DOI:10.21276/sjpm.2016.1.2.2

Saudi Journal of Pathology and Microbiology
Scholars Middle East Publishers
Dubai, United Arab Emirates
Website: http://scholarsmepub.com/

ISSN 2518-3362 (Print)
ISSN 2518-3370 (Online)

Original Research Article

Synthesis, Characterization and Antibacterial Activities of Mixed Ligand Complexes of Symmetrical Schiff Base and 8-Hydroxyquinoline with Zn(II), Cd(II) and Hg(II)

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Abstract: The current work reports a new Schiff base [N1-benzylidenebenebenzene-1,2-diamine(L) = $C_{20}H_{16}N_2$] has been synthesized from benzaldehyde (C_6H_5CHO) and O- aminoaniline ($O\text{-}C_6H_4(NH_2)_2$. Metal mixed ligand complexes of the Schiff base were prepared from chloride salts of Zn(II), Cd(II) and Hg(II) in ethanol and 8-hydroxyquinoline(8HQ)(C_9H_7NO) containing sodium hydroxide. All the complexes were characterized on the basis of their; FT-IR and U.V spectra, melting point, molar conductance, and determination of the percentage of the metal in the complexes by flame (AAS). In the all complexes, (8HQ) behaves as a bidentate ligand as primary ligand through –-OH phenolic group and –N groups of pyridine group. Also, the prepared ligand (L) was bidentate in all complexes coordinating through two nitrogen atoms as a secondary ligand. Mixed ligand complexes of bivalent ions of Zn(II), Cd(II) and Hg(II) of the according to the formula $[M(L)(Q)_2]$ in 1:1:2 of molar ratio. The suggest geometry of the complexes appears to be octahedral. The synthesis complexes were tested in vitro for antibacterial activity of ligands and metal complexes to the pathogenic bacteria activity against bacteria (gram +ve) and (gram -ve) has been studied.

Keywords: 8-Hydroxyquinoline, Schiff base, Mixed ligand complexes, and Antibacterial activities.

INTRODUCTION

A Schiff base (or azomethine) is a functional group that contains a carbon nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group but not hydrogen[1, 2]. Schiff bases are characterized by the −N=CH− (azomethine) group and are also known to have biological activities such as antimicrobial [3-5], antifungal [6], anticancer [7] activity. Interactions of metal ions with (N, O and S) atoms have attracted much attention in recent years [8]. Schiff's bases have been playing an important part in the development of coordination chemistry [9-10].

8-Hydroxyquinoline (8HQ) and its derivative originating in plants as well as from synthesis, has been used as a fungicide in agriculture and a preservative in the textile, wood, and paper industries [11] and widely used for metal complexation [12-14].

All the hydroxyquinoline derivatives, In medicinal field, (8HQ) derivatives can be used as insecticides, antibacterial, fungicidal, neuroprotective, and anti-HIV agents [15-17]. In addition, due to their chelating ability toward a great number of metal cations, derivatives of (8-HQ) have found many applications.

The aim of the present research in the synthesis ,physicochemical study and antibacterial activity of Zinc(II), Cadmium(II) and Mercury(II) coordination complexes of (8HQ) as primary ligand with new Schiff base ligand (L) as a secondary ligand. The antibacterial activity was tested of ligands and metal complexes to the pathogenic bacteria activity has been studied.

EXPERIMENTAL

Materials and measurement

All chemicals are highest purity and used as supplied. All metal(II) salts were used as chlorides. $ZnCl_2$, $CdCl_2.H_2O$, $HgCl_2$ and NaOH (supplied by either Merck or Fluka). Ethanol, methanol, dimethylforamaide (DMF), dimethylsulphoxide (DMSO), acetone, benzene, diethylether, tetrachlorocarbon and chloroform from (B.D.H). Benzaldehyde and O-aminoaniline (Merck).

