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Synthesis, Characterization, and Biological Efficacy on new mixed ligand complexes based from azo dye of 8-hydroxy quinoline as a primary ligand and imidazole as a secondary ligand with some of transition metal ions

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Abstract:

New series of mixed ligand complexes of Mn(II), Co(II), Ni(II) , Cu(II) , and Hg(II) ions were prepared in two general formula [M (L1)$(L_2)_2$]Cl , and [M $(L_1)_2(L_2)_2$] for each ion with E-5-((4-nitro phenyldiazanyl)quinoline-8-ol (L_1) as primary ligand , and imidazole molecule (L_2) as a secondary ligand . Free ligands and their complexes characterized via MS , UV-Vis. , FTIR , ^{1}HNMR, Magnetic suscbtibility, and Molar Conductivity . The results indicating the octahedral geometry for all compounds with [M$(L_1)_2(L_2)_2$] formula while the complexes which have general formula [M$(L_1)(L_2)_2$]Cl articulate tetrahedral geometry except [Cu$(L_1)(L_2)_2$]Cl which has square planer geometry . (L_1) ligand behaved as bidentate through nitrogen atom and oxygen atom of hydroxyl group in the basic medium whereas imidazole coordinated through nitrogen (3) as a neutral monodintate ligand. Antibacterial efficiency of compounds were tested against (*Enterococcus faecalis* , *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeroginosa*, *Proteus mirabilis* and *Klebsiella pneumoniae*) multi-drug resistant bacteria (MDR). All compounds appeared significant efficacy contra MDR bacteria, but ligand L_1 appeared maximum inhibition zone and anti-bacterial efficacy contra all MDR bacteria while the minimum inhibition zone was marked in ligand L_2 antibacterial efficacy. The complexes generally have high antibacterial activities in gram +ve bacteria contrasted to gram -ve bacteria, where Hg (II) ion complexes showed higher biological efficacy on all bacteria than other mixed ligand complexes of other ions. Ni (II) ion complexes showed lower antibacterial activity compare to other metal complexes.

Key words: Azo compounds , 8-hydroxyquinoline , imidazole , mixed ligand compounds , biological efficacy.

INTRODUCTION:

Mixed ligand complexes of transition metal ions have great interesting from the researchers who study their coordination behavior and exploiting their properties in a different fields especially the antibacterial activity [1-3] , 8-hydroxy quinoline is an important compound which has the ability to coordinate with a various ions as bidentate through nitrogen atom of quinoline ring and oxygen atom after deprotonation of hydroxyl group [4-7] to format five member ring between this ligand with the central metal ion that helps to increase the stability of the complexes , as well as its known biological activity [8] , Imidazole molecule is a part of the installation of many biological systems such as histidine and many of its derivatives have been used as antibacterial, antifungal and anticancer agents also the important using to estimation of metal ions in drugs[9,10]. This molecule has an ability to coordinate alone with metal ions as monodintate ligand through (N_3) atom [11] .

Pathogenic bacteria have caused dangerous illnesses and a lot of mortality in numerous countries, chiefly in the developing nations. These factors commonly diffusion speedily, and the common contagion to them have been appointed to the immune-compromised individuals, gravid women, children, and elderly persons [12]. Along with the gradual resistance of bacteria to the existing antibiotics as a consequence of irregular antibiotic exhaustion in medicine, the health and general hygiene of people are strongly at risk, and, thence , to avoid this threat, recognition and using new anti-bacterial compounds are requested [13]. In the lately years, empirical research have showed some of the imidazole derivatives, numerous features such as the antifungal, antiviral, anti-parasitic, and in-vitro inhibition of cancer cells have been showed the antibacterial effects of these compounds has confirmed their capability to inhibit pathogenic bacteria such as *E. faecalis*, *S. aureus*, and *P. aeruginosa* [14,15].

The purpose of the present study is attended of mixed ligand complexes of azo dye of 8-hydroxy quinoline as a primary ligand and imidazole as a secondary ligand with Mn(II) , Co(II) , Ni(II) , Cu(II) , while Hg(II) in a different ratios of the primary ligand and char action them by spectrometric techniques and examine the biological activity against different species of MDR bacteria .

MATERIALS AND METHODS

Chemicals and Instruments :

All chemical compounds used in this study were supplied by Merck , and B.D.H companies chemical company with 99% of purity , Electronic spectra measured by (UV-Vis)T80 , PG instruments Ltd. UK , while IR spectra recorded by (FTIR)-Platinum –ATR Bruker using KBr disk (400-4000)cm$^-$, Molar conductivity performed on 720(WTW) , Mass spectra was carried out by AB SCIEX 3200 QTRAP Mass analyzer , The element analysis was measured by Costech ECS Elemental 4010 , while magnetic measurements of complexes carried out by Balance Magnetic Susceptibility Model –M.S.B Auto , and ^{1}HMR in DMSO-d6 solvent recorded by Bruker Avance-111 300 MHz NMR Spectrometer .

Preparation of (L_1) ligand

4-nitro aniline (1.38 gm,10 mmole) dissolved in a mixture of (3 ml of HCl, and 15 ml of distilled water) in an ice bath with temperature below (5)^{o}C , then diazotized by adding a mixture of (0.70 gm $NaNO_2$, and 10 ml of cold distilled water) drop by drop with continues stirring , The resulting diazonuim salt was coupled with an alcoholic (0.44 gm NaOH , and 15 ml of ethanol) solution of (1.45 gm,10 mmole) 8-hydroxy quinoline . After neutralization with diluted HCl solution the ligand was separated by filtration then dried in air , The yellow precipite was produced with 79% of yield as shown in **scheme (1).**

Preparation of complexes (general method)

The solid complexes were prepared by mixing (10) mmole of the primary ligand (L1) for [M$(L_1)(L_2)_2$]Cl formula , and (20)mmole for [M$(L_1)(L_2)_2$] formula with (20) mmole of imidazole (L_2) , and (10) mmole of metal chloride in (25) ml of absolute ethanol. The drops of (1)N of NaOH added to this mixture reflux the

mixture for (2) hours until the precipitation was formed then filtered , dried in air , and recrycltized from ethanol. The schemes (2) and (3) show the general reaction to prepare the complexes , and table(1) illustrate some of physicochemical properties of ligands and its complexes.

Biological Activity

Bacterial Isolates:

The following multi drug resistance (MDR) pathogenic bacterial isolates: two gram +ve bacteria (*Staphylococcus aureus* and *Enterococcus faecalis*) while four gram –ve bacteria (*Proteus mirabilis, Escherichia coli, Pseudomonas aeroginosa* and *Klebsiella pneumoniae*) were isolated from different clinical specimens like sputum, stool, CSF, wound, blood and urine. The isolates were diagnosed using a range of morphological as well as biochemical technicalities [16] , and then finally confirmed by using Vitek-2 compact system GP and GN card automated bacterial identification instrument. All bacterial isolates were stocked on brain heart infusion broth with (15%) glycerol at (-20 °C). The isolates were sub-cultured on brain heart infusion agar and incubated at 37 °C for 24h before use.

