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Synthesis, Characterization, Antibacterial study and Efficiency of Inhibition of New di- β -enaminone Ligand and its Complexes

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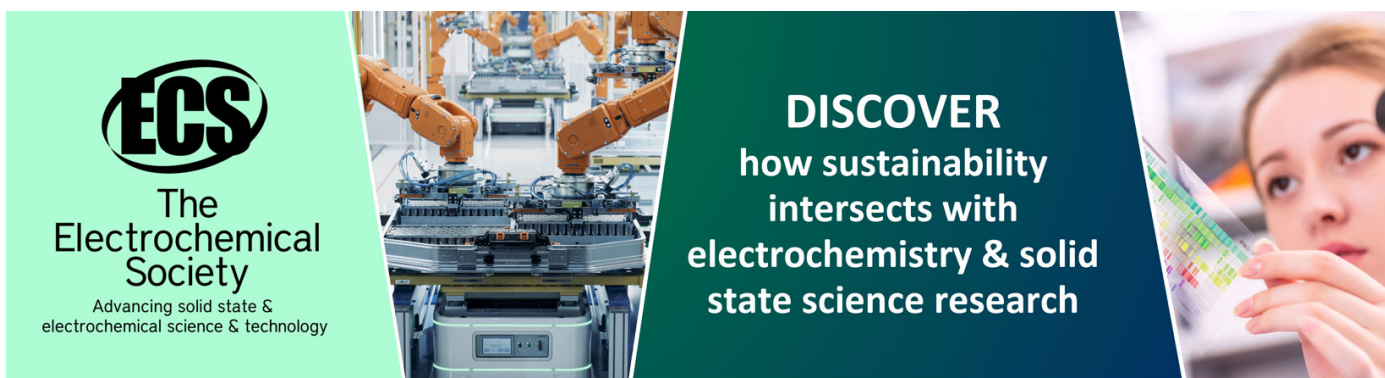
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Synthesis, Characterization, Antibacterial study and Efficiency of Inhibition of New di- β -enaminone Ligand and its Complexes.

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Abstract. The new ligand [3,3'-(1,2-phenylenebis(azanediyl))bis(5,5-dimethylcyclohex-2-en-1-one)] (L) derived from 5,5-Dimethylcyclohexane-1,3-dione with 1,2-phenylenediamine was used to prepare a new chain of metal complexes of Mn(ii), Co(ii), Ni(ii), Cu(ii), Cd(ii) and Zn(ii) by inclusive formula $[M(L)]Cl_2$. Characterized compounds on the basis of 1H , ^{13}C NMR (for ligand (L)), FT-IR and U.V spectrum, melting point, molar conduct, %C, %H and %N, the percentage of the metal in complexes %M, Magnetic susceptibility, thermal studies (TGA), while its corrosion inhibition for (plain steel) in tap water is studied by weight loss. These measurements proved that by (O and N) atoms in the ligand, the metal ions are coordinated in a tetra dentate form and the tetrahedral structure of these complexes is suggested. Using the pathogenic bacteria such as (*Escherichia coli*) (G⁻) and (*Staphylococcus aureus*) (G⁺) and fungi (*Candida albicans*) and (*Trichomoniasis*), the anti-microbial action of both (L) and their complexes was studied by diffusion method.

Keywords. 1,2-phenylenediamine, β -enaminone, Transition metal complexes.

1. Introduction

Enaminones contain of an (NH₂) group connected by (C=C) to a (C=O) group. These components of enamenon make it as bidentates system. Providing the required stability of the system is done through the carbonyl group which facilitates prepare the complex and then isolate and store [1-3]. Enamino carbonyl group chemistry is widely considered. Due to its use as an intermediary for many useful synthetic compounds, Enaminone has received considerable attention over the past decade. In order to find different ways to synthesize enaminones, a lot of work has been done. Enaminones are used in the synthesis different hetero cyclic and biological activity analogues and in the pharmaceutical development because it is an important organic intermediates. Enaminones were considered to be good chelating ligands for the transition metals in coordination chemistry [4-7]. They are used for the synthesis of many important compounds including α,β -amino acids, γ -amino alcohol, heterocycles, alkaloids, quinolines, azocompounds, etc . In conclusion, it should be noted that the biological activity of enaminones compounds is attributed to the presence of the active group N=C-C=O within a ring system [8-11]. Dimidone is also called 5,5-Di methyl cyclo hexane -1,3-di one and is acyclic di ketone in the form of white to light yellow crystals used in organic chemistry. Dimidone and its derivatives



have many biological properties such as anti-histaminic, anti-cancer inorganic, anti-coagulant and anti-oxidant. One of its main applications is its use in green organic reactions. Also used in different anti-microbial agents such as macro cyclic metal complexes, tetrahydro quinolone diones and acridine based compounds, xanthenes, quinazoline derivatives and substituted [12-14]. Dimedone is an alicyclic compound contain 1,3-dicarbonyl groups surrounded by a (-CH₂-) group and it is there in a tautomer trans-enol form where inter-molecular (H- bond) is impossible. Because there are (2C) atoms in the dimedone that are part of the pack bone of the formed heterocyclic, it is a good precursor for partial hydro genated fused hetero cyclic. Its ability to build a wide range of spiral bi-hetero cycles came from its formation of effective derivatives due to its good structural properties [15-17]. The purpose of this research is to prepare a fresh ligand [3,3'-(1,2-phenylenebis (azanediyl))bis(5,5-dimethylcyclohex-2-en-1-one)] (L) and their transition metal complexes with Mn(ii), Co(ii), Ni(ii), Cu(ii), Cd(ii) and Zn(ii) ions.

