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## Synthesis, Characterization, Theoretical, thermal Studies and Bio Activities of Metal Complexes with Schiff base mannich ligand.

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### ABSTRACT

New bidentate ligand 1-[(2-{1-[(Dicyclohexylamino)-methyl]-1H-indol-3-yl}-ethylimino)-methyl]-naphthalen-2-ol (HL), was incorporated from the response of 1-[[2-(1H-Indol-3-yl)-ethylimino] methyl]-naphthalen-2-ol and dicyclohexyl amine. Monomeric complexes of this ligand, of general formulae  $[Pt^{(IV)}(L)(H_2O)_2Cl_2]Cl$ ,  $[M^{(III)}(L)(H_2O)_2]Cl$  with  $M^{(III)} = Co, Ni, Cu$  and  $Zn$ , and  $[Re^{(V)}(L)(H_2O)_2Cl_2]2Cl$  are reported. The method of holding and general geometry of the complexes were resolved through  $^1H$ -NMR, FT-IR, UV-Vis, TGA and mass spectral reviews, magnetic effective estimations, essential investigation, metal substance, chloride containing and molar conductance. These reviews uncovered octahedral geometries for the  $Re^{(V)}$ ,  $Pt^{(IV)}$  complexes, and tetrahedral for  $Co^{(III)}$ ,  $Ni^{(III)}$ ,  $Cu^{(III)}$  and  $Zn^{(III)}$  complexes. The investigation of complexes development by means at molar proportion and occupation strategy in DMF solution has been researched and results were reliable to those found in the solid complexes with a proportion of (M:L) as (1:1). The thermodynamic parameters, for example  $\Delta E^*$ ,  $\Delta H^*$ ,  $\Delta S^*$ ,  $\Delta G^*$  and  $K$  are computed from the TGA bend utilizing Coats-Redfern method. Hyper Chem-8 program has been utilized to foresee structural geometries of compounds in gas stage the warmth of arrangement ( $\Delta H_f^\circ$ ), restricting vitality ( $\Delta E_b$ ) up to vitality, electronic vitality, dipole moment at 298 k. Moreover the electrostatic potential of the free ligand (HL) was computed to investigate the reactive sites of molecules. The compounds were also screened for their bioactive such as *staphylococcus aureus*, *Pseudomonas aeruginosa*, as well fungi like *Penicillium expansum*, *Fusarium graminearum*, *Macrophomina phaseolina*, and *Candida albicans*.

**Keywords:** bidentate ligand, tryptamine, mannich Schiff base complexes.

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## INTRODUCTION

The Tryptamine class of chemistry incorporates normally occurring, engineered and semi-synthetic medication based on the base skeleton "Tryptamine". The important auxiliary of the tryptamine class of chemicals is its estimation to the neurotransmitter serotonin. These medications are ordinarily alluded to as drugs. Tryptamine sort ligands, one of the most seasoned classes of ligands in coordination science have been utilized widely on complex move and primary gathering metals [1]. Schiff base complexes containing diverse metal particles, for example Ni and Cu have been examined in detail for their different crystallographic high lights, structure–redox connections and enzymatic responses, mesogenic qualities and catalysis properties [2-5]. Transition metal complexes of Schiff bases are paramount scientific enthusiasm, due to their different uses as biomimetic frameworks of proteins in the transport, stockpiling and activation of dioxygen [6-10].  $\text{CuN}_2\text{O}_2$  coordination is exceptionally regular in copper chemistry and redox conduct of a wide arrangement of mononuclear  $\text{Cu}^{(II)}$  Schiff base complexes was assessed a few years ago in relation to their auxiliary changes [11]. Isatin has known (1H-indole-2,3-dione) have both amide and keto carbonyl. The C-3 carbonyl group of isatin is unequivocally electrophonic and it promptly condensation and expansion response [12], and through NH group compounds of the isatin arrangement are equipped for going into N-alkylation, N-acylation and into Mannich and Michael reaction [13].

## EXPERIMENTAL

### *Materials and measurements*

All reagents were commercially available and used without further purification. Solvents were distilled from appropriate drying agents immediately prior to use. Elemental analyses (C, H and N) were performed using a Perkin-Elmer C.H.N 2400 elemental analyzer. The content of metal ions were calculated gravimetrically as metal oxides. Molar conductance measurements of the ligand and its complexes with  $10^{-3}$  mol/l in DMSO were carried out using Jenway 4010 conductivity meter. Magnetic measurements were carried out on a Sherwood Scientific magnetic balance using the Gouy method. Electron impact (70 eV) mass spectra were recorded on a Finnegan-MAT model 8430 GC-MS-DS spectrometer. The UV Vis spectra were obtained in DMF solution ( $10^{-3}$  M) for the ligand and their metal complexes with a Jenway 6405 spectrophotometer using 1 cm quartz cell, in the range 200–900 nm. IR spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) were recorded as KBr pellets on a Bruker FT-IR spectrophotometer. ( $^1\text{H}$ ,  $^{13}\text{C}$ ) NMR spectra were acquired in DMSO- $d_6$  Solution using a Bruker AMX 400 MHz spectrometer with tetramethylsilane (TMS) as an internal standard for  $^1\text{H}$  NMR analysis and thermal analysis studies of the ligand and complexes were performed on a Perkin-Elmer Pyris Diamond DTA/TG thermal system under nitrogen atmosphere at a heating rate of 10C/min from 25–700 °C.

### *Preparation of 1-[[2-(1H-Indol-3-yl)-ethylimino] methyl]-naphthalen-2-ol (A)*

Equimolar (0.01 mol) quantity of 2Hydroxy-naphthalene-1-carbaldehyde and 2-(1H-Indol-3-yl)-ethylamine were dissolved in sufficient amount of ethanol and refluxed for 3 hrs in presence of glacial acetic acid. After standing for approximately 24 hrs. at room temperature, the products were separated by filtration, dried under vacuum and recrystallized from war methanol.

### *Preparation of 1-[(2-{1-[(Dicyclohexylamino)-methyl]-1H-indol-3-yl}-ethylimino)-methyl]-naphthalen -2-ol (HL)*

Equimolar quantity of dicyclohexyl amine (0.01mol) in 25 ml of ethanol was added to the solution containing Schiff bases and formaldehyde (37% v/v). The reaction mixture was stirred for 2 hrs at room temperature and heating for 3 hrs followed kept under refrigeration for 24 hrs. The products were separated by suction filtration, dried under vacuum and recrystallized from ethanol. The molecular formula, molecular weight, melting point, yield and elemental analysis are shown in table 1.

### *Preparation of Complexes*

The preparation of all complexes is essentially the same and so a generic description will be presented. To a solution of (HL) (1mmole) in ethanol was added slowly to a solution of metal salt ( $\text{CoCl}_2.6\text{H}_2\text{O}$ ,  $\text{NiCl}_2.6\text{H}_2\text{O}$ ,  $\text{CuCl}_2.2\text{H}_2\text{O}$ ,  $\text{ZnCl}_2.2\text{H}_2\text{O}$ ,  $\text{H}_2\text{PtCl}_6.6\text{H}_2\text{O}$  and  $\text{ReCl}_5$ .) in (ethanol and water) ratio (1:1) with stirring the

mixture was refluxed for (2hrs). The solid was collected by filtration, recrystallized from methanol and dried at room temperature. Elemental analysis data, color and yield for the complexes are given in table 1.

#### Microbiological investigations

All the metal complexes, ligand and metal salts were screened against *staphylococcus aureus* (gram positive ) and *Pseudomonas aeruginosa* (gram negative) bacteria as well fungi like *Penicillium expansum*, *Fusarium graminearum*, *Macrophomina phaseolina*, and *Candida albicans*, by using the wall agar diffusion method using solvent (DMSO), the concentration of the compounds in this exposure was ( $10^{-3}$  M) by using disc sensitivity test. This method involves the exposure of the zone inhibition toward the diffusion of micro-organism on agar plate. The plates were incubated for 24 and 48 hours of bacteria and fungi respectively at 37 °C.

