



# Synthesis, Characterization and Antimicrobial Study on Ni(II), Cu(II) and Zn(II) Complexes with N,N-di (o-hydroxybenzenoylmethylene) ethylenediamine

<sup>a\*</sup> Ali Mohammed Yimer

*Department of Chemistry, College of Natural Sciences, Arba Minch University, P.O.Box 21, Arba Minch, Ethiopia.*

<sup>a</sup>*E-mail: ali.mohammed@amu.edu.et*

## Abstract:

The Ni(II), Cu(II) and Zn(II) complexes with a tetradentate ligand obtained by condensation of ethylenediamine with 2-(2-hydroxyphenyl)-2-oxoacetaldehyde have been synthesized and characterized by elemental analysis, molar conductance and magnetic susceptibility measurements, IR, UV-Visible and atomic absorption studies. The Ni(II) and Cu(II) complexes possess four coordinate square planar geometry whereas Zn(II) complex possesses tetrahedral structure. Bactericidal and fungicidal activities of the compounds were evaluated in vitro by disc diffusion method.

**Key words:** ethylenediamine, ortho-hydroxyphenylglyoxal, tetradentate ligand, thin-layer chromatography

## 1. Introduction

Ketoanil Schiff's bases with O and N donor binding sites have attracted considerable attention because of their preparative accessibility, potential biological properties [1, 2] applications in industries as dyes [3] and versatile coordination properties leading to formation of stable complexes with transition metal ions in unusual coordination numbers and isomeric structures [4-7]. The multifarious biological including antipathogenic behavior of these metal-Schiff's base complexes is of paramount importance for designing metal-based drugs.

-----  
\* Corresponding author. Tel.: +251910078572; fax: +2510468810279.  
E-mail address: ali.mohammed@amu.edu.et.

In view of mentioned distinguished features of these compounds we report here the synthesis, magnetic, spectral and antimicrobial studies of Ni(II), Cu(II), and Zn(II) complexes with ethylenedianil of ortho-hydroxyphenylglyoxal (or N,N-di(o-hydroxybenzenoylmethylene) ethylenediamine).

## 2. Experimental

The ligand ethylenedianil of ortho-hydroxyphenylglyoxal(L) was synthesized by the condensation of ethylenediamine and ortho-hydroxyphenylglyoxal. The reaction mixture containing ethylenediamine (0.25 mol) and ortho-hydroxyphenylglyoxal (0.5 mol) in ether was stirred at room temperature ( $\sim 20^{\circ}\text{C}$ ). The yellow brawn precipitate obtained was crystallized from acetone and product was finally washed with ether and dried in air.

The complexes of Ni(II) and Zn(II) were synthesized by refluxing their reaction mixtures containing metal chloride (0.01 mol) and ligand (0.01 mol) in acetone/methanol for 1h at  $\sim 75^{\circ}\text{C}$ . Concentrated reaction mixtures on cooling in ice bath yielded solid powders which were washed with cold water and acetone/methanol successively and dried in air. The monoligand Cu(II) complexes precipitated from their reaction mixtures immediately were filtered out, washed with acetone and dried in air. To the filtrate of monoligand Cu(II) complex on further adding the ligand Cu(II)-bis-ligand complex precipitated was filtered out, washed with acetone and dried in air.

The purity of the compounds was tested by TLC on silica gel layers using chloroform, acetone and butanol solvents.

For the bacterial and fungicidal activities, compounds were screened in viro by Disc Diffuion method [8] against animal pathogens, viz. *Escherichia coli*, *Staphylococcus aureus* and *xanthomonas holcicola* (bacteria) and *Aspergillus niger*, *Colletotrichum gloeosporioides* and *Fusarium oxysporm* (fungi).

Melting pints were determined in open glass capillaries with Stuart SMP-10 melting point apparatus and are uncorrected. Microanalyses were performed on a Vario EL-III analyzer. IR spectra were recorded on Shimadzu Prestize-21 FT-IR spectrophotometer in  $4000\text{-}200\text{ cm}^{-1}$  region in KBr medium. The electronic spectra were recorded on SP65 UV-Vis. spectrophotometer in methanol solvent. Magnetic susceptibility was measured at room temperature ( $295^{\circ}\text{C}$ ) on MSB-Auto (Sherwood Scientific Ltd) balance. The molar conductance of complexes was measured in methanol at room temperature on Jenway digital conductivity bridge. Metal contents of the complexes were determined by atomic absorption spectroscopy using BUCK Scientific spectrophotometer.