2. Experimental

2.1. Chemicals

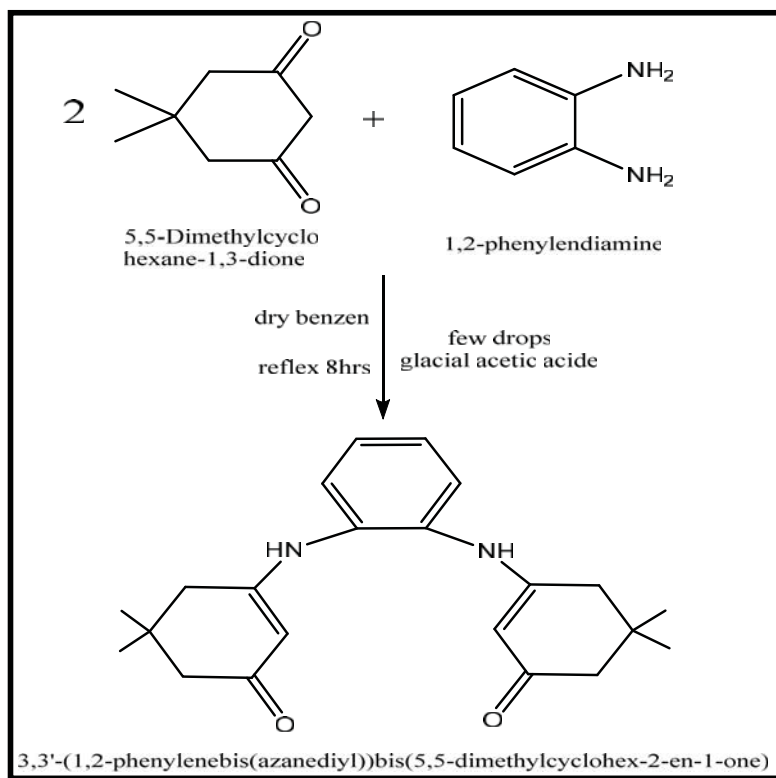
All chemicals were purchased from Fluka and Sigma-Aldrich to complete the research and were used without purification

2.2. Analytical and physical measurements

Shimadzu-FTIR-8300-Spectrophotometer is used within the range (400-4000)cm⁻¹ to perform FT-IR measurement of compounds prepared by KBr pellets. By an Stuart SMP10 Melting Point Apparatus with an open capillary tube, the melting point of the prepared compounds was measured. By Shimadzu UV-160 UV Visible Spectrophotometer with a quartz cell length of 1.0 cm and a concentration of 10⁻³ M from the samples in the DMSO solvent at laboratory temperature, the electronic spectra of the compound were measured. Using 300 MHz NMR spectrometer, the NMR spectra ¹H and ¹³C in a dimethyl sulfoxide solution (DMSO-d₆ with TMS) have been recorded. By Electron-Impact (EI) on Shimadzu GCMSQPA 1000 spectrometer, mass spectra were obtained. Through the Atomic Absorption (A.A) technique by a (AA-680. Shimadzu), the percentage of metals has been determined. Using the conductivity meter EUTECH CON 150, the conductivity measurements at room temperature and 10⁻³M concentration of the sample solution in the DMSO solvent were conducted. A Linseis STA PT1000 at the temperature range of 0-600 °C and used argon gas, thermal gravity analysis (TGA) was performed. With the Sherwood Scientific's Magnetic Susceptibility Balances, magnetic moments (μ_{eff} B.M) at 25 °C have been identified. By Elemental Analyzer EURO EA 3000, Micro elemental analysis for carbon, hydrogen and nitrogen has been determined.

2.3. Synthesis of the ligand (L)

1,2-phenylenediamine (0.97g, 9mmol) solution in dry benzene (10 ml) was slowly added to 5,5-Dimethylcyclohexane-1,3-dione (2.5g, 18mmol) solution in dry benzene (10 ml). A light brown solution has emerged by allowing the mixture to stir continuously until it is completely dissolved. Glacial acetic acid in the form of a few drops has been added to the solution. For 8 hours, the solution was refluxed until a light yellow precipitate appeared; by TLC the solution was monitored. The reaction mixture was left to cool to the laboratory temperature and then the reaction mixture was filtered to obtain a light yellow product that was isolated and washed with benzene several times, then allowed to dry and give a yellow precipitate. Yield (87 %), m.p (160-162) °C, Fig.(1). Scheme (1) shows the path of the ligand synthesis, table (1) shows some physical data and microanalysis of the results of (L) and their complexes.



Scheme 1. The structure of the prepared (L)

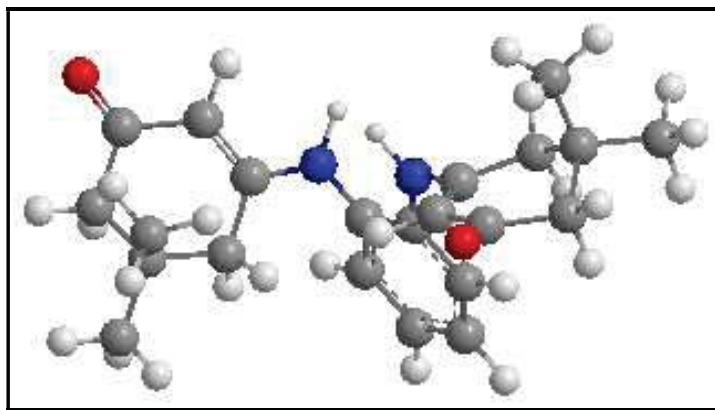


Fig. (1) 3D –Structure of (L)

2.4. Synthesis of complexes with ligand (L)

The metals chloride solution ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ and ZnCl_2) (0.14 - 0.24 g, 1mmol) in (10ml) ethanol was added to the ligand solution (0.35g, 1mmol) in (10ml) ethanol. For 4 hours, heat the reaction mixture under the reflux. After collecting the precipitate, filtrate and wash with EtOH , CH_3COCH_3 and Et_2O and in a laboratory atmosphere, leave dry, Fig. (2)

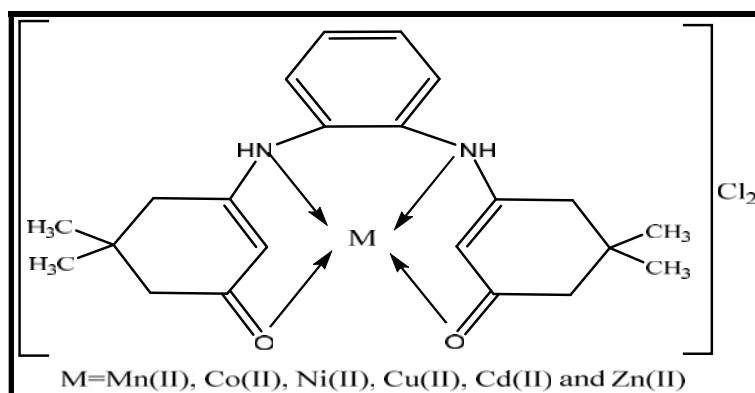


Figure 2. The suggested chemical structure of the complexes

3. Results and Discussion

One of the most important characteristics of mineral complexes is that it is thermally stable and solid color. They are soluble in Dimethyl formamide and Dimethyl sulphoxide. The results of Theoretical and practical atomic absorption results were compared for all compounds. They were close together

3.1. Mass spectral of the ligand (L)

To determine fragmentation pattern and molecular weight of (L), mass spectrum was performed, Fig. (3) [18].