#### Programs used in theoretical calculation

#### Materials and methods

Hyper chem. is a sophisticated molecular modeler, editor and powerful computational package, that is known for its' quality, flexibility and ease of use [15, 16]. It can plot orbital wave functions resulting from semi-empirical quantum mechanical calculations, as well as the electrostatic potential, the total charge density or the total spin density can also be determined during semi-empirical calculation, this information is useful in determining reactivity and correlating calculation results with experimental data.

-Computational methods:

- a) Semi -empirical quantum mechanical
- b) Molecular mechanics
- c) Mopac 2000

Types of calculations: The types of prediction possible of Molecules are [17,18]:

- a) Geometry optimization calculations employ energy minimization algorithms to locate stable structures.
- b) Bond distances
- c) Molecular dynamics which provide the thermodynamic calculations and dynamic behavior of molecules
- d) Plot the electrostatic potential field (HOMO and LUMO).
- e) Vibrational spectrum (I.R and Raman spectra).

#### The thermal analysis

From the TGA curves recorded for the successive steps in the decomposition process of these ligand and complexes it was possible to determine the following characteristic thermal parameters for each reaction step: Initial point temperature of decomposition ( $T_i$ ): the point at which TG curve starts deviating from its base line. Final point temperature of decomposition ( $T_f$ ): the point at which TG curve returns to its base line. Peak temperature, i.e. temperature of maximum rate of weight loss (TDTG): the point obtained from the intersection of tangents to the peak of TG curve. Mass loss at the decomposition step ( $D_m$ ): it is the amount of mass that extends from the point  $T_i$  up to the reaction end point  $T_f$  on the TG curve, i.e. the magnitude of the ordinate of a TG curve. The material released at each step of the decomposition is identified by attributing the mass loss ( $D_m$ ) at a given step to the component of similar weight calculated from the molecular formula of the investigated complexes, comparing that with literatures of relevant compounds considering their temperature. This may assist identifying the mechanism of reaction in the decomposition steps taking place in the complexes under study. Activation energy ( $E$ ) of the composition step: the integral method used is the Coats–Redfern equation [19], for reaction order  $n=1$  or  $n=2$ , which when linearized for a correctly chosen  $n$  yields the activation energy from the slope;

$$\log \left[ \frac{1 - 1(1 - \alpha)^{1-n}}{T^2(1-n)} \right] = \log \frac{ZR}{qE} \left[ 1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT} \quad n = 1$$

$$\log \left[ \frac{-\log \cdot (1 - \alpha)}{T^2} \right] = \log \left[ \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{2.303RT} \quad n = 1$$

$\Delta S^* = 2.303 R [\log(Ah/K T_{max})]$ ,  $\Delta H^* = E - RT_{max}$ ,  $\Delta G^* = \Delta H^* - T_{max} \Delta S^*$ . Where  $\alpha$  = fraction of weight loss,  $T$  = temperature (K),  $n$  = order of reaction,  $A$  or  $Z$  = pre-exponential factor,  $R$  = molar gas constant,  $E$  = activation energy and  $q$  = heating rate. Order of reaction ( $n$ ): it is the one for which a plot of the Coats–Redfern expression gives the best straight line among various trial values of  $n$  that are examined relative to that estimated by the Horovitz–Metzger method [20, 21].

## RESULTS AND DISCUSSION

The new (NO) dentate ligand HL was obtained in good yield by the reaction of 1-([2-(1H-Indol-3-yl)-ethylimino] methyl)-naphthalen-2-ol and dicyclohexyl amine scheme 1. In general the ligand was characterized by elemental analysis (table 1), IR table 2, UV-Vis table 3, mass spectroscopy. Monomeric complexes of the ligand with  $Co^{(III)}$ ,  $Ni^{(III)}$ ,  $Cu^{(III)}$ ,  $Zn^{(III)}$ ,  $Pt^{(IV)}$  and  $Re^{(V)}$  were synthesized by heating (1 mmol) of each ligand with (1 mmol) of metal salt, using ethanolic. However, in ethanolic, deprotonation of the ligand occur facilitating the formation of the complexes  $[Pt^{(IV)}(L)(H_2O)_2Cl_2]Cl$ ,  $[M^{(III)}(L)(H_2O)_2]Cl$  with  $M^{(III)} = Co, Ni, Cu$  and  $Zn$ , and  $[Re^{(V)}(L)(H_2O)_2Cl_2]2Cl$  are reported, scheme 1. The complexes are air-stable solids, soluble in DMF and DMSO, sparingly soluble in MeOH,  $CHCl_3$ ,  $CH_2Cl_2$  and not soluble in other common organic solvents. The analytical data table 1 agree well with the suggested formulae.

