ISSN 0974-3618 (Print)
0974-360X (Online)

www.rjptonline.org

RESEARCH ARTICLE

Synthesis, Characterization and Theoretical Study for certain Copper (II) complexes using Organic Chalcone Schiff bases as Ligands

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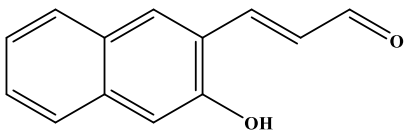
ABSTRACT:
This paper describes the synthesis of new Cu(II) complexes using copper (II) chloride and four ligands. L_1 has been used to synthesize the (M1) complex. Three azomethine ligands have been used to synthesize the (M2, M3, M4) complexes. The synthesized compounds were characterized by FT-IR, ^{1}H NMR and UV-Vis spectroscopy, moreover melting point. Molar ratio method has been used to determination of ligand to metal ratio, metal percentage in complexes has been evaluated by atomic absorption technique. Results showed that the complexes were square planar, and these compatibles with the proposed formula. Theoretical study was performed using Gaussian program W09 and AM1 method to evaluate HOMO, LUMO and some physical properties.

KEYWORDS: Copper (II) Complexes, Chalcone, Schiff's bases, Ligands, Molar ratio, atomic absorption.

1. INTRODUCTION:
Copper (II) complexes are an important compound in coordination chemistry and play an important role in many biological processes, such as electron transfer in living organisms,[1] copper (II) Complexes have a high capacity to bind with DNA, so they are used as anti-tumors[2] and enzyme regulation.[3] When the azomethine group (-N=C-) is presence in a compound, it is known as Imines compound, which can be synthesis by reaction of primary amine and carbonyl compound, imines have many significant applications in the pharmaceutical field including antibacterial,[4,5] antitumor activity[6,7], antifungal[8,9]. Recently, more imine metal complexes have gained a lot of attention, due to their biological aspects, such as antifungal [10] and antitumor. [11] Rai et al. reported that the antimicrobial capability of copper imines complexes enhanced by withdrawing substituent groups.[12]

Study has shown that metal complexation with imine as ligands enhance the bioactivity than the free ligand, due to the stability of the complexes.[13,14] The goal of this study is to investigate the complexation potential of chalcone schiff bases with Cu (II) metal.

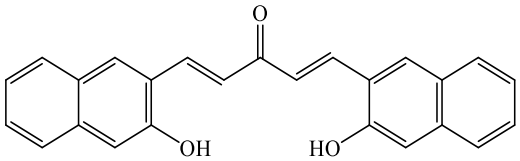
2. MATERIALS AND METHODS:
2. 1. (3-hydroxynaphthalen-2-yl)acrylaldehyde.



To 100 mL round bottomed flask immersed in ice bath contains 30 mL ethanol solution of 16 mmol of 3-hydroxy-2-naphthaldehyde and 8 mmol of acetaldehyde was added 15 mL of 10% NaOH solution drop wise through separation funnel, the reaction mixture was stirred for 5 hrs., then maintained overnight in refrigerator, the precipitate was filtered washed successively with distilled water and then recrystallized from ethanol

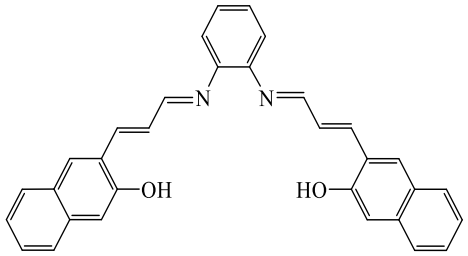
Received on 29.05.2021 Modified on 18.06.2021
Accepted on 04.07.2021
Research J. Pharm.and Tech 2022; 15(3):1008-1012.
DOI: 10.52711/0974-360X.2022.00168

2. 2. 1,5-Bis(3-hydroxynaphthalen-2-yl) penta-1,4–dien-3-one ligand. (L_1)



