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Synthesis, Characterization, and Antimicrobial Studies of Propionaldehyde Schiff base Metal (II) Complexes

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Abstract Metal complexes of Mn(II), Cu(II) and Ni(II) with Schiff base ligand (HL) derived from condensation of propionaldehyde with ethylenediamine were synthesized in alcoholic medium. The complexes were characterized on the basis of melting point, conductivity, solubility, IR and UV/Visible spectral studies. The *in-vitro* antibacterial activities of the complexes were tested against different strains of bacteria which includes Gram positive (*Staphylococcus aureus, Streptococcus pyogenes*), Gram negative (*Escherichia coli, Salmonella typhi*) and fungus *Candida albicans*. The complexes were formed in moderate yields (30-87%) and they were of various colours and had sharp melting points. The complexes were either soluble or slightly soluble in most of the polar solvents used. The IR spectra revealed that the complexes coordinated through azomethine nitrogen and phenolic oxygen of the ligands. Further conclusive evidence of the coordination of the Schiff bases with the metal ions was shown by the appearance of new bands due to v(M-N) and v(M-O) in the metal complexes. The UV/visible electronic spectra further revealed that the Complexes are non-electrolytes. The results of the anti-microbial study showed that the complexes had more potent activities than their free ligands.

Keywords Schiff base, propionaldehyde, ethylenediamine, synthesis, antimicrobial studies

Introduction

Schiff's base ligands and their metal complexes have been extensively studied over the past few decades [1]. The metal complexes with Schiff bases as ligands play an important role in the development of coordination chemistry [2]. Schiff bases have therefore provided a foundation stone for the building of contemporary coordination chemistry and have found extensive applications in different fields [3]. Schiff bases are derived from aromatic carbonyl compounds and have been widely studied in connection with metallo protein models and asymmetric catalysis, due to versatility of their steric and electronic properties. Schiff base ligands can be able to coordinate different metals with various oxidation states, rendering the use of Schiff base metal complexes for a large variety of useful catalytic transformations [4]. Schiff bases were first reported by Hugo Schiff in 1864 [1, 5-7]. The compounds containing an azomethine group (-CH=N-) are known as imines, anils or Schiff bases [1,7]. They result from the condensation of primary amines with ketones or aldehydes to give imines containing a C=N bond [1,5].



Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields, whose examples include: biological, inorganic and analytical chemistry [8]. Among the organic reagents actually used, Schiff bases possess excellent coordination characteristics, structural similarities with natural biological substances, relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural properties [6].

Propionaldehyde (figure 1) is an aldehyde also known as propanal, propionic aldehyde or methylacetaldehyde, with a boiling point of 49°C and a melting point 81°C. Propionaldehyde is a colourless liquid with a suffocating, fruity-like odour. It is highly flammable and soluble in water. It is used in the manufacture of propionic acid, polyvinyl and other plastics. It is also used in the synthesis of rubber chemicals as a disinfectant and preservative. Propionaldehyde can form explosive peroxides and may polymerize with the addition of acids, bases, amines and oxidants, resulting in a fire or explosion hazard. It decomposes on burning, producing toxic gases and irritating fumes [9].



Figure 1: Propionaldehyde

Materials and Methods

All the chemicals and solvents used were of Analar (AR) grade and were used without further purification. They are propionaldehyde, ethylenediamine, MnCl₂.4H₂O, CuCl₂.2H₂O, NiCl₂.6H₂O, methanol, ethanol, acetone, chloroform, ethyl acetate, benzene, petroleum ether and concentrated sulphuric acid. Melting point of all compounds were determined using Griffin melting point apparatus. The solubility of the complexes was determined in some polar and non-polar solvents such as water, methanol, ethanol, acetone, chloroform, ethyl acetate, benzene and petroleum ether and then warmed over a water bath for complexes that did not dissolve in cold solvents. Molar conductivity was measured by using Metler P163 conductivity meter in methanol solution (10⁻³ M) at 25°C, in the Department of Soil Science, University of Maiduguri. The infrared (IR) spectra were recorded as NaBr disc on Perkin Elmer 1310(IR) at Multi-User Laboratory, Faculty of Science, Abubakar TafawaBalewa University, (ABTU) Bauchi, in the range of (200-4000) cm⁻¹ for the ligand and their complexes. Electronic spectra of all the complexes were measured in methanol solution (10⁻³ M) at 25°C using UV-2550PC Series Shimadzu Spectrophotometer in the wavelength range of 250–800 nm at the National Research Institute for Chemical Technology (NARICT), Federal Ministry of Science and Technology, Zaria, Nigeria.

