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Synthesis, Characterization and Antibacterial Activities of New Metal Complexes of Unsymmetrical Tetradentate Schiff Bases

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ABSTRACT

Unsymmetrical Schiff baseH_2L^1=2-((8-((E)-1-((2-hydroxy phenyl) ethylidene amino) naphthalen-1-ylimino) methyl)-6-methoxyphenol and H_2L^2=1-((E)-(8-((E)-1-(2-hydroxy phenol) ethylidene amino) naphthalen-1-ylimino)methyl)naphthalen-2-ol which derived from 1,8-diaminonaphthalene and 2-hydroxy acetophenone and then with 2-hydroxy-3-methoxy benzaldehyde or 2-hydroxy-1-naphthaldehyde and their complexes of the type [M L^n], where n=1,2 and M=Co(II) Ni(II),Cu(II)and Zn(II) have been synthesized.Adduct complexes of the type [$ML^n(py)_2$] were also prepared in(1:2)(complex: py) molar ratio. The complexes and adducts were characterized by elemental analysis (C.H.N), metal content, (IR,UV-Vis,^{1}H-NMR)spectroscopy, conductivity and magnetic measurements. The resulting data suggested that the Schiff bases containing ONNO donor atoms act as dibasic tetradentate ligands through coordination with metal ions. Conductivity data in DMF solution showed that all complexes are non-electrolyte. Magnetic moment and electronic spectra dada indicate that the complexes have either squar planer or octahedral geometry, the ligands and their complexes gram negative bacteria (*Salmonella typhi* and*Escherichia coli*).

Keywords: unsymmetrical tetradentate, Schiff base, Antibacterial activity.

تحضير وتشخيص معقدات جديدة لقواعد شيف رباعية السن غير المتماثلة وفعاليتها البايولوجية

الملخص

حضرت قواعد شيف غير المتماثلة H_2L^1 = [1- ((E)- ((3- (((E) -2- hydroxybenzylidene) amino)phenyl)imino)methyl) naphthalene- 2- ol], H_2L^2 = [1-((E)-((3-(((E) -1- (2 - hydroxphenyl) ethylidene) amino) phenyl) imino) methyl) naphthalene - 2 – ol], والمشتقة من m- phenylenediamine و 2 - hydroxynaphthaldehyde مع Salicyaldehyde او 2-hydroxyacetophenone، ومعقداتها نوع [$M_2L^n{}_2$] حيث n = 1, 2 M = Mn(II), Co(II), Ni(II), Cu(II), وحضرت ايضا معقدات الاضافة نوع [$M_2L^n{}_2(py)_4$] بنسبة مولية (4 : 1) (بريدين : معقد). شُخَصت الليكاندات ومعقداتها بالتحليل الدقيق للعناصر (C.H.N)، تقدير المحتوى الفلزي، الطرق الطيفية (الاشعة تحت الحمراء، الاشعة المرئية - فوق البنفسجية والرنين النووي المغناطيسي)، قياسات التوصيلية المولارية والحساسية المغناطيسية. أوضحت نتائج القياسات أن قواعد شيف الحاوية (ONNO) كذرات مانحة تسلك كليكاندات ثنائية القاعدة رباعية السن من خلال تناسقها مع الايون الفلزي، بينًت نتائج قياسات التوصيلية في محلول DMSO أن المعقدات غير موصلة. ومن خلال نتائج العزوم المغناطيسية والأطياف الإلكترونية تم اقتراح ترتيب رباعي السطوح او ثماني السطوح للمعقدات، في حين اتًخذت معقدات [$Ni_2L^n{}_2$] شكل المربع المستوي. قيمت الفعالية البايولوجية المضادة لبكتريا (*Staphylococcus aureus*) و (*Escherichia Coli*) لليكندات ومعقداتها ووجد بأنها تمتلك فعالية جيدة.

الكلمات الدالة: الفعالية المضـادة للبكتريا، ميتا- فنيلين ثنائي الامين، قواعـد شيف، رباعية المنح غير المتماثلة.

INTRODUCTION

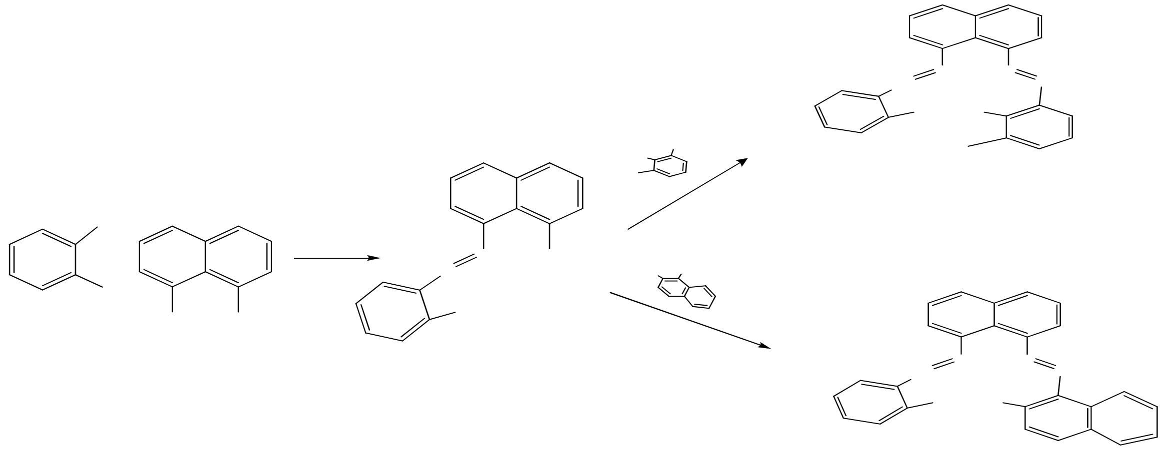
Metal complexes of Schiff bases play a central role in coordination chemistry for analytical, physical, and biochemical purposes (Attarie *et al.*,1997). Both symmetrical and unsymmetrical Schiff bases and their metal complexes contributedimmensely the development ofcoordination chemistry because of structural variety, to preparative accessibility,and bioactivity(Sakunthaland Subramanian, 2012). But in biological system, transition metal ions are usually bound to a macrocycle such as heme ring or to donor atoms of peptide chains in distorted environment (Yaul *et al.*, 2014). This unsymmetrical coordination of ligands around central metal ions had led to agrowing interest in the design and synthesis of transition metal complexes of unsymmetrical substituted Schiff base ligands as synthetic models (Nejo *et al.*, 2009). In addition, this class of compounds presents also a wide range of interesting properties, including biological (Pandy *et al.*, 2012), magnetic (Pietroandand and Sergio, 2004), nonlinear (NOL)(Rightto andBella, 2014), and the most commonly explored catalytic activity (Gupta and Sutar, 2007). In view of aforesaid importance of unsymmetrical Schiff bases and their complexes, we report synthesis and characterization of Schiff bases ligands (H_2L^1 and H_2L^2)from1,8-diaminonaphthalene with 2-hydroxyacetophenon the resulted compound react with 2-hydroxy-3-methoxy benzaldehyde and 2-hydroxy-1-naphthaldehyde respectively.

