International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.12 No.03, pp 72-79, 2019

Synthesis, Characterization and Antimicrobial Studies Of A Schiff Base Derived From 1,8 Diaminonaphthalene And 2-Hydroxy-1-Naphthaldehyde With Its Metal Complexes

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Abstract : The metal complexes of Mn(II), Hg(II), Pb(II), Cd(II), Fe(III) and Cr(III) have been synthesized from a Schiff base ligand (HL) derived from the condensation of 2- hydroxy-1-naphthaldehyde with 1,8 diaminonaphthalene. The compounds were characterized by elemental analysis, M.pt, IR and ^{1}HNMR. The elemental analysis revealed a 1:2 molar ratio (amine:aldehyde) for the ligand (HL) and 1:1 molar ratio (M:L) for the complexes. The IR spectra showed the azomethine (>C=N) bond around 1624 cm^{-1} in the ligand. This was shifted to higher frequencies in the complexes. The doublet signals in the range δ10.08-10.82 ppm in the ^{1}HNMR of the ligand is assigned to the azomethine proton (>C=N) group. The multiplet signals in the range δ6.30-8.90 ppm, indicated aromatic proton. The synthesized compounds were assayed for antibacterial activity against some pathogenic bacteria such as Gram positive: *Staphylococcus aureus, Streptococcus pyogenes)* and two Gram negative *(Escherichia coli, Klebsiella pnuemonae)* and two fungi *(Aspergillus niger* and *Candida albicans)* using filter paper disc agar diffusion method.

Keywords : 2- hydroxy-1-naphthaldehyde , 1,8 diaminonaphthalene, Schiff base, metal(II) complexes, infrared, antimicrobial activity.

Introduction

The chemistry of Schiff bases is an area of increasing interest. The metal chelates derived from aromatic aldehydes are a class of compounds having biological activity such as antibacterial, antitumor and antiviral agents depending on the parent aldehyde and the metal ion. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerizable while those of aromatic aldehydes having effective conjugation are more stable (Nejo, 2009; Sahu *et al.*, 2012).

Naomi,P. Ndahi *et al* /International Journal of ChemTech Research, 2019,12(3): 72-79.

DOI= http://dx.doi.org/10.20902/IJCTR.2019.120312

Schiff bases are generally bidentate or polydentate ligands capable of forming very stable complexes with transition metals. They can only act as coordinating ligands if they bear a functional group, usually the hydroxy, sufficiently near the site of condensation in such a way that a five or six membered ring can be formed when reacting with a metal ion. Tetradentate Schiff bases with N_2O_2donor atom is of the type reported in this work. Structure and mechanism of the formation of the Schiff base complexes and stereochemistry of four coordinate chelate complexes formed from Schiff bases and their analogues have been discussed in several reviews (Calligaris and Randaccio, 1987., Cimerman *et al*., 2000)