Preparation of Schiff base ligand (HL)

The Schiff base ligand (HL) was prepared using a standard literature procedure described by [8]. This was done by the condensation of 20ml of propionaldehyde (14.43ml, 0.2mol) with ethylenediamine (6.685ml, 0.1mol) in ethanol (2:1 molar ratio). 2-3 drops of conc. H_2SO_4 was added. The resulting mixture was refluxed for 3-4 hours. On cooling, the solid product obtained was filtered, washed with ethanol and dried in a desiccator over fused calcium chloride (CaCl₂).

Equation for the Reaction

aldehyde + amine \rightarrow HL + H₂O Where HL = Schiff-base



Figure 2: Proposed structure of Schiff base (HL)



Preparation of the Metal(II) Complexes

An ethanolic (20 ml) solution of Schiff base ligand (0.01mol, 2.8g) was added drop wise to 25ml of the metal(II) salts (1.9791g, 0.01mol) of $MnCl_2.4H_2O$, (2.3771 g, 0.01mol) of $NiCl_2.6H_2O$, and (1.7048g, 0.01mol) of $CuCl_2.2H_2O$ in boiling ethanol (78.3^oC). The reactions took place in 2:1 (ligand-metal). The reaction mixture was refluxed for 2 hours, cooled, filtered, washed with ethanol/acetone/ether and the product obtained was dried in a desiccator containing calcium chloride (CaCl₂).

Equation for the Reaction

$$\begin{split} HL + MX_2.nH_2O \rightarrow [ML]X_2+ \quad nH_2O \\ Where \ HL = Schiff \ base, \ M = Mn(II), \ Ni(II) \ and \ Cu(II), \ X = Cl, \ n = 2, \ 4, \ or \ 6 \end{split}$$

Antimicrobial Test

The *in-vitro* antimicrobial properties of the Schiff base ligands and the metal complexes were assayed against different strains of organisms such as Gram positive (*Staphylococcus aureus, Streptococcus pyogenes*), Gram negative (*Escherichia coli, Salmonella typhi*) and fungus (*Candida albicans*) using a standard method described [2,8]. For the detection of the antimicrobial activities, the filter paper disc agar diffusion method was used. A disc of blotting paper was impregnated with a known volume and appropriate concentration of the ligand and the metal complexes, this was placed on a plate of sensitivity testing agar uniformly inoculated with the test organism at 37 °C for 24 hours. The ligand and the complexes diffused from the disc that was related to the sensitivity of the organism. Strains sensitive to the ligand/complexes were inhibited at a distance from the disc whereas resistant strains have smaller zones of inhibition or grow up to edge of the disc. After incubation, the average inhibition zone was measured and recorded.

Table 1: Some physical characteristics for the ligand and their metal(II) complexes						
Compounds	Molecular	Colour	Melting point	Yield	Molar conductivity	
	formula		(° C)	(%)	(scm ² mol ⁻¹)	
	(Molar mass)					
HL	$C_8H_{16}N_2$	Light	196	18	11.00 x 10 ⁻³	
	(140.2)	orange				
$Mn(L^{1}-$	$Mn[(C_8H_{16}N_2)_2]Cl_2$	Light	172	87	12.10 x 10 ⁻³	
L^1) X_2	(406.0)	brown				
, ,					2	
$Cu(L^1-L^1)X_2$	$Cu[(C_8H_{16}N_2)_2]Cl_2$	Light green	176	30	36.00 x 10 ⁻³	
	(414.8)					
$Ni(L^1-L^1)X_2$	$Ni[(C_8H_{16}N_2)_2]Cl_2$	Purple	184	66	13.50 x 10 ⁻³	
	(410.0)					

Results and Discussion

The Schiff base ligand (HL), on interaction with Mn(II), Cu(II) and Ni(II) formed complexes with moderate yields (18-87 %) corresponding to the general formula $M(L^{1}-L^{1})X_{2}$ where M = Mn(II), Cu(II) and Ni(II), L–L deprotonated Schiff base ligand and X= Cl. All the complexes are air stableand have sharp melting points (172-196°C). The sharp melting point indicates that the complexes are probably pure [10]. The molar conductivity of the complexes were within the range of (11.00 x $10^{-3} - 36.00 x 10^{-3} \text{ Scm}^2 \text{mol}^{-1}$). These values indicate the non-electrolytic behaviour of these complexes [1, 11-13]. The solubility of the complexes are either soluble or slightly soluble in all the solvents except petroleum ether and ethyl acetate.



