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Synthesis, characterization, and antimicrobial studies of some vanillin schiff base metal (II) complexes

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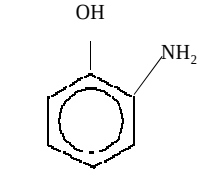
ABSTRACT

Some new transition metal complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with Schiff base ligand (HL) derived from condensation of vanillin with 2-aminophenol was synthesized in alcoholic medium. Both the ligand/complexes were characterized on the basis of microanalysis, melting point, conductivity, solubility, IR, and UV/VIS spectral studies. The in vitro antibacterial activities of the complexes were tested using number of bacteria species such as Escherichia coli, Salmonella typhi, Klebsiella pneummiae, Pseudomonas aeruginosa, Staphylococcus aureus, Streptocuccus pyogenes, corynebacterium specie, and Basillus subtilis. The complexes were formed in moderate yields and they are of various colours and have sharp melting points. The purity and composition of the Schiff bases and the metal(II) complexes were established by elemental analysis which suggests a metal: ligand ratio of 1:2. The IR spectra revealed that the complexes coordinated through azomethine nitrogen and methoxy 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. Based on the electronic spectral transitions, an octahedral structure has been assigned to all the complexes except Zn(II) complexes which has been assigned tetrahedral structure. Measured molar conductance showed that the complexes are non electrolytes and are soluble in protic solvents like methanol and ethanol. Some complexes showed good antibacterial activities against the tested bacteria at 100, 200 and 300 mg/ml. therefore, the possible use of the complexes as antibiotic can be suggested.

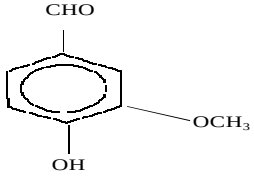
Key words: Synthesis, characterization, antimicrobial studies, schiff base, vanillin, 2- aminophenol.

INTRODUCTION

The synthesis of Schiff base ligands and their metal complexes have been extensively studied because of their interesting biological activities [1-4]. They have been reported to be useful in medicine, catalyst, as antibiotics, antifungal, antituberculius and have applications in various fields [5-8]. A search through literature reveals that schiff bases and their metal complexes have been studied for their corrosion inhibition properties [9].



2-aminophenol



vanillin

Vanillin is a phenolic aldehyde organic compound with the molecular formula $C_8H_8O_3$. The functional groups include aldehyde, ether, and phenol. It is the primary component of the extract of the vanilla bean. Vanillin Schiff-bases have been demonstrated to possess polyvalent metal ions [10]. Condensation product of vanillin with amines confers biological activity; as well as having good complexation ability with metal ions [11-13]. There are only few reports on the synthesis and physicochemical studies of vanillin Schiff-bases and their metal (II) complexes. In view of the above, this paper is intended to report the synthesis, characterization and antimicrobial studies of some vanillin Schiff-base metal(II) complexes.

EXPERIMENTAL SECTION

All the chemicals and solvents used were of Analar(AR) grade and were used without further purification. They are vanillin, 2-aminophenol, $MnCl_2.4H_2O$, $CoCl_2.6H_2O$,$NiCl_2.6H_2O$, $Cu(CH_3COO)_2$. H_2O, $Zn(CH_3COO)_2.2H_2O$, methanol, ethanol petroleum ether, chloroform, benzene, ethylacetate and acetone.

The percentage (%) Mn, Co, Ni, Cu and Zn were determined by EDTA complexo metric titration [14]. Microanalysis of Carbon, Hydrogen, and Nitrogen (C, H, N) was performed using Perkin Elmer model 2400 series 11CHN S/O Elemental analyzer in South Africa. 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, petroleum ether, chloroform, benzene, ethyl acetate and acetone. Molar conductivity was measured by using metler P 163 conductivity meter in methanol solution (10^{-3} M) at 25^{o}C, in the Department of Soil Science of the University of Maiduguri.