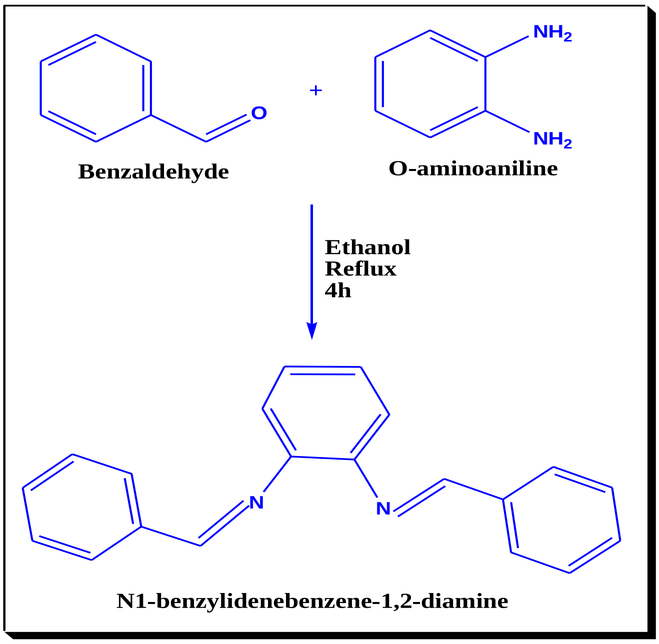
The C, H and N content of the Schiff base (L) were prepared were determined by the micro analytical unit of Eurverctor EA 3000A Elemental Analyzer. While metal contents of the complexes were determined by Atomic Absorption (A.A) Technique / Flame Emission Spectrophotometer using AA – 680 Shimadzu . The (FT-IR) spectra were recorded in 4000-400 cm^{-1} rang of ligands and 4000-200 cm^{-1} of metal complexes on FT-IR-600 FT-IR Spectrophotometer using KBr pelts . The (HNMR) for ligand was recorded by NmReady60pro.60 mhz .The electric spectra (UV) of the complexes in DMSO solution (10^{-3}) were monitored at 25^{o}C in the 200-1100 nm rang with a Shimadzu-U.V-160.Altra Violet-Visible- Spectrophotometer with 1.000±0.001 cm matched quartz cell .

The measured molar conductance values (Λm) in DMSO solution of the complexes were measured at 25^{o}C for 10^{-3}M solution of the samples using CON 510 Conductivity. Melting points were determined by using Stuart Scientific melting point Apparatus.

Preparation of Schiff base ligand

The new Schiff base was prepared by condensation [0.8490gm;4mmol] of benzaldehyde in 30mL of ethanol with [0.43256gm;2mmol] of O-aminoaniline in 15mL of ethanol was performed by heating under reflex, in the presence of 5 drops of acetic acid as a catalyst for 4hr. The yellow colored solid mass formed was cooled and then condensed solid product and isolated by filtration and washed with distilled, water to get a pure sample. Yield: 75%.). m p: 82-85^{0}C. M.W=284.364g/mol, ($C_{20}H_{16}N_2$).

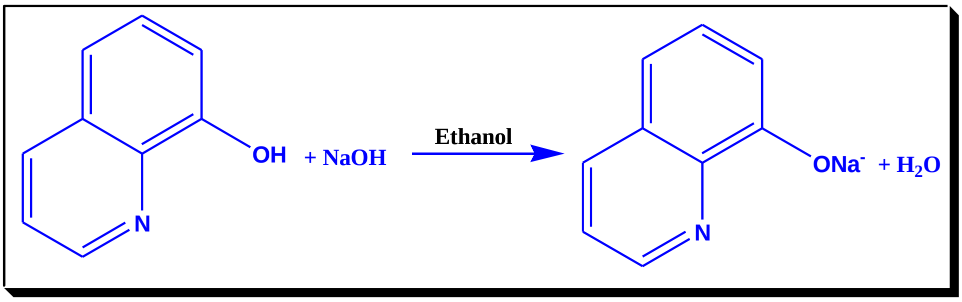
Found: C: 83.81% H: 5.33%, N: 8.96%. % Calculated :C: 84.48%; H: 5.67%; N: 9.85



Scheme 1: Preparation of the N1-benzylidenebenezene-1,2-diamine(L)