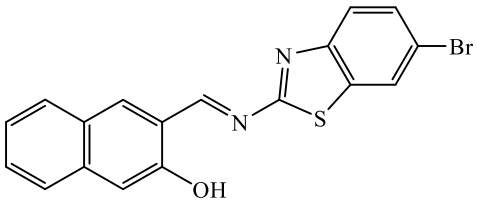
To 100 mL round bottomed flask contains 30 mL ethanol solution of 10 mmol of 3-hydroxy-2-naphthaldehyde and 5 mmol of acetone was added 10 mL of 10% NaOH solution dropwise through separation funnel, the reaction mixture was stirred for 4 hrs., then maintained overnight in refrigerator, the precipitate was filtered washed successively with distilled water and then recrystallized from ethanol.

2. 3. (1, 2- Phenylene bis (azaneylylidene)) bis (prop-1- en- 1- yl- 3- ylidene)) bis (naphthalene -2 -ol). (L_2)



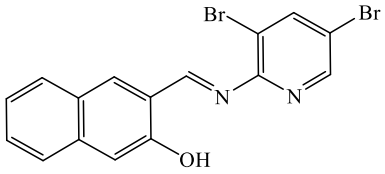
A solution of *O*-phenylenediamine (10 mmol) dissolved in 25mL EtOH was added to 50mL round bottom contains (20 mmol) of (*E*)-3-(3-hydroxynaphthalen-2-yl) acrylaldehyde, five drops of glacial acetic acid and EtOH (25 mL). The mixture was refluxed for 3 hrs. the obtained precipitate was filtered, washed with EtOH and recrystallized from EtOH .[15-19]

2. 4. (6-bromobenzothiazol-2-yl)imino)methyl) naphthalen-2-ol. L_3



A solution of 2-amino-6-bromobenzothiazol (18 mmol) dissolved in 20 mL absolute ethanol was added to round bottomed flask contains 20 mL absolute ethanol and (18 mmol) of 3-hydroxy-2-naphthaldehyde, the mixture was refluxed for 3 hrs. the precipitate was filtered, washed with EtOH and recrystallized from EtOH.[20]

2. 5. (((3,5-dibromopyridin-2-yl)imino)methyl) naphthalen-2-ol. L_4



A solution of 2-amino- 3,5-dibromopyridin (18 mmol) dissolved in 20 mL absolute ethanol was added to round bottomed flask contains solution of 3-hydroxy-2-naphthaldehyde (18 mmol) dissolved in 20 mL absolute ethanol, the mixture was refluxed for 3 hrs., the precipitate was filtered, washed with water, recrystallized from ethanol.[21]

2. 6. Complexes of M_1-M4:

(2 mmol) of (L_1-L_4) dissolved in 16 mL of EtOH was added (1 mmol) of copper (II) chloride dissolved in 19 mL of EtOH, the resulting mixture was refluxed for 1.5 hrs in 75 mL round bottom, the precipitate filtered and recrystallized from ethanol.

3. RESULTS AND DISCUSSION

The most popular experimental method for chalcones synthesis is the Claisen-Schmidt reaction, compound Z was synthesized by reaction equimolar of 3-hydroxy-2-naphthaldehyde and acetaldehyde in presence of NaOH as catalyst, while ligand L1synthesized by reaction of (2:1) mole ratio of 3-hydroxy-2-naphthaldehyde and acetone, in presence of NaOH as catalyst, L2,L3 and L4 were synthesized by condensation of primary amine and aldehyde using ethanol as a solvent, in good yields. Cu(II) complexes were synthesized by reaction of (L1,L2,L3 and L4) and copper (II) chloride using ethanol as a solvent, see table 1.

Table 1. Properties of compounds (L1-L4) and their complexes.

