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Synthesis and characterization of new Schiff bases complexes with ions elements (Co(II), Ni(II), Cu(II) Mn(II), Zn(II),) and evaluation of the bacterial activity

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***Abstract*---**This paper consists of three main parts: First part: includes the synthesis of ligand for Schiff bases (L_1, L_2) from the reaction of aldehydes (vanillin, isovanillin) with amines (cytosine), which are shown in the following: L_1: 4-(I^1-azaneyl)pyrimidin-2(1H)-one2-methoxy-4-vinylphenol; L_2: 4-(I^1-azaneyl)pyrimidin-2(1H)-one2-methoxy-5-vinylphenol. Second part: Synthesis of new divalent metal complexes through the reaction of ligand (L_1, L_2) prepared in this study with chlorides salts and metal sulfates (nickel, cobalt, copper, manganese, and zinc) in a ratio of (1:1) (ligand: salt metal). The prepared ligands and complexes were characterized by physical and spectroscopic methods, including conductivity measurements, magnetic susceptibility measurements, melting point, atomic absorption spectroscopy, micro elemental analysis - CHN, UV-Vis, FT-IR, and H-NMR spectroscopies. From the results of these measurements, it was found that the ligands (L_1, L_2) prepared in this study behave like a bidentate ligands behavior as donor atoms are associated with metals via the nitrogen atoms in the (C=N) group and the (NH2) group, as well as in the pyrimidine ring. Also, it was found that all the complexes possess the proposed geometric shapes, which are the tetrahedral geometry and the square planar geometric shape. By measuring the molar electrical conductivity, it was found that all the prepared complexes are electrically neutral, so the sulfate and chloride ions are inside the coordination sphere and are directly related to the ionic metals in these prepared complexes. Third part: The biological activity of some prepared Schiff base complexes was tested against two kings of bacteria (E.coli) and (Staphylococcus

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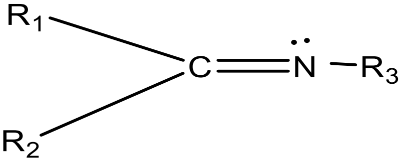
aureus) and showed a high inhibitory ability against the chosen bacteria. Bidentate ligands.

***Keywords*---**schiff bases, complexes of nickel, cobalt, zinc, copper, and manganese, and biological activity.

Introduction

Schiff bases are defined: as the organic compounds containing azomethine group (C=N)) and have the general formula shown in Figure (1-1) ⁽¹⁾. These bases were named after the scientist Hugo Schiff discovered, who first attended them (1864) through a simple condensation reaction of carbonyl compounds such as (aldehydes, aliphatic and aromatic ketones) with primary amines, as shown in (Figures 1- 2) and as a result, these imines are called Schiff Base ⁽²⁾.



R_1, R_2, and R_3= alkyl, aromatic, and aliphatic group
Figure 1-1. The general structure of the Schiff bases

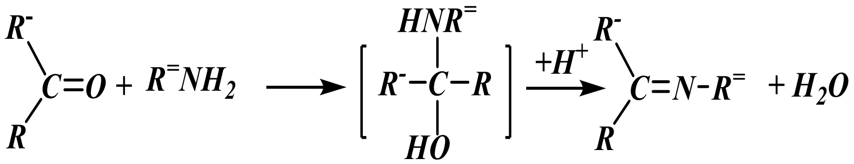


Figure 1-2. Condensation of an aldehyde or a ketone with a primary amine

The Schiff bases are considered to be the most important ligands used in the field of coordination chemistry, which have a significant role to play in the preparation of a large number of complexes of metal ions in general and transitional ones in particular due to their ability to coordinate with ionic metals and to form stable complexes with them ⁽³⁾. The general chemical formula for Schiff's bases is RR'C=NR''. These compounds are called Imines, Azomethines, Aniles, or Benzanils, where each of the R and R' in the enyls represents an aliphatic or aromatic group or a hydrogen atom. and R'' compensated or uncompensated benzene ring, in the imines, R is a substituted or unsubstituted benzene ring, R' is a hydrogen atom, and R'' is an alkyl or aryl group. They are also called ketimines when derived from ketones, as both R and R' are an alkyl or aryl group, and they are called Aldimines when derived from aldehydes, i.e. R is an alkyl or aryl group and R' is a hydrogen atom ⁽⁴⁾. Schiff bases resulting from the interaction of aromatic amino compounds with ketones or aliphatic or aromatic aldehydes have been characterized as the most stable among Schiff bases ⁽⁵⁾, while Schiff bases prepared from condensation of aliphatic amino compounds were found unstable, as they quickly disintegrate into their primary components (6).

One of the main characteristics of these compounds is the formation of colored complexes with many metal ions (7). Many reports highlight the importance of Schiff's bases as antimicrobial agents, as the azomethine group is found in some marketed drugs such as. Nifuroxazide (INN) 4 and Thiacetazone 5) (8).. Schiff bases have gained significance in the medical and pharmaceutical fields due to a wide range of biological activities such as antibacterial, antifungal, antiproliferative, antiviral, anti-inflammatory, and antineoplastic. Thus, the complexes of Schiff bases possess more biological activity than the ligands that make up those complexes, as was observed when converting compounds with biological activity to Schiff bases, thereby improving the biological activity of these compounds, specifically in the case of using amino compounds such as amino acids (9). A nitrogen atom in the (–CH = N-) group may participate in the formation of a hydrogen bond with the active centers of cell parts and interfere with normal cell processes (10). Some Schiff bases and their complexes were also used as catalysts, such as the ruthenium-Schiff base complex, which is a good catalyst for synthesis interaction "tri zoacetates-dia aiiyl substituted complex". There are other catalysts factors such as the Schiff base (Tri dentate ligands), which is of great importance in the organic-life reactions, through which it is possible to link between amino acids and Schiff bases to create important effective sites (11).

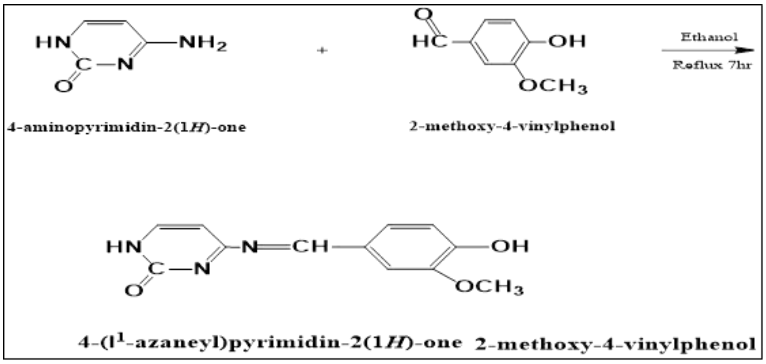
Experimental part

Synthesis of Schiff bases ligands

The ligand was prepared for Schiff's bases (L_1, L_2) through the reaction of amines such as (cytosine) with aldehydes such as (vanillin, and iso vanillin), which are described below:

Synthesis of the first ligand (L_1), in a ratio of (1:1) (cytosine: vanillin)

