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# Potentiometric and Theoretical Studies of 2-((4-Morpholinobenzylidene)amino)phenol With Some Transition Elements

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**Abstract**

The stability constants of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and La(III) metal ions with 2-((4-morpholinobenzylidene)amino)phenol (HL) were determined in 25 % (v/v) ethanol-water medium at 25 $^o$C (I = 1 M NaClO$_4$). The calculations of the metal-ligand stability constants were obtained by Calvin-Bjerrum pH-metric method using the Miniquad-75 computer program. The dissociation constant (pK$_a$) value of monoprotic ligand HL was found as 10.36. The order of the formation constant values (log K$_i$) of metal ion complexes with HL increases in the order La(III) > Fe(III) > Cu(II) > Co(II) > Ni(II) > Mn(II). Optimization of the geometries of the HL metal complexes was done with the density functional theory method (DFT) using the Gaussian 09 program package as DFT methods.

**Keywords**: 2-((4-morpholinobenzylidene)amino)phenol, stability constants, Miniquad-75, DFT methods.

### 1. Introduction

Morpholine derivatives play an important role in the treatment of several diseases, anti-inflammatory, analgesic, local anesthetic, anticancer, appetite suppressant, and antimicrobial activity [1-4]. Moreover, the metal complexes obtained from the Schiff base ligands are important due to their various applications in pharmaceutical, antimicrobial, anticarcinogenic reagents, industrial and analytical fields [5, 6]. However, morpholine is nitrogen containing heterocyclic compound,

which is present in anticancer and antibiotic drugs such as gefitinib and linezolid [7, 8]. If an -OH group is present in the ring of the azomethine at ortho position, it is observed in many instances that it forms chelate rings which in turn enhances the stability of the complex.

In this work, some di and trivalent metal complexes of 2-((4-morpholinobenzylidene)amino)phenol were studied by the pH metric technique. Also, the quantum-chemical calculations of geometries for metal chelates with the density functional theory method (DFT) using the Gaussian 09 program package have been discussed.

## 2. Experimental

Schiff base ligand of 2-((4-morpholinobenzylidene)amino) phenol (HL) was prepared in ethanol solution by refluxing and stirring equimolar amount of 4-morpholinbenzaldehyde (1 mmol) with o-aminophenol (1 mmol) for 3 hours. The yellow precipitate obtained was filtered, washed with ethanol-water mixture and recrystallized from methanol, the final precipitate dried under vacuum (Figure 1). Di and trivalent metal ion solutions of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and La(III) were prepared in distilled water and determined by EDTA [9].

The sodium hydroxide solution was used as a titrant and standardized against oxalic acid [10]. The following mixtures were prepared and titrated at room temperature against a standard solution of $0.2\,M$ NaOH in a 25 % ethanol-water mixture at ionic strength of $1\,M$ $NaClO_4$. The volume in all solution mixtures was made up to 50 ml with ethanol-water mixture before the titration. The following titrations were carried out: (i) 5 ml of $HClO_4$, (ii) Solution (i) + 5 ml of the ligand under investigation $(1\ \times10^{-3}\,M)$, and (iii) Solution (ii) + 10 ml $(2\ \times10^{-4}\ M)$ of metal ion. The pH measurements were performed with a KF and potentiometric titrator equipped with a combined porolyte electrode. The electrode system and the proton-ligand equilibrium constant of the HL under experimental conditions were determined by Calvin-Bjerrum pH-metric titration method [11-13]. The measurements are usually carried out at a constant ionic strength higher than the metal ion concentration. The calculations were obtained from the data points in each titration using the computer program Miniquad-75 [14-16].
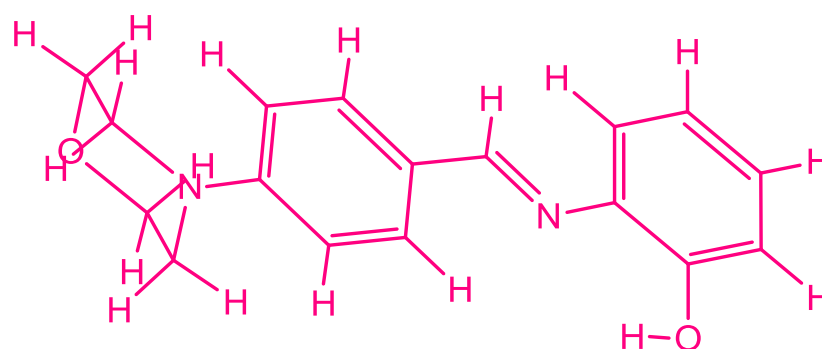


**Fig. 1** Structure of the 2-((4-morpholinobenzylidene)amino)phenol.

# 3. Results and discussion

## 3.1. Acidity constants of the free ligand

The proton-ligand formation ($\overline{n}_A$) of HL at different pH values, was calculated from the titration curves of the acid in the absence and presence of HL (equation 1).

