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Synthesis, Structural Characterization And Antimicrobial Activities of Fe(*II*),Co(*II*) and Ni(*II*) Schiff Base Complexes Derived From *L-arginine* and Benzaldehyde

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Abstract— **Fe(II), Co(II) and Ni(II) metal complexes with new Schiff base derived from L-arginine and Benzaldehyde have been synthesized and characterized based on their conductivity measurements, elemental analysis, infrared and electronic spectra. The spectral analysis reveals that the ligand acts as a bidentate molecule coordinating through the nitrogen atom of the azomethine group and the oxygen atom of the carboxylate group forming chelates with 1:2 metal to ligand stoichiometry. The complexes of Fe(II) and Co(II) were found to be tetrahedral whereas that of Ni(II) was proposed to be square planar. Antimicrobial activities of the Schiff base ligand and their metal complexes reveal that the Schiff base transition metal complexes show significant inhibitory activities against some fungi and bacteria.**

Keywords: *Schiff base ligand, L-arginine, Benzaldehyde, Antimicrobial activities*

I INTRODUCTION

Metal Schiff base complexes have played significant roles in the development of coordination chemistry [1]. Schiff bases are condensation product of primary amines with carbonyl compounds [2]. They are widely studied because of their increasing recognizable roles in biological systems. The versatility of Schiff base ligands and their biological, analytical and industrial applications of their complexes make further investigations in this area highly desirable [3,4,5]. The interest on Schiff bases and their metal complexes is heightened by the fact that they provide synthetic docking models for development of new chemotherapeutic drugs that fit well into binding sites of macro-molecular targets [6,7]. This is usually achieved by providing unhindered entry sites for deoxyribonucleic acid structure and conformation [4,8,9]

Literature review reveals that transition metal complexes of Schiff bases show promising antitumor property. The complexes of Schiff base exercise their biological activity in mammalian cells by inhibiting ribonucleotide reductase which is an essential enzymes in DNA precursors synthesis [9,10]. Iron, Nickel and Cobalt complexes have indicated that they can be more active in the inhibition of DNA synthesis than the free ligand itself [6,11,13]. In this study, we present the synthesis, characterization and antimicrobial activity of Schiff base ligand and its metal(II) complexes as broad-spectrum antibacterial agents

II EXPERIMENTAL

All the chemicals and solvents used were obtained from Fluka and Aldrich. They are benzaldehyde, L-arginine, acetic acid, copper (II) nitrate, Iron(II) sulphate, Ni(II) Chloride, sodium hydroxide, fused calcium choride, methanol, Distilled water, ethanol and hexane.

Melting point of all compounds were determined using Gallenkemp melting point apparatus. The solubility of the ligand and complexes was determined in some polar and non-polar solvents such as water, methanol, ethanol, acetone, hexane. Molar conductivity was measured by using meter P163 conductivity meter in methanol solution (10-3 M) at 25oc in the Department of Applied Chemistry of the University of Calabar, Nigeria.

The infrared (IR) spectra were recorded as KBr disc on FTIR – 8400s Fourier 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 ligand and the complexes. Electronic spectra of all the complexes were measured in methanol solution (10-3m) at 250c using UV-2530 Shimadzu spectrophotometer in the wavelength range of 250-600nm in the Department of Pure and Applied Science Chemistry, University of Calabar, Nigeria.

III PREPARATION OF SCHIFF BASE LIGAND

A 0.01M (0.4g) of sodium hydroxide was dissolved in 30ml of ethanol, to this solution; 0.01M(1.7g) of L-arginine was added and stirred magnetically until it became homogenous. 0.01M (1.06g) of benzaldehyde was added and stirred magnetically for 2hours. The solution was left to stand

overnight. The isolated colourless precipitate was filtered off, washed with methanol and dried over fused calcium chloride in

Equation for the reaction;

BH + LA = LABH + H2O

where

LABH = Schiff base,

BH = benzaldehyde,

LA = L- arginine

Preparation of the Schiff base metal(II) complexes

The Schiff base synthesis procedure was repeated and the solution was added drop wisely to 20ml of the metal(II) salts [0.01M, 2.4g 0f $NiCl_2.6H_20$; 1.9g of $FeSO_4.6H_2O$; 2.9g of $CoCl_2$. $6H_2O$] respectively.

The solutions were mixed in a 1:2 molar ratio of metal(II) to ligand. The solution was stirred magnetically for 2hours and then allowed to stand overnight. The products obtained were filtered, washed with methanol and dried in dessicator over $CaCl_2$.