EXPERIMENTAL

All chemicals were used reagent grad from Barco Phrma Lab companies, as supplied.Melting point or decomposition temperature was determined on Mellting point apparatus, Digital, SMP1O, and SMP2O, IR spectra were recorded on 300 spectrometer (Thermo Mattson) (400-4000 cm^{-1}) using KBr disc. Electronic spectra were recorded in DMF(10^{-3}M) solution on SPECTRO UV-VISAUTO,11v60 Hz or220v.50Hz at room temperature using 1 cm quartz cell(200-800)nm. Molar conductance was measured for (10^{-3}) M solution in DMF using conductivity meter JENWAY product Manuals 430/PH/cond, Meter JENWAY. Magnetic susceptibility Measurements of the complexes were carried out at $25C^0$ on the solid state by (Sherwood instruments). Metal content of complexes was determined spectrophotometrically using pg istroments, AA500 Atomic Absorption Spectrophotometer(Flame and graphite analysis) in Scientific Research Center. Elemental analysis of the ligands and complexes were performed on Euro EAE Elemental Analyzer EuroEA 3000Italy. ^{1}H-NMR Spectra were recorded in DMSO-d6 using NMRedy 60 Prrouser, Manual Version 1.0(Nanalysis Crop, c 2015) in the college of Education For Pure Sciences/ Ibn Al-Haitham in the university of Baghdad.

Preparation of ligands:

The unsymmetrical Schiff base ligands were prepared according to the reported procedure (Abubakar *et al.*, 2011). by reacting equimolar amounts of 1,8-diamino naphthalene (1.58 g ,0.01 mole) in (10ml) methanol wasadded slowly to methanol solution (10 ml)containing -2-hydroxyacetophenone (1.36 g, 0.01 mole) and refluxed for 1h. Then, (1.52g,0.01mole) of 2-hydroxy-3-methoxy benzaldehyde or (1.72 g,0.01 mole)of 2- hydroxy-1-napthaldehyde, each one dissolved in (10 ml) methanol, the resulting colored mixture was refluxed with stirring for 4h and then was cooled. The resulting precipitate was filtered off, washed with methanol and dried under vacuum, (Schem 1).



Scheme 1 : Synthesis of Schiff bases ligands (H_2L^1) and (H_2L^2)

Preparation of complexes

The ligand H_2L^1 (4.10g ,0.01mole) or(4.30 g ,0.01mole) of H_2L^2 was dissolved in 30 ml of ethanol in 100ml round bottom flask. A solution of (0.01 mole) of metal salt [$CoCl_2$. $6H_2O$(2.37gm) $NiCl_2$. $6H_2O$(2.37 gm), $CuCl_2.2H_2O$ (1.70gm) and $ZnCl_2$(1.36 gm)] in (20ml) of ethanol was addedwise drop for 10-15 min. with continuous stirring at room temp.The mixture was refluxed for (3-4) h, After cooling, the precipitate was filtered off and washed with cold ethanol then dried under vacuum.

Preparation of adduct Complexes

These complexes were prepared by the addition of pyridine (1.58g ,0.02 mole)to (0.01,mole) preparedin ethanol (50ml) with the continuous stirring until complete precipitation (Osowole, 2008). The precipitate was filtered off, washed with ethanol and dried under vacuum.

