*ChemSearch Journal 8(2): 1 – 5, December, 2017*
Publication of Chemical Society of Nigeria, Kano Chapter

Received: 29/06/2017 Accepted: 20/08/2017

# Synthesis and Antimicrobial Studies Of Mn(II), Co(II), Ni(Ii), Zn(II) and Cd(II) Complexes Derived from Schiff Base: 2-Amino-N-(2-(R)-2-Amino-1-Hydroxy-3-Phenylpropylidene)Amino)Ethyl)-3-Phenylpropanimidic

**Muhammad Saleh Salga and Saadatu Hassan DanAli**
[1]Department of Chemistry, Umaru Musa Yaradua University katsina.
[2]Isakaita College of Education Dutsinma, Katsina.
**Email:** muhammad.saleh@umyu.edu.ng

## ABSTRACT

The Schiff base 2-amino-N(2-(R)-2-amino-1-hydroxy-3-phenylpropylidene)amino) ethyl)-3-phenylpropanimidic was obtained by refluxed condensation of ethylenediamine with phenylalanine. The ligand was isolated by filtration, washed with water-ethanol mixture and characterized by FTIR, UV-visible spectroscopy, melting point determination and conductivity test. The compound was used to prepare the complexes of Mn(II), Co(II), Ni(II), Zn(II) and Cd(II). The metal-ligand ratio was determined using the Job's method of continuous variation. From the result of IR spectroscopy, the structure of the proposed ligand showed an absorption of 1558cm$^{-1}$ due to azomethine which was shifted to higher frequency range of 1559-1624cm$^{-1}$ upon complexation with metal ions that coordinated the ligand through both oxygen and nitrogen.

**Keywords**: Antimicrobial, schiff bases, synthesis, tetradentate ligands

## INTRODUCTION

Schiff bases are generally bi, tri, tetra-dentate ligands capable of forming very stable complexes with transition metals Tetradentate Schiff bases with $N_2O_2$ donor atoms are well known to coordinate with various transition metal ions (Costamagna *et al*,. 2000).

The complexes of transition metal(II) which involves derivatives of amino acids and diamine have been of interest due to their pharmacological activities complexes have been increasingly studied because of their interesting structure as well as their antimicrobial and anticancer properties. However, complexes of transition metals with Schiff bases have been reported to show better biological activity than the free ligands (Hamil *et al*. 2009). The synthetic flexibility and selectivity towards the central metal ion of the Schiff bases make them special and attractive (Cesar and Angela 2000). This important feature makes them relevant in the coordination chemistry as they readily form stable complexes ( Salga *et al*, 2011). Literature indicates that the biological activity of Schiff bases relies at the azomethine linkage which is expected to change upon complexation (Revinder, 2014). Being transition metals mostly biometals, they show special properties on reacting with schiff bases. The present study was aimed to synthesize, characterized and study the antimicrobial properties of tetradentate Schiff base derived from the condensation of ethylenediamine with phenylalanine and its complexes.

## EXPERIMENTAL

### Materials and Methods

All the chemicals and solvents used in this research are of Analar grade, purchased from Zayo-Sigma. SMP1 Stuart scientific melting point apparatus, EC215 conductivity meter and Nicolet100 FTIR spectrophotometer was used for IR spectral analysis. All the glass wares are borosilicates and were washed, rinsed and dried in an oven before use.