Preparation of ligands and Complexes solutions:

The following concentrations were used in the antibacterial test:

1- Ligand concentration: 0.01 g of powder each ligand (L_1 and L_2) were dissolved in 1ml of DMSO to give concentration 10 mg/ml.

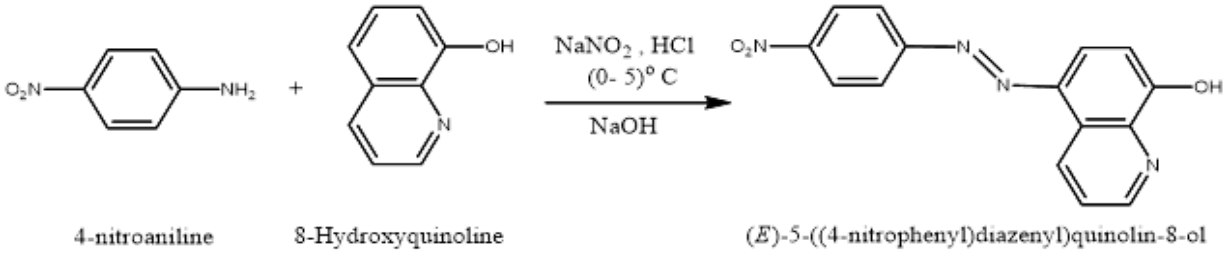
2- Mixed ligand complexes of ions: 0.01 g of powder of each complexes of Mn(II), Co(II), Ni(II), Cu(II) and Hg(II) for $[M(L_1)(L_2)_2Cl]$, and $[M(L1)_2(L_2)_2]$ formulas were dissolved in 1ml of DMSO to give 10mg/ml concentration.

Antibacterial activity experimental

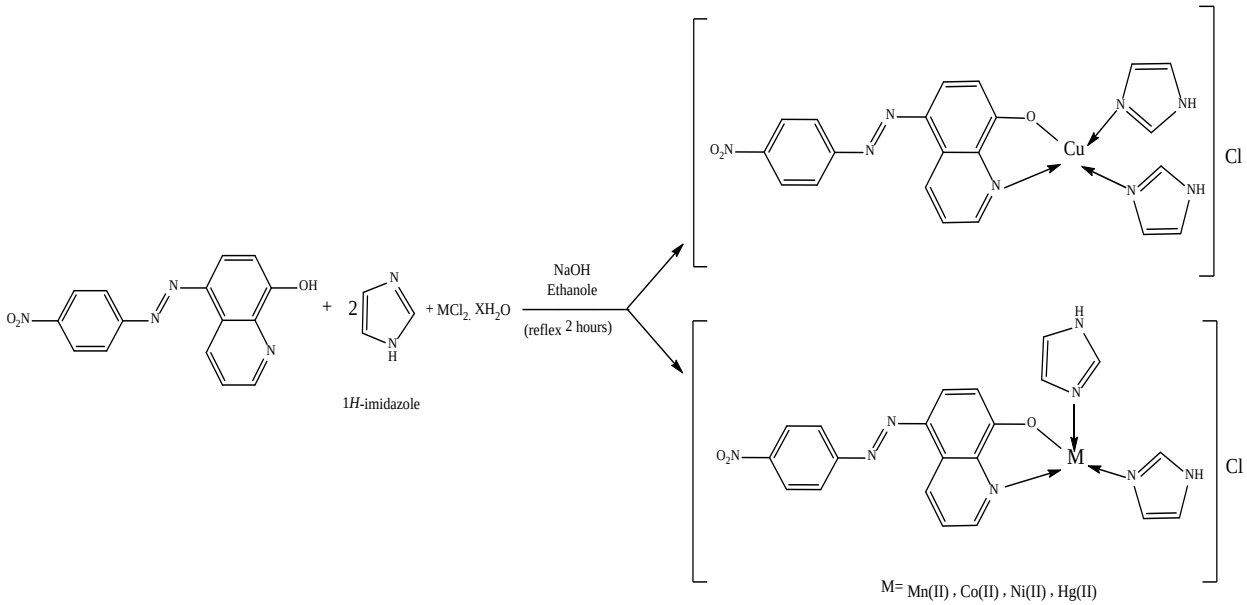
Bacterial suspensions were prepared as explained by [**17]** . Agar well diffusion method used to determine the antibacterial activity of ligands and mixed ligand complexes of ions against bacterial isolates **[18].** Brain heart infusion broth (BHIB) was used for the elaboration of MDR bacterial cultures. Muller Hinton agar (MHA) was used to determine the activity of ligands and mixed ligand complexes of ions against bacterial . These media were attended similarity to the industrial's prescript.

Agar well diffusion assay

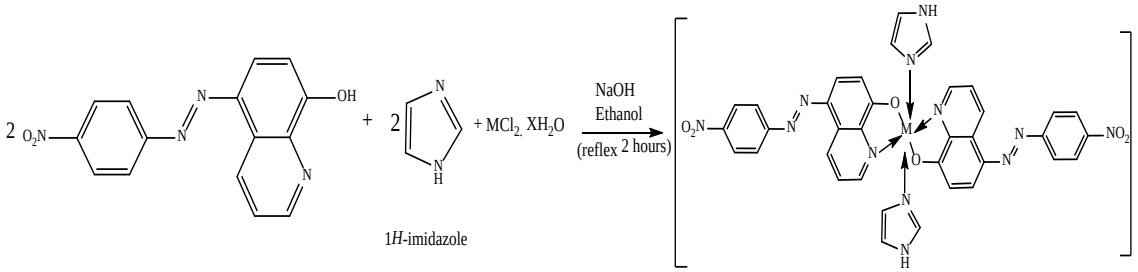
Bacterial isolates suspensions were attended to resemble 0.5 McFarland standards. Utilizing the micropipette, 100 µl of bacterial suspensions BHIB was diffuse up the superficies of MHA plate. This procedure was utilized for all experimental MDR bacteria. Utilizing an antiseptic cork borer, punctures were perforation in all of the culture plates. One of the punctures was perforation in the center of the plate where 100 µl of Gentamicin was inserted as positive control; 100µl of DMSO was inserted as a negative control in the other hole; 100µl of each ligands and mixed ligand complexes of ions were alone placed in the remaining holes [five holes to the $[M(L_1)(L_2)_2]Cl$ complexes and five holes to other ratio $[M(L_1)_2(L_2)_2]$ complexes. The culture plates were then incubated at 37°C for 24 h. The clear zone of inhibition around holes was calculated in mm. The tests were carried out in triplicate **[19]**.