Antibacterial Activity

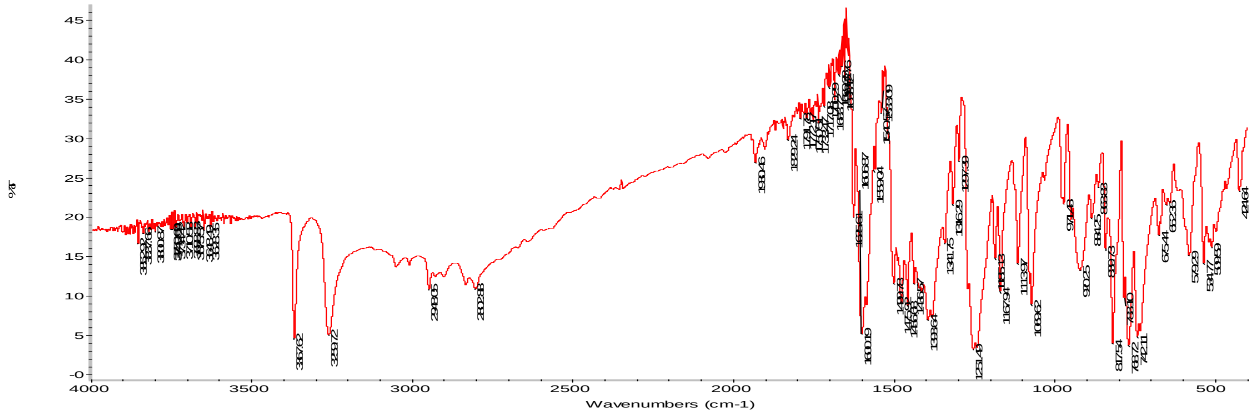
Antibacterial activity was evaluated using agar diffusion method (Bauer *et al*., 1966)Gram-negative(*Salmonella typhi* and *Escherichia coli*). Which were cultivated in nutrient agar on petri dishes. The test solution was prepared by dissolving (10 gm) of the tested substances in DMSO(1 ml). A6mm diameter filter discs were socked in the tested solutions. After 2h cultivation at37°C, dimeter of zones of inhibition was determined. DMSO was inactive under applied conditions.

Result and discussion

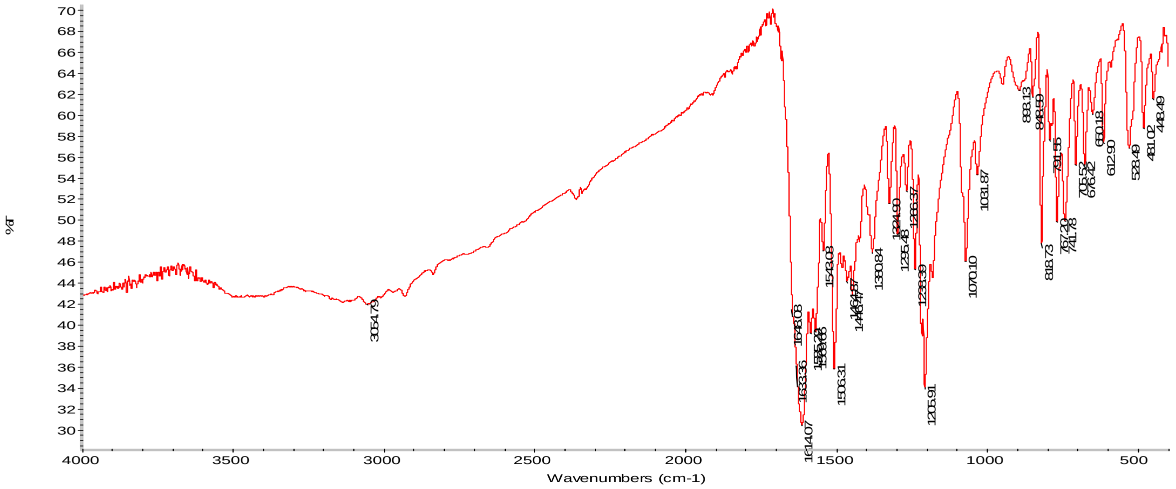
All the metal complexes are quite stable in dry air and insoluble in common organic solvents but soluble in DMF and DMSO.The elemental analysis shows(1:1) (M:L) molar ratio for[M L^n] and(1:1:2) [M :L^n: py].Some physical properties of ligands and their complexes are listed in (Table 1).The molar conductance in 10^{-3} M DMFsolution of complexes are in the range (0.4-26.18) ohm^{-1} cm^2 mol^{-1}, indicating a non-electrolytic nature of the complexes (Padmaja *et al.,* 2011).

