Synthesis, Characterization and Antimicrobial Studies of Mn(II) Co(II) AND Zn(II) SCHIFF Base Complexes Derived from L-Arginineand 2-Hydroxy-1-Naphthaldehyde

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Abstract: ***The ligand, L-arginine-2-hydroxy-1-naphthaldehyde (LAHN) was synthesized and used for the preparation of Mn(II), Co(II) and Zn(II) complexes. These were characterized using infrared, electronic absorption data, molar conductivity and elemental analysis. The infrared spectra data of this ligand and its metal complexes show that the ligand is a bidentate molecule which coordinated to the metal ions through the azomethine nitrogen and the carboxylate oxygen atom of the L-arginine-2-hydroxy-1-naphthaldehyde, the Schiff base.From theelectronic absorption spectra data available, tetrahedral geometry have been assigned to the prepared complexes. The ligand and all complexes have good antimicrobial effect onEscherichia coli, Staphylococusaureus, Salmonella typhi Candida albicanand Aspergilliusnigerstrains at different concentrations. The complexes show enhanced activities and their activities against the microorganisms increased with increasing concentrations.***

Keywords: Schiff base complex, bidentate ligand, antimicrobial activity

1. Introduction

Schiff bases also called imines are characterized by the presence of the azomethine functional group (-C=N-) and are usually formed by condensation of an aldehyde or ketone with a primary amine [1]. This condensation reaction is a facile reaction due to the good electrophylic characteristic properties of the carbonyl towards the amine group [2]. Over the years, Schiff bases have been used extensively as versatile ligands with transition metals which are able to form very stable complexes because they donateelectrons into the vacant d-orbitals of the metal atoms /ions and in some cases these ligands accept electrons from these low oxidation state metals thus effecting strong bonding through syngerstism[3]. It has been observed that such complexation is the explanation for their therapeutic effects against many diseases including cancer [4]. This versatility of Schiff base ligands is shown in the biological, analytical and industrial applications of their metal complexes. This also makes further investigations in this area highly desirable [5], and as such, current researches dealing with metal complexes of hetero atoms in Schiff bases have expanded their applications enormously to include a vast diverse fields of human endeavors.

The interest on Schiff bases and their metal complexes is heightened by the fact that they provide synthetic docking models fordevelopment of new chemotherapeutic drugs that fit well into binding sites of macromolecular targets [6]. This is usually achieved by providing unhindered entry sites for Deoxyribonucleic Acid (DNA) structure and conformation [7]. Many Schiff bases and their complexes are known to show promising antifungal, antibacterial, antiviral including anti HIV and anticancer activities [8]. In addition, some Schiff bases containing N & O donor atoms are also effective anti-corrosion agents and serve in manyother analytical purposes in organic and inorganic chemistry fields, hence their wide applications in industries. [9][10].This research work reports on the synthesis of Mn(II), Co(II) and Zn(II) complexes of L-arginine-2-hydroxy-1-naphthaldehyde, their characterization and their antimicrobial effectiveness.

2. Experimental

Synthesis of L-arginine-2-hydroxy-1-naphthaldehyde (LAHN)

Ethanolic solutions of L-arginine (1.742g, 0.01mol) and2-hydroxy-1-naphthaldehyde (1.722g,0.01mol) were slowly mixed together while stirring. Three drops of glacial acetic acid were added to the mixture and magnetically stirred for two hours. The resulting yellow precipitate was filtered and washed several times with ethanol then dried over fused calcium chloride in a dessicator.

Synthesis of the metal(II) L-arginine-2-hydroxy-1-naphthaldehyde

The Schiff base ligand, L-arginine-2-hydroxy-1-naphthaldehyde (1.742g, 0.01M)was dissolved in 30ml ethanol. To this solution,warmed ethanolic solution of metal(II) chloride hydrate(0.01M) was added, followed by few drops of sodium hydroxide. This mixture was magnetically stirred for two hour and the precipitate formed was filtered, washed and dried in a dessicator over fused calcium chloride.

Table 1: Physical data of the compounds

Compound	Molecula Formula	Colour	Melting point(^{0}C	Conductivity (Ω^1cm^2 mol^{-1})	% yield	Found (Cald)(%) M C H N
LAHN	$C_{17}H_{19}N_4O_3$	Yellow	203.7	1.17	87.73	- 63.25.8 17.1 (62.7)(4.9) (16.8)
[Mn(LAHN)$_2$]Cl$_2$	$MnC_{34}H_{38}N_8O_6Cl_2$	Brown	>300	1.65	54.04	7.1 52.3 4.9 14.4 (7.3)(53.3)(4.8)(14.6)
[Co(LAHN)$_2$]Cl$_2$	$CoC_{34}H_{38}N_8O_6Cl_2$	Brown	219.2	3.82	51.19	7.5 52.0 4.8 14.4 (7.5)(52.3)(4.7)(14.3)
[Zn(LAHN)$_2$]Cl$_2$	$ZnC_{34}H_{38}N_8O_6Cl_2$	Yellow	213.4	1.53	52.28	8.2 51.6 4.8 14.2 (7.9)(51.5) (4.8) (14.2)

