Bajopas Volume 11 Number 1 June, 2018

http://dx.doi.org/10.4314/bajopas.v11i1.6

Bayero Journal of Pure and Applied Sciences, 11(1): 32 - 36
Received: November, 2017
Accepted: April, 2018
ISSN 2006 – 6996

SYNTHESIS, CHARACTERISATIONAND ANTIMICROBIAL ACTIVITIES OF MIXED LIGAND COMPLEXES OF Mn(II), Fe(II) AND Co(II) CONTAINING N,N′-BIS(O-ANISALDEHYDE) P-PHENYLENEDIAMINE (TETRADENTATE SCHIFF BASE) AND GLYCINE

*** Siraj, I. T. and Sule, M.**
Department of Pure and Applied Chemistry, Bayero University Kano, Nigeria
*Corresponding author: itsirajo.chm@buk.edu.ng

ABSTRACT

Complexes of Mn(II), Fe(II) and Co(II) containing N, N′-bis[o-anisaldehyde]p-phenylenediamine tetradentate Schiff base as primary ligand and glycine as secondary bidentate ligand have been synthesized by reflux in 1:1:1 mole ratio and characterized both analytically and spectroscopically. Molar conductance measurement (69.02 to 86.30Ω^{-1}cm^{2}mol^{-1}) of the complexes indicated they are weak electrolyte and magnetic susceptibility measurement shows values in range of 4.53 to 5.59BM indicating their paramagnetism. The infrared data suggested that the Schiff base coordinated via the two nitrogen atoms of the azomethine groups (1628 to 1680 cm^{-1}) and the oxygen atoms of the adjacent methoxy groups (1341 to 1389 cm^{-1}), while glycine coordinated via the nitrogen atom of the amino group (3060-3324 cm^{-1}) and the oxygen atom of the carboxylate anion. Based on the analytical and spectroscopic data the complexes may be assigned an octahedral geometries and molecular formulae of the form [M(L)Gly], where M = Mn, Fe and Co, L =Schiff base and Gly = glycine. The Schiff base and its mixed ligand complexes were screened for antimicrobial activity against Staphylococcus aureus, Escherichia coli, Salmonella typhi, Mucor inducus and Aspergillus fumigatus. The complexes exhibited enhanced antimicrobial activity (10mm to 18mm) at 60 µg/disc as compared to 10mm activity of the uncoordinated Schiff base at the same concentration.

Keywords: Mixed ligand complex; Schiff base, Glycine, p-phenylenediamine, o-anisaldehyde.

INTRODUCTION

Ligands with more than one denticity (bidentate and polydentate) are capable of forming very stable complexes with transition metals. Most of them can act as chelating ligands especially if they bear functional group(s) that areclose enough to the site of condensation in such a way that a 5 or 6-memberring can be formed when reacting with a metal ion. The Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications for example they are noted for their applications as anti-corrosion agent and also in catalysis of many reactions like carbonylation, hydroformylation, oxidation, reduction and epoxidation (Wail and Young, 2016). Schiff bases containing nitrogen and oxygen donor atoms and their complexes have been used as drugs and have shown good biological activities against wide range of bacterial and fungal species (Wail, 2013).

Amino acids are the structural units of proteins. They are essential constituents of all living cells and contain one or more amino and carboxylic groups and have good coordination sites for metal chelation (Naikwade *et al.,* 2013). Therefore, mixed ligand complexes containing amino acid as secondary ligands would be of immense importance as they play significant roles in biological system (Anwar *et al.,* 2013). In continuation of our work on the amino acids (Siraj and Sadiq, 2016), we here report the synthesis of mixed ligand complexes of Mn (II), Fe (II), and Co (II) with a Schiff base derived from anisaldehyde and phenylenediamine incorporating amino acid(glycine) as a secondary ligand. We also report the antimicrobial activities of the Schiff base and the complexes.

