

## Metal Complexes of Multidentate Schiff Base-Azo Ligand: Synthesis, Characterization and Biological Activity

Abbas Ali Salih Al-Hamdani \*

### ABSTRACT

A series of transition metal complexes have been synthesized from the new Schiff base-azo ligand ( $H_2L$ ) derived from 4-(2-Amino-4-hydroxy-phenylazo)-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-5-one and *o*-phenylene diamine. The structural features have been confirmed from their elemental analyses, metal content, magnetic moment measurement, molar conductance, FT-IR, UV-Vis and NMR spectral studies. The data show that the complexes have the composition of  $[MH_2L]$  type and octahedral geometry, with  $M=Zn(II)$ ,  $Cu(II)$ ,  $Ni(II)$  and  $Co(II)$ .

Structural geometries of compounds were also suggested in gas phase by using theoretical treatments, using HyperChem-6 program for the molecular mechanics and semi-empirical calculations for  $\Delta H_f^\circ$  and  $\Delta E_b$  at 298 K. Biological evaluations of considerable number of these compounds were done using organisms *Escherichia coli* and *Staphylococcus aureus*.

**Keywords:** 4-Aminoantipyrine, Schiff Base-Azo, Biological Activity, Structural Studies.

### INTRODUCTION

In recent years, a considerable amount of work has been done on the coordination chemistry of metal ion (II) complexes with Schiff base ligands to model the physical and chemical behavior of biological copper systems. Schiff bases of 4-aminoantipyrine and its complexes have a variety of applications in biological, clinical, analytical and pharmacological areas (Hitoshi *et al.*, 1997, Raman *et al.*, 2007). Studies of new kinds of chemotherapeutic Schiff bases are now attracting the attention of biochemist (Choi *et al.*, 1995, Katia *et al.*, 1996) The coordinating properties of 4-aminoantipyrine have been modified to give a flexible ligand system, formed by condensation with a variety of reagents like aldehydes, ketones, thiosemicarbazides and carbazides etc (Dharmaraj *et al.*, 2001, Agarwal *et al.*, 1997, Singh *et al.*, 1999, Kriza *et al.*, 2000, Raman *et al.*, 2002). Schiff bases derived from the 4-aminoantipyrine are well known as polydentate ligands coordinating in neutral forms. The interaction of these donor ligands and metal ions give

complexes of different geometries and these complexes are potentially biologically active (Mathew *et al.*, 2005, Harikumaran *et al.*, 2009, Mohanan *et al.*, 2009, Zhao *et al.*, 2007, Zhang *et al.*, 2002, Chandra *et al.*, 2009, Agarwal *et al.*, 2006). Azo compounds are very important class of chemical compounds receiving attention in scientific research.

Azo dyes derived from the 4-aminoantipyrine are well known as polydentate ligand and complexation with metal ions give different geometries and many uses (Raman *et al.*, 2009, El-Saied *et al.*, 1993, Shosho *et al.*, 2008). A new method for the synthesis of azo Schiff base ligand in which the azo and azomethine groups are coordination sites was developed through a Schiff base precursor (Abdelhamid *et al.*, 2010).

### Experimental

The following chemicals were commercially available products of analytical reagent grade. 4-Aminoantipyrine, *o*-phenylenediamine, 3-amino phenol, DMF (Dimethyl formamide), DMSO (dimethyl sulfoxide), ethanol,  $K_2CO_3$ , HCl, NaOH,  $NaNO_2$  were obtained from Fluka and Riedel-de Haen).  $ZnCl_2$ ,  $CoCl_2 \cdot 6H_2O$ ,  $NiCl_2 \cdot 6H_2O$  and  $CuCl_2 \cdot 2H_2O$  from (BDH). (FT-IR) the spectra were recorded in the range (4000-200)  $cm^{-1}$  on a Shimadzu

\* Department of Chemistry, College of Science for girls, University of Baghdad. Baghdad- Iraq. Received on 27/9/2010 and Accepted for Publication on 26/2/2012.

3800, spectrometer, using CsI Pellets. Electronic absorption spectra were recorded in the range (200-1100) nm on a Shimadzu 160 Spectrophotometer, in freshly prepared  $10^{-3}$  M solutions in (DMF) at room temperature using quartz cell (1.000) cm. The metal contents of the complexes were determined using a Shimadzu A.A680G atomic absorption Spectrometer. Molar conductivity measurements of the complexes at 25°C in freshly prepared  $10^{-3}$  M solutions in DMF were determined using a PW9526 Digital Conductivity meter. The chlorine content was determined gravimetrically (Skoog *et al.*, 1969). Magnetic properties were using (Balance magnetic susceptibility model MSR-MKi).  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR spectra were recorded using Bruker 400 MHz spectrometer and elemental (C, H and N) analyses were carried out on a Perkin-Elmer automatic equipment model 240.B. The melting points of the prepared complexes were measured using Gallen Kamp .

#### **Synthesis of the 4-(2-Amino-4-hydroxy-phenylazo)-1, 5-dimethyl-2-phenyl-1, 2-dihydro-pyrazol-3-one (I)**

A 250 mL beaker, equipped with a magnetic stirring bar, contain a mixture of HCl (37%, 2 mL), ethanol (10 mL) and (10 mL) of distilled water, was charged with 4-amino-2,3-dimethyl-1-phenyl-3-pyrozoline-5-one ( 0.203 g, 1mmol). 8 mL of aqueous  $\text{NaNO}_2$  (0.069 g, 1mmol) was added drop-wise while maintaining the temperature between 0—5 °C. The diazonium chloride formed was added drop wise with stirring to cold ethanolic solution of 3-amino phenol (0.11 g, 1 mmol), and then (25 mL) solution of 1M NaOH was added to the dark colored mixture. The mixture was stirred for 1 h at 0 °C and acidified with 1 mL of conc. HCl. The brown product formed was suction filtered and recrystallized from ethanol-water and dried.

