www.ThePharmaJournal.com

The Pharma Innovation

ISSN: 2277- 7695
TPI 2016; 5(1): 81-86
© 2016 TPI
www.thepharmajournal.com
Received: 12-11-2015
Accepted: 15-12-2015

**Rehab K. Al-Shemary**
Department of Chemistry, College of Education for Pure Sciences, Ibn -Al-Haitham, University of Baghdad, Iraq.

**Ali M.A. Al-khazraji**
Department of Chemistry, College of Education for Pure Sciences, Ibn -Al-Haitham, University of Baghdad, Iraq.

**Ali N Niseaf**
Department of Chemistry, College of Education for Pure Sciences, Ibn -Al-Haitham, University of Baghdad, Iraq.

**Correspondence:**
**Rehab K. Al-Shemary**
Department of Chemistry, College of Education for Pure Sciences, Ibn -Al-Haitham, University of Baghdad, Iraq.

# Preparation, spectroscopic study of Schiff base ligand complexes with some metal ions and Evaluation of antibacterial activity

**Rehab K. Al-Shemary, Ali M. A. Al-khazraji, Ali N Niseaf**

**Abstract**
The new bidentate Schiff base ligand namely [(E)-$N^1$-(4-methoxy benzylidene) benzene-1, 2-diamine] was prepared from condensation of 4-Methoxy benzaldehyde with O-Phenylene diamine at 1:1 molar ratio in ethanol as a solvent in presence of drops of 48% HBr. The structure of ligand (L) was characterized by, FT-IR, U.V-Vis., $^1$H-, $^{13}$C- NMR spectrophotometer, melting point and elemental microanalysis C.H.N.
Metal complexes of the ligand (L) in general molecular formula [$M(L)_3$], where M= Mn(II), Co(II), Ni(II),Cu(II) and Hg(II); L=($C_{14}H_{14}N_2O$) in ratio (1:3)(Metal:Ligand) were synthesized and characterized by Atomic absorption, FT- IR, U.V-Vis. spectra, molar conductivity, chloride content, melting point and magnetic susceptibility from the above data the geometrical formula was octahedral for all complexes. And in vitro tests for antibacterial activity showed that most of the prepared compounds display activity to (*Staphylococcus aureus*), (*Escherichia coli*), (*Bacillus subtilis*) and (*Pseudomonas aeruginosa*).

**Keywords:** Schiff base, 4-Methoxy benzaldehyde, Antibacterial activity and Complexess.

## 1. Introduction
Compounds which are formed by the condensation of an active carbonyl group with primary amine or N-substituted imine containing an imino group (R-C=N-), are known as Schiff bases [1, 2]. They have been used extensively as ligands in the field of coordination chemistry, furthermore the Schiff bases are very important tools of the inorganic chemists as these are widely used to design molecular ferromagnets, in catalysis [3], in biological modeling applications [4], as liquid crystals and as heterogeneous catalysts [5]. Schiff bases have been widely used as ligands because of high stability of the coordination compounds and their good solubility in common solvents [6]. The π-system in a Schiff base often imposes a geometrical constriction and affects the electronic structure as well [7]. Thermo chemical properties of Schiff bases have attracted much researcher attention in view of their ability to coordinate metal ions, acting as bidentate ligands in metal chalets involving NN Schiff-base donor atom sets [8]. They are regarded as privileged ligands [9]. Schiff base and their metal complexes are very popular due to their diverse chelating ability [10]. They play an important role in both synthetic and structural research because of their preparative accessibility and structural diversity [11]. Schiff bases composed of NN donor atoms are important chelating ligands for designing supramolecular synthons, medicinal and catalytically useful metal complexes [12]. Schiff bases derived from aromatic diamines such as o-phenylene diamine have received attention due to their synthetic flexibility [13], application in catalysis and coordination chemistry [14], in understanding the process of metal binding in metalloproteins and metalloenzymes in the body [15]. Schiff bases of o-phenylene diamine and its complexes have a variety of applications including biological, clinical and analytical [16]. Earlier work has shown that some drugs showed increased activity when administered as metal chalets rather than as organic compounds and that the coordinating possibility of o-phenylene diamine has been improved by condensing with a variety of carbonyl compounds [17].
In this paper, we describe the preparation and characterization of ligand namely [(E)-$N^1$-(4-methoxy benzylidene) benzene-1,2-diamine] by condensation of 4-Methoxy benzaldehyde with O-Phenylene diamine (1:1) and its complexes with Mn(II),Co(II), Ni(II), Cu(II) and Hg(II) in ratio (1:3) (M:L) were prepared. Also the antimicrobial studies of the Schiff base and its complexes were done by disc diffusion method. Its final version, if changes had been made to the initial version. The submitted typeset scripts of each contribution must be in their final

form and of good appearance because they will be printed directly. The document you are reading is written in the format that should be used in your paper.