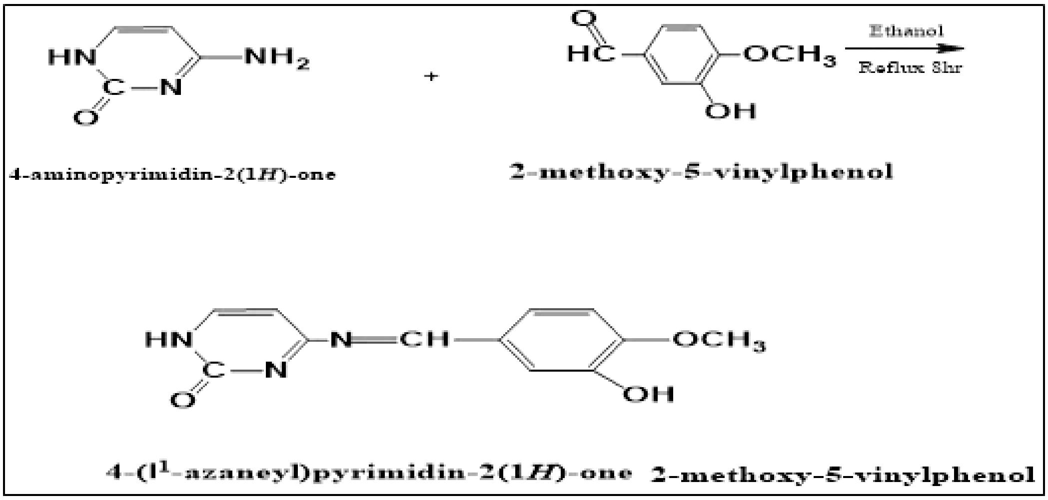
This ligand was prepared by dissolving (1gm, 0.0096) of Cytosin in (20ml) of hot ethanol in a Round-bottom flask (Rb-flask) with a capacity (100ml), then added to it a solution of dissolving (1.369 gm, 0.0096 mol.) of vanillin in (20ml) of hot ethanol. A few drops of snowy acetic acid were added to the previous mixture, then stirred the mixture with a magnetic stirrer with thermal escalation to 80°C with continuous stirring for (7hr) to complete the reaction. After that, the solution was evaporated to a quarter of its original volume and then left for (24) hours to complete the sedimentation process. Then the precipitate was filtered and washed with ethanol and then with ether several times and then recrystallized with ethanol, then dried in an electric oven at 50 ° C. Then the formed precipitate was weighed and calculated the percentage which is found 62%. The equation (1-2) shows the above reaction.



Equation (2-1). The reaction of preparing the first ligand (L_1) Schiff's base.

Synthesis of the second ligand (L_2), in a ratio of (1:1) (cytosine: isovanillin)

This ligand was prepared by dissolving (1gm, 0.0096) of Cytosin in (20ml) of hot ethanol in an Rb-flask with a capacity (100ml), then added to it a solution of dissolving (1.369 gm, 0.0096 mol.) of isovanillin in (20ml) of hot ethanol. After that a few drops of snowy acetic acid were added to the solution, then stirred with a magnetic stirrer by increasing the temperature up to 80 °C and continuing the stirring for 8h) until the reaction was completed. After that, the solution was evaporated to a quarter of its original volume and then left for (24) hours to complete the sedimentation process. Then the precipitate was filtered and washed with ethanol and then with ether several times, recrystallized with ethanol, and dried in an electric oven at 50 ° C. Then the formed precipitate was weighed and calculated the percentage which is found 72%. The equation (2-2) shows the above erection.



Equation (2-2). The reaction of preparing the second ligand (L_2) Schiff's base

Preparation of Schiff base complexes

Preparation of first ligands (L_1) complexes with hydrate metals chlorides

($NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $CoCl_2.6H_2O$, $ZnCl_2.4H_2O$, $MnCl_2.4H_2O$) in a ratio (1:1) (ligand: metal salt). 0.0008 mol of the metal salt solution dissolved in (15 ml) of hot ethanol with (0.0008 mol) of the first ligand solution (L_1) dissolved in (15 ml) of hot ethanol is put gradually in a Round-bottom flask of capacity (100 ml) with continuous stirring. After that, the thermal escalation of the mixture was carried out for (3 hrs), then the solution was evaporated to a quarter of the original volume and cooled. The precipitate was filtered, then washed with ethanol, and then with ether and it was dried in a furnace at 50°C. Then the precipitate was weighed and the percentage of precipitate was calculated.

Preparation of second ligand complexes (L_2) with hydrate metal sulfate

($NiSO_4.6H_2O$, $CuSO_4.5H_2O$, $CoSO_4.7H_2O$, $ZnSO_4.7H_2O$, $MnSO_4.\ H_2O$) in a ratio of (1:1) (ligand: metal salt). 0.0016 mol of the metal salt solution dissolved in (15 ml) of hot ethanol with (0.0016 mol) of the second ligand solution (L_2) dissolved in (15 ml) of hot ethanol is put gradually in a Round-bottom flask of capacity (100 ml) with continuous stirring. After that, the thermal escalation of the mixture was carried out for (3 hrs), then the solution was evaporated to a quarter of the original volume and cooled. The precipitate was filtered, then washed with ethanol, and then with ether and it was dried in a furnace at 50°C. Then the precipitate was weighed and the percentage of precipitate was calculated.

Results and Discussion

This study included the preparation of ligands for Schiff bases (L_1, L_2) derived from amines (cytosine) and aldehydes (vanillin and isovanillin) in a ratio of (1:1). These ligands are combined with the following hydrometallic chlorides and sulfates ($NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $CoCl_2.6H_2O$, $ZnCl_2.4H_2O$, $MnCl_2.4H_2O$) and ($NiSO_4.6H_2O$, $CuSO_4.5H_2O$, $CoSO_4.7H_2O$, $ZnSO_4.7H_2O$, $Mn\ SO_4.\ H_2O$) in a ratio of (1:1) (ligand: metal) and the formation of new complexes that were characterized by different spectroscopic techniques, and physical and chemical methods. In this work, we evaluation of the biological activity of a number of prepared complexes on the two types of bacteria: (E-coli) and (Staphylococcus aureus).

The ligands prepared and used in this study

L_1: 4-(I^1-azaneyl)pyrimidin-2(1H)-one2-methoxy-4-vinylphenol
L_2: 4-(I^1-azaneyl)pyrimidin-2(1H)-one2-methoxy-5-vinylphenol

The complexes prepared and used in this study are shown in Table (3-1) below

Table 3-1
Prepared complexes and used in this work

Sr. No.	Prepared complexes	Sr.No.	Prepared complexes
1	[Ni (L_1)C_{l2}]	11	[Ni (L_2)C_{l2}]

2	[Co (L_1)Cl_{12}]	12	[Co (L_2)Cl_{12}]
3	[Cu(L_1)Cl_{12}]	13	[Cu(L_2)Cl_{12}]
4	[Zn (L_1)Cl_{12}]	14	[Zn (L_2)Cl_{12}]
5	[Mn(L_1)Cl_{12}]	15	[Mn(L_2)Cl_{12}]
6	[Ni(L_1) SO_4]	16	[Ni(L_2) SO_4]
7	[Co (L_1) SO_4]	17	[Co (L_2) SO_4]
8	[Cu(L_1) SO_4]	18	[Cu(L_2) SO_4]
9	[Zn (L_1) SO_4]	19	[Zn (L_2) SO_4]
10	[Mn(L_1) SO_4]	20	[Mn(L_2) SO_4]

Characterization of the prepared complexes and ligands.

The prepared ligands and complexes were characterized by the following spectroscopic techniques and physical measurements:

Atomic Absorption

The proportions of the elements Co(II), Cu(II), Ni(II), Zn(II), and Mn(II) for all the prepared complexes were estimated by atomic absorption spectrometry, which was prepared by concentrated nitric acid and then completing the required volume to (100ml) with deionized water, the complexes solutions were prepared with concentrations located within the concentrations of standard models compatible with the linear range of the standard curve of the elements measured in the device and attended standard solutions of ion salts Co (II), Cu (II), Ni (II), Zn (II), Mn (II), Mn (II) by the standard additionality method, and determine the quantity of the element present in each of these prepared metal complexes. The practical results obtained are close to those calculated theoretically as in Table (3-2). These results can be relied upon with a number of other measurements to support the validity of the suggested structural formulas for prepared complexes.

Micro Elemental Analysis - CHN

Carbon (C), hydrogen (H), and nitrogen (N) ratios were measured for ligand and some prepared complexes, and the results were shown in Table (3.2). When comparing the practically obtained percentages with the theoretically calculated percentages, we note that there is a clear convergence between their values, and this indicates the correctness of the molar ratios (ligand: metal) used to prepare these complexes, as well as the validity of the spectral measurements, and these results can be relied upon to support the validity of suggested formulas for the prepared complexes.