MATERIALS AND METHODS

General

All chemicals and solvents used were of analytical grade and were used without further purification. The glass wares used were washed with detergent, rinsed with distilled water and dried in an oven at 110°C before use. All weighing were carried out on an electric Mettle balance model H3OAR. Melting points and decomposition temperatures were determined using GallenKamp melting point apparatus. Molar conductance measurements were carried out using Jenway conductivity meter (4010 model). Magnetic susceptibility measurement was carried out at room temperature using a magnetic susceptibility Gouy balance (MK1 model). FTIR analysis was conducted using Fourier Transform Infrared spectrophotometer, Agilent Technolgies Cary model (650 to 4000cm^{-1}). Biological activity studies were carried out at the Microbiology Laboratory, Bayero University Kano, Nigeria.

Synthesis of the Schiff base (ligand)

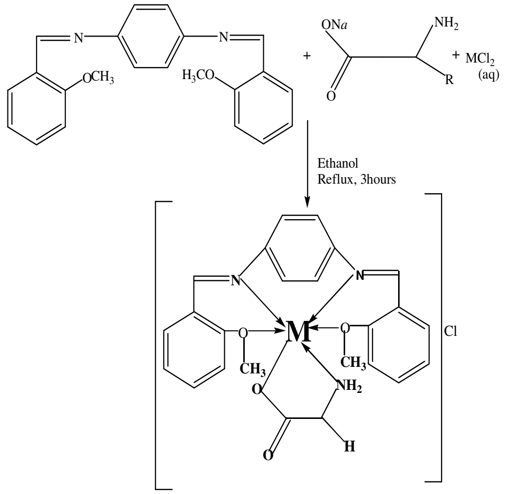
A solution of p-phenylenediamine (0.10814g, 1mmol) and o–anisaldehyde (0.272g, 2mmol) in ethanol (25cm^{3}) was refluxed for 2 hours and the product allowed to cool at room temperature. The crystalline precipitate obtained was filtered and washed with anhydrous diethylether and dried in a desiccator (Ketul *et al.*,2011).

Synthesis of the mixed ligand complexes

Schiff base (0.344g, 1.00 mmol) in 25cm^3 ethanol and metal (II) chloride (1.00 mmol) was mixed with a solution of the amino acid (1.00 mmol) containing sodium hydroxide (0.1M). It was refluxed for 3 hours, concentrated on water bath and the precipitate obtained was filtered and washed with absolute ethanol and then washed again with anhydrous diethylether and dried in a dessicator (Mikkat and Ihsan, 2013).

Metal analysis

The percentage of the metals and chlorine in the complexes was estimated gravimetrically by digestion of the complexes using nitric acid and subsequent precipitation of the metal and chloride ions with appropriate precipitating agents. The precipitates formed were dried and weighed. The masses of the precipitate obtained were used to determine the percentage of the metal in the complexes in accordance with a reported procedure (Vogel, 1989).



M = Mn(II), Fe(II) or Co(II).
Scheme 1: Preparation of mixed lignd complexes.

Antimicrobial activity

The antibacterial and antifungal tests of the Schiff base and mixed ligand complexes were carried out by disc diffusion method. The bacterial species used in the screening were *Staphylococcus aureus, Eschericia coli* and *Salmonella typhi* and the fungal species were *Mucor inducus* and *Aspergillus fumigatus*. Three different concentrations 60µg/disc, 30µg/disc and 15µg/disc of each complex and ligand were prepared using DMSO. Gentimycine and Mancozef were adopted as standard antibiotic for the bacterial and fungal isolates respectively (Yushau and Sadisu, 2011, Hassan *et al.,* 2006).

RESULTS AND DISCUSSION

Physicochemical parameters

The Schiff base was formed by condensation reaction of p-phenylenediamine and o-anisaldehyde. The formed Schiff base was reacted with the metal (II) chloride and glycine to form the mixed ligand complexes (Scheme 1). The physical properties of the formed tetradentate Schiff base and the mixed ligand complexes are shown in Table1.