***Aim of the work:*** Schiff bases and their transition metal complexes possess a number of biological applications. Metal complexes show higher activity than free ligands. Among transition metal complexes the activity of copper complexes is high.These compounds shows bright path towards pharmaceutical as well as chemical sciences. But still there is need to explore the biological properties of these already synthesized copper complexes and to synthesize new complexes with more properties.

## 2. Experiment

### 2.1 Materials and Methods

All chemicals used were of the analytical reagent grade (AR), and of highest purity available. The chemicals used included o-phenylene diamine and4-methoxy benzaldehyde were purchased from sigma Chemical Co.(USA).The metal salts used for complexation: Copper(II) chloride dihydrate; Manganese (II) chloride tetra hydrate; Nickel(II) chloride hexahydrate; Cobalt(II) chloride hexahydrate and Mercury (II) chloride were obtained from British Drug House (BDH) Chemical Limited Company. Glacial acetic acid reagent and all other Organic solvents were spectroscopic pure from BDH included ethanol, diethyl ether and DMSO. DMF and sodium hydroxide (A.R.) were used.

### 2.2 Instrumentation

Melting point was determined on "Gallen kamp Melting point Apparatus". Carbon, hydrogen and nitrogen were analyzed by using Euro Vector EA 3000 A Elemental Analyses (Italy). FT-IR measurements were recorded on Shimadzu- 8300 Spectrophotometer in the range of (4000-400 $cm^{-1}$) as KBr disc. Electronic spectra were recorded using U.V-Vis. spectrophotometer type CECIL, England, with quartz cell of (1 cm) path length in rang (200-1000) nm in ethanol at room temperature.$^{1}$H and $^{13}$C-NMR spectra were recorded by using a Bruker 300 MHZ (Switzerland), Chemical shift of were recorded in δ(ppm) unit downfield internal reference (TMS), using DMSO as a solvent. Conductivity measurements were obtained from WTW conductivity meter by using ethanol as a solvent of $10^{-3}$ M concentration at room temperature. The chloride content determined using potentiometric titration method on 686–Titro Processor–665 Dosim A–Metrohm /Swiss. Magnetic susceptibility measurements were obtained at room temperature on the solid state applying Faraday's Method using Bruker BM6 instrument. Metal analyses of complexes were determined by Atomic Absorption (A.A.) technique. Using a shimadzu PR-5.ORAPHIC PRINTER atomic absorption spectrophotometer.

### 2.3Study of Biological Activity

The antimicrobial activity of the Schiff base ligand and its metal complexes were determined by the agar well diffusion assay [12]. The bacteria strains (*Staphylococcus aureus*), (*Escherichia coli*), (*Bacillus subtilis*) and (*Pseudomonas aeruginosa*) were maintained on Nutrient agar, using Ethanol as a solvent, the concentration of the compounds in this exposure was ($10^{-3}$ M) by using disc sensitivity test. The plates were incubated aerobically at 37 °C for 24 hours and the antimicrobial activity was assessed by measuring the inhibition halo of microbial growth around the well. This method involves the exposure of the zone inhibition toward the diffusion of micro-organism on agar plate.

## 3. Synthesis

### 3.1 Synthesis of Schiff base Ligand

(0.121mL.1mmole) of4-methoxy benzaldehyde was added to ethanolic solution of (0.108 g. 1mmole) of O- phenylene diamine in (15 mL) of ethanol with presence of drops of 48% HBr. The solution mixture was stirred and refluxed for 4 hours, a pale brown precipitate observed. The resulting precipitate was filtered off, recrystallized from a hot menthol and dried at 50 $^{0}$C. The preparation method of the ligand (L) is represented in scheme (1).

### 3.2 Synthesis of the chelates

A similar method to that the preparation pathway described in literature [19-23] using all the complexes were prepared by refluxing respective hydrated cobalt(II), nickel(II), copper (II) Manganese(II) and Mercury (II)chlorides in ethanolic solution of ligand in molar ratio of and 1:3(M:L) in (15 ml)ethanol on water bath for 4-7 hrs. at 80 °C. The colored product separate out on cooling which was collected by filtration, washed with dry diethyl ether. The resulting product was recrystallized from a hot ethanol and dried in vacuum desiccators over $CaCl_2$ anhydrous (yield 66-88%). All the metal complexes were found to be and soluble in water, ethanol and most of common organic solvents. Physical properties of the prepared complexes were given in (Table 1).