General Preparing of the Mixed Ligands Metal Complexes

The metal complexes were prepared using metal chlorides and the Schiff base by the general method. The complexes were preparing by a similar method of synthesis using the reagents in molar ratio of M: L: 2(Q) . A ethanolic solution (10mL, 1mmol) of the appropriate $ZnCl_2$ [0.136gm, 1mmol), $CdCl_2.2H_2O$ [0.201gm,1mmol] and $HgCl_2$ [0.271gm, 1mmol] ; was added to a ethanolic solution (10ml) of the Schiff base, primary ligand (L)[0.2843g/mol,1mmol) in ethanolic solution and (0.145gm,2mmol) of the secondary ligand sodiumquinolate in 20ml of ethanol and added [0.08gm,1mmol] of the sodium hydroxid according to the following Scheme (2) , was added to the previous solution and leave it in the laboratory atmosphere for 24hr . The complexes precipitated were filtered and washed with distilled water.



Scheme (2): Sodiumoxyquinolate

Study of biological activity [5-6]

Evaluation of chemical compounds against bacterial activity:

Method is used the agar well diffusion to evaluate higher activity of the chemical compound against bacterial growth against Gram positive bacteria (G+ve), (*Staphylococcus* and *Bacillus*) and Gram negative bacteria(G-ve), (*Providencia* and *Pseudomonas Aeruginosa*).

RESULTS AND DISCUSSION

Physical Properties

Ligand (L) is soluble in (DMF),(DMSO),(MeOH), (EtOH),$(CH_3)_2CO$ and completely insoluble in water (H_2O), (CCl_4), (C_6H_6), Petroleum ether and $CHCl_3$. all complexes were soluble in (DMF) and (DMSO).Molar conductance values of the soluble complexes in DMSO show value ranging from (5.65-7.69) Ω^{-1} cm^2 mol^{-1} indicating that they are all non-electrolytic [18].

The FT-IR spectral data of (8-QH) and (L) and their complexes as KBr spectra discs are described Tables 2. The band at (3240-3047)cm^{-1}due to the O-H stretching vibration of the OH group of 8-HQ [16]. This observation leads to the conclusion that the complex formation takes place by de protonation of the (OH) group of (8-HQ) moiety , suggesting the displacement of the hydroxyl proton by M(II) ion leading to covalent (M–O) bonding with the (8-QH) ligand [19].A strong ν (C-O) band observed at 1108 cm^{-1} indicates the presence of oxine moiety in the complexes coordinated through its (N) and (O) atoms as uninegative bidentate ligand [14]. The ν (CH=N) group vibration of the (L)Showed a strong band in the 1678 cm^{-1} shifted in the 1712–1636 cm^{-1} range on coordination [20]. Accordingly, one can deduce that the (L) binds the metal ion as bidentate fashion (NN).The spectra of three complexes showed new bands around (523-648) cm^{-1} and (482-503) cm^{-1} due to υ M-N and υ M- O respectfully bonds supported the formation of the complexes under investigation [15]. The integral intensities of each signal in the 1HNMR spectrum of ligand, Figure (2), was found to agree with the number of different types of protons present. The signals obtained in range δ (7.22. -7. 51) ppm were assigned for aromatic protons. In the 1H NMR spectrum of the ligand (L), the formation of Schiff base is supported by the presence of a singlet signal at δ (8.19) ppm corresponding to the azomethine proton (–N=CH–). The NMR spectral data of (L) was compared with the spectral data for the similar ligands reported in literatures .[21] The electronic spectrum of 8-HQ show an absorption band at 316 nm (32786cm^{-1}) in DMSO this band is attributed to ($n\rightarrow\pi^*$). The electronic spectrum of (L) show an absorption band at 301 nm (33222cm-1) is attributed to ($n\rightarrow\pi^*$) within the organic ligands. The [Zn(II),Cd(II)and Hg(II)] (d^{10})complexes did not display any peak in the visible region and the bands which appeared in the spectra of three complexes (as shown in table (3) could be attributed to the charge transfer (CT) transition. In fact this result agrees with the previous work of octahedral geometry [19].