#### **Synthesis of the Ligand :4,4'-(3Z,3'Z)-3,3'-(phenyl-1,2-diylbis(azan-1-yl-1-ylidene)) bis(1,5-dimethyl-2-phenyl-2, 3-dihydro-1H-pyrazole-yl-3-ylidene) bis(diazene-2,1-diyl) bis (3-aminophenol) ( $\text{H}_2\text{L}$ )**

To a mixture of 4-(2-amino-4-hydroxy-phenylazo)-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-one (3.23 g, 10 mmol) in absolute ethanol (25 mL) containing 5 drops of glacial acetic acid, was added a solution of phenyl-1,2-diamine ( 0.3 g, 5 mmol) in ethanol (15 mL). The reaction mixture was heated on water bath at (40-50 °C) for 40 h. in presence of  $\text{K}_2\text{CO}_3$  after the addition of excess of Ethanol

(50 mL). A brown solid was formed, and then recrystallised from methanol. The product was dried over anhydrous  $\text{CaCl}_2$  in vacuum. Yield is 55%, mp 175 °C.

#### **Syntheses of Complexes**

A solution of the Schiff base-azo ligand (1 mmol) in ethanol (20 mL) was allowed to stir for 30 min. An ethanolic solution (15 mL) of the metal salt (1 mmol) (metal salts are hydrated chlorides except zinc as the anhydrous chloride) was then added dropwise. The resulting mixture was refluxed under  $\text{N}_2$  for 6 h, resulting in the formation of a solid mass which was washed several times with hot ethanol and dried under vacuum. Elemental analysis data, colours, and yields for the complexes are given in Table 1.

#### **Mole Ratio Method**

The absorption spectra were measured for many mixed solutions containing (1mL ) of the metal ion salt, in the optimum concentration, and variable volumes of the ligand solution in the same concentration. M:L ratio was obtained by plotting the relation between the mole ratio in the X-axis and absorbance in the Y-axis. The intercept of the two straight lines represent the M:L ratio the (1:1).

#### **Programs used in theoretical calculations**

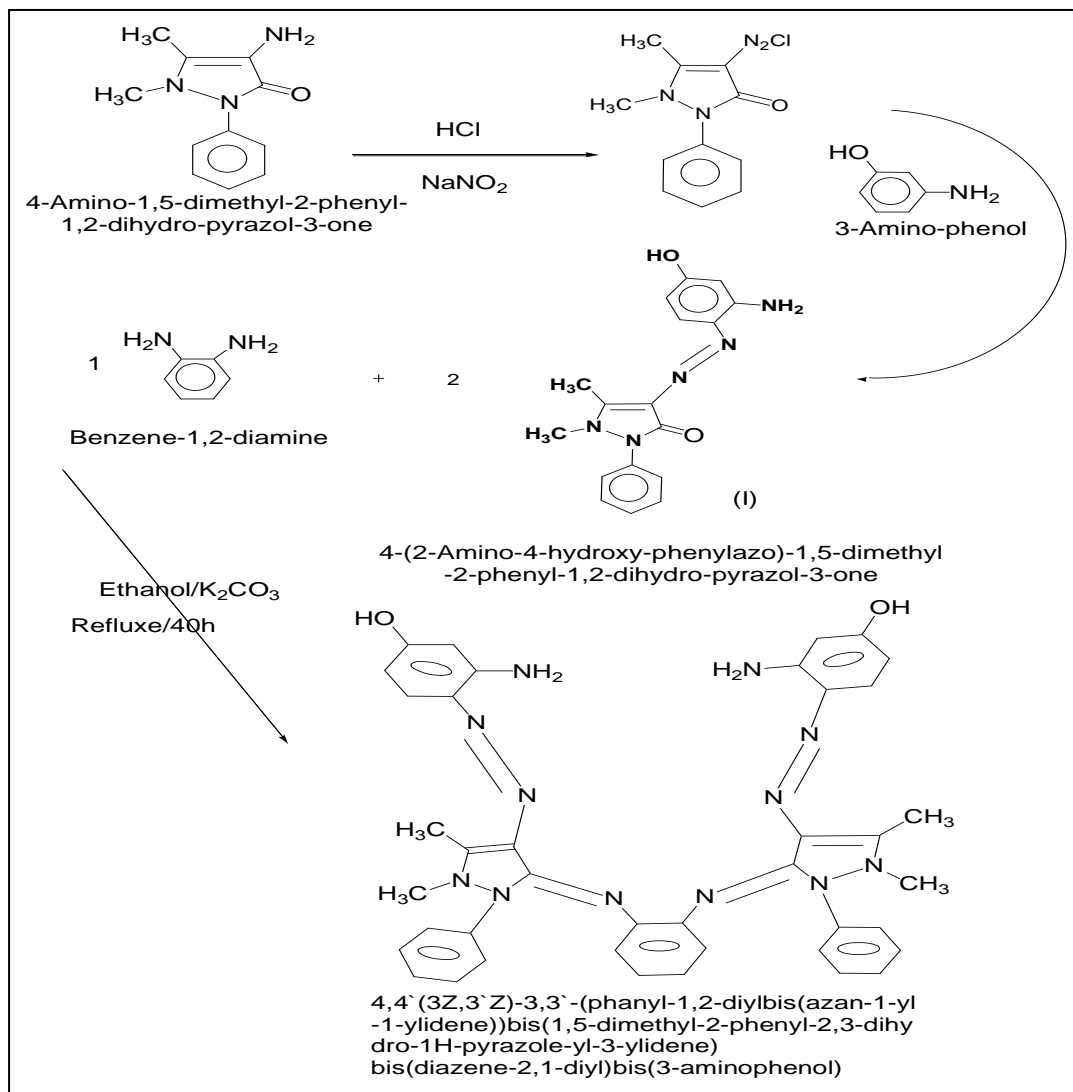
Hyper Chem-6 program is a sophisticated molecular modeler, editor and powerful computational package, that is known for its quality, flexibility and ease of use. Uniting 3D visualization and animation with quantum chemical calculations, molecular mechanics and dynamic (Dorestt, 1996). In the present work, parameterization method 3(PM3) was used for the calculation of heat of formation and binding energy for all metal complexes. PM3 is more popular than other semi-empirical methods due to the availability of algorithms and more accurate than with other methods (Foresman *et al.*, 1996). PM3/TM is an extension of the PM3 method to include orbital's for use with transition metals. It has parameterized primarily for organic molecules and selected transition metals.

#### **Bacteriological Activity**

Two pathogenic microbials were used to test the antimicrobial activity of the ligand and their metal complexes; they were *Escherichia coli* and *staphylococcus aureus*. The nutrient agar medium was prepared and a

quantity of 10 mL of the medium was poured into the sterilized petri plates and allowed to solidify (Majdan *et al.*, 1996). The plates were inoculated with spore suspensions of pathogenic bactericides. By using the sterilized cork, borer, wells were dug in the center of the culture plates. The test

complex solution in DMSO was added (0.5 mL) to these wells, and the plates were incubated at 25°C for 24h. Then the inhibition zone appeared around the wells in each plate was measured and recorded as the cytotoxic effect of the appropriate complexes.