### Preparation of the Schiff base

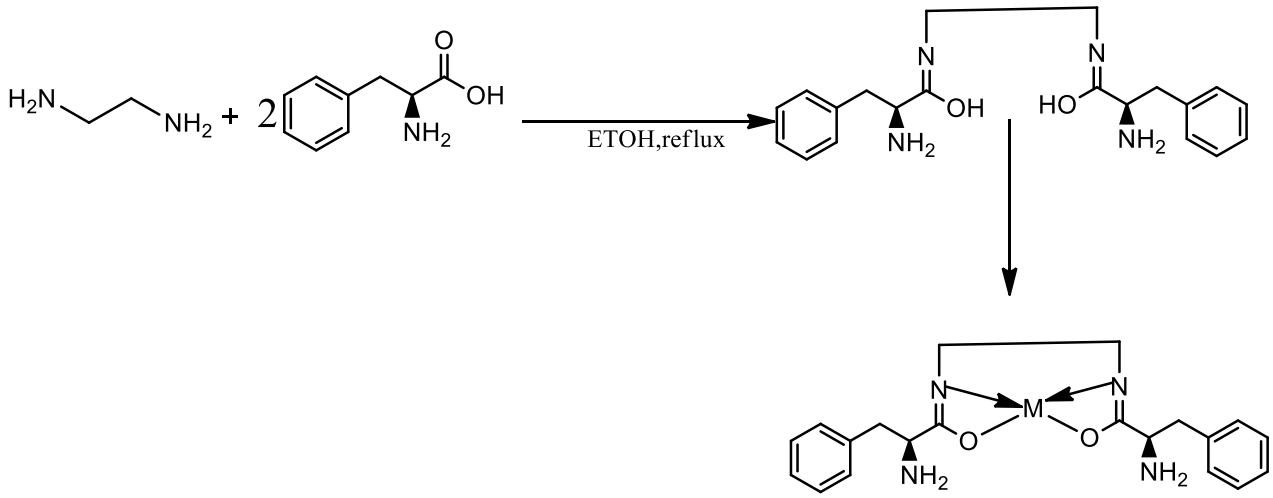
Ethylenediamine (3ml, 0.05mol) was dissolved in ethanol (50ml) and stirred for 10minutes. The solution was added into a hot ethanolic solution of phenylalanine (16.5g, 0.1mol) and the stirring continued for 10minutes.The mixture was then refluxed at 60$^0$C for 3hour. The precipitate formed was filtered, washed with ethanol-water mixture at 70:30 ratio, and dried in desiccator over phosphorous pentoxide (Salga, 2008, Meizhu *et al*, 2012).

### Preparation of metal (II) Schiff base complex

To the methanolic solution (20ml) of the metal salts (0.001mol), a solution of the ligand (0.001mol) taken also in methanol was added with stirring for 5 minutes. The mixture was then

refluxed for 2hrs at $80^0$C. After cooling overnight at room temperature, a precipitate was formed which was filtered, washed with ethanol-water mixture (30:70) and dried over phosphorous pentoxide. (Iffet *et al*., 2004 and Meizhu *et al*., 2012) as shown in the scheme below:

**SCHEME OF THE REACTION**




**Antimicrobial Screening**

The Schiff base and its metal complexes were screened for *in-vitro* antimicrobial activities against bacterial and fungal strains using disc diffusion method. The antibacterial activity studies were carried out using *Staphylococcus aureus* (gram positive) and *Escherichia coli* (gram negative) isolates while the antifungal activity studies were conducted using *Aspergillus niger* and *Aspergillus flavus*. The isolates were cultured on Mueller hinton agar (MHA) and potato dextrose agar (PDA) for the bacterial and fungal strains respectively. The media MHA (39g) and PDA (65g) were dissolved in 1litre of distilled water, the media was autoclaved at 121°C for 15minutes, 20ml of each media was poured in each plate and allowed to solidify before inoculation. The compounds were dissolved in 10ml distilled water using a serial dilution method with a stock of 1g in 1ml, forming different concentrations. 6mm disc was made in the laboratory using Whatman filter paper which was sterilized in an autoclave before inserting into the prepared concentrations of the compounds (Deeni and Husseini, 1991). Ciprofloxacin and ketoconazole were used as reference standard (positive control) while distilled water was used as negative control. The zones of inhibition was observed and recorded.