Table2.Selected Infrared Bands (KBr disc,cm^{-1})

Compound	υOH	NH	C=O	C=N	COO^-	M-N	M-O
LAHN	3400	3797w	1681s	1629s	1342s	590w	455w
Mn(LAHN)$_2$Cl$_2$	3368s	3760m	1687s	1629w	1393s	489s	424s
Co(LAHN)$_2$Cl$_2$	3386s	3589w	1687m	1623w	1356s	581w	469w
Zn(LAHN)$_2$Cl$_2$	3240s	3678w	1681m	1627w	1346s	606m	455w

Table 3: Electronic Spectral data

Compound	Band(cm^{-1})	Assignment
LAHN	47,846 30,395 30,211	n-σ* π-π* n-π*
Mn(LAHN)$_2$Cl$_2$	48,076 30,487 24,027 21,038	n-σ* π-π* $^6A_1 \rightarrow {}^4T_1(^4P,^2D)$ $^6A_1 \rightarrow {}^4E(^4G)$
Co(LAHN)$_2$Cl$_2$	47,846 30,487 25,000	n-σ* π-π* $^4A_2 \rightarrow {}^4T_1$
Zn(LAHN)$_2$Cl$_2$	47,846 38,759 30,120	n-σ* $\pi - \pi^*$ L→M

Table 4: Antimicrobial studies of L-arginine-2-hydroxy-1-naphthaldehyde and its metal complexes

Ligands/complexes	Zone of inhibition in (mm)					
	Concentrations (μg/ml)	*S. typhi*	*E.coli*	*S. aureus*	*C. albican*	*A.niger*
LAHN	1000 500	14 9	15 9	15 10	19 9	15 10
[Mn(LAHN)$_2$]Cl$_2$	1000 500	17 10	24 10	16 10	22 12	18 12
[Co(LAHN)$_2$]Cl$_2$	1000 500	14 7	12 8	12 8	10 8	14 9
[Zn(LAHN)$_2$]Cl$_2$	1000 500	23 12	22 10	17 12	25 13	21 14
Streptomycin	1000 500	25 15	23 15	23 13	-	-
Ketoconazole	1000 500	-	-	-	24 13	26 16

***Measure**ments are in mm diameter, ≥8.0 mm indicates no inhibition

3. Discussion

All the synthesized ligand and complexes arevariedly coloured solids; soluble in common coordinating solvents like DMF, DMSO, acetone and ethanol as shown in Table 1. They are stable in air and exist in powdery form indicating their polymeric nature. The molar conductance values are very low in the range of 1.17-3.82s cm^{2}mol^{-1} suggesting their non electrolytic nature and only littledegree of polarity.[11]. The melting points ofthe complexes are high indicating strong bonding system within the compounds. [12]

Infrared of LAHN and its complexes

The IR spectrum (Table 2) ofthe ligand gave a characteristic band at 3400cm^{-1} assignable to v(O-H)intramolecular hydrogen bond. [13]. The band at 1629cm^{-1} is characteristic of azomethine v(C=N) stretching vibration while the bands at 1342cm^{-1} is assigned to carboxylate ion v(COO$^-$). The v(C=N) vibration at 1629cm^{-1} in the ligands was shifted to lower wave number of 1625cm^{-1}, 1623cm^{-1} and 1624cm^{-1} at coordination to Mn(II), Co(II) and Zn(II) respectively. The v(O-H) intramolecular hydrogen bond at 3400cm^{-1} disappeared on complexation with another band emerging at 1342cm^{-1} in eachcomplex, thus confirming participation of the carboxylateoxygen atom in coordination. The bands at 489, 581 and 610cm^{-1} in the spectra of the metal complexes are due to v(M-N) while the band at 424cm^{-1}, 460cm^{-1} and 455cm^{-1} are due to v(M-O). This shows that the ligand acted as a bidentate ligand coordinating to the metal ions through the carboxylate oxygen and azomethine or imino nitrogen.