## 4. Results and Discussion

The present study aims to investigate the structure of Co (II), Ni (II), Cu(II), Mn(II) and Hg(II) complexes with the prepared Schiff base ligand and metal ions. This ligand has many centers of chelation; thus, making the elucidation and assignment of the chelation centers a challenge, the solving of this problem is tried through the investigation of the separated complexes using molar conductance, elemental analyses, electronic absorption and infrared, $^{1}$H&$^{13}$C-NMR analysis. All the complexes are have melting points >200 °C, and they are easy soluble in ethanol, methanol DMF and DMSO and slightly insoluble in non-polar solvents. The C, H, N, and atomic contents of both theoretically calculated and measured values are in accordance with the tentative formula of the complexes. The analytical and physical data of the metal complexes ligand are shown in Table 1. The observed molar conductance values measured in $10^{-3}$mol $L^{-1}$ solution of the given complexes were, Table 5. All cheated complexes prepared in the work showed conductivity values ranged between(72-88) $ohm^{-1}cm^{2}$ $mol^{-1}$ in ethanol at room temperature these values indicate that conductive species exist [7]. According to these results the structural formulas of these complexes may be proposed in scheme (2).

### 4.1 NMR spectrum for the ligand (L)

The $^{1}$H NMR spectrum of the new Schiff base L in DMSO-$d_6$ solution showed the following signals in δppm at:(2.479, singlet,6H for DMSO protons); (3.82,singlet,3H for O-C$\underline{H}_3$ group); (6.834-8.76 to 2 benzene ring protons (8.12, singlet,2H for -N$\underline{H}_2$) and the rang at (6.540-8.126) for 2 benzene ring protons [19, 20]. The peak observed at (9.34 attributed to $\underline{H}$C=N imine proton) [21].

The $^{13}$C NMR spectrum of L in DMSO-$d_6$ solution showed the signals at: group (40.586 for DMSO); (55.783 for=O-$\underline{C}H_3$); (111.426-136.336 to 2 benzene rings);( 143.211 for $\underline{C}$-C=N

group); ( 153.646 for C-$NH_2$) [22]. The peaks observed at (160.854 attributed to C=N imine moiety) and the signal at (161.07 for C-$OCH_3$ group) [23].

### 4.2 IR spectra

The IR spectra provide valuable information regarding the nature of the functional group attached to the metal ion. The IR spectrum of the [L] Fig. (1) Showed new strong band at (1611) $cm^{-1}$ is due HC=N imine [8,9] compared with the precursors, which indicate the ligand [10, 11]. In the IR spectra of the complexes, a medium intensity band due to υ(C=N) was shifted towards lower side about 20-30 $cm^{-1}$ compared to ligand spectra and appeared in the range of 1581-1591 $cm^{-1}$. This supports the fact that the ligand coordinate to the metal ions through the nitrogen of C=N group in all the complexes [12, 13].

The IR spectrum of the ligand exhibited bands at 3402 $cm^{-1}$and3361 $cm^{-1}$were assigned to υ($NH_2$) stretching frequency [14], In the complexes (table 3) the IR spectra showed characteristic bands in the region3382 –3231 $cm^{-1}$ which is lower in comparison with free $NH_2$. Hence, it can be concluded that the nitrogen of the amino group is involved in metal coordination [15].Bands corresponding to (C–H) aromatic stretching in the range of (3024-3070)$cm^{-1}$,$(C–H)_{aliphatic}$ stretching in the range of (2924-2962) $cm^{-1}$,$υ(C=C)_{aromatic}$ in the range of (1530-1540) $cm^{-1}$[16]. Absorption band corresponding in the range of (1242-1252) $cm^{-1}$ due to υ (C-O) [17]. Finally the complexes exhibited bands at the ranges (437-472) and (522-562) $cm^{-1}$ which could be assigned to the ν (M - O) and ν (M-N) stretching vibration modes respectively [18].

### 4.3 The electronic absorption spectral and magnetic studies

The U.V-Vis spectrum of ligand (L) Fig.(4) displayed two absorption peaks, the first peak at (265) nm (37735 $cm^{-1}$) may be assigned to π–π* electronic transition. The second peak at (332) nm (30120 $cm^{-1}$) was attributed to n–π* electronic transition [24]. The U.V-Vis spectral data of the ligand (L) were given in Table (5).