**RESULTS AND DISCUSSION**

**TABLE 1:** The Physical Properties of the Synthesized Ligand and Metal Complexes

| S/N | MOLECULAR FORMULAR | COLOUR | YIELD (%) | Mol. Wt. | M.P. (°C) | D.T .(°C) | Conductivity ($ohm^{-1}cm^2mole^{-1}$) |
|---|---|---|---|---|---|---|---|
| 1 | $C_{20}H_{26}N_4O_2$ | White | 83 | 354.5 | 180 | - | - |
| 2 | $C_{20}H_{24}MnN_4O_2Cl_2$ | White | 68 | 478.27 | | 296 | 5 |
| 3 | $C_{20}H_{24}CoN_4O_2Cl_2$ | Blue | 74 | 482.27 | | 285 | 4 |
| 4 | $C_{20}H_{24}NiN_4O_2Cl_2$ | Pale green | 73 | 482.03 | | 278 | 5 |
| 5 | $C_{20}H_{24}ZnN_4O_2Cl_2$ | White | 69 | 488.72 | | 249 | 7 |
| 6 | $C_{20}H_{24}CdN_4O_2Cl_2$ | Milky | 78 | 535.75 | | 230 | 9 |

The results of the melting/decomposition temperature of the ligand and its metal complexes were found to be between 180°- 296°C. These sharp values indicate the high purity of the compounds under study. However, the higher decomposition temperature of the complexes when compared with the melting points of the ligands designates high thermal stabilities of the

compounds. Moreover, the colors observed for the ligand and its metal complexes were white, cream, pale-green, cream and blue colors for (Cd(II), Zn(II),) Mn(II), Ni(II), and Co(II) respectively. The color of the ligand may be due to the presence of chromophores or electronic/charge transfer within the structure of the complex (Gao *et al* 2013). The compounds gives significant yields between the ranges 68-83% (Table 1). The conductance measurement values were quite low indicating the non-electrolytic nature of the compounds under study (Table 2).

**TABLE 2:** Solubility test of the ligand and Metal Complexes

| S/N | Compounds | Chloroform | DMSO | Ethanol | Methanol | Water | Acetone | $CCL_4$ |
|---|---|---|---|---|---|---|---|---|
| 1 | Ligand | IS | IS | SH | SH | S | S | IS |
| 2 | Mn(II)complex | IS | IS | SH | SH | S | S | IS |
| 3 | Co(II)complex | IS | IS | SH | SH | S | S | IS |
| 4 | Ni(II)complex | IS | IS | SH | SH | S | S | IS |
| 5 | Zn(II)complex | IS | IS | SH | SH | S | S | IS |
| 6 | Cd(II)complex | IS | IS | SH | SH | S | S | IS |

KEY: S=soluble SS=slightly soluble IS=insoluble SH=soluble when hot

**TABLE 3:** Job's Method (Complexes of the Ligand)

| Mole fraction, | Absorbance(s) (nm) | | | | |
|---|---|---|---|---|---|
| | Mn(II) | Co(II) | Ni(II) | Zn(II) | Cd(II) |
| 0.1 | 0.09 | 0.19 | 0.25 | 0.12 | 0.15 |
| 0.2 | 0.15 | 0.21 | 0.42 | 0.24 | 0.36 |
| 0.3 | 0.23 | 0.39 | 0.55 | 0.36 | 0.41 |
| 0.4 | 0.29 | 0.47 | 0.68 | 0.49 | 0.57 |
| 0.5 | 0.54 | 0.76 | 0.85 | 0.59 | 0.60 |
| 0.6 | 0.48 | 0.41 | 0.59 | 0.42 | 0.51 |
| 0.7 | 0.30 | 0.36 | 0.31 | 0.37 | 0.42 |
| 0.8 | 0.21 | 0.31 | 0.22 | 0.28 | 0.33 |
| 0.9 | 0.10 | 0.22 | 0.13 | 0.14 | 0.24 |

The results of the solubility test shows that the compounds were partially soluble in most organic solvents and soluble only in water, hot ethanol and hot methanol (Table 2). The metal-ligand ratio of the compounds was estimated to be 1:1 as obtained from the method of continuous variation (Job's) method Table (3).