## 3. Results and Discussion

All the metal complexes are stable in air. Microanalytical data (Table 1) are consistent with the molecular formulae of the compounds. The molar conductance values account for [9] non-electrolytic nature of Ni(II) complex, and 1:2 and 1:1 electrolytic nature of the two Cu(II) and Zn(II) complexes respectively.

In order to identify the binding modes of the ligand in the complexes, IR spectrum of the free ligand was compared with that of complexes. The free ligand displayed  $\nu\text{OH}$  and  $\nu\text{C-O}$  bands at  $3458\text{ cm}^{-1}$  and  $1066$  &  $1129\text{ cm}^{-1}$  of phenolic/enolic groups. In the spectra of the complexes the absence of  $\nu\text{OH}$  band, lowering in frequency of  $\nu\text{C-O}$  bands (ca.  $1045$  & ca.  $1103\text{ cm}^{-1}$ ) and appearance of a new band in  $488\text{-}561\text{ cm}^{-1}$  attributed to  $\nu\text{M-O}$  reveal coordination of deprotonated phenolic/enolic group of the ligand; an additional band appeared in  $453\text{-}473\text{ cm}^{-1}$  region in the spectra of Cu(II) and Zn(II) complexes could be attributed to  $\nu\text{M-O-M}$  vibrations. The azomethine group stretching vibration, displayed in ligand spectrum at  $1613\text{ cm}^{-1}$ , appeared at low value ( $1457\text{-}1538\text{ cm}^{-1}$ ) in complexes indicates coordination of azomethane nitrogen with metals. The appearance of new band in  $465\text{-}489\text{ cm}^{-1}$  range in complex spectra attributed to  $\nu\text{M-N}$  supported the presence of azomethane group in the coordination zone of the metals. The shifting of  $\nu\text{C=O}$  band of ligand ( $1646\text{ cm}^{-1}$ ) on complexation in  $1602.1642\text{ cm}^{-1}$  range is a strong evidence in support of the view regarding coordination of deprotonated enolic group of quinonoid structure of the ligand [1].

A band at  $375\text{ cm}^{-1}$ ,  $303\text{ cm}^{-1}$  and  $247\text{ cm}^{-1}$  in Zn(II) and mono-ligand trinuclear Cu(II) are assigned to  $\nu\text{M-Cl}$  and  $\nu\text{Cu-Cl-Cu}$  vibrations of monodentate and bidentate chloride respectively. [10,11].

Lattice water exhibited symmetric and antisymmetric stretching and bending vibrations in  $3209\text{-}3493\text{ cm}^{-1}$  and  $1601\text{-}1630\text{ cm}^{-1}$  regions respectively, whereas coordinated water displayed wagging ( $\rho_w$ ), twisting ( $\rho_t$ ), rockng ( $\rho_r$ ) vibrations and  $\nu\text{M-OH}_2$  peak in  $832\text{-}1044\text{ cm}^{-1}$  and  $252\text{-}399\text{ cm}^{-1}$  regions respectively of complex spectra.

The lower magnetic moment of Ni(II) complex, 1.25 BM, than spin-only value of spin free  $d^8$  configuration (2.83 BM) indicates the presence of both spin paired and spin free, states in equilibrium in the solid. However spectral bands occurring at  $23529\text{ cm}^{-1}$  and  $28572\text{ cm}^{-1}$  are characteristic of  $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$  and  $^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$  d-d transitions respectively of square planar spin paired geometry [12, 16] of this complex. High frequency bands spreading over  $33898\text{-}45456\text{ cm}^{-1}$  region correspond to charge transfer transitions.