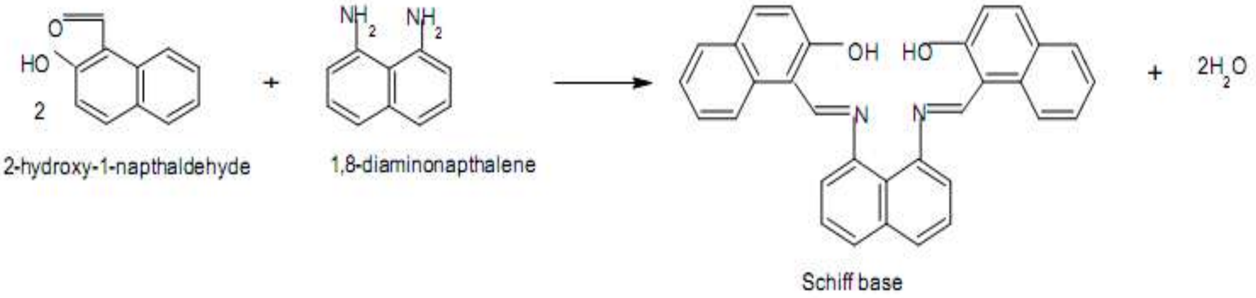
Materials and Methods

All the chemicals and solvents used were of analar grade and were used without further purification. The metal contents were determined by EDTA-complexometric titration. Melting points and decomposition temperature of the ligand and complexes were determined on a Griffin melting point apparatus. Microanalysis was performed on Thermo Flash EA CHNS-O elemental analyzer. The infrared (IR) spectra were recorded on FTIR – 84005 Model in the range 4000 – 350cm^{-1} for the ligand and complexes. The electronic absorption spectra of the ligand and the complexes were obtained on UV/Visible Spectrophotometer Model 721.The ^{1}HNMR spectra of the Schiff base ligand was recorded on PROTON /Brucker/Top Spin 3.2T-D-65536 using DMSO as an internal reference. The conductivity of the complexes was determined at room temperature (30^{0}C)on freshly prepared 10^{-3} MeOH solutions using estick(R) Series Model EC 500/Conductivity and Temperature Meter. Antibacterial activities of the ligand and metal complexes were screened against two strains of Gram positive bacteria*(Staphylococcus aureus, Streptococcus pyogenes)* and two Gram negative *(Escherichia coli, Klebsiella pnuemonae)* and two fungi *(Aspergillus niger* and *Candida albicans)*using filter paper disc agar diffusion method.

Mn(II), Hg(II), Pb(II) and Fe(III) were used as chlorides while Cd(II) and Cr(III) salts were used as acetates. 2- hydroxy-1- naphthaldehyde, and 1,8 diaminonaphthalene were purchased from Sigma.

Synthesis of the Ligand (HL)

The ligand was prepared according to litereture procedures (Abd-Elzar, 2001; Nevin and Memet, 2009; Tawfiq, 2011). This was done by the condensation of 2- hydroxy-1- naphthaldehyde, and the corresponding amine in 1:2 (amine: aldehyde) molar ratio in ethanol. A 30 ml ethanolic solution of 2-hydroxy-1-naphthadelyde (20 mmol, 3.444g) with 30 ml ethanolic solution of 1,8- diaminonaphthalene (10 mmol. 1.582g) were placed in a quick fit conical flask, after which 2-3 drops of conc. H_2SO_4 was added. The mixture was refluxed for 3hrs and left to stand for 2-3 days. The solid product obtained were filtered, washed with ethanol and dried in a desiccator over calcium chloride ($CaCl_2$).



Scheme 1: Preparation of the ligand (HL)

Synthesis of the Metal Complexes

The metal complexes were prepared according to litereture procedures (Abd-Elzar 2001; Nevin and Memet, 2009; Tawfiq, 2011). Metal salts of Mn(II), Cd(II), Hg(II), Pb(II) Cr(III) and Fe(III) were added to the Schiff base ligand in a mole ratio 1:1 (metal: ligand). A mixture of the Schiff base (HL) under investigation (1 mmol, 0.4665g) in 30ml ethanolic solution and the same amount of the same solution of Mn(II) salt (1 mmol, 0.1979g) were refluxed for 2 hours, after which it was cooled, filtered and the product obtained were dried in a desiccator containing calcium chloride ($CaCl_2$) as a desiccant. The same procedure was applied to each metal salt. The masses of the products were determined by weighing after drying and percentage (%)yields calculated.

Results and Discussion

The ligand (HL) on interaction with the metal ions Hg(II), Pb(II), Mn(II), Cd(II), Fe(III) and Cr(III) formed complexes with good yields ranging from 50-83%. All the compounds formed are air stable. The complexes showed various colours ranging from light brown to dark brown and black (Table 1). The colours of some of the complexes may be dueto charge transfer from the ligand to the metal ions , and for the others it might be due to d-d transitions of the metal ions (Sunil *et al.*, 2011).