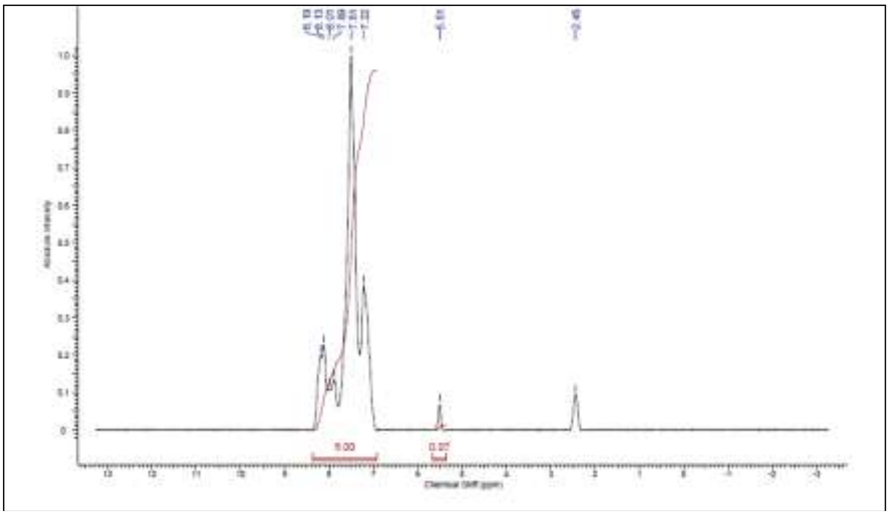


Fig-1: ^{1}H-NMR spectrum of the N1-benzylidenebenezene-1,2-diamine (L)

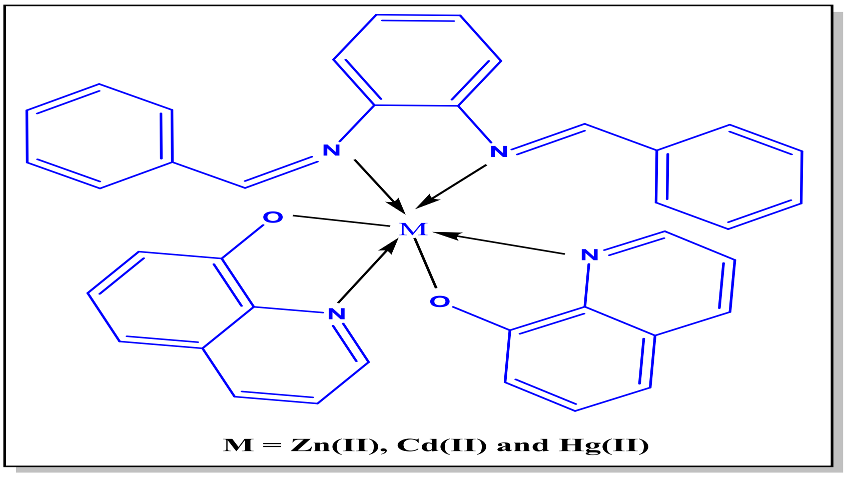


Fig-2: The proposed structural formula of the metal chelate complexes

Antibacterial study

The results obtained for antibacterial test models studies by agar well – diffusion bioassay revealed biological activity of the ligands and metal complexes after 24h in Table 4 [24].

A comparative study of ligands and their metal complexes showed that free ligands (8-HQ) exhibited a lower antibacterial activity than their complexes while Schiff higher activity except for Providencia. All complexes showed negative effect against growth of Providencia except [Hg(L)(Q)$_2$] which showed moderately effect. The [Hg(L)(Q)$_2$] complex showed positive effect against four organisms which exhibits moderately to high activity and the zone of inhibition 12 -30mm [19, 25].

The increased inhibition activity of the metal complexes can be explained on the basis of Tweedy's chelation theory [25]. In metal complexes, on chelation the polarity of the metal ion might be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups [19, 25].