IR Spectra of the Ligand and their Metal(II) Complexes

The selected vibrational frequencies for the Schiff base ligand and its metal complexes are presented in Table 2. The IR spectral data of the free ligand showed a band at 1570 cm⁻¹ which is characteristics of the azomethine nitrogen present in the Schiff base ligand (HL) [14-15]. In all the complexes, the bands for azomethine group underwent a shift to a lower frequencies (1500-1560 cm⁻¹) indicating coordination of azomethine nitrogen with the metal ion [16]. Both the ligand and their metal complexes showed broad bands at 3200 cm⁻¹–3240 cm⁻¹ which is assigned to v(OH) [7]. The v(C-O) phenolic stretching frequencies of the ligand was observed at 1180 cm⁻¹. This band was shifted to a lower frequency range (1040 – 1100 cm⁻¹) in the complexes, and this is indicative of bonding through phenolic oxygen [1, 15]. The ligand (HL) also showed strong band at 1340 cm⁻¹ which was assigned to v(C-N) stretching. The band was shifted to 1240 cm⁻¹ – 1310 cm⁻¹ region in all the complexes. The v(M-N) bands was observed at 600 cm⁻¹–640 cm⁻¹as new bands. This occurrence indicates that there is coordination between the metal and the lone pair of electron on the nitrogen atom of the ligand. Also, bands observed at 530 cm⁻¹ – 610 cm⁻¹ lindicates the formation of v(M-O) bond for the complexes [7]. These bands were absent in the spectra of the free ligand.

Table 2: Relevant vibrational bands for the Schiff base ligand and their metal(II) complexes

Compounds	v(O-H)	v(C=N)	v(C-N)	v(C-O)	v(C-H)	v(M-N)	v(M-O)
HL	3540br	1570w	1340m	1180m	2880s	-	-
$Mn(L^1-L^1)X_2$	3200br	1570s	1310m	1040w	2860sh	640sh	610w
$Cu(L^1-L^1)X_2$	3520sh	1500s	1240m	1100br	2860sh	600w	570sh
$Ni(L^1-L^1)X_2$	3240s	1560sh	1240sh	1040br	2860sh	630sh	530w

Electronic Spectra

UV-VIS spectra of the Mn(II), Cu(II) and Ni(II) complexes were recorded at 250 - 800 nm using methanol as a solvent. The absorption regions, band assignment and the proposed geometries of the complexes are given in Table 3. The UV/Visible spectra of Mn(L¹-L¹)X₂ complex showed broad bands at 13809 cm⁻¹, 14035 cm⁻¹ and 14596 cm⁻¹ respectively. The band at 13809 cm⁻¹ correspond to ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}$ transition,14035 cm⁻¹ correspond to ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}$ (G) transition respectively [17]. The complex [Cu(L¹-L¹)X₂] also showed broad band in the visible region at 13550 cm⁻¹, 13869 cm⁻¹ and 14714 cm⁻¹ assignable to ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ transition and ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}$ transition respectively [18]. The UV/Visible spectrum of [Ni(L¹-L¹)X₂] complex also, showed broad bands at 15596 cm⁻¹ and 15821 cm⁻¹ which were assigned to ${}^{3}A_{2g}$ (F) $\rightarrow {}^{3}T_{1g}$ (P) transition and ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ (F) transition respectively [19].

Compounds	Absorption(cm ⁻¹)	Band assignments	Geometry
HL	34917	$n \rightarrow \pi *$	
$Mn(L^1-L^1)X_2$	13809	${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}(n)$	Octahedral
	14035	${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}(G)$	
	14596	${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}(G)$	
$Cu(L^1-L^1)X_2$	13550	${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$	Octahedral
	13869	${}^{2}E_{g} \rightarrow {}^{2}T_{2g}$	
	14714	$^{2}B_{1g} \rightarrow ^{2}A_{1g}$	
$Ni(L^1-L^1)X_2$	15596	${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$	Octahedral
	15821	$^{3}A_{2g} \rightarrow ^{3}T_{1g}(F)$	





Figure 3: Proposed structure of the metal complexes

M = **Mn**(**II**), **Ni**(**II**) or **Cu**(**II**)