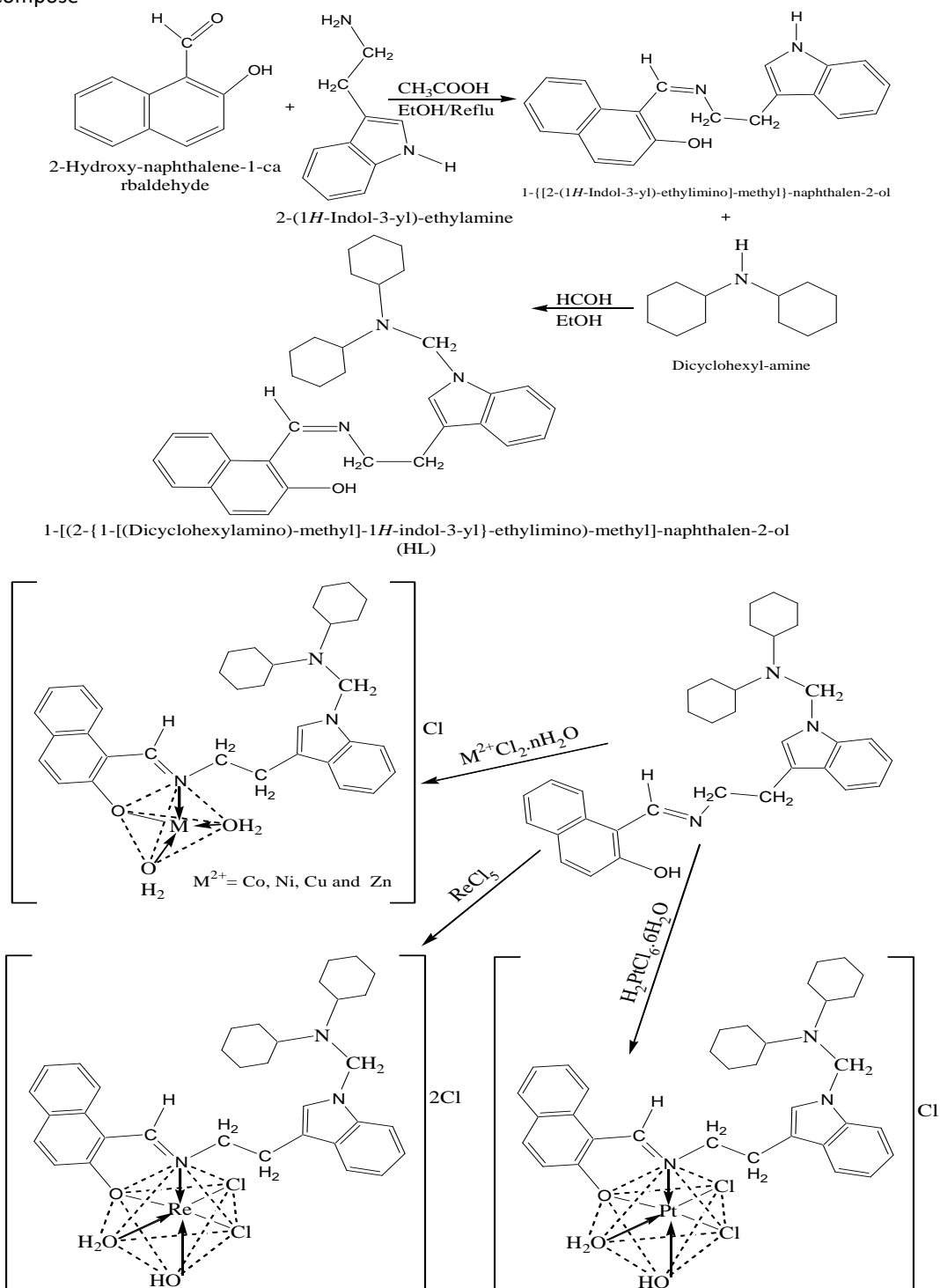
### IR spectra

The IR spectra bands of the ligand (HL) and its complexes were characterized at 3462, 3035, 2960, 2905 and 1673  $cm^{-1}$  due to the  $\nu(OH)$  phenol,  $\nu(CH)$  aromatic,  $\nu(CH)$  aliphatic,  $\nu(CH)$  aldehyde and  $\nu(C=N)$  functional groups, respectively, for the ligand [22]. The IR Spectra of the complexes exhibited ligand bands with the appropriate shifts due complexes formation [23]. Moreover, the  $\nu(C=N)$ , bands of the ligand were observed at (1653-1635)  $cm^{-1}$  and these bands were shifted to the lower frequencies by (38-20)  $cm^{-1}$  in the spectra of the complexes. This indicates that the ligand was coordinated with the metal ions through the O phenol group and N azomethine group atoms, respectively. At lower frequency the complexes exhibited bands around 536–469  $cm^{-1}$  assigned to the  $\nu(M-N)$  and exhibited bands around 413–420  $cm^{-1}$  assigned to the  $\nu(M-O)$  for complexes and new bands in complexes the (3593- 3507)  $cm^{-1}$  and (880- 835)  $cm^{-1}$  assigned to the  $\nu(H_2O)$  and  $\delta(H_2O)$  This indicates that the ligand was coordinated with the metal ion through the  $H_2O$  atom [24,25].

**Table 1. Analytical and physical data of the ligand and its complexes**

| Compounds                | Formula<br>M. wt                         | color          | m. p<br>°C  | Yield% | Elemental analysis, found / Calc.% |      |      |       |       |
|--------------------------|--|----------------|-------------|--------|------------------------------------|------|------|-------|-------|
|                          |  |                |             |        | C                                  | H    | N    | M     | Cl    |
| HL                       | $C_{34}H_{41}N_3O$<br>507.71             | Orange         | 188-<br>190 | 88     | 81.21                              | 7.99 | 7.97 |       |       |
|                          |  |                |             |        | 80.43                              | 8.14 | 8.28 |       |       |
| $[Co(L)(H_2O)_2]Cl$      | $C_{34}H_{44}N_3O_3Cl$<br>Co<br>637.12   | Dark<br>green  | 221d        | 78     | 63.76                              | 7.32 | 7.11 | 10.01 | 5.87  |
|                          |  |                |             |        | 64.10                              | 6.96 | 6.60 | 9.25  | 5.56  |
| $[Ni(L)(H_2O)_2]Cl$      | $C_{34}H_{44}N_3O_3Cl$<br>Ni<br>636.88   | Dark<br>green  | 243d        | 90     | 63.74                              | 5.98 | 7.97 | 10.07 | 5.55  |
|                          |  |                |             |        | 64.12                              | 6.96 | 6.60 | 9.22  | 5.57  |
| $[Cu(L)(H_2O)_2]Cl$      | $C_{34}H_{44}N_3O_3Cl$<br>Cu<br>641.73   | Brown          | 251d        | 84     | 62.86                              | 7.21 | 7.65 | 10.78 | 5.87  |
|                          |  |                |             |        | 63.63                              | 6.91 | 6.55 | 9.90  | 5.52  |
| $[Zn(L)(H_2O)_2]Cl$      | $C_{34}H_{44}N_3O_3Cl$<br>Zn<br>643.57   | Light<br>Brown | 222d        | 88     | 64.33                              | 5.93 | 7.54 | 10.98 | 5.54  |
|                          |  |                |             |        | 63.45                              | 6.89 | 6.53 | 10.16 | 5.51  |
| $[Pt(L)(H_2O)_2Cl_2]Cl$  | $C_{34}H_{44}N_3O_3Cl_3$<br>Pt<br>844.17 | Red            | 193d        | 71     | 47.78                              | 5.01 | 6.13 | 22.76 | 13.05 |
|                          |  |                |             |        | 48.37                              | 5.25 | 4.98 | 23.11 | 12.60 |
| $[Re(L)(H_2O)_2Cl_2]2Cl$ | $C_{34}H_{44}N_3O_3Cl_4$<br>Re<br>870.75 | Red-<br>brown  | 199d        | 87     | 47.24                              | 5.46 | 5.35 |       | 15.97 |
|                          |  |                |             |        | 46.90                              | 5.09 | 4.83 |       | 16.29 |

d= decompose



Scheme 1. Synthesis route of the ligand Proposed structures of metal complexes

**Table 2. FTIR spectral data (wave number  $\nu$ )  $\text{cm}^{-1}$  for the ligand and its complexes**

| Compounds  | $\nu(\text{OH})$ | $\nu(\text{CH})$<br>aromatic | $\nu(\text{CH})$<br>aliphatic | $\nu(\text{CH})$<br>aldehyde | $\nu(\text{C}=\text{N})$ | $\nu(\text{M}-\text{N})$ | $\nu(\text{M}-\text{O})$ | $\text{H}_2\text{O}$<br>rocking |
|--|------------------|------------------------------|-------------------------------|------------------------------|--------------------------|--------------------------|--------------------------|---------------------------------|
| HL   | 3462             | 3035                         | 2960                          | 2905                         | 1673                     | -                        | -                        |                                 |
| [Co (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | -                | 3065                         | 2952                          | 2921                         | 1635                     | 556                      | 489                      | 3540<br>880                     |
| [Ni (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | -                | 3057                         | 2955                          | 2944                         | 1652                     | 534                      | 463                      | 3553<br>875                     |
| [Cu (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | -                | 3074                         | 2957                          | 2911                         | 1653                     | 568                      | 500                      | 3507<br>867                     |
| [Zn (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | -                | 3015                         | 2985                          | 2919                         | 1650                     | 539                      | 490                      | 3593<br>853                     |
| [Pt(L)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]Cl  | -                | 3061                         | 2936                          | 2914                         | 1638                     | 580                      | 486                      | 3553<br>853                     |
| [Re(L)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]2Cl | -                | 3036                         | 2983                          | 2943                         | 1647                     | 573                      | 489                      | 3589<br>835                     |

### Mass spectrum

#### Ligand (HL)

The electron impact spectrum of the ligand (HL) confirms the probable formula by showing a peak at 507 m/z, corresponding to Schiff base moiety [(C<sub>34</sub>H<sub>41</sub>N<sub>3</sub>O), calculated atomic mass 507.71]. The series of peaks in the range of 491, 353 and 142 m/z may be assigned to various fragments. Their intensity gives an idea of the stability of fragments.

#### Complex of Co

The electron impact spectrum of [Co (L) (H<sub>2</sub>O)<sub>2</sub>]Cl confirms the probable formula by showing a peak at 637m/z, corresponding to Complex moiety [(C<sub>34</sub>H<sub>44</sub>N<sub>3</sub>O<sub>3</sub>ClCo), calculated atomic mass 637.12]. The series of peaks in the range of 422.3, 421.3, 215.2 and 214.3 m/z may be assigned to various fragments.

#### Complex of Cu

The electron impact spectrum of [Cu (L) (H<sub>2</sub>O)<sub>2</sub>]Cl confirms the probable formula by showing a peak at 641 m/z, corresponding to Complex moiety [(C<sub>34</sub>H<sub>44</sub>N<sub>3</sub>O<sub>3</sub>ClCu), calculated atomic mass 641.73]. The series of peaks in the range of 570, 215.2 and 214.3m/z may be assigned to various fragments.

