



Ring Opening polymerization of caprolactone And Antibacterial activity by Mixed Ligand of Metal(II) and (III) Complexes

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Abstract

Reaction of L^1 [(E)-N¹-(nitrobenzylidene)benzene-1,2-diamine] and L^2 (m-aminophenol), and one equivalent of di- or tri-valent metals (Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II)) afforded the complexes $[M(L_1)(L_2)_2]Cl$, $M=Cr(III)$ and Fe(III) and the complexes $[M(L_1)(L_2)_2]$ $M= Mn(II), Co(II), Ni(II), Cu(II)$ and Zn(II). The structure of the Schiff base ligand and their complexes are characterized by (C:H:N), FT.IR, UV-Vis, ¹HNMR, ¹³CNMR and mass spectral. The presence of metal in the complexes are characterized by flame atomic absorption. The spectral data of the complexes have revealed the octahedral geometry. The (L_1), (L_2) and mixed ligand metal complexes were screened for their ability as catalysis for ring opening polymerization and toward antibacterial and antifungal activities on different species of pathogenic bacteria and fungi.

Key words : Schiff base, mix ligand , Ring-opening polymerization, Metal complexes, Spectral analysis , Biological activity .

1. Introduction

The use of mixed ligand complexes allows to produce a different feature, lead to increase selectivity, sensitivity and change limitation properties of the single ligand[1-3]. Schiff base with mix ligand and its complexes have a variety of applications including biological[4], analytical[5], catalysts[6, 7]. The chemistry of mixed ligand that are capable of binding different ligand with metal center continues to be of great interest[8]. Over the last few years, our attention has focused mostly on the coordination chemistry of calix[n]arenes[9], Schiff base and phenolic compounds[10] and their use in catalysis. But use mix ligand complexes in this area still remains rare. In catalysis, we have observed how remote metal centres bound to a Schiff-base exhibited beneficial cooperative effects in the ring-opening polymerization of ϵ -caprolactone. In this work the synthesis and characterization of Cr³⁺, Mn²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ complexes with Schiff base ligand (L_1) and mixed ligand complexes with m-aminophenol (L_2). The Schiff base complexes

were characterized by ¹HNMR, ¹³CNMR, FT.IR, UV-Vis, mass spectra elemental microanalysis(C:H:N), magnetic moment and molar conductance. The biological activities and ability of complexes as catalysts for ring-opening polymerization of cyclic esters were investigated

2. Experimental :

2.1. Materials :

All reagents used in the present study includes o-phenylenediamine, m-nitrobenzaldehyde, m-aminophenol, sodium hydroxide, methanol, ethanol, benzene and carbon tetrachloride DMF and DMSO (Merck and Aldrich chemicals). The metal chlorides, CrCl₂.6H₂O, MnCl₂.4H₂O, FeCl₃, CoCl₂.6H₂O, NiCl₂.6H₂O. CuCl₂.2H₂O and ZnCl₂(Merck, BDH and Riedel company) and used without further purification.

2.2. Preparation of the Schiff Base Ligand (L_1) :

O-Phenylenediamine (2.1629g, 20 mmole) in of ethanol(50 mL) was stirred with m-

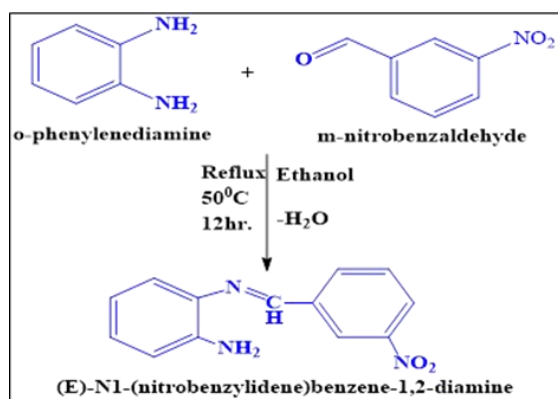
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Receive Date: 19 July 2022, Revise Date: 05 September 2022, Accept Date: 06 September 2022

DOI: 10.21608/EJCHEM.2022.151187.6544

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nitrobenzaldehyde, (3.0224g, 20 mmole) in ethanol(50 mL) and 5 drops of acid were added slowly. The mixture was refluxed for 12hr at 50°C. The deep brown solid was filtered, washed with distilled water and dried in a desiccator. The yield of the reaction was 85%. The following structure represents the the Schiff base formation in Scheme(1).