Comp.	Molecular Formula	M.Wt g / mole	M.P. C^0	Colour	Yield %
L1	$C_{20}H_{20}Cl_2O_3$	379.28	122-124	Orange	73
L2	$C_{27}H_{28}Cl_2N_2O_2$	483.43	213-214	Red brown	87
L3	$C_{21}H_{19}BrN_2OS$	427.36	201-203	White	83
L4	$C_{19}H_{18}Br_2N_2O$	447.98	225-227	Yellow	78
M1	$C_{50}H_{28}Br_4CuO_6$	1107.93	>300	Dark purple	70
M2	$C_{24}H_{16}Br_2CuN_2O_2$	587.76	>300	Light Brown	75
M3	$C_{36}H_{20}Br_2CuN_4O_2S_2$	828.06	>300	Dark Brown	68
M4	$C_{32}H_{18}Br_4CuN_4O_2$	873.68	>300	Black	65

FT-IR spectrum for L_1 appear vibration (O-H group) at 3405 cm-1 and vibration of azomethine group (C=N) at

1616-1623 cm-1. All the results of all ligands are given in table 2. See fig. 1 of the FT-IR spectrum of the L_1.

Table 2. FT-IR spectrum of synthesized ligands

Comp.	νO-H	νC-H ar	νC=O	νC=N	νC=C ring	
L1	3405	3055	1600	-	1595	1488
L2	3431	3053	-	1616	1587	1481
L3	3439	3055	-	1622	1612	1489
L4	3424	3037	-	1623	1601	1490

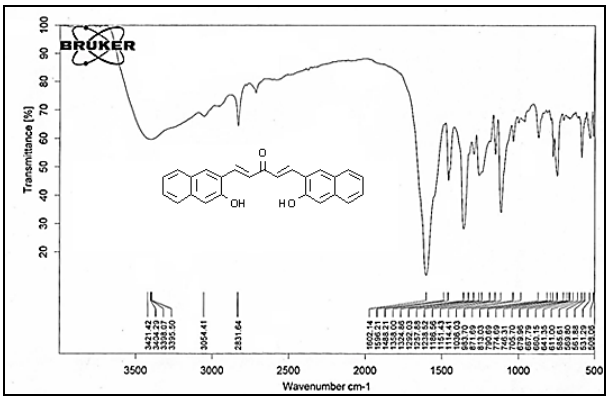


Figure 1: FT-IR spectrum for L1.

The ^{1}H-NMR spectra for synthesized compounds were recorded in DMSO-d_6, ligands spectra consisted of a singlet signals within the range (10.53-10.62 ppm) for L1 and L2 ligand, while within the range (12.01-12.11 ppm) for L3 and L4 attributable to phenolic hydrogen, the shift of hydroxyl group signals for L3 and L4 is due to the hydrogen bonding for hydroxyl proton and nitrogen atom of the azomethine group (fig. 2), multi signals were observed within the range (7.0-8.33 ppm), these can be attributed for aromatic protons, olefinic protons signals were observed within the range (6.37-6.61 ppm), (fig. 3 for L1 ligand), data are listed in table 3.

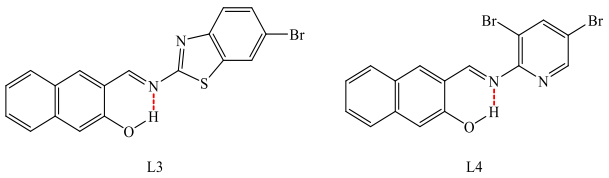


Figure 2 : Hydrogen bonding for L3 and L4 ligands.

Table 3: ^{1}H-NMR chemical shift (ppm) for synthesized [L_1, L_2, L_3, L_4] compounds.