The Schiff base was found to be light green crystalline solid, which changes to various colours upon complexation. It was found to be air stable, non-hygroscopic and relatively thermally stable with melting point of 135°C. This melting point significantly changes when complexed with the respective metal ions which decomposed at a temperature range of 177 to 186°C.

Table1.Physical properties of the compounds

Compound	Colour	M.P/Decomp.Temp	Yield	Molar conductivity ($\Omega^{-1}cm^2mol^{-1}$)
L	Green	135	83.2	-
[Mn(L)Gly]Cl	Grey	186	76.4	69.02
[Fe(L)Gly]Cl	Brown	184	70.2	86.30
[Co(L)Gly]Cl	Blue	177	72.2	70.50

Key: L = $C_{22}H_{20}N_2O_2$, Gly = glycinato

The molar electrical conductance measurement of the complexes in DMSO at 10^{-3}M concentration was conducted as reported in the literature (Geary, 1971).The results presented in Table 1, suggested that the complexes are weakly electrolytic. The values obtained are in the range of 69.02 to 86.30 $\Omega^{-1}cm^2mol^{-1}$which are within the range reported for 1: 1 electrolytes in a related complexes (Mikkat and Ihsan, 2013, Kailash and Saxena, 2011). These results indicated that the chloride ion from the metal salts acted as a counter ion outside the coordination sphere, indicating that the complexes are cationic in nature, similar conclusion was reported by Surendra *et al.*, (2012).

Table 2. Magnetic properties of the complexes

Compound	$\Psi g(\times10^{-6})g^{-1}$	$\Psi m(mol^{-1})$	μeff (BM)
[Mn(L)Gly]Cl	25.76	0.0131	5.59
[Fe(L)Gly]Cl	19.63	0.0110	4.89
[Co(L)Gly]Cl	16.78	0.0086	4.53

Key: L = $C_{22}H_{20}N_2O_2$, Gly = glycinato

The spin magnetic moment of the complexes was determined by Gouy balance and the values obtained are in the range of 4.53 to 5.59 B.M. (Table2), which are consistent with the number of unpaired electrons observed in the d-orbitals of the respective metal (II) ions in octahedral geometry (Temitayo *et al*., 2012).

The percentage of the metals and chlorine in the complexes was estimated by gravimetric methods (Vogel, 1989) and results presented in Table 3. The values obtained were found to be in good agreement with the theoretical values. This corroborates the proposed molecular formula of the complexes [M(L)Gly]Cl as shown in Scheme 1.

Table 3. Percentage of metals and chlorine in the complexes

Compound	%Metal Found(calculated)	%Cl Found(calculated)
[Mn(L)Gly]Cl	10.94(10.82)	7.02(6.98)
[Fe(L)Gly]Cl	10.40(10.99)	6.92(6.97)
[Co(L)Gly]Cl	11.40(11.51)	7.03(6.93)

Key: L = $C_{22}H_{20}N_2O_2$, Gly = glycinato

Infrared Spectral studies

The comparison of the IR spectra of the tetradentate Schiff base and the complexes suggested the complexation sites of the ligand. The spectrum of the Schiff base showed a sharp peak at 1605 cm^{-1} assigned to azomethine vibrational peak. This peak was observed to shift to higher wave lengths in the range of 1628 to 1680 cm^{-1}in the spectra of the complexes which indicated the participation of the azomethine nitrogen in complex formation, similar results was reported by Kailash and Saxena, (2011).The spectrum of the Schiff base indicated a peak at 1303cm^{-1} (Table 4) which can be attributed to υ(C-O) stretching, also these peaks were observed to shift to higher wave lengths in the spectra of the complexes in the range of 1341 to 1389 cm^{-1} indicating that the oxygen atom of the methoxy group has coordinated to the metal ions. Appearance of new peaks in the range of 3060 to 3324 cm^{-1}which were absent in the Schiff base affirmed the presence of amino group of the glycinato secondary ligand in the complexes (Temitayo *et al*., 2012).