Scheme(1): Preparation Method of Schiff Base Ligand (L₁)

2.3. Preparation of the Mixed Ligand Complexes[11]:

The complexes were preparing in the molar ratio of M:L₁:2L₂ (1:1:2). Aqueous solution (10 mL) of the required CrCl₃.6H₂O(0.26gm, 1mmole), MnCl₂.4H₂O(0.19g,1mmole),FeCl₃(0.16gm,1mmole), CoCl₂.6H₂O(0.23g,1mmole),NiCl₂.6H₂O(0.23g,1mmole), CuCl₂.2H₂O(0.17g, 1mm) and ZnCl₂(0.136g,1mmole). Has been added into an ethanolic solution(30ml) for the (L₁), (0.24gm,1mmole) and (0.2183gm,2mmole) of m-aminophenolate (L₂) in (30ml) of ethanolic solution and sodium hydroxide (0.08 gm,2mmole) was added into the solution. The solution was refluxed for 2hr then the precipitate were filtered and washed thoroughly with diethylether and dried in vacuo.

2.4. Physical Measurements:

FT-IR spectra of the samples were recorded on using FT-IR-600 FT-IR spectrophotometer using KBr pellet. The UV-Vis spectra were measured on a Shimadzu-U.V-160. Ultraviolet spectrometer using DMSO solution 10⁻³ in the range (200-1000) nm. Magnetic moments were measured as powder samples using Faraday method, with Auto magnetic

susceptibility balance Sherwood Scientific was employed for this purpose. The molar conductance of the complexes was measured using a CON 510 Conductivity in DMSO (10⁻³ M) solution at room temperature. In addition, the mass spectra was measured at the ms model 5973 network mass selection technology (HP) with triple-axis detector by the analyzer quadrupole at 230 °C. Elemental analysis (C:H:N) were carried out by the micro analytical unit at Euro EA elemental analyzer for the (L₁) and mixed ligand complexes. Atomic absorption (A.A)technique / flame emission spectrophotometer using AA – 680. NMR spectra were employed to detrain metal contains. (¹H-, ¹³CNMR) were acquired in DMSO-d₆ solution using Nmr bruker400mhz in the DMSO-d₆ with TMS as the internal standard. Melting point were obtained on stuart melting point apparatus. well-diffusion method is used to check the antimicrobial activities.

2.5. ROP polymerization activity.

Screening of the complexes toward ring-opening polymerization was carried out as following literature[12].

2.6. Antimicrobial Screening:

The in vitro biological screening effects of the investigated the Schiff base (L₁), (L₂) and mixed ligand complexes were assessed against the bacteria: (*Steptococcus sp.*, *Pseudomonas Aeruginaso*, *Staphylococcus aureus*, *Staphylococcus epidermidis* *Escherichia coli* and *Klebsiella sp.*) Also, the well diffusion methods was used to investigate antifungal activity of the compounds against the fungi viz, *Candida albicans* (Yeast) by [13]. (10⁻³M) of the stock solution of compounds in DMSO was prepared

3. Results and Discussion

3.1 Elemental Analysis and Molar Conductivity:

The (C:H:N) analysis of (L₁) and mixed ligand complexes were in good agreements with the calculated value, Table (1) includes elemental analysis, molar conductance and physical properties. of the complexes as (10⁻³M) in DMSO indicating their non-electrolytic nature except Cr³⁺ and Fe³⁺complexes show electrolyte behaviour at ratio (1:1), [14]as mention in Table(2).