$$\bar{n}_A = Y - \frac{(V_1 - V_2)(N^o + E^o)}{(V^o + V_1)\,TC_L^o} \quad (1)$$

where, Y is the total number of dissociable proton attached to the ligand molecule and equal 1, $V_1$ and $V_2$ are the volume of sodium hydroxide (ml) required to reach the same pH in acid and ligand titration curves, respectively, $N^o$ is the concentration of the alkali, $E^o$ is the initial concentration of free acid, $V^o$ is the initial volume (50 cm$^3$) of the mixtures and $TC_L^o$ is the concentration of ligand in 50 ml solution. The titration curves obtained by plotting the pH values against the volume of NaOH are given in Figures 2–3.
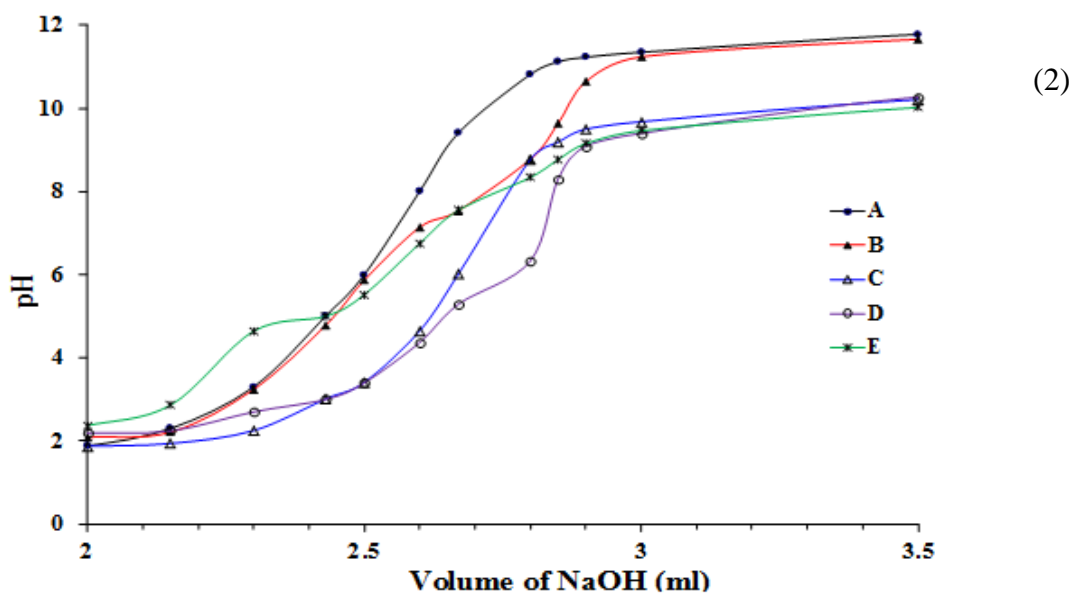
Figures 2–3 show different trends, indicating that the titration curve of ligand solution shift to lower pH value, due to releasing of proton from HL. The magnitude of the horizontal displacement of the curves (C–E) from the free HL curve (B) reveals that the titration curves are going to produce the complexes. It is observed that Mn(II) complex (curve C) begin to form at the higher pH value (2.92) than Co(II) complex (curve E) (2.83). The complexes are quite stable up pH = 10. In the present study the HL is monoprotic ligand and has a phenolic group, so it can donate a proton and became anion. The value of pK$_{OH}$ is found to be 10.36 due to the deprotonation of the phenolic group, it is clear that the HL is of lower acidic character [17, 18].

## 3.2. Stability constants of binary metal complexes

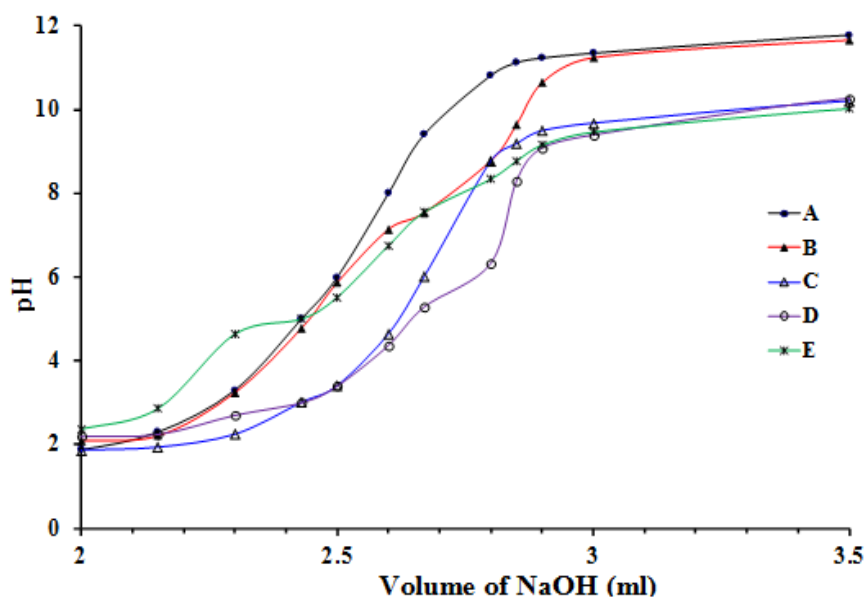The formation functions $\overline{n}$ and pL can be computed from equations 2, 3.



$$(2)$$

**Fig. 2** Titration curves of HL with different metal ions at 25 ℃ in I = 1 M NaClO$_4$ (25 % (v/v) ethanol-water mixture). (A): HClO$_4$, (B): A + HL, (C): B + Mn(II) ion, (D): B + Fe(III) ion and (E): B + Co(II) ion.

**Fig. 3** Titration curve of HL with different metal ions at 25 ℃ in 1 M NaClO$_4$ (25 % (v/v) ethanol-water mixture). (A): HClO$_4$, (B): A + HL, (C): B + Ni(II) ion, (D): B + Cu(II) ion and (E): B + La(III) ion.

$$\bar{n} = \frac{(V_3 - V_2)(N^O + E^O)}{(V^O + V_2)\ \bar{n}_A\ TC_M^O} \tag{2}$$

$$pL = log_{10} \frac{\sum_{n=0}^{n=i} \beta_n^H \left(\frac{1}{antilog\,pH}\right)^n}{TC_L^O - \bar{n}\ TC_M^O} \cdot \frac{V^O + V_3}{V^O} \tag{3}$$

where, $V_3$ is the volume (ml) of alkali employed to reach the same pH value, $TC_M^O$ is the total concentration of metal ions present in the solution and $\beta_n^H$ is the overall stability constant.

The pH- metric titrations were carried out in a restricted range of pH values from 2 to 11, since the solutions became cloudy at higher pH values, probably due to the formation of sparingly soluble polymeric complexes or hydroxo-species [19, 20]. Also, the calculations were restricted to data obtained before the precipitation. The $\bar{n}$ and p[L] values were calculated at different points in the pH-metric range (Figure 4). The stoichiometry of the binary complexes proved that the form 1:l, 1:2 and 1:3 (metal:ligand) binary complexes. The formation curves of the obtained chelates show that, the maximum value of $\bar{n}$ was around 3 indicating the formation of 1:1, 1:2 and 1:3 (metal:ligand) type of some species. These species are M–L, M–L$_2$ and M–L$_3$ types and based on the three inflections after the addition of one, two and three moles of NaOH per 1 M of ligand [21].