The infrared (IR) spectra were recorded as KBr discs on FTIR 8400S Shimadzu Spectrophotometer at National Research Institute for Chemical Technology (NARICT), Federal Ministry of Science and Technology, Zaria, Nigeria, in the range 4000 – 350cm^{-1} for the Schiff base ligands and their complexes. Electronic spectra of all the complexes were measured in methanol solution (10^{-3} M) at 25^{o}C using UV-2550 Shimadzu Spectrophotometer in the wavelength range of 250 – 600nm also at 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 as described by Raman et al., 2004 [15]. This was done by the condensation of 20ml of vanillin (0.03g, 10mmol) with 2-aminophenol (0.022g, 10mmol) in ethanol (1:1 molar ratio). The mixture was then refluxed for 3h.The product obtained was filtered, washed in distilled water, dried, and preserved in a desiccator containing $CaCl_2$.

Equation for the reaction

aldehyde + amine → HL + H_2O

Where HL= Schiff-base

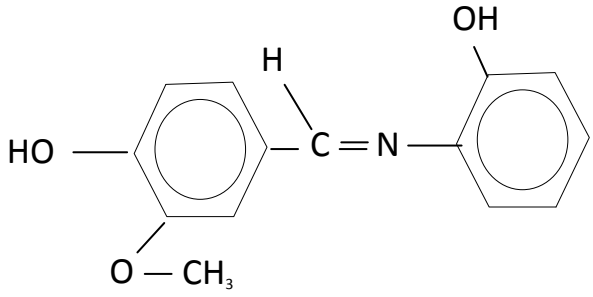


Fig 1: Proposed structure of Schiff base (HL)

Preparation of the Schiff base metal (II) complexes

An ethanolic (10 ml) solution of schiff base ligand (20mmol, 0.055g) was added drop wise to 10ml of the metal(II) salts [10mmol, 0.02g of $MnCl_2.4H_2O$, 0.024g of $CoCl_2.6H_2O$, 0.024g of $NiCl_2.6H_2O$, 0.02g of $Cu(CH_3COO)_2.H_2O$ and 0.022g of $Zn(CH_3COO)_2.2H_2O$] in boiling ethanol(78.3^{0}C). The reactions took place in 1:2 mole ratio of metal(II):HL. The reaction mixture was refluxed for 3h on a water bath and the volume of the solution was reduced to half of the initial volume. The product obtained was filtered, washed with water, diethyl ether and then dried in a vacuum over $CaCl_2$ [16, 17].

Equation for the reaction

$MX_2 .nH_2O + 2HL \rightarrow M L_2 X_2 + nH_2O$

Where
M= Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)
n = 1, 2, 4 or 6
X= Cl or OAC

Antimicrobial test

The *in vitro* antimicrobial properties of the Schiff base ligands and the metal complexes were assayed with the following bacteria: *Escherichia coli, Salmonella typhi, Klebsiella pneumoniae, Pseudomonas aeruginosa, Staphylococcus aureus, Streptocuccus pyogenes, Corynebacterium specie, and Basillus subtilis* using disc diffusion method [18]. The suspension of each microorganism was added to a sterile agar medium, then poured into sterile Petri plates and left to solidification. Different concentrations (100, 200 and 300 mg/ml) of the Schiff base ligands and the metal complexes in methanol were placed on the culture media and incubated for 24h. Activities were determined by measuring the diameter of the zone showing complete inhibition (mm) [19].

RESULTS AND DISCUSSION

Determination of purity

The analytical data along with some physical properties are summarized in Table 1. The Schiff base ligand (HL) on interaction with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) formed complexes with moderate yields(24-53%). All the complexes are air stable and have sharp melting points (130-190^{o}C) except the ligand (HL) which melted above 350^{0}C. The sharp melting point indicates that the complexes are probably pure. The lower value of the molar conductivity (0–1.4 x 10^{-2} Scm^2mol^{-1}) indicates the non electrolytic behavior of these complexes, since a value in the range 75 – 90 Scm^2mol^{-1} is expected for a 1:1 electrolytic. [1]. Solubility test revealed that the complexes of Mn(II), Co(II), Ni(II) and Cu(II) are soluble in all the solvents used except water and petroleum ether. In addition the Cu(II) complexes were soluble in petroleum ether.