#### Complex of Re

The electron impact spectrum of [Re(L)(H<sub>2</sub>O)<sub>2</sub>Cl<sub>2</sub>]2Cl confirms the probable formula by showing a peak at 868m/z, corresponding to Complex moiety [(C<sub>34</sub>H<sub>43</sub>N<sub>3</sub>O<sub>3</sub>Cl<sub>4</sub>Re), calculated atomic mass 868.74]. The series of peaks in the range of 764, 421.3 and 214.3 m/z may be assigned to various fragments.

### Electronic spectral, magnetic moments, and conductivity measurements

The electronic spectrum at the ligand (HL) exhibits intense absorption at (282,330) and 348 nm attributed to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$ , respectively. The electronic spectra of the Co<sup>(II)</sup> complex with ligand exhibit one absorption band at 677 nm which is attributed to  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_{1\text{P}}$ . Furthermore, the magnetic moment of the Co<sup>(II)</sup>(d<sup>7</sup>) complex was found to be 4.1 B.M., All the above mentioned data correspond to a tetrahedral geometry. The electronic spectra of the Ni<sup>(II)</sup> complex with ligand exhibit one absorption band at 797 nm which is attributed to  ${}^3\text{T}_1 \rightarrow {}^3\text{T}_{1\text{P}}$ . Furthermore, the magnetic moment of the Ni<sup>(II)</sup>(d<sup>8</sup>) complexes is found to be 3.9 B.M., All the above mentioned data correspond to a tetrahedral geometry. The electronic spectra of the Cu<sup>(II)</sup> complex exhibit one and two absorption bands with ligand at 953 nm which is attributed to  ${}^2\text{T}_2 \rightarrow {}^2\text{E}$ . Furthermore, the magnetic moment of the Cu<sup>(II)</sup> (d<sup>9</sup>) complexes is found to be 2.01 B.M., All the above

mentioned data correspond to an tetrahedral geometry [26,27]. The electronic spectra of the Pt<sup>(IV)</sup> and Re<sup>(VI)</sup> complexes with ligand exhibit three and two absorption band at 368, 492, 790 nm and 587, 892 nm which is attributed to C. T,  ${}^3T_{1g} \rightarrow {}^3A_{2g}$ ,  ${}^3T_{1g} \rightarrow {}^3T_{1g}$  (P) and  ${}^1A_{1g} \rightarrow {}^1T_{2g}$ ,  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  Furthermore, the magnetic moment of the Re<sup>(VI)</sup>(d2) and Pt<sup>(IV)</sup> (d6) complexes was found to be 3.05 and diamagnetic B.M respectively, complexes of together with the  $\mu_{\text{eff}}$  value table 3 suggest octahedral geometry around for complexes. The molar conductivity value of the complexes were consistent with non-electrolytes all complexes and 1:1 electrolytes for Re<sup>(VI)</sup> complex. See for the scheme proposed structures of metal complexes [26-29].

**Table 3. Electronic data and molar conductivity for the metal complexes**

| Complexes  | $\lambda$<br>nm   | Assignment   | $\Omega$ Ohm <sup>-1</sup><br>cm <sup>2</sup> mol <sup>-1</sup> | $\mu_{\text{eff}}$<br>B.M | Suggested<br>Formula |
|--|-------------------|--|---|---------------------------|----------------------|
| [Co (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | 677               | ${}^4A_2 \rightarrow {}^4T_{1(P)}$   | 88  | 4.10                      | Tetrahedral          |
| [Ni (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | 797               | ${}^3T_1 \rightarrow {}^3T_{1(P)}$   | 80  | 3.9                       | Tetrahedral          |
| [Cu (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | 953               | ${}^2T_2 \rightarrow {}^2E$  | 70  | 1.63                      | Tetrahedral          |
| [Zn (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | 385               | C. T   | 76  | diamagnetic               | Tetrahedral          |
| [Pt(L)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]Cl  | 587<br>892        | ${}^1A_{1g} \rightarrow {}^1T_{2g} \nu_2$<br>${}^1A_{1g} \rightarrow {}^1T_{1g} \nu_1$ | 71  | diamagnetic               | Octahedral           |
| [Re(L)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]2Cl | 368<br>492<br>790 | C. T<br>${}^3T_{1g} \rightarrow {}^3A_{2g}$<br>${}^3T_{1g} \rightarrow {}^3T_{1g}$ (P) | 156   | 3.05                      | Octahedral           |

#### Study Complexes in Gas Stat (Theoretical studies)

##### Electrostatic Potentials:

Electron distribution governs the electrostatic potential of the molecules. The electrostatic potential (E.P) describes the interaction of energy of the molecular system with a positive point charge. (E.P) is useful for finding sites of reaction in a molecule; positively charged species tend to attack a molecule where the electrostatic potential is strongly negative (electrophonic attack) [30]. The (E.P) of the free ligand (HL) was calculated and plotted as 2D contour to investigate the reactive sites of the molecules, figure 1. Also one can interpret the stereochemistry and rates of many reactions involving "soft" electrophiles and nucleophiles in terms of the properties of frontier orbital (HOMO, highest occupied molecular orbital) and (LUMO, lowest unoccupied molecules). The results of calculations show that the LUMO of metal ions prefer to react with the HOMO of two-donor atoms with nitrogen of azomethane and oxygen of the hydroxyl group for free ligand (HL).

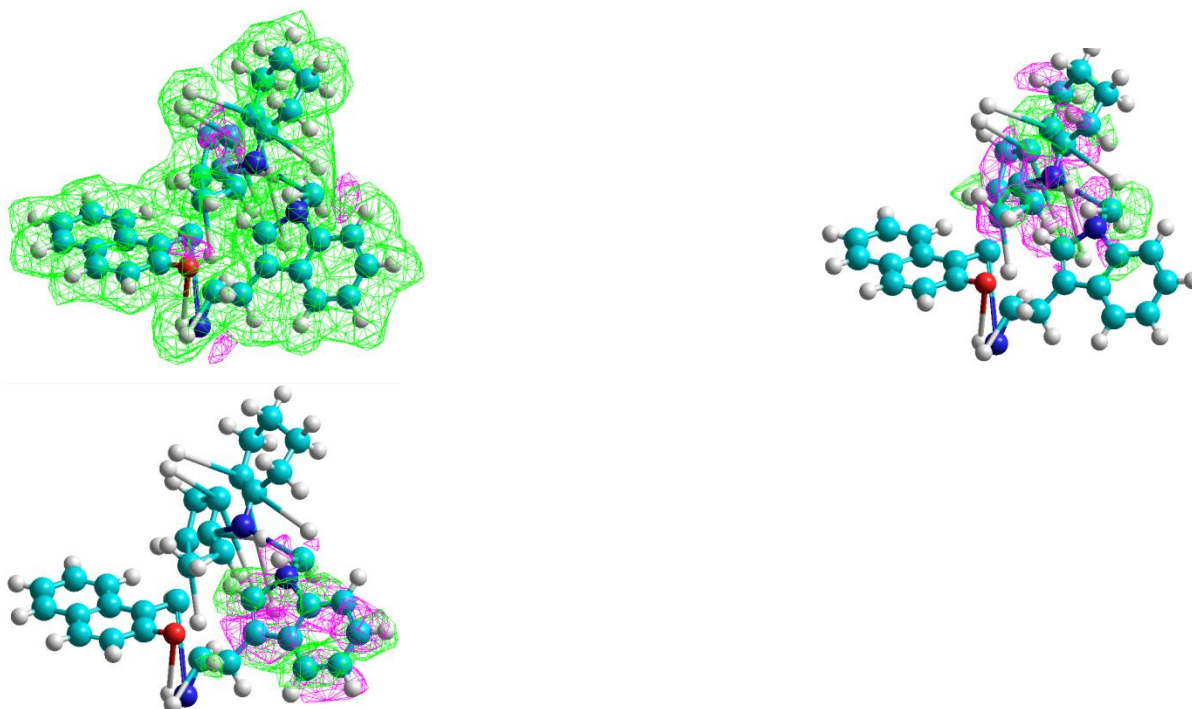
##### Optimized energies:

The program Hyperchem-8 was used for the semi-empirical and molecular mechanics calculations. The heat of formation ( $\Delta H_f^\circ$ ) and binding energy ( $\Delta E_b$ ) for free ligand and their metal complexes were calculated, (table 6).