Scheme 1. Preparation of the ligand (H<sub>2</sub>L)

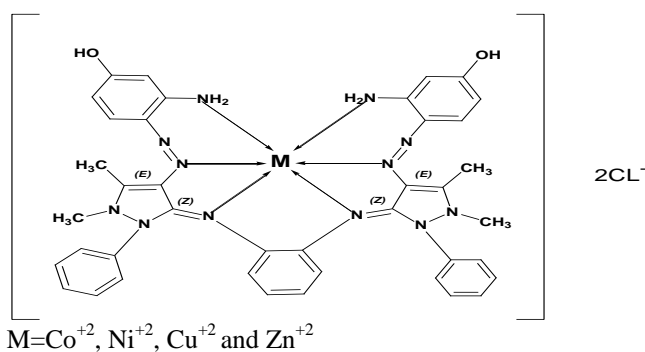


Figure 1. Proposed structure of the ligand H<sub>2</sub>L complexes

## RESULTS AND DISCUSSION

### Physico-chemical characterizations and geometrical configuration of the complexes:

Metal (II) salts react with Schiff base ligand in 1:1 molar ratio in alcoholic medium. The ligand and its complexes are stable at room temperature and are non hygroscopic. The ligand is soluble in common polar organic solvents, such as ethanol, methanol, and chloroform but partially soluble in hexane. The Schiff base complexes are relatively soluble in DMF and

DMSO. The synthesized ligand and its complexes were characterized by elemental analysis (C, H, N, M and Cl) in good agreement with their formulation as in (Table 1). The composition of the complexes formed in solution has been established by mole ratio. In both cases the results reveal (1:1) metal to ligand ratio. The geometry of the newly synthesized compounds has been elucidated based on their elemental analysis, molar conductivity and spectral data.

**Table 1. Physical characteristics and analytical data for (H<sub>2</sub>L) and its metal complexes**

Mol. Formula Mol. Weight	Color	Yield %	M.p. (°C)	C%	H%	N%	M%	Cl%
				Calcd	Calcd	Calcd	Calcd	Calcd
				C%	H%	N%	M%	Cl%
				Expt	Expt	Expt	Expt	Expt
(C <sub>17</sub> H <sub>17</sub> N <sub>5</sub> O <sub>2</sub> ) I=323.35	Brown	67	175	63.15	5.30	21.66	-	-
				63.01	5.88	21.05	-	-
(C <sub>40</sub> H <sub>38</sub> N <sub>12</sub> O <sub>2</sub> ) H <sub>2</sub> L=718.81	Brown	55	210	66.584	5.33	23.38	-	-
				66.65	6.12	22.34		
[CoH <sub>2</sub> L]2CL =848.6	Red	66	>360	56.56	4.47	19.79	6.94	8.35
				55.89	5.90	20.32	7.08	8.12
[NiH <sub>2</sub> L]2CL =848.4	Green	81	>360	56.57	4.47	19.80	6.91	8.35
				56.07	5.55	18.87	7.77	7.81
[CuH <sub>2</sub> L]2CL =853.25	Black	64	>360	56.25	4.45	19.68	7.44	8.30
				55.94	5.06	18.85	6.66	7.65
[ZnH <sub>2</sub> L]2CL =855.1	Pale Brown	58	>360	56.13	4.44	19.64	7.64	8.29
				56.66	5.65	21.01	7.62	7.99

### FT-IR Spectra of the free Ligand and complexes

The IR spectrum of the ligand shows characteristic bands at 3406, 1635, 1562 and 1034 cm<sup>-1</sup> due to the ν(O-H), ν(C=N), ν(N=N) and ν(N-N) functional groups, respectively (Raman *et al.*, 2009; Chandra *et al.*, 2009). The IR spectra of the complexes exhibited ligand bands with the appropriate shifts due to complex formation (Table 2). The ν(C=N) and ν(N=N) at 1635 and 1562 cm<sup>-1</sup> in the free ligand shift to as shown in 1601–1619 and 1519–1534 cm<sup>-1</sup>, respectively, for the complexes. The reduction in bond order, upon complexation, can be attributed to delocalization of metal electron density (*t<sub>2g</sub>*) to the π-system of the ligand. These shifts confirm the coordination of the ligand *via* the nitrogens of azomethine and the azo groups to metal ions. The ν(N-H) band at 3400–3350 cm<sup>-1</sup> in the free ligand was shifted to lower frequency and by ca. 12 cm<sup>-1</sup> for the complexes, confirm

the involvement of the amine group in complexation. At lower frequency the complexes exhibited bands around 412–471 cm<sup>-1</sup> assigned to the ν(M-N) (Abbas *et al.*, 2009; Nakamoto, 1997).

### Magnetic Moments and Electronic Spectra

The electronic spectrum of the Schiff base ligand exhibits intense absorption at [(37174.7 and 31250) and (27027)] cm<sup>-1</sup> attributed to π → π\* and n → π\*, respectively. The magnetic moment value 4.22 B.M of Co(II) complex is typical for a distorted octahedral geometry (Lever, 2003). The electronic spectrum for this complex showed two broad peaks at 15384.6 and 19607.8 cm<sup>-1</sup>, assigned to <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>A<sub>2g</sub>(ν<sub>2</sub>) and <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(P)(ν<sub>3</sub>) transition, respectively. The Ni(II) complex exhibits peaks at [(18484.2 and 17391.3) and (16000 and 14430)] cm<sup>-1</sup> which assign to <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub>(P) and <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub>(F)

transition, respectively suggesting an octahedral geometry around the Ni(II) ion. The magnetic moment value of this complex is consistent with octahedral geometry structure. The spectrum of Cu(II) complex of together with the  $\mu_{\text{eff}}$  value (Table 3) suggest octahedral

geometry around Cu(II) complex (Chandra, 2009). The spectrum of Zn(II) complex gave band assigned to C.T.

The molar conductivity values of the complexes were consistent with 2:1 electrolytes (Temel, 2004).