The U.V-Vis spectrum of the Co (II) complex displayed four absorption peaks. The first peak at (276) nm (3623 $cm^{-1}$) was assigned to charge transfer electronic transition, while the second, third and fourth peaks at (448) nm (22282) $cm^{-1}$, (633) nm (15782) $cm^{-1}$ and (798) nm (12521) $cm^{-1}$ were attributed to (d-d) electronic transition type $^4T_1g_{(F)} \rightarrow {}^4T_1g_{(p)}$, $^4T_1g_{(F)} \rightarrow {}^4A_2g_{(F)}$ and $^4T_1g_{(F)} \rightarrow {}^4T_2g_{(F)}$ were suggesting a high spin octahedral geometry around Co(II) central ion [25].

The U.V-Vis spectrum of the Ni(II) complex displayed three absorption peaks. The first peak at (280) nm (35714 $cm^{-1}$) peak was refer to charge transfer electronic, while the second peak at (420) nm (23809 $cm^{-1}$) and third peak at (838) nm (23809 $cm^{-1}$) were attributed to (d-d) electronic transition type $^3A_2g_{(F)} \rightarrow {}^3T_1g_{(F)}$ and $^3A_2g_{(F)} \rightarrow {}^3T_2g_{(F)}$ respectively, that is a good suggestment with high spin octahedral geometry [26].

The U.V-Vis spectrum of the Cu(II) complex exhibited two absorption peaks. The first peak at (272) nm (36764 $cm^{-1}$) was assigned to charge transfer electronic transition, while the second peak at (708) nm (14113 $cm^{-1}$) were attributed to (d-d) electronic transition type $^2Eg_{(F)} \rightarrow {}^2T_1g_{(F)}$ that is a good suggestment with high spin octahedral geometry [27].

The U.V-Vis spectrum of the Mn(II) complex exhibits three absorption peaks. The first peak at (282) nm (35460 $cm^{-1}$) was assigned charge transfer electronic transition. The second and third peaks at (344) nm (28990 $cm^{-1}$) (421) nm (23748 $cm^{-1}$) were assigned to (d-d) electronic transition type $^6A_1g \rightarrow {}^4A_1g_{(G)}$, $^4Eg_{(G)}$ and $^6A_1g \rightarrow {}^4T_2g_{(G)}$ have a high spin octahedral coordination environment around Mn(II) centeral ion[28].

The U.V-Vis spectrum of the Hg complex displayed two absorption peaks. The first peak at (290) nm (38022 $cm^{-1}$) and the second peak (324) nm (30864 $cm^{-1}$) refer to charge electronic transition only [29]. The U.V-Vis spectrum of the Hg (II) complex showed no d-d transitions in the visible region, indicating for Hg (II) shown Tables (2&3). According to the elemental analysis Table (1) and FT-IR spectra, the structures of these complexes can be suggested octahedral.

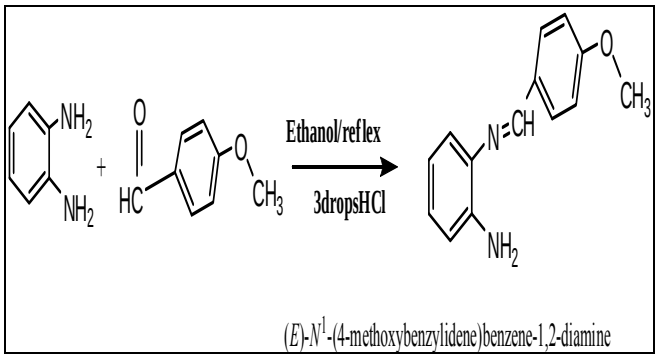
The magnetic moment values are listed in Table 1. The magnetic moment values are found to be 4.65, 1.78, 2.81, 5.64, BM for Co(II),Ni(II),Cu(II)andMn(II) complexes respectively, suggesting an octahedral geometry [28,29]. The Hg(II) complex is diamagnetic and according to its empirical formula, an octahedral geometry was proposed for this complex.

