



Synthesis, Spectroscopic and Preliminary Antimicrobial Studies of Some Schiff Base Ligands; N,N'-Ethylene Bis(salicylideneimine) and N,N'-Bis (salicylidene)-3,5-Diaminobenzoic Acid and their Metal Complexes

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Abstract: The Mg (II), Fe(II), Pb (II), Cd(II) and Co(II) metal complexes, were synthesized by coupling the above metals with two Schiff bases, N,N'-ethylene bis-(salicylideneimine) and N,N' bis (salicylidene)-3,5-diaminobenzoic acid respectively. The first ligand, N,N'-ethylene bis (salicylideneimine) was obtained by the condensation reaction of salicylaldehyde and ethylenediamine while the second, N,N' bis (salicylidene)-3,5-diamino benzoic was formed by the reaction of salicylaldehyde and 3,5-diaminobenzoic acid. The characterization of these ligands and their complexes was on the basis of their melting points, electronic spectra, and IR. These ligands as well as their complexes were screened for anti-microbial activity against some gram negative and gram positive organisms and they showed some measure of inhibition against the organisms.

Keywords: N,N'-Ethylene bis-(salicylideneimine), N,N'bis-(salicylidene)-3,5-diaminobenzoic acid, Salicylaldehyde, Ethylenediamine, Gram positive, Gram negative.

1. INTRODUCTION

Schiff bases are organic ligands which contain azomethine group R-C=N. They are generally prepared by condensation of primary amines (-NH₂) with active carbonyl compounds like aldehyde or ketones (C=O). [1] [2]. Schiff base derived from aromatic amines and aromatic aldehydes have a wide variety of application in many fields such as biological, inorganic and analytical chemistry [3]. Transition metals are known to form complexes with Schiff bases and these bases are used as chelating ligands in the field of coordination chemistry [4]. They are also useful in transamination processes [5]. Schiff bases have many important biological activities which include antimicrobial, antitumor and anti-HIV activities etc. [6][7] [8][9]. The aim of this study is to synthesize some new Schiff base ligands by capping the amine groups in diaminobenzoic acid and ethylenediamine with the carbonyl group from salicylaldehyde, couple the following transition metals, Cd(II), Co(II), Fe(II), Mg(II) and Pb(II) with the above ligands to form complexes as well as characterize these ligands and their metal complexes on the basis of their melting points, electronic spectra, infrared spectroscopy and finally, determine their biological activities.

2. EXPERIMENTAL

2.1. Material and Instrumentation

All the chemicals used for the synthesis of the ligands and their metal complexes were of analytical grade. IR spectra used in the characterization of the ligands and their metal complexes were recorded using Shimadzu, FTIR-8400S, and UV model: V2.30

2.2. Preparation of N, N'-ethylene Bis (Salicylideneimine), EL₁

The ligand, EL₁ was synthesized by mixing a solution of salicylaldehyde (11.630g, 0.095mol) in 250ml hot ethanol (99%) and of ethylenediamine (2.861g, 0.048mol). The mixture was refluxed for

2hours and the yellow precipitate formed was filtered off, re-crystallized with ethanol and dried. This was kept in desiccators for farther use. [10]

2.3. Preparation of N, N'-Bis (salicylidene)-3,5-Diaminobenzoic Acid, BL₂

A solution of 3,5-diaminobenzoic acid (0.33g, 0.0021 mol) in 99% absolute ethanol (15ml) and 0.01M NaOH (12ml) was slowly added to a solution of salicylaldehyde (0.48g, 0.004mol) in absolute ethanol (20ml). The reaction mixture was refluxed for 4hours at 60°C. The mixture was cooled and the colored precipitate formed was filtered and dried in a desiccator. [11] [12]

2.4. Synthesis of EL₁ Complexes

Generally, the metal compounds and the various Schiff base ligands were reacted together in a stoichiometric mole ratio of 1.1. The Fe (II), Pb (II) and Mg (II) EL₁ complexes were prepared as fellows: The metal chlorides and nitrates (0.01mole, 1.26g, 3.312g, and 1.48g) respectively in warmed ethanol (25ml) were added to a solution of EL₁(0.01mole) in 85% of warmed ethanol respectively. The mixtures were refluxed for one hour and after the reactions, the resulting solutions were filtered and re-crystallized with ethanol and allowed in desiccators.