**Table 2. Characteristic IR bands ( $\text{cm}^{-1}$ ) of the compounds studied**

compound	$\nu\text{NH}_2$	$\nu\text{O-H}$	$\nu\text{N=N}$	$\nu\text{C=N}$	$\nu\text{N-N}$	$\nu\text{M-N}$
I	3390-3340	3435	1612	-	1034	-
H <sub>2</sub> L	3400-3350	3406	1562	1635	1034	-
[CoH <sub>2</sub> L]2CL	3403-3354	3400	1519	1601	1033	454 ,447
[NiH <sub>2</sub> L]2CL	3409-3358	3402	1534	1618	1035	453 ,441
[CuH <sub>2</sub> L]2CL	3389-3347	3409	1530	1612	1034	452 ,444
[ZnH <sub>2</sub> L]2CL	3388-3341	3410	1521	1619	1032	450 ,441

**Table 3. UV-Visible spectra of the free ligand and complexes in  $10^{-3}$  M DMF, Magnetic moments and molar conductance in  $10^{-3}$  M DMSO .**

Compound	$\lambda_{\text{max}}$ nm	Wave Number $\text{cm}^{-1}$	$\epsilon_{\text{max}}$ ( $\text{L.mol}^{-1}.\text{Cm}^{-1}$ )	(d-d) Transitions	Molar Conductance $\Lambda_{\text{m}}(\Omega^{-1}\text{cm}^2\text{mol}^{-1})$	$\mu_{\text{eff}}$ (BM)
H <sub>2</sub> L	269 320 370	37174.7 31250 27027	1100 1670 1270	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-
[CoH <sub>2</sub> L]2CL	650 510	15384.6 19607.8	420 310	${}^4\text{T}_{1\text{g}} \rightarrow {}^4\text{A}_{2\text{g}}(\nu_2)$ ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{1\text{g}}(\text{P})(\nu_3)$	71	4.22
[NiH <sub>2</sub> L]2CL	541 575 625 693	18484.2 17391.3 16000 14430	380 380 360 350	${}^3\text{A}_{2\text{g}} \rightarrow {}^3\text{T}_{1\text{g}}(\text{P})$  ${}^3\text{A}_{2\text{g}} \rightarrow {}^3\text{T}_{1\text{g}}(\text{F})$	76	2.87
[CuH <sub>2</sub> L]2CL	537 632	18621.9 15822.7	510 360	${}^2\text{B}_{1\text{g}} \rightarrow {}^2\text{E}_{\text{g}}$ ${}^2\text{B}_{1\text{g}} \rightarrow {}^2\text{B}_{2\text{g}}$	77	1.75
[ZnH <sub>2</sub> L]2CL	-	-	-	-	79	Diamagnetic

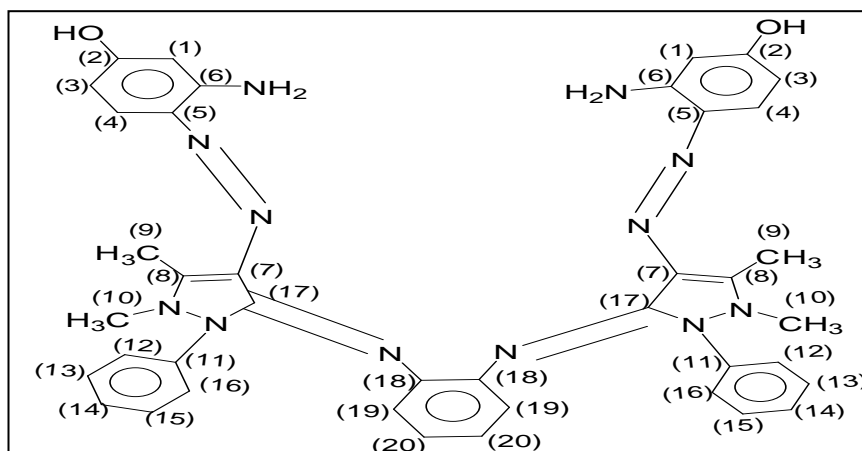
### Nuclear Magnetic Resonance Spectral Studies ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR

The newly synthesized ligand gave a satisfactory spectral data and the molecular structure was assigned on the basis of  ${}^1\text{H}$ NMR and  ${}^{13}\text{C}$ NMR chemical shift. NMR spectra were determined in  $\text{CDCl}_3$  with TMS as an internal reference. The identification was based on using simple splitting patterns that were produced by the coupling of protons and carbons which have very different chemical shifts. According to the results obtained from the spectra.  ${}^1\text{H}$  NMR spectrum of ligand (H<sub>2</sub>L) in  $\text{CDCl}_3$  gives the following signals: phenyl as multiple at 6.9-7.18 ppm, =C-CH<sub>3</sub> at 3.1 ppm, -N -CH<sub>3</sub> at

1.6 ppm, peak at 11.4 ppm is attributable to the phenolic -OH group present in the 3-amino phenol of the free ligand. The presence of this peak noted for the zinc complex confirms the -OH proton free from complexation and showed a signal at 4.5 ppm attributable to the amine NH<sub>2</sub> group present in the 3-amino phenol of the free ligand. The spectrum of the Zn, Ni and Co complexes are shifted downfield compared to the free ligand, suggesting deshielding of the NH<sub>2</sub> group due to coordination with metal ions. There is appreciable change in this complexes. The molecular structure was illustrated as follows:  ${}^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , ppm, 400MHz):  $\delta = 126(\text{C-1}), 176(\text{C-2}), 119(\text{C-3}), 135(\text{C-4}), 137(\text{C-5}),$

179(C-6), 87(C-7), 155.6(C-8), 11.2(C-9), 37.9(C-10),  
164.3(C-11), 123.6(C-12), 168.8(C-13), 121.6(C-14),

131.6 (C-15), 146.2(C-16), 187.9(C-17), 168.3(C-18),  
169.6(C-19), 137.6(C-20).



