as co-ligand: Synthesis, spectroscopic and redox activity, *Indian J. Chem., Sect. A*, **29**,1131 (2000)
- Mukhopadhyay, Uday and Ray, Debashis, *Indian J. Chem., Sect. A*, **40**, 228 (2001)
- Krishnankutty K. and Ummathur, Mohammed Basheer, Metal complexes of schiff bases derived from dicinnamoylmethane and aromatic amines , *J. Indian Chem Soc.* **83**, 663 (2006)
- Debey Raj Kumar, *J. Indian Chem. Soc.*,**83**, 1087 (2006)
- Saritha P., Reddy B. Satyanarayan and Jayatyagaraju, Synthesis and structural studies on divalent transition metal complexes of 5-acetyl 2,4-dihydroxy acetophenone semicarbazone, *J. Indian Chem. Soc.*, **83**, 1204 (2006)
- Arora K., Sharma K.P., *Synth. React. Inorg. Met.-Org. Chem.*, **32**, 913 (2003)
- Vigato, P. A., Tamburini, S. *Coord. Chem. Rev.*, **248**, 1717 (2004)
- Katsuki T. *Coord. Chem. Rev.*, **140**, 189 (1995)
- Spinu C. and Kriza A, Co(II), Ni(II) and Cu(II) complexes of bidentate schiff bases, *Acta Chim. Slov.*, **47**, 179 (2000)

10. Sun B. Chen J., Hu J.Y. and Lix, *J Chin Chem. Lett.*, **12(II)**, 1043 (2001)
11. Boghaei D.M. and Mohebi S, Non-symmetrical tetradentate vanadyl schiff base complexes derived from 1,2 phenylene diamine and 1,3-naphthalene diamine as catalysts for the oxidation of cyclohexene *Tetrahedron.*, **58 (26)**, 5357 (2002)
12. Liu J, Wu B, Zhang B and Liu Y, Synthesis and Characterization of Metal Complexes of Cu(II), Ni(II), Zn(II), Co(II), Mn(II) and Cd(II) with Tetradentate Schiff Bases *Turk. J. Chem.*, **30**, 41 (2006)
13. Britovsek G J P, Gibson V. V., Mastroianni S, Oakes D C H, Red Shaw C, Solan G. A., White A. J. P. and Williams D. J., Imine versus Amine Donors in Iron-based Ethylene Polymerisation Catalysts , *Eur. J. Inorg. Chem.*, (2), 431 (2001)
14. Budakoti A., Abid M. and Azam A., Synthesis and antiamoebic activity of New 1-N- substituted thiocarbamoyl-3,5-diphenyl—pyrazoline derivatives and their Pd(II) complexes , *Eur. J. Med. Chem.*, **41(I)**, 63 (2006)
15. Jin V.X., Tan S.I. and Ranford J.D., *Inorg. Chim. Acta.*, **358(3)**, 677 (2005)
16. Mehta N.K. and Agarwala V.S., *Int. Corros. Cong. Proc.*, **13 (319)**, 1 (1996)
17. Chohan Z.H., *Synth. React. Inorg. Met. Org. Chem.*, **31(1)**, 1 (2001)
18. Thangadurai T.D. and Natarajan K., *Trans. Met. Chem.*, **26**, 500 (2001)
19. Jejurkar C.R. and Parik H.K., *Asian J. Chem.*, **9(4)**, 624 (1997)
20. Felico R.C., Dasilva G.A., Ceridorio L.F. and Dockal E.R., *Synth. React. Inorg. Met.–Org. Chem.*, **29(2)**, 171 (1999)
21. Osowole A.A., Woods J.A.O. and Odunola O.A., Synthesis and Physico-chemical properties of some Copper(II)  $\pi$ - $\sigma$ -ketoamines and their adducts with 2,2-bipyridyl and 1,10-phenanthroline, *Synth. React. Inorg. Met. Org. Chem.*, **33(2)**, 167 (2003)
22. Perrin D.D., Armarego W.F.F. and Perrin D.R., Purification of laboratory Chemicals, Pergamon Press, Oxford, (1980)
23. Hiari Y.M. Al., Sweileh B. A., Novel synthesis and antimicrobial activity of 3,7-dimethylphenoxathiin nucleus and some related analogs, *Asian J. Chem.* **18**, 2285-2298 (2006)
24. Golebiewski W.M., Wilkowska E., Synthesis and Biological Activity of New Diarylalkenes, *Polish J. Chem.* **74**, 759-766 (2000)
25. Speca A.N., Karayani N.M., Pytlewski L.L., *Inorg. Chim. Acta.*, **9**, 87 (1974)
26. Greary W.L., *Co-ord. Chem. Rev.*, **13**, 47 (1971)
27. Thornback J.R. and Wilkinson G., Schiff-base complexes of ruthenium(II), *J. Chem. Soc., Dalton Trans.* 110 (1978)
28. Bush P.H., Boular J.C., *J. Am. Chem. Soc.*, **8**, 110 (1956)
29. Agarwal R.K., *J. Indian Chem. Soc.*, **65**, 448 (1988)
30. S. Srivastav Anuraag, Pratibha Tripathi, K. Srivastava singh Ajay, K. Nand, Sharma Rajendra, Bioactivity of novel transition metal complexes of N'-(4-methoxy) thiobenzoyl] benzoic acid hydrazide, *Eur. J. Med. Chem.*, **43**, 577 (2008)