Melting Point Measurement

The melting point was measured for all the prepared complexes and their values are shown in Table (3-2).

Molar Electrical Conductivity

The molar electrical conductivity of the complexes prepared in this study was measured at a concentration of (10^{-3}M) and using (DMSO) after obtaining a thermal equilibrium state of the solution at a temperature of (25 °C). It was found from the results of the molar electrical conductivity measurements that it agrees with the suggested structural formulas for the complexes, and it is noted in Table (3-3) that the molar electrical conductivity values for all the prepared complexes fall within the range of the classification of complexes with equivalent behavior, i.e. (non-electrolytic) or poorly conductive in the solution.

Table (3-2).
Results of the micro-analysis of CHN, the ratio of the elements, and some physical properties of the ligands and the prepared complexes

No. of complex	Expected formula for complexes	Color	Melting point	conductivity (ohm^{-1}cm^{2} mol^{-1}) DMSO	Results of the analysis of elements % (theoretical and practically)			
					M	C	H	N
1	L_1	white	286-288	---	---	58.77 58.15	4.52 4.45	17.13 17.10
2	L_2	milky	168-170	-----	---	58.77 58.15	4.52 4.45	17.13 17.10
3	$[Ni(L_1)(Cl_2)]$	light green	263-265	19.7	15.65 15.33	38.44 38.33	2.95 2.88	11.20 11.13
4	$[Co\ (L_1)(Cl_2)]$	blue	200-203	13.5	15.70 15.62	38.41 38.33	2.95 2.88	11.20 11.15
5	$[Cu\ (L_1)(Cl_2)]$	light blue	256-258	12	15.97 15.94	36.23 36.21	2.78 2.76	10.56 10.52
6	$[Zn\ (L_1)(Cl_2)]$	white	296-299	13.2	17.13 17.11	37.77 37.66	2.90 2.77	11.01 10.96
7	$[Mn\ (L_1)(Cl_2)]$	white	269-271	9.4	14.80 14.66	38.83 38.33	2.98 2.93	11.32 11.19
8	$[Ni(L_2)(SO_4)]$	light green	294-292	14.5	14.66 14.27	36.02 35.90	2.77 2.74	10.50 10.43
9	$[Co(L_2)(SO_4)]$	dark purple	289-292	16.4	14.72 14.62	36.00 36.00	2.76 2.66	6.99 6.96
10	$[Zn(L_2)(SO_4)]$	white	296-299	14.8	16.07 16.03	35.42 5.38	2.72 2.70	10.32 10.29
11	$[Cu(L_2)(SO_4)]$	light blue	240-243	11	15.69 15.67	35.59 35.51	2.73 2.67	10.37 10.25
12	$Mn(L_2)(SO_4)]]$	yellow	277-288	18.7	13.86 13.81	36.37 ------	2.79 ------	10.60 ------

Magnetic Susceptibility Measurements

The magnetic susceptibility of the prepared complexes was measured at (25°C) and the results are shown in Table (3-3) which shows the values of (xM), (xg), (xA), (D), and μ_{eff} for the nickel, cobalt, copper and manganese complexes.

Table (3-3)
The values of (xM), (xg), (xA), (D), and μ_{eff} for the nickel, cobalt, copper, and manganese complexes

No.	Complex	Gram sensitivity xg × 10-6 (c.g.s.u)	Molar sensitivity $xM\times10^{-6}$ (c.g.s.u)	Diamagnetic correction factor $D\times 10^{-6}$ (c.g.s.u)	Atomic sensitivity $xA\times10^{-6}$ (c.g.s.u)	μ_{eff} (B.M)
1	$[Ni(L_1)(Cl_2)]$	15.865	5948.438	131.97	6080.4089	3.80
2	$[Ni(L_1)(SO_4)]$	16.000	6406.4	125.27	6531.67	3.94
3	$[Co\ (L_1)(Cl_2)]$	5.5000	2063.325	131.97	2195.295	2.28
4	$[Co\ (L_1)(SO_4)]$	17.999	7205.899	125.27	7331.169	4.17
5	$[Cu\ (L_1)(Cl_2)]$	4.34667	1728.801	131.97	1860.771	2.10
6	$[Cu\ (L_1)(SO_4)]$	4.405000	1783.1665	125.27	1908.9866	2.13
7	$[Mn\ (L_1)(Cl_2)]$	38.444	14269.023	133.97	14402.993	5.80
8	$[Mn\ (L_1)(SO_4)]$	36.999	14661.223	127.27	14788.493	5.93
9	$[\ Ni\ (L_2)(Cl_2)]$	0.00005	0.0187	131.97	131.988	0.4
10	$[\ Ni\ (L_2)(SO_4)]$	0.00001503	0.006	125.27	125.2760	0.1
11	$[\ Co\ (L_2)(Cl_2)]$	18.65333	6977.785	131.97	7129.755	4.11
12	$[Co\ (L_2)(SO_4)]$	5.001	2002.1503	125.27	2127.4203	2.25
13	$[\ Cu\ (L_2)(Cl_2)]$	3.407	1355.0661	131.97	1487.0361	1.88
14	$[\ Cu\ (L_2)(SO_4)]$	2.922000	1183.2054	125.27	1308.4754	1.76
15	$[\ Mn\ (L_2)(Cl_2)]$	37.22275	13815.595	133.97	13949.5658	5.70

- The nickel (II) complexes prepared in this study (1 and 2) have given a magnetic moment of (3.80 and 3.94 B.M.), respectively, these values apply to tetrahedral nickel (II) complexes, while the prepared (9 and 10) nickel (II) complexes gave a magnetic moment of (0.4 and 0.1B.M), respectively, and these values apply to the square planar nickel (II) complexes, so it diamagnetic complexes that do not show a magnetic moment (12,13).
- The cobalt (II) complexes prepared in this study (11 and 4) gave magnetic moments estimated at (4.11 and 4.17 B.M.), respectively, as these values are in agreement with the paramagnetic tetrahedral cobalt complexes, while the cobalt complexes (II) (3, 12) gave a magnetic moment of (2.28, 2.25 B.M), that values apply to cobalt complexes of flat square shape (14).
- Copper (II) complexes prepared in this study (5 and 6) showed magnetic moments (2.10 and 2.13 B.M), respectively, and these values are in

agreement with the tetrahedral copper (II) complexes, while the prepared copper (II) complexes (13 and 14) gave a magnetic moment (1.88 and 1.76 B.M), respectively, and these values apply to the flat square Cu (II) complexes (15, 16).

- Manganese complexes prepared in this study gave (7,8 and15) gave magnetic moments of (5.80, 5.70, and 5.93 B.M) respectively, and these values apply to tetrahedral manganese (II) complexes (17).

Electron Spectra

Electronic absorption spectra measurements are a necessary part of the process of characterization and studying the structure of new complexes. In this study, the electronic spectra of the ligands and complexes prepared using the solvent (DMSO) and at a concentration of (10^{-4}) molar were measured. The first ligand (L_1) showed two absorption bands (37037 and 50000 cm^{-1}) due to the (π→π*), and (n →π*) transitions. The second ligand (L_2) appeared in two absorption bands (50000, and 35087) due to the (π→π*), and (n→π*), (n→π) transitions). while the complexes prepared showed spectra that contain bands of transitions (the ligand spectrum and the charge transfer spectra), as well as the (d-d) spectra that appear with very weak intensities in the spectra of the complexes, which indicate the occurrence of coordination between the ligand and the metal ion.

Based on previous studies and research (18,19,20,21,22,23), the electronic transitions of the complexes were explained and their geometric shapes were determined, as shown in Tables (3-4), (3-5), (3-6), (3-7), (3-8), and (3-9) and Figures (3-1), (3-2), (3-3) (3-4), (3-5), and (3-6) that show the structure of the prepared complexes and the values of the electron spectra in (nm)) and (cm^{-1}) for ligands (L_1, L_2) and their complexes.