**Table 4.**  $^1\text{H}$ NMR data for (I),  $\text{H}_2\text{L}$  and its complexes

Compound	$\delta(\text{OH})$	$\delta(\text{NH}_2)$	$\delta(=\text{C}-\text{CH}_3)$	$\delta(\text{CH})$ aromatic	$\delta(-\text{N}-\text{CH}_3)$
I	9.98 (1H)	4.9 (2H)	2.23(3H)	7.12-7.53(8H)	2.7(3H)
$\text{H}_2\text{L}$	11.4 (2H)	4.5 (4H)	3.1 (6H)	6.9-7.18( 20H)	1.6 (6H)
$[\text{CoH}_2\text{L}]_2\text{CL}$	11.4 (2H)	3.6 (4H)	3.5(6H)	6.9-7.18( 20H)	1.8(6H)
$[\text{NiH}_2\text{L}]_2\text{CL}$	11.4 (2H)	3.8 (4H)	3.4(6H)	6.9-7.18( 20H)	1.2(6H)
$[\text{ZnH}_2\text{L}]_2\text{CL}$	11.4 (2H)	3.8 (4H)	3.5(6H)	6.6-7.18( 20H)	1.4(6H)

### Theoretical study

The vibration spectra of the schiff base-azo ( $\text{H}_2\text{L}$ ) were calculated by using a semi-empirical (PM3) method. The results obtained for wave numbers are presented in (Table 5), and the comparison with the experimental values indicate some deviations. These deviations may be due to the harmonic oscillator approximation and lack of electron correlation. It was reported (Chamberlain, *et al.*, 1999) that frequencies coupled with Hartree- Fock Theory (HFT) approximation and a quantum harmonic oscillator approximation tend to be 10% too high.

### Optimized Geometries Energy of metal complexes for Schiff base-Azo

A theoretically probable structures of metal complexes with Azo Schiff base were calculated to search for the most probable model building stable structure, these shapes, show the calculated optima geometries for ( $\text{H}_2\text{L}$ ) and their metal complexes. The results of PM3 method of calculation in gas phase for the binding energies and heat of formation of

Co(II), Ni(II), Cu(II) and Zn(II) complexes, are described in (Table 5).

### Electrostatic Potential (E.P)

Electron distribution governs the electrostatic potential of molecules and describes the interaction of energy of the molecular system with a positive point charge, so it is useful for finding sites of reaction in a molecule where the E.P. is strongly negative electrophilic attach (Druckerey, *et al.*, 2006). The E.P of free ligand was calculated and plotted as 3D contour to investigate the reactive sites of the molecules, and one can interpret the stereochemistry and rates of many reactive in involving soft electrophiles and nucleophiles in terms of the properties of frontier orbitals (HOMO and LUMO). Overlap between the HOMO and LUMO values were plotted as 3D contour to get more information about these molecules. The results of calculation showed that the LUMO of transition metal ion prefers to react with the HOMO of nitrogen atoms of Schiff base-azo ligand.

**Table 5. Conformation energetic in (kJ. mol<sup>-1</sup>) for the ligand and its metal complexes.**

Conformation	PM3	
	$\Delta H_f^\circ$	$\Delta E_b$
H <sub>2</sub> L	174.5514459	-9503.8221462
CoH <sub>2</sub> L	-1034.143706	-40977.950698
NiH <sub>2</sub> L	-1897.098098	-5980.458084
CuH <sub>2</sub> L	-10094.675909	-29780.167430
ZnH <sub>2</sub> L	-1567.976044	-30890.078964

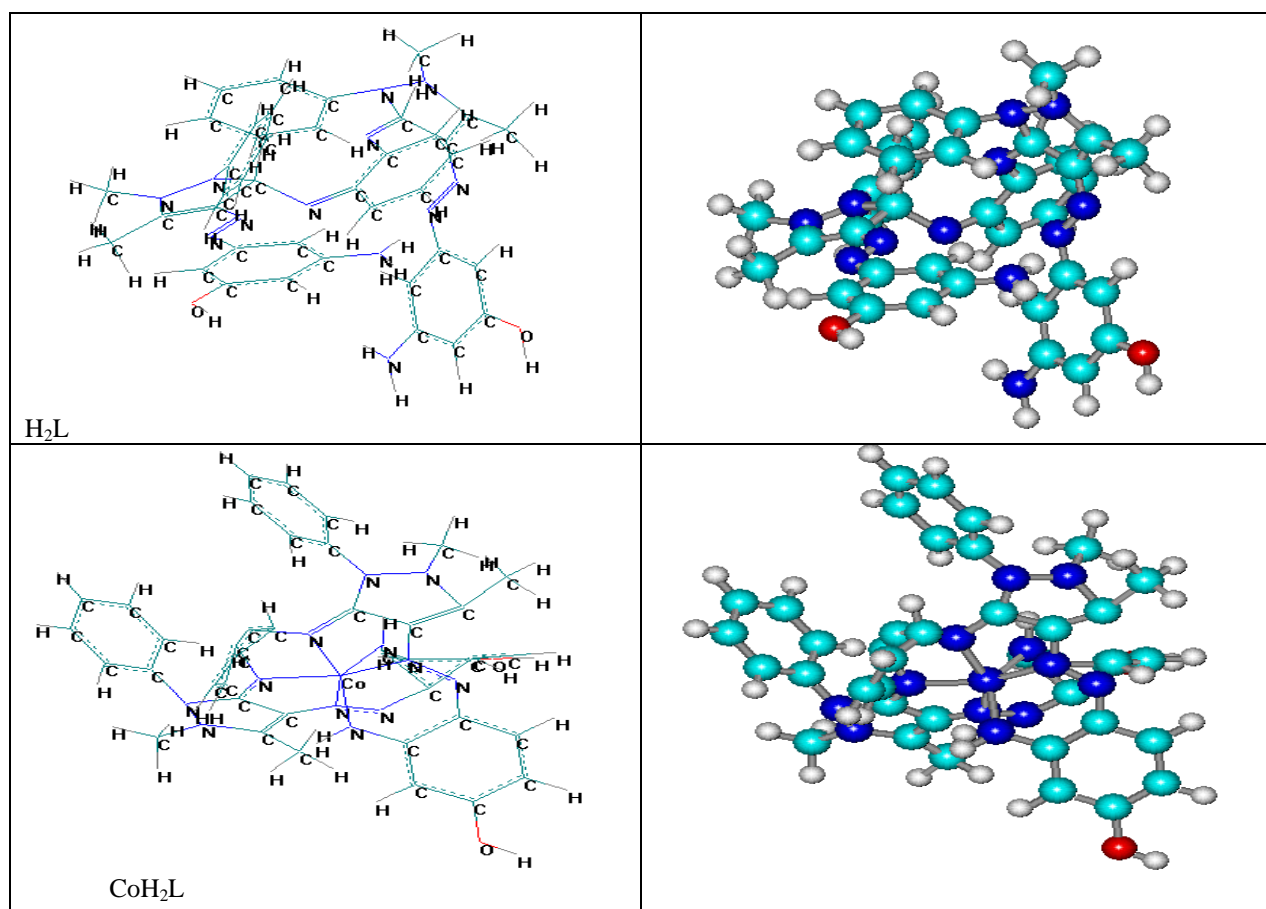
**Table 6. Comparison of experimental and theoretical vibration frequencies for H<sub>2</sub>L.**