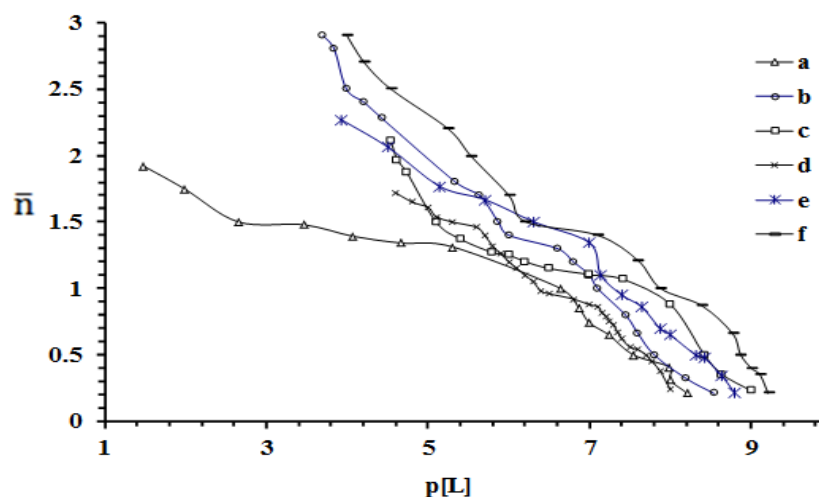**Fig. 4** Formation curves of metal ions complexes with HL, (a) Mn(II)–HL (b) Fe(III)–HL, (c) Co(II)–HL, (d) Ni(II)–HL, (e) Cu(II)–HL and (f) La(III)–HL systems.

**Table 1:** The proton-ligand and stability constants of the metal-ligand complexes

| $pK^H$ | $\log K_i$ | Mn(II) | Fe(III) | Co(II) | Ni(II) | Cu(II) | La(III) |
|--------|-----------|--------|---------|--------|--------|--------|---------|
| 10.36 | $\log K_1$ | 7.54 | 7.80 | 8.42 | 7.71 | 8.30 | 8.87 |
| | $\log K_2$ | 2.65 | 5.87 | 5.10 | 5.32 | 6.13 | 6.22 |
| | $\log K_3$ | - | 3.99 | - | - | - | 4.54 |
| | $\log \beta$ | 10.19 | 17.66 | 13.52 | 13.03 | 14.43 | 19.63 |

The concentration of the metal ion solution was $2 \times 10^{-4}$ M, hence there was no precipitation or polynuclear complexes [22]. The decrease in pH values for the metal titration curves relative to ligand titration curve points to the formation of strong metal complexes [23]. The overall formation constants (equation 4) are compared using standard procedures based on the calculation of the average number of ligand bound per metal ion [24, 25].

$$(\log \beta = \log K_{ML}^M + \log K_{ML_2}^M + \log K_{ML_3}^M) \quad (4)$$

In the following Table 1, the dissociation constants ($pK_a$) of the HL as well as the stability constants ($\log K_i$) of the metal ion complexes have been listed. The stability constants of metal-ligand complexes were very close to those already published after allowing for

changes in experimental works and conditions [26, 27]. The properties of the studied central metal ions and the stability constants of their complexes were discussed in an effort to give information about the nature of chemical bonding in complexes and make possible the calculation of the stability constants. The stability constants of 1:2 ratio (metal-ligand) complexes are lower than those of the corresponding 1:1 ratio compounds, as expected from statistical considerations [28]. The formation constants of the obtained complexes of HL are arranged as follows: La(III) > Fe(III) > Cu(II) > Co(II) > Ni(II) > Mn(II). The order of stability constants of 1:1, and 1:2 metal-ligand complexes are in the expected

Irving-Williams arrangement [29]. This arrangement largely reflects the changes in the heat of complex formation across the some influence of the crystal-field stabilization energies and the polarizing abilities of the metal ion [30, 31]. Also, the Fe(III) and La(III) metal ions are a hard Lewis acids with a high charge and the presence of negatively charged O,N donor atoms in both azomethine and phenol groups producing thermodynamically stable complexes with Fe(III) and La(III) [32]. Good linear relationships exist for these data which demonstrate that metal ion affinity for a particular chelate increases with increasing metal ion charge [33, 34]. The obtained results agree with the progressive coordination of a bidentate ligand of HL through the O,N atoms, until the formation of the octahedral complexes $FeL_3$ and $LaL_3$. This can be illustrated further by the lowest energy structures obtained from the semi-empirical calculations: the $\Lambda$ and $\Delta$ structures are characterized by the same lowest energy values and are in very good agreement

with the X-ray results reported by Charalambous [35], who found both forms in the crystal lattice. This gives confidence on the use of semi-empirical calculations in defining the chemical structures corresponding to the complex models found from solution equilibrium studies.

### 3.3. Distribution diagrams

The degree of formation of each species involved in the complexation reaction has been calculated using the HYSS computer program [36]. Following a procedure similar to that presented for ligand speciation and distribution diagrams can be developed for species involved in the complexes. The concentration distribution diagrams of the protonated ligand in 25 % ethanol-water mixture and ionic strength 1 M $NaClO_4$ is shown in Figure 5. In acidic solution (pH < 9), HL initially exists in the fully protonated form as HL. On raising the pH, the species (HL) lose its proton to give the full deprotonated species (L$^-$), which is the predominant species at pH > 10.5.
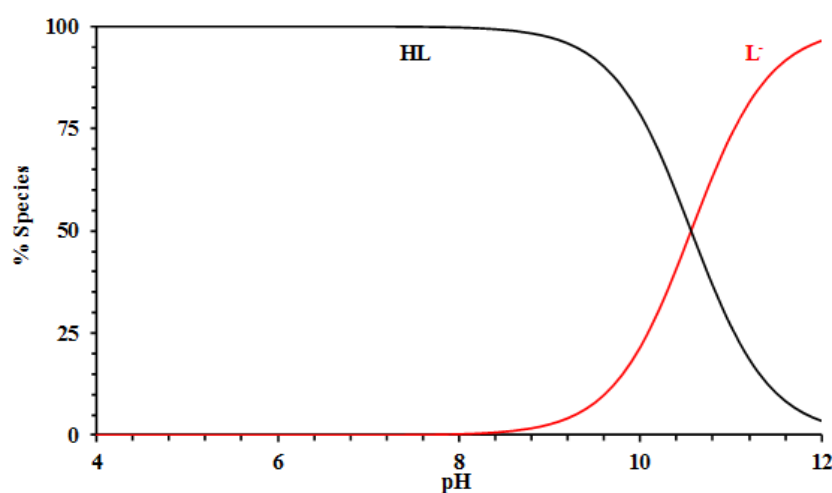