Table (3-4)
Values of electronic transitions in units (nm and cm^{-1}) for ligands (L_1, L_2)

No	Prepared ligand	Wavelength (λ)		Transitions type
		nm	cm^{-1}	
1	L_1	200	50000	π→π*
		270	37037	n→π*
2	L_2	200	50000	π→π*
		285	35087	n→π*

Table (3-5)
Values of the electronic spectra in units (nm) and (cm^{-1}) for nickel (II) Ni complexes

No	Prepared complex	Wavelength (λ)		Transitions type	Structure
		nm	cm^{-1}		
1	$[Ni(L_1)(SO_4)]$	275	36363	π→π*	T.d
		345	28985	n→ π*	
		565	17699	C . T	
		785	12738	$^3T_1(F) \rightarrow {}^3T_1(P)$	

		885	11299	$^3T_1(F) \rightarrow {}^3T_1(P)$	
2	$[Ni(L_2)(Cl_2)]$	269	37174	$\pi \rightarrow \pi^*$	Sq.p
		324	30864	$n \rightarrow \pi^*$	
		340	29411	C . T	
		540	18518	$^1A_1(g) \rightarrow {}^1A_2$ (g)	
		430	23255	$^1A_1(g) \rightarrow {}^1B_2$ (g)	

Table (3-6)
Values of the electronic spectra in units (nm) and (cm^{-1}) for Cobalt(II) Co. complexes

No	Prepared complex	Wavelength (λ)		Transitions type	Structure
		nm	cm^{-1}		
1	$[Co(L_1)(SO_4)]$	275	36363	Ligand	T.d
		490	20408	C . T	
		785	12738	$^4A_2$ (F)$\rightarrow {}^4T_1$ (F)	
		870	11494	$^4A_2$ (F)$\rightarrow {}^4T_2$ (F)	
2	$[Co\ (L_2)(Cl_2)]$	238	42016	$\pi \rightarrow \pi^*$	T.d
		275	36363	$n \rightarrow \pi^*$	
		402	24875	C . T	
		615	16260	$^4A_2$ (F)$\rightarrow {}^4T_1$ (P)	
		698	14326	$^4A_2$ (F)$\rightarrow {}^4T_1$ (F)	

Table (3-7)
Values of the electronic spectra in units (nm) and (cm^{-1}) for Copper(II) Cu. Complexes

No	Prepared complex	Wavelength (λ)		Transitions type	Structure
		nm	cm^{-1}		
1	$[Cu(L_1)(\ Cl_2)]$	245	40816	$\pi \rightarrow \pi^*$	T.d
		277	36101	$n \rightarrow \pi^*$	
		380	26315	C . T	
		890	11231	$^2T_2 \rightarrow {}^2E_2$	
2	$[Cu\ (L_2)(Cl_2)]$	240	41666	$\pi \rightarrow \pi^*$	Sq.p
		292	34246	$n \rightarrow \pi^*$	
		306	32679	C . T	
		680	14705	$^2B_1g \rightarrow {}^2A_1g$	

Table (3-8)
Values of the electronic spectra in units (nm) and (cm^{-1}) for zinc(II) Zn. Complexes

No	Prepared complex	Wavelength (λ)		Transitions type	Structure
		nm	cm^{-1}		
1	$[Zn\ (L_1)(\ Cl_2)]$	247	40485	$\pi \rightarrow \pi^*$	T.d
		266.50	37523	$n \rightarrow \pi^*$	
		356	28089	C . T	
2	$[Zn\ (L_2)(Cl_2)]$	244	40983	$\pi \rightarrow \pi^*$	T.d
		277	36101	$n \rightarrow \pi^*$	

		340	29411	C . T	

Table (3-9)
Values of the electronic spectra in units (nm) and (cm^{-1}) for Manganese(II) Mn. Complexes

No	Prepared complex	Wavelength (λ)		Transitions type	Structure
		nm	cm^{-1}		
1	[Mn (L_1)(Cl_2)]	245	40816	$\pi\rightarrow\pi^*$	T.d
		268.50	37243	$n\rightarrow \pi^*$	
		343	29154	C . T	
2	[Mn (L_2)(Cl_2)]	244	40983	$\pi\rightarrow\pi^*$	T.d
		269.50	37105	$n\rightarrow \pi^*$	
		354	28248	C . T	

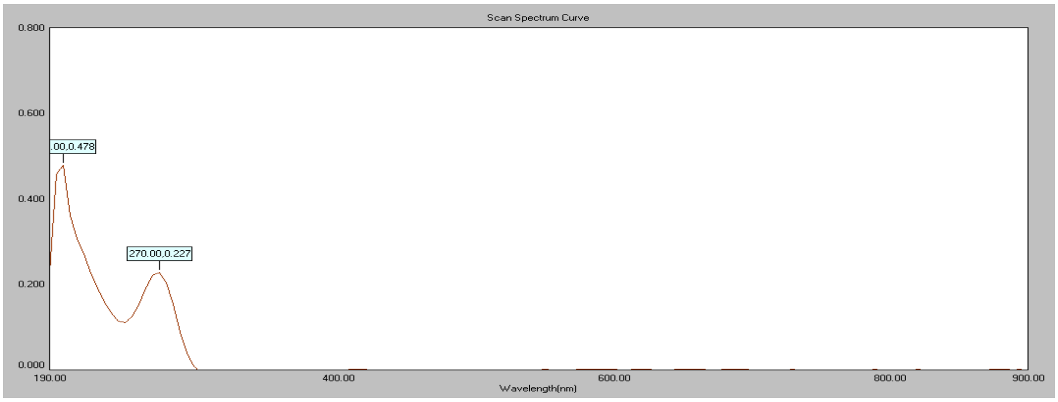


Figure (3-1). UV-visible spectrum of ligand (L_1)

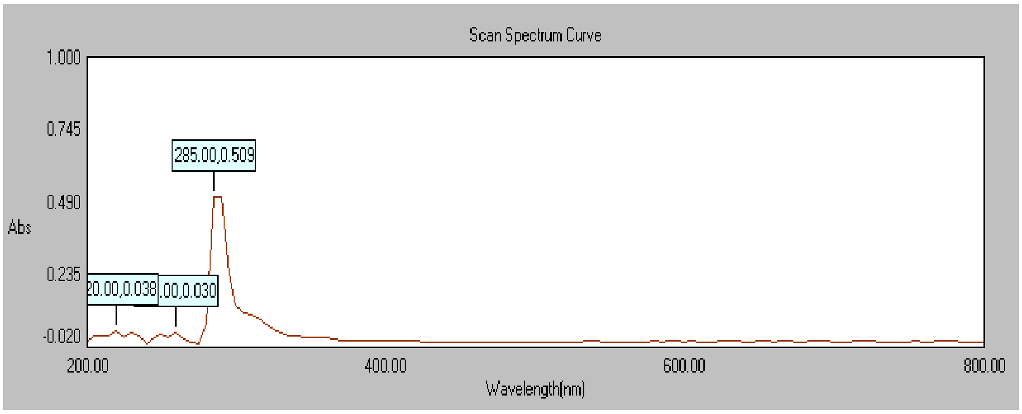


Figure (3-2). UV-visible spectrum of ligand (L_2)

