http://dx.doi.org/10.4314/bajopas.v11i1.4

Bayero Journal of Pure and Applied Sciences, 11(1): 20 - 24
Received: November, 2017
Accepted: April, 2018
ISSN 2006 – 6996

SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITIES OF SCHIFF BASE DERIVED FROM THIOUREA AND ANISALDEHYDE AND ITS Mn(II), Fe(II) AND Co(II) COMPLEXES

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ABSTRACT
Complexes of Mn(II), Fe(II) and Co(II) with a Schiff base derived from condensation reaction of thiourea and o-anisaldehyde has been synthesized and characterized analytically and spectroscopically. Melting point of the Schiff base was found to be 160°C and the complexes decomposed within a temperature range of 215 to 275°C. Molarconductances of the complexes were found to be within 1.1 to 3.5$\Omega^{-1}cm^2mol^{-1}$ range. Magnetic moment indicated the complexes to be paramagnetic (4.03 to 5.71BM). Infrared spectrum of the Schiff base showed the azomethine peak at 1601cm^{-1} which shifted up to1687cm^{-1} in the complexes. The analytical and spectral studies revealed that all the metal(II) complexes are in 1:3 metal ligand ratio, with the Schiff base acting as tetradentate ligand towards the metal ion via azomethine – N, and methoxy –O and two chlorine atoms were further coordinated to the metal(II) ion. The synthesized ligand and its respective metal (II) complexes were screened for their antibacterial activity against Staphylococcus aureus and Escherichia coli strains and antifungal activity against Aspergillus flavus and Mucorindicus. The results revealed that, the Schiff base and the metal (II) complexes showed significant antibacterial and antifungal activities at high concentration.
Key word: Metal complexes, thiourea, anisaldehyde, characterization, antimicrobial

INTRODUCTION

Schiff base ligand and their complexes continue to attract broad attention in coordination chemistry, due to their facile synthesis, electronic properties and applications (Clieton, 2011; Arulmurugan *et al*., 2010, Wail and Young, 2016). Transition metal complexes, particularly with oxygen and nitrogen donor Schiff bases are of specific interest because of their ability to adapt to many types of configurations including even the odd type, tunable structural ability and their sensitivity to molecular environments (Golcu *et al.,* 2005). Schiff bases can accommodate different metal centers involving various coordination modes in which the homo and hetero metallic complexes with varied stereochemistry have been synthesized successfully (Wail and Young, 2016). They have numerous applications in many fields including antibacterial, antiviral, antifungal agents, homogenous or heterogeneous catalysis and magnetism (Abu-Dief and Mohamed, 2015, Brodowska and Elzbieta, 2014, Wail and Young,2016).

We hereby report the synthesis, characterization and antimicrobial activities of Schiff base derived from thiourea and anisaldehyde and its Mn(II), Fe(II) and Co(II) complexes.

MATERIALS AND METHODS

All reagents 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 Mettler balance model H_3OAR, melting/decomposition temperature were determined using Galenkamp melting point apparatus. Molar conductance measurements were carried out in DMSO using Jenway conductivity meter 4010 model. Jenway 6305 UV-Visible Spectrophotometer was used for UV-absorbance measurements. Magnetic susceptibility measurement was conducted using magnetic susceptibility balance MK1 model, infrared spectral analysis were recorded using Cary 630 Fourier transform infrared (FTIR) Agilent technologies in the range of (650–4000) cm^{-1}. Biological activities were carried out at the Microbiology Department, Bayero University Kano, Nigeria.

Synthesis of the Schiff base

Anisaldehyde (2.723g, 0.02mol) in 25cm^3 ethanol was added to a solution of thiourea (0.07612g, 0.01 mol) also in ethanol (25cm^3) and few drops of 10% sodium hydroxide (NaOH) were added to adjust the pH, the mixture was then refluxed with stirring for two hours. The obtained solution was concentrated using water bath and the concentrate was cooled using ice cubes. The resulting precipitate was collected by filtration and then washed with anhydrous diethyl ether and dried in a desiccator over calcium chloride (Abdlseed and El-ajaily, 2012)

Synthesis of the Schiff base complexes

The synthesized Schiff base (3.12g, 0.01mol) solution in ethanol (25cm^3) was added to 25cm^3 ethanolic solution of the appropriate metal (II) chloride (0.01mol). Few drops of ammonium hydroxide solution were added slowly to adjust the pH and then the mixture was refluxed for 4hrs.

The obtained solution was concentrated using water bath and the concentrate was cooled using ice cubes. The resulting precipitate was collected by filtration and then washed with anhydrous diethyl ether and dried in a desiccator over $CaCl_2$ (Abdlseed and El-ajaily, 2012).