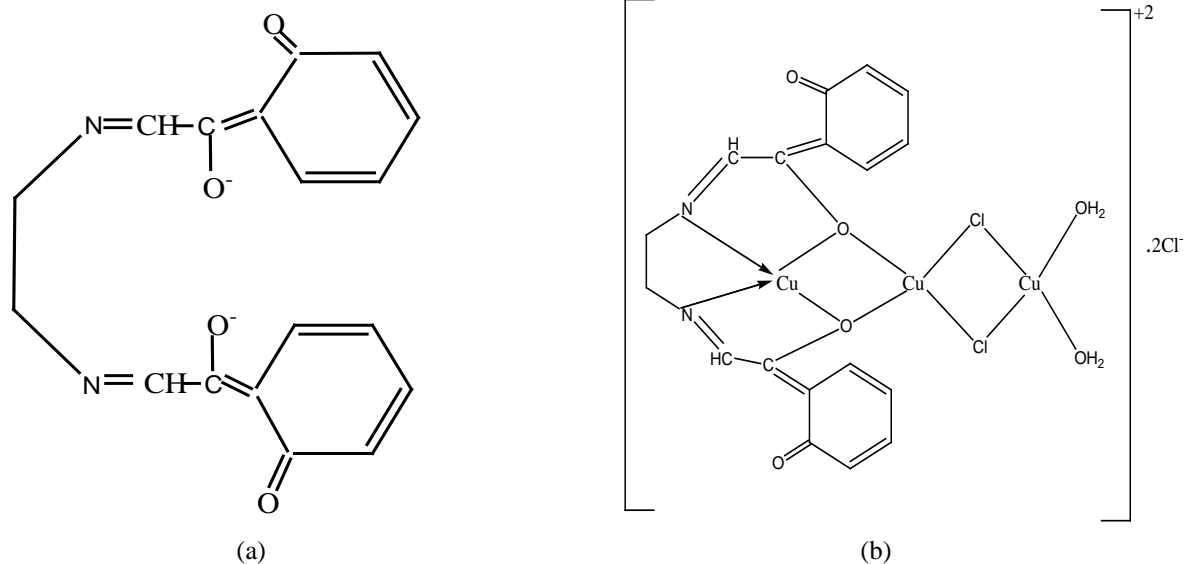
The magnetic moments of both Cu(II) complexes, 1.23 BM and 1.19 BM, are lower than spin-only value of  $d^9$  configuration most probably due to the presence of antiferromagnetic interactions in these trinuclear paramagnetics. Three bands occurring in  $24390\text{-}25000\text{ cm}^{-1}$ ,  $26316\text{-}27027\text{ cm}^{-1}$  and  $28986\text{-}30303\text{ cm}^{-1}$  regions of electronic spectra attributed to  $^2\text{B}_{1g} \rightarrow ^2\text{A}_{1g}$ ,  $^2\text{B}_{1g} \rightarrow ^2\text{B}_{2g}$  and  $^2\text{B}_{1g} \rightarrow ^2\text{E}_g$  transitions respectively of their square planar geometry [17,18]. As a typical example structure of monoligand trinuclear Cu(II) complex is shown in Figure 1.

The perusal of antimicrobial activities of the compounds (Table 2) reveals that the complexes possess greater bactericidal and fungicidal activities against all the microbes in comparison to ligand which is due to their higher lipophilicity. This modified antimicrobial behavior of the complexes may be accounted for on the basis of Chelation Theory and Overtones Concept [18]. Among all the compounds Zn(II) complex which showed highest antimicrobial activity against both test bacteria and antifungal activity against *A. niger* and greater than standard drugs, could be considered a promising drug against these microbes.

**Table 1. Analytical data, magnetic moment and physical properties of compounds**

S.No.	Compounds	Color	Yield (%)	M.P (°C)	Molar Cond. ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ )	$\mu_{\text{eff}}$ (B.M.)	Elemental analysis (%)			
							Calculated. (Found)			
							C	H	N	M
1	$\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_4$	Yellow	41	152±2	-	-	66.67 (67.01)	4.94 (4.62)	8.64 (8.43)	-
2	$[\text{NiL}]\cdot\text{H}_2\text{O}$	Brown yellow	64	245±2	39.7	1.25	54.18 (54.42)	4.01 (4.86)	7.59 (8.06)	14.72 (15.56)
3	$[\text{Cu}_3\text{L}_2]^{+2}\cdot 2\text{Cl}^-\cdot 4\text{H}_2\text{O}$	Black green	58	278±2	159.7	1.23	44.20 (43.55)	3.30 (3.44)	7.59 (8.02)	19.50 (20.27)
4	$[\text{Cu}_3\text{LCl}_2(\text{H}_2\text{O})_2]\cdot 2\text{Cl}^-$	Green brown	42	283±2	154.2	1.19	31.28 (32.13)	2.32 (2.49)	4.05 (4.42)	28.99 (30.10)
5	$[\text{Zn}_2\text{LCl}(\text{H}_2\text{O})]^{+1}\cdot \text{Cl}^-\cdot 4\text{H}_2\text{O}$	Light yellow	82	>300	86.5	Diamag.	35.19 (34.83)	3.58 (3.89)	4.59 (5.06)	14.25 (14.93)