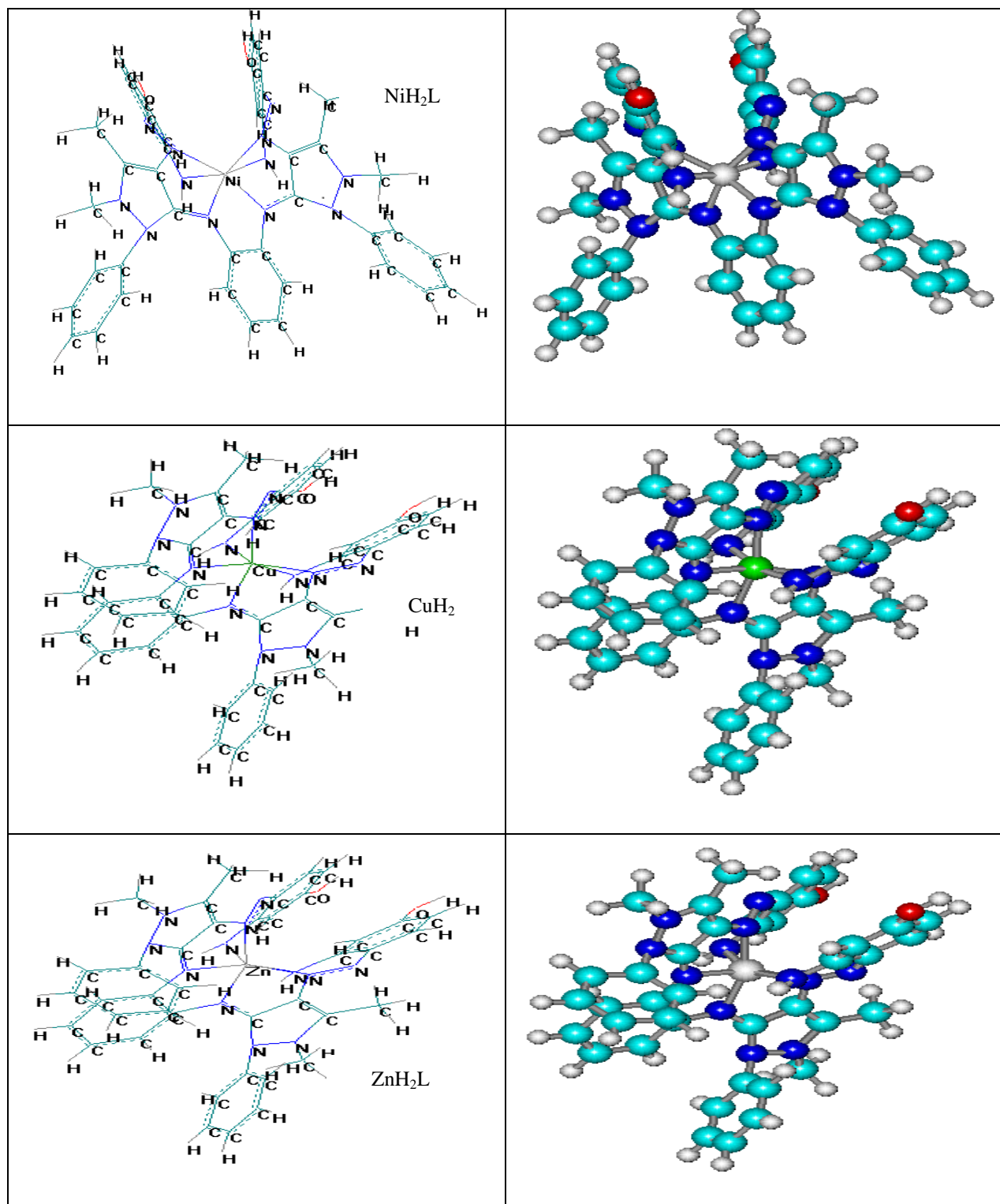
Symb.	H <sub>2</sub> L
$\nu_{\text{NH}}$	(3400,3350) <sup>*</sup> (3486,3610) <sup>**</sup> (-2.5,-7.7) <sup>***</sup>
$\nu(\text{C}=\text{N})$ iso	(1635) <sup>*</sup> (1647) <sup>**</sup> (-0.7) <sup>***</sup> (1635) <sup>*</sup> (1630) <sup>**</sup> (0.3) <sup>***</sup>
$\nu_{\text{OH}}$	(3406) <sup>*</sup> (3501) <sup>**</sup> (-2.7) <sup>***</sup>
$\nu_{\text{N-N}}$	(1034) <sup>*</sup> (1055) <sup>**</sup> (-2.0) <sup>***</sup> (1034) <sup>*</sup> (1022) <sup>**</sup> (1.1) <sup>***</sup>
$\nu_{\text{N=N}}$	(1562) <sup>*</sup> (1552) <sup>**</sup> (0.6) <sup>***</sup> (1562) <sup>*</sup> (1600) <sup>**</sup> (-2.4) <sup>***</sup>