IR Spectra

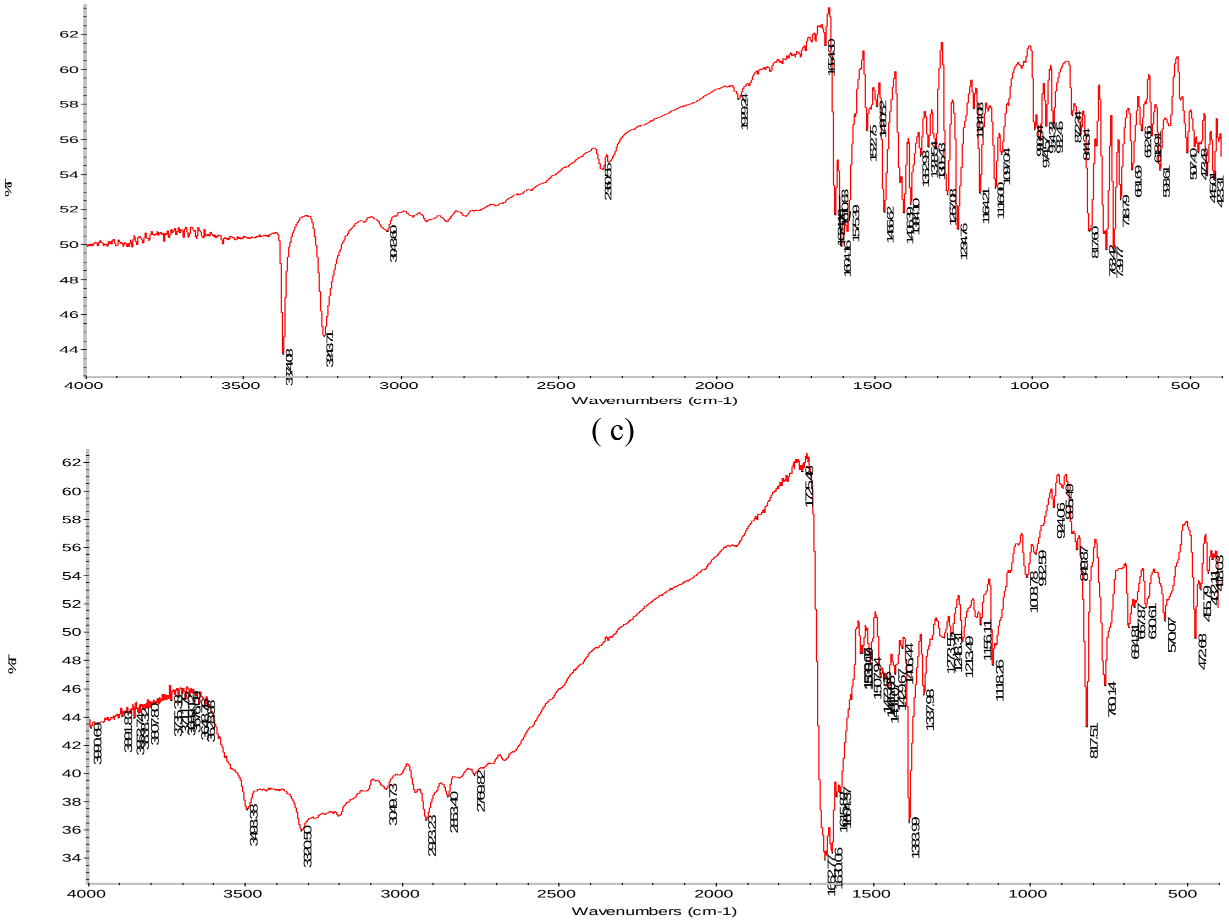
The position of the important bands of Schiff bases and their complexes are shown in the (Table 2). Due to the unsymmetrical nature of the ligands and their complexes two bands were observed for each of the following groups. υ (C=N); υ (C-O) and υ (OH) taking their origin from the different aldehyde (Nejo *et al*., 2009; Hegzy and Gaafar, 2012). The ligands (H_2L^1 and H_2L^2) exhibited characteristic υ(C=N)stretching frequencies at(1606,1625)and(1610,1624)cm^{-1} respectively, which shift to higher frequencies, upon complexation (Al-kattan and Al-Nidaa, 2014).This indicates participation of azomethine nitrogen in bonding (Arhana *et al.,* 2007). The IR spectrum of the free ligands shows bands at (3259, 3367) cm^{-1} and (3243,3374) cm^{-1} due to phenolic υ(OH) group for H_2L^1 and H_2L^2 respectively (Pethe *et al.*, 2017). The absence of these bands in the spectra of allcomplexes and adducts indicates the coordination of phenolic oxygen to the metal after deprotonation (Munde[1]*et al.*, 2010;Yaul *et al.*, 2009). This is further supported by the shifting of υ(C-O)phenolic bands (1185,1251)cm^{-1} and(1234,1267) cm^{-1} for H_2L^1 and H_2L^2 respectively to higher wave numbers in the complexes(Maurya *et al.*, 2001). Thus, it can be concluded that the Schiff bases act as dibasic tetradentate ligands via the azomethine N and phenolic O atoms (Hancock and Thornton, 1969). Assignment of the proposed coordination sites is further supported by the appearance of new band at (450-481) cm^{-1} and(503-580) cm^{-1} which could be attributed to υ (M-N) and υ(M-O) respectively (Joel, 2015; Bagat *et al.*, 2009). For (5,6,7,12.13,14) complexes the band of υ (C=N) was observed at (1473-1506)cm^{-1} which means the coordination of the N atom of pyridine ring with the metal ions (Srinivasan *et al.*, 2010).The I.R spectra of the ligands and their Ni(II) complexes have been shown in Fig1.



(a)



(b)



(c)

(d)

Fig 1:The I.R spectrum of (a) H_2L^1(b)[NiL^1] (c) $H_2L^2$and(d)**[NiL^2]**

Electronic Spectra and Magnetism

The magnetic moments and electronic spectral data at 25^{0}C of the ligands and theircomplexes are listed in (Table 3).The electronic spectra of the ligands H_2L^1 and H_2L^2 in DMF solution show the aromatic intense bands at (34233and 35000)cm^{-1} attributed to π→π* transitionand at (32333 and 33232) cm^{-1} due to the n→π* transition of non-bonding electrons present on the nitrogen of the azomethine group. These transitions are also found in spectra of complexes but they are shifted, confirming the coordination of ligands to metal ions (Zeyrek *et al.*, 2005). The new bands in spectra of all complexes at the range (27027-30027) cm^{-1}may be associated with the charge transfer transition(Khandar *et al.*, 2011). The magnetic moment values of Co(II) complexes (1,8) are found to be (2.89,2.15)B.M respectively indicating square-planar (Bailar andVraban,1973). Their electronic spectra show absorption band at (16528,16728) cm^{-1} respectively, attributed to the ^2A_1g→ $^2E'g$ transition, indicating a square-planer geometry for Co(II) complexes(Ahmed *et al.*, 2009),while the magnetic moment of Co(II) complexes (5,12) equal(4.91, 4.96) B.M indicating octahedral geometry (Pathan *et al.*, 2012) and the electronic spectra of these complexes showed d-d transitions at (15151 ,15251)cm^{-1},(20000 and 20618)cm^{-1}assignable to$^4T_1g(F)$→$^4A_2p(F)$ and$^4T_1g(F)$→$^4T_1g(p)$ respectively indicating octahedral geometry around Co(II) ions (Matrtell, 1971).