The ligand melted at 240 ^{O}C and the complexes melted in the range of 210-287 ^{O}C. This indicates the high thermal stability of the compounds. The conductance values(Λ_m) in methanol are found in the range of 15-28 Scm^2 mol^{-1} which indicates that all the complexes are non-electrolytes. (Table 1)

The microanalysis(C,,H,N) of the ligand and the complexes are presented in Table 2.The results indicated that the experimental data are in close agreement with the theoretical values and agrees with the formation of 1:1 (M:L) molar ratio for the complexes.

Table 1: Physical Properties of the Schiff Base Ligand and its Complexes

S/No	Compound	Colour	Yield, g(%)	M.P/D.T (^{0}C)	Λ_m (Scm^2 mol^{-1})
1	HL	Light brown	5.38 (58)	240	
2	[Hg(HL)Cl]	Black	1.47 (70)	230 -233	23.40
3	[Pb(HL)Cl]	Dark brown	1.70 (80)	260	18.50
4	[Mn(HL)Cl]	Black	0.238 (51)	210 -212	16.30
5	[Fe(HL)Cl]	Dark brown	0.362 (65)	255 -256	28.00
6	[Cd(HL)]	Black	0.481 (83)	220	25.00
7	[Cr(HL)]	Light brown	0.499 (96)	285 -287	15.00

Table 2: Microanalysis of the Schiff Base Ligand and Complexes

S/No	Compound	C Found (Calcd)	H Found (Calcd)	N Found (Calcd)	M % Found (Calcd)
	HL				
1	$C_{32}H_{22}N_2O_2$	82.63	4.99	7.49	-
	(466.56)	(82.30)	(4.71)	(6.00)	-
2	$Hg(C_{32}H_{22}N_2O_2)Cl$	54.97	3.36	3.95	28.94
	(703.06)	(54.61)	(3.12)	(3.98)	(28.59)

3	Pb($C_{32}H_{22}N_2O_2$)Cl	54.74	3.20	3.47	29.72
	(709.06)	(54.41)	(3.10)	(3.94)	(29.20)
4	Mn($C_{32}H_{22}N_2O_2$)Cl	68.71	3.98	5.49	9.87
	557.06	(68.93)	(3.94)	(5.02)	(9.46)
5	Cr($C_{32}H_{22}N_2O_2$)	74.71	4.26	5.88	10.03
	(518.56)	(74.05)	(4.24)	(5.39)	(10.19)

Table 3:^{1}H Nuclear Magnetic Resonance data of the Ligand (ppm)

Ligand		**Phenolic proton δ (OH)**	**Azomethine δ (-HC=N)**	**Aromatic proton δ (C – H)**	**Solvent (DMSO)**
HL		12.00	10.08 – 10.82	6.30 – 8.90	2.51 – 3.32

The ^{1}HNMR Spectra of the ligand was recorded in DMSO. The chemical shifts, expressed in ppm are given in Table 3. ^{1}HNMR spectra of similar Schiff base ligands have been reported (Nevin and Mement, 2011, Ahmad *et al*., 2011). The free ligand (HL) exhibited a singlet signal at δ 12:00 ppm due to hydrogen-bonded phenolic proton. The doublet signals which gave sharp peaks were observed in the range δ 10.08 -10.82 ppm assigned to azomethine proton (-HC=N) group. The multiplet signals in the range of δ 6.30 - 8.90 ppm indidicates aromatic proton. DMSO protons appeared at δ 2.51-3.32 ppm.