3.2.Mass spectrum:

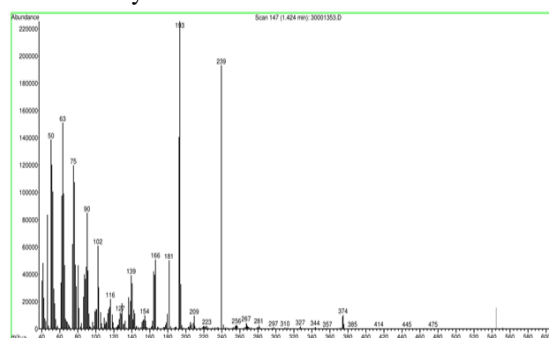
The mass spectrum of the mixed ligand complexes shows a molecular ion peak at (544.5, 512, 548.5, 516, 515, 521 and 522 m/z) to the

[Cr(L₁)(L₂)₂]Cl, [Mn(L₁)(L₂)₂], [Fe(L₁)(L₂)₂]Cl, [Co(L₁)(L₂)₂], [Ni(L₁)(L₂)₂], [Cu(L₁)(L₂)₂] and [Zn(L₁)(L₂)₂] complexes respectively. The molecular ion peak for the [Cr(L₁)(L₂)₂]Cl and [Mn(L₁)(L₂)₂] complexes shown in Figure (1-2). This composition is conformed by the mass spectra for all complexes. It is in good agreement with the microanalytical data.

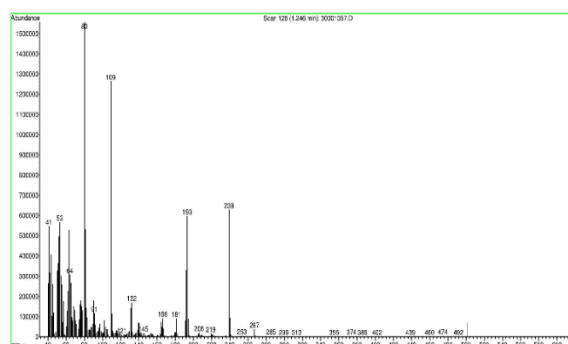
E. Absorption Spectral Studies and the Magnetic Moment:

The electronic spectrum of (L₁), (L₂) and mixed ligand complexes in DMSO solution were recorded in the 200 to 1000 cm⁻¹. The results obtained for mixed ligand complexes are given in Table(2). The electronic spectrum of the (L₁) exhibits intense absorption at (275, 301 and 324)nm attributed to (π-π*) and (n-π*) transitions[15]. But the spectrum of the (L₂) shows peaks at (273 and 294)nm due to (π-π*) electronic transitions[16]. The electron spectrum of the Cr³⁺ complex with (L₁) and (L₂) exhibits three peaks in (275 and 301)nm described to ligand field (L.F) and at 325nm related to charge transfer (MLCT). Also, peaks at (450, 825 and 938)nm were appeared the electronic transition type ⁴A_{2g}(F)→⁴T_{1g}(P) (U₃), ⁴A_{2g}(F)→⁴T_{1g}(F) (U₂) and ⁴A_{2g}(F)→⁴T_{2g}(F) (U₁) transitions[17]. This complex had an effective magnetic moment of μ_{eff} value 3.70B.M., corresponding to three unpaired electronic,

which suggests a high spin octahedral stereochemistry.



