

Original Research Article

Preparation and Characterization of Some Transition Metal Complexes of New Tetradentate Schiff Base Ligand Type N₂O₂

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Abstract: Mn(II), Co(II), Ni(II), Cu(II) and Hg(II) metal complexes of Schiff base (2,2'-(1E,1'E)-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(phenyl methan-1-yl-1-ylidene)di benzoic acid) derived from 2-benzoylbenzoic acid and ethylene diamine have been synthesized and characterized by IR, ¹H-, ¹³C-NMR (only ligand) and electronic spectra, elemental analysis, in addition of magnetic moment measurements and molar conductance. It has been found that the Schiff base ligand behaves as tetradentate (N₂O₂) ligand forming chelates with 1:1 (ligand: metal) stoichiometry. The conductivity data for all complexes are consistent with those expected for non-electrolyte nature. It found that all complexes showed octahedral geometries. And in vitro tests for antibacterial and antifungal activity showed that most of the prepared compounds display a good activity to (*staphylococcus aureus*), (*Escherichia coli*), (*Bacillus subtilis*) and (*Pseudomonas aeruginosa*).

Keywords: Schiff base, Characterization, 2-benzoyl benzoic acid and ethylene diamine.

INTRODUCTION

Schiff bases, named after Hugo Schiff, are formed when any primary amine reacts with an aldehyde or a ketone under specific conditions [1, 2]. Structurally, a Schiff base (also known as imine or azomethine) is a nitrogen analogue of aldehyde and ketone in which the carbonyl group (C=O) has been replaced by an imine or azomethine group. Schiff bases are some of the most widely used organic compounds [3, 4]. They are used as pigments and dyes, catalysts [5], intermediates in organic synthesis [6], as polymer stabilizers [7], and separation of trace amount of metal ions [8]. Schiff bases have also been shown to exhibit a broad range of biological activities [9]. Imine groups are present in various natural, natural-derived, and non-natural compounds [10]. Generally ligands are Lewis bases that have lone pair on nitrogen, oxygen, etc and that bind with transition metals (Lewis acids) [11]. Ligands can be divided into monodentate, bidentate and multidentate types [12], according to the availability of one [13], two or more donor atoms bonding with metal [14]. Active and well-designed Schiff base ligands are considered as 'privileged ligands' because they are easily prepared by the condensation between aldehydes or ketones and amines and are able to stabilize different metals in various oxidation states [15]. Metal complexes of Schiff bases have been widely studied due to the versatility of their steric and electronic properties, which can be fine-tuned by choosing the appropriate amine precursors and ring substituents [16]. N₂O₂- tetra dentate ligands (soft and

hard donor) possess many advantages such as facile approach [17], relative tolerance [18], readily adjusted ancillary ligands [19], and tunable steric and electronic coordination environments on the metal center [20]. They were well known that N and O atoms play a key role in the coordination of metals at the active sites of numerous metal bimolecular [21]. Chelating ligands containing O and N donor [22]. Because of the tetradentate N₂O₂ ligands and their transition metal complexes, act as catalyst [23]. Thus, this group of compounds has attracted significant attention being relevant to their application in agrochemical and pharmaceutical industries [24].

Schiff base ligands are well known for their wide range of applications in pharmaceutical and industrial fields, dye industries, plastic, Agriculture, biochemistry, physiology and providing liquid crystal [25]. Schiff base and their complexes have received considerable scrutiny from both experimental and theoretical stand, which were used in several areas such as homogenous catalysis [26], Bio inorganic chemistry [27], and inorganic pharmacology [28]. Schiff bases are very important in development of coordination chemistry [29]. The aim of the present research in the synthesis and antibacterial activity studies of (II), Cobalt (II), copper(II) and Mercury(II) complexes containing Schiff base derived from 2-benzoyl benzoic acid and ethylene diamine by available techniques.

EXPERIMENTAL

Materials and measurements: 2-benzoyl benzoic acid, ethylene diamine and glacial acetic acid were purchased from sigma Chemical Co. (USA). All other solvents used in this work were reagent grade (BDH/Aldrich) and used without further purification. The elemental analyses were carried out in Ahl-Al Bat University/ Jordan by means of Micro analytical unit of EA 300 AC.H.N Elemental analyzer. IR spectra were recorded using KBr discs 4000-400 cm^{-1} on FT-IR Test scan Shimadzu model 8000 UV-Vis spectra were recorded in DMSO on Shimadzu model 1700 UV-Vis spectrophotometer. Magnetic susceptibilities measurements were obtained at room temperature using Bruker BM6 instrument [16]. Molar conductance measurements were determine in DMSO by using Alpha Digital conductivity meter model 800. Electro thermal malting point model 9300 was used to measure the melting points of the ligand and its complexes.