Antibacterial Activity Test

The Schiff base ligand and its complexes were dissolved separately in DMSO to have three different concentrations of 15µg/disc, 30µg/disc and 60µg/disc. The samples were placed on the surface of the inoculated culture media (nutrient agar) and incubated at 37°C for 24hrs. Then *in vitro* antibacterial activity against *Staphylococcus aureus* (gram positive) and *Escherichia coli* (gram negative) of the ligand and its complexes were carried out by disc diffusion method. The diameter of the zone of inhibition produced by the ligands and the complexes were compared with the standard (Yusha'u and Sadisu, 2011).

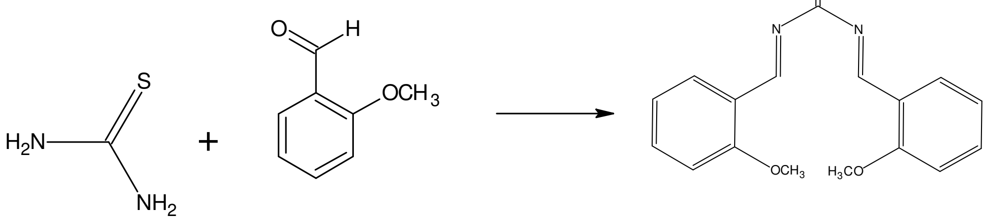
Antifungal Activity Test

The ligand and its complexes were dissolved separately in DMSO for the concentrations of 15µg/disc, 30µg/disc and 60µg/disc. The samples were placed on the surface of the inoculated culture media (potatoes dextrose agar) and incubated at room temperature for 48hrs. The *in vitro* antifungal activity against *Aspergillus flavus* and *Mucor inducus specie* of the ligand and its complexes were carried out by disc diffusion method. The diameter of zone of inhibition produced by the ligand and the complexes were compared with the standard (Hassan *et al.*, 2006).

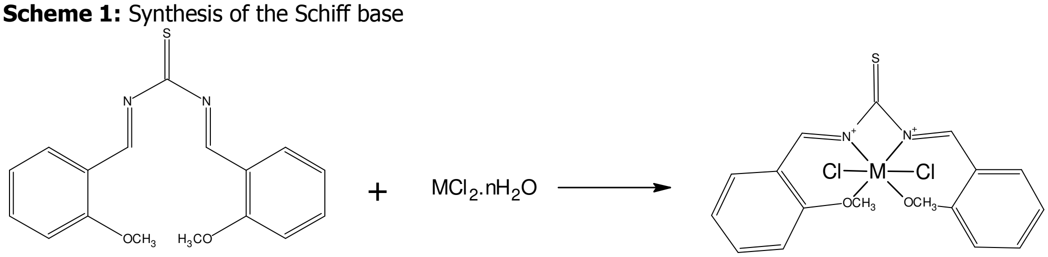
RESULTS AND DISCUSSION

Synthesis and physicochemical studies

The Schiff base was synthesized from thiourea and o-anisaldehyde and its complexes from Mn(II), Fe(II) and Co(II) chlorides (Scheme 1). The observed physical data of the Schiff base and the complexes are shown in Table 1



Scheme 1: Synthesis of the Schiff base



M=Mn(II), Fe(II) and Co(II)

Scheme 2: Synthesis of the metal complexes

The Schiff base was air stable with melting point of 160°Cas shown in Table 1. The higher melting point observed for the Schiff base is an indicative of its high thermal stability and the much higher values recorded by the complexes 215 °C to 275°C showed that, the thermal stability improved considerably upon complexation. The solubility data of the Schiff base and the complexes are presented in Table 2. The complexes are more soluble in the relatively polar solvent methanol, ethanol and acetone but insoluble in the non-polar solvents, hexane and pet ether. DMSO has dielectric constant as such it dissolved all the compounds as expected.

Table 1: Physical Properties of the Schiff base and it's metal(II) complexes

S/N	Compound	% Yield	Colour	Melting Point Temp (C)	Decomposition Temp (°C)
1	$C_{17}H_{16}O_2N_2S$	53.5	Cream	160	–
2	$[MnLCl_2].4HO$	70.7	Milk	–	275
3	$[FeLCl_2].4H_2O$	79.0	Reddish brown	–	230
4	$[CoLCl_2].4H_2O$	58.8	Deep blue	–	215

L = $C_{17}H_{16}O_2N_2S$

Table 2: Solubility Test of the Schiff Base and its Metal (II) Complexes

Solvent	$C_{17}H_{16}O_2N_2S$	$[MnLCl_2].4H_2O$	$[FeLCl_2].4H_2O$	$[CoLCl_2].4H_2O$
DMSO	S	S	S	S
Methanol	S	S	S	S
Ethanol	S	SS	SS	SS
Acetone	S	SS	SS	SS
Water	SS	SS	IS	IS
DMF	SS	SS	IS	SS
Chloroform	IS	IS	IS	IS
n-hexane	IS	IS	IS	IS
Pet-ether	IS	IS	IS	IS
Carbon tetrachloride	IS	IS	IS	IS