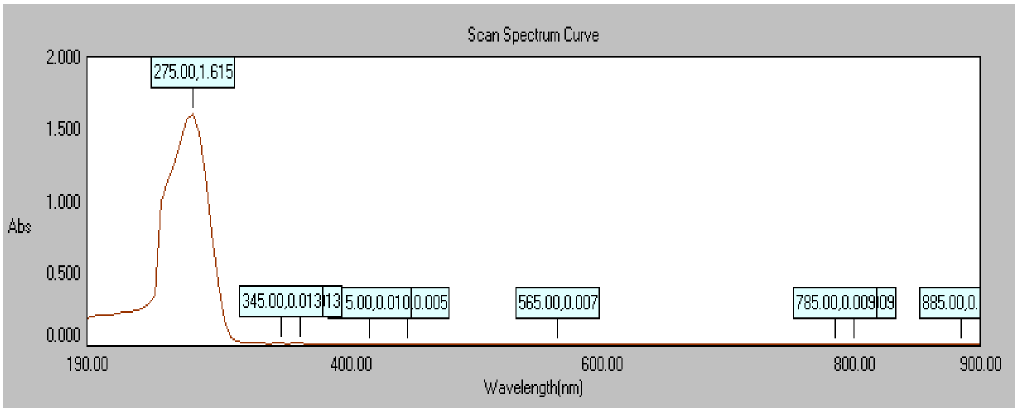


Figure (3-3). UV-visible spectrum of the complex [Ni(L_1)(SO_4)]

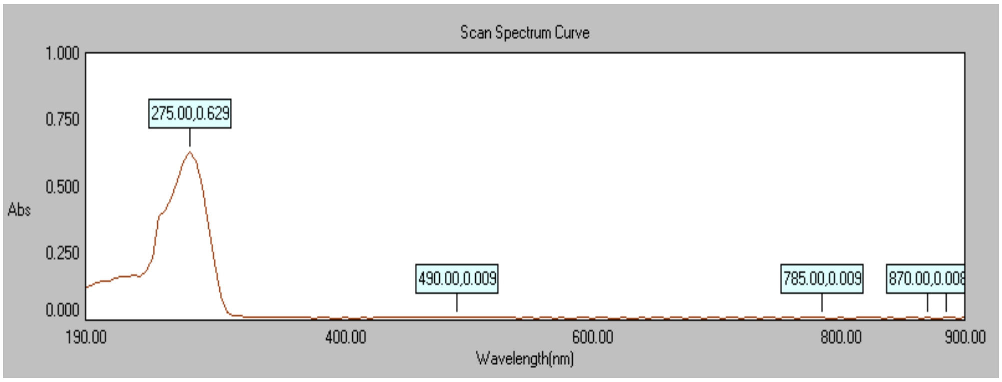


Figure (3-4). UV-visible spectrum of the complex [Co(L_1)(SO_4)]

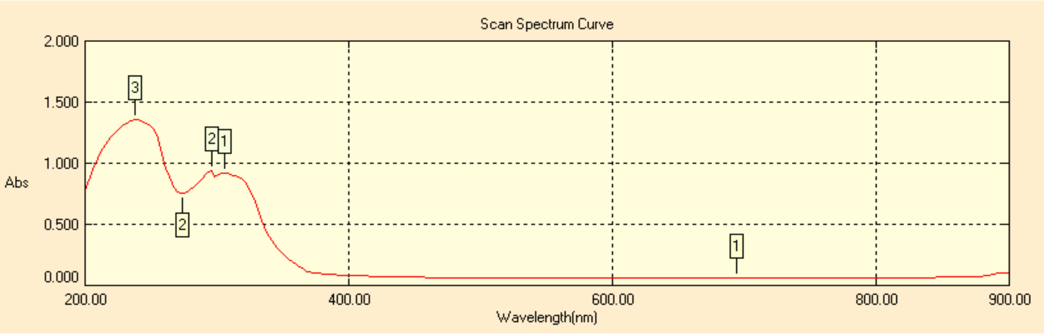


Figure (3-5). UV-visible spectrum of the complex [Cu (L_2)(Cl_2)]

Figure (3-6). UV-visible spectrum of the complex $[Zn(L_2)(Cl_2)]$

FT-IR Spectra

This study measured the vibratory spectrometry (infrared spectrometry) of ligands (L_1, L_2) and their complexes in the range (400-4000 cm^{-1}) and (200-4000 cm^{-1}). The spectra of the complexes were compared with the spectra of the ligands in our study to ascertain the bonding sites or coordination between the metal and the ligands, so we focus on the important vibration groups of the following (stretching vibration group υ(C=N)), (stretching vibration group υ (M-N)), (stretching vibration group υ (M-SO_4)) and (stretching vibration group υ (M-Cl)). The IR spectra have been determined for these active groups found in ligands (L_1, L_2)) and their complexes based on previous research and studies related to a similar relationship by many workers in this field.

- The stretching vibration bands of the group (C = N) appeared in ligands (L_1, L_2) at (1649,1666 cm^{-1}), respectively, but when the ligands are coordinated with ionic metals, we notice that there is a shift in these values to lower frequencies in some complexes, which indicates coordination between the nitrogen atom of (C= N) group and the metal ion, and this displacement shows the weakness that occurs in the property of the double bond for the isomethane group, which agrees with ref (24, 25).
- The stretching vibration of the (M-N) band appeared in a low-frequency region within the infrared spectrum of the metal complexes between the range (416-572) cm^{-1} of the infrared spectrum of the prepared complexes, which indicates the bonding of metals with the four ligands of the Schiff bases through the nitrogen atoms present in the prepared ligands (26).
- The stretching vibration bands of the (M-Cl) appear in the (250-350 cm^{-1}) region of the infrared spectrum (27), and in this study, the stretch-frequency bands of the metal-chlorine band of the prepared complexes within the region (220-340) cm^{-1}
- The complexes prepared in this study and containing the (SO_4) group showed three to four absorption bands for each complex within the confined area between (876-1184) cm^{-1}, and this confirms the presence of the (SO_4) chelating group in the complex and its association with the metal with two bonds (28)
- The stretch frequency bands of the alcoholic or phenolic (OH) group appear in the form of broad and wide absorption bands and appeared in the first

ligand (L_1) within the region (3209-3419) cm^{-1} and in the second ligand (L_2) at the region (3215-3437) cm^{-1}, while these bands also appeared in the prepared complexes from ligands (L_1, L_2) at the same frequencies or close to them. In the curvature of the (OH) group, a frequency band appears at the region 1(300-1370) cm^{-1} (29).

All of these bands mentioned above are recorded in Tables (3-10) and (3-11) based on Figures (3-7), (3-8), (3-9), and (3-10), which shows the infrared spectra of the ligands and complexes prepared in this study.

Table (3-10)
values of frequencies of some important bands in the infrared spectrum in units (cm-1) for ligand (L_1)

Compound	ῡ(C=N)	ῡ(M-Cl)	ῡ(M-N)	ῡ (OH)	ῡ(SO_4)
L_1	1649	---	---	3419	---
[Ni (L_1)Cl_2]	1615	293	448	3395	---
[Co (L_1) SO_4]	1637	---	422	3327	879,976 1085,1109
[Zn (L_1)Cl_2]	1624	319	455	3406	---
[Cu(L_1) SO_4]	1653	---	422	3317	873,968 1084,1112
[Mn(L_1) Cl_2]	1657	295	438	3284	--

Table (3-10)
values of frequencies of some important bands in the infrared spectrum in units (cm-1) for ligand (L_2)

Compound	ῡ(C=N)	ῡ(M-N)	ῡ(M- Cl)	ῡ(SO_4)	ῡ (OH)
L_2	1666	---	---	----	3437
[Ni (L_2) SO_4]	1662	418	---	960,1010 1099,1149	3309
[Co (L_2) Cl_2]	1654	425	242	----	3406
[Zn (L_2) SO_4]	1633	430	----	972,1014 1080,1114	3381
[Cu(L_2) Cl]	1671	441	270	-----	3242
[Mn(L_2) Cl]	1670	446	220	-----	3486