Preparation of Schiff base (H_2L)

The Schiff base (2,2'-(1E,1'E)-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(phenyl methan-1-yl-1-ylidene) dibenzoic acid) was prepared by adding (25mL) of 2-benzoyl benzoic acid ethanolic solution (0.002mmol) with 4drops from glacial acetic acid to the same volume of ethanolic solution of ethylene diamine (0.001mmol). The mixture was refluxed with stirring for (5-6) hrs. The resulting solution was evaporated to half volume and the precipitated product was collected by filtration, washed twice with (5mL) hot ethanol and dried. Condensation of ethylene diamine and 2-benzoyl benzoic acid in ethanol gives single product according to the following reaction shows in scheme (1).

Preparation of the complexes

A general method has been used for the preparation of all chelated complexes. A solution (0.001mmol) of ligand dissolved in (25 mL) of hot ethanol was added with stirring a stoichiometric amount (1:1) (ligand: metal) ratio for Mn(II), Co(II), Ni(II), Cu(II) and Hg(II) chloride salts and the mixture were refluxed for 30 min. They were filtered, washed with (5mL) ethanol and dried on cooling at room temperature, the coloured complexes precipitated out in each case, shows in scheme (2).

Biological Screening studies

The in-vitro biological screening effects of the investigated compounds were tested against the bacteria (*staphylococcus aureus*), (*Escherichia coli*), (*Bacillus subtilis*) and (*Pseudomonas aeruginosa*) by disc diffusion method using nutrients agar as the medium. All the blank discs were moistened with the solvent. The sample solutions (10^{-2}M) were prepared by dissolving the compounds in DMSO and the solutions were loaded on the wells of the culture and in culture incubated at 37°C for 24 h for the bacterial culture. During this period, the test solution was diffused and affected the growth of the microorganisms. Hence, the

inhibition zones were developed on the plate around the disc.

RESULTS AND DISCUSSION

General

The ligand is pink powder, which was a soluble in common organic solvent except water. The reaction between the ligand and the metal ions mentioned above gives vary in colour solids, depending on the nature of metal ions. All complexes are quiet air-stable, but it's soluble in DMSO and DMF. Some physical and chemical properties for (H_2L) ligand and its chelated complexes with Mn (II), Co(II), Ni(II), Cu(II) and Hg (II) metal ions. The melting points of the complexes were different (higher) than that of the Schiff base ligand, an evidence for complexation. The complexes were in a good agreement with those required by the proposed formula $[\text{M}(\text{L})(\text{H}_2\text{O})]$ where $\text{L}=(\text{C}_{30}\text{H}_{24}\text{N}_2\text{O}_4)$; $\text{M}=\text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II})$ and $\text{Hg}(\text{II})$ that all the prepared complexes are agreement with the stoichiometric ratio (1:1) metal : ligand. The result of the elemental analysis of the prepared compounds which are recorded in Table (1) NMR spectrum for the ligand (L): $^1\text{H-NMR}$ spectrum of the ligand (L) in DMSO-d_6 illustrated in Fig. (5), Table (2) is multiples corresponding to aromatic protons at (6.86-7.67) ppm. [14]. The characteristic signal at (6.02) ppm. is assigned to $\text{HC}=\text{N}$. The COOH signal is found proton at (12.48) ppm. [5]. The DMSO signal appeared at (2.50) ppm.

$^{13}\text{C-NMR}$ of the free ligand (L) Fig (2), Table (3) shows the COOH peak at (161.07) ppm, the $\text{HC}=\text{N}$ peak at (143.50) ppm. carbon peaks for aromatic are appeared at (114.64-129.27) ppm and carbon peaks for aliphatic are detected at (47.41-55.78) ppm. the peak at (40.31) ppm. assigned to DMSO [6].