##### Optimized vibrational spectra for ligand (L):

The vibrational spectra of the free ligand and their metal complexes have been calculated, table 7. The theoretically calculated wave numbers for this ligand showed that some deviations from the experimental values, these deviations are generally acceptable in theoretical calculations [31]. The most diagnostic calculated vibrational frequencies were chosen for the assignment of ligand (HL) and metal complexes which are included in table 7 and their respective experimental vibrational modes are shown in the same table 2. The results obtained for the theoretical calculations of the frequencies agreed well with those obtained for the experimental values, table 2.





**Figure 1. Electrostatic potential (HOMO and LUMO) as 2D contours for (HL)**

*Bond length measurements for the (HL) and their metal complexes:*

Calculation of parameters has been optimized bond lengths of the free ligand (HL) and their metal complexes by applying the Semi-empirical (PM3) at Geometry Optimization ( $0.001 \text{ K.Cal.mol}^{-1}$ ), which to give excellent agreement with the experimental data [32, 33] as shown in table 8.

**Table 6. Conformation energetic (in  $\text{KJ. mol}^{-1}$ ) for Naringin and its metal complexes**

| Compounds  | $\Delta E_{\text{tot}}$ | $\Delta H^{\circ}_f$ | $\Delta E_b$  | Dipole (Debyes) |
|--|-------------------------|----------------------|---------------|-----------------|
| HL   | -125392.57133           | 102.2404773          | -8242.7605227 | 4.581           |
| [Co (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | -142058.72311           | 2015.461668          | -4326.4163316 | 9.648           |
| [Ni (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | -114221.76535           | 1981.34446           | -4112.78009   | 8.156           |
| [Cu (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | -219901.1675            | 1652.1165            | -3998.176532  | 7.114           |
| [Zn (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | -29998.11537            | 1763.5667            | -3389.1997001 | 9.875           |
| [Pt(L)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]Cl  | -1626.463316 (AMBER)    |                      |               | 9.453           |
| [Re(L)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]2Cl | -3357.82801 (AMBER)     |                      |               | 10.44           |

**Table 7. Comparison between the experimental and theoretical vibrational frequencies ( $\text{cm}^{-1}$ ) for free ligand (HL) metal complexes**

| Compounds  | $\nu \text{ C=N}$ |        | $\nu \text{ M-N}$ |       | $\nu \text{ M-O}$ |       | $\text{H}_2\text{O}$ roring |       |
|--|-------------------|--------|-------------------|-------|-------------------|-------|-----------------------------|-------|
|  | $\nu$             | $\nu$  | $\nu$             | $\nu$ | $\nu$             | $\nu$ | $\nu$                       | $\nu$ |
| HL   | 1677*             | 1673** | -                 | -     | -                 | -     | -                           | -     |
| [Co (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | 1643*             | 1635** | 555*              | 556** | 491*              | 489** | 882*                        | 880** |
| [Ni (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | 1655*             | 1652** | 533*              | 534** | 465*              | 463** | 880*                        | 875** |
| [Cu (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | 1650*             | 1653** | 566*              | 568** | 501*              | 500** | 866*                        | 867** |
| [Zn (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | 1655*             | 1650** | 535*              | 539** | 495*              | 490** | 855*                        | 853** |
| [Pt(L)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]Cl  | 1640*             | 1638** | 581*              | 580** | 488*              | 486** | 855*                        | 853** |
| [Re(L)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]2Cl | 1644*             | 1647** | 577*              | 573** | 488*              | 489** | 833*                        | 835** |

Where:-\*Theoretical frequency; \*\*Experimental frequency.



**Table 8. Selected bond lengths (Å) for (E) ligand and their metal complexes**

| Compounds  | C=N   | C-O   | M-N   | M-O   | M-Cl |
|--|-------|-------|-------|-------|------|
| HL   | 1.347 | 1.363 | -     | -     | -    |
| [Co (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | 1.357 | 1.366 | 1.691 | 1.979 | 1.83 |
| [Ni (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | 1.355 | 1.367 | 1.690 | 1.978 | 1.79 |
| [Cu (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | 1.359 | 1.369 | 1.689 | 1.980 | 1.80 |
| [Zn (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | 1.366 | 1.368 | 1.691 | 1.980 | 1.81 |
| [Pt(L)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]Cl  | 1.356 | 1.361 | 1.692 | 1.977 | 1.99 |
| [Re(L)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]2Cl | 1.351 | 1.360 | 1.693 | 1.977 | 1.98 |

#### Theoretical electronic spectra for the metal complexes

The electronic spectra of the metal complexes have been calculated and the wave number for these compounds showed some deviations from the experimental values as shown in table 9. These deviations in theoretical calculation are generally acceptable due to couplings between the electronic spectra modes and the approximation that each normal mode of the electronic spectra inter acts independently electronic spectra beam [34-36]. The most diagnostic calculated electronic spectra were chosen for the assignment of the metal complexes. Experimental electronic modes are shown in table 3. All the theoretical electronic spectra of all compounds were calculated by using the semi-empirical (PM3) method at geometry optimization (0.01 K.Cal. Mol<sup>-1</sup>) was used, and the comparison between of the experimental data and theoretical data of the electronic spectra for metal complexes in table 9.

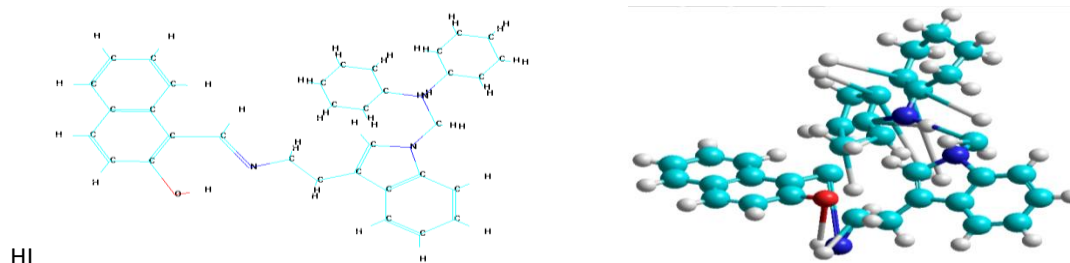
**Table 9. Comparison between experimental and theoretical of the electronic spectra for complexes**