Figure(1): Mass Spectrum of [Cr(L₁)(L₂)₂]Cl



Figure(2): Mass Spectrum of [Mn(L₁)(L₂)₂]

Table(1): Elemental Analysis and Physical properties for (L₁), and prepared Complexes

Compounds	Empirical Formula	M. weight (g/mol)	Color	M.P°C	C.H.N Calc (Found)			
					M%	C%	H%	N%
Schiff base(L ₁)	C ₁₃ H ₁₁ N ₃ O	241	Deep brown	300 Dec.	-	64.72 (63.22)	4.60 (4.04)	17.42 (16.02)
[Cr(L ₁)(L ₂) ₂]Cl	CrC ₂₅ H ₂₃ N ₅ O ₃ Cl	544.5	Olive	210	9.55 (8.18)	55.15 (54.24)	4.26 (3.01)	12.86 (11.70)
[Mn(L ₁)(L ₂) ₂]	MnC ₂₅ H ₂₃ N ₅ O ₃	512	Blackish gray	300 Dec.	10.74 (9.59)	58.65 (57.70)	4.53 (3.70)	11.73 (10.40)
[Fe(L ₁)(L ₂) ₂]Cl	FeC ₂₅ H ₂₃ N ₅ O ₃ Cl	548.5	Raddish brown	185	10.21 (9.47)	54.74 (53.55)	4.23 (3.10)	12.77 (11.75)
[Co(L ₁)(L ₂) ₂]	CoC ₂₅ H ₂₃ N ₅ O ₃	516	Deep green	230	11.43 (10.98)	58.19 (57.15)	4.49 (3.12)	13.57 (12.25)
[Ni(L ₁)(L ₂) ₂]	NiC ₂₅ H ₂₃ N ₅ O ₃	515	Light olive	300 Dec.	11.46 (10.13)	58.31 (57.62)	4.50 (3.11)	13.60 (12.08)
[Cu(L ₁)(L ₂) ₂]	CuC ₂₅ H ₂₃ N ₅ O ₃	521	Blackish gray	300 Dec.	12.28 (11.68)	57.63 (56.58)	4.45 (3.35)	13.44 (12.88)
[Zn(L ₁)(L ₂) ₂]	ZnC ₂₅ H ₂₃ N ₅ O ₃	522	Olive	230	12.45 (11.21)	57.52 (56.79)	4.44 (3.08)	13.42 (12.91)

The electronic spectrum of the Mn²⁺ complex with (L₁) and (L₂) show peaks at 274, 322 and 345)nm due to (L.F) and (MLCT). The other peaks at (729 and 920)nm were conformed the transition types ⁶A_{1g}→⁴T_{2g}, ⁴E_g(G) and ⁶A_{1g}→⁴T_{1g}(G)[18]. Furthermore, the magnetic moment of the Mn²⁺

complex was found to be μ_{eff} value 5.72B.M., corresponding to unpaired electrons, which suggests octahedral geometry[19]. The electron spectra of the Fe³⁺ complex with (L₁) and (L₂) shows a peak at (275,301 and 319)nm due to (L.F.) and (MLCT)respectively and the peaks at (515 and 674)nm due to transition type ⁶A_{1g}→⁴T_{2g}, ⁴E_g(G) and

${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$ respectively, which obscures the low intensity d-d absorption bands[20]. The magnetic moment value was found μ_{eff} value 5.83B.M., which is very close to the octahedral spatial structure of high spin state[21]. The electronic spectrum of Co^{2+} complex with (L_1) and (L_2) showed peaks at (275 and 301)nm was related to (C.T.), the other two peaks at (325 and 828)nm were assigned to electronic transition type ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transitions respectively[17], also the μ_{eff} value 4.80B.M. may be possessed as extra confirmation to be high spin octahedral geometry[22]. The electronic spectrum of Ni^{2+} complex with (L_1) and (L_2) appeared absorption peaks at (275,301 and 322)nm due to (C.T.) and (MLC), the other three peaks at

(365, 797 and 920)nm were assigned to electronic transitions type ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3), ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (ν_1) respectively, the Ni^{2+} complex shows the μ_{eff} value 3.22B.M., which was much close to the octahedral geometry[23].

Two peaks absorbed at at (275 and 346)nm belong to the electronic spectrum of Cu^{2+} complex with (L_1) and (L_2) due to (C.T.) and (MLCT) respectively, others peaks at (369, 676 and 921)nm were caused by electronic transitions type ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ respectively[38], The value of μ_{eff} was 1.91B.M this which mean suggested octahedral environment.