**Fig. 5** Representative concentration distribution curves as pH values of the HL ligand ($C_{HL}$ = 0.001 M).

The MnL$^+$ system starts to form at pH value 1.20, reaching a maximum concentration (98.75 %) in the pH range 1.20–9.40 (Figure 6). On the other hand, MnL$_2$ system concentration was found to increase with increasing the pH and becomes predominant (98.6 %) at pH 9.65. In Figur 7, the distribution diagram of the Fe(III)–HL system is shown the deprotonated complex FeL$^{+2}$ in an acidic medium and its concentration reaches the maximum percentage 81.10 % (pH 5.0). The complex species FeL$_2$$^+$ starts to from pH 4.22 and reaches its maximum percentage 82.2 %. Whereas, the deprotonated complex species FeL$_3$

starts to form at pH 6.22 and reaches its maximum percentage 97.5 %.In the pH range 3.25–10.25, reaching a maximum concentration of the CoL$^+$ system is 95.8 % (Figure 8). The hydrolyzed species CoL$_2$ has been formed above pH 6.10 and has 97.4 % relative concentration at pH 9.89. The deprotonated complex NiL$^+$ formed in the acidic medium and its concentration reaches the maximum percentage 88.5 % at pH 6.60. Whereas, the complex species NiL$_2$ starts to form at pH 6.15 and reaches its maximum percentage 98.2 % (Figure 9).
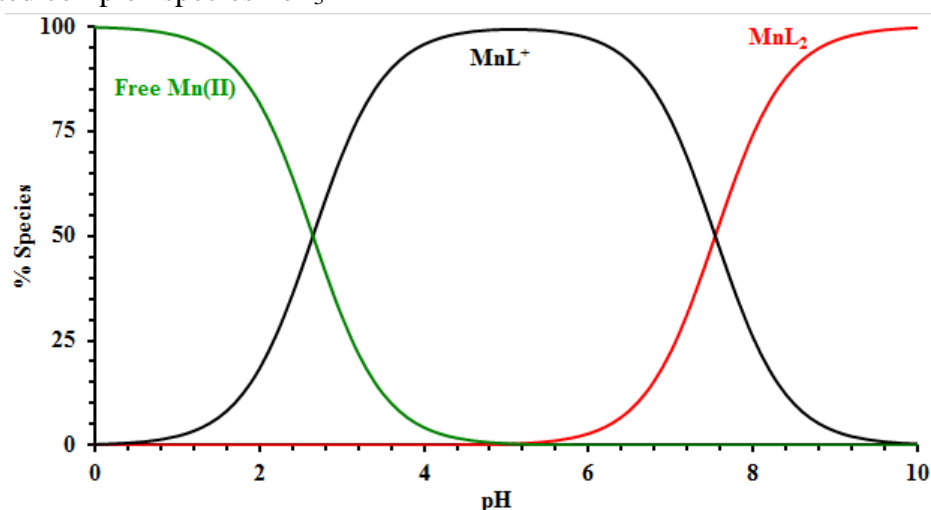


**Fig. 6** Species distribution curves as a function of *pH* calculated for Mn(II)-HL system.
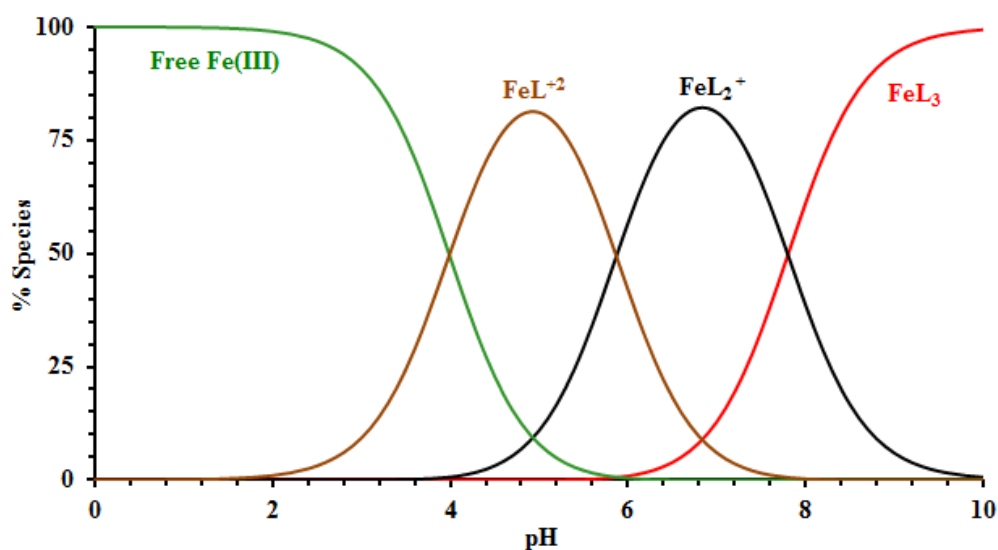