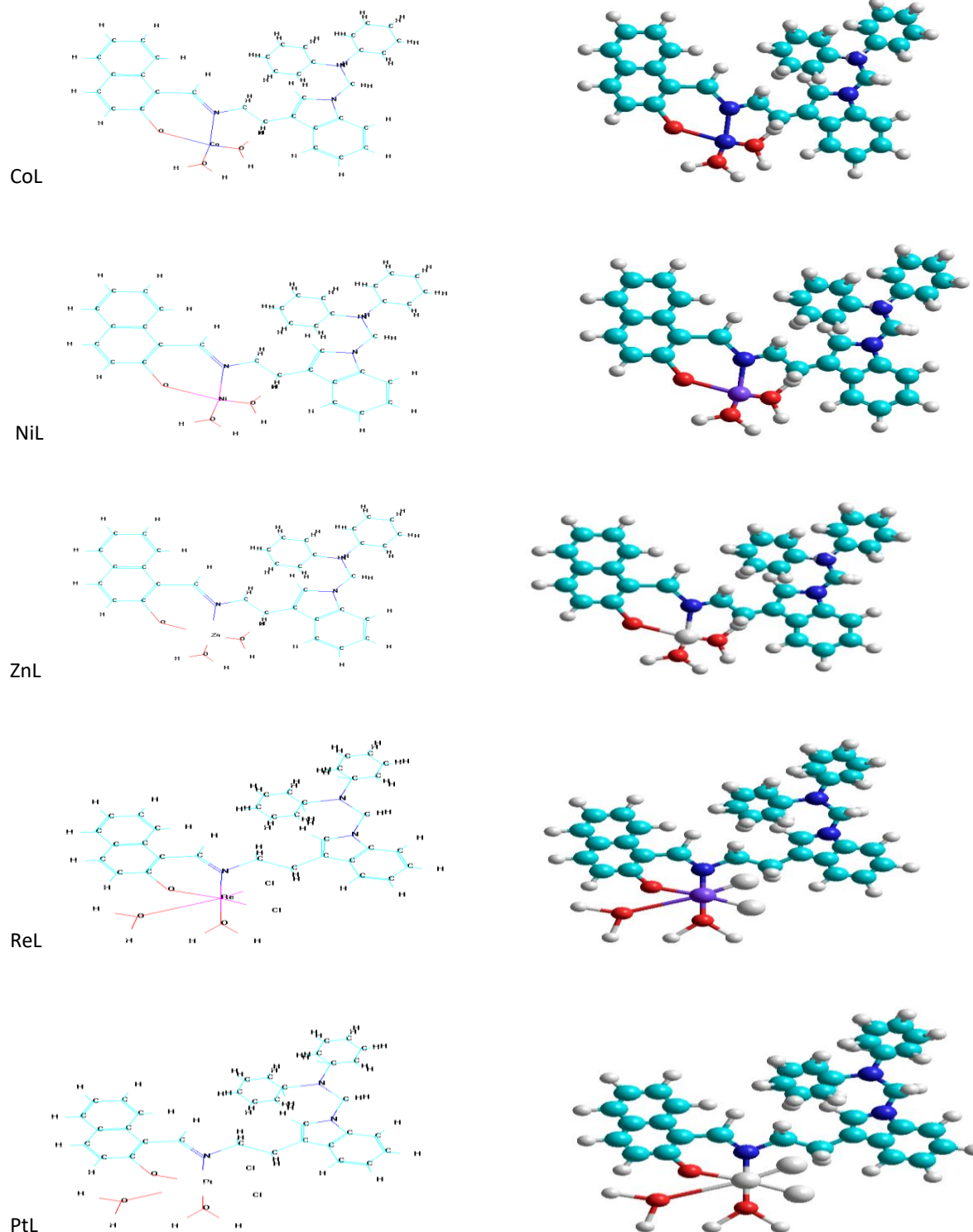
| Complexes  | Maximum absorption (nm) |       | Band assignment  | Suggested geometry |
|--|-------------------------|-------|--|--------------------|
| [Co (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | 677*                    | 670** | <sup>4</sup> A <sub>2</sub> → <sup>4</sup> T <sub>1(p)</sub>               | Tetrahedral        |
| [Ni (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | 797*                    | 790** | <sup>3</sup> T <sub>1</sub> → <sup>3</sup> T <sub>1(p)</sub>               | Tetrahedral        |
| [Cu (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | 953*                    | 944** | <sup>2</sup> T <sub>2</sub> → <sup>2</sup> E                               | Tetrahedral        |
| [Zn (L) (H <sub>2</sub> O) <sub>2</sub> ]Cl                | 385*                    | 391** | C. T   | Tetrahedral        |
| [Pt(L)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]Cl  | 587*                    | 592** | <sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>2g</sub> v <sub>2</sub> | Octahedral         |
|  | 892*                    | 888** | <sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1g</sub> v <sub>1</sub> |                    |
| [Re(L)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]2Cl | 368*                    | 370** | C. T   | Octahedral         |
|  | 492*                    | 500** | <sup>3</sup> T <sub>1g</sub> → <sup>3</sup> A <sub>2g</sub>                |                    |
|  | 790*                    | 800** | <sup>3</sup> T <sub>1g</sub> → <sup>3</sup> T <sub>1g</sub> (P)            |                    |

Where: \*Theoretical frequency.; \*\*Experimental frequency

#### Optimized geometries of (HL) and their complexes:

All theoretically probable structures of free ligand and their complexes have been calculated by (PM3) method in gas phase to search for the most probable model building stable structure, figure. 2.





**Figure 2. Conformational Structure of (HL) and their metal complexes**

#### *Thermal analysis*

The results of thermo gravimetric analyses of (HL) and metals complexes are given in table 10. The thermograms have been carried out in the range of 25–700°C at a heating rate of 10°C/min in nitrogen atmosphere; they showed an agreement in weight loss between their results obtained from the thermal decomposition and the calculated values, which supports the results of elemental analysis and confirms the suggested formulae.

Thus, the ligand HL showed a common general behavior as the first step ( $C_{34}H_{41}N_3O$ ) was loss of  $C_{12}H_{16}N_3$  moiety followed by the other parts of the ligand, the final step of the thermolysis reactions of the complexes was found to give the metal oxide see table 10.

(HL)- $C_{34}H_{41}N_3O$  [99.34% Found (100 % Cal)]  
 (199.1-313.7°C) →  $C_{12}H_{16}N_3$  [29.8% Found (29.53% Cal)]  
 (313.7-589.3°C) →  $C_{22}H_{25}N_2O$  [69.54% Found (70.47%Cal)]

(NiL)- $C_{34}H_{44}N_3O_3NiCl$  [86.977% Found (88.188 % Cal)]  
 (33.5-132.8°C) →  $2H_2O$  [4.163 % Found (5.271% Cal)]  
 (133-433.7°C) →  $C_{15}H_{13}Cl$  [22.794% Found (22.821%Cal)]  
 (462.9-699.4°C) →  $C_{19}H_{27}N_3$  [60.02% Found (60.096 %Cal)]

(CoL)- $C_{34}H_{44}N_3O_3CoCl$  [91.330% Found (91.552 % Cal)]  
 (33.7-96.9°C) →  $2H_2O$  [3.634 % Found (4.095% Cal)]  
 (146 - 175°C) →  $C_{15}H_{10}Cl$  [34.143% Found (35.687%Cal)]  
 (298 - 698°C) →  $C_{19}H_{30}N_3$  [53.553% Found (51.77 %Cal)]

**Table 10. Thermal analysis data of some metal complexes of HL.**

| Com. | TG range (°C) | DTG max (°C) | % Estimated (calculated) |                    | Assignment  |
|------|---------------|--------------|--------------------------|--------------------|---|
|      |               |              | Mass loss                | Total mass lose    |   |
| HL   | 199.1-313.7   | 287.9        | 29.8(29.53)              | 99.34              | $C_{12}H_{16}N_3$<br>$C_{22}H_{25}N_2O$                 |
|      | 313.7-589.3   | 524.4        | 69.54(70.47)             | (100)              |   |
| NiL  | 33.5-132.8    | 70.32        | 4.163(5.271)             | 86.977<br>(88.188) | $2H_2O$<br>$C_{15}H_{13}Cl$<br>$C_{19}H_{27}N_3$<br>NiO |
|      | 133-433.7     | 319          | 22.794(22.821)           |                    |   |
|      | 462.9-699.4   | 611.6        | 60.02(60.096)            |                    |   |
| CoL  | 33.7-96.9     | 141.5        | 3.634 (4.095)            | 91.330<br>(91.552) | $2H_2O$<br>$C_{15}H_{10}Cl$<br>$C_{19}H_{30}N_3$<br>CoO |
|      | 146- 175      | 232          | 34.143 (35.687)          |                    |   |
|      | 298- 698      | 482          | 53.553 (51.77)           |                    |   |