Comp.	(s,2OH)	(s,1H)	H aromatic rings	s CH=CH
L1	10.82	8.8-8.91	7.0-8.24	6.41-6.5
L2	10.53	8.48-8.60	7.29-8.11	6.37-6.61
L3	12.01	8.71-8.92	7.34-8.33	-
L4	12.11	8.95-9.01	7.19-8.22	-

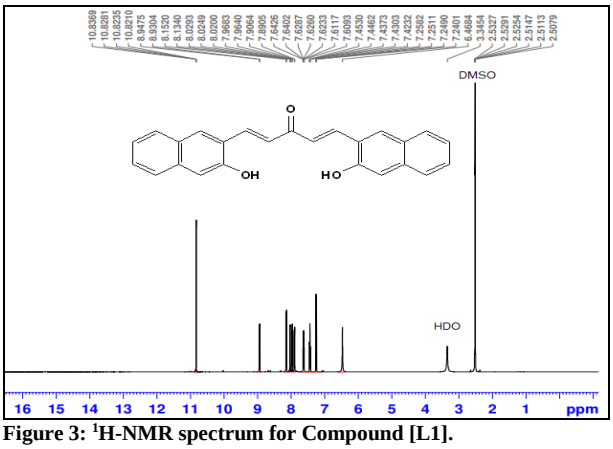


Figure 3: ^{1}H-NMR spectrum for Compound [L1].

All synthesized compounds have hydroxyl groups, these were used as a donor groups to formation the complexes, FT-IR spectra for complexes reveals to disappearance of hydroxyl group band within the range (3402-3439 cm^{-1}), then appearance absorption bands for M-O within the range (948-910 cm^{-1}) and M-N within the range (548-550 cm^{-1}),[22, 23] absorption bands data are listed in table 4., (fig. 4 for L3 ligand).

Table 4. The FT-IR spectrum of M_1-M_4:

Comp.	νC-H		νC=O	νC=N	νC=C		M-O	M-N
	Ar.	Aliph.						
M1	3052	-	1603	-	1595	1493	948	-
M2	3055	-	-	1624	1592	1498	910	548
M3	3061	-	-	1622	1616	1499	936	550
M4	3064	-	-	1626	1549	1486	959	540

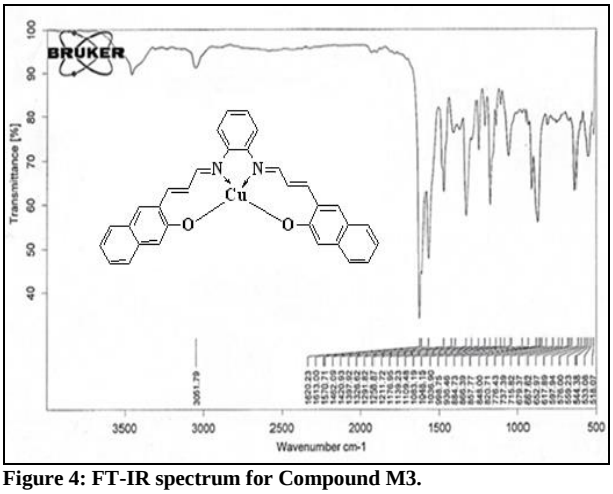


Figure 4: FT-IR spectrum for Compound M3.

DMF was used to record electronic spectra of all ligands and their complexes at room temperature. Spectra of L1 consist of a broad band at max 528 nm corresponding to π→π* and n→π*, this due to conjugated system for chalcone compound, the bands within range 370–455 nm are attributed to the π→π* transition of long conjugated azomethine group, π→π* transition for aromatic rings are observed within the range (320–358 and 260–270 nm). See table 5.

Table 5. $_{max}$ of L_1-L_4 and M_1-M_4

Compound						
	max nm	cm-1	max nm	cm-1	max nm	cm-1
L1	516	19379	355	28169	269	37171
L2	410	24390	330	30303	266	37037
L3	415	24096	343	29154	264	37878
L4	438	22831	302	33112	263	38461
M1	374	26737	308	32467	265	37735
M2	331	30211	320	3125	290	34482
M3	466	21459	332	30120	268	37134
M4	456	21929	322	31055	260	38461