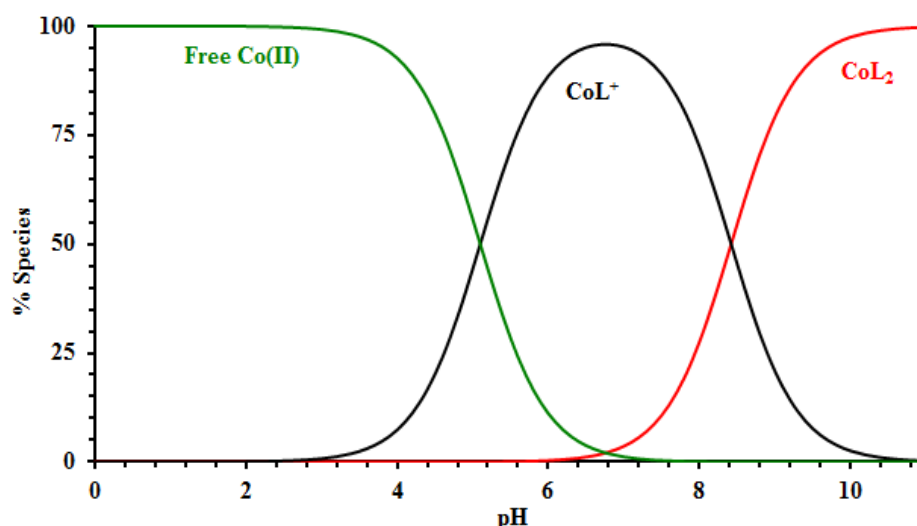**Fig. 7** Species distribution curves as a function of pH calculated for Fe(III)–HL system.

**Fig. 8** Species distribution curves as a function of pH calculated for Co(II)–HL system.
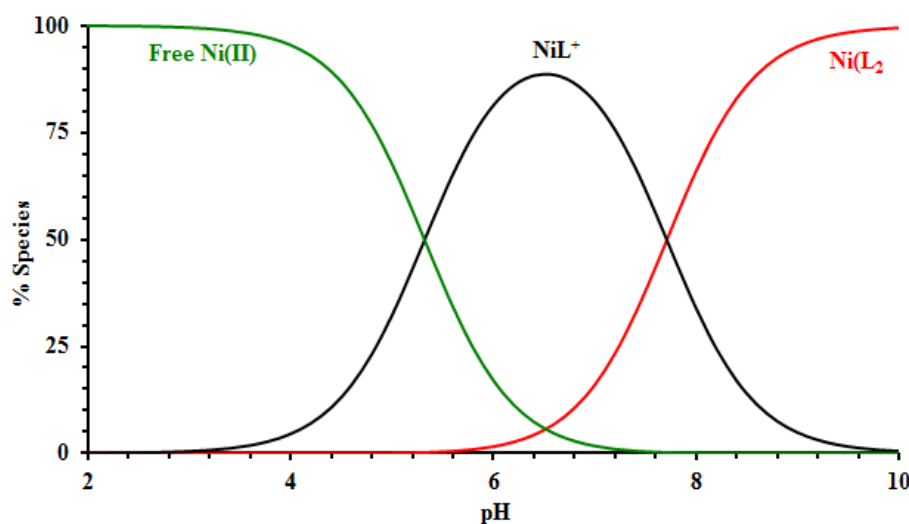


**Fig. 9** Species distribution curves as a function of pH calculated for Ni(II)-HL system.

The distribution curves of the Cu(II)−HL system calculated on the basis of the pH-metric results (Figure 10). The hydrolyzed species $CuL^+$ has been formed above pH 4.10 and has 95.9 % relative concentration at pH 7.25 and $CuL_2$ shows the predominance at pH 9.85 with 97.5 %. The $LaL^{+2}$ system starts to form at pH value 2.28, reaching a maximum concentration (77.6 %) in the pH range 2.28–7.90 (Figure 11). On the other hand, $LaL_2^+$ system concentration was found to increase with increasing the pH and becomes predominant (91.3 %) at pH 7.65, whereas, the deprotonated complex species $LaL_3$ starts to form at pH 7.25 and reaches its maximum percentage 98.2 %.
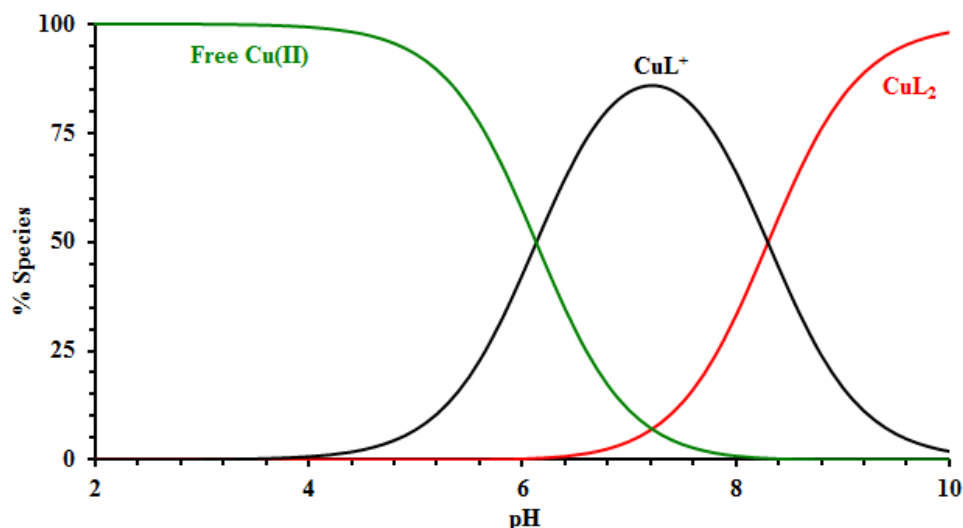
**Fig. 10** Species distribution curves as a function of pH calculated for Cu(II)-HL system.
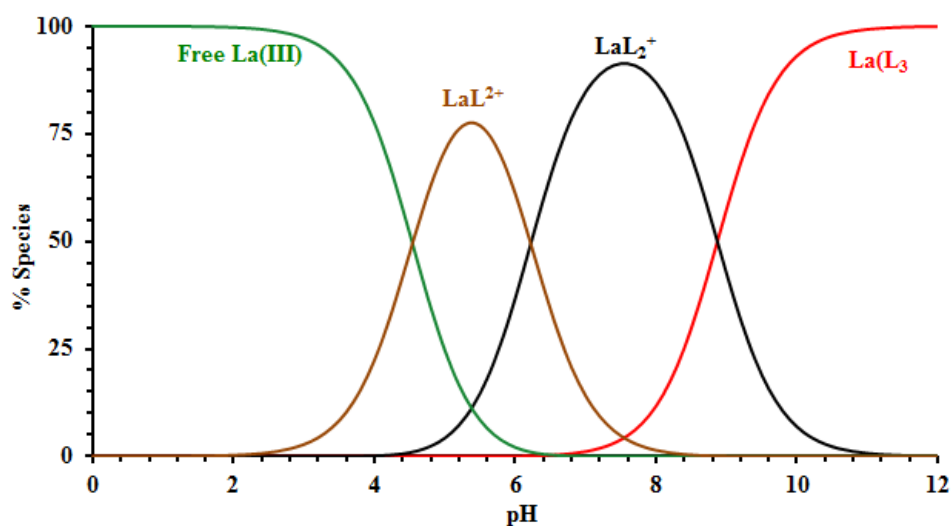