Equation for the reaction

MX_2. nH_2O + 2LABH

$MLABH_2X_2$ + nH_2O where M = Ni(II), Fe(II) and Co(II)

n = 1,2,4, or 6

X = Cl or SO_4

Antimicrobial Test

The *in vitro* antimicrobial properties of the ligand and the metal complexes were assayed with the following bacteria; *Staphyloccus aureus, Eschereshia coli, Klebsiella pneumioa, Proteus mirabilis, Candida albicans, Aspergillus niger and Penicillum digitatum* using disc diffusion method. The suspension of each microorganism was added to a sterile agar medium, then poured into sterile petri plates and left to solidified. Different concentration of the Schiff base ligand and the metal complexes in methanol were placed on the culture media and incubated for 24hr. Activities were determined by measuring the diameter of the zone showing complete inhibition.

IV RESULTS

Table 1 Physical data of the compounds

Compound	Calcd(found)% C	H	N	Color	Melting point (^oC)	% Yield	Conductivity (Ω^1cm^2-mol^{-1})
LABH ($C_{13}H_{18}N_4O_2$)	59.8 (57.9)	6.9 (5.9)	21.4 (21.5)	White	190	32	0.10
[Ni(LABH ($^{NiC}{}_{13}{}^{H}{}_{17}{}^{N}{}_{4}{}^{O}{}_{2}$)	48.7 (48.5)	5.3 (5.4)	17.6 (17.3)	Pale green	210	48	0.10
[Fe(LABH ($FeC_{13}H_{17}N_4O_2$)	49.1 (48.9)	5.3 (5.2)	17.6 (17.7)	Brown	227.3	36	0.11
[Co(LABH ($CoC_{13}H_{17}N_4O_2$)	48.9 (48.6)	5.3 (5.2)	17.5 (17.6)	Brown	220	62	0.15

Table 2 Selected IR spectra bands (KBr, disc, cm^{-1})

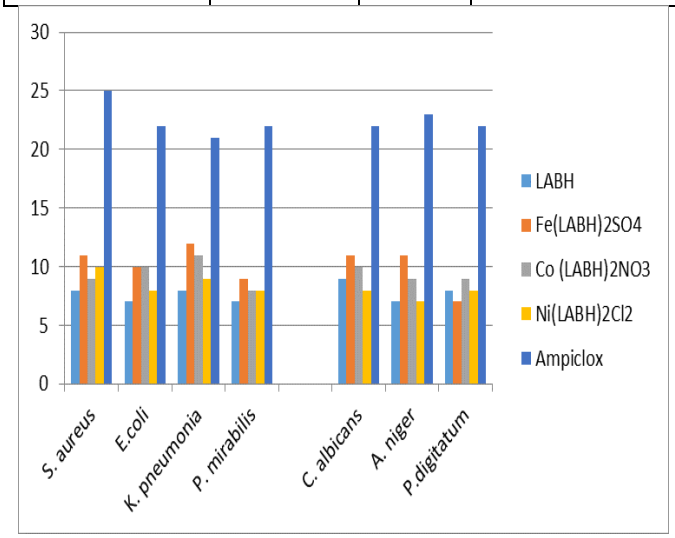
COMPOUND	NH	OH	C=0	C=N	M-N	M-O
LABH	3901	3338	1667	1561	-	-
Ni $(LABH)_2Cl_2$	3355	3175	1663	1584	521	463
Fe $(LABH)_2$ SO_4	3871	3327	1621	1521	509	394
Co $(LABH)_2$ NO_3	3869	3390	1736	1646	530	404

Table 3 Electronic spectra data

Compound	Band (nm)	Assignment
LABH	331	$n - \pi^*$
	310	$\pi - \pi^*$
	210	$n - \delta^*$
$Ni(LABH)_2$ Cl_2	515	$A_1 - {}^4E_4$
	430	${}^6A_1 - {}^4A_1$
	350	$n - \pi^*$
$Fe(LABH)_2$ SO_4	355	$\pi - \pi^*$
	322	$L \longrightarrow M$
	210	$n - \delta^*$
$Co(LABH)NO_3$	390	${}^4A_2 \longrightarrow {}^4T_1$
	445	${}^6A_1 \longrightarrow {}^4T_1$
	210	$n - \delta^*$