Infrared Spectra

The relevant IR frequencies exhibited by the Schiff base ligand(HL) and its corresponding metal(II) complexes are presented in Table 4. The ligand showed a broad band at 3406 which is due to the hydroxyl group,**ν(**OH) of the ligand. However, a shift to lower wave number occurred in the spectra of the complexes in the range of (3402 – 3398 cm^{-1}) band which may be due to coordination. The azomethine**ν**(C=N) band in the spectra of the ligand appeared at 1624 cm^{-1} as a broad band. A shift to a higher frequency was observed in the spectra of the metal complexes in the region (1627 – 1639 cm^{-1}) as medium intensity bands. The shift indicates that the metals are coordinated through the nitrogen atom of the azomethine group (Rafeye and Anita ,2015), reported that the Schiff base ligand of ethylenediamine with benzaldehyde derivatives show a strong band at 1636 cm^{-1} which is characteristic of the azomethine group.The phenolic C – O appeared at 1327 cm^{-1} in the free ligand, this reflects the higher acidity of the OH group in the ligand which in turn affects the strength of the C – O band. Similar observation was reported by Nevin and Memet (2011). The C=O stetching vibration band occurred at 1340 cm^{-1}. This value was shifted to higher frequency in the complexes due to participation of oxygen in the formation of C – O bond which was observed in the range of 1342-1411 cm^{-1}.

The **ν**(C=C) mode appears at 1477 cm^{-1} in the Schiff base ligand. On coordination with the metal ion these bands shifted to higher frequencyin the spectra of Hg(II), Cd(II) and Cr(III) complexes at 1496 cm^{-1}. This showed that coordination occurred through the phenolic oxygen and amino nitrogen. A shift to a lower frequency was also observed in the spectra of Pb(II), Mn(II) and Fe(III) complexes at 1411 cm-^{1} due to C=C skeletal ring structure. This is in agreement with similar assignments by Abd El-Naby *et al*, (2013).

M-O appeared in the range of 500-658 cm^{-1} and M-N was observed in the range of 430-482 cm^{-1}as a weak band in the complexes. These bands were not observed in the spectra of the ligand. This indicates that the metal ions are coordinated through the phenolic oxygen and azomethine nitrogen. Several reviews have indicated the band assignments for the M-O bond in the range of 500-750 cm^{-1} and M-N bond occur in the range of 320-490 cm^{-1} (Parameswari *et al*.,2013; Widad, 2014; Shawnt *et al*., 2013).

Table 4: Relevant Infrared Frequencies (cm^{-1}) for the Schiff Base Ligand and Complexes

S/No	Compounds	v(OH)	v (C=N)	v (C-O)	v (C=C)	M-O	M-N
1	HL	3406	1624	1327	1477	-	-
2	[Hg(HL) Cl]	3402	1639	1411	1496	501	447
3	[Pb(HL) Cl]	3402	1635	1342	1411	644	478
4	[Mn(HL)Cl]	3406	1639	1354	1411	509	455
5	[Fe(HL)Cl]	3402	1635	1346	1411	621	451
6	[Cd(HL)]	3402	1639	1411	1496	648	439
7	[Cr(HL)]	3398	1627	1404	1496	597	482