**Fig. 11** Species distribution curves as a function of pH calculated for La(III)-HL system.

### 3.4. Quantum chemical calculation

Quantum chemical calculations were utilized to find the geometrically optimized structures of these complexes. Optimization of geometries was done with the density functional theory method (DFT) using the Gaussian 09 program package as DFT methods are very effective in modeling compounds [37, 38]. The DFT method was treated according to hybrid Becke's three parameters and the Lee–Yang–Parr function (B3LYP) level of theory using 6311++G(d,p), LanL2MB basis set. Gauss view 5 and Chemdraw version 15 are used to draw the structures, the most popular density functional method [39, 40]. Some parameters of quantum calculation such as $E_{Homo}$, $E_{Lumo}$, energy gap ($E_g$), ionization potential (I) and electron affinity (A) are given in the following relations (4-6):

$$A = - E_{Lumo} \tag{4}$$

$$I = - E_{Homo} \tag{5}$$

$$E_g = E_{Lumo} - E_{Homo} \tag{6}$$

These data give a good correlation between the experimental and theoretical calculation where, the sequence of stability of metal complexes 1:1 arranged as La(III) > Co(II) > Cu(II) > Ni(II) > Fe(III) > Mn(II) as a result of values of energy gap between $E_{Homo}$ and $E_{Lumo}$ (Table 2). The La(III)-complex has an energy gap higher than the other metal complexes. A low value of the energy bond gab ΔE of Mn(II)-complex gives more activity (less stable), because the energy to remove an electron from the last occupied orbital will be low [41]. On the other hand, for complexes 1:2 for the same metals the sequence of stability arranged as Co(II) > Fe(III) > La(III) > Mn(II) > Cu(II) > Ni(II), while in complexes 1:3 the stability arranged as La(III) > Fe(III) according to values of the energy gap. The molecular properties of optimized geometrical of some metal complexes 1:1, 1:2 and 1:3 ratios are shown in Figures 12-14.

**Table 2:** The molecular properties of metal-HL complexes 1:1, 1:2 and 1:3 ratios calculated with DFT (B3LYP) level of theory using standard basis 6-311++G(d,p)

| Complex (M:L) | Metal ion | $E_{Homo}$ (ev) | $E_{Lumo}$ (ev) | Energy gap (ev) | Ionization potential | Electron affinity |
|---|---|---|---|---|---|---|
| 1:1 | Mn(II) | - 0.25736 | - 0.25621 | 0.00115 | 0.25736 | 0.25621 |
|  | Fe(III) | - 0.25554 | - 0.24360 | 0.01194 | 0.25554 | 0.24360 |
|  | Co(II) | - 0.27366 | - 0.24490 | 0.02876 | 0.27366 | 0.24490 |
|  | Ni(II) | - 0.25540 | - 0.24062 | 0.01478 | 0.25540 | 0.24062 |
|  | Cu(II) | - 0.20408 | - 0.18921 | 0.01487 | 0.20408 | 0.18921 |
|  | La(III) | - 0.26247 | - 0.19087 | 0.07160 | 0.26247 | 0.19087 |
| 1:2 | Mn(II) | - 0.26608 | - 0.25778 | 0.00830 | 0.26608 | 0.25778 |
|  | Fe(III) | - 0.25606 | - 0.22903 | 0.02703 | 0.25606 | 0.22903 |
|  | Co(II) | - 0.25992 | - 0.23089 | 0.02903 | 0.25992 | 0.23089 |
|  | Ni(II) | - 0.24104 | - 0.23927 | 0.00177 | 0.24104 | 0.23927 |
|  | Cu(II) | - 0.22213 | - 0.21671 | 0.00542 | 0.22213 | 0.21671 |
|  | La(III) | - 0.25524 | - 0.24490 | 0.01034 | 0.25524 | 0.24490 |
| 1:3 | Fe(III) | - 0.18654 | - 0.17801 | 0.00853 | 0.18654 | 0.17801 |
|  | La(III) | - 0.24189 | - 0.23163 | 0.01026 | 0.24189 | 0.23163 |
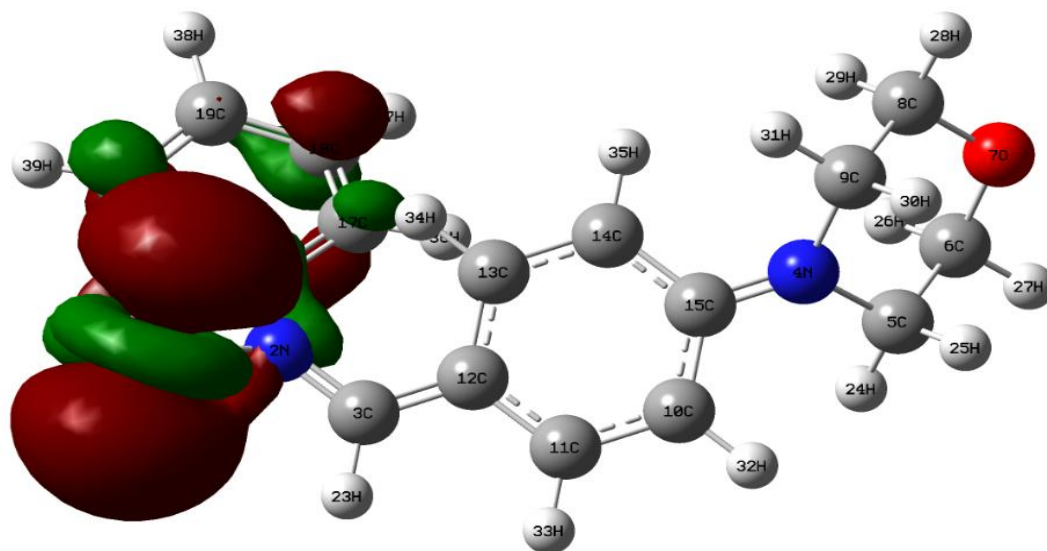
A ($E_{Homo}$)
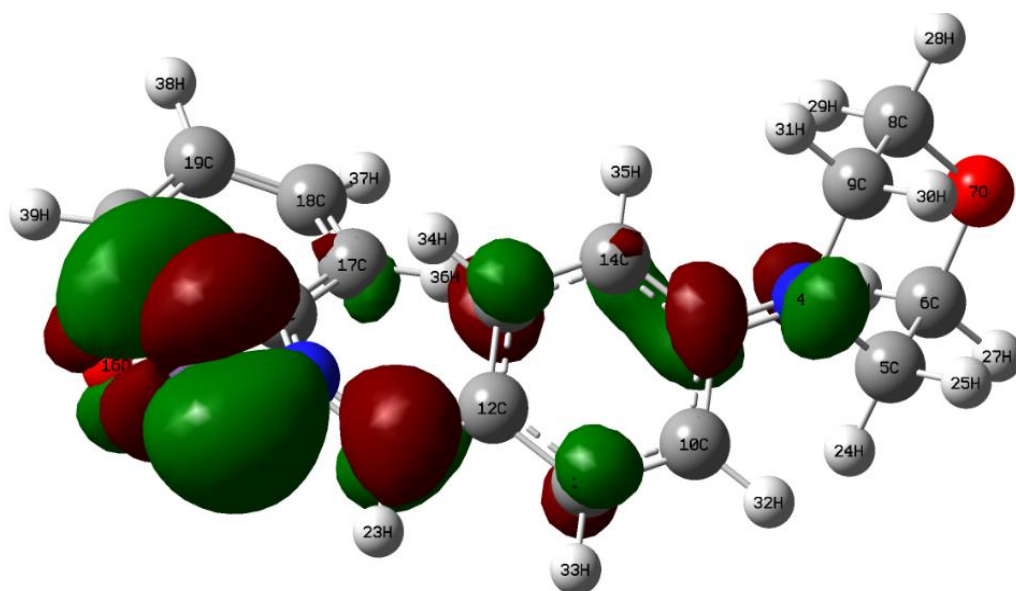
B ($E_{Lumo}$)