The Ni(II) complexes (2,9) are diamagnetic moiety because its magnetic moment is almost zero. Therefore, the Schiff bases ligands coordinate to Ni(II)ion as tetradentate chelating agent with a square-planar environment(Raman *et al.*, 2007). The electronic spectra of these complexes show absorption bands at (17666and17680) and (23529 and 23727) cm^{-1} attributed to the^1A_1g→^1A_2g and^1A_1g →^1B_1g transitionrespectively. This shows that Ni(II) complexes have a square–planer geometry (Fierro *et al.*, 2011). For Ni(II) complexes (6,13) the magnetic moment values are

(2.83,3.15) B.M, indicating the octahedral configuration with two unpaired electrons (Al-Daher and Mohammed, 2018) and The electronic spectra of those complexes show bands at (17857,18518) cm^{-1} and (23419,23529) cm^{-1} assignable to$^3A_2g(F)\rightarrow{}^3T_1g(F)$ and $^3A_2g(F)\rightarrow{}^3T_1g(P)$; these bands are characteristicsof octahedral geometry (Singh *et al*., 1989).

The obtained magnetic moment values for Cu(II) complexes (310) are (1.80 and 1.82) B.M indicating square-planar system (Lever, 1968).The electronic spectra of Cu(II) complexes showed weak bands at (17600 and 17857) and (24810 and 24814)cm^{-1} is attributed to the $^2B_1g\rightarrow{}^2A_1g$ and $^2B_1g\rightarrow{}^2Eg$ transition respectively which is comparable with complexes having square-planar structure (Lever *et al*., 1984).The obtained magnetic values of Cu(II) complexes (7,14) at (1.94 ,1.98)B.M indicating octahedral system (Pathan *et al*., 2012). The electronic spectra of Cu(II)complexes showed one broad band at (13888,14705) cm^{-1} which might be assigned to$^2Eg\rightarrow{}^2T_2g$ transition suggesting an octahedral (Cotton *et al*.,1999) geometry around Cu(II) in these complexes.

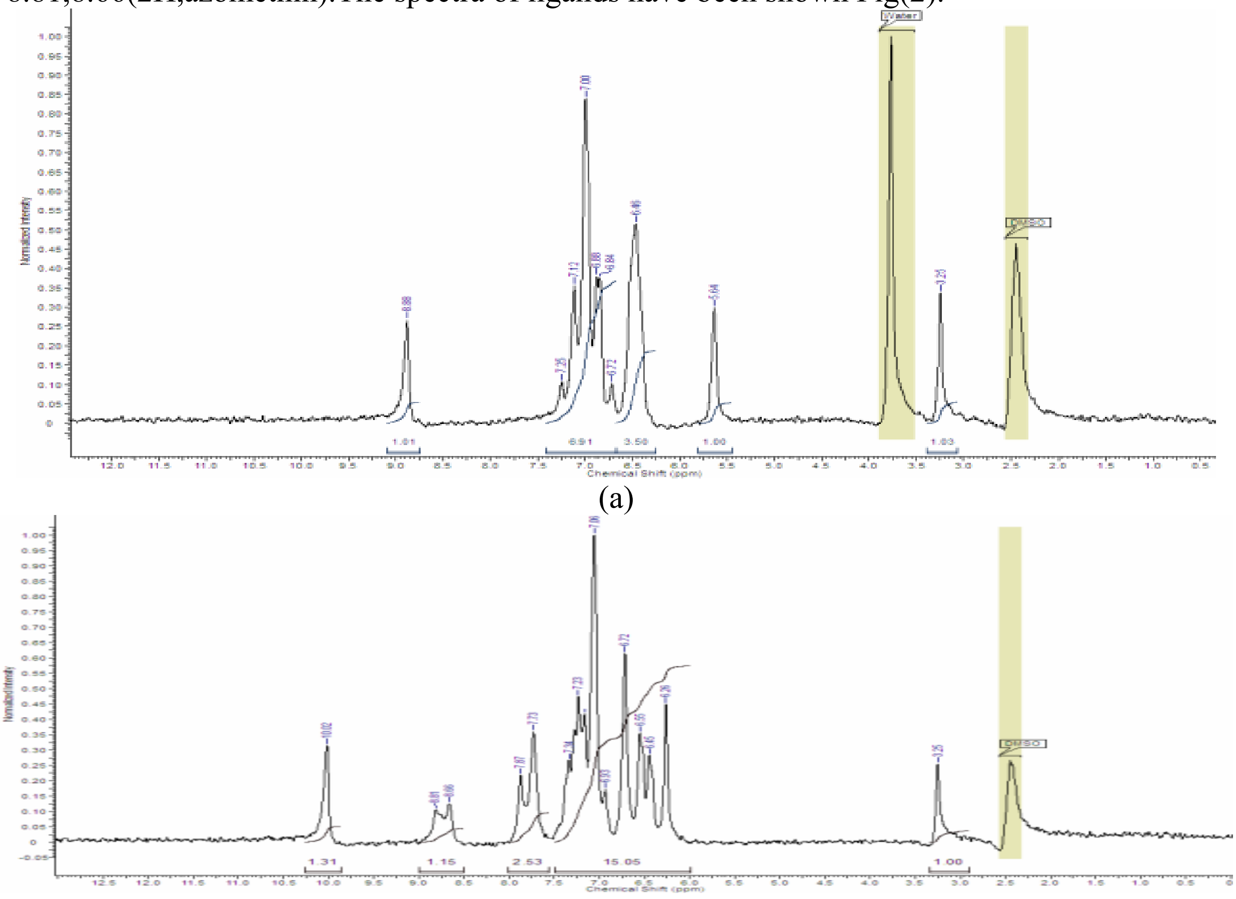
The electronic spectrum of Zn(II) complexes (4,11) show only a band at (28277-29250) cm^{1}attributed to the ligands charge transfer transition. The Zn (II) complexes are expected to be diamagnetic and their geometry is most probably similar to the Co(II),Ni(II) and Cu(II) complexes, depending on the data of other measurements namely metal content and I.R spectra(Geary 1971).