Scheme(1): Preparation of (L_1)

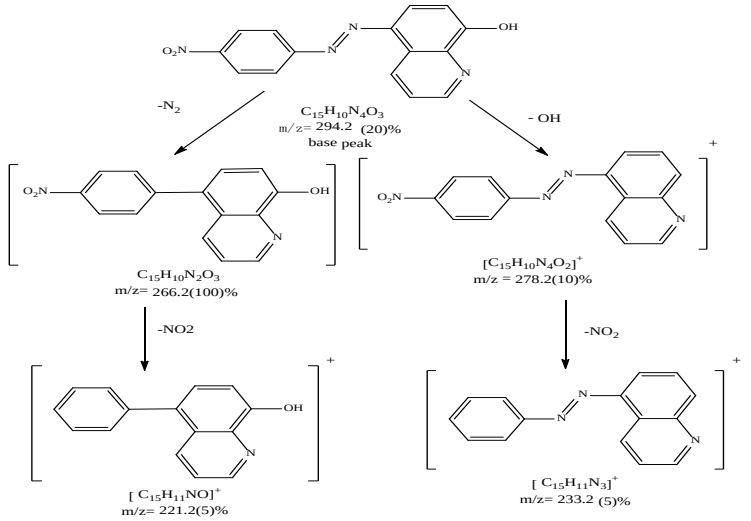


Scheme (2) : Synthesis of $[M(L_1)(L_2)_2]Cl$ Complexes

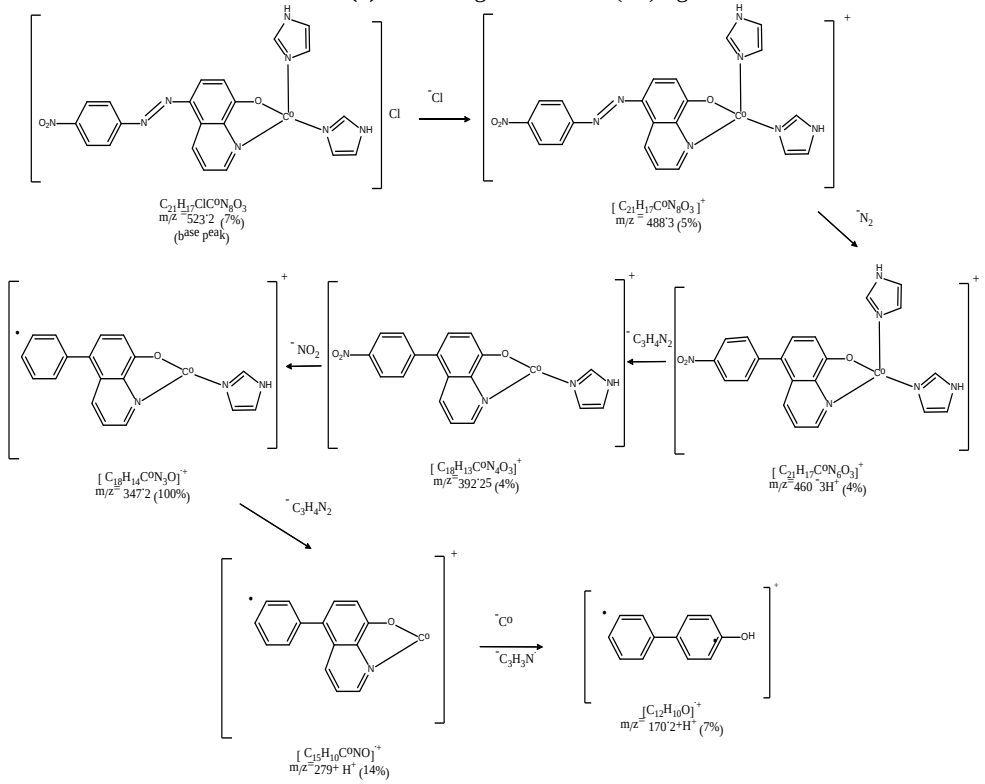


(*E*)-5-((4-nitrophenyl)diazenyl)quinolin-8-ol

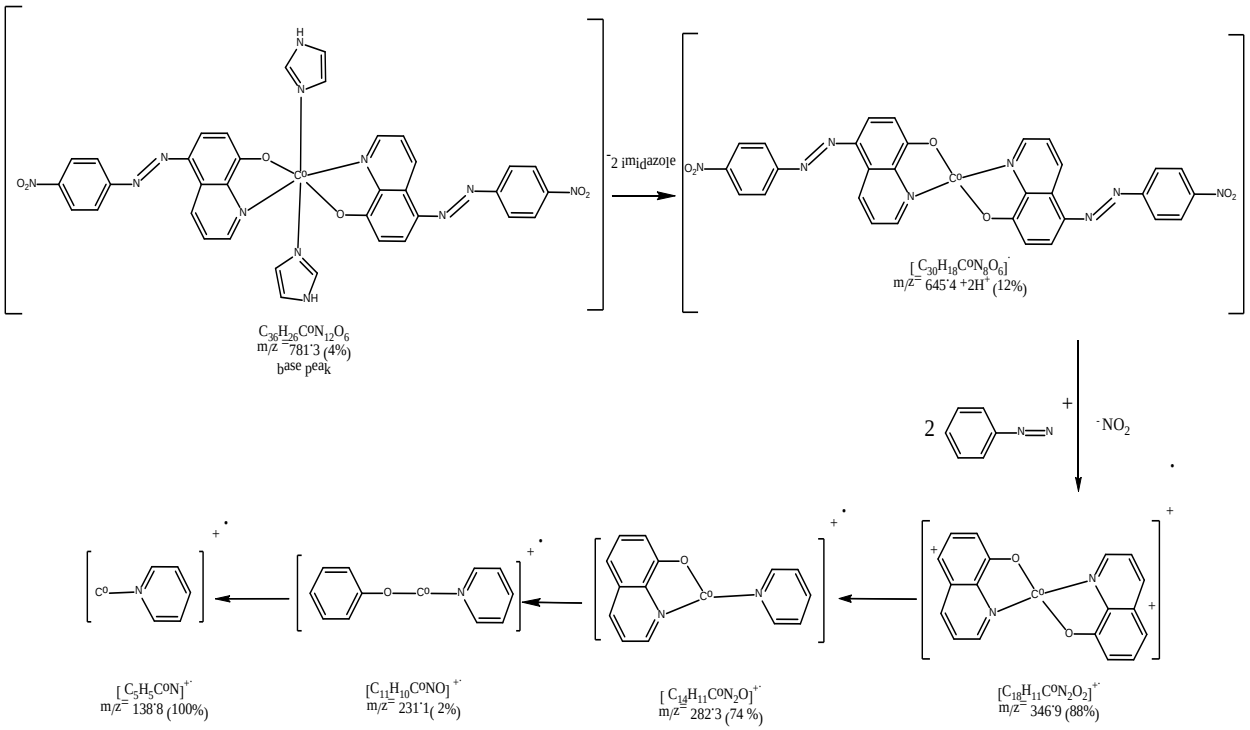
Scheme (3) : Synthesis of $[M(L_1)_2(L_2)_2]$ Complexes