Table 4: Antimicrobial susceptibility studies of HL and its metal complexes

Compounds	Conc.	Antimicrobial activity with zone of inhibition (mm)					
	(µg/ml)	Staphylococcusaureus	Streptococcus	Escherichia	Salmonella	Candida	
			Pyogenes	coli	typhi	albicans	
HL^{1}	30	$0.00{\pm}0.00^{a}$	0.00 ± 0.00^{a}	$0.00{\pm}0.00^{a'}$	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	
	20	$0.00{\pm}0.00^{\mathrm{a}}$	$0.00{\pm}0.00^{a}$	0.00 ± 0.00^{a}	$0.00{\pm}0.00^{a}$	0.00 ± 0.00^{a}	
	10	$0.00{\pm}0.00^{a}$	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	$0.00{\pm}0.00^{a}$	0.00 ± 0.00^{a}	
$Mn(L^{1}-$	30	$9.67 {\pm} 0.58^{b,b'}$	$12.33 \pm 0.58^{b,b'}$	$9.33 \pm 0.58^{b,b'}$	12.67 ± 0.58^{b}	0.00 ± 0.00^{a}	
L^1) X_2	20	7.33±0.58 ^{c,c'}	7.33±1.15 ^{c,c'}	7.00 ± 0.00^{c}	$9.00{\pm}0.00^{c,c'}$	0.00 ± 0.00^{a}	
	10	$0.00{\pm}0.00^{a}$	$0.00{\pm}0.00^{a}$	$0.00{\pm}0.00^{a}$	$7.00{\pm}0.00^{d}$	$0.00{\pm}0.00^{a}$	
$Cu(L^1-L^1)X_2$	30	13.00 ± 0.00^{d}	10.00 ± 0.00^{d}	11.67 ± 0.58^{d}	$10.00 \pm 0.00^{e,c'}$	$12.00 \pm 0.00^{b,b'}$	
	20	$10.67 \pm 0.58^{e,d'}$	$8.00\pm0.00^{e,c'}$	$8.67 \pm 0.58^{e,b'}$	$8.33 \pm 0.58^{f,c'}$	$8.67 \pm 0.58^{c,c'}$	
	10	$7.00{\pm}0.00^{f,c'}$	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	$0.00{\pm}0.00^{a}$	$7.00\pm0.00^{d,c'}$	
$Ni(L^1-L^1)X_2$	30	14.67 ± 0.58^{g}	$12.00 \pm 0.00^{f,b'}$	0.00 ± 0.00^{a}	$10.33 \pm 1.15^{g,c'}$	14.67 ± 0.58^{e}	
	20	$11.00\pm0.00^{h,d'}$	$8.67{\pm}0.00^{g,c'}$	0.00 ± 0.00^{a}	$8.67{\pm}0.58^{h,c'}$	$11.00 \pm 1.73^{f,b'}$	
	10	$9.00 \pm 0.00^{i,b'}$	$7.00{\pm}0.00^{h,c'}$	0.00 ± 0.00^{a}	$0.00{\pm}0.00^{a}$	7.67±0.58 ^{g,c'}	
LZ	30	31.67 ± 0.58^{j}	30.00 ± 0.00^{i}	-	-	-	
ER	30	$0.00{\pm}0.00^{a}$	24.67 ± 0.58^{j}	-	-	-	
GN	30	-	-	20.00 ± 0.00^{f}	15.00 ± 0.00^{i}	-	
NOR	30	-	-	22.00 ± 0.00^{g}	34.00 ± 0.00^{j}	-	
KET	30	-	-	-	-	37.00 ± 0.00^{h}	

*Different superscript letters along the same column are significantly (P<0.05) different.

Key: HL^2 = Schiff base ligand, X_2 = Cl, LZ = Linczolid, ER = Erythromycine,

GN = Gentamicin, NOR = Norfloxacin, KET = Ketazol.

Antibacterial activity

The antimicrobial activity of the Schiff base ligand and their metal complexes [Mn(II), Cu(II) and Ni(II) complexes] at concentrations of 10, 20 and 30 µg/ml were evaluated against Gram positive (*Staphylococcus aureus, Streptococcus pyogenes*) and Gram negative(*Escherichia coli, Salmonella typhi*) bacteria as well as fungal specie – *Candida albicans* are presented in table 4. The Schiff base ligand (HL¹) did not show efficacy against all the microorganisms tested. But, on complexation with Mn(L¹-L¹)X₂ showed increased activity (P<0.001) against all the organisms that were previously resistant to the parent ligand except *C. albicans* which was resistant to the Mn(II) complex. At concentration of 30 µg/ml, it was observed that all the test organisms were susceptible [20] on Cu(L¹-L¹)X₂ complex. Ni(L¹-L¹)X₂ was found to be resistant to *E. coli* while *S. typhi,S. aureus, S. pyogenes* and*C. albicans* were found to be susceptible [20-21] to Ni(II) complex. Enhanced activity (P<0.001) was observed for Cu(II) complex on comparison with Mn(II) and Ni(II). It was also observed that increase in concentrations, increases the



activity of the complexes. The increased potency of the metal complexes may be attributed to their increased lipophilic nature arising due to chelation [22].

Conclusion

In this paper the synthesis of a Schiff base ligand derived from condensation of propionaldehyde with ethylenediamine and its metal(II) complexes have been described. The Schiff base ligand coordinated through its azomethine nitrogen with metal ion. This is supported by infrared spectral data. The electronic spectral band observed are consistent with an octahedral geometry for Mn(II), Cu(II) and Ni(II). The molar conductivity data of the complexes in methanol indicated that they are non-electrolytes. All the complexes are air stable and soluble in some of the solvents used except petroleum ether and ethyl acetate. The *in-vitro* antimicrobial study shows that the complexes have higher activities compared to the free ligand.

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