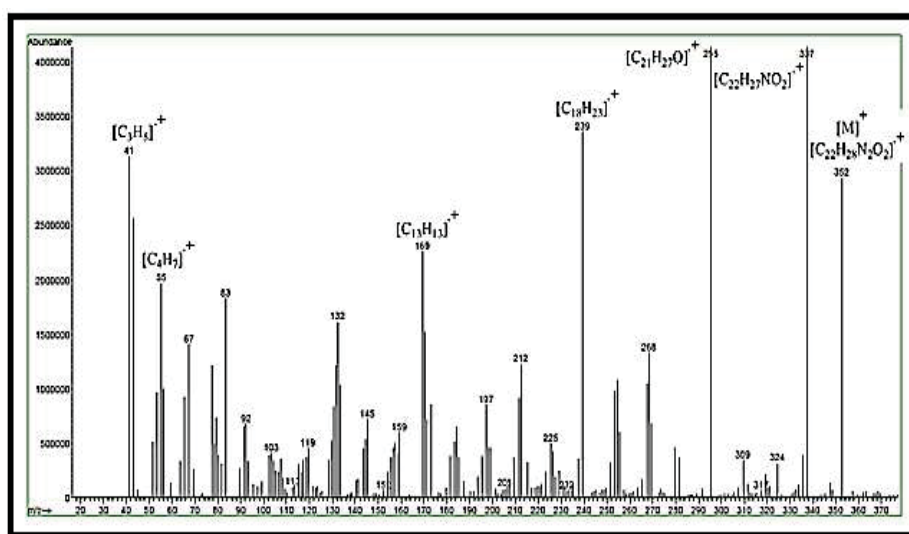


Figure 3. Mass Spectrum of (L)

3.2. Nuclear magnetic resonance spectra of the ligand (L)

3.2.1. $^1\text{H-NMR}$ spectra of (L)

The Proton-1, Nuclear magnetic resonance spectrum for (L) in Fig.(4) display the next character chemical shift in DMSO- d_6 (solvent) : A single signal belonging to the proton of the N-H group ($\delta = 8.38\text{ppm}$) within the spectrum has been exhibited. Chemical shift of protons (C_2) to the C-H aromatic group at ($\delta = 7.28\text{ppm}$) has been specified. Signal appeared at chemical shift ($\delta = 4.91\text{ppm}$) of a proton (C_3) from the $C_2\text{H}$ group, while chemical shifts at ($\delta = 2.52$ and 2.46ppm) indicated (C_4

and C₅) protons of the CH₂ groups. Lastly a signal at (1.04 -1.08ppm) on (C₆) proton CH₃ groups was determined. Spectral data of ¹H-NMR of (L) in the literature were reported [19-23]. These results are reported in Table(2)

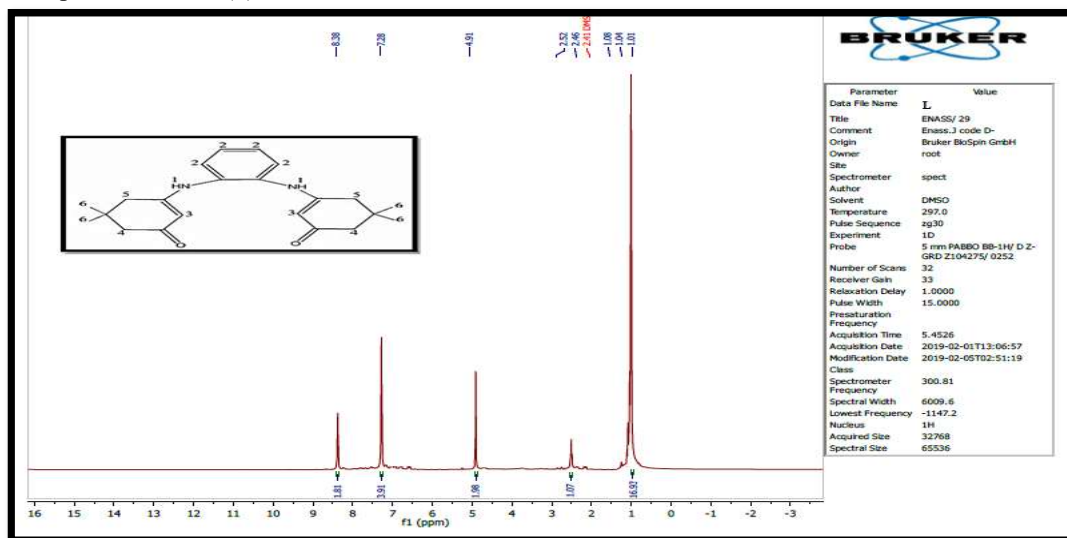


Figure 4. ¹H-NMR spectra of (L)

3.2.2. ¹³C-NMR spectrum of (L)

The Carbon -13 Nuclear magnetic resonance spectrum for (L) , Fig.(5) in DMSO-d₆ (solvent) display many of signals back to (L), explain as follows: The ligand spectrum showed a signal at (δ = 195.51 ppm) that return to the carbon atom (C₁) of the C=O group. A chemical shift was also found at (δ= 161.24 ppm) attributed to a carbon atom (C₂). Signals at (δ=133.88, 127.37 and 126.77 ppm) attributed to (C₃, C₄ and C₅) respectively. Also the resonances at (δ=97.07, 50.73, 42.23, 32.83 and 28.53 ppm) attribute to (C₆, C₇, C₈, C₉ and C₁₀), respectively [24-27]. The results are listed in Table (3)