Scheme (4): Mass fragmentation of (L1) ligand



Scheme (5) : Fragmentation of [Co (L_1) (L_2) $_2$] Cl Complex



Scheme (6) : Fragmentation of [Co $(L_1)_2$ $(L_2)_2$] Complex

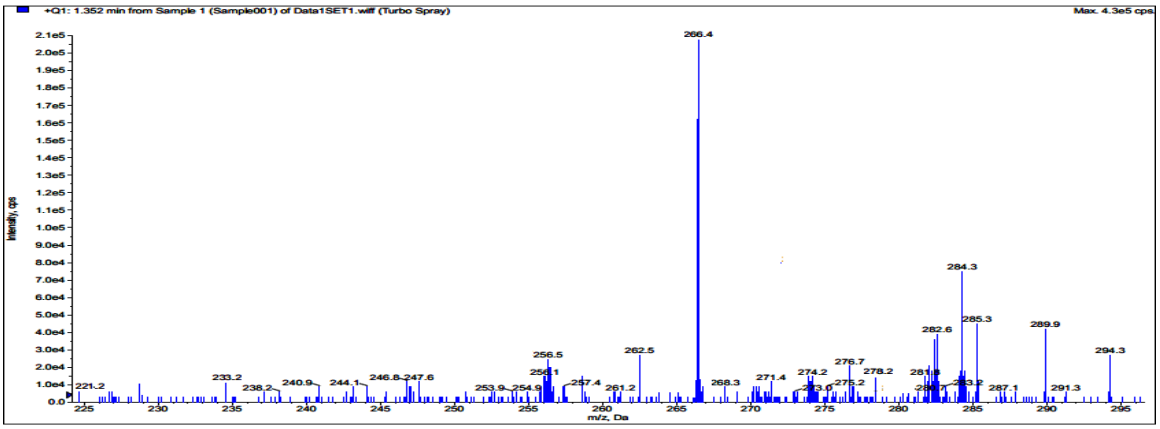


Figure 1: Mass spectrum of(L_1)ligand

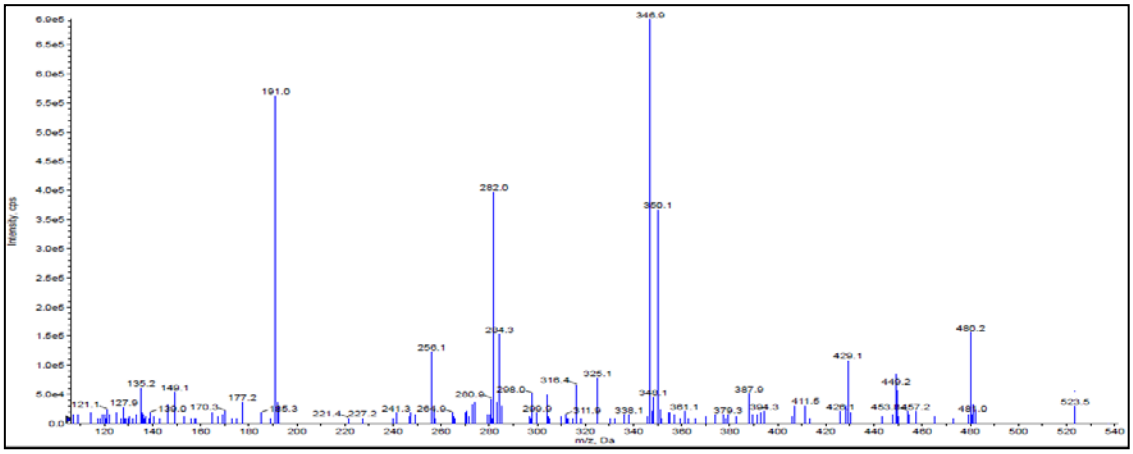


Figure (2) : Mass spectrum of [Co (L_1) $(L_2)_2$]Cl complex

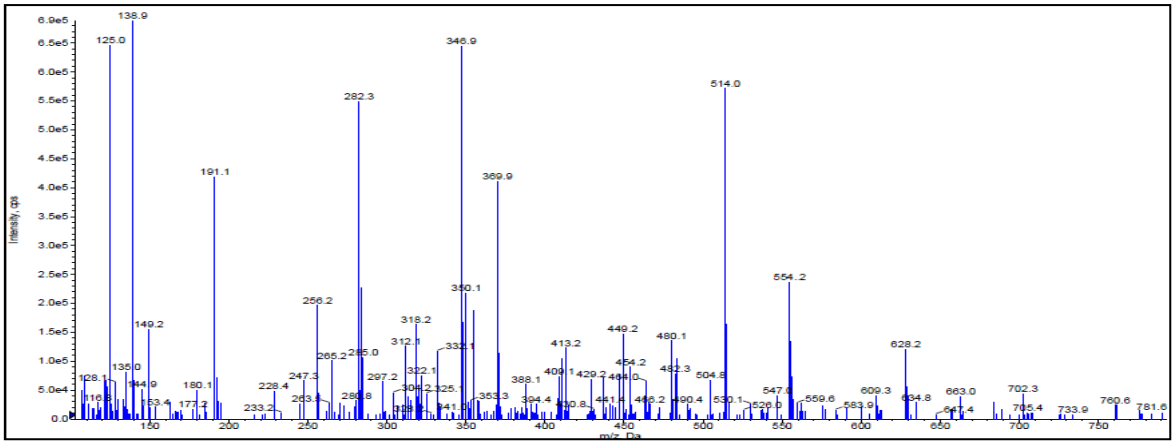


Figure 3: Mass spectrum of Co $(L_1)_2(L_2)_2$ complex

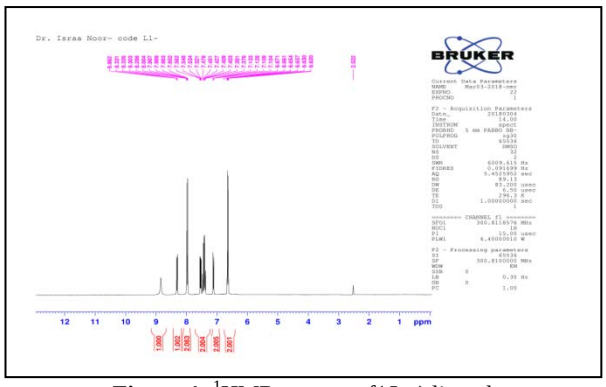


Figure 4: ^{1}HMR spectra of(L_1) ligand

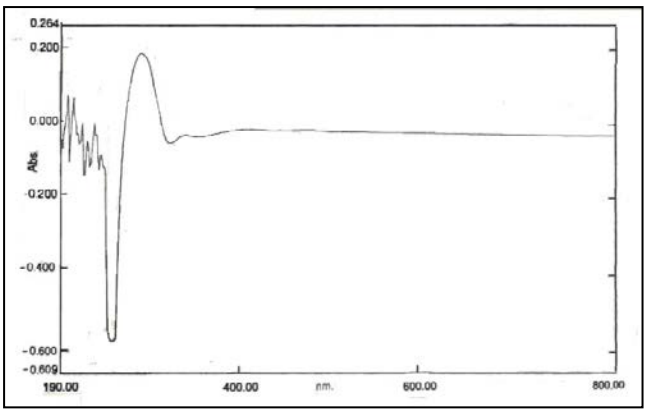


Figure 7 : Uv-Vis spectra of (L_2)