Table(2): UV Spectra Data and Molar Conductivity for Mixed Ligand Complexes

Compounds	(λ . nm)	ABS	Wave number) (cm^{-1})	Molar conductivity .cm ² .Mol ⁻¹	Λ_m	μ_{eff} (B.M)
[Cr(L₁)(L₂)₂]Cl	301	2.191	33222	33.79		3.70
	325	2.330	30769			
	450	0.312	22222			
	825	0.026	12121			
	938	0.026	10660			
Mn(L₁)(L₂)₂	322	2.057	31055	25.91		5.72
	345	2.037	28985			
	729	0.015	13717			
	920	0.004	10869			
[Fe(L₁)(L₂)₂]Cl	275	1.988	36363	37.08		5.83
	301	1.953	33222			
	319	1.891	31347			
	515	0.211	19417			
	674	0.034	14836			
Co(L₁)(L₂)₂	275	2.165	36363	24.80		4.80
	301	2.207	33222			
	325	2.348	30769			
	828	0.039	12077			
Ni(L₁)(L₂)₂	275	2.041	36363	24.50		3.22
	301	2.050	33222			
	322	2.078	31055			
	365	2.041	27397			
	797	0.029	12547			
	920	0.024	10869			
Cu(L₁)(L₂)₂	275	1.779	36363	23.77		1.91
	346	1.292	28901			
	369	0.880	27100			
	676	0.052	14792			
	921	0.028	10857			
Zn(L₁)(L₂)₂	274	1.985	36496	18.32		Dia
	301	1.977	33222			
	350	0.975	28571			

The electronic spectrum Zn^{+2} complex with (L_1) and (L_2) showed absorption peaks at (274,301 and 320)nm due to (C.T.) and (MLCT) respectively, the absence of absorption peaks in the visible region indicated not (d-d) electronic transitions happened, this is a good result for octahedral complex and the magnetic susceptibility seemed the complex has diamagnetic moments[24]

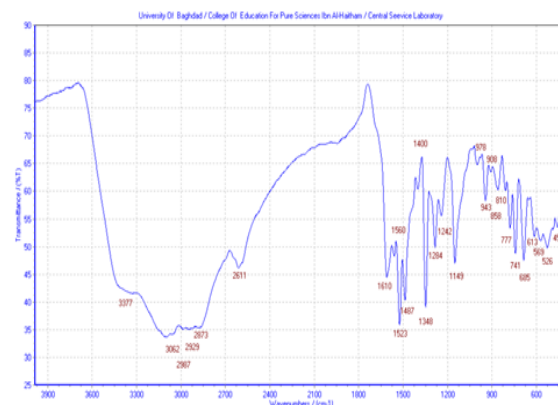
F. Infrared Spectral Studies of the (L_1), (L_2) and their Complexes:

The main vibrational bands of the FTIR spectrum were assigned to the functional group of the complexes have been recorded in Table(3) and Figures(3-4) to the (L_1), (L_2) and (Cr^{3+} and Co^{2+}) complexes. Bands at (3452 and 3182) cm^{-1} which were attributed to $\nu(NH_2)$ group, shifted to less frequency has been observed during complexation for metal ion[25]. Band at 1685 cm^{-1} belong to azomethine group was shifted to lower frequency (1595-1651) cm^{-1} . confirming the coordination of nitrogen atom with the metal ion[26]. (L_2) spectrum appeared band at 3325 cm^{-1} was assigned to stretching vibration of $\nu(OH)$, deprotonated of phenol group confirmed by FT-IR [27]. $\nu(NH_2)$ at (3325 and 3215) cm^{-1} also disappear from the complexes spectrum indicated to form coordination bond with metals ions. New bands at (598-459) cm^{-1} observed in the regions around (598-459) cm^{-1} may be ascribed to $\nu(M-N)$ and $\nu(M-O)$ vibration respectively[28].