### 4.4 Biological Activities

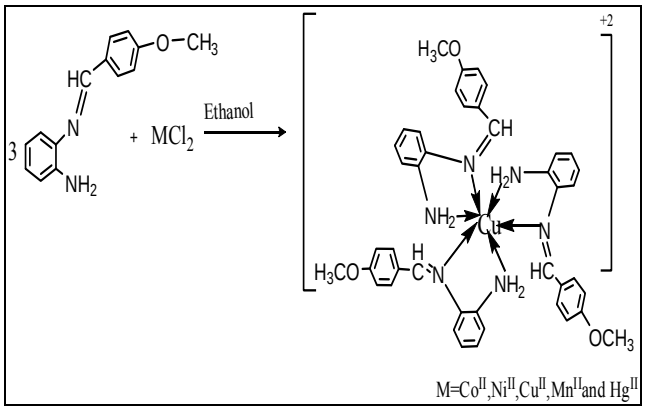
Bidentate Schiff base ligand derived by the condensation of 4-Methoxy benzaldehyde with O-Phenylene diamine and it's Co(II), Mn(II), Cu(II) and Hg(II) complexes showed biological activities against the type of bacterial (*Escherichia coli*) in Fig(5). The compounds showed inhibition diameter against the type of bacterial (*Staphylococcus aureus*) except ligand, the results indicate that the complexes showed more activity than the ligand under similar experimental conditions, this may be due to that the chelation considerably reduces the polarity of the metal ion mainly because of partial sharing of its positive charge with the donor groups and possible electron delocalization over the whole chelate ring such, chelation could also enhance the lipophilic character of the central metal atom, which subsequently favors its permeation through the lipid layer of the cell membrane [32-35]. All compounds ligand and its complexes have good biological activity against the type of bacterial (*Bacillus*) except Ligand and $[Mn(L)_3]$. Also the compounds against the type of bacterial (*Pseudomonas*) except $[Hg(L)_3]$ complex. Table (6) Diameter of zone of inhibition.

### 4. Conclusions

The new Schiff ligand (E)-N1-(4-methoxybenzylidene) benzene-1,2-diamineand metal complexes were a prepared $[Mn(L)_3]$, $[Co(L)_3$, $[Ni(L)_3]$, $[Cu(L)_3]$ and $[Hg(L)_3]$. The metal (II) ions are coordinated by two imine (H-C=N) atoms. Spectroscopic, structurical and magnetic data show that all complexes are six-coordinate metal complexes owing to the ligation of bidentate Schiff base moieties as fellow in scheme (1&2):




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




**Scheme 2:** Synthetic route of the ligand's metal complexes

**Table 1:** Some physical properties of prepared lignad (L) and its complexes and weight of metal salts

| *Empirical Formula* | *Molecular Weight* | *Yield %* | *M.P °C* | *Color* | *Metal salt* | *Weigh(g) 1mmol* | *Calc.) %(Found* | | | | *Solubility* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | *C* | *H* | *N* | *Metal* | |
| *L=$C_{14}H_{14}N_2O$* | *226.28* | *80* | *178* | *Pale brown* | *-* | *-* | *(74.31) 73.82* | *(6.24) 6.87* | *(12.38) 12.72* | *-* | *Methanol, Ethanol, DMSO, DMF* |
| *[Co(L)$_3$]* | *742.37* | *70* | *234* | *Dark brown* | *$CoCl_2.6H_2O$* | *0.238* | *(67.95) 68.12* | *(5.70) 6.20* | *(11.32) 11.20* | *(8.56) 7.85* | *=* |
| *[[Ni(L)$_3$]* | *737.51* | *66* | *200* | *brown* | *$NiCl_2.6H_2O$* | *0.238* | *(68.40) 68.70* | *(6.74) 6.22* | *(11.4) 11.87* | *(7.96) 8.10* | *=* |
| *[Mn(L)$_3$]* | *742.37* | *88* | *232* | *greenth brown* | *$MnCl_2.4H_2O$* | *0.198* | *(6.24) 6.87* | *(6.24) 6.87* | *(6.24) 6.87* | *(10.95) 10.35* | *=* |
| *[Cu(L)$_3$]* | *741.26* | *78* | *194* | *brown* | *$CuCl_2.H_2O$* | *0.201* | *(67.95) 68.23* | *(5.70) 5.11* | *(6.24) 6.87* | *(8.56 8.31* | *=* |
| *[Hg(L)$_3$]* | *1* | *86* | *187* | *Dark brown* | *$HgCl_2$* | *0.271* | *(6.24) 6.87* | *(6.24) 6.87* | *(6.24) 6.87* | *(30.96) 30.41* | *=* |

**Table 2:** $^1$H-NMR Chemical Shifts for Ligand (L) (ppm in DMSO)

| *DMSO* | *O-CH$_3$* | *C=CH* | *NH$_2$* | *HC=N* |
|---|---|---|---|---|
| *2.5* | *3.82* | *6.834-8.76* | *8.12* | *9.34* |

**Table 3:** $^{13}$C-NMR Chemical shifts for Ligand (L) (ppm in DMSO)

| DMSO | O-CH$_3$ | C=CH | C-HC=N | CH=N | C-O |
|---|---|---|---|---|---|
| 40.30 | 55.50 | 111.4-136.3 | 143.2 | 160.8 | 161. |