Table 4. spectral data of the compounds

Compound	$v(C=N)cm^{-1}$	$v(NH_2)cm^{-1}$	$v(C\text{-}O)cm^{-1}$
L	1605	-	1303
[Mn(L)Gly]Cl	1628	3324	1382
[Fe(L)Gly]Cl	1631	3132	1341
[Co(L)Gly]Cl	1680	3060	1389

Key: L = $C_{22}H_{20}N_2O_2$, Gly = glycinato

Antimicrobial studies

The antibacterial and antifungal activity of the Schiff base and the complexes at three concentrations (60, 30 and 15 µg/disc) were determined. It was observed that the Schiff base and Mn(II) complex have similar antibacterial activities, they both recorded no activity (6 mm) against *Salmonella typhi* and *Escherichia coli* at all concentrations but active (10 mm) against *Staphylococcus aureus* at 60 µg/disc. However, Fe(II) and Co(II) complexes have shown remarkable activities against the bacterial isolates used at all concentrations. *Salmonella typhi* was found to be resistant to the free ligand and the complexes at all concentration used as no activity (6 mm) was recorded(Table 5). Cobalt(II) complex demonstrated good activity of 20 mm, 15 mm and 13 mm at 60µg/disc, 30µg/disc and 15 µg/disc respectively against *Aspergillus fumigates* similar observation was reported (Ajay *et al*.,(2012), Sanap and Patil(2013).However,all other compounds are without activity against the fungal isolates tested (Table 6).

Table 5:Antibacterial data of the Schiff base and Metal complexes

Compound	**Concentration and zone of inhibition(mm)**								
	60µg/disc			**30µg/disc**			**15µg/disc**		
	S. aureus	***E. coli***	***S. typhi***	***S. aureus***	***E. coli***	***S. typhi***	***S. aureus***	***E. coli***	***S. typhi***
L	10	06	06	06	06	06	06	06	06
[Mn(L)Gly]Cl	10	06	06	06	06	06	06	06	06
[Fe(L)Gly]Cl	15	18	06	13	13	06	10	06	06
[Co(L)Gly]Cl	15	16	06	15	10	06	12	06	06
Gentamycine (10mg/disc)	20	35	30						

Key: L = $C_{22}H_{20}N_2O_2$, Gly = glycinato

Table 6. Antifungal data of the Schiff base and Metal complexes

Compound	**Concentration and zone of inhibition(mm)**					
	60µg/disc		**30µg/disc**		**15µg/disc**	
	M. indicus	***A. Fumigatus***	***M. indicus***	***A. Fumigatus***	***M. indicus***	***A. Fumigatus***
L	06	06	06	06	06	06
[Mn(L)Gly]Cl	06	06	06	06	06	06
[Fe(L)Gly]Cl	06	06	06	06	06	06
[Co(L)Gly]Cl	06	20	06	15	06	13
Mancozef (10mg/disc)	20	30				

Key: L = $C_{22}H_{20}N_2O_2$, Gly = glycinato

In general, the antimicrobial activities of the complexes against some of the isolates were found to be significantly enhanced by coordination, which may be attributed to the chelation factor, however the activity recorded by the complexes are lower than the Gentimycin and Mancozef drug used as standard antibacterial and antifungal reference respectively. The fungal isolates were found to be more resistant to the compounds synthesized than the bacterial isolates.

CONCLUSION

The analytical and spectroscopic data suggested the synthesis of the Schiff base and the mixed ligand complexes. The synthesized ligand has acted as a new tetradentate Schiff base coordinating to the metal via the nitrogen atoms of the two azomethine groups and the oxygen atoms of the methoxy groups. The glycine acted as a secondary ligand coordinating through the nitrogen and oxygen donor atoms. Results of the antimicrobial studies have indicated the Fe(II) and Co(II) complexes have exhibited enhanced activities against the microbes compared to the free ligand and Mn (II), however, only Co(II) complex exhibited antifungal activity. The coordination improves the activity of the ligand and the Fe(II) and Co(II) complexes shows potential of being use as antimicrobial agents.