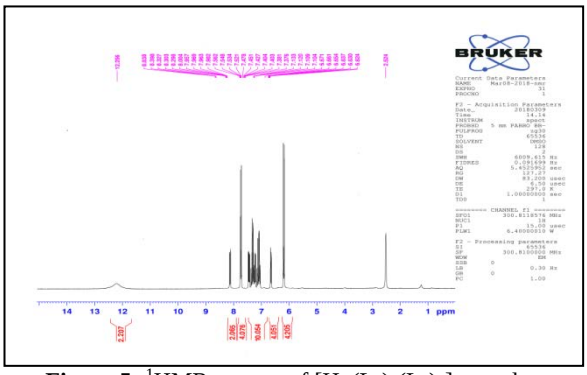


Figure 5 :^{1}HMR spectra of $[Hg(L_1)_2(L_2)_2]$ complex

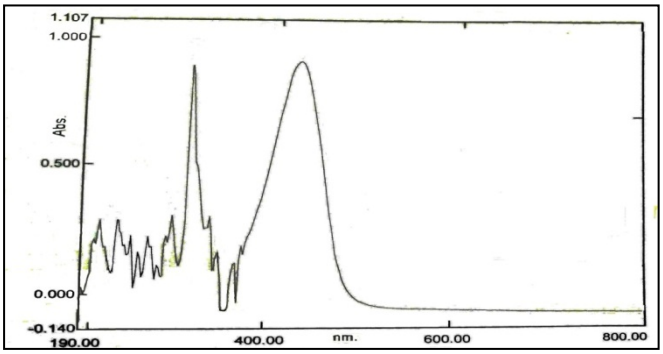


Figure 8: Uv-Vis spectra of $[Ni\ (L_1)(L_2)_2]Cl$ complex

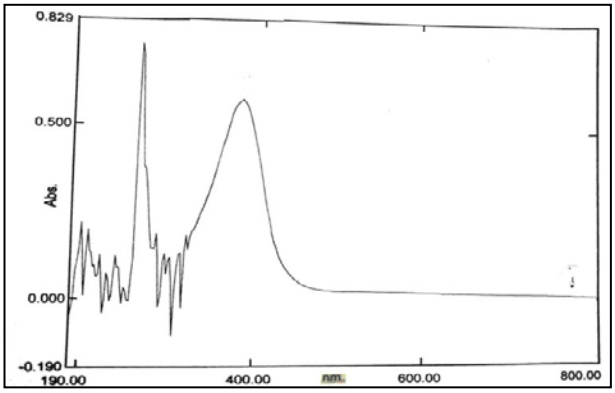


Figure 6: Uv-Vis spectra of (L_1)

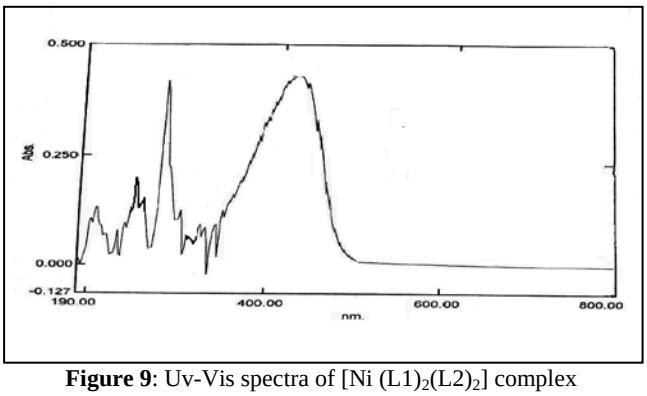
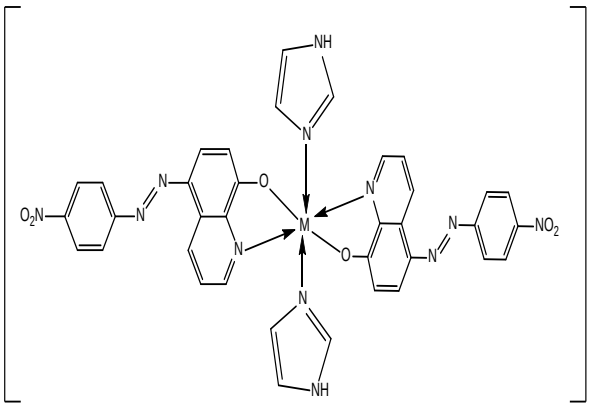
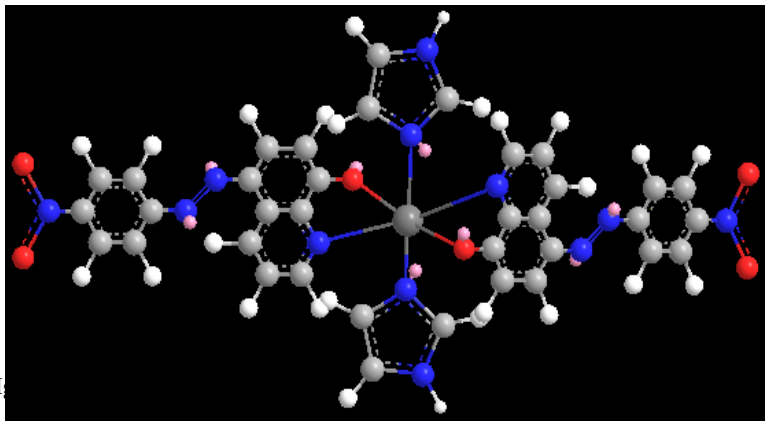


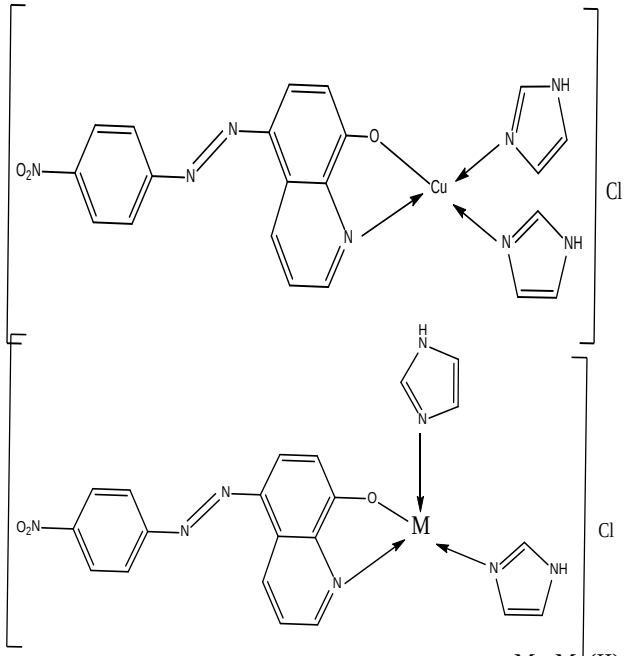
Figure 9: Uv-Vis spectra of $[Ni\ (L1)_2(L2)_2]$ complex