Electronic Spectra

The UV-Vis spectra of the ligand and its complexes were recorded in methanol solution in the wavelength range of 200-800 nm. In the ligand , the two absorption bands at 27777 and 25641cm^{-1},are attributed to $\pi - \pi^*$ and $n - \pi^*$ transition of the non-nonbonding electrons present on the nitrogen of the azomethine group (Zeyrek *et al.*, 2005). The absorption bands shifted to a lower frequency on coordination with the metal ions. This shift confirmed the coordination of the ligand to the metal ion. The electronic spectra of the Hg(II) complex shows strong absorption band at 25641 cm^{-1} which was assigned to charge transfer from the ligand to metal ion (LMCT) .For this complex, d-d transition is not expected because of d^{10} configuration as reported by (Hagar *et al.*, 2010). The electronic spectrum of Pb(HL)Cl complex reveals two absorption bands at 25000 cm^{-1} and 22727 cm^{-1} due to the presence of charge transfer transition. Mn(II) complex shows absorption band at 25641 cm^{-1} attributed to charge transfer transition and two bands occurring at 22727 cm^{-1} and 20833 cm^{-1} were assigned to $^5T_2g(F) \rightarrow {}^5Eg$ and $^6A_1g \rightarrow {}^4T_2g$ (G) respectively. Square pyramidal structure was suggested for the complex. The electronic spectra of Fe(III) complex display three absorption bands at 25641cm^{-1}, 23809cm^{-1} and 17857cm^{-1} which are probably due to metal to ligand charge transfer transition and$^5T_2(F) \rightarrow {}^5Eg$ transition respectively, characteristics of square pyramidal structure. The electronic spectra of Cd(II) shows a band at 25000 cm^{-1} attributed to ligand to metal charge transfer transitions. Tetrahedral geometry was proposed for this complex (Tawfiq, 2011).The electronic spectral data of Cr(III) complex shows a band at 26315cm^{-1} attributed to charge transfer transition. Another band occurring in the visible region at 23255cm^{-1} and 20833cm^{-1} is assigned to $^4A_2g(F) \rightarrow {}^4T_1g(F)$ transition. A tetrahedral structure was proposed for this complex (Pedro *et al.*, 2006).

Table 5:Electronic Spectra for the Schiff Base Ligand and its Metal Complexes

S/No.	Compound	λ_{max} nm	λ_{max} cm^{-1}	Σ	Assignment
1	HL	360	27777	13420	$n - \pi^*$
		400	25000	12360	$\pi - \pi^*$
2	[Hg(HL)Cl]	390	25641	1573	MLCT
3	[Pb(HL)Cl]	400	25000	4500	
		440	22727	1045	MLCT
4	[Mn(HL)Cl]	310	32258	1196	MLCT
		440	22727	1191	$^6A_1g \rightarrow {}^4T_1g$
		480	20833	1116	$^6A_1g \rightarrow {}^4T_2g$
5	[Fe(HL)Cl]	390	25641	1121	MLCT
		420	23809	1018	$^5T_2g(F) \rightarrow {}^5Eg$
		560	20000	520	$^5T_2g(F) \rightarrow {}^5Eg$
6	[Cd(HL)]	380	26315	1190	MLCT
7	[Cr(HL)]	380	26315	897	MLCT
		430	23255	1202	$^4A_2g(F) \rightarrow {}^4T_2g(F)$
		480	20833	1225	$^4A_2g(F) \rightarrow {}^4T_1g(F)$

Antimicrobial Activity

The Schiff base ligand derived from 2-hydroxyl-1- napthaldehyde with I,8-diaminonapthalene were tested against different pathogenic microorganisms such as:*Staphylococcus aureus*, *Streptococcus pyogene*, *Escherichia coli*, *Klebsielia pneumonea*, *Candida albicans* and *Aspergillus niger* at concentrations of 400 mg/ml, 300 mg/ml, 200 mg/ml and100mg/ml. All tests were performed in triplicate. At all concentrations with all tested microorganisms, no activity was observed on the ligand.Hg(II) complex showed activity at all concentrations against all the tested microorganisms with inhibition zones in the range of 7.0±0.00 - 25.0±0.00. This is in good agreement with similar studies that biological activity of chelating compounds is enhanced on chelation with metal ions. Some of the inactive ligands have been found to develop such properties upon chelation (Ahmad *et al.*, 2011). At the concentration of 400 mg/ml, the complex was highly active against *Klebsiella pneumonea* with inhibition zone of20.0±0.00 and *Candida albicans*(25.0±0.00)when compared with the standard drugs (Ciprofloxacin,17.33±0.58 and Amphotericin B,22.33±0.58). Complexes of Pb(HL)Cl, Mn(HL)Cl, Fe(HL)Cl, Cd(HL)Cl, and Cr(HL)Cl showed no activity against all the tested microorganisms at all concentrations.