Infrared spectral Studies

In order to study the binding mode of the ligand with the metal ions, a comparison was made for the FT-IR spectra of the free ligand and this of the prepared complexes and the data was given in (Table-3). The IR spectral data of the ligand showed a band at 1627cm^{-1} , which is assigned to $\nu(\text{C}=\text{N})$ stretching vibration, a feature found in Schiff bases [7]. This band was also showed at the range (1603-1614) cm^{-1} in the complex compounds, which was shifted to a lower frequency, indicating the involvement of $-\text{C}=\text{N}$ nitrogen of the ligand in coordination with metal ions, resulting in the formation of the five complexes [8]. The free ligand (H_2L) exhibits strong absorption band at (1695) cm^{-1} due to the stretching vibration of $\nu(\text{C}=\text{O})$ of carboxylic group [9]. This band disappeared in the spectra of its complexes accompanied by the appearance in frequencies at (1519-1533) cm^{-1} and (1456 -1481) cm^{-1} due to $\nu_{\text{asymm}}(\text{COO}^-)$ and to $\nu_{\text{symm}}(\text{COO}^-)$ for all the complexes, ($\Delta \nu_{\text{asym.}} - \Delta \nu_{\text{sym.}}$) = (48-81) cm^{-1} , supporting the idea that the ligand coordinate through deprotonated oxygen of carboxylate

[10]. The new observed bands in the regions (489-520) cm^{-1} and (418-441) cm^{-1} are tentatively attributed to ν (M-N) and ν (M-O) (Metal-Ligand) stretching vibrations respectively, confirming the coordination of the Schiff base to the respective metal ions [11, 12]. The IR spectrum of the ligand (L) (Fig-4) exhibited broad band in the regions (2520-3337) cm^{-1} was assigned to ν (OH) stretching frequency [13], absent this band in the spectra of all complexes, which indicated deprotonation and involvement of the oxygen of carboxylate in chelating [14]. The broad bands in the region (3321-3482) cm^{-1} and the weak bands at (829-810) cm^{-1} were indicate ν (O-H) and δ (OH) for all the complexes [15], a feature indicating the presence of coordinated aqua (H_2O) (Table 4). The water analysis of the complexes suggested two water molecules per complex compound. Therefore from IR spectra, it is concluded that the ligand behave as anion tetra dentate and bind with the metal ions by two O atoms of carboxylate and the two N atoms of imine [16].

Molar conductivity

The molar conductance values of the complexes in DMSO lie in the range 10 to 17 $\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ which is quite lower than that expected for an electrolyte and reveal their non-electrolytic nature as in Table(5) [17, 18, 19].

The electronic absorption spectral and magnetic studies

The spectral data of the compounds were presented in Table 1. The electronic absorption spectrum of the synthesized H_2L showed UV bands at 37735 and 30120 cm^{-1} . The bands at 37735 cm^{-1} is assigned to $n \rightarrow \pi^*$ transition of azomethine group [20, 21]. This transition was also found in the spectra of the complexes, but they were shifted towards lower in range (30769 -28571) cm^{-1} [22].

In the present investigation, brownish Co(II) complexes generally exhibited absorption band 11792 cm^{-1} corresponding to (ν_1), which was attributed to the transitions ${}^4\text{T}_{1g(\text{F})} \rightarrow {}^4\text{T}_{2g(\text{F})}(\nu_1)$. This band was the characteristic of high spin octahedral Co (II) complex [23].

The greenish brown Ni(II) complexes exhibited two bands at 12626 and 15764 cm^{-1} for the complex, which are attributed to the ${}^3\text{A}_{2g(\text{F})} \rightarrow {}^3\text{T}_{2g(\text{F})}(\nu_1)$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g(\text{F})}(\nu_2)$ transitions respectively indicating octahedral geometry around Ni(II) ion [24].

The electronic spectrum of Cu (II) complex display one high intensity band with shoulder bidden at 13765 cm^{-1} for the complex is due to $\text{E}_{g(\text{F})} \rightarrow {}^2\text{T}_{2g(\text{F})}$ transition. On the basis of electronic spectra distorted octahedral geometry around Cu (II) ion is suggested [25].

The brown Mn(II) complex exhibited electronic transition at 12903 cm^{-1} for the expected for

six-coordinated d^5 octahedral complexes. The electronic spectra of Mn(II) d^5 complex exhibits electronic transition at 12658 cm^{-1} . This transition is assigned to ${}^6\text{A}_{1g(\text{F})} \rightarrow {}^4\text{T}_{1g(\text{D})}(\nu_1)$ for Mn(II) complexes in octahedral environment due to large crystal field splitting [26].