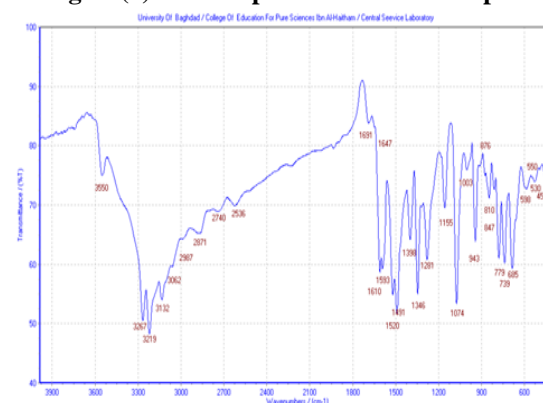
G. Ring-opening polymerisation (ROP) of ϵ -caprolactone:

The mixed ligand complexes of chromium, manganese and iron were selected to screening their ability toward ROP of ϵ -caprolactone (Table 4). ROP of ϵ -CL: were carried out in the presence of

benzyl alcohol (BnOH). It is obvious the increase of molecular weight from chromium complex to iron complex this is because of the increase in electronegativity of iron complex(3) as compared with chromium complex(1) and manganese complex(2). In term of yield percent all catalysts gave high yield percent and narrow PDI



Figure(3): FTIR Spectra for Cr^{+3} Complex



Figure(4): FTIR Spectra for Co^{+2} Complex

Table(3): The FTIR Spectra Bands (cm^{-1}) of the (L_1), (L_2) and Mixed Ligands Complexes

Compounds	$\nu(OH)$	$\nu(NH_2)$	$\nu(C=N)$	$\nu(M-N)$	$\nu(M-O)$
Schiff base(L_1)	-	3452 s. 3182 s.	1685 s.	-	-
$[Cr(L_1)(L_2)_2]Cl$	-	3377 br. 3280 br.	1610 sh.	569 w.	526 w.
$Mn(L_1)(L_2)_2$	-	3361 br. 3186 br.	1612 s.	540 w.	469 w.
$[Fe(L_1)(L_2)_2]Cl$	-	3357 sh. 3294 sh.	1595 sh.	544 w.	492 w.
$Co(L_1)(L_2)_2$	-	3267 sh. 3219 sh.	1610 sh.	598 w.	530 w.
$Ni(L_1)(L_2)_2$	-	3334 s. 3278 s.	1595 sh.	503 w.	459 w.
$Cu(L_1)(L_2)_2$	-	3338 s. 3262 s.	1651 s.	575 w.	469 w.
$Zn(L_1)(L_2)_2$	-	3273 sh. 3226 sh.	1608 sh.	528 w.	459 w.

Table 4. Polymerization of ϵ -CL using complexes 1-3

Cat.	Conv.%	M_n^a	PDI ^b
Complex-1	50	3420	1.17
Complex-2	70	3700	1.25
Complex-3	91	5440	1,13

Under nitrogen : runs were follow in toluene. ^b M_n GPC in THF with a Mark–Houwink factor of 0.56. ^bMw/Mn) from GPC, $t^{\circ}c=80$, time 3hour, CL: Cat :BnOH=100:1:1.

I. Microbiological Investigation of the (L₁), (L₂) and Mixed Ligand Metal Complexes:

(L₁), (L₂) and mixed ligand complexes screened for their biological activities against antibacterial strains (*Staphylococcus aureus*, *Pseudomonas Aeruginosa* and *Staphylococcus epidermidis*) (G⁺) and (*Streptococcus sp.*, *Klebsiella sp* and *Escherichia coli*)(G⁻) and antifungal studies as *Candida albicans* (Yeast) by agar well diffusion method using Mueller Hinton agar medium for antibacterial activity. The measured size related to the inhibition zones against the growth of various micro-organisms has been stated in Table (4) and Figure(5), which shows the impact of the prepared compounds on the bacterial species and fungi. From the obtained data, one can notice that, in comparison to the (L₁) indicated anti-microbial activities against *Staphyl-ococcus aureus* and

Pseudomonas Aeruginosa and (L₂) against *Staphyl-ococcus aureus* and *Streptococcus sp.*.