L =  $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_4$



**Figure 1.** Structures of a) quinonoid Ligand and b) Cu(II) monoligand complex

Table 2. Antimicrobial activity data of Compounds

S.N	Compounds	Inhibition Zone (mm)							
		<i>S. aureus</i>		<i>X.holcicola</i>		<i>F.oxysporm</i>		<i>A. niger</i>	
		10μl	20μl	10μl	20μl	10μl	20μl	10μl	20μl
1	Ligand	7	9	-	-	-	-	7	10
2	[NiL].H <sub>2</sub> O	15	18	13	22	15	20	15	22
3	[Cu <sub>3</sub> L <sub>2</sub> ] <sup>+2</sup> .2Cl <sup>-</sup> .4H <sub>2</sub> O	17	19	25	31	13	20	8	25
4	[Cu <sub>3</sub> LCuCl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].2Cl <sup>-</sup>	17	20	22	27	8	12	10	15
5	[Zn <sub>2</sub> LCuCl(H <sub>2</sub> O)] <sup>+</sup> .Cl <sup>-</sup> .4H <sub>2</sub> O	23	25	25	32	12	18	19	27
6	DMSO (Control)	-	-	-	-	-	-	-	-
7	<i>Chlroamphinicol</i>	21	23	25	30	-	-	-	-
8	<i>Bavistin</i>	-	-	-	-	15	20	20	25

#### 4. Conclusion

In the present project a new Schiff's base ligand, obtained by the coordination of ethylenediamine with orthohydroxyphenylglyoxal, has been used in the preparation of Ni(II), Cu(II) and Zn(II) complexes. All the new products were characterized by using spectroscopic (UV-visible, FT-IR and AAS), molecular weight, elemental analysis, molar conductance and magnetic susceptibility measurements. FT-IR studies reveal the coordination of azomethine nitrogen and phenolic oxygen atoms to the metal ions. Magnetic measurements data in conjugation with

electronic spectrum data revealed square planar geometry of Ni(II) and Cu(II) complexes, tetrahedral stereochemistry of diamagnetic Zn(II) complex. Molar conductance values showed 1:2 and 1:1 electrolytic nature of both Cu(II) and Zn(II) complexes respectively whereas Ni(II) complex was non-electrolytic. Elemental and metal analysis results are consistent to the molar formulae of the complexes. Antimicrobial studies conducted on two bacteria and two fungi revealed highest antimicrobial activities by Zn(II) complex against all the microbes used. But Schiff's base ligand showed lowest activity than complexes of the metals.

On the bases of recent reports that Schiff's bases and their complexes are getting enhanced importance in their applications in treatment of diverse infections including HIV and in other areas like in making light emitting diodes, water purification etc. I therefore, propose and recommend with confidence that the present Schiff's base ligand and other Schiff's bases could be synthesized to prepare complexes with transition metals of 3d,4d and 5d series and products should be characterized for their structures and explored for their applications in different fields of interests.

## References

- [1] S. Upadhyay, Ph.D. Thesis, C.C.S. Univ., Meerut, 2006.
- [2] Madhu, Ph.D. Thesis, C.C.S. Univ., Meerut, 2000.
- [3] R.K. Upadhyay, N. Agarwal, Nat. Acad. Sci. Letters, 14, 251 (1991).
- [4] R.K. Upadhyay. (1997). *J. Indian Chem. Soc.*, 75, 535.
- [5] R.K. Upadhyay, A.K. Bajpai and K. Rathore, *Transition Met. Chem.*, 10, 24 (1985).
- [6] R.K. Upadhyay, V. Sharma, V.P. Singh. (1982). *J. Liq. Chromatogr.*, 5, 1141.
- [7] R.K. Upadhyay, A.K. Bajpai, K. Rathore, *Chromatographia*, 18, 618 (1984).
- [8] D.L. Drew, A.L. Barry, R.O. Toole, J.C. Sherris. (1972). *Appl. Environ. Microbiol.*, 24, 240.
- [9] W.J. Greay, *Coordination Chemistry Reviews*, Vol. 7, No.1, 81-122 (1971).
- [10] R.K. Upadhyay, A. Rani, *Acta Chim. Hung.*, 126, 195 (1989).
- [11] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, N.Y., P. 295, 1970.
- [12] A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, the Netherlands, 1978.
- [13] G.H. Anuradha, A.V. Chandrapal. (2011). *E-J. Chem.*, 8, 421.
- [14] P.S. Badami, A.D. Kulkarni, S.A. Patil, *J. Electrochem. Sci.*, 4, 717 (2019).
- [15] A.A. Elamari, A.N. El-Tajoury, S.A. I. Sharif. (2011). *E-J. Chem.*, 8, 43.
- [16] A.A. Del Paggio, D.R. McMillin, *Inorg. Chem.* 22, 691 (1983).
- [17] R.K. Upadhyay, Ph.D. Thesis, Meerut Univ, Meerut, 1972.
- [18] S. Chandra, D. Jain, A.K. Sharma, P. Sharma, *Molecules*, 14, 174 (2009).