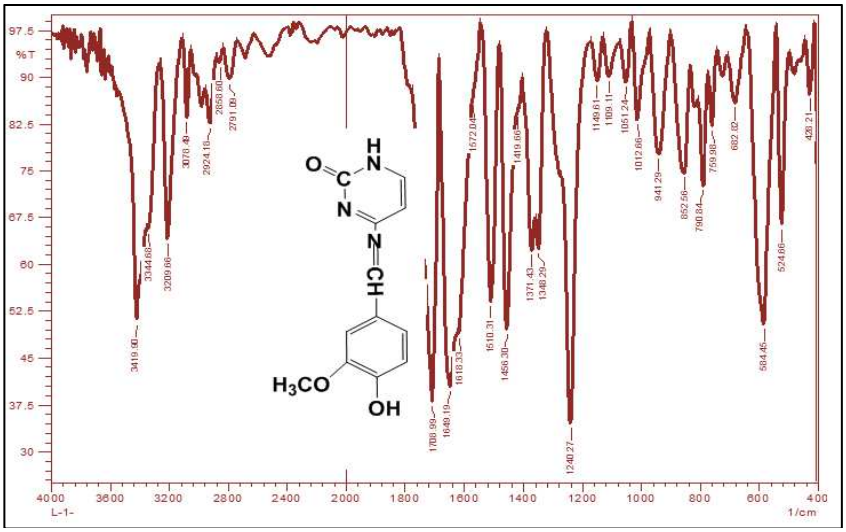


Figure (3-7). Infrared spectrum of Ligand 1 (L_1)

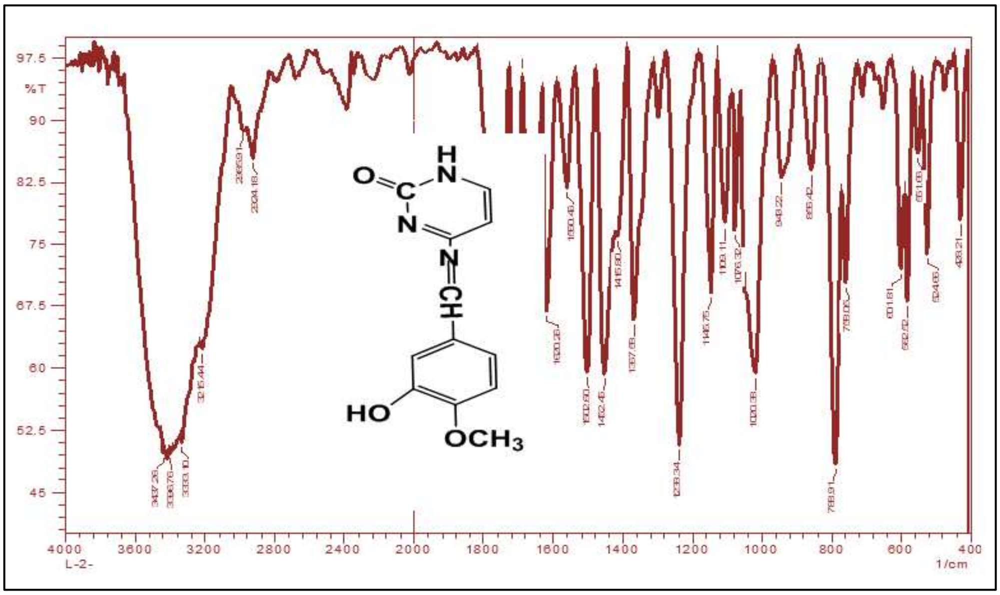


Figure (3-8). Infrared spectrum of Ligand 2 (L_2)

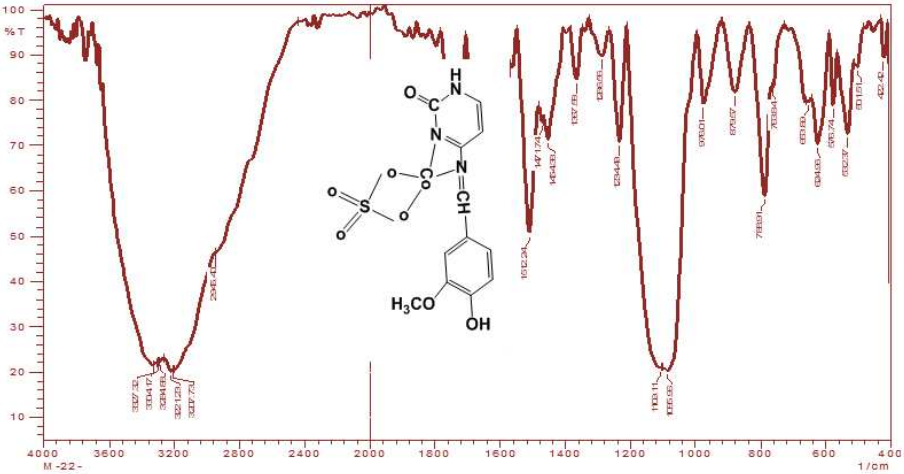


Figure (3-9). Infrared spectrum of [Co (L_1) SO_4]

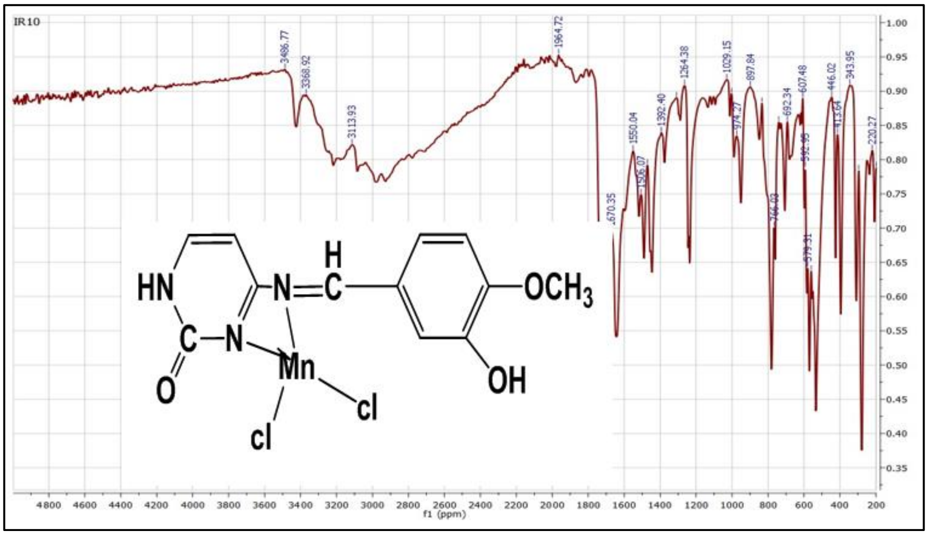


Figure (3-10). Infrared spectrum of [Mn (L_2) Cl_2]

^{1}H-NMR Spectra

The **^{1}H NMR** spectrum of the first ligand (L_1) in an acetic acid solvent showed that a single signal at the range δ H = 2.17 ppm belonged to the protons of the acetic acid solvent and a single signal at the position δ H = 3.52 ppm belonged to the protons of the (OCH_3) group, also, single signals appeared at δ H = 5.56 ppm and δ H = 6.56 ppm returning to the two protons in the pyrimidine ring, the multiple signals (a triple signal) appeared at δ H = 7.45, 7.56, and 7.66 ppm attributed to the three protons in the aromatic ring, and a signal appeared at the δ H = 8.50 ppm belonging to the proton in the (N = C-H) group. The signal at the δ H = 9.30 ppm belonged to the proton in the phenolic (OH) group, while, a signal appeared at the δ H = 11.01 ppm belonging to the proton of the (NH) group, as shown in Figure (3-11).