2.5. Synthesis of BL₂ Complexes

The synthesis of Co & Cd complexes of N,N'-bis(salicylidene)-3,5-diaminobenzoic acid was carried out thus; A solution of a BL₂ (0.33g, 0.01mole) in absolute ethanol (20ml) and those of the Co and Cd (II) chlorides respectively in (99%) ethanol (25ml) were mixed and refluxed for 4hours. Black colored precipitates of Cd(II) and Co(II) were obtained and then filtered, followed by repeated washing with cold ethanol. They were later dried in desiccators.

3. RESULT AND DISCUSSION

3.1. Physical Properties of the Synthesized Compounds

N, N'-Ethylene bis (salicylideneimine), EL₁ and its Mg (II) complex, [MgEL₁] were observed to be crystalline yellowish compound melting at 90°C and 104°C, respectively. The PbEL₁, was a whitish crystalline complex with melting at over 369°C, while FeEL₁ was a brownish powdery compound with a melting point of 70°C.

N, N'-Bis (salicylidene)-3, 5-diaminobenzoic acid, BL₂ was observed to be a black in powdery substance at 200°C. Both cadmium complex (CdBL₂) and cobalt complex (CoBL₂) were observed blackish powdery compounds; however their melting points were not determined. Generally, the all the synthesized compounds gave good percentage yields; the only exceptions are lead (IV) complex (PbEL₁) and iron (II) complex (FeEL₁) respectively.

The physical properties and the percentage yields of the ligand and the metal complexes are presented in Table 3.1 below;

Table1. Physical properties of the ligands and the metal complexes

Compound	Colour	Texture	Melting point (°C)	% Yield
EL ₁	Yellow	Crystalline	90	76.27
MgEL ₁	Yellow	Crystalline	104	65.06
PbEL ₁	Milky	Crystalline	>369	31.78
FeEL ₁	Brownish	Powdery	70	20.43
BL ₂	Black	Powdery	200	65.71
CdBL ₂	Black	Powdery	ND	63.82
CoBL ₂	Grey	Powdery	ND	63.82

ND= Not determined

3.2. UV-Visible Spectra of Ligand and their Metal Complexes

The electronic spectra of EL₁, and its MgEL₁, PbEL₁, and FeEL₁ complexes as shown in Table 3.2 below are similar to each other with regards to the positions of the absorption bands and their intensities. The spectra of EL₁ shows broad band at 408.5nm with an absorbance of 0.757 and a

molar absorptivity of 3160.79. These absorption bands observed are due to $\pi \rightarrow \pi^*$ transitions and $n \rightarrow \pi^*$ transitions of the non-bonding in the ligand.

In the spectrum of MgEL₁, a broad band at 408nm with an absorbance of 0.405 and a molar absorptivity of 3156.92 was observed. These values when compared to the ligand showed no difference. This is mainly because complexation did not take place owing to the fact that Mg (II) ion used is not a transition metal.

In the spectrum of PbEL₁, three weak absorption bands at 756.00nm, 713.00nm and 494.50nm were observed. Their absorbances were obtained at 0.090, 0.091 and 0.125 respectively while their molar absorptivities were calculated as 5849.59, 5516.87, and 3826.22 respectively. These weak bands displays bathochromic shifts when compared to their ligand and also their absorption is attributed to $\pi \rightarrow \pi^*$ transitions.

In the spectrum of FeEL₁, two absorption bands ranging from strong to weak intensities were observed at 457.5nm, and 291nm were observed. Their absorbances were obtained at 0.744 and 2.783 respectively while their molar absorptivities were calculated as 3539.93 and 2251.62 respectively. The strong bands displays a hypsochromic shifts when compared to their ligand and also this is an evidence that complexation has occurred.

The electronic absorption spectral data of the Schiff bases and their metal complexes are presented in Table 3.2 below;

Table2. Electronic spectral data of the Schiff bases and their metal complexes

Compound	Wavelength(nm)	Absorbance	Molar Absorptivity
EL ₁	408.50br	0.757	3160.79
MgEL ₁	408.00br	0.405	3156.92
PbEL ₁	756.00w	0.090	5849.59
	713.00w	0.091	5516.87
	494.50w	0.125	3826.22
FeEL ₁	457.50w	0.744	3539.93
	291.00s	2.783	2251.62
BL ₂	366.50s	5,00	2835.81
CdBL ₂	427.00m	0.180	3303.93
	362.50w	0.100	2804.86
	312.50s	0.270	2417.98
	280.50s	0.572	2170.38