^{1}H-NMR-Spectra of ligands.

The^{1}H-NMR.spectra of free ligand at room temperature in DMSO-d^6 shows the following singles(Shelke *et al*., 2012;Wahba *et al.,* 2017).

ForH$_2$L^1:δ=3.25(3H,-CH$_3$),δ=3.25(3H- OCH$_3$), δ=5.64 (2H,phenolic), δ= (6.46-7.25) (13 H, aromatic),δ=8.88 (2H, azomethine).

ForH$_2$L^2:δ=10.02(2H,phenolic),δ=((6.26-7.34)),(7.737.87))(16 H, Aromatic), δ=3.25 (3H,CH$_3$), δ=8.81,8.66(2H,azomethin).The spectra of ligands have been shown Fig(2).



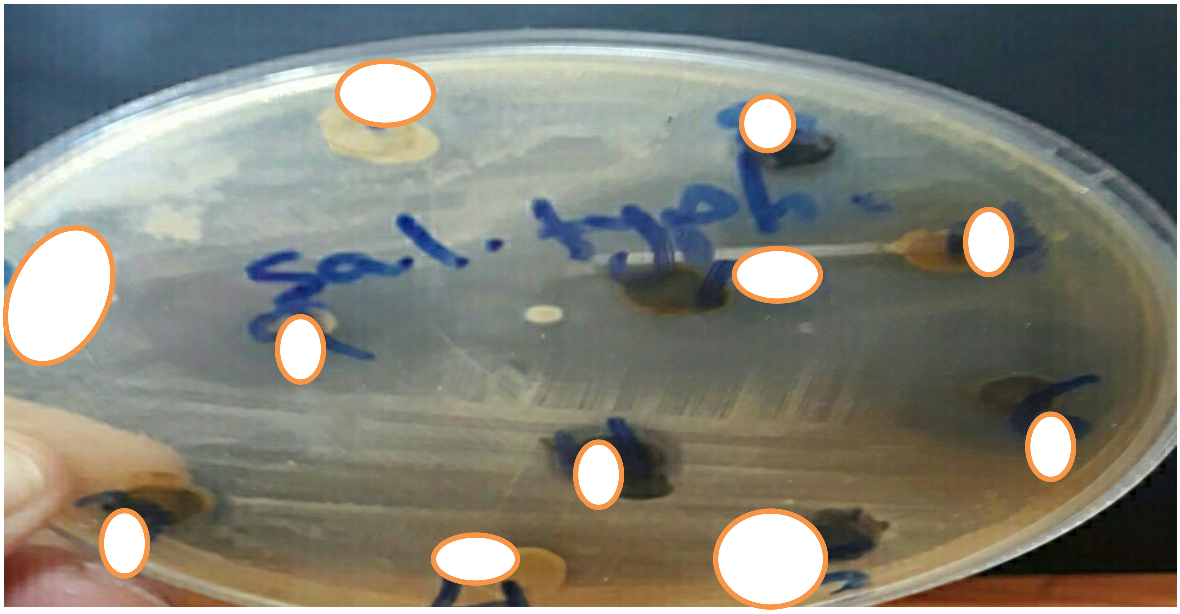
(a)

(b)

Fig 2: ^{1}HNMR of(a) H$_2$L^{1}and (b) H$_2$L^2

Antibacterial Activity:

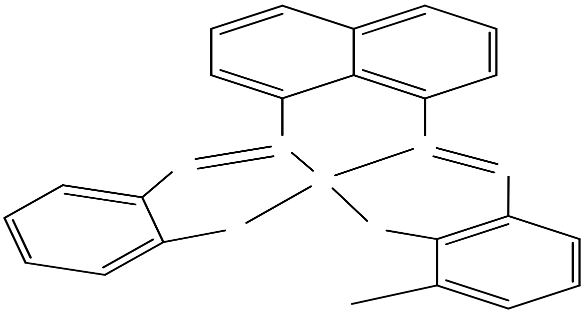
The tested compounds were screened in vitro for their antibacterial activity against bacteria gram negativebacteria(*Salmonella typhi* and *Escherichia coli*). The anti- bacterial results are given in (Table 4), Compared with those of the standard drug ceftriaxone. The results evidently show that metal(II) complexes have been shown to be more effective than the free ligands. Theactivity order of the synthesized compound against *Salmonella styphi* of synthesized compounds is as follows$[NiL^2(py)_2]>[CoL^1]>[NiL^2]>$ $[NiL^1(py)_2]>[CoL^1(py)_2]$ while the antibacterial activity of ligands and other complexes =zero. The activity order of the synthesized compound against *Escherichia coli*$[NiL^1]=[NiL^2]>[NiL^1(py)_2]>[NiL^2(py)_2]>$ $[CoL^1(py)_2]$ while the antibacterial activity of ligands and other complexes = zero ligands higher antibacterial activity of some metal complexes than the free Schiff base ligands that can be explained by chelation of Schiff base with metal ions (Joseyphus and Nair, 2008) as chelates display both polar and nonpolar properties; this makes them suitable for permeation into cells and tissues.