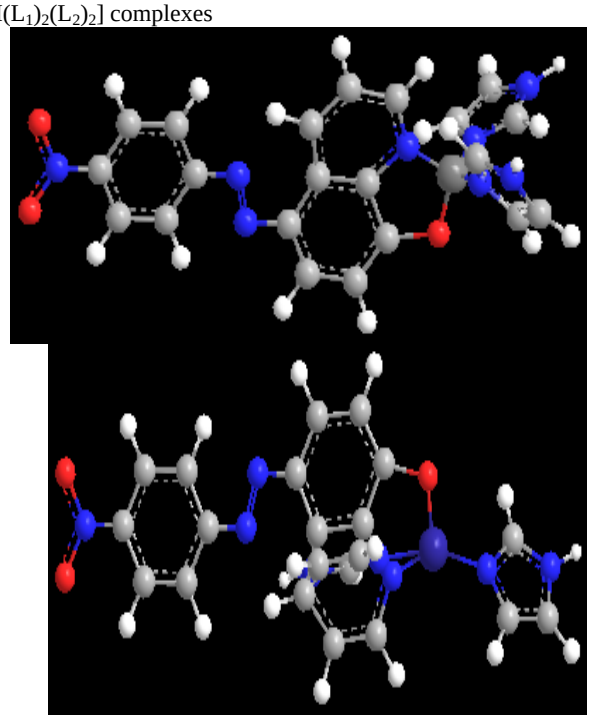




M= Mn(II) , Co(II), Ni(II) , Cu(II) , H

Figure 10 : Suggested structure of $[M(L_1)_2(L_2)_2]$ complexes





M= Mn(II) , Co(II), Ni(II), Hg(II)

Figure 11: Suggested structure of $[M(L_1)\ (L_2)_2]Cl$ complexes

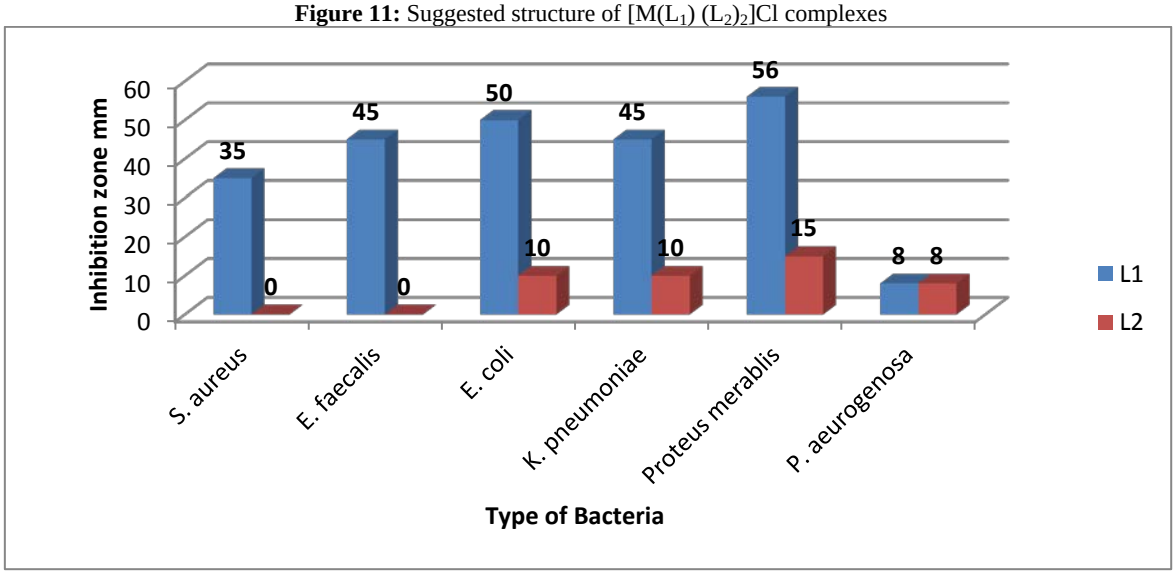


Figure 12: Comparing of antibacterial activity (inhibition zone, mm) of two ligands against pathogenic bacteria**.**

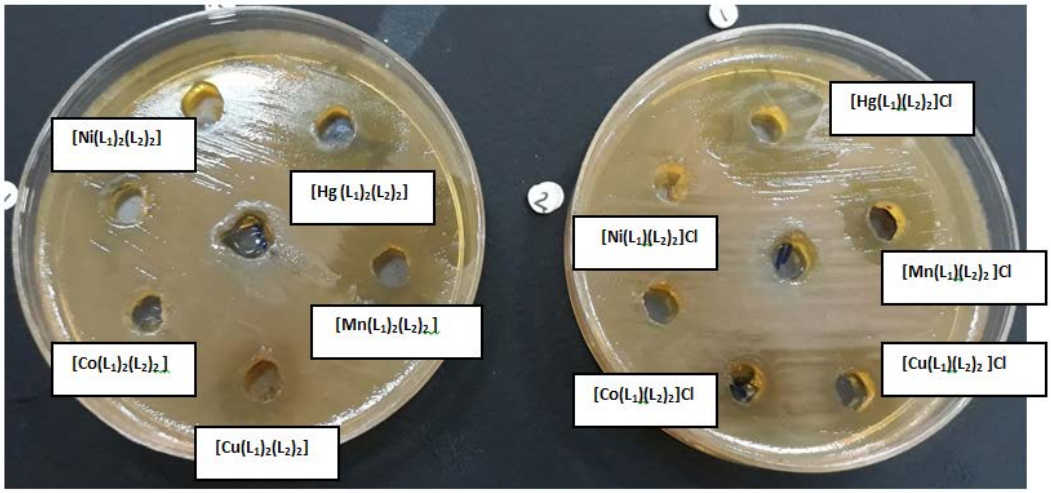


Figure 13: Antimicrobial activity activity (inhibition zone, mm) of mixed ligand complexes of Mn(II), Co(II), Ni(II) , Cu(II) , and Hg(II) ions against *Escherichia coli*.

Table(1) : Some of physicochemical properties of ligands and their complexes

Empirical Formula	Mwt	Yield(%)	Elemental Analysis Calcl. (Found)				m.p (^{o}C)
			C%	H%	N%	M%	
$C_{15}H_{10}N_4O_3$ (L_1)	294.20	79	61.22 (61.20)	3.43 (3.41)	19.04 (19.06)	------	124 – 126
$C_3H_4N_2$ (L_2)	68.07	-	52.93 (52.91)	5.92 (5.90)	41.15 (41.14)	-------	90 - 92
$MnC_{21}H_{17}N_8O_3Cl$	519.80	70	48.52 (48.68)	3.30 (3.32)	21.56 (21.52)	10.57 (10.59)	134-136
$CoC_{21}H_{17}N_8O_3Cl$	523.80	68	48.15 (48.20)	3.27 (3.24)	21.39 (21.18)	11.25 (11.28)	139-141
$NiC_{21}H_{17}N_8O_3Cl$	523.56	73	48.18 (48.20)	3.27 (3.26)	21.40 (21.42)	11.21 (11.16)	146-148
$CuC_{21}H_{17}N_8O_3Cl$	528.41	80	47.73 (47.58)	3.24 (3.26)	21.21 (21.08)	12.03 (12.07)	153-155
$HgC_{21}H_{17}N_8O_3Cl$	665.45	71	37.90 (37.94)	2.57 (2.60)	16.84 (16.85)	30.14 -------	166-169
$MnC_{36}H_{26}N_{12}O_6$	777.61	75	55.60 (55.64)	3.37 (3.36)	21.62 (21.63)	7.07 (6.95)	189-191
$CoC_{36}H_{26}N_{12}O_6$	781.60	81	55.32 (55.35)	3.35 (3.32)	21.50 (21.46)	7.49 (7.50)	216-219
$NiC_{36}H_{26}N_{12}O_6$	781.36	76	55.34 (55.32)	3.35 (3.37)	21.51 (21.50)	7.51 (7.53)	221-225
$CuC_{36}H_{26}N_{12}O_6$	786.21	70	55.00 (54.86)	3.33 (3.34)	21.38 (21.36)	8.08 (7.97)	226-228
$HgC_{36}H_{26}N_{12}O_6$	923.26	77	46.83 (46.81)	2.84 (2.87)	18.21 (18.17)	21.73 -------	232-235