**Table 4:** Infrared spectral data (wave number υ) cm$^{-1}$for the ligand (L), precursors and its complexes

| *Compound* | *υ(N-H)* | *υ(C-H) aromatic* | *υ(C-H) aliphatic* | *υ(HC=N)$_{imine}$* | *υ(C=C)* | *υ(C-O)* | *M–N M–O* |
|---|---|---|---|---|---|---|---|
| L | 3402 3361 | 3058 | 2962 | 1611 | 1505 | 1252 | - |
| [Co(L)$_3$] | 3378 3267 | 3070 | 2954 | 1575 | 1510 | 1250 | 522 437 |
| [Ni(L)$_3$] | 3345 3244 | 3057 | 2924 | 1591 | 1510 | 1246 | 549 472 |
| [Cu(L)$_3$] | 3351 3279 | 3024 | 2929 | 1579 | 1506 | 1249 | 543 468 |
| [Mn(L)$_3$] | 3382 3231 | 3066 | 2926 | 1585 | 1508 | 1248 | 562 443 |
| [Hg(L)$_3$] | 3370 3264 | 3068 | 2937 | 1582 | 1506 | 1246 | 532 |

**Table 5:** Electronic spectral data of the ligands and its metal complexes

| *Compound* | *$\Lambda_m$ ohm.cm$^2$mole$^{-1}$* | *$\mu_{eff}$* | *λnm* | *υ'wave number cm$^{-1}$* | *Assignments* |
|---|---|---|---|---|---|
| *L* | *-* | *-* | *260* | *37735* | *π→π** |
| | | | *332* | *30120* | *n→π** |
| *[Co(L)$_3$]* | *76* | *4.65* | *276* | *36231* | *C.T* |
| | | | *448* | *22282* | *$^4T_1g_{(F)}\rightarrow{}^4T_1g_{(P)}$* |
| | | | *633* | *15782* | *$^4T_1g_{(F)}\rightarrow{}^4A_2g_{(F)}$* |
| | | | *798* | *12521* | *$^4T_1g_{(F)}\rightarrow{}^4T_2g_{(F)}$* |
| *[Ni(L)$_3$]* | *85* | *1.78* | *280* | *35714* | *C.T* |
| | | | *420* | *23809* | *$^3A_2g_{(F)}\rightarrow{}^3T_1g_{(F)}$* |
| | | | *838* | *11933* | *$^3A_2g_{(F)}\rightarrow{}^3T_2g_{(F)}$* |
| *[Cu(L)$_3$]* | *72* | *2.81* | *272* | *36764* | *C.T* |

| | | | | | |
|---|---|---|---|---|---|
| | | | *708* | *14113* | $^2Eg_{(F)} \rightarrow {}^2T_1g$ |
| *[Mn(L)$_3$]* | *88* | *5.64* | *282* | *35460* | *C.T* |
| | | | *344* | *28990* | $^6A_1g_{(F)} \rightarrow {}^4A_1g_{(G)}, Eg_{(G)}$ |
| | | | *421* | *23748* | $^6A_1g_{(F)} \rightarrow {}^4T_2g_{(G)}$ |
| *[Hg(L)$_3$]* | *80* | - | *324* | *30864* | *C.T* |

**Table 6:** Diameter of zone of inhibition (mm)

| *Compound.* | *L* | *[Co(L)$_3$]* | *[Mn(L)$_3$]* | *[Ni(L)$_3$]* | *[Cu(L)$_3$]* | *[Hg(L)$_3$]* |
|---|---|---|---|---|---|---|
| *Escherichia. Coli* | *5* | *8* | *11* | *10* | *14* | *9* |
| *Staphylococcus aurous* | - | *12* | *10* | *14* | *9* | *11* |
| *Bacillus* | - | *11* | - | *15* | *13* | *7* |
| *Pseudomonas* | *8* | *10* | *17* | *13* | *15* | - |