Table 1: Some Physical properties of the compounds

Compounds Chemical (Formula)	**M. wt.**	**Color**	**M .p °c (dec) °c**	**Λm Ω^{-1} cm^2 mol^{-1} in DMSO (10^{-3}M)**	**Analysis Calc (Found)**	
					M% Found	**M% Calculated**
L	284.364	yellow	82-85^0	1.95	-	-
(8HQ)	145.150	Pale brown	277(dec)	1.95	-	-
[Zn(L)(Q)$_2$]	638.074	Greenish yellow	330(dec)	6.04	9.91	10.25
[Cd(L)(Q)$_2$]	685.524	Pale yellow	320(dec)	5.65	15.62	16.39
]Hg(L)(Q)$_2$[	773.064	Pale yellow	246(dec)	7.69	24.53	25.95

Table 2: Infrared spectral data of Schiff base (L),(8HQ)and their mixed ligand complexes

Compounds	υ (O-H)	υ(C-H) aromatic	υ (C=C) aromatic	υ(C=N)	M-N	M-N	M-O
(L)	-	3057	1583	1678	-		
(8HQ)	3417	3600	1593		-		
[Zn(L)(Q)$_2$]	-	3075	1576	1716	648	598	503
[Cd(L)(Q)$_2$]	-	3075	1576	1712	646	604	498
[Hg(L)(Q)$_2$]	-	3053	1539	1736	586	523	482

Table 3: UV-Vis, and magnetic moment data for the ligand and their metal complexes

Compounds	**λ_{max} (nm)**	**Wave number** υ′(cm^{-1})	**€$_{max}$ (L.mol^{-1}.cm^{-1})**	Assignment
(L)	301	33222	2332	n→π*
(8HQ)	316	31645	2357	n→π*
$[Zn(L)(Q)_2]$	277 301	36101 33222	1730 1424	CT CT
$[Cd(L)(Q)_2]$	285	35087	2369	CT
$[Hg(L)(Q)_2]$	284	35211	2125	CT

Table 4: Showed the Inhibition Circle Diameter in (mm) for the Bacteria After 24hr. Incubation at 37^{0}C for the compounds

Compound	***Staphylococcus Aureus* (G-ev)**	***Bacillus* *(G+ev)***	***Pseudomonas Aeruginosa* *(G-ev)***	***Providencia* *(G+ev)***
Control (DMSO)	1	2	2	1
(L)	34	21	27	-
(8HQ)	18	15	17	-
$[Zn(L)(Q)_2]$	23	20	16	-
$[Cd(L)(Q)_2]$	25	23	19	-
$[Hg(L)(Q)_2]$	21	30	18	12

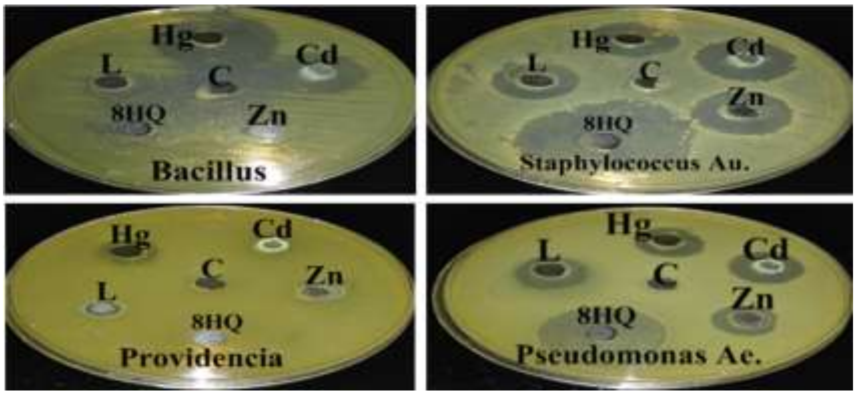


Fig-3: Shows the antimicrobial activity of complexes appear the inhibition zones against pathogenic bacteria (*Staphylococcus Aureus, Pseudomonas Aeruginosa, Providencia* and *Bacillus*

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