Key:$C_{17}H_{16}O_2N_2S$S = Soluble, SS = Slightly Soluble, IS = Insoluble

Molar conductance's of the complexes were determined at room temperature using a procedure reported by Geary, (1971) to establish the charge of the complexes synthesized.The results obtained indicated a low value for all the complexes. The values are within the range of 1.1 to 3.5$\Omega^{-1}cm^{-2}mol^{-1}$(Table 3) which shows that these complexes are neutral and therefore non-electrolytes.The results are in good agreement with the propose formulation of the complexesand also in agreement with similar results and conclusion reported by Misbah*et al.*,(2013) for similar compounds.

Table 3: Molar Conductivity Values of the Metal (II) Complexes

S/N	Compound	Electrical Conductivity ($\Omega^{-1}cm^{-1}$)	Molar Conductivity ($\Omega^{-1}cm^2mol^{-1}$)
1	$[MnLCl_2].4H_2O$	221×10^{-6}	1.1
2	$[FeLCl_2].4H_2O$	691×10^{-6}	3.5
3	$[CoLCl_2].4H_2O$	486×10^{-6}	2.5

L = $C_{17}H_{16}O_2N_2S$

Results of the magnetic susceptibility measurement of the synthesized complexes (Table 4) indicated that they are all paramagnetic in nature. The values obtained 4.03 BM, 4.88 BM and 5.71 BM for Co (II), Fe (II) and Mn (II) complexes respectively are all within the normal range of values observed for octahedral metal (II) complexes as reported in the literature (Gehad*et al.,* 2006). Therefore, suggesting consistency between the results obtained and the propose formula of the compounds. These values showed that all the complexes mentioned above are six coordinated and probably octahedral in shape. The coordination number was found to be completed by the chlorine atom from the metal (II) chloride and this was confirmed by treating the complex with silver ion. Precipitate of AgCl was only observed when the complex was digested with nitric acid this is in agreement with reported literature (Fatima, 2015).

Table 4: Magnetic Susceptibility values of the metal (II) complexes

S/N	Compound	$\Psi_g(g^{-1})$	$\Psi_m(mol^{-1})$	μeff(BM)
1	$[MnLCl_2].4H_2O$	2.6804×10^{-5}	1.0802×10^{-2}	5.71
2	$[FeLCl_2].4H_2O$	1.953×10^{-5}	7.889×10^{-3}	4.88
3	$[CoLCl_2].4H_2O$	1.7465×10^{-5}	7.108×10^{-3}	4.03

L= $C_{17}H_{16}O_2N_2S$

IR Spectral Studies

The IR spectrum of the free Schiff base ligand with that of the complexes were compared to study the bonding mode of the ligand and the metal complexes to note any changes that may occur which may signify complexation have occurred (Table 5). The IR spectrum of the ligand showed a band at 1601cm^{-1}assigned to the azomethine bond (-C=N-) which was absent in the spectra of the starting aldehyde and the amine. The azomethine peak was observed to be shifted to 1687cm^{-1} in the spectra of the complexes suggesting complexation might have occurred. Furthermore, new bands in the regions (657 to 758) cm^{-1} attributed to ν(M–N) stretching vibration were observed. The band at 1289 cm^{-1} assigned to ν(C–O) vibration in the spectrum of the Schiff base has shifted to (1240 to 1246) cm^{-1} in the spectra of the complexes indicating its involvement in coordination through the oxygen atom. These data suggested that the azomethine–nitrogen and methoxy–oxygen were involved in the coordination with the metal (II) ion in the complexes.

A broad band in the region of 3136 to 3347 cm^{-1} assigned to ν(O–H) was observed in the spectra of all the complexes which is a feature indicating the presence of water of hydration. Similar results were reported in the work of Abdlseed and El-ajaily, (2012) on similar compounds.