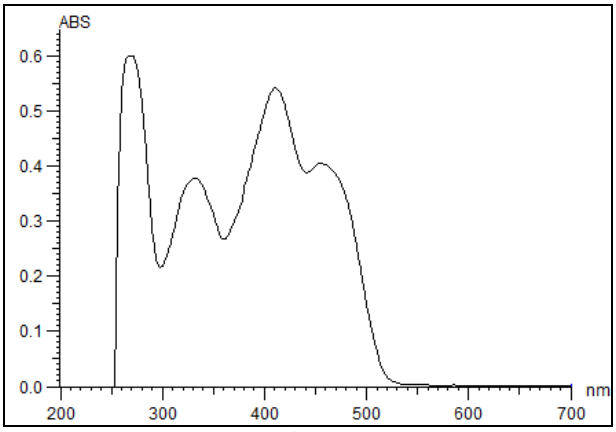


Figure 5: UV-Visible spectrum for compound L2.

Molar conductivity was determined using DMSO solvent (10^{-3} mole L^{-1}), using (Conductivity Meter - Model CRISON Basic 30 EC), the conductivity values indicates that the complexes were non-electrolytic nature, see table 6.

Table 6. Molar conductivity M_1-M_4

Complexes	(ohm^{-1}. cm^2 . mol^{-1})
M1	29.5
M2	23.8
M3	20.1
M4	12.1

4. COMPUTATIONAL STUDY:

All calculations were performed with Gaussian 09. The ground-state geometries were fully optimized at AM1 theory (Austin Model1 is semi empirical method that is most often used to model organic molecules).

The highest occupied molecular orbital (HOMO) , the lowest unoccupied molecular orbital (LUMO) were calculated. See the following equations: [24-25]

A **(**Electron Affinity**)= (-E_{LUMO})**
I **(**Ionization Potential**)= (-E_{HOMO})**

while absolute electronegativity μ, absolute hardness η and electrophilcity ω calculated by the following equations :

$$\mu = 1/2(I+A)$$

$$\eta = 1/2(I-A)$$

$$\omega = \mu^2/2\,\eta$$

Electronic properties for synthesized ligands are listed in Table 6.

Table 6: Calculated HOMO , LUMO and some Electronic properties synthesized ligands

L	E_{HOMO}	E_{LUMO}	*A*	*I*	μ	η	Ω
L1	-0.3179	-0.0363	0.03625	0.31792	0.17709	0.14084	0.00140
L2	-0.3067	-0.0303	0.03032	0.30673	0.16853	0.13821	0.00132
L3	-0.3250	-0.0416	0.04164	0.32495	0.1833	0.14166	0.00142
L4	-0.3179	-0.0502	0.05016	0.31794	0.18405	0.13389	0.00120

A = Electron affinity, *I* = Ionization potential, μ = Electronegativity, η = Hardness, ω = Electrophilicity

5. CONCLUSIONS:

All synthesized M_1-M_4 complexes are described by stability and its resistance for heating and air, they characterized by spectroscopic technique, Physical and spectrophotometry results indicates that the geometry of Cu II complexes is square planar. Fig. 5 Show the shape for synthesized complexes.

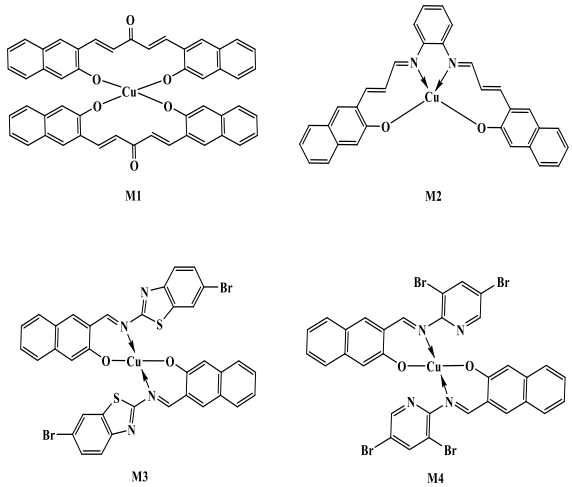


Figure 5: structures for synthesized complexes

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