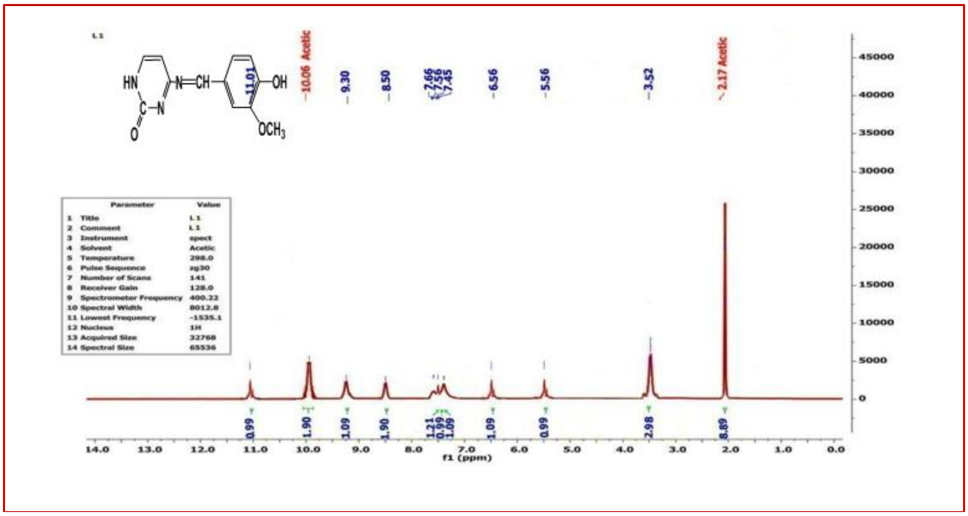


Figure (3-11). ^{1}H-NMR spectrum of the first ligand (L_1)

The **^{1}H NMR** spectrum of the second ligand (L_2) in acetic acid solvent gave a single signal at the range δ H = 2.17 ppm which belongs to the acetic acid solvent protons and a single signal at the position δ H = 3.48 ppm which is due to the protons of the (OCH_3) group. It also gave a single signal at the range δ H = 6.87 ppm that belongs to the protons of the pyrimidine ring and showed multiple signals (a quadrupole signal) at the positions δ H = 7.45, 7.56, 7.66, and 7.87 ppm attributed to the aromatic ring protons. As well as a signal at the position δ H = 8.45 ppm which is attributed to the proton in the group (N = C-H), a signal at the position δ H = 9.28 ppm attributed to the proton in the phenolic (OH) group and a signal appeared at the position δ H = 11.11 ppm due to the proton of the (NH) group as shown in Figure (3-12).

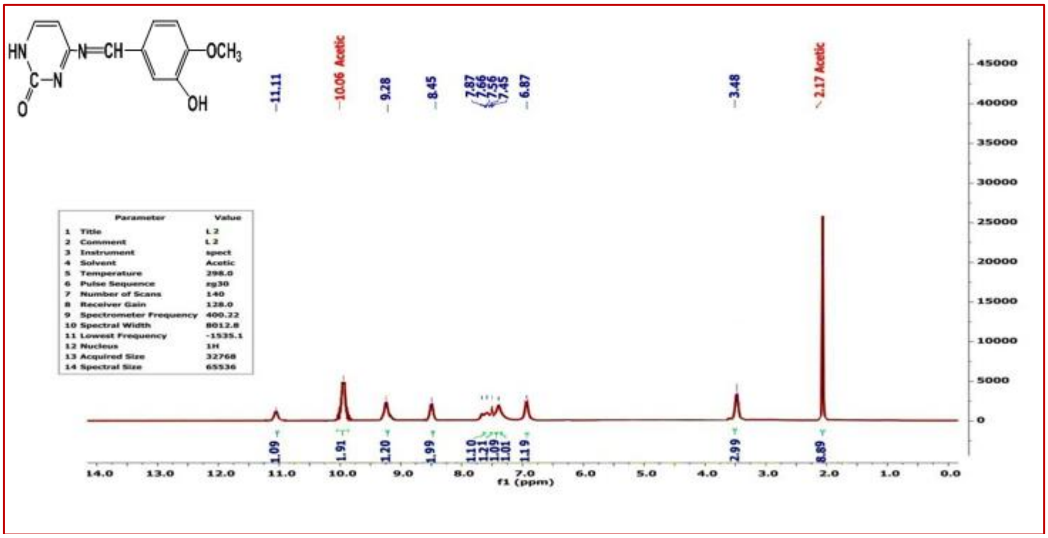
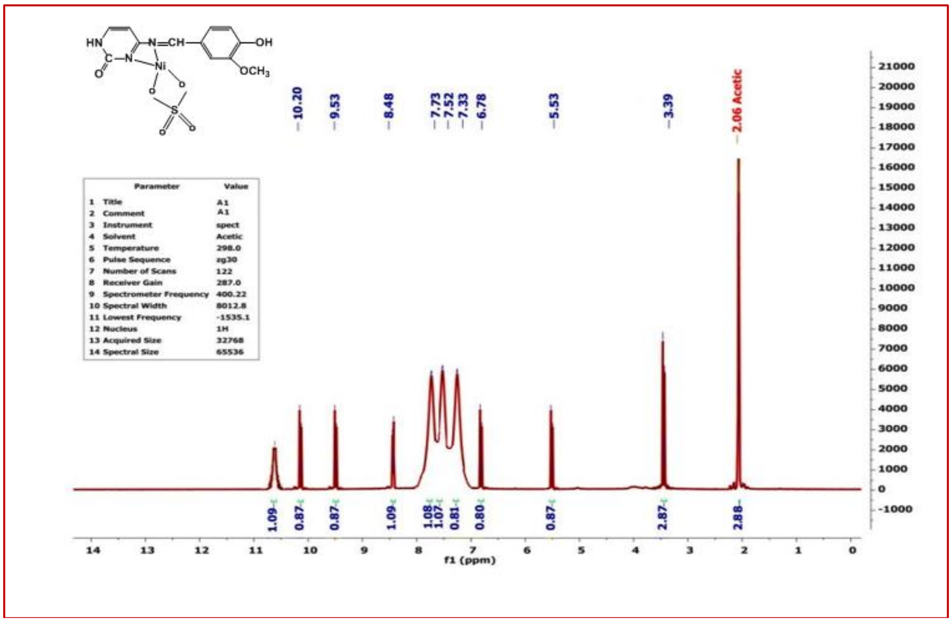
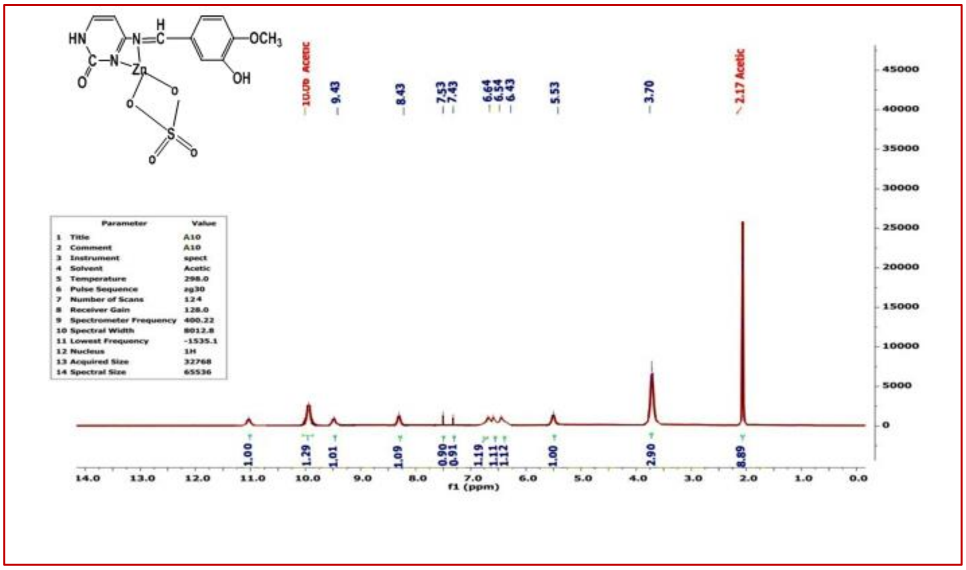


Figure (3-12). ^{1}H-NMR spectrum of the second ligand (L_2)