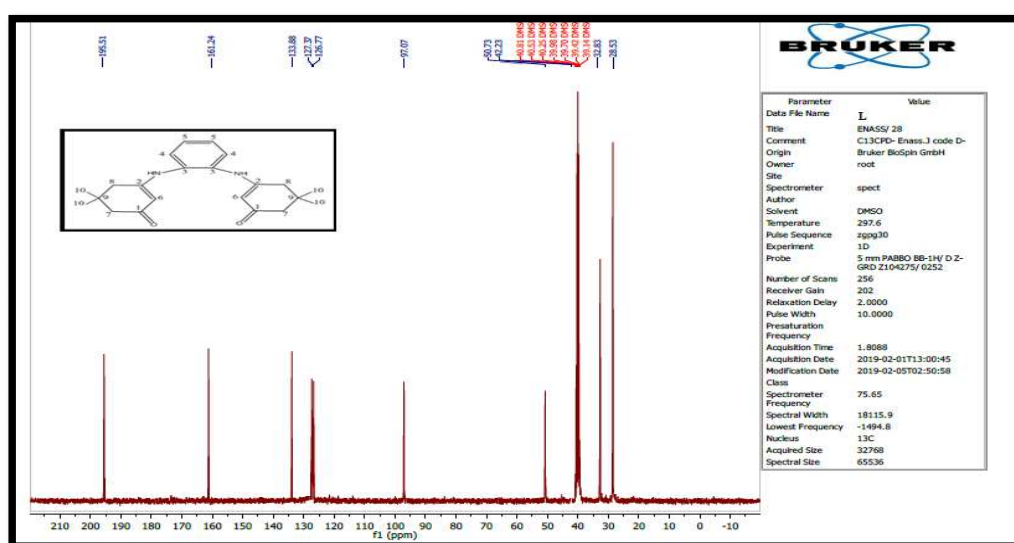


Figure 5. ¹³C-NMR spectra of (L)

3.3. FT-IR Spectra of ligand (L) and its metal complexes

The spectrum of FT-IR due to (L), Fig.(6) shows the emergence of a band at $(3240) \text{ cm}^{-1}$ due to ν (N-H) stretching vibration, which was observed to disappear when the complexes were formed. This confirms the coordination with the metal ions by nitrogen atoms of the enamine groups [28]. The band at $(1573) \text{ cm}^{-1}$ is due to carbonyl groups $\nu(\text{C=O})_{\text{dimedone}}$ stretching vibration for (L) in the range between $(1589\text{--}1585) \text{ cm}^{-1}$ which is shifted towards higher frequencies, confirming that the ligand is coordinated by O atom in the C=O [29]. The new bands in the range between $(528\text{--}513) \text{ cm}^{-1}$ were attributed to ν (M-N) for complexes, indicating that to the nitrogen (enamine group) of (L) are contribute in coordination with metal ions [30]. The new bands in the range between $(497\text{--}489) \text{ cm}^{-1}$ were attributed to $\nu(\text{M-O})$ for complexes [31], indicating that the oxygen (carbonyl groups) of (L) are contribute in coordination with metal ions, Table (4), Fig. (7).

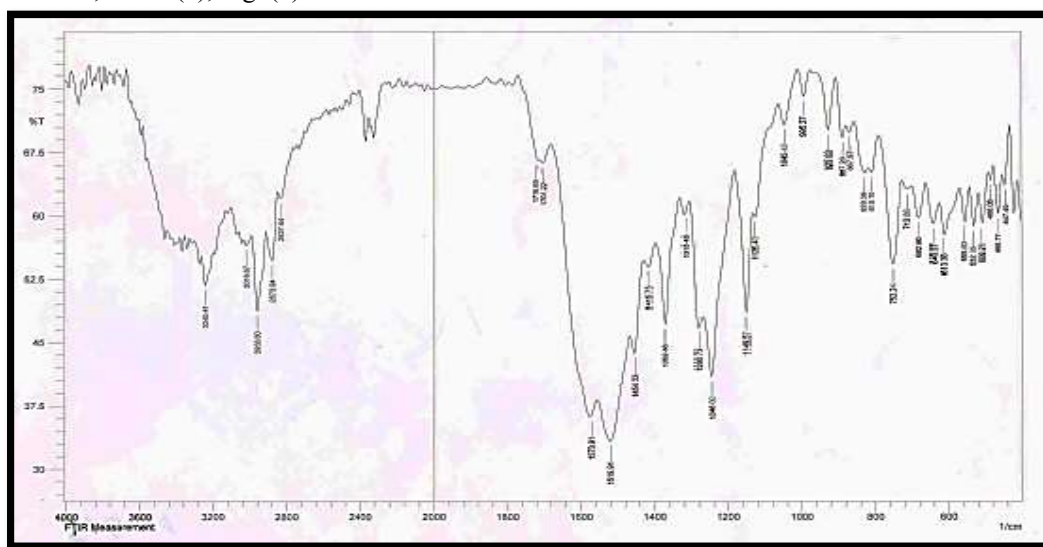


Figure 6. FTIR spectrum of (L).

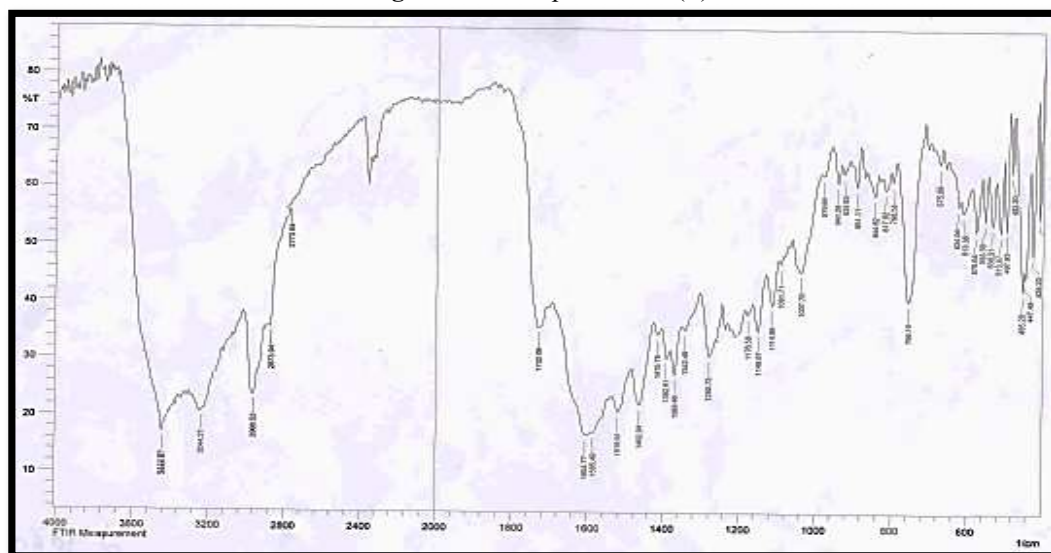


Figure 7. FTIR spectrum of $[\text{Ni}(\text{L})]\text{Cl}_2$ complexes.