Table 1: Physical characteristics and analytical data for the Schiff base ligand and the metal(II) complexes

Compound	Molecular formula (Molar mass)	Colour	Melting point (^{0}C)	Yield (%)	Molar conductivity (Scm^2mol^{-1})
HL	$C_{14}H_{13}NO_3$ (243.26)	Black	>350	32	0
$Mn(L - L)X_2$	$Mn(C_{14}H_{13}NO_3)_2$ (543.98)	Brown	130	33	4 x 10^{-3}
$Co(L - L)X_2$	$Co(C_{14}H_{13}NO_3)_2$ (545.47)	Brown	190	49	1.4 x 10^{-2}
$Ni(L - L)X_2$	$Ni(C_{14}H_{13}NO_3)_2$ (545.21)	Brown	180	24	6 x 10^{-3}
$Cu(L - L)X_2$	$Cu(C_{14}H_{13}NO_3)_2$ (550.07)	Brown	190	53	0
Zn(L - L)	$Zn(C_{14}H_{13}NO_3)_2$ (551.93)	Red	140	34	4 x 10^{-3}

X= Cl or OAC

Table 2: The microanalysis and metal estimation data of the Schiff base ligands and their metal complexes

Compounds	Molecular formula (Molar mass)	Microanalysis, % found (calc.)			
		C	H	N	M
HL	$C_{14}H_{13}NO_3$ (243.26)	66.35 (69.12)	4.98 (5.38)	6.86 (5.76)	–
$Mn(L - L)X_2$	$Mn(C_{14}H_{13}NO_3)_2$ (543.98)	62.39 (61.90)	4.56 (4.82)	5.45 (5.50)	10.23 (10.09)
$Co(L - L)X_2$	$Co(C_{14}H_{13}NO_3)_2$ (545.47)	61.75 (61.65)	4.38 (4.80)	7.41 (5.10)	10.91 (10.80)
$Ni(L - L)X_2$	$Ni(C_{14}H_{13}NO_3)_2$ (545.21)	46.69 (61.68)	4.93 (4.81)	7.49 (5.14)	11.07 (10.77)
$Cu(L - L)X_2$	$Cu(C_{14}H_{13}NO_3)_2$ (550.07)	48.99 (61.14)	4.63 (4.76)	8.55 (5.09)	11.50 (11.55)
Zn(L - L)	$Zn(C_{14}H_{13}NO_3)_2$ (551.93)	59.69 (60.33)	4.52 (4.73)	4.73 (5.08)	12.03 (11.85)

Microanalysis

The microanalysis of the ligands and their metal(II) complexes are presented in Table 2. The results revealed that the % C, H and N are in good agreement with the proposed structures. From the data obtained, it appears that the compounds analyzed as $[M(L\text{-}L)X_2]$ indicating a 1:2 mole ratio (M:L). Metal ion percentage also agrees with proposed structures (Figure 2 and 3).

IR spectra of Schiff base ligand (HL)