* Intensities: *s*-strong, *m*-moderate, *br*-broad, *w*-weak, *sh*-shoulder

3.3. IR Spectra of Ligands and their Metal Complexes

The infrared spectra of EL₁ and its complexes are presented in Table 3.3a. The spectrum of EL₁ was much as expected. Bond formations were revealed by the presence of absorption bands in the 3500-3300cm⁻¹ region of the spectrum which is assigned to O-H stretching. The presence of bands at 1750.46 cm⁻¹ indicates the formation of an imine linkage (C=N). A broad absorption band at 1361.79cm⁻¹ indicates the presence of C=C aromatic and C=O stretching. At 1036.77cm⁻¹ a moderate band was observed indicating CH₂ rocking and C-H out of plane bend. Bands assignable to (C-C) ring stretching vibrations were obtained. Far-infrared analysis was not recorded for this ligand.

The spectra for MgEL₁, PbEL₁ and FeEL₁ revealed no alteration in the stretching or bending frequencies of the C=C aromatic, C=O stretching, CH₂ rocking and C-H out of plane bend. Bands assignable to (C-C) ring stretching were still observed. A moderate shift of the absorption frequency of the ligand from 1750.46 cm⁻¹ to lower frequencies of 1600.97cm⁻¹, 1630.87cm⁻¹, and 1620.26cm⁻¹ as observed in the complexes MgEL₁, PbEL₁ and FeEL₁ respectively suggests that complexation has occurred by involving the imine nitrogen as has been observed for some other schiff base complexes reported. Also the shift observed in the O-H stretch of the ligand at 3371.64cm⁻¹ and those from the complexes i.e. 3007.12cm⁻¹, 3349.50cm⁻¹, and 3343cm⁻¹ for MgEL₁, PbEL₁ and FeEL₁ respectively suggests that complexation has occurred by involving the oxygen end as has been observed for some other reported cases.

Table3. Infrared Spectra of EL_1 and its Complexes (cm^{-1})

EL_1	$MgEL_1$	$PbEL_1$	$FeEL_1$	Functional group
3371.64br	3007.12w	3349.50w	3343w	O-H stretching
2737.08m	2907.72m	2738.05w	2925.16m	C-H aromatic stretching
1750.46m	1600.97m	1630.87m	1620.26s	C=O stretching
1361.79br	1406.15s	1367.58br	1448.59s	C=C Aromatic, C=N
1036.77m	1027.13s	1037.74w	1042.56m	C-C, C-O
757.09w	749.37s	753.23w	759.98s	CH_2 rocking, C-H out of plane bend
389.63s	467.75m	386.74s	430.14s	C-C ring

The infrared spectral data of BL_2 and its complexes are presented in Table 3.4 below. The spectrum of BL_2 was much as expected. Bond formations were revealed by the presence of absorption bands at $3760.35cm^{-1}$ region of the spectrum which is assigned to O-H stretching. The presence of bands at $1687.77 cm^{-1}$ indicates the presence of a carbonyl functionality (C=O). A strong absorption band at $1453.14 cm^{-1}$ indicates the formation of an imine linkage (C=N) as well as C=C aromatic stretching. At $1137.07cm^{-1}$ a strong band was observed indicating C-C, C-O stretching. Bands assignable to (C-C) ring stretching vibrations were observed at $430.14 cm^{-1}$. Far-infrared analysis was not recorded for this ligand.

The spectra for $CdBL_2$ and $CoBL_2$ revealed no alteration in the stretching or bending frequencies of the C=C aromatic, C=O stretching, CH_2 rocking and C-H out of plane bend. Bands assignable to (C-C) ring stretching were still observed. A moderate shift of the absorption frequency of the ligand to lower frequencies as observed in the complexes suggests that complexation has occurred by involving the imine nitrogen as has been observed for some other schiff base complexes reported. Also the shift observed in the O-H stretch of the ligand and those from the complexes suggests that complexation has occurred by involving the oxygen end as has been observed for some other reported cases.