All the complexes show good antibacterial activity, when compared to the (L₁) and (L₂). This elevated activities of the could be associated to chelation theory [29]. Thus, chelation reduces the metal atom polarity and that will lead to partial sharing regarding its positive charge with donor group and potential π – electron delocalization throughout whole ring [24]. However, the Zn⁺² complex is highly active against *Staphyl-ococcus aureus*, *Pseudomonas Aeruginaso*, *Streptococcus sp.*, *Escherichia coli* and *Klebsiella sp.*, when compared to (L₁), (L₂) and other mixed ligand complexes. In the case of *Candida albicans* that represent a class of fungi type of yeast that has a clear impact with (L₁), Mn⁺² and Zn⁺² complexes, but no effect on the rest.

Table (5): Effect of (L₁), (L₂) and Mixed Ligand Complexes on the Growth of Tested Bacteria and Fungi

Sample Bacteria	Cr ^{III-} complex	Mn ^{II} comp lex	Fe ^{III} com plex	Co ^{II} com plex	Ni ^{II} co mplex	Cu ^{II} co mplex	Zn ^{II} compl ex	(L ₁)	(L ₂)	Control (DMSO)
<i>Staphyl-ococcus aureus</i> (G+ev)	-	11	10	10	-	12	12	12	11	-
<i>Staphyloco-ccus epidermidis</i> (G+ev)	-	12	13	12	12	9	9	-	-	-
<i>PseudomonasAeruginaso</i> (G+ev)	11	11	-	-	-	10	14	11	-	-
<i>Streptococcus sp.</i> (G-ev)	-	10	-	-	11	10	12	-	10	-
<i>Escherichia coli</i> (G-ev)	-	12	11	-	-	11	16	--	-	-
<i>Klebsiella sp.</i> (G-ev)	-	12	11	10	9	11	14	-	-	-
<i>Candida albicans</i> (Yeast)	-	13	-	-	-	-	10	13	-	-