Table 5: IR Spectral Data of the Schiff Base and its Metal (II) Complexes

S/N	Compound	$\upsilon(C=N)$ cm^{-1}	$\upsilon(M-N)$ cm^{-1}	$\upsilon(C-O)$ cm^{-1}	$\upsilon(OH)$ cm^{-1}
1	$C_{17}H_{16}O_2N_2S$	1601	–	1289	
2	$[MnLCl_2].4H_2O$	1670	670	1240	3267
3	$[FeLCl_2].4H_2O$	1687	657	1246	3136
4	$[CoLCl_2].4H_2O$	1657	758	1246	3347

L= $C_{17}H_{16}O_2N_2S$

Antimicrobial Studies

The antibacterial activity test of the Schiff base and its metal (II) complexes have been determined and the results is presented in Table 6. Generally, the activity increase with increase in concentration of the compounds. The diameter of the inhibition zone was measured and recorded for each treatment.The data revealed that, the Schiff base showed weak activity against the tested organisms at all concentrations which relatively increase upon complexation.The complexes showed a relatively significant activity but lower than the standard antibacterial drug (Ampiclox)used.*Staphylococcus aureus* was found to be susceptible to Mn(II) complex as high activity was recorded. Co (II) complexes was found to be active against both *Staphylococcus aureus* and *Escherichia coli* while Fe(II) showed moderate activity against all the tested organisms. However, *Escherichia coli* was found to be resistant to Mn(II) complex. The increase activity in the complexes may be attributed to the chelation which reduce the polarity of the compound therefore enhancing lipophilicity of the complexes and consequently increasing its antimicrobial activity Chohan*et* al.,(2006).

Table 6: Antibacterial activity of the Schiff base and its Metal (II) Complexes

Test organism	Compound	Zone of Inhibition (mm)/Concentration) (μg/disc) 60	30	15	Control (mm) (60μg/disc)
Staphylococcus aureus	$C_{17}H_{16}O_2N_2S$	11	10	09	Ampiclox 22
	$[MnLCl_2].4H_2O$	16	14	12	
	$[FeLCl_2].4H_2O$	11	08	06	
	$[CoLCl_2].4H_2O$	18	16	14	
Escherichia coli	$C_{17}H_{16}O_2N_2S$	13	10	08	Ampiclox 22
	$[MnLCl_2].4H_2O$	06	06	06	
	$[FeLCl_2].4H_2O$	13	10	09	
	$[CoLCl_2].4H_2O$	25	24	17	

L = $C_{17}H_{16}O_2N_2S$

Table 7: Antifungal activity of the Schiff base and its Metal (II) Complexes

Test organism	Compound	Zone of Inhibition (mm)/Concentration (μg/disc) 60	30	15	Control (mm) (60μg/disc)
Aspergillus flavus	$C_{17}H_{16}O_2N_2S$	06	06	06	Grisofulvin 32
	$[MnLCl_2].4H_2O$	06	06	06	
	$[FeLCl_2].4H_2O$	06	06	06	
	$[CoLCl_2].4H_2O$	13	11	10	
Mucorindicus spp.	$C_{17}H_{16}O_2N_2S$	11	09	06	Grisofulvin 31
	$[MnLCl_2].4H_2O$	06	06	06	
	$[FeLCl_2].4H_2O$	06	06	06	
	$[CoLCl_2].4H_2O$	20	17	14	

L = $C_{17}H_{16}O_2N_2S$

Sensitivity of the fungal isolates to the ligand and its respective metal (II) complexes indicated that Co(II) complex showed high activity against all the two isolates while Mn(II) and Fe(II) complexes showed no activity. The ligand recorded no activity against *Aspergillus aureus* and low activity against *Mucor indicus*, the results are shown in Table 7.

The antimicrobial data revealed that the Schiff base and the complexes exhibited varying degrees of inhibition on the growth of the tested organism. The results further indicated that, the activity of Schiff base is enhanced upon coordination to the metal ions. The Co (II) complex was found to record a well enhance activity against *Escherichia coli,* infact it is even more active than the reference standard antibacterial drug (Ampiclox) used in the test.

CONCLUSION

Schiff base derived from the reaction of o-anisaldehyde and thiourea and its metal complexes with Mn(II), Fe(II) and Co(II) ions have been prepared and investigated. The synthesized Schiff base acted as tetradentate ligand. Infrared, conductivity, magnetic and other studies indicated that the metal (II) ions coordinated to the azomethine-nitrogen and methoxy-oxygen. All the respective metal (II) complexes were evaluated *in vitro* against two bacterial (Gram positive and Gram Negative) and two fungal strains. The antimicrobial data revealed that the activity of the ligand and its respective metal (II) complexes against the tested microorganisms increases with the increase in concentration. Most of the compounds showed low activity compared to the standard antimicrobial drugs,Ampiclox and Grisofulvin used for bacteria and fungi respectively. However, they may still be a potent antimicrobial agents looking at their activity at higher concentration. Interestingly, Co(II) showed higher activity than the standard antimicrobial drug used with respect to *Escherichia coli* with 25mm zone of inhibition as against the Ampiclox at 22mm as shown in Table 6. The results suggested that if further work is done on the Co (II) complex, it might be a better antibacterial agent against *Escherichia coli* compared to Ampiclox.

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