The selected vibrational frequencies for the Schiff base ligand and its metal complexes are presented in Table 3. Very strong band at 1569cm^{-1} is characteristics of the azomethine nitrogen present in the Schiff base ligand (HL) [15]. This was shifted to 1553-1595 cm^{-1} in the complexes, which indicates the coordination of the metal to the azomethine nitrogen. The metal complexes showed broad bands at 3261-3406 cm^{-1} which is characteristic of v(OH). This indicates that the phenolic –OH group does not participate in bond formation with the metals. The infrared spectrum of the Schiff base ligand showed strong bands at 1486, which was assigned to v(C-N) stretching. This was shifted to 1492-1589 cm^{-1} region in all the complexes. The spectral bands of the complexes at 1286-1291 were assigned to v(C-O) which did not show considerable shift from the region 1290 cm^{-1}of the ligand. Thus it is suggested that the oxygen atoms of terminal methoxy and hydroxyl group are not coordinated to the metal ions. V(M-N) and v(M-O) were observed in the far infrared region. These bands are absent in the spectra of the ligand. The v(M-N) was observed at 525-971cm^{-1} as new bands. This occurrence indicates that there is coordination between the metal and the lone pair of electron on the nitrogen atom of the ligands. Also bands observed at 439-579 cm^{-1}, indicates the formation of M-O bond for the complexes [20].This support the coordination mode of ligand through oxygen atom of the methoxy group.

Electronic spectra

UV-VIS spectra of the Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes were recorded at 250 – 600nm using methanol as a solvent. The absorption regions, band assignment and the proposed geometries of the complexes are given in Table 4. The orgel diagram for d^5 configuration for Mn(II) shows the three bands at 22935, 23901 and 2823 cm^{-1} assigned for $^6A_1g \rightarrow {}^4T_1g$, $^6A_1g \rightarrow {}^4T_2g$, and $^6A_1g \rightarrow {}^4A_2g$. The electronic transition observed for Mn(II) complex suggest the octahedral geometry [15]. Three peaks are predicted in their electronic spectra, namely, $^4A_2g(F) \rightarrow {}^4T_1g(P)$, $^4A_2g(F) \rightarrow {}^4T_1g(F)$ and $^4A_2g(F) \rightarrow {}^4T_2g(F)$ found at 11274, 15083 and 24067 respectively for the cobalt(II) complex. These are in conformity with octahedral arrangement for Co(II) ion [21].

Table 3: Relevant infrared frequencies (cm^{-1}) of the Schiff base ligands and their metal(II) complexes.

Compound	v(OH)phenolic	v(C-O)	v(C-N)	v(C=N)	v(O-CH_3)	v(M-N)	v(M-O)
HL	3408w	1290m	1486m	1569sh	2934w	-	-
Mn(L - L)X_2	3406b	1286s	1512vs	1589vs	3406m	748s	579m
Co(L - L)X_2	3364b	1286b	1510s	1588s	3364br	635m	571m
Ni(L - L)X_2	3316sh	1290vs	1492vs	1595vs	3258sh	596m	503m
Cu(L - L)X_2	3261m	1291vs	1492vs	1553w	3190w	525s	439m
Zn(L - L)	3405w	1288vs	1589vs	1589vs	2947w	971m	569br

b = broad m = medium s = strong vs = very strong sh = sharp w = weak X= Cl or OAC

Table 4. Electronic absorption spectral data for the metal complexes

Compounds	Absorption(cm^{-1})	Band assignment	Geometry
Mn(L - L)X_2	22935, 23901, 2823	$^6A_1g \rightarrow {}^4T_1g$, $^6A_1g \rightarrow {}^4T_2g$, $^6A_1g \rightarrow {}^4A_2g$	Octahedral
Co(L - L)X_2	11274, 15083, 24067	$^4A_2g(F) \rightarrow {}^4T_1g(P)$ $^4A_2g(F) \rightarrow {}^4T_1g(F)$ $^4A_2g(F) \rightarrow {}^4T_2g(F)$	Octahedral
Ni(L - L)X_2	22883	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Octahedral
Cu(L - L)X_2	23753	$^3A_{2g} \rightarrow {}^3T_{2g}$	Octahedral
Zn(L - L)	22988	d-d transition	Tetrahedral

The appearance of a band at 22883 cm^{-1} assigned to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition favours an octahedral geometry for Ni(II) complex. Copper(II) has a (d^9)configuration and showed only one transition at 23753cm^{-1} assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition ,which is in good agreement with distorted octahedral configuration around the copper(II) ion. Though three transitions are expected in this case, they are very close in energy and often appear in the form of one broad band envelope [18]. The bands observed in the complex at 22988 cm^{-1} is tentatively assigned to the spin allowed d-d transitions. This is consistent with a tetrahedral geometry. Based on the microanalysis, IR and Electronic spectral data the proposed structures for the Schiff base ligand and the complexes are shown in Figures 1 – 3.