Table(2) : IR vibrations of (L_1) and (L_2) ligands and their metal ion complexes

Compound	v (C-O) in plane	*v* (C-O) out of plane	v(C-O) phenolic	*v*(C=N) imidazole	v(C=N) quinoline	*v*(M-N)	*v*(M-O)
(L_1)	671 w	840 w	1224 w	-	1506 m	-	-
(L_2)	-	-	-	1541 m	-	-	-
[Mn (L_1)(L_2)$_2$]Cl	659 w	836 m	1271 m	1546 m	1523 m	511 w	418 m
[Mn(L_1)$_2$(L_2)$_2$]	657 w	823 w	1232 m	1464 m	1462 m	534 w	420 w
[Co (L_1)(L_2)$_2$]Cl	634 w	821 w	1236 m	1550 m	1498 m	553 w	412 w
[Co(L_1)$_2$(L_2)$_2$]	667 w	823 w	1228 w	1579 m	1496 m	504 w	414 w
[Ni (L_1)(L_2)$_2$]Cl	661 w	842 m	1228 w	1548 m	1529 m	514 w	432 w
[Ni(L_1)$_2$(L_2)$_2$]	665 w	821 w	1232 w	1570 m	1462 m	505 w	428 w
[Cu(L_1)(L_2)$_2$]Cl	648 w	832 w	1234 w	1548 m	1467 m	518 w	414 w
[Cu(L_1)$_2$(L_2)$_2$]	663 w	835 w	1230 w	1577 m	1470 m	520 w	432 w
[Hg (L_1)(L_2)$_2$]Cl	651 w	842 m	1227 w	1552 m	1488 m	516 w	436 w
[Hg(L_1)$_2$(L_2)$_2$]	663 w	826 w	1232 w	1564 m	1458 m	534 w	410 w

Table(3) : Molar Conductivity, Magnetic Susbtibility , and Electronic Transitions of ligands and their complexes .

Compound	Molar Conductivity $S.cm^2.mole^-$		μ.eff. (B.M.)	λ max (nm)	Transitions	Geometry
	DMF	DMSO				
(L_1)	-----	-------	-----	256 389	π-π* C.T	-----
(L_2)	-----	-----	-----	226 278	π-π* n-π*	-----
$[Mn (L_1)(L_2)_2]Cl$	78.8	75.6	5.93	238 262 422	π-π* π-π* MLCT	Tetrahedral
$[Mn(L_1)_2(L_2)_2]$	20.1	18.3	5.72	232 259 418	π-π* π-π* MLCT	Octahedral
$[Co (L_1)(L_2)_2]Cl$	76.4	74.7	3.87	234 264 432	π-π* π-π* MLCT	Tetrahedral
$[Co(L_1)_2(L_2)_2]$	18.6	16.5	4.72	230 258 429	π-π* π-π* MLCT	Octahedral
$[Ni (L_1)(L_2)_2]Cl$	76.2	74.5	3.53	236 267 435	π-π* π-π* MLCT	Tetrahedral
$[Ni(L_1)_2(L_2)_2]$	18.4	16.4	2.85	232 260 432	π-π* π-π* MLCT	Octahedral
$[Cu(L_1)(L_2)_2]Cl$	74.6	72.8	1.81	267 456	π-π* MLCT	Square planar
$[Cu(L_1)_2(L_2)_2]$	17.2	15.8	1.71	264 448	π-π* MLCT	Distorted octahedral
$[Hg (L_1)(L_2)_2]Cl$	82.7	81.4	-----	271 256 478	π-π* π-π* MLCT	Tetrahedral
$[Hg(L_1)_2(L_2)_2]$	23.5	20.4	-----	268 480	π-π* MLCT	Octahedral

Table (4): Antibacterial activity (inhibition zone, mm) of ligands against pathogenic bacteria

Type of bacteria	**L1**	**L2**
Staphylococcus aureus	35	0
Enterococcus faecalis	45	0
Escherichia coli	50	10
Klebsiella pneumoniae	45	10
Proteus mirabilis	56	15
Pseudomonas aeroginosa	35	8

Table (5): Antibacterial activity (inhibition zone, mm) of mixed ligand complexes of Mn(II), Co(II), Ni(II) , Cu(II) , and Hg(II) ions against pathogenic bacteria

Compound	***S. aureus***	***E. faecalis***	***E. coli***	***K. pneumoniae***	***P. mirabilis***	***P. aeroginosa***
$Mn (L_1)(L_2)_2Cl$	25	25	25	7	0	16
$Mn(L_1)_2(L_2)_2$	30	27	29	15	14	18
$Co (L_1)(L_2)_2Cl$	15	17	0	2	0	0
$Co(L_1)_2(L_2)_2$	24	19	13	22	20	28
$Ni (L_1)(L_2)_2Cl$	20	0	0	0	0	0
$Ni(L_1)_2(L_2)_2$	23	0	11	0	11	0
$Cu (L_1)(L_2)_2Cl$	40	0	19	7	24	5
$Cu(L_1)_2(L_2)_2$	40	13	27	12	28	3
$Hg (L_1)(L_2)_2Cl$	34	26	30	25	25	24
$Hg(L_1)_2(L_2)_2$	28	24	27	22	14	21

RESULTS AND DISCUSSION:

Mass spectra show a peak at m/e (294.3) represents the molecular ion peak of the free ligand (L_1) , the primary fragmentation of (L_1) take place in two paths the first one by loose (N_2) of azo group at m/e(266.4) while the second bath was started by loose (-OH) group at m/e (277) than loose ($-N_2$) from this fragment at m/e (249) as shown in scheme (4) and figure (1) , Mass fragmentation of $[Co(L_1)(L_2)_2]Cl$ complex that started by loose ($-N_2$) from (L_1) ,and $[Co(L_1)_2(L_2)_2]$ complexes which fragmenting by loose two imidazole molecules respectively are being studied , The appearance of molecular peaks of these compounds gave agreement confirms of molecular formulas, as shown in figures (2 ,3) and schemes(5 ,6).