**Table 11 Thermodynamic data of the thermal decomposition of ligand and their complexes.**

| Sam | T range (°C) | n   | R <sup>2</sup> | Tmax (K) | Ea (kJ mol <sup>-1</sup> ) | ΔH* (kJ mol <sup>-1</sup> ) | A (sec <sup>-1</sup> ×10 <sup>7</sup> ) | ΔS* (J mol <sup>-1</sup> K <sup>-1</sup> ) | ΔG* (kJ mol <sup>-1</sup> ) | K ×10 <sup>-7</sup> |
|-----|--------------|-----|----------------|----------|----------------------------|-----------------------------|---|--|-----------------------------|---------------------|
| HL  | 199.1-313.7  | 1   | 0.997          | 287.9    | 10.160737                  | 5.70751                     | 3.661                                   | -104.996                                   | 61.946                      | 9.095102            |
| HL  | 313.7-589.3. | 1   | 0.998          | 524.4    | 13.851965                  | 13.1808                     | 7.791                                   | -102.075                                   | 95.086                      | 6.45457             |
| NiL | 33.5-132.8   | 0.9 | 0.997          | 70.32    | 5.96778                    | 3.09795                     | 1.53783                                 | -108.5589                                  | 40.5703                     | 7.25169             |
| NiL | 133- 433.7   | 0.9 | 0.993          | 319      | 9.1435                     | 3.8845                      | 5.42426                                 | -103.1137                                  | 69.1081                     | 0.19629             |
| NiL | 462.9-699.4  | 0.9 | 0.997          | 611.6    | 14.46375                   | 8.22775                     | 6.5654                                  | -102.943                                   | 85.4412                     | 0.112099            |
| CoL | 33.7- 96.9   | 0.9 | 0.997          | 141.5    | 6.289644                   | 2.88339                     | 2.02715                                 | -107.688                                   | 47.0031                     | 0.101652            |
| CoL | 146-175      | 0.9 | 0.989          | 232      | 11.69165                   | 4.65185                     | 13.0333                                 | -98.24933                                  | 87.8435                     | 0.38090             |
| CoL | 298-698      | 0.9 | 0.99           | 482      | 15.989                     | 6.448                       | 15.07571                                | -76.445                                    | 97.4027                     | 0.52368             |

Antimicrobial activity of ligand and all complexes

Ligand, metal salts and their complexes of transition metals were screened for antibacterial and antifungal activity. The entire tested compound exhibited variable antibacterial activity and antifungal activity as shown in figure.3 and 4.

Ligand activity exhibited antibacterial against *S. aureus* and *P.aeruginosa* but activity was found to be lower than the metal complexes and salts metals. Ligand also exhibited activity antibacterial against *S. aureus* and *P.aeruginosa* but activity high in complexes and metal salts as shown in, figure. 3. ligand which did not exhibit have antifungal activity but exhibited activity was in some metal complexes and salts metals as shown in, figure 3. Where exhibited CuL and CoL complex activity lower compared with salts of Cu and Co against *P.expansum* and *F. graminearum*. While the HL and some salts metals exhibiting antifungal strong activity against *P.expansum* and *C. albicans*, by not exhibited antifungal activity against *F.graminearum* and *M. phaseolina* as compared with the antimicrobial activity with some mixed ligand metal complexes which exhibited antifungal activity top than ligand as shown in (3). Exhibited some complexes Prepared antifungal activity strong against *F.graminearum* and *M. phaseolina* as compared with the ligands which did not exhibit antimicrobial activity. From the data shown in the figure 5- 9 allot of compounds exhibited bio activity against 2 kinds of bacteria and 4 kinds of fungal.

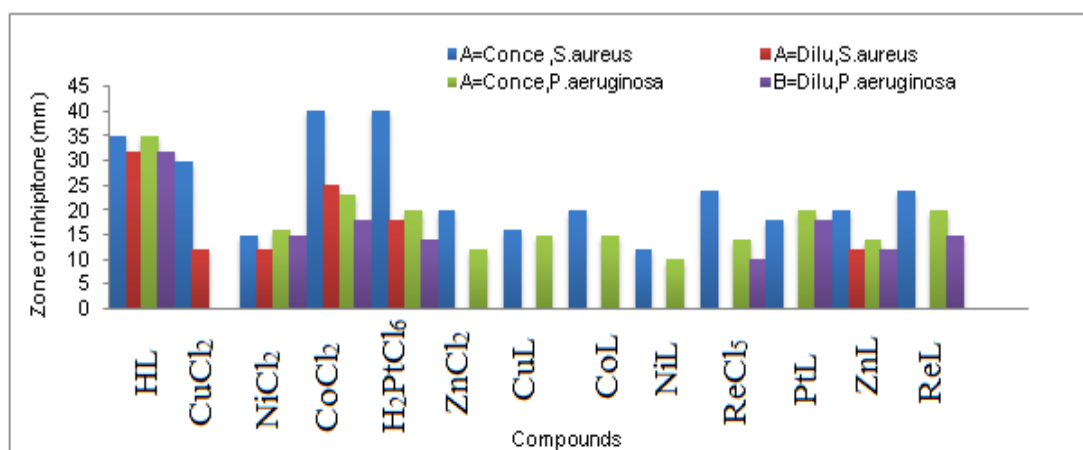


Figure 3. The antibacterial activity of compounds against *S. aureus* and *P.aeruginosa*

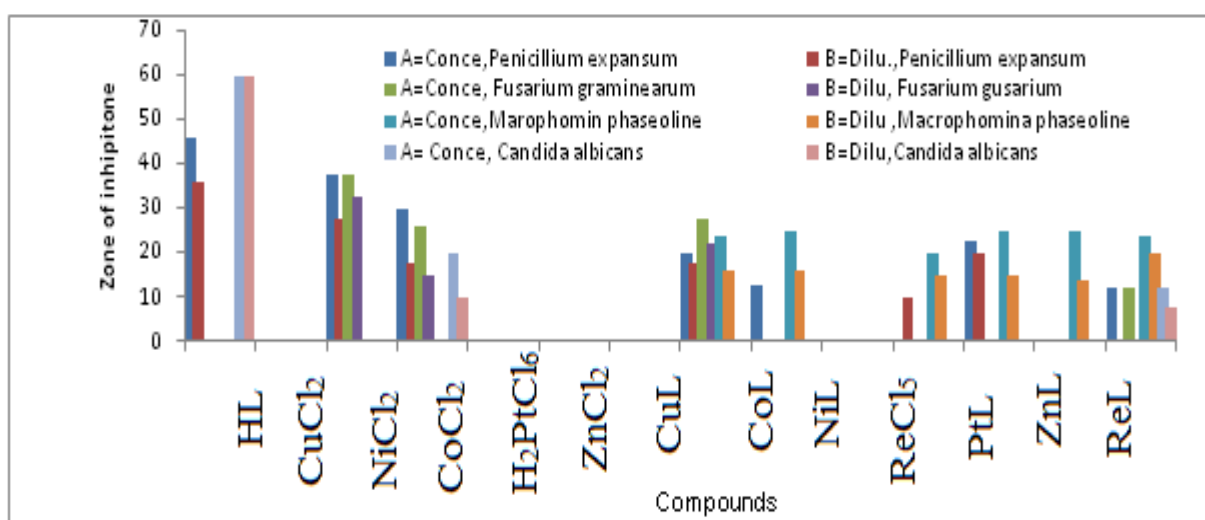


Figure 4. The antibacterial activity of compounds against *P.expansum*, *F.graminearum*,

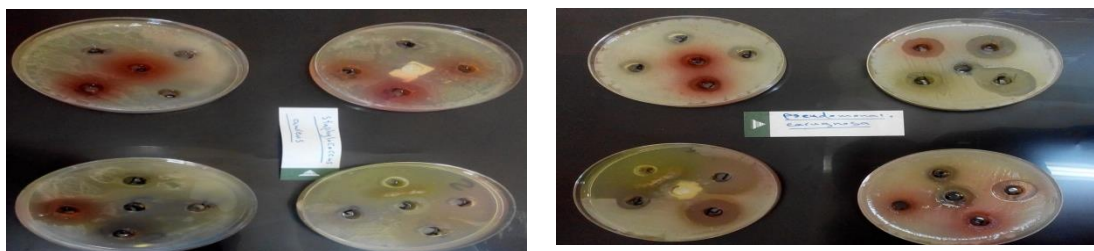


Figure 5 Effect of the ligand complexes towards the *Staphylococcus aureus* and *Pseudomonas aeruginosa*