3.4. UV-Vis spectra of ligand (L) and their metal complexes

Table (5) gives the UV-Vis spectra of (L) and their complexes that measured in DMSO, in the range (200-1000) nm.

The ligand (L): Two bands have appeared in the ligand spectrum at 42553 and 30581 cm^{-1} due to the electron transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively, Fig.(8) [32].

[Mn(L)]Cl₂: Three absorption bands were diagnosed in the electronic spectrum of manganese complex at 35335, 25000 and 16667 cm^{-1} attributed to Intra ligand, C.T and ${}^6A_1 \rightarrow {}^4T_{1(G)}$ respectively and this shows the tetrahedral geometric shape of the complex [33].

[Co(L)]Cl₂: The electronic spectrum of Co complex display four absorption bands at 42372, 35460, 25125 and 12330 cm^{-1} due to Intra ligand, Intra ligand, C.T and ${}^4A_2 \rightarrow {}^4T_{1(P)}$, respectively, which indicate an tetrahedral geometry, Fig.(9)[34].

[Ni(L)]Cl₂: Three absorption bands of Ni(II) complex at 35460, 26315 and 14144 cm^{-1} due to Intra ligand, C.T and ${}^3T_{1(F)} \rightarrow {}^3T_{1(P)}$, respectively, which indicate an tetrahedral geometry [35].

[Cu(L)]Cl₂: Electronic spectrum of the prepared copper complex display four bands at 35971, 29411, 25000 and 12437 cm^{-1} which are attributed to the transitions: Intra ligand, Intra ligand, C.T and ${}^2T_2 \rightarrow {}^2E$ respectively [36].

[Cd(L)]Cl₂: The electronic spectrum of cadmium complex display tow absorption bands at 35587 and 25000 cm^{-1} due to Intra ligand and C.T, respectively, which indicate a tetrahedral geometry [37].

[Zn(L)]Cl₂: Electronic spectrum of the prepared Zn (II) complex display tow bands at 35211 and 25000 cm^{-1} which are attributed to the transitions: Intra ligand and C.T, respectively [38].

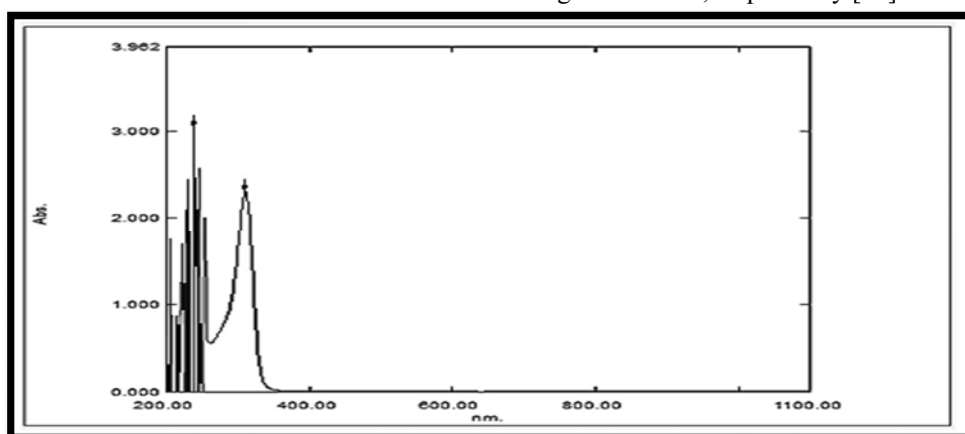


Figure 8. UV-Vis spectrum of (L).

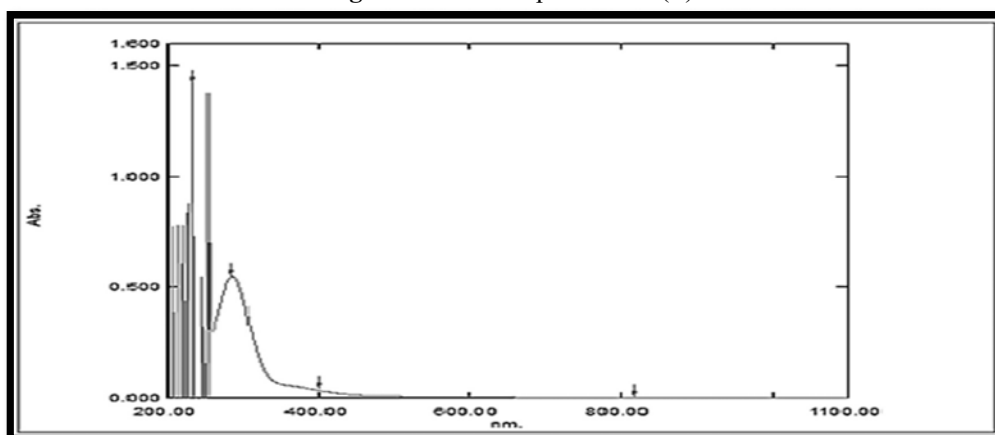


Figure 9. UV-Vis spectrum of [Co(L)]Cl₂ complex.