**TABLE 4:** Infrared Absorption Frequencies ($cm^{-1}$) of the ligand and Metal Complexes

| **S/N** | **COMPOUNDS** | **(C=N) ($cm^{-1}$)** | **(M-N) ($cm^{-1}$)** | **(M-O) ($cm^{-1}$)** | **C=C ($cm^{-1}$)** | **C-C ($cm^{-1}$)** |
|---|---|---|---|---|---|---|
| 1 | $C_{20}H_{26}N_4O_2$ | 1558 | - | - | 697 | 1408 |
| 2 | $C_{20}H_{24}MnN_4O_2Cl_2$ | 1555 | 699 | 468 | 604 | 1409 |
| 3 | $C_{20}H_{24}CoN_4O_2Cl_2$ | 1624 | 696 | 470 | 603 | 1410 |
| 4 | $C_{20}H_{24}NiN_4O_2Cl_2$ | 1620 | 625 | 470 | 603 | 1412 |
| 5 | $C_{20}H_{24}ZnN_4O_2Cl_2$ | 1621 | 682 | 469 | 603 | 1409 |
| 6 | $C_{20}H_{24}CdN_4O_2Cl_2$ | 1559 | 681 | 468 | 604 | 1409 |

IR spectrum of the schiff base does not show any band corresponding to primary amine or carbonyl group which indicates the formation of the Schiff base and complete elimination of water molecule due to condensation of the amino group with the carbonyl group of the phenyalanine. The IR spectra of the free Schiff base shows bands in the region of 1558cm$^{-1}$, which can be assigned to (C=N) stretching vibration, a fundamental feature of azomethine group that is confirming the formation of the Schiff base. This band has shifted to various frequencies in the spectra of the metal complexes indicating that the Schiff base has coordinated to the metal ions used. The bands at the wavelengths of 603-648cm$^{-1}$, 1398-1439cm$^{-1}$ and 468-470cm$^{-1}$ can be ascribed to the aromatic carbon (C=C) and (C-C), metal to oxygen (M-O) and ligand to metal charge transfer (M←N) respectively (Table 4). This is in agreement with the literature reported by Aliyu and Adamu, 2009.

**TABLE 5:** Anti bacterial screening Data of the ligand and Metal (II) Complexes

| Compound | *Escherichia coli* | | | *Staphylococcus aureus* | | |
|---|---|---|---|---|---|---|
| | Concentration and Zones of inhibition(mm) | | | Concentration and Zones of inhibition(mm) | | |
| | $10^{-1}$ | $10^{-2}$ | $10^{-3}$ | $10^{-1}$ | $10^{-2}$ | $10^{-3}$ |
| Ligand | 8 | 8 | 7 | 7 | 6 | 6 |
| Mn(II)complex | 22 | 17 | 11 | 9 | 7 | 7 |
| Co(II) complex | 23 | 20 | 13 | 24 | 16 | 15 |
| Ni(II) complex | 19 | 16 | 11 | 16 | 14 | 10 |
| Cd(II) complex | 10 | 10 | 7 | 6 | 6 | 6 |
| Zn(II) complex | 22 | 19 | 11 | 9 | 7 | 7 |
| ciprofloxacin (+) | 35 | - | - | 16 | - | - |
| Water (-) | | | | | | |

**TABLE 6:** Antifungal screening Data of the ligand and Metal (II) Complexes

| Compound | *Aspergillus flavus* | | | *Aspergillus niger* | | |
|---|---|---|---|---|---|---|
| | Conc.and Zone of inhibition(mm) | | | Concentration and Zone of inhibition(mm) | | |
| | $10^{-1}$ | $10^{-2}$ | $10^{-3}$ | $10^{-1}$ | $10^{-2}$ | $10^{-3}$ |
| Ligand | 8 | 7 | 7 | 7 | 6 | 6 |
| Mn(II)complex | 19 | 16 | 15 | 17 | 15 | 12 |
| Co(II) complex | 13 | 10 | 9 | 10 | 8 | 8 |
| Ni(II) complex | 14 | 11 | 10 | 20 | 18 | 15 |
| Cd(II) complex | 26 | 17 | 12 | 23 | 13 | 10 |
| Zn(II) complex | 12 | 11 | 10 | 25 | 19 | 16 |
| Ketoconazole (+) | 32 | - | - | 20 | - | - |
| Water (-) | | | | | | |