Table 4 Antimicrobial Results

	S. aureus	*E.coli*	*K.* pneumonia	*P. mirabilis*		*C. albicans*	*A. niger*	*P.digitatum*
LABH	8	7	8	7		9	7	8
$Fe(LABH)_2SO_4$	11	10	12	9		11	11	7
$Co(LABH)_2NO_3$	9	10	11	8		10	9	9
$Ni(LABH)_2Cl_2$	10	8	9	8		8	7	8
Ampiclox	25	22	21	22	Fluco n..azo le	22	23	22



V DISCUSSION

All the synthesized ligand and complexes are variedly colored solids; soluble in common coordinating solvents like ethanol and methanol as shown in the table above. They are stable in air and exist in crystalline form indicating their polymeric nature. The molar conductance values implicating the very weak electrolytic nature of these compounds are very low in the range of 0.10-0.15cm^2 mol^{-1}. The melting points of the complexes are high indicating strong bonding network within the compounds.

Infrared spectra

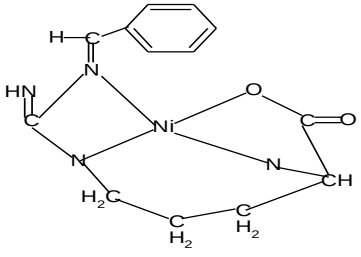
The IR spectrum (Table 3) of the ligand gave a characteristics band at 3338cm^{-1}assignable to v(0-H) intramolecular hydrogen bond. The band at 1561cm^{-1} is characteristic of azomethineV(C=N) stretching vibration while the bands at 1667cm^{-1}, 1663cm, 1621cm^{-1} and 1763cm^{-1} are assigned to carboxylate ion v(C=0). The v(C=N) vibration at 1561cm^{-1} in the ligands was shifted to different wave number of 1584, 1521 and 1646cm^{-1} on coordination to Ni(II), Fe(II) and Co(II) respectively. The v(O-H) intramolecular hydrogen bond at 3338cm^{-1} disappeared on complexation with emerging bands at 3175, 3327 and 3390cm^{-1} in each complex, thus confirming participation of the carboxylate oxygen atom in coordination. The bands of 463cm^{-1}, 509cm^{-1} and 404cm^{-1} are due to v(M-O), v(M-N) and v(M-O) for Ni(II), Fe(II) and Co(II) complexes respectively. This indicates that the ligand acted as a bidentate ligand coordinating to the metal ions through the carboxylate oxygen and azomethine or imine nitrogen. Also the bands at 3901, 3355, 3871 and 3869$cm^{-1}$are ascribed to NH stretching vibrations.

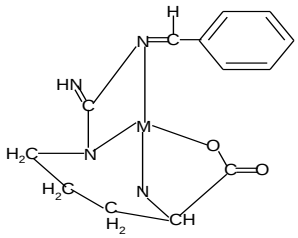
Electronic absorption spectra

The absorption bands and assignment of the ligand and metal complexes are given in table 4. The electronic absorption spectra of the Schiff base have bands at 331nm, 310nm and 210nm. These are assigned n-π^*, π-π^* and n-δ^* transitions respectively which are attributed to intraligand transfer. These bands were hypsochromically shifted in the spectra of the complexes implying the coordination of the ligand to the metal ions.

The metal ions also display some d-d transitions. The spectrum of the $[Ni(LABH)_2]Cl_2$ gave a single d-d transition band at 430nm assignable to forbidden $^6A_1$-$^4A_1$ transitions which are typical of square planar Ni(II) complex. The electronic spectra of $[Fe(LABH)_2]SO_4$ at 322nm is assignable to LMCT transition. The electronic spectrum of $[Co(LABH)]Cl_2$ has a double d-d transitions at 445nm and 390nm which can be assigned to $^6A_1$-$^4T_1$ and $^4A_2$-$^4T_1$ transitions characteristics of tesstrahedral cobalt(II) complex.

Proposed structure of Ni (II) complex





Proposed structure of the complexes M=Fe(II)and Co(II)

VI CONCLUSION

The synthesis of Schiff base ligand from condensation reaction of L-arginine with benzaldehyde was achieved and its metal(II) complexes have been described. The Schiff base ligand coordinated to the metal ions through its azomethine nitrogen and oxygen atom of the carboxylate group. This is affirmed by infrared spectral data. The electronic absorption spectra indicate transitions consistent with a tetrahedral geometry for Fe(II) and Co(II) complexes while Ni(II) complex adopt a square planar structure. The complexes were formed from 1:2 metal to ligand molar ratio. The *in vitro* antimicrobial study shows that the complexes have higher activities compared to the free ligand.

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