3.5. Magnetic and Conductive measurements of metal complexes prepared from ligand (L)

The measured magnetic measurement values and (μ_{eff}) of the complexes Mn(ii), Co(ii), Ni (ii), Cu(ii), Cd(ii) and Zn(ii) are listed in Table (1). The values of μ_{eff} showed results for the complexes mentioned (5.82, 4.93, 3.05, 1.79) B.M respectively, these values are proportional to the tetrahedral form of complexes. All prepared complexes showed electrolytic properties according to measurements of molar conductivity, Table (1) [39]

3.6. The corrosion studies of ligand (L) and $[\text{Zn(L)}]\text{Cl}_2$ complex

3.6.1. The role of ligand (L) in inhibition of corrosion on (plain steel) in tap water.

A systematic study was carried out in this research to test the action of the inhibitor representing the prepared ligand (L) and one of its complexes $[\text{Zn(L)}]\text{Cl}_2$ on the corrosion of (plain steel) in tap water in a submerged way and measure the weight loss for the purpose of developing corrosion inhibitors of low toxicity and high efficiency. Represents the chemical composition of specimens plain steel (wt %) was: C, 0.16; Mn, 0.43; Cu and Sn, 0.01; P, Si, S and Ni, 0.02 and the remainder Fe. The plain steel samples having dimension $2.0\text{cm} \times 2.0\text{cm} \times 0.1\text{cm}$ were used for this experiment. The solution of the experimented ligand (L) and its complex were prepared in (10:1 ratio) (tap water: Dimethyl sulfoxide) mixture to ensure solubility. The plain steel specimens were abraded with emery paper (multi size) and a mixture of distilled water and acetone was washed. After weighing, they were immersed in 250 ml beaker contain 125 ml of solution of 10:1 tap water: DMSO without and with the addition of different concentration (10^{-4} , 10^{-2} M) of the ligand and $[\text{Zn(L)}]\text{Cl}_2$ complex. All the beakers were open to air, in laboratory temperature these measurements were made. The experiment was repeated at 24, 48 hours. The results of these tests were determined, and are given in Table (6) [40-42].

3.6.2. Study the effect of immersion time and inhibitor concentration on corrosion inhibition

When testing for inhibition efficiency and its correlation with inhibitor concentration, maximum efficiency was found at 10^{-2} M. The best inhibition in high concentration can be attributed to the actuality that the inhibitor molecules coverage more metals. The inhibitory efficiency of the inhibitor was increased over time to 48 hours and then almost proved and this explains the formation of persistent film above the metal surface.

At the same concentration of inhibitors, the order of inhibition efficiency was found to be as follows: $[\text{M(L)}]\text{Cl}_2 > \text{ligand}$. In the Table (6) reported values (Θ) and (% E.I), equation (1)

$$\% \text{ E.I} = \Theta \times 100 = [1 - (W_{\text{inh}}/W_{\text{free}})] \times 100 \dots \dots \dots (1)$$

% E.I= the inhibition efficiency

Θ = degree of surface coverage

W_{inh} = the weight losses per unit area in the presence of the inhibitors

W_{free} = the weight losses per unit area in the absence of the inhibitors

3.6.3. Thermal analysis studies of ligand (L) and $[\text{Cu(L)}]\text{Cl}_2$

Based on methods (TGA / DTG and DSC) and within the temperature range of ambient temperature to 600°C , the thermal properties of Ligand (L) have been diagnosed. For the purpose of suggesting a inclusive scheme of thermal decomposition of Ligand (L), these methods were used to obtain data about the thermal stability of the new Ligand (L). Based on the supporting information, the heat separators and the percentage of mass loss are listed in Table (7). In four consecutive steps of decomposition, the ligand (L) $[\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_2]$ has been decomposed. The loss of fragment $\text{C}_3\text{H}_{16}\text{N}_2\text{O}_2$ in the temperature range $25-366^\circ\text{C}$ is due to the estimated mass loss of 32.11% (calculated mass loss = 31.78%) within the first and second steps of decomposition. The DSC curve gives maximum peak temperatures at 123.7 and 180°C , both of them refer to an endothermic decomposition. The loss of fragment C_3H_4 in the temperature range

366–595°C is due to the estimated mass loss of 11.432% (calculated mass loss = 11.33%) within the third and fourth steps of decomposition, Fig.(10).

In three consecutive steps of decomposition, The complex $[\text{Cu(L)}]\text{Cl}_2$ has been decomposed. The loss of fragment Cl_2 , N_2O_2 and C_2H_3 in the temperature range 25–273°C is due to the estimated mass loss of 32.303% (calculated mass loss=32.226%) within the first step of decomposition. The loss of fragment C_7H_5 in the temperature range 273–495°C is due to the estimated mass loss of 20.413% (calculated mass loss =20.321%) within the second step of decomposition. The loss of fragment (C and 5H_2 molecules) in the temperature range 495–595°C is due to the estimated mass loss of 4.536% (calculated mass loss =4.515%) within the final (third) step of decomposition. The Differential scanning calorimetry analysis point to four an endothermic peak at 96.8 , 221.6, 307.4 and 387.2°C may refer to decomposition of the organic ligand in (an organ) atmosphere, the last peak at 595°C refer to an exothermic decomposition process, this confirms the breaking of the bond between the metal and the ligand, Table (7),Fig.(11) [43–45].

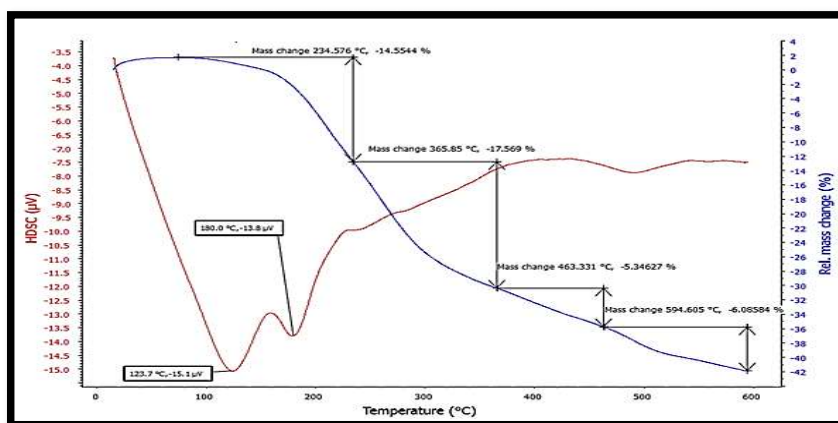


Figure 10. Thermal study of (L)