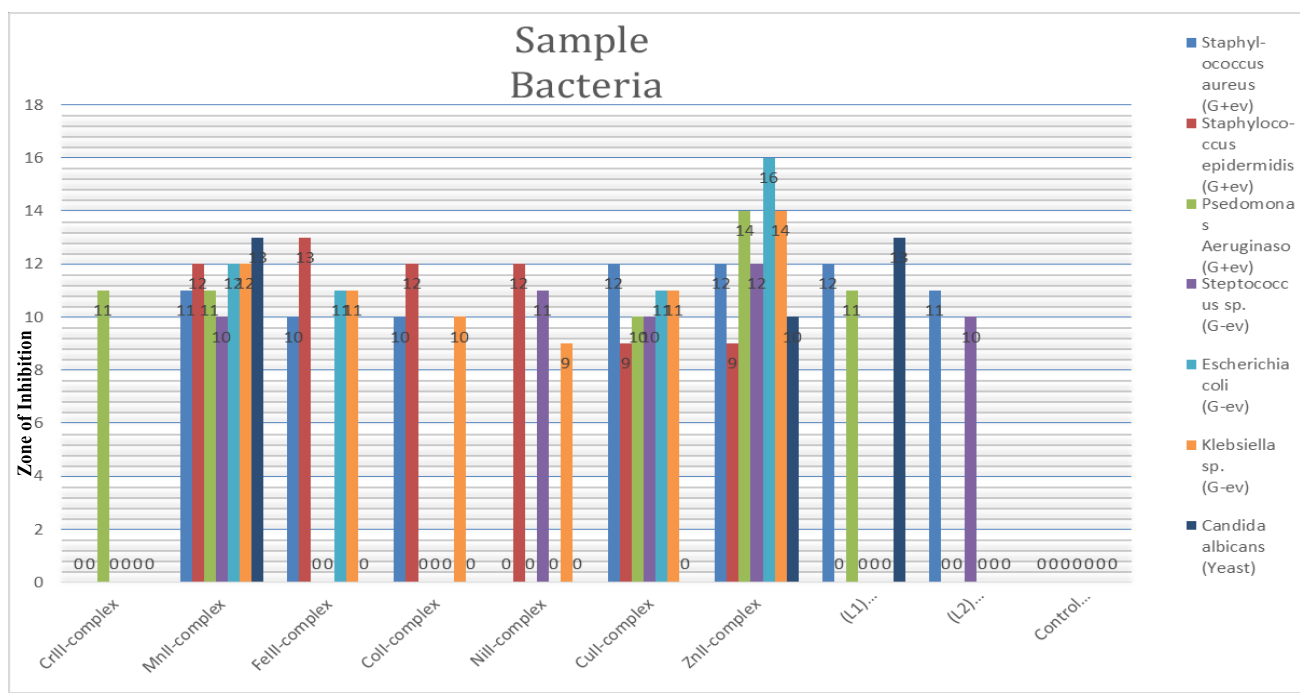


Figure (5): Bioactivity of the (L₁), (L₂) and Mixed Ligand Complexes Against the Bacteria Species and Fungi.

4. Conclusion

The work presents spectroscopic characterization and biological activity of mixed ligand complexes of Cr³⁺, Mn²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ with Schiff base ligand (L₁) as a primary ligand and m-aminophenol (L₂) as a secondary ligand. The analytical and physicochemical data show satisfactory agreement with the proposed formula prepared complexes. In brief, the results obtained can be summarized as follows:

1-The stoichiometric ratio of the complexes is (M:L₁:2L₂), (1:1:2) and the complexes are fairly stable in air and have non electrolytic nature except Cr³⁺ and Fe³⁺ complexes show electrolyte nature at ratio (1:1).

2-Schiff base ligand (L₁) acts a bidentate ligand coordinate to metal ion through two group are linked in the form of coordination bonds during the azomethine nitrogen and NH₂ group through the coordination links of m. The m-aminophenol (L₂) acts a bidentate ligand to phenol group linked in the form of ionic bond and the -N of NH₂ group coordinated in the compose of coordination bind.

3-Octahedral geometry is proposed for mixed ligand complexes depending on the magnetic moment values of each metal ion, these include Cr³⁺, Mn²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ in Figure (12).

4- Generally, the results showed that the Zn²⁺ complex has a highly significant activity toward *Staphylococcus aureus*, *Pseudomonas Aeruginoso*, *Streptococcus sp.*, *Escherichia coli* and *Klebsiella sp.*, when compared to (L₁), (L₂) and other mixed ligand complexes, due to their molecular weight as well as their electronic configuration (d¹⁰ system) in comparison to the other metal complexes.

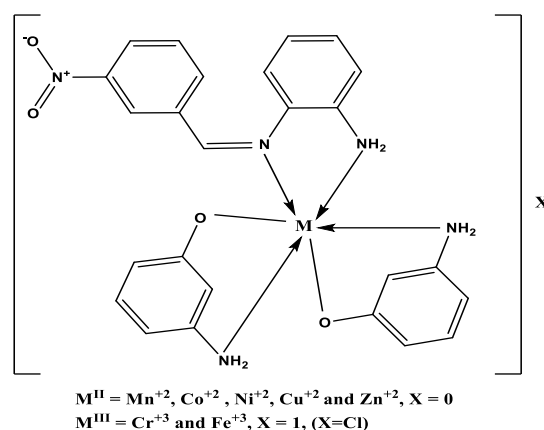


Figure (12): Propose Structure for the Mixed Ligand Complexes

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