The electronic spectrum of the Hg (II) complex showed no d-d transitions in the visible region, indicating for Hg (II), this is mean electronic transitions happened octahedral geometry has been assigned to the Hg (II) complex. According to the elemental analysis Table (1) and FT-IR spectra, the structures of these complexes can be suggested octahedral [27].

The magnetic moment values are listed in Table 1. The magnetic moment values are found to be 4.71, 1.81, 2.85, 5.64, BM for Co(II), Ni(II), Cu(II) and Mn(II) complexes, respectively, suggesting an octahedral geometry [28,29]. The Hg(II) complex is diamagnetic and according to its empirical formula, an octahedral geometry was proposed for this complex.

Biological Activities

We investigated the applicability disc diffusion method for determining the susceptibility of bacterial (*staphylococcus aureus*), (*Escherichia coli*), (*Bacillus subtilis*) and (*Pseudomonas aeruginosa*) species against newly synthesized tetradentate Schiff base ligand derived by the condensation of 2-benzoyl benzoic acid with ethylene diamine and its Mn(II), Co(II), Ni(II) Cu(II), and Hg(II) complexes. The minimum inhibition concentration value of the compounds against the growth microorganisms are summarized the Table 6. A comparison of the value of ligand with its complexes indicates that the metal chalets exhibited higher antimicrobial activity than ligand and the control sample. Such increased activity of the complexes can be explained based on the Overtone's concept and the Tweedy chelating theory [32]. According to the Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favors the passage of only lipid soluble materials, due to which lip solubility is an important factor that controls antimicrobial activity [33]. On chelating, the polarity of the metal ion will be reduced due to the partial sharing of positive charges with donor groups. Furthermore, it increases the delocalization of π -electrons over the whole chelated ring that enhances the lipophilicity of the complexes [34]. This increased lipophilicity enhances the penetration of the complexes into lipid membranes and the blocking of the metal binding sites in the enzymes of microorganisms [35]. Due to the presence of more functional groups (hydroxyl groups and azomethine groups), which forms hydrogen bonding with proteins present in the cell walls of the organisms, resulting in interference with the normal cell process [36]. Comparatively, Table (6) diameter of zone of inhibition.

Table 1: Some physical properties of prepared ligand (H₂L) and its complexes and weight of metal salts

Empirical Formula	Yield %	M.P ^o C	Colour	Metal salt	Weight (g) 1mmol	Λ_m ohm.c m ² mol ⁻¹	(Calc.)% Found			
							C	H	N	Metal
L=C ₃₀ H ₂₄ N ₂ O ₄	87	121	Pink	-	-	-	(75.61) 75.15	(5.08) 5.00	(5.88) 6.04	-
[Co(L)(H ₂ O) ₂].H ₂ O	89	<256	brownish	CoCl ₂ .6 H ₂ O	0.238	17	(67.55) 67.50	(4.16) 6.00	(5.25) 5.42	(11.50) 11.20
[[Ni(L)(H ₂ O) ₂].2 H ₂ O	81	200	brown	NiCl ₂ .6 H ₂ O	0.238	10	(67.58) 77.50	(4.16) 5.40	(5.25) 8.42	(11.01) 11.30
[Mn(L)(H ₂ O) ₂].H ₂ O	82	232	greenish brown	MnCl ₂ .4 H ₂ O	0.198	15	(68.08) 67.98	(5.00) 49.40	(5.29) 5.42	(10.38) 10.35
[Cu(L)(H ₂ O) ₂].H ₂ O	78	194	Blue	CuCl ₂ .H ₂ O	0.170	12	(66.97) 66.50	(4.12) 4.40	(5.21) 5.02	(20.03) 19.80
[Hg(L)(H ₂ O) ₂]	80	187	pale brown	HgCl ₂	0.271	13	(53.37) 77.50	(5.00) 5.40	(6.04) 8.42	(30.96) 30.41

Table 2: ¹H-NMR Chemical Shifts for Ligand (H₂L) (ppm in DMSO)

HC=CH	DMSO	HC=N	COOH
6.68-6.96ppm.	2.46 ppm	6.02 ppm	12.67ppm

Table 3: ¹³C-NMR Chemical shifts for Ligand (H₂L) (ppm in DMSO)