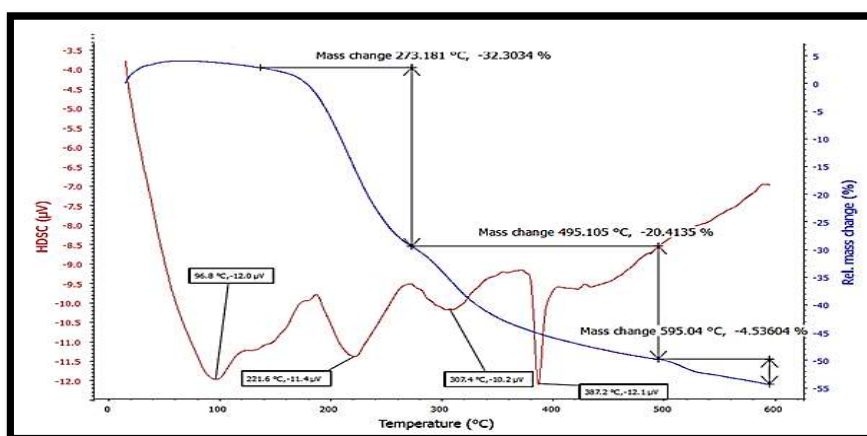


Figure 11. Thermal study of $[\text{Cu(L)}]\text{Cl}_2$ complex

3.6.4. Antimicrobial Activity

Using a good diffusion method by agar nutrient as a medium, a biological test has been carried out in vitro for compounds prepared on certain types of bacteria which include (*Escherichia coli*) as (G^-) and (*Staphylococcus aureus*) as (G^+) and the fungus, (*Candida albicans*) and (*Trichomoniasis*). By dissolving the compounds in DMSO, stock solutions (10^{-3} M) have been prepared. A well has been

performed on the agar medium inoculated with microorganisms as a typical procedure. The plate was incubated at 37 °C for 24 hrs after the well was filled with a test solution using a micro pipette. The test solution was spread and the growth of pollinated microorganisms was affected within this period, Table (8), Fig.(12) [46-47].

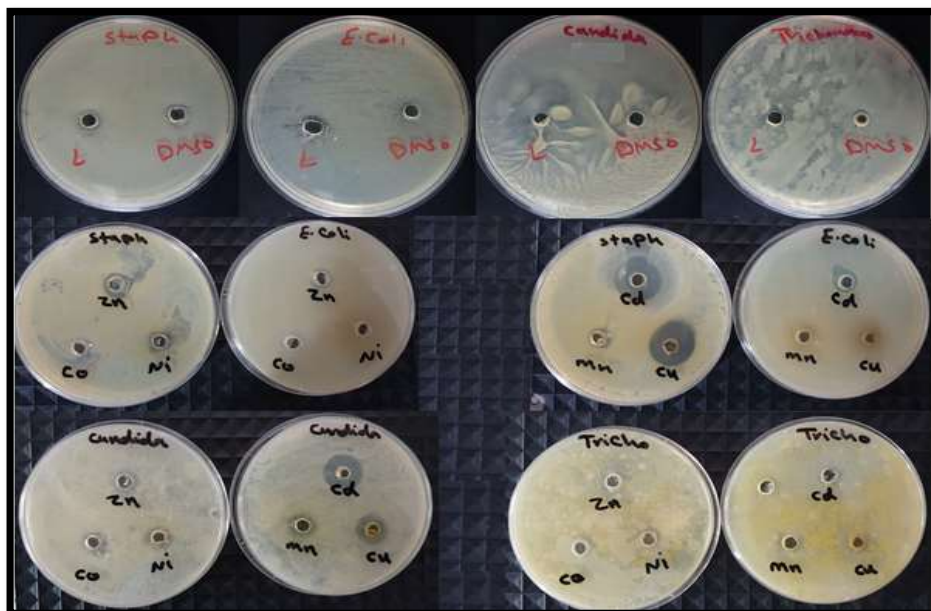


Figure 12. The diameter values of inhibition of (L) and some complexes prepared against selected microbial

4. Acknowledgement

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5. Conclusion and Recommendation

Based on the reported results, it is concluded that the ligand (L) act as a tetra dentate coordinated donor by O atoms of (CO) groups and N atoms of (NH₂) groups. The tetrahedral structure of the synthesis compound was suggested by data (¹H-¹³C Nuclear magnetic resonance for (L) only), conductivity and magnetic measurement for the complexes. The Ligand (L) display corrosion inhibition marked action on corrosion of (plain steel) in tap water. Multi-step decomposition patterns for their organic frameworks, TGA studies show for (L) and their complexes. The (L) and their complexes were examined for their biological actions against selected types of bacteria and the fungus. The results of these studies showed that their complexes are more activity than free ligand.

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Appendix

Table 1. Some physical data, percentage of metal (%M), melting point, molar conduct and magnetic measurement of the prepared compounds.

Comp.	M. wt (g/ mole)	Color	m. p (°C)	M % Calculation (actual)	Molar Cond. Ohm ⁻¹ cm ² mol ⁻¹ (DMSO)	μ _{eff} (B.M)
(L) C ₂₂ H ₂₈ N ₂ O ₂	352.48	Yellow	160-162 °C	----	----	----
[Mn(L)]Cl ₂	478.32	Brown	195-197 °C	11.49 (11.52)	72.6	5.82
[Co(L)]Cl ₂	482.31	Brown	180-182 °C	12.22 (12.25)	68.5	4.93
[Ni(L)]Cl ₂	482.07	Brown	177-179 °C	12.18 (12.23)	82.3	3.05
[Cu(L)]Cl ₂	486.92	Green	175-177 °C	13.05 (13.00)	75.2	1.79
[Cd(L)]Cl ₂	535.79	Yellow	190-192 °C	20.98 (20.89)	79.34	0
[Zn(L)]Cl ₂	488.76	Yellow	188-190 °C	13.38 (13.43)	69.62	0

Table 2. Show data (¹H-NMR) and chemical shift in (DMSO-d⁶) for (L)

Comp.	Active groups	ppm (δ)
(L)	(NH) group	8.38 (1 H, s)
	C ₂ for (CH) (Ar-ring)	7.28 (4 H, d)
	C ₃ for (C ₂ H) group	4.91 (1 H, d)
	C ₄ for (CH ₂) group	2.52 (2 H, m)
	C ₅ for (CH ₂) group	2.46 (2 H, m)
	C ₆ for (CH ₃) groups	1.04 -1.08 (6 H, s)

Table 3. Show data (^{13}C -NMR) and chemical shift in (DMSO- d_6) for (L)

Comp.	Active groups	ppm (δ)
(L)	C ₁ for CO group (di medone)	195.51
	C ₂ for dimedone ring	161.24
	C ₃ for (Ar- ring)	133.88
	C ₄ for (Ar- ring)	127.37
	C ₅ for (Ar- ring)	126.77
	C ₆ for dimedone ring	97.07
	C ₇ for dimedone ring	50.73
	C ₈ for dimedone ring	42.23
	C ₉ for dimedone ring	32.23
	C ₁₀ for methyl groups	28.53

Table 4. The FTIR band for (L) and their metal complexes.