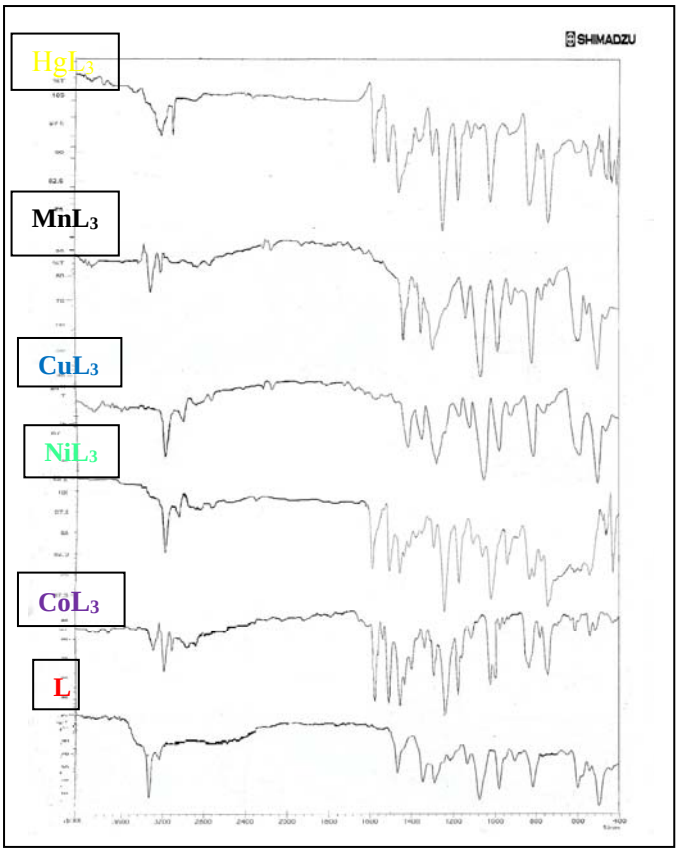



**Fig 1:** The IR spectra of the ligand (L) and its complexes

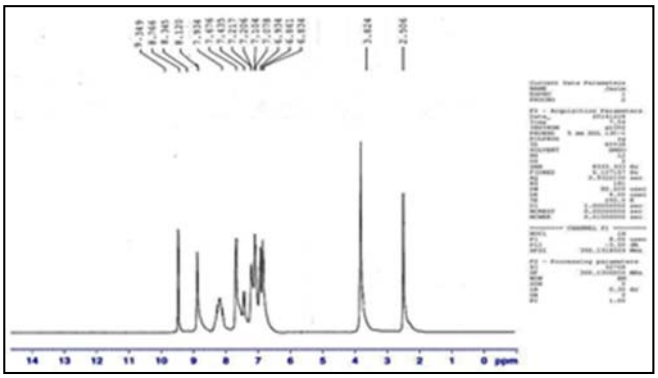


**Fig 2:** $^1H$- *NMR of Ligand* (L)

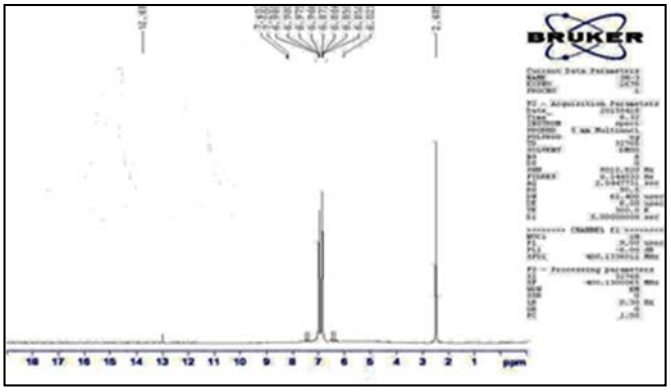



**Fig 3:** $^{13}C$- *NMR of Ligand* (L)

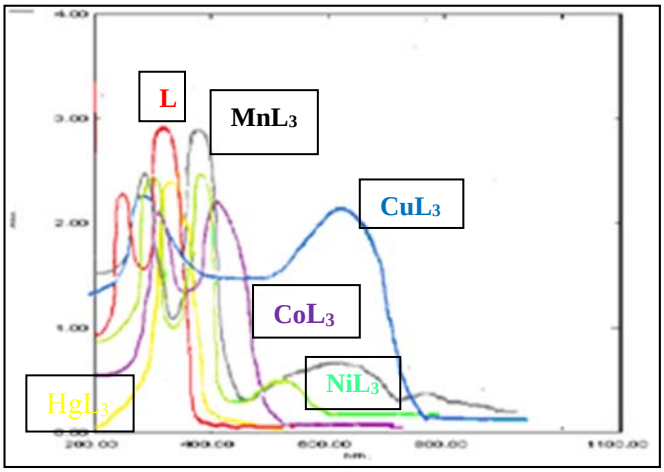



**Fig 4:** UV. Vis spectra of Ligand and its complexes

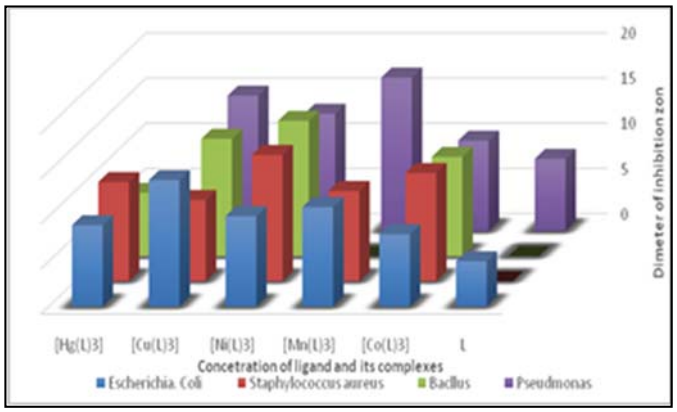



**Fig 5:** Difference between the antimicrobial activity of ligand & metal complexes

**References**


1. Cimerman Z, Miljanic Z, Galic N. Croatica *Chemica Acta* 2000; 73:81-95.
2. Perry BF, Beezer AE, Miles RJ, Smith BW, Miller J, Nascimento MG. International Journal of Chem Tech Research. 1988; 45:181.
3. Dominik C, Branko K. *crysteng-comm* 2011; 13:4351-4357.
4. Cemal S, Zeliha H, Hakan D. J Molec Strc. 2011; 977:53-59.
5. Singh P, Goel RL, Singh BP. J Indian Chem Soc. 1975; 52:958-959.
6. Elmali A, Kabak M, Elerman Y. J Mol Struct. 2000; 477:151.
7. Patel PR, Thaker BT, Zele S. Indian Acad. Sci. (Chem. Sci.) 2001; 113:183-189.
8. Valcarcel M, Laque de Castro MD. Flow- Throgh Biochemical Sensors. *Elsevier*. Amsterdam, 1994.
9. Lawrence JF, Frei RW. Chemical Derivatization in Chromatography. Elsevier. Amsterdam, 1976.
10. Raafat Issa M, Abdalla Khedr M, Rizk H. Journal of the ChineseChemical Society. 2008; 55:875-884.
11. Maurer RI, Blover PI, Dilworth JR, Reynoh CA. J Med Chem. 2002; 45:1420.
12. Selbin J. Coord. Chem. Rev. 1966; 1:293-314.
13. Vasin SV, Cetralla J, Genogel RA. J Inorg Chem.1990; 29:885.
14. Gaber M, Tarek A Fayed, S El-Daly, Y.S.Y El-Sayed. *Elsevier*. *Spectrochimica Acta* Part A. 2007; 68:169-175.