Antibacterial activity

The zone of Inhibition of the Schiff base ligand and its metal complexes at a concentration of 100,200 and 300 mg/ml, against eight pathogenic bacteria are presented in Table 5. The antimicrobial results revealed that the ligand showed moderate activity against *Escherichia coli, Staphylococcus aureus, Streptococcus pyogenes and Bacillus subtilis* with maximum zone of inhibition of 25mm against *Escherichia coli.* Mn(II) show considerable activity at all concentrations against *Escherichia coli, Salmonella typhi, Staphhlococcus aureus and Bacillus subtilis* with maximum zone of inhibition of 30mm at 300mg/ml against *Salmonella typhi.* Co (II) showed very low activities against *Klebsilla pneumoniae, Steptococus pyogenes and Bacillus subtilis* with zone of inhibition range within 07-08, 08-12 and 07-10 respectively. Ni (II) complex was found to be reasonably active against *Escherichia coli, salmonella typhi , Staphylococcus aureue, Streptococcus pyogenes and Bacillus subtilis* with highest zone of inhibition of 36mm against *Salmonella typhi.*

Cu(II) complex exhibited only moderate inhibitory activity range between 07-18mm against *Salmonella typhi, Klebsella pneumonia Streptococcus pyogenes and Bacillus subtilis.* From Table 5, it is evidenced that Zn(II) complex did not produce any inhibitory zones against all the Gram-negative bacteria used, but it was found to be effective at all concentrations, against all the Gram-positive bacteria.

Table 5: Antimicrobial activities of the Schiff base ligand and the metal complexes

Compound	Concentration (mg/ml)	*E.Coli* (mm)	*S.Typhi* (mm)	*K.Pneumonia* (mm)	*Ps.Aeruginosia* (mm)	*St.aureous* (mm)	*St.Pyogenes* (mm)	*C.Bacterium* (mm)	*B.Subtilis* (mm)
HL	100	15	00	00	00	17	18	00	07
	200	20	00	00	00	20	20	00	08
	300	25	08	00	00	22	23	00	10
Mn $(L\text{-}L)X_2$	100	21	23	00	00	07	00	00	08
	200	23	27	00	00	09	00	00	11
	300		30	07	00	11	00	00	13
Co $(L\text{-}L)X_2$	100	00	00	00	00	00	08	00	07
	200	00	00	07	00	00	10	00	09
	300	00	00	08	00	00	12	00	10
Ni $(L\text{-}L)X_2$	100	21	30	00	00	28	07	00	11
	200	25	34	00	00	30	09	00	13
	300	27	36	07	00	34	11	00	15
Cu $(L\text{-}L)X_2$	100	00	10	09	00	00	00	00	07
	200	00	11	12	00	00	08	00	08
	300	00	14	18	00	00	09	00	10
Zn (L-L)	100	00	00	00	00	11	16	10	09
	200	00	00	00	00	14	18	14	11
	300	00	00	00	00	20	22	18	14