Comp.	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{C-N})$	Ph(N)_2	$\nu(\text{M-N})$	$\nu(\text{M-O})$
(L)	3240(m)	1573(s)	1246(b)	752(s)	-	-
[Mn(L)]Cl ₂	3248(b)	1587(m)	1230(m)	752(m)	516(m)	497(w)
[Co(L)]Cl ₂	3248(m)	1589(s)	1232(b)	748(s)	516(w)	497(w)
[Ni(L)]Cl ₂	3244(b)	1585(m)	1226(s)	756(m)	513(w)	497(m)
[Cu(L)]Cl ₂	3248(b)	1589(s)	1230(b)	752(s)	528(w)	489(w)
[Cd(L)]Cl ₂	3245(m)	1586(s)	1229(m)	756(s)	524(m)	489(m)
[Zn(L)]Cl ₂	3244(m)	1586(m)	1232(m)	756(m)	516(w)	489(m)
b=broad s=strong m=medium w=week						

Table 5. UV-Vis data of (L) and their complexes in solvent (DMSO).

Comp.	$\lambda(\text{nm})$	$\nu(\text{cm}^{-1})$	ϵ_{max} molar $^{-1}\text{cm}^{-1}$	Assignment	Suggested geometry
(L)	235	42553	3026	$\pi \rightarrow \pi^*$	-
	327	30581	2315	$n \rightarrow \pi^*$	
[Mn(L)]Cl ₂	283	35335	2.392	I.L	T.h
	400	25000	8	C.T	
	600	16667	6	${}^6\text{A}_1 \rightarrow {}^4\text{T}_1$	
				(G)	
				I.L	
[Co(L)]Cl ₂	236	42372	1425	I.L	T.h
	282	35460	545	I.L	
	398	25125	96	C.T	
	811	12330	60	${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ (P)	
[Ni(L)]Cl ₂	282	35460	2185	I.L	T.h
	380	26315	413	C.T	
	707	14144	17	${}^3\text{T}_1$ (F) $\rightarrow$ ${}^3\text{T}_1$	
				(P)	
[Cu(L)]Cl ₂	278	35971	2335	I.L	T.h
	340	29411	1117	I.L	
	400	25000	410	C.T	
	804	12437	23	${}^2\text{T}_2$ (F) $\rightarrow$ ${}^2\text{E}$	
[Cd(L)]Cl ₂	281	35587	2355	I.L	T.h
	400	25000	10	C.T	
[Zn(L)]Cl ₂	284	35211	1964	I.L	T.h
	400	25000	8	C.T	

C.T = Charge Transfer

I.L=Intra Ligand

T.h=Tetrahedral

Table 6. Data of Weight before and after immersion of (L) on low carbon steel (plain steel) in tap water at laboratory temperature.

Comp.	Time(hr)	Concentration [M]	wt before immersion(g)	wt after immersion(g)	wt difference (g)	% wt loss	Θ	% E.I
Ligand (L)	24	-	0.6579	0.4668	0.1911	29.04	-	-
		10^{-4}	0.6682	0.4924	0.1758	26.30	0.0943	9.43
		10^{-2}	0.6546	0.4946	0.1600	24.44	0.1584	15.84
	48	-	0.6563	0.4128	0.2435	36.75	-	-
		10^{-4}	0.6690	0.4603	0.2087	31.19	0.1429	14.29
		10^{-2}	0.6584	0.4677	0.1907	28.96	0.2168	21.68
[Zn(L)]Cl ₂	24	-	0.6512	0.4592	0.1920	29.48	-	-
		10^{-4}	0.6610	0.5044	0.1566	23.69	0.1843	18.43
		10^{-2}	0.6558	0.5189	0.1369	20.78	0.2869	28.69
	48	-	0.6535	0.3957	0.2578	39.44	-	-
		10^{-4}	0.6702	0.4692	0.2010	29.99	0.2203	22.03
		10^{-2}	0.6571	0.4836	0.1735	26.64	0.3269	32.69

Table 7. Temperature data for thermal decomposition with weight loss.

Comp.	Step	TG range ($^{\circ}$ C)	%Found (Calculate)		Assignment
			Mass loss	Total mass loss	
Lignd (L)	1 and 2	25-366	14.55(14.47)	32.11(31.78)	-C ₃ H ₁₆ N ₂ O ₂
	3 and 4	366-595	17.56(17.31)		-C ₃ H ₄
			11.43(11.33)	11.43(11.33)	
[Cu(L)]Cl ₂	1	25-273	32.303(32.226)		-Cl ₂ , N ₂ O ₂ , C ₂ H ₃
	2	273-495	20.413(20.321)	57.252	-C ₇ H ₅
	3	495-595	4.536(4.515)	(57.062)	-C, 5H ₂

Table 8. The inhibition diameter (mm) of the microbial after (24 hrs) (37 $^{\circ}$ C) in cubation paid.

Comp.	Staphylococcus aurea (G+)	Escherichia coli (G-)	Candida albicans	Trichomoniasis
Lignd (L)	0	0	0	0
[Mn(L)]Cl ₂	11	11	11	0
[Co(L)]Cl ₂	0	0	12	0
[Ni(L)]Cl ₂	11	0	12	0
[Cu(L)]Cl ₂	20	0	15	0
[Cd(L)]Cl ₂	31	12	18	22
[Zn(L)]Cl ₂	13	11	0	0