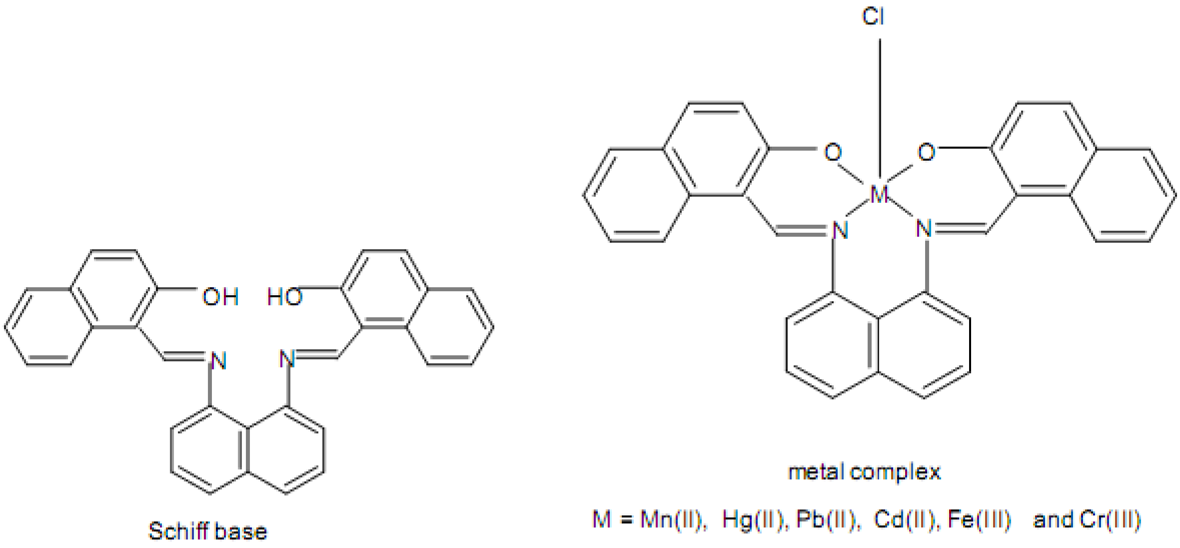


Figure 1: Proposed structures for the ligand and the metal complexes

Minimum Inhibition Concentration

MIC is defined as the lowest concentration where no visible turbidity is observed in the test tube. The Schiff base compound in which inhibition zone was observed were selected for MIC with broth dilution technique. Hg(HL)Cl had an MIC value in the range 100– 50mg/ml on all the organisms except for *K. pneumonea* with MIC value at 25mg/ml. This indicates that the compound is more potent on *K. pneumonea* than the other organisms

Minimum Bactericidal Concentration

Minimum bactericidal concentration which is the lowest concentration of the metal complex that will prevent the bacterial growth was determined. Hg(HL)Cl complex showed high MBC value on *K. pneumonea* then followed by *E. coli* and *S. pyogene* while *S. aureus* has the least MBC value at 100 mg/ml.

Conclusion

From the IR results, it may be concluded that the Schiff base ligand is tetradentate and coordinated with the metal ions through the phenolic oxygen and azomethine nitrogen atoms. The electronic spectral measurement of the complexes in methanol suggested the complexes to be either four or five coordinated. The analytical data obtained suggested 1:1 (M:L) stoichiometry for all the compounds. The antimicrobial and antifungal activities of the ligand and the metal complexes against pathogenic microorganisms such as *S. aureus*, *S.pyogene*, *K.pneumonea*, *E.coli*, *C.albicans* and *A. niger* were determined. Based on the results obtained, Hg(HL)Cl complex showed high inhibition zones on different species at the same concentrations while the other compounds showed moderate activity.

Acknowledgments

The authors are grateful to the authorities of the University of Maiduguri for providing some of the research facilities. Also, to Bangor University, United Kingdom (UK) for running the proton n.m.r and also to MEDAC Limited, United Kingdom (UK) for microanalysis.

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