\*: Experimental frequency

\*\* : Theoretical frequency

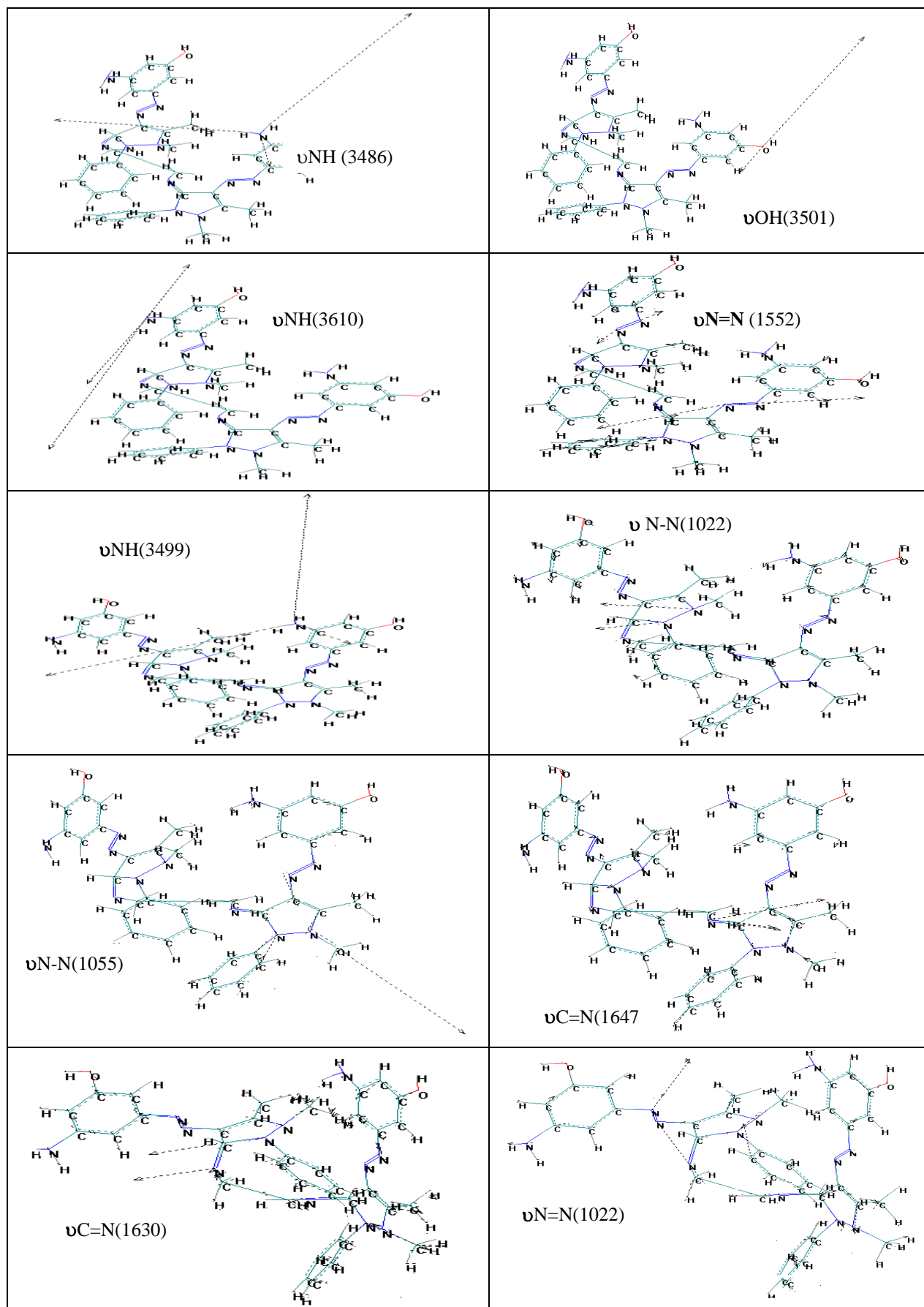
\*\*\*: Error % due to main difference in the experimental measurements and theoretical treatments of vibration spectrum.



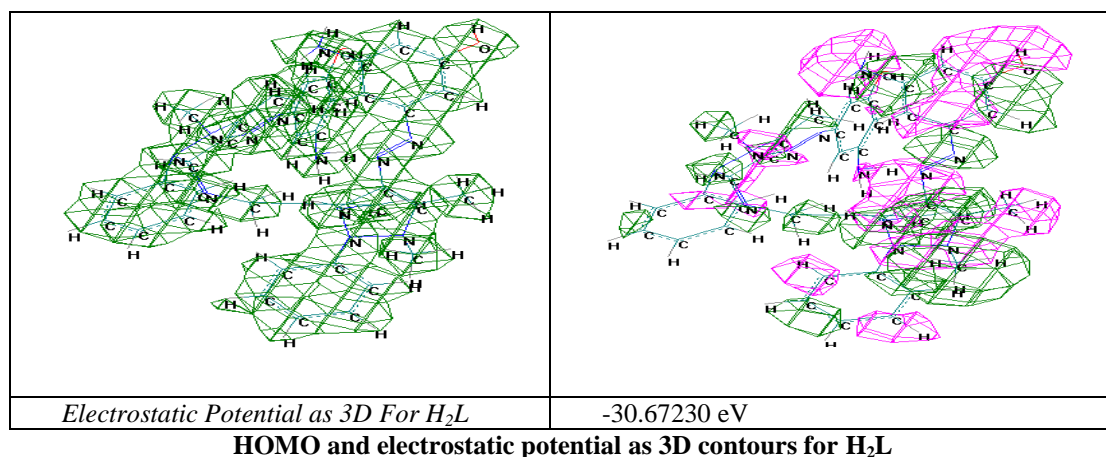


Conformational structure of the ligand and its complexes





The calculated vibrational frequencies of  $\text{H}_2\text{L}$

**Table 7. Antibacterial activities for the Schiff base and its complexes**

Compounds	<i>Staphylococcus aureus</i> (+)		<i>Escherichia coli</i> (-)	
	5mM	10mM	5mM	10mM
Ligand	-	-	+	-
Cobalt Complex	-	+	-	++
Copper Complex	-	++	+	++
Nickel Complex	-	-	+	-
Zinc Complex	-	-	+	-

(-) = No inhibition = inactive, (+) = (2-5) mm = active, (++) = (5-8) mm = highly active.

### Bactericidal activity

The data of antimicrobial activities of the prepared ligand and its complexes are given in (Table 6). The result showed that the complexes have more toxicity against the bacterial species than the free ligand. This can be attributed to the tweeds chelation theory (Morad *et al.*, 2007), according to which the chelation reduces the polarity of the metal atom mainly because of the partial sharing of its positive charge with donor group and possible electro delocalization over the whole ring. This increases the lipophilic character lipid layers of the cell membranes. Furthermore, the mode of action of compounds may involve the (C=N) and (N=N) groups with active centers of cell constituents resulting in the interference with normal cell process

### CONCLUSION

In this paper we have explored the synthesis and

coordination chemistry of some monomeric complexes obtained from the reaction of the hexadentate ligand H<sub>2</sub>L with some metal ions. The mode of bonding and overall structure of the complexes were determined through physico-chemical and spectroscopic methods. Complex formation study via molar ratio has been investigated and results were consistent with those found in the solid complexes with a ratio of (M:L) as (1:1). Hyper Chem-6 program has been used to predict structural geometries of compounds in gas phase, and biological activity studies of the ligand and its metal complexes against several organisms, *Escherichia coli* and *Staphylococcus aureus* are reported. Compounds exhibited some activity.