**Fig. 12** Molecular properties of Mn(II)-HL system (1:1), A (Homo) and B (Lumo).
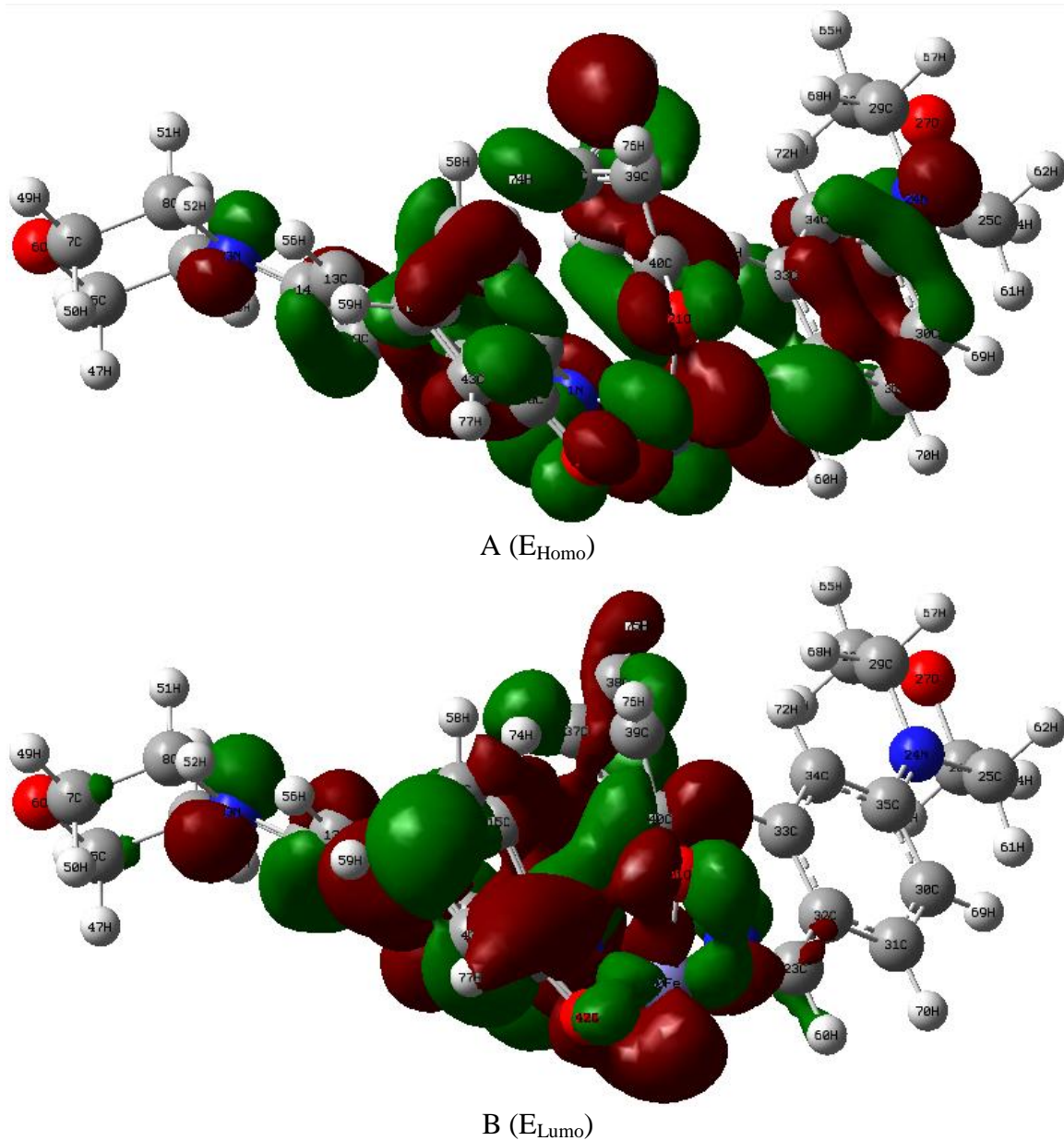
A (E$_{Homo}$)