^{1}HNMR spectrum of (L_1) in DMSO-d6 solvent show singlet at (8.86) ppm due to the proton of hydroxyl group of Quinoline moiety [20] which disappeared in $[Hg(L_1)_2(L_2)_2]$ complex spectrum that indicate the coordination process through hydroxyl group after losing its proton , the fourth protons of aromatic aryl ring [21-24]obvious as a doublet signals in (6.62) and (6.65) ppm, while the protons of Quinoline appears at (7.10-8.3) ppm [25], The signal of (N1) proton of imidazole ring [26] was also observed at (12.25) ppm in the $[Hg(L_1)_2(L_2)_2]$ complex spectrum, as shown in figures (4,5).

IR spectra of (L_1) ligand show vibration frequencies of *v* (C-O) for phenolic group**[27, 28]** in (1224) cm^- which proceed to higher frequencies in the complexes, as well the frequencies of this bond in plane and out of plane in (671) cm- and (840)cm- respectively, were priced to lower values in the complexes compared to free ligand, The *v* (O-H) of phenolic group**[29]** that appear in (3473) cm^- minefield in the complexes, These above results indicated the coordination through oxygen atom of (-OH) group after it's deprotonation. The vibrational frequencies of v(C=N) of Quinoline ring in (L_1) , and *v* (C=N) of imine group in (L_2) which appear in [30,31] (1506) cm^- and (1541) cm^- consecutively where observed to be shifted towards lower frequencies in the complexes If compared to the free ligands suggesting that the coordination through nitrogen atoms of quinoline and imidazole rings of these ligands while there was no significant changes of *v*(N=N) in complexes spectra which appear in (1444) cm^- **[32]** in (L1) , as demonstrated in table (2) .

Molar Conductivity was carried out in both of (DMF) and (DMSO) solvents at (25)^oC and (10^{-3})M for the prepared complexes , The resulting values for $[M(L_1)(L_2)_2]Cl$ complexes were between (74.6-82.7) $S.cm^2.mole^-$ in (DMF) solvent , and (72.8 – 81.4) $S.cm^2.mole^-$ in (DMSO) indicating (1:1) electrolyte type , The white precipitate formed when a drops of (0.1) M of $AgNO_3$ was added to the complexes which confirms existence of chlorine out of the coordination sphere **[33]**, while $[M(L_1)_2(L_2)_2]$ showed values ranging between (23.5-17.5) $S.Cm^2.mole^-$ in (DMF) , and (15.8-20.4) $S.Cm^2.mole^-$ in (DMSO) confirmed the non-ionic character of these complexes **[34]** .

Magnetic susbtibility measurements indicates that complexes formula $[M(L_1)(L_2)_2]Cl$ have tetrahedral geometry bating Cu(II) complex which has square planar while that all of $[M(L_1)_2(L_2)_2]$ complexes were possessive the octahedral **[35]** .

UV-Vis spectra of the complexes and free ligands measured in DMF solvent at room temperature , (L_1) resulted in two bands in 389 nm(25706 cm^-) , and 256 nm (39062 cm^-) due to the charge transfer and $\pi - \pi^*$ transitions while (L_2) showed two bands 287 nm (34843 cm^-), and 226 nm(44247 cm^-) consequent to n-π^* and π-π^* transitions , All of these bands showed bathochromic shift in the complexes comparing to the ligands indicating the coordination process , while $[Cu(L_1)(L_2)_2]Cl$ complex show single band at 616 nm (16233 cm^-) due to ^2B_1g ^2A_1g transition of square planar geometry [34,36], The data of transitions is summarized in table (3), and figures (6 - 9) represent the electronic spectra of the free ligands and Ni(II) complexes

The capacity of antimicrobial efficiency of two ligand (L_1,L_2) and five mixed ligand complexes of Mn(II), Co(II), Ni(II), Cu(II), and Hg(II) in two formulas [$M(L_1)(L_2)_2Cl$] and $[M(L_1)_2(L_2)_2]$ for each ion against six multidrug resistance bacteria (two G +ve bacteria (*E. faecalis* and *S. aureus*) and four G –ve bacteria (*P. mirabilis*, *E. coli*, *P. aeroginosa* and *K. pneumoniae*) were assessed by the existence or the absence of inhibition zone. The results of antibacterial efficiency of the ligands and mixed ligand complexes of ions are listed in table (4), table (5) and figure (13). The results indicate that L_1 ligand had better antibacterial activities on all bacterial isolated than L_2 ligand and other mixed ligand complexes of ions. The results also indicated that L_2 ligand have no influence on G +ve MDR bacterial isolates compared to the influence on G –ve MDR bacterial isolates .

As for the effectiveness of the metal complexes, they generally have a high antibacterial activities on G +ve bacteria compared to G-ve bacteria, where Hg (II) ion complexes had higher biological efficacy on all bacteria than other metal complexes. Ni (II) ion complexes showed lower antibacterial activity compare to other metal complexes (table 5).

The complexes $[M(L_1)_2(L_2)_2]$ of Cu(II), Mn(II), Ni(II) and Co(II) ions given higher antibacterial activity against all bacteria compare to $[M(L1)_1(L_2)_2Cl]$ except $[Hg(L_1)_2(L_2)_2]$ of complex showed lower antibacterial activity compare to $[Hg(L_1)(L_2)_2Cl]$ (figure 13).

The enhancement of antimicrobial activity of the ligand (L_1) may be due to chelation of transitional metals with it. Complicated decrease the polarity of metal ion by coordinating with ligands and rises the lipophilicity of the metals **[37]**. Thus it easiness the new synthesized complex to permeate the lipoid cell membrane of microorganisms and prevent their growth.

This variation in efficacy and inhibition vigor of(L_2) ligand is compatible to the existence of chlorine and phenyl compounds **[38]**. Beside the reduction of influences on G +ve bacteria, experiments demonstrated the potency of methyl nitro imidazole to inhibit the growth of the G-ve bacteria such as *Proteus merablis*, *P. auroginosa*, *K. pneumoniae* and *E. coli*, This ligand could liberate free radicals that damage bacteria and murder them **[39] .**

CONCLUSIONS

Series of new mixed ligand complexes were prepared with (E)-5-nitrophenyl)diazenyl0quinolin-8-ol as a primary ligand (L_1) and imidazole as a secondary ligand (L_2) with Mn(II), Co(II), Ni(II) , Cu(II) , and Hg(II) , in two different ratios of (L_1) as two formulas $[M(L_1)(L_2)]Cl$ which have tetrahedral geometry except $[Cu(L_1)(L_2)]Cl$ has square planer and $[M(L_1)_2(L_2)_2]$ were octahedral geometry .

The ligand (L_1) has maximum inhibition zone and antibacterial efficacy against all tested MDR bacteria while the minimum inhibition zone was determined ligand L_2 antibacterial efficacy. Retained The complexes generally appeared high antibacterial activities in G +ve bacteria compared to G -ve bacteria, where Hg (II) ion complexes has higher biological efficacy on all bacteria than other mixed ligand complexes of other ions. Ni (II) ion complexes has lower antibacterial activity compare to other metal complexes.

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