HC=CH	DMSO	H ₂ C-C=N	=C-C=N	COOH
142.69-145.22 ppm	40.30ppm	64.54ppm	166.07 ppm	169.69ppm

Table 4: Infrared spectral data (wave number ν) cm⁻¹ for the ligand (H₂L), precursors and its complexes

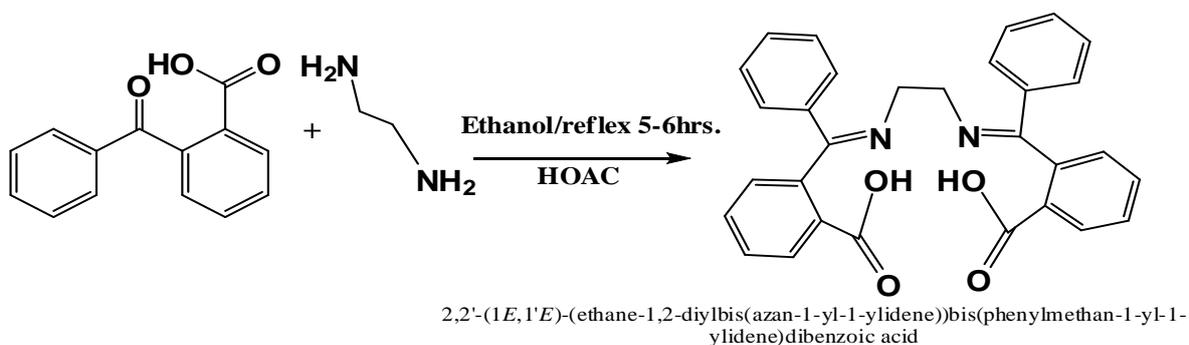
Compound	ν (OH)	ν (C-H) _{arom.}	C=O carbonate	ν (C-H) _{aliph.}	ν (HC=N) _{imine}	ν (C=O) _{asy}	ν (C=O) _{sym}	$\Delta\nu$ cm ⁻¹	δ (OH)	M-N M-O
H ₂ L	2520-3337	3020	1695	2993	1627	-	-	-	-	-
[Co(L)(H ₂ O) ₂].H ₂ O	3482	3018	-	2964	1612	1529	1467	62	810	489 421
[Ni(L)(H ₂ O) ₂].2H ₂ O	3423	3082	-	2904	1614	1519	1467	52	810	493 412
[Mn(L)(H ₂ O) ₂].H ₂ O	3321	3026	-	2993	1604	1529	1481	48	987	499 418
[Cu(L)(H ₂ O) ₂].H ₂ O	3367	3042	-	2910	1609	1533	1456	77	823	520 432
[Hg(L)(H ₂ O) ₂]	3464	3111	-	2962	1603	1530	1462	68	821	495 441

Table 5: Electronic spectral data of the ligand (L) and its metal complexes

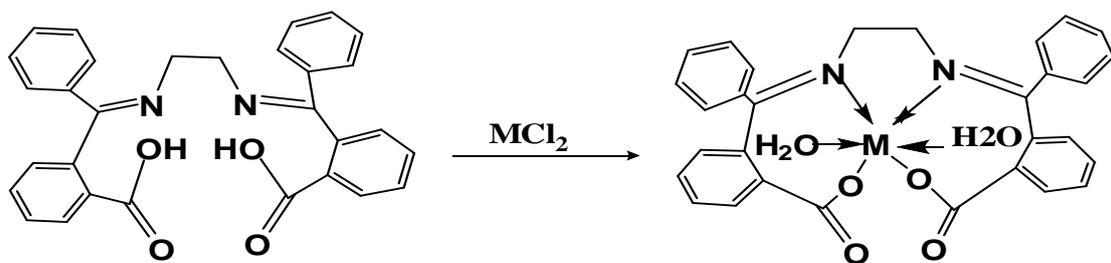
Compound	Λ_m ohm.cm ² mol ⁻¹	μ_{eff}	λ_{nm}	ν wave number cm ⁻¹	Assignments	Proposed structure
H ₂ L	-	-	265	37735	$\pi \rightarrow \pi^*$	-
			332	30120	$n \rightarrow \pi^*$	
[Co(L)(H ₂ O) ₂].H ₂ O	17	4.71	312	32051	C.T	Octahedral
			848	11792	${}^4T_{1g(F)} \rightarrow {}^4T_{2g(F)}$	
[Ni(L)(H ₂ O) ₂].2H ₂ O	10	1.81	320	30769	C.T	Octahedral
			634	15764	${}^3A_{2g(F)} \rightarrow {}^3T_{1g(F)}$	
			792	12626	${}^3A_{2g(F)} \rightarrow {}^3T_{2g(F)}$	
[Cu(L)(H ₂ O) ₂].H ₂ O	15	2.85	324	30864	C.T	Octahedral
			726	13765	$E_{g(F)} \rightarrow {}^2T_{2g(F)}$	
[Mn(L)(H ₂ O) ₂].H ₂ O	12	5.72	325	30769	C.T	Octahedral
			775	12903	${}^6A_{1g(F)} \rightarrow {}^4E_{g(D)}$	
[Hg(L)(H ₂ O) ₂]	13	-	350	28571	C.T	Octahedral