Table4. Infrared Spectra of BL_2 and its Complexes (cm^{-1})

BL_2	$CdBL_2$	$CoBL_2$	Functional Group
3760.35w	3403.51w	3757.46s	O-H stretching
2978.19w	2902.96br	2902.00br	C-H aromatic stretching
1687.77s	1619.29m	1634.73m	C=O stretching
1453.14s	1420.62w	1438.94w	C=C Aromatic, C=N bending
1137.07s	1038.7m	1041.6w	C-C, C-O stretching
430.14br	468.72w	431.1w	C-C ring

* Intensities: *s*-strong, *m*-medium, *br*-broad, *w*-weak

The proposed structures of the ligands and their metal complexes are given below:

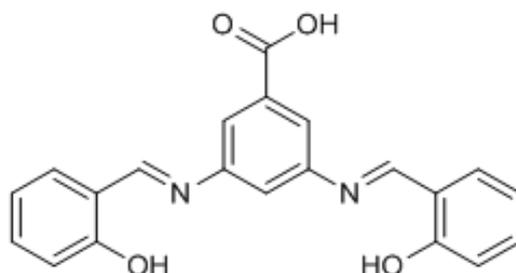


Fig1. N, N'-Bis (salicylidene)-3, 5-diaminobenzoic acid, (BL_2) [11]

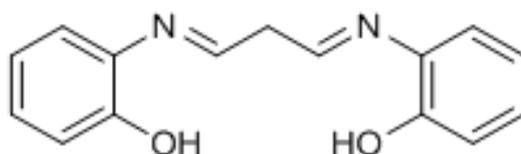


Fig2. N, N'-Ethylene bis (salicylideneimine) (EL_1) [10]

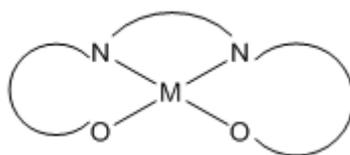


Fig3. Representation of the metal complexes

Where M= Fe, Pb, Cd, and Co [10]

3.4. Antimicrobial Properties

In fig 4 below, the result of the activity on both gram positive and gram negative was shown with CoBL_2 having the highest zone on the gram negative while BL_2Cd produced the highest zone on gram positive organism. The lowest zone was produced on gram positive, while ligand BL_2 and metal complex of MgEL_1 and CoBL_2 has no activity on positive organism.

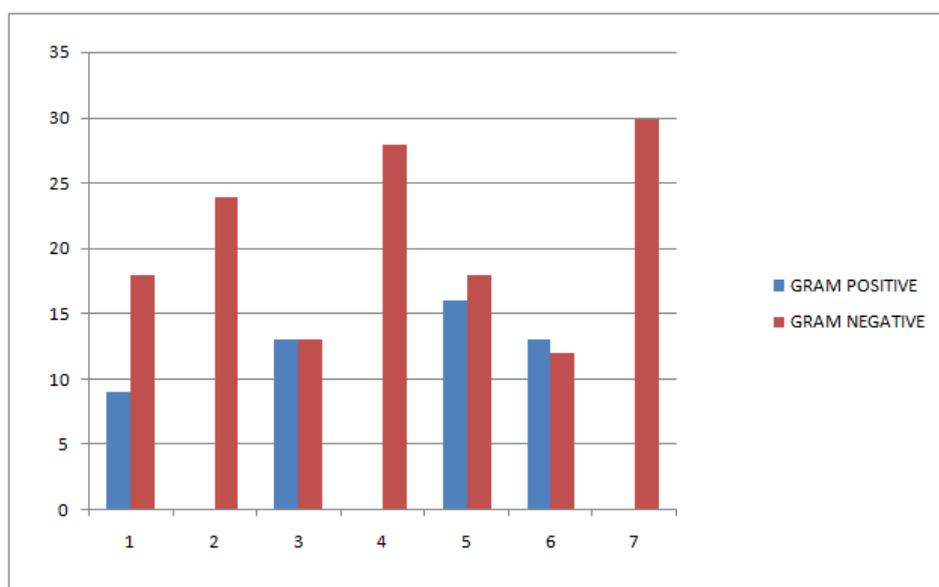


Fig4. Representation of gram negative and gram positive organism

4. CONCLUSION

The Mg (II), Fe(II), Pb (II), Cd(II) and Co(II) complexes were synthesized by coupling with the Schiff base *N,N'*-ethylene bis (salicylideneimine) and (*N,N'* bis (salicylidene)-3,5-diamino benzoic acid. The result of the electronic spectra and infrared spectra shows that there was coordination between the ligands and metal complexes. The antimicrobial result showed that the compounds have significant activities on the gram negative organism than on the gram positive organism.

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