REFERENCES

Ajay R.P., Kamini J.D., Sambhaji S.R., Vishwanath P. P. and Rama S. L. (2012). Synthesis, Characterization amd Biological activities of Mixed Ligand Co(II) Complexes of Schiff base, 2- Amino – 4 – Nitrophenol – n – Salicylidene with Some Amino Acids. .*Journal of Chemical and Pharmaceutical Research*. 4(2): 1413 – 1425.

Anwar M.D., Saidul-IslamM., Asraful-Alam M.D. and Tupal S. (2013). Synthesis, Physicochemical Studies and Antimicrobial Screening of Metal Complexes of Fe(III) and Au(III) with Amino Acids. *International Journal of Scientific and Technology Research,* 2(7): 2277-8616.

Geary W.J. (1971): The use of Conductivity Measurement in Inorganic Solvents for Characterization of Coordination Compounds. *Coordination Chemistry Reviews,* 7(1): 82-110.

Hassan S.W., Umar R.A., Lawal M., Bilkis L.S. and Muhammad B.Y. (2006). Evaluation of Antifingal Activity of *Ficussycomprus* (moraceae*): Biological and Environmental Science Journal for the Tropics,*3(2): 18-25.

Kailash K. A. and Sexena P.N. (2011) Synthesis and Characterization of New Oxovadium (IV) and Vanadium (III) Complexes with Aldimines on the Bases of Some Physicochemical Studies. *International Journal of Research in Pharmacy and Chemistry*, 1(4): 765-769.

Ketul P.N., Thathor Y.J. and Patel S.G. (2011): Synthesis, Characterization and Biocidal Studies of Some Metal (II) Complexes with Tetradentate Schiff Base and Neutral Bidentate Schiff Base*. Der ChemicaSinica,* 2(1): 143-151.

Mikkat Z.H. and Ihsan A.M (2013): Mixed Ligand Complexes of Gold (III) with some Amino Acids and Dithiocarbamates or Dithiophosphates. *Science Journal of Analytical Chemistry,* 1(2): 21- 27.

Naikwade S.D., Thakur S. and Mazahar F. (2013). Mixed Ligand Complexes of Cobalt (II) with Imipramine and Adenosine in Mixed Solvent System. *International Journal of Pharmtech Research,* 5(4): 974.

Sanap S. V. and Patil R. M. (2013). Synthesis, Characterization and Biological Activity of Chiral Mixed Ligand Ni(II) Complexes. *Research Journal of Pharmaceutical Sciences.* 2(1): 1 – 10.

Siraj I. T**.** and Sadiq I. A. (2016), Synthesis, Characterization and Antimicrobial Activities of a SchiffBase Derived from Phenylalanine and Acetylacetone and its Mn(II), Ni(II) And Cu(II) Complexes. *Chemsearch Journal*: 7(2): 34-39

Surendra C. D., Sivakumar V. and Joseph J. P. (2012). Synthesis and Characterization of Macrocyclic Complexes of Co(II), Ni(II) and Cu(II). *Indian Journal of Chemical Technology.* 19: 351 – 356.

Temitayo O. A., Isaac A. O., Adeleke C. A., Grace O. O., Olayinka O., Ezekiel O. A. and Adebowale O. A. (2012). Synthesis, Characterization and Antimicrobial Activities of Some Metal(II) Amino Acids Complexes. *Advances in Biological Chemistry*, 2: 268 – 273.

Vogel T. (1989): *Practical Inorganic Chemistry,* 4th edition, John Wiley Inc. England*: 133-325.*

Wail A. Z. (2013). Biological Activities of Schiff Bases and their Complexes. *International Journal of Organic Chemistry,* 3:73-95.

Wail A. Z. Young G. K. (2016). OrganometallicComplexes of Schiff bases: Recent Progress in Oxidation Catalysis. *Journal of organometallic Chemistry*822(3) 173-188

Yusha'u M. and Sadisu F. U. (2011): Inhibition Activity of Deuterium Microcarpum Extracts on some Clinical Isolates. *Biological and Environmental Science Journal for the Tropics,* 8(4): 113-117.