Table 6: Diameter of zone of inhibition (mm)

Compound	H ₂ L	[Co(L)(H ₂ O) ₂] H ₂ O	[Ni(L)(H ₂ O) ₂] 2H ₂ O	[Cu(L)(H ₂ O) ₂] H ₂ O	[Mn(L)(H ₂ O) ₂] . H ₂ O	[Hg(L)(H ₂ O) ₂]
<i>Escherichia coli</i>	1	3	1	2	3	2
<i>Staphylococcus aureus</i>	4	6	6	5	7	8
<i>Bacillus subtilis</i>	3	2	3	4	5	1
<i>Pseudomonas aeruginosa</i>	1	2	3	1	2	5



Scheme (1): Synthetic route of the Schiff base ligand (H₂L)



M=Cu^{II}, Ni^{II}, Co^{II}, Mn^{II} and Hg^{II}

Scheme (2): Synthetic route of the metal complexes

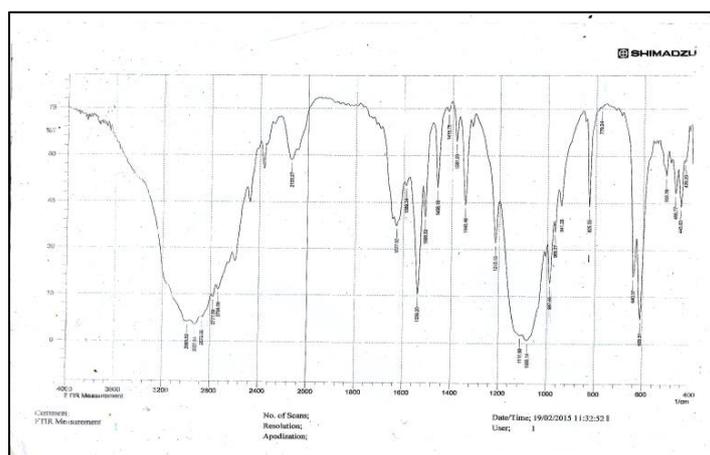


Fig. (1) Spectrum of complex (H₂L)