B (E$_{Lumo}$)

**Fig. 13** Molecular properties of Fe(III)-HL system (1:2), A (Homo) and B (Lumo).
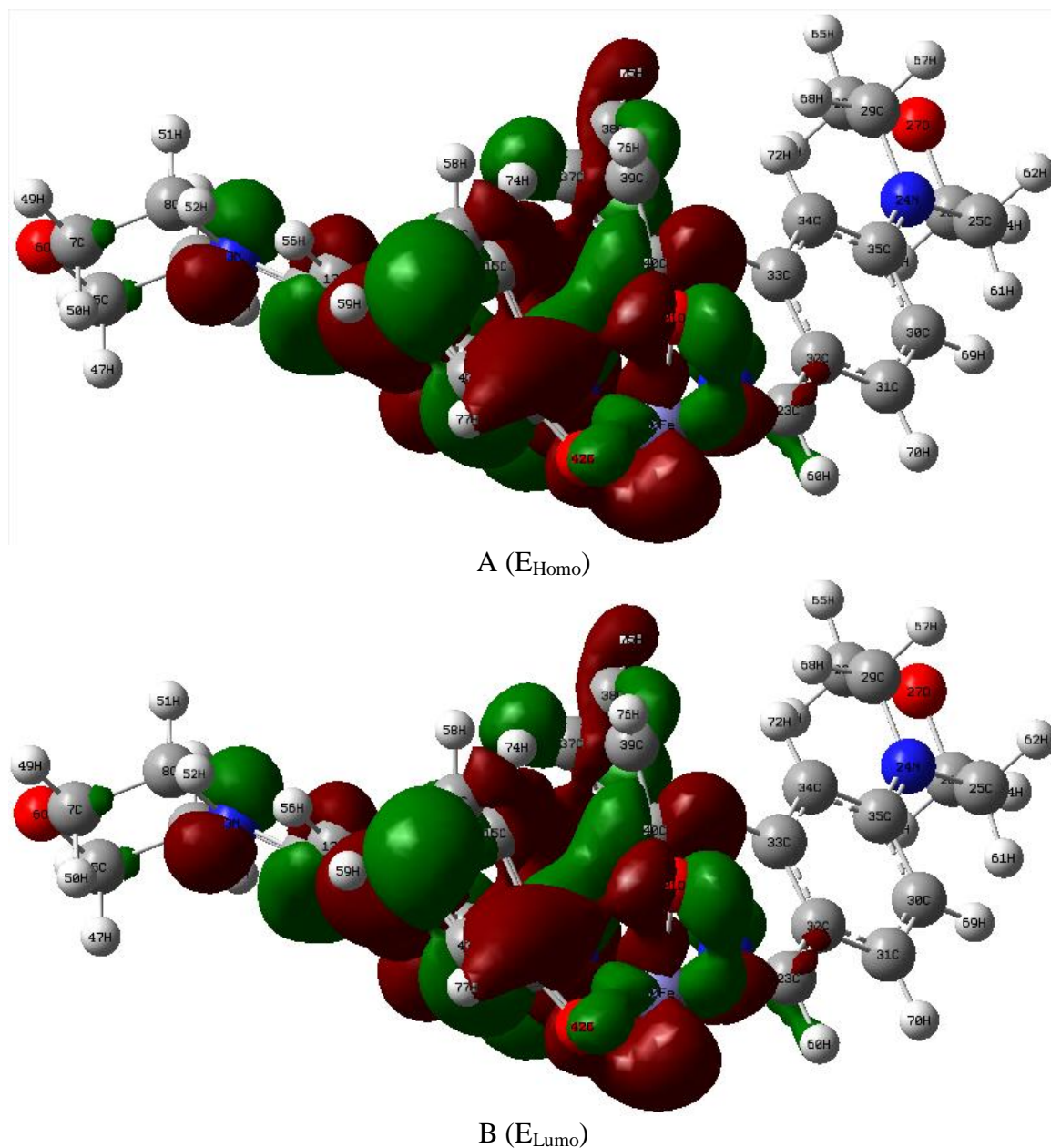
A ($E_{Homo}$)



B ($E_{Lumo}$)

**Fig. 14** Molecular properties of La(III)-HL system (1:3), A (Homo) and B (Lumo).

## 4. Conclusion

The formation constant values of the obtained complexes were very different, indicating no simultaneous metal ion chelates formation with ligand occurring . The average number of metal ion associated with the ligand ( $\overline{n}$ ) was 3, indicating that 1:1, 1:2 and 1:3 metal-ligand complexes were formed. The solution of metal ions was $2 \times 10^{-4}$ M to

avoid the possibility of hydrolysis or formation of dimer complexes. The order of stability constants of the complexes was founded to be La (III) > Fe(III) > Cu(II) > Co(II) > Ni(II) > Mn(II). The stability of Fe(III) and La(III) with the ligand under study was high because Fe(III) and La(III) are hard Lewis acids with a high oxidation number. Also, the presence of negatively charged O,N donor atoms in

both azomethine and phenol groups plays a major role in producing thermodynamically stable complexes with Fe(III) and La(III). Quantum chemical calculation gives a good correlation between the theoretical and experimental calculation. In this work, the sequence of stability of the formation complexes 1:1 ratio can be arranged as La(III) > Co(II) > Cu(II) > Ni(II) > Fe(III) > Mn(II) according to the values of energy gap between $E_{Homo}$ and $E_{Lumo}$. While, the complexes of 1:2 ratio for the same metals have a sequence of stability arranged as Co(II) > Fe(III) > La(III) > Mn(II) > Cu(II) > Ni(II), and for the complexes of 1:3 ratio the stability is arranged as La(III) > Fe(III).

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