The compounds were further assayed for antibacterial and antifungal activities. The metal complexes were found to show more activity than the free ligands. Moreover, Ni(II) and Co(II) complexes demonstrated activity higher than the referenced drug in the antibacterial screening (Table 5), while Cd(II), Zn (II) and Ni(II) complexes illustrated activity higher than the reference drug in the antifungal screening (Table 6). These outstanding activities may be attributed to the high molecular weights of the compounds and possible metal ions toxicities, (Anna-Maj, 1989 and Michalak (2006).

**REFERENCES**

Aliyu H., and Adamu H., (2009), Synthesis and characterization of n-(i-morpholinobenzyl) semicarbazide manganese (II) and iron (II) complexes. *J. Pure and Appl sci.*, 2, 143-148.

Anna-Maj B. P., (1989) Toxicity of heavy metals (Zn, Cu, Cd, Pb) to vascular plants, Water, Air and Soil Poll. J. Bioorg. & Med. Chem. 47(3), 287–319.

Cesar Spinu and Angela Kriza (2000), Co(II), Ni(II) and Cu(II) complexes of bidentate schiff bases. *Acta Chim. Slov.* 47, 179-184.

Costamagna J., Ferraudi G., Matsuhiro B., Campos-Vallette M., Canales J., Villagran M., Vargas J. and Aguirre M. J. (2000) *Coord. Chem. Rev.,* 196-215.

Deeni S., and Husseini M., (1991) In-vitro assay of some plant extracts against Fusariumoxysporum f. sp. Lycopersici causal agent of tomato wilt. *J. Med. Chem.* 30, 67-72.

Gao J., Guoa Y., Wang J., Wang Z., Jin X., Cheng C., Li Y., and Li K., (2013) Synthesis, Characterization and Antimicrobial Studies of Some Vanillin Schiff base Metal (II) Complexes. *J. Chem. & Pharm. Res.* 7, 32-39.

Hamil A. M., Khalifa K. M., AL-Houni A., and El-ajaily M. M., (2009) Synthesis, spectroscopic investigation and antimicrobial activity of schiff base complexes of cobalt (ii) and copper (ii) ions. *Ras. J. Chem.*. 2, 261-266

Iffet S., Elif L., Seza A., Nursen S., and Nazmiye S., (2004), Antimicrobial, activities of N-(2-hydroxy-1-naphthalidene)-amino acid(glycine,alamine,phenylalanine, histidine, tryptophane) Schiff bases and their manganese(III) complexes. *Biometals* 17(2), 115-120.

Meizhu R., Juan W., Yanping S., and Jinyu H., (2012) Catalytic oxidation of alcohols by a novel manganese Schiff base ligand derived from salicylaldehyde and L-Phenylalanine in ionic liquids. *Catal. Commun*, 20(5), 51-53.

Michalak, A., (2006) Phenolic Compounds and Their Antioxidant Activity in Plants Growing under Heavy Metal Stress, Polish. *J. Environ. Stud.* 15(4), 523-530

Muhammad S. S. (2008) Comparative analysis on physical properties of the ligand N, N Bis (salicyl) biphenyl-4,4-diimine and N,N-bis (salicyl) ethylenediamine and their divalent metal complexes of Cr, Co, Mn, Ni and Cu. *Int. J. Phy. Sci.* 3, 37-42

Muhammad S. S., Hapipah M. A., Mahmood A. A., Siddig I. A., Pouya D. H., Hamid A., Hadi A., (2011) Mechanistic Studies of the antiulcerogenic activity and acute toxicity evaluation of dichlorido-Copper (II)-4-(2-5- bromo-benzyllideneamino)ethyl Piperazin-1-ium phenolate complex against ethanol induced gastric injury in rats. *Molecules,* 16, 86-90

Revinder Kumar Ravikant (2014) Review on synthesis and application of Schiff base and its transition metal complexes. *Res., J. Chem. Environ. Sci.* 2, 122-127.