Figure 6. Effect of the ligand and complexes towards the *Penicillium expansum*

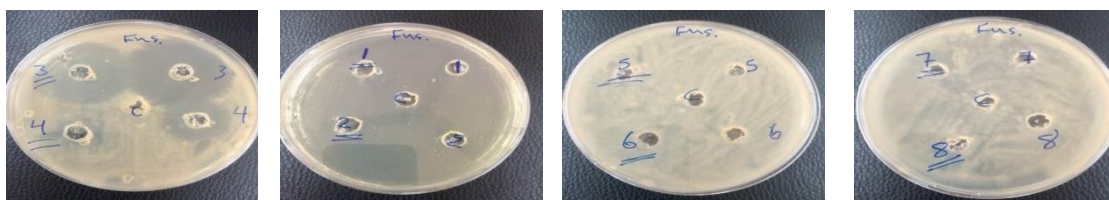


Figure 7. Effect of the ligand and complexes towards the *Fusarium graminearum*

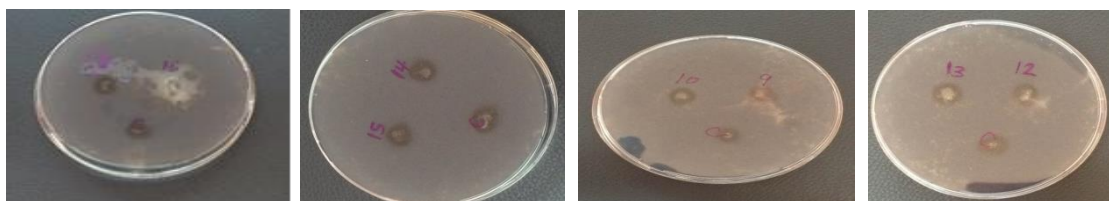


Figure 8. Effect of the ligand and complexes towards the *Macrophomina phaseolina*



Figure 9. Effect of the ligand and complexes towards the *Candida albican*

### CONCLUSION

In this paper synthesis and characterization of new bidentate ligand 1-[(2-{1-[(Dicyclohexylamino)-methyl]-1H-indol-3-yl}-ethylimino)-methyl]-naphthalen -2-ol, and prepared complexes general formulae  $[Pt^{(IV)}(L)(H_2O)_2Cl_2]Cl$ ,  $[M^{(III)}(L)(H_2O)_2]Cl$  with  $M^{(III)} = Co, Ni, Cu$  and  $Zn$ , and  $[Re^{(V)}(L)(H_2O)_2Cl_2]2Cl$  are reported. The thermodynamic parameters, such as  $\Delta E^*$ ,  $\Delta H^*$ ,  $\Delta S^*$ ,  $\Delta G^*$  and  $K$  are calculated from the TGA curve using Coats–Red fern method. Hyper Chem-8 program has been used to predict structural geometries of compounds in gas phase. The compounds were also screened for their bioactive such as *staphylococcus aureus*, *Pseudomonas aeruginosa*, *Penicillium expansum*, *Fusarium graminearum*, *Macrophomina phaseolina*, and *Candida albicans*.



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## REFERENCES

- [1] Al-Hamdani, A. A. S, Balkhi, A. M, Falah, A, Shaker, Sh. A. J. *Chil. Chem. Soc.* 2015, 60 (1): 2774-2785.
- [2] Aiello, I, Ghedini, M, Neve, F, Pucci, D. *Chem. Mater.* 1997, 9: 2107.
- [3] Klement, R, Stock, F, Elias, H, Paulus, H, Valko, M, Mazur, M. *Polyhedron.* 1999, 18:3617.
- [4] Santos, I. C, Vilas-Boas, M. M, Piedade, F. M, Freire, C, Durate, M. T, Castro, B. *Polyhedron.* 2000, 19: 655.
- [5] Stemmler, A. J, Burrows, C. T. *J. Am. Chem. Soc.* 1999, 121: 6956.
- [6] Bryliakov, K. P, Talsi, E. P. *Angew. Chem., Int. Ed.* 2004, 43: 5282.
- [7] Dyers, J. L, Que, S. Y, Van Derveer, D, Bu, X. R. *Inorg. Chim. Acta.* 2006, 359: 197.
- [8] Pui, A, Pierre, M.J. *Polyhedron.* 2007, 26: 3143-3152.
- [9] Ueno, T, Yokoi, N, Unno, M, Matsui, T, Tokita, Y, Yamada, S. M, Ikeda, S. M, Nakajima, H, Watanabe, Y. *PNAS.* 2006, 103: 9416.
- [10] Vigato, P. A, Tamburini, S. *Coord. Chem. Rev.* 2004, 248: 1717.
- [11] Bernal, I. *Stereochemical Control, Bonding and Steric Rearrangements.* Elsevier, Amsterdam, 1990; (Chapter 3).
- [12] Abdulghani, A. J, Ahmed, Z. Z. *Pakistan J. of Chemistry.* 2011;1(3): 100-113;
- [13] AL-Bayati, Kh. A. *Tikrit J. of Pure Sci.* 2012; 17 (2):40-45.
- [14] Ramadoss, G, Andy, R. M. Athiappan, Bioino. *Chem. and Appli.* 2014: 1-12.
- [15] Stewart, J. J. *Reviews in Computational Chemistry*, Lipkowitz, K. B, Boyd, D. B. (eds.), VCH publishers, New York, 1996; 9(1): 72-80.
- [16] Cook, D. B. *Hand book of Computational Quantum Chemistry*, New York, Oxford univ.Press, 1998; 149.
- [17] Choinacki, H, Pruchnik, F. *Quantum Chemical studies on molecular and Electronic structure of complexes adducts*, *Int. J. Mol. Sci.* 2001; 2(44): 11-17.
- [18] Nahari, T. T. *Iserco Sci. and Technology Vision*, 2007; 3(3): 32-40.
- [19] Coats, A. W, Redfern, J. P. *Kinetic parameters from thermo gravimetric data.* *Nature*, 1964; 201: 68-79.
- [20] Al-Hamdani, A.A.S, Zainab, A. H. *Baghdad Sci. J.* 2016; 13(3): 511-523.
- [21] Horovitz, H.H, Metzger, G. *Thermochim. Acta*, 1963;159: 43-54.
- [22] Al-Hamdani, A.A.S, Shayma, Sh. A. J. *Oriental Chem* 2011; 27: 835-845.
- [23] W. Al Zoubi, F. Kandil, M.K. Chebani, *Int. J. Chem Tech Res.USA*, 2011; 3, :1612-1621.
- [24] Sliverstein, R. M. Webser, X. F. *Spectrometric Identification of Organic Compounds.* 7<sup>th</sup> Ed., Jon Wiley and Son, Inc. USA, 2005.
- [25] Nakamoto, N. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 6<sup>th</sup>Ed, Part 2 John Wiley and Sons, Inc., New Jersey, 2009.
- [26] Lever, A. B. P. *Inorganic Electronic Spectroscopy.* New York, 1968; 6: 121.
- [27] Al-Hamdani, A. A. S. *Dirasat, Pure Scie.* 2013; 39 (1): 61-72.
- [28] Al-Hamdani, A. A. S, Al-Zoubi, W. *Spectrochimica Acta Part A: Mole. and Biomol. Spect.* 2015; 137: 75-89.
- [29] Al-Hamdani, A. A. S, Balkhi, A. M. Falah, A. *Damascus University J. for Basic Sci.* 2013; 29(2): 21-41.
- [30] Nagesha, K, Kotove, A. *Concepts in theoretical chemistry* Elsevier publishing company, New York, London. 1978.
- [31] Azhary, A. A. J. *Phys. Chem.* 1998, 102: 620-629.
- [32] Kunkeler, D. J, Cornelissen, K. Ree Dig, *J. Am. Chem. Soc.* 1996; 118: 2190-2197.
- [33] Keypour, H. K Wainwright, Taylor, P. M. *Iran. Chem. Soc. J.* 2004; 1(1): 53- 64.
- [34] Henryk, C, Wojciech, K. Florian, P. "Quantum chemical studied on molecular and electronic structure of some metal complexes", *Int. Mol. Sci.* 2001, 2.
- [35] Nagesha, D.K, Kotov, N. A. *Material.* 2003; 8 (4):
- [36] Al-Hamdani, A. A.S, Rehab, G. H. *Baghdad Sci. J.* 2016; 13(4): 770-781.