Electronic spectra of LAHN and its complexes

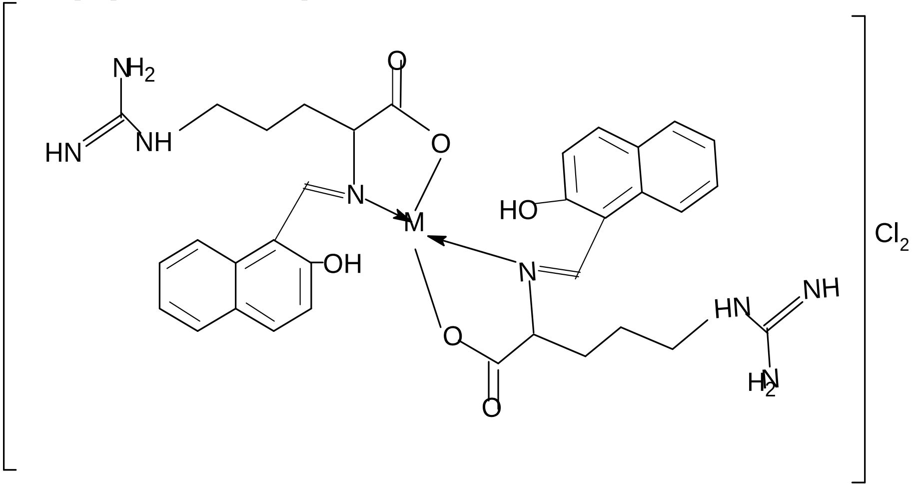
The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods for structural identification. The electronic absorption measurements (Table 3) are hereby used for assigning the stereochemistry of metal ions [14].The electronic absorption spectra of the Schiff base have bands at 47,846, 30,395 and 30,211cm^{-1} These are assigned n - σ*, π- π* and n- π* transitions respectively which are attributed to intra-ligand transition which are due to the presence of lone pair of electrons on the hetero oxygen atoms and double bonds in the structure of the ligand [12][14]. The π- π* transitions are associated with azomethine group. In the spectra of the complexes, these bands were shifted to higher absorption wave numbers indicating the coordination of the ligand to the metal ions. The metal ions also show some d-d transitions.The spectrum of the $[Mn(LAHN)_2]Cl_2$ gave a single d-d transition band at 24,038cm^{1} assignable to forbidden $^6A_1 \rightarrow {}^4A_1$ transitions which are typical of tetrahedral manganese(II) complex [15]. The electronic spectrum of $[Co(LAHN)_2]Cl_2$ has a single d-d transition at 25,000cm^{-1} which can be assigned to $^4A_2 \rightarrow {}^4T_1$ transition, a characteristic of tetrahedral cobalt(II) complex [15]. The electronic spectra of the $[Zn(LAHN)_2]Cl_2$ complex gave no d-d transition as expected for a d^{10} configuration where all the electrons are paired. Thus giving the diamagnetic properties of the zinc complex [16]

AntimicrobialActivity

The procedure used for screening is as reported by [17][18]. The synthesized compounds dissolved in DMF were examined *in vitro* by Paper Disk Diffusion method. In this method, all wares used were sterilized in a hot air oven . The gram-positive bacteria,*Staphyloccocusaureus*, *salmonella typhi* and gram-negative*Escherihia coli* and the fungi *Candida albican* and *Asperigillusniger*were subcultured and incubated for 6-8hours inNutrient andSabouraud Dextrose agar respectively. The viable bacterial cells were evenly swabbed onto the Nutrient agar plates while the fungal spores were swabbed onto the Sabourud Dextrose agar plates. The paper disks,6.0 mm diameter, were soaked in thedifferent test samples (concentrations,1000& 500µg/ml), drained and using sterilized forceps placed in the agar plates. The plates were then incubated for 48 hours (bacteria) and 72 hours (fungi)at 37^{oc}.After theincubation period, the zones of inhibition were measured in mm (Table 3).

The ligands and the metal complexes show very good antimicrobial properties against *Escherichia coli, Staphylococusaureus, Salmonella typhi and Candida albican*strains with the metal complexes having a higher inhibition activities (14—25mm diameter inhibition zones) compared to the free ligands (14—19mm diameters). In all the cases studied, the zinc complexes proved to be a better antimicrobial agent (up to 25mm diameter inhibition zone against *C.albican*) followed by Mn(II) complexes (24mm diameter against *E.coli*)as compared to the free ligands.

The following structure is proposed for the complexes



4. Conclusion

The Schiff base and novel complexes of Mn(II), Co(II) and Zn(II) L-arginine-2-hydroxynaphthaldehyde and the Schiff base ligand were synthesized and characterized using infrared spectra, electronic absorption spectra, molar conductivity and elemental analysis. These complexes and the ligand were stable to air, non hygroscopic and variedly coloured. Their electronic and infrared spectra datarevealled the bidentate nature of the ligand through which it coordinates to the metal ions using the azomethine nitrogen and carboxylate oxygen. Tetrahedral geometries are assigned to these complexes. The ligand and complexes showed very good antimicrobial properties against

Escherichia coli Staphyloccocusaureus Salmonella typhi and *Candida albicans* strains with the metal complexes having a higher inhibition activities than the free ligand.

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