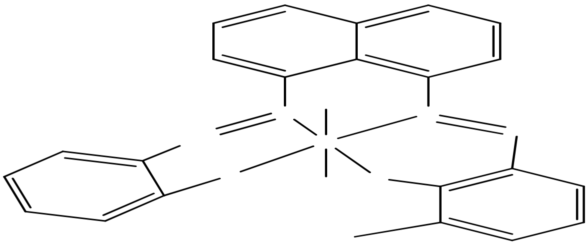
(a) (*Salmonila taphi*)

(b)(*Escherichia coli*)

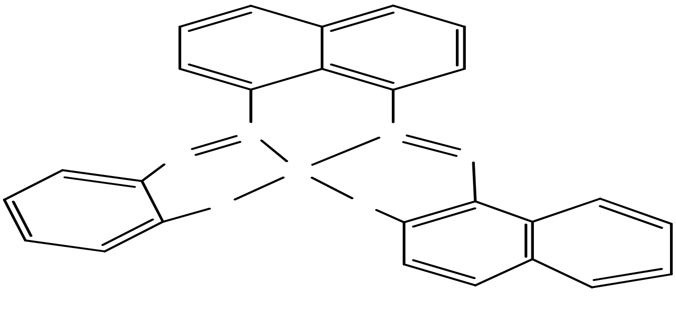
Fig 3 : Antibacterial Bacterial Activity of ligands and complexes for (a) *Salmonella typhi*,(b) *Escherichia coli*



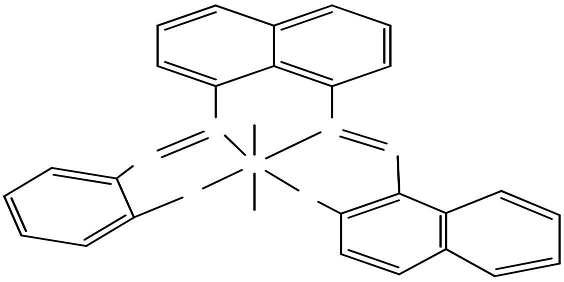
[ML[1]]
Complexes (1,2,3,4)
M=Co(II),Ni(II),Cu(II),Zn(II)



[ML[1](py)$_2$]
Complexes (5,6,7)
M=Co(II),Ni(II),Cu(II)



[ML[2]]
Complexes(8,9,10,11)
M=Co(II),Ni(II),Cu(II) ,Zn(II)



[ML[2](py)$_2$]
Complexes(12,13,14)
M=Co(II),Ni(II),Cu(II)

Fig 4 :Suggested structure of complexe

Table 1: Some physical properties and analysis of the ligands and their complexes

NO.	Complexes	Color	m.p(C^0)	Analysis calc.(found)%			M% Calc. (found)	Λm(ohm^{-1} cm^2 mol^{-1})
				%C	%H	%N		
H_2L^1	$C_{26}H_{22}N_2O_3$	Milky	190-191	76.07 (76.03)	5.40 (5.20)	6.82 (6.50)	-----	----
1	[Co L^1]	Dark green	>300 d	----	-----	-----	12.60 (12.50)	5.19
2	[Ni L^1]	Orange	238 d	66.84 (66.40)	4.31 (4.10)	5.99(4.45)	12.56 (12.30)	7.00
3	[Cu L^1]	Drack grey	>300 d	----	-----	-----	13.46 (13.10)	16.88
4	[Zn L^1]	Orange	219 d	----	----	-----	13.79 (13.52)	4.47
5	[Co L^1 $(py)_2$]	Drack brown	257 d	-----	-------	------	9.42 (9.28)	11.55
6	[Ni$L^1(py)_2$]	Green-Yellow	293 d	-----	-----	-----	9.38 (9.15)	5.05
7	[Cu $L^1(py)_2$]	Drack grey	>300d	68.61 (68.30)	4.79 (4.36)	8.89 (8.72)	10.08 (10.01)	10.41
H_2L^2	$C_{29}H_{22}N_2O_2$	Off white	182-184	80.90 (80.70)	5.15 (5.02)	6.50 (6.32)	------	-
8	[Co L^2]	Orange	228 d	71.46 (71.30)	4.13 (4.05)	5.74 (5.30)	12.09 (11.98)	10.55
9	[Ni L^2]	Black	167 d	-----	-----	------	12.05 (12.00)	26.18
10	[Cu L^2]	Drack grey	>300 d	-----	------	------	12.91 (12.42)	19.89
11	[Zn L^2]	Drack orange	184-186	-----	-----	-----	13.23 (13.08)	0.4
12	[Co $L^2(py)_2$]	Medium brown	144 d	72.55 (72.50)	4.68 (4.51)	8.67 (8.34)	9.12 (9.02)	5.57
13	[Ni $L^2(Py)_2$]	Yellow	234 d	------	------	------	9.09 (8.99)	24.96
14	[Cu L^2 $(py)_2$]	Drack Green	246 d	------	------	------	9.77 (9.50)	9.09

Table 2: Characteristic Infrared spectral data of the ligands and their complexes