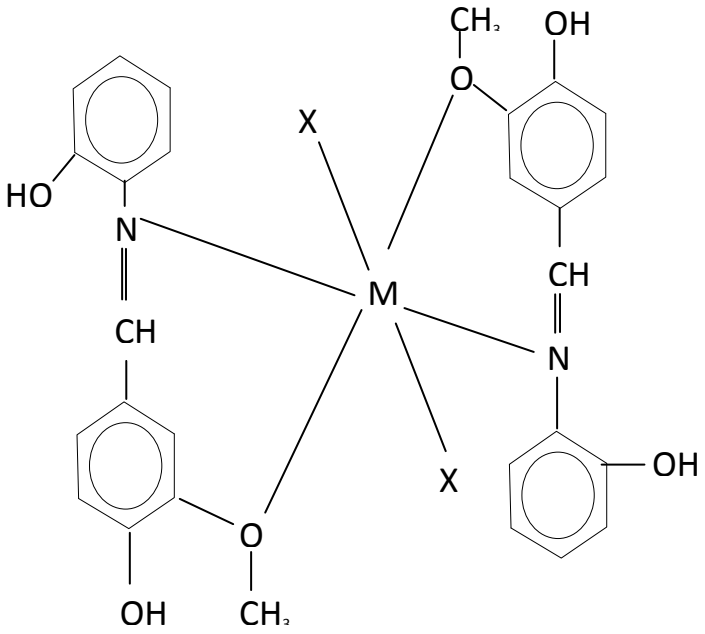


Fig 2: Proposed structure of the metal complexes M = Mn(II), Co(II), Ni(II) or Cu(II)

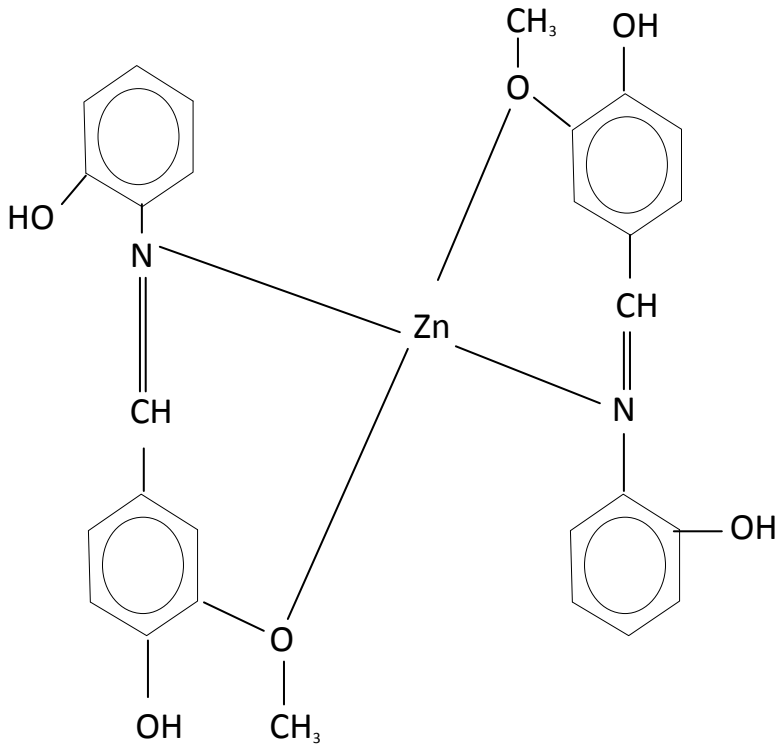


Fig 3: Proposed structure of Zn(II) complex

CONCLUSION

In this paper the synthesis of a Schiff base ligand derived from condensation of vanillin with 2-aminophenol and its metal(II) complexes have been described. The Schiff base ligand coordinated through its azomethine nitrogen and oxygen atom of methoxy group of the vanillin. This is supported by infrared spectral data. The electronic spectral band observed are consistent with an octahedral geometry for Mn(II), Co(II), Ni(II) and Cu(II) complexes while Zn(II) complexe adopt a tetrahedral geometry. The complexes were formed in 1:2(metal:ligand) ratio as confirmed by the microanalysis. The molar conductivity data of the complexes in methanol indicated that they are non electrolytes. All the complexes are air stable and soluble in protic solvents like methanol and ethanol. The *in vitro* antimicrobial study shows that the complexes have higher activities compared to the free ligand.

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