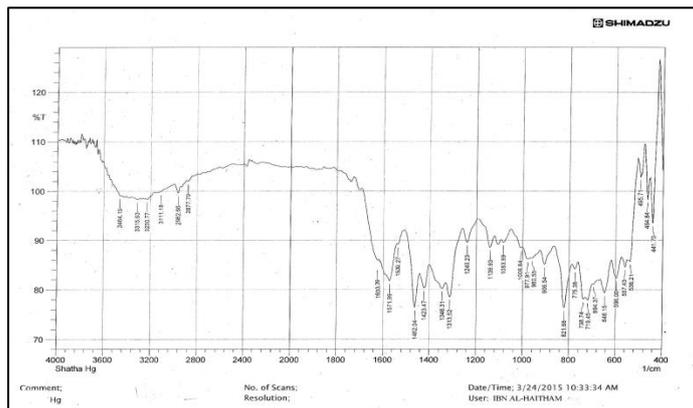


Fig. (2) Spectrum of complex $[Hg(L)(H_2O)_2]$

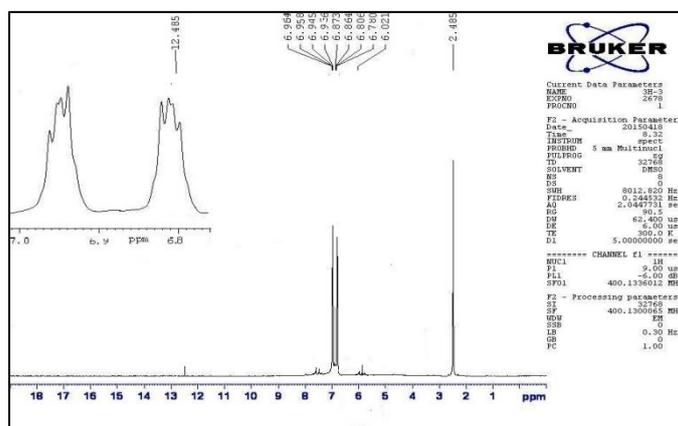


Fig.(3) 1H NMR spectrum of Ligand(H_2L)

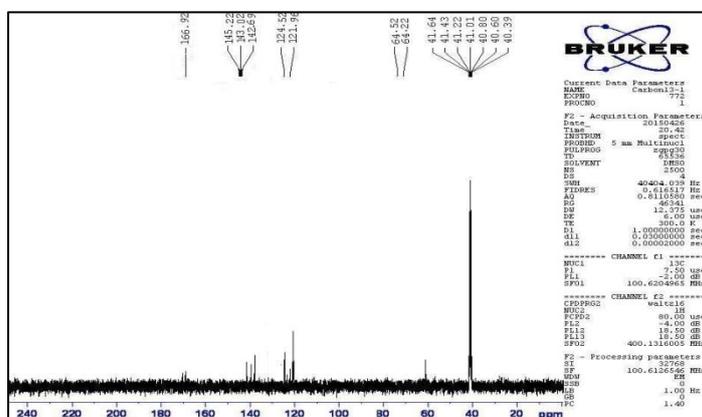


Fig.(4) ^{13}C NMR spectrum of Ligand (H_2L)

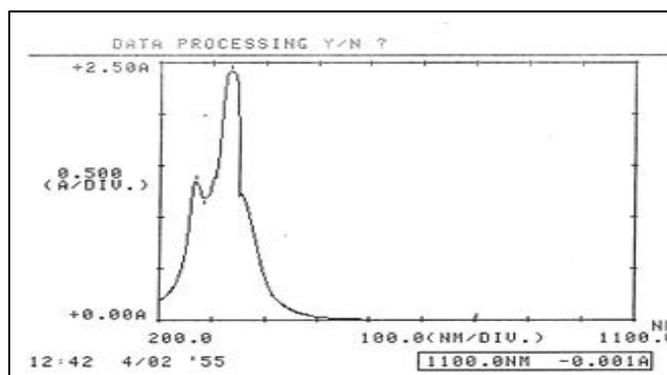


Fig.(5)UV-Vis spectrum of Ligand (H_2L)