15. Cimerman Z, Miljanić S, Antolić J. Spectrosc. Lett. 1999; 32:181-196.
16. Issa RM, Khedr AM, Rizk HF. Spectrochimica Acta Part A. 2005; 62:621-629.
17. Souza P, Garcia-Vazquez JA, Masaguer JR. Transition Met. Chem. 1985; 10:410.
18. J Costamagna, J Vargas, R Latorre, A Avlvarado, G Mena. *Coord. Chem. Rev* 1992; 119:67.
19. Mahindra AM, Fisher JM. Rabinovitz Nature (London), 1983; 303:64.
20. Palet PR, Thaker BT, Zele S. Indian J Chem. 1999; A38:563.
21. Patel KV, Bhattacharya PK. Indian J Chem. 1982; A21:1110.
22. Purohit KM, Ramana Rao DV. Indian J Chem. 1984; A23:967.
23. Srivastava S, Singh D. Asian J Chem. 1999; 11:1517.
24. Kumar RN, Chauhan NK, Das AK, Singh SK. Asian J Chem. 2000; 12:428.
25. Lewis NA, Ray S, Patra GK, Datta D. Indian J Chem. 1999; A38A:991.
26. Sevagapandian S, Nehru K, Athappan PR. Proc. Indian Acad. Sci. (Chem. Sci.). 2000; 112:389.
27. Kanthimathi M, Nair BV, Ramasami T, Shibahara T. Proc. Indian Acad. Sci. (Chem.Sci.). 1995; 109:235.
28. Rai HC, Kumar A, Kumari A. Asian J Chem. 2000; 12:557.
29. Maurya RC, Trivedi PK, Singh H. Natl. Acad. Sci. Lett. 1997; 20:1.
30. Jha NK, Joshi DM. Synth. React. Inorg. Met. Org. Chem. 1986; 16:947.
31. Nour EM, Al-Kority AM, Sadeek SA, Teleb SM. Synth. React. Inorg. Met. Org. Chem. 1993; 23:39.
32. Singh P, Goel RL, Singh BP. J Indian Chem Soc. 1975; 52:958.
33. Bansod A.D, R.G Mahale, A.S Aswar. J Inorg Chem. 2007; 52(6):882.
34. Bolos C.A, G.S Nikolov, L Ekateriniadou, A Kortsaris, D.A Kyriakidis. *Metal-Based Drugs,* 1998; 5(6):323.
35. Hamurcu F, A.B Gunduzalp, S Cete, B Erk. *Trans. M. Chem.* 2008; 33:141.