NO.	Complexes	IR spectral bands (cm-1)					
		υ (C=N imin)	υ (C-O) phenol	υ(O-H)	υ (M-N)	υ(M-O)	υ C= Npyridine ring
H_2L^1	$C_{26}H_{22}N_2O_3$	(1606,1625)s	(1185,1251)s	(3259, 3367)s	----	----	-----
1	[Co L^1]	(1618, 1635)s	(1247,1293)m	-----	473m	527s	------
2	[Ni L^1]	(1633,1648) s	(1238, 1266) s	-----	481 w	528 m	------
3	[Cu L^1]	(1616,1652) s	(1245, 1256) s	-----	458 w	520m	------
4	[Zn L^1]	(1612,1654) s	(1240, 1260) m	------	478 w	520 s	------
5	[Co L^1 $(py)_2$]	(1615,1666) s	(1194, 1273) s	-----	472w,475m	575 w	1473m
6	[Ni$L^1(py)_2$]	(1620,1635) s	(1248,1271) s	------	475w,480w	520 m	1506s
7	[Cu $L^1(py)_2$]	(1622,1658) s	(1250 , 1268) s	--------	470 m,475w	530 w	1500s
H_2L^2	$C_{29}H_{22}N_2O_2$	(1610,1624) s	(1234, 1267)s	(3243, 3374)s	-----	------	-----
8	[Co L^2]	(1615,1666) s	(1251, 1275) s	-------	480 w	516m	-----
9	[Ni L^2]	(1630,1652)s	(1248, 1273) s	-------	472 w	570 m	-----
10	[Cu L^2]	(1628,1635) s	(1244,1274) s	-------	472 w	529 m	------
11	[Zn L^2]	(1612,1630) s	(1248,1270) s	------	472w	503 m	-----
12	[Co $L^2(py)_2$]	(1616,1635) s	(1245, 1271) s	-------	450 w,472m	569 m	1488m
13	[Ni $L^2(Py)_2$]	(1640,1655) s	(1255, 1280) s	------	481 m,475,	580 w	1500m
14	[Cu L^2 $(py)_2$]	(1630,1642) s	(1250, 1286) s	------	450m,480 m	560 m	1498w

s= strong ,m=medium , w= weak

Table 3 : Magnetic moments and the electronic spectral data of the ligands and their complexes

No.	Complexes	μ_{eff} (B.M)	assignment	Band maxima λ(cm^{-1})	Strut.
H_2L^1	$C_{26}H_{22}N_2O_3$	----	n→π*, π → π*	32333 ,34233	----
1	$[CoL^1]$	2.89	$^2A_1g \rightarrow {}^2E'g$, C.T	16 528 , 27397	S.q
2	$[NiL^1]$	Diamagnetic	$^1A_1g \rightarrow {}^1A_2g, {}^1A_1g \rightarrow {}^1B_1g$, C.T	17680 , 23529 ,28857	S.q
3	$[CuL^1]$	1.80	$^2B_1g \rightarrow {}^2A_1g, {}^2B_1g \rightarrow {}^2Eg$,C.T	17857 ,24810,27777	S.q
4	$[Zn\ L^1]$	Diamagnetic	C.T	29 250	S.q
5	$[Co\ L^1(py)_2]$	4.69	$^4T_1g(F) \rightarrow {}^4A_2g(F), {}^4T_1g(F) \rightarrow {}^4T_1g(p)$	15251,20618,27777	oct
6	$[NiL^1\ (py)_2]$	3.15	$^3A_2g(F) \rightarrow {}^3T_1g(F), {}^3A_2g \rightarrow {}^3T_1g(p)$	17857,23419,30027	oct
7	$[Cu\ L^1(py)_2]$	1.98	$^2Eg \rightarrow {}^2T_2g$	14705,27777	oct
H_2L^2	$C_{29}\ H_{22}\ N_2\ O_2$	----	n→π*, π → π*	33232 , 35000	----
8	$[Co\ L^2]$	2.15	$^2A_1g \rightarrow {}^2E'g$, C.T	16728,28345	S.q
9	$[NiL^2]$	Diamagnetic	$^1A_1g \rightarrow {}^1A_2g, {}^1A_1g \rightarrow {}^1B_1g$, C.T	17666, 23727, 27777	S.q
10	$[Cu\ L^2]$	1.82	$^2B_1g \rightarrow {}^2A_1g, {}^2B_1g \rightarrow {}^2Eg$, C.T	17600,24814,29500	S.q
11	$[Zn\ L^2]$	Diamagnetic	C.T	28277	S.q
12	$[Co\ L^2(py)_2]$	4.91	$^4T_1g(F) \rightarrow {}^4A_2g(F), {}^4T_1g(F) \rightarrow {}^4T_1g(p)$	15151,20000,27777	oct
13	$[Ni\ L^2(py)_2]$	2.83	$^3A_2g(F) \rightarrow {}^3T_1g(F), {}^3A_2g \rightarrow {}^3T_1g(p)$	18518,23419,29221	oct
14	$[Cu\ L^2(py)_2]$	1.94	$^2Eg \rightarrow {}^2T_2g$	13888,27027	oct

Table 4: The antibacterial activities of Schiff base and their complexes

complexes	*Salmonila styphi*	*Escherichia coli*
H_2L^1	0	0
$[CoL^1]$	22	0
$[NiL^1]$	0	22
$[CuL^1]$	0	0
$[ZnL^1]$	0	0
$[CoL^1(py)_2]$	15	13
$[NiL^1(py)_2]$	17	20
$[CuL^1(py)_2]$	0	0
H_2L^2	0	0
$[CoL^2]$	0	0
$[NiL^2]$	18	22
$[CuL^2]$	0	0
$[ZnL^2]$	0	0
$[CoL^2(py)_2]$	0	0
$[NiL^2(py)_2]$	35	18
$[CuL^2(py)_2]$	0	0

Inhibition zone diameter(mm)(%inhibition)(6-10)(27-45%;10-14(45-64%);14-18(62-82%);18-22(82-100%)

CONCLUSION

Unsymmetrical Schiff bases and their complexes were prepared and characterized by spectral and analytical data. The synthesized Schiff base acts as adibasic tetradentate ligand coordinated via phenolic oxygen and azomethine nitrogen atoms illustration Fig (4). Magnetic and electronic spectral studies reveal square-planar structure for[ML] complexes and octahedral structure for $[ML^n(py)_2]$ adducts and from the test of bacteria we found that Some complexes have high activity towards gram negativebacteria (*Salmonella typhi* and *Escherichia coli*).

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