## REFERENCES

- Agarwal, R. K. Garge, P. Agarwal, H. Chandra, J. 1997. *Synth. React. Inorg. Met-Org Chem.*, 27, 251.
- Agarwal, R.K. Singh, L. and Sharma, D. K. 2006. *Bioinorganic Chemistry and Applications.*, ID 59509.
- Abdelhamid, A.O. Afifi, A. M. M. 2010. *Journal of Advanced Research*, 1, 137-144.
- Choi, Y. K. Chjo, K. H. Park, S. M. and Doddapaneni, N. 1995. *J. Electrochem. Soc.*, 142, 4107.
- Chandra, S Jain, D. Sharma, A. K. and Studies, K. 2009. *Molecules*, 14, 1, 174-190.
- Chamberlain, B. M. Sun, Y. Hagadorn, J. R. Hemmesch, E. W Hillmyer,. A.V. and Tolman, W.B. 1999. *Macromolecules*, 32, 2400.
- Dharmaraj, N. Iswanathamurthi, P. V. and Natarajan, K. 2001. *Transition Met. Chem.*, 26, 105.
- Dorestt, H. A. 1996. A review of quantum chemical studies of energetic materials, DSTO Technical report.
- Druckerey, H. and Mark, H. F. 2006. *Benzene Diazonium Salts-Azo Dyes*, 1, 123.
- El-Saied, F.A. Aly, M.M. and Anwar, A.M. 1993. *Transition Met. Chem.*, 18, 588-590.
- Foresman, J.C. Frisch, C. 1996. Exploring Chemistry With Electronic Structure Methods" 2<sup>nd</sup> ed, Gaussian Inc.
- Hitoshi, T. Tamao, N. Hideyyki, A. Manabu, F. and Takayuki, M. 1997. *Polyhedron*, 16, 3787.
- Habiban, M. A. 1999. Ph.D. Thesis College of Science University of Baghdad, Iraq.
- Harikumar, M. L. and Siji, V. L. 2009. *J. Indian Chem. Soc.*, 86, 441-448.
- Kriza, A. Reiss, A. Florea, S. Caproiu, T., 2000. *J. Indian Chem. Soc.*, 11, 207.
- Katia, B. Simon, L. Anne, R. Gerard, C. Francoise, D. and Bernard, M. 1996. *Inorg. Chem.*, 35, 387.
- Lever, A.B.P. 2003. From Coelho to Inorganic Chemistry: A Lifetime of Reactions - By Fred Basolo, Profiles in Inorganic Chemistry, John P. Fackler Jr. (Series Ed.), Kluwer Academic Publishers/Plenum Press, New York, NY, Hardbound., *Coordination Chemistry Reviews.*, 247, 1, 197-197.
- Mohanan, K. Athira, C. J. Sindhu, Y. and Sujamol, M. S. 2009. *Journal of Rareearths*, 27, 5, 705.
- Mathew, G and Hari Kumaran, M L. 2005. *Asian J. Chem.*, 17, 1.
- Majdan, M. Fuks, L. and Maidan. 1996. *I. Mineralia Slovaca* , 28, 412.
- Morad, F. M. ELajaily, M. Ben Gweirif, M. S. 2007. *J. Indian Chem. Soc.*, 1, 1, 72-78.
- Nakamoto, K. 1997. Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley-Inter Science, New York.
- Raman, N. Raja, J. J. Joseph, J. and Raja, J. D. 2007. *J. Chil. Chem. Soc.*, 52, 2, 1138-1141.
- Raman, N. Kulandaisamy, A. and Jeyasubramanian, K. 2002. *Polish J. Chem.*, 76, 1085.
- Raman, N Raja, S. J. Sakthivel, A. 2009. *J. Coord. Chem.*, 62, 1, 691-709.
- Singh, L. Tyagi, N. Dhaka, N.P. and Sindhu, S. K. 1999. *Asian J. Chem.* 11, 503.
- Shosho, C. E. Higgins, G. T. and Bisulca, A.A. 2008. United States Patent, 7, B2, 621-625.
- Skoog, D. and West, D. 1969. Fundamentals of Analytical Chemistry, Hott, Rinehart and Winston, Inc.
- Temel, T. Cukir, U. Tolan, B. Otludil, H and Vgras, V. 2004. *J. Coord. Chem.* 57, 7, 571.
- Zhao, W. N. 2007. *Acta Cryst.* E63, 2095.
- Zhang, Y. Yizhi, L. and Hanbin, T. 2002. *Acta Cryst.*, E 58, 24.

## معقدات العناصر لليكاند آزو- قاعدة شف متعددة السن :تحضير،تشخيص وفعالية بيولوجية

عباس علي صالح الحمداني \*

### ملخص

تم تحضير سلسلة من معقدات العناصر الانتقالية مع آزو- قاعدة شف الجديدة المشتقة من (آزو) 4-(2-امينو-4-هايدروكسي-فنييل آزو)-1،5-ثنائي مثل 2-فنييل -1،2-ثنائي هايدرو-بايروزول-3-اون مع أورثوفيلين ثنائي الأمين. تم تحليل عناصر المركبات الجديدة المحضرة وتحديد محتوى الكلور والفلزات وقياس الناقلية المغناطيسية والتوصيلية المولارية، كما درست أطيف الأشعة تحت الحمراء وفوق البنفسجية - المرئية والرنين النووي المغناطيسي. أظهرت النتائج ان المعقدات ثمانية السطوح والصيغة العامة هي  $[MH_2L]$ . إذ ان  $M =$  الكوبلت (II) ، النيكل (II)، النحاس (II) والخرصين (II). أجريت معالجة تكوين المعقدات نظريا في الطور الغازي بأستخدام برنامج (Hyper Chem-6) بتطبيق الميكانيكة الجزيئية والشبه تجريبية في حساب  $\Delta H_f^\circ$  و  $\Delta E_b$  بدرجة 298كلفن . كما درست الفعالية البيولوجية للمركبات ضد انواع منتخبة من البكتريا *Escherichia coli and Staphylococcus aureus*.  
الكلمات الدالة: معقدات العناصر لليكاند آزو، فعالية بيولوجية.

\* قسم الكيمياء، كلية العلوم للبنات، جامعة بغداد، بغداد، العراق. تاريخ استلام البحث 2012/9/27 وتاريخ قبوله 2013/2/26.