	Parameter	Value
1	Title	A1
2	Comment	A1
3	Instrument	spect
4	Solvent	Acetic
5	Temperature	298.0
6	Pulse Sequence	zg30
7	Number of Scans	122
8	Receiver Gain	287.0
9	Spectrometer Frequency	400.22
10	Spectral Width	8012.8
11	Lowest Frequency	-1535.1
12	Nucleus	1H
13	Acquired Size	32768
14	Spectral Size	65536

Figure (3-13). ^{1}H-NMR spectrum for the complex [Ni(L$_1$)(SO$_4$)]



	Parameter	Value
1	Title	A10
2	Comment	A10
3	Instrument	spect
4	Solvent	Acetic
5	Temperature	298.0
6	Pulse Sequence	zg30
7	Number of Scans	124
8	Receiver Gain	128.0
9	Spectrometer Frequency	400.22
10	Spectral Width	8012.8
11	Lowest Frequency	-1535.1
12	Nucleus	1H
13	Acquired Size	32768
14	Spectral Size	65536

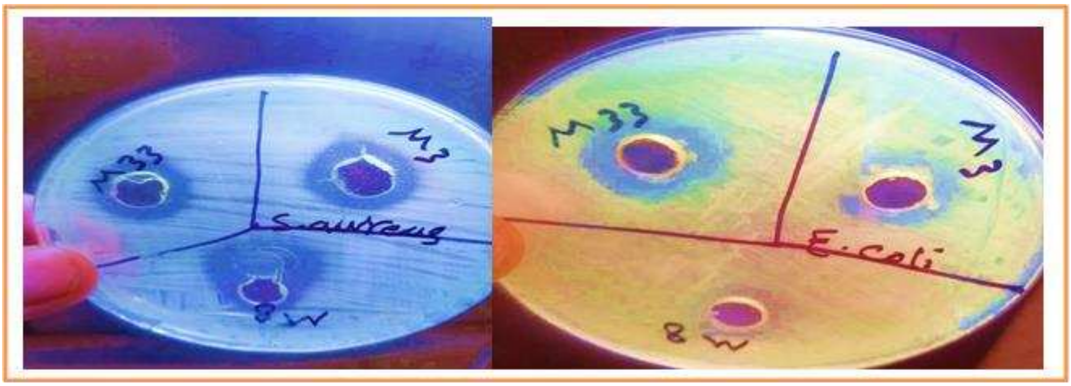
Figure (3-14). ^{1}H-NMR spectrum for the complex [Zn((L$_2$)(SO$_4$)]

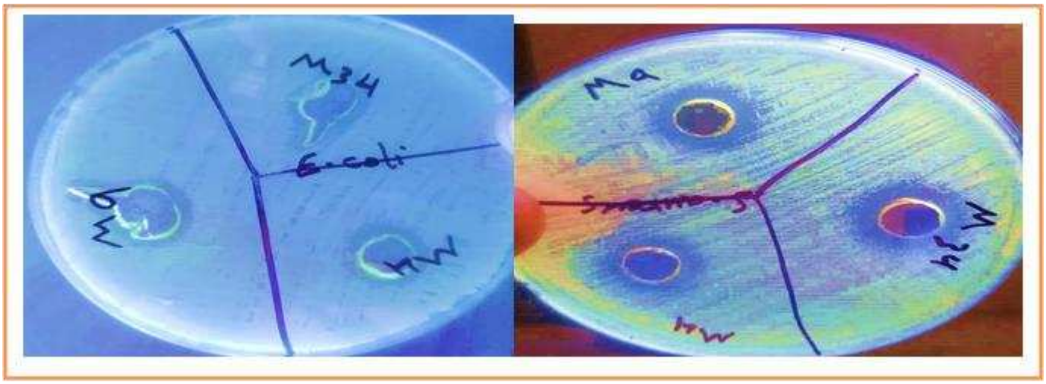
Biological activity screening of the prepared complexes

The biological activity of the prepared complexes (Schiff's base complexes) was conducted against two types of Gram-negative bacteria (*E.coli*) and Gram-positive bacteria (*Staphylococcus aureus*). Some of the complexes showed high inhibitory activity against (*Staphylococcus aureus*) and (*E. coli*) bacteria, while some of the complexes showed moderate to weak or no inhibitory activity as shown in Table (3-12) and Figure (3-15).

Table (3-12)
The average inhibition range of the complexes prepared at a concentration of (1000 ppm) using a DMSO solvent against two types of bacteria (*E.Coli* and *Staphylococcus aureus*) measured in millimeters

NO	Complex symbol	Chemical formula	Inhibition zone diameter in mm	
			(G-ve) E .coli	(G+ve) Staph
1	M3	$[Zn (L_1)(Cl_2)]$	15	25
	M8	$[Zn (L_2)(Cl_2)]$	13	30
	M33	$[Zn (L_2)(SO_4)]$	17	24
2	M4	$[Cu (L_1)(Cl_2)]$	8	17
	M9	$[Cu (L_2)(Cl_2)]$	10	20
	M34	$[Cu(L_1) SO_4]$	12	24
3	M2	$[Co (L_1)(Cl_2)]$	19	0
	M12	$[Co (L_2)(Cl_2)]$	0	14
	M37	$[Co (L_3)SO_4]$	15	20





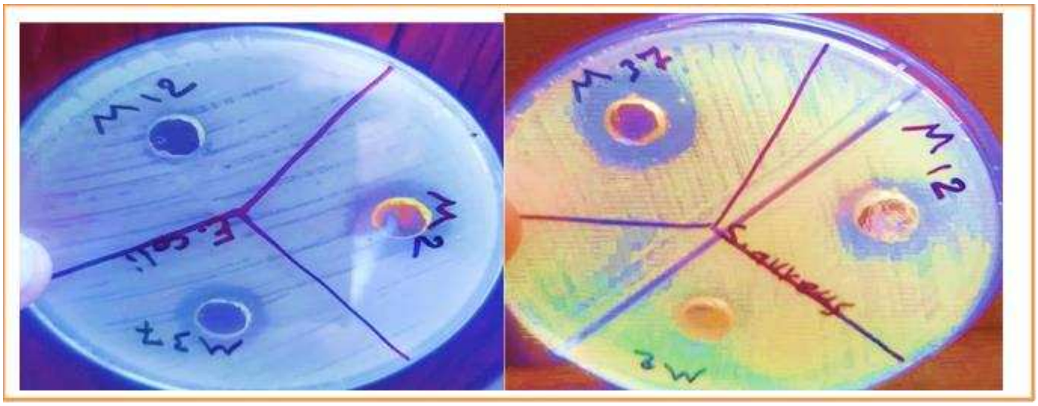


Figure (3-15). Average inhibition range of the prepared complexes against *E.Coli* and *Staph measured* bacteria measured by mm

Conclusion

- Through the physical and spectroscopic measurements that include molar conductivity, melting point, magnetic sensitivity, and micro elemental analysis - CHN, as well as spectroscopic measurements that include UV-vis, FT-IR, and proton nuclear magnetic resonance ^{1}H-NMR. which conduct on the ligands and complexes prepared in this study, it was found that all of the ligands (L_1 and L_2) that were prepared exhibit a bidentate ligands behavior and coordinate with chlorides and sulfates of hydrated metals ($NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $CoCl_2.6H_2O$, $ZnCl_2.4H_2O$, $MnCl_2.4H_2O$, $NiSO_4.6H_2O$, $CuSO_4.5H_2O$, $CoSO_4.7H_2O$, $ZnSO_4.7H_2O$, $MnSO_4$. H_2O) bivalent by nitrogen atoms present in the group (C=N) and group (NH_2) as well as present in the pyrimidine ring, in all complexes.
- By measuring the molar electrical conductivity, it was found that all the complexes prepared in this study are electrically neutral, so the sulfate and chloride ions are inside the coordination sphere and are directly related to the ionic metals in these complexes.
- Through magnetic susceptibility measurements, it was found that the prepared complexes possess the following geometric shapes (tetrahedron, and planar square)
- Some of the complexes showed a high inhibitory ability against *Staphylococcus aureus* and *E. coli.*

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