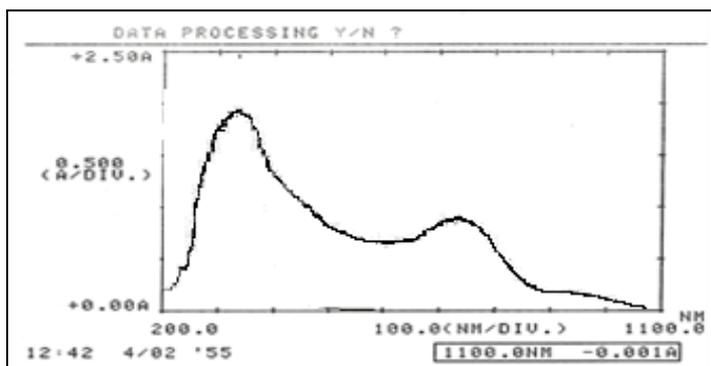


Fig.(6)UV-Vis spectrum of *Complex[Co(L)(H₂O)₂]*

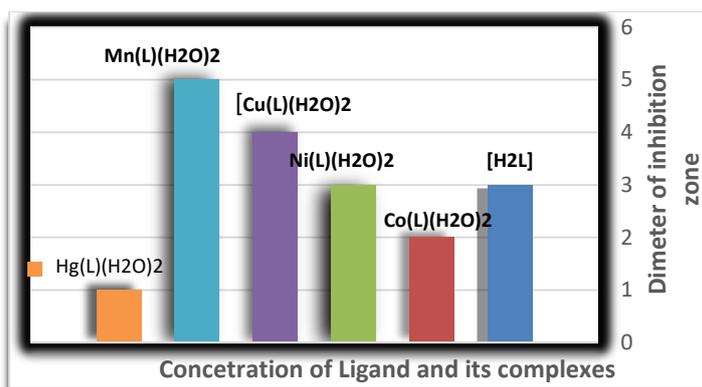


Fig.(7) Effect of *Escherichia coli*

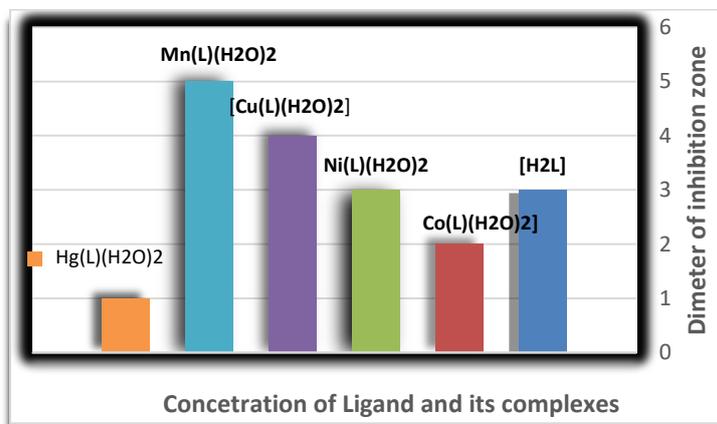


Fig.(8) Effect of *staphylococcus aureus*

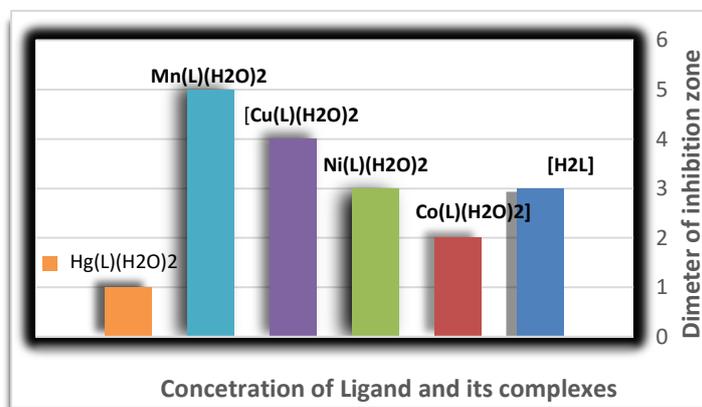


Fig.(9) Effect of *Bacillus subtilis*

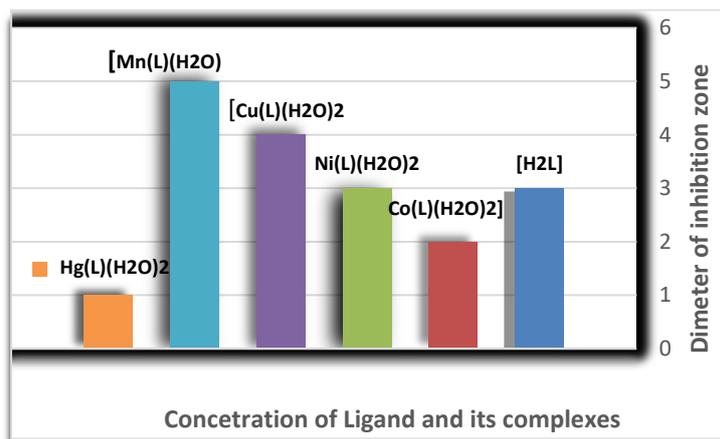


Fig.(10) Effect of *Pseudomonas aeruginosa*

CONCLUSION

The new Schiff ligand (L) and metal complexes were prepared [Mn(L) (H₂O)₂],[Co(L) (H₂O)₂], [Ni(L)(H₂O)₂], [Cu(L)(H₂O)₂] and [Hg(L)(H₂O)₂]. The metal (II) ions are coordinated by two N atoms for imine (H-C=N) groups and two O atoms for carboxylate (COOH) groups. Spectroscopic, structural and magnetic data show that all complexes are six-coordinate metal complexes owing to the ligation of tetradentate ligand moieties with two coordinated water shows schemes (1&2).

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