

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Synthesis, Spectral, Bioactive And Theoretical Studies Of New Schiff Base And Metal Complexes.

Veyan Taher Suleman¹, Vian Yamin Jirjees¹, Abbas Ali Salih Al-Hamdani^{2*}, and Suzan Duraid Ahmed³.

¹Department of Chemistry, College of Science, University of Dohuk, Iraq.

²Department of Chemistry, College of Science for Women, University of Baghdad, Iraq.

³Department of Chemistry, College of Education for pure Science (Ibn Al-Haitham/ University of Baghdad, Iraq

ABSTRACT

The new Schiff base (H₄L) has been synthesized from reaction of 5,5-Dimethylcyclohexane-1,3-dione with 6-Amino-pyrimidine-2,4-diol. Use ligand and metal ions to prepared complexes with the general formula: [M(H₄L) (Cl)₂] where M(II)=Co, Ni, Cu, Zn, Cd and Hg are report. The structure of compounds mode of bonding and overall were determined through ¹H-NMR, FT-IR, Mass and UV-Vis spectroscopy, elemental analysis (C.H.N.O), Flame Atomic absorption, magnetic moment measurement, chloride containing, molar conductance and TGA curve, Nature for produced compounds, have been studied, obeyed mole ratio as well, methods of continuous, were observed for complex solutions. On origin data a tetrahedral geometry were assigned for the produced complexes. The ligand and their complexes have been evaluated for vitro antibacterial. In the DFT studies the geometries of Schiff base and metal complexes were fully optimized.

Keywords: 6-Amino-pyrimidine-2,4-diol, Schiff base Complexes, 5,5-Dimethyl-cyclohexane-1,3-dione Theoretical Studies.

**Corresponding author*

INTRODUCTION

Schiff base derivatives attract from 5, 5- dimethyl cyclohexane-1,3- dione a significant interest and occupy an important large in development of coordination chemistry [1-3]. Schiff base play an important role in inorganic chemistry as they easily form stable complexes with most metal ions. The presence of donor atoms (N,O,S) in the ligand will play an important role in the formation of a stable chelating and this situation facilitates the complexation process [4]. Metal complex with Schiff base derived from 6-Amino-pyrimidine-2,4-diol and 5,5-Dimethyl-cyclohexane-1,3-dione are an important class of ligands to their preparability, selectivity towards the metal ion, geometry similarities with natural biological substances, and also due to the presence of (C=N) and hydroxyl groups which elucidate the mechanism of reaction in biological systems [5-7] also have been studied for their application in clinical, analytical and pharmacological areas [8].

EXPERIMENTAL

Instrumentation: Electronic absorption spectroscopies were recorded using Shimadzu 160, $^1\text{H-NMR}$ spectra were recorded using (Bruker 400MHz). Mass-spectrometer were obtained by LC-Mass 100P Shimadzu, chlorine content. Magnetic properties by using model MSR-MKi. Analysis microelement (C.H.N.O.) using PerkinElmer model 240B. Melting points by using (Buchi SMP-20) Molecular conductivity was measured using a Jenway 4071 digital. Thermal analysis of compounds was measured using a PerkinElmer pyris Diamond DTA/TG. Metal Content Select by (Shimadzu 680G) F.A.A. Spectrometer and I-R spectrometer by using (Shimadzu 3800).

Materials: The following chemicals were commercially available products of analytical reagent grade. 6-Amino-pyrimidine-2,4-diol, 5,5-Dimethyl-cyclohexane-1,3-dione, DMSO, pure ethanol, methanol, NaOH, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, CaCl_2 , $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$, HgCl_2 and $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ were obtained from Fluka, Aldrich.

Synthesis of Ligand (H₄L): (20 cm³) Pure ethanol to dissolve 5,5-dimethyl-cyclohexane -1,3-dione (1.4g, 0.01mol) was added to mixture containing a neutral ethanolic solution by (sodium hydroxide + glacial acetic acid) (10 ml) of 6-Amino-pyrimidine-2,4-diol (2.542g, 0.02mol). The resulting mixture was refluxed for 12 hours with stirring. A light red crystals glossy was formed and then re-crystallized from mixture of methanol. The product was dried in vacuum, yield (88%), mp 197-200 °C.

The singlet signal observed at ($\delta=2.248$ ppm, 2.345 ppm) in the spectrum of free Schiff base, was assigned to the methyl group ($\text{C}-(\text{CH}_3)_2$), singlet signal showed at ($\delta=2.845$ ppm, 3.394 ppm), was attributed to the ($-\text{CH}_2$), singlet signal showed at ($\delta=4.838$ ppm), was attributed to the ($-\text{C}-\text{OH}$), singlet signal showed at ($\delta=6.623$ ppm) was attributed to the ($-\text{C}-\text{H}$), the signal appeared at ($\delta=2.5$ ppm) can be assigned to the (solvent-DMSO) show in (Fig.-1) $^1\text{H-NMR}$ Spectrum of free ligand. The molecular ion peak for the free ligand (H₄L), was observed at $m/z = 359$ (M) (relative abundance is 70%) for $\text{C}_{16}\text{H}_{18}\text{N}_6\text{O}_4$ which is in excellent agreement with the (358.35) theoretical value and the fragmentation pattern (311, 255, 215 and 211 m/z) show in (Fig.-2). The fragmentation pattern is shown in

Synthesis of Complexes: A solution of the ligand (3.55g, 0.01 mol) in methanol (25 cm³), and distilled water solution (25 cm³) the metal salt prepared (0.01 mol) was then added drop wise.

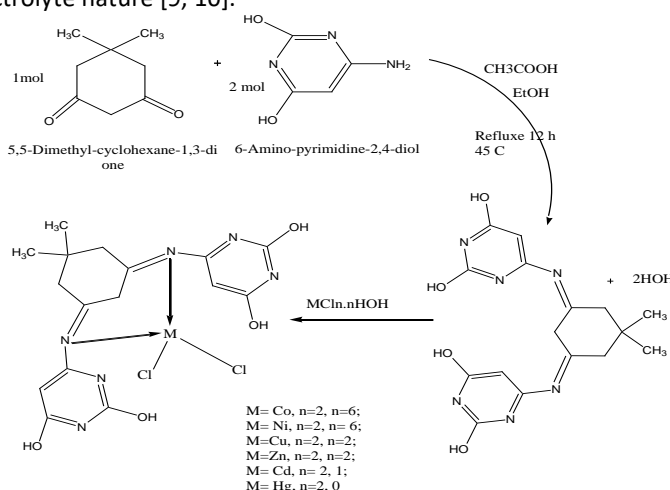
The resulting mixture was stirred three hours in (40-50) °C, resulting in the formation of a solid material which was washed several times with (hot ethanol:distilled water) (1:2) and dried in room temperature. Physical properties for the complexes are given (Table 1), and show (Scheme 1) Synthesis of metal complexes with Ligand.

RESULTS AND DISCUSSION

To prepare for ligand (H₄L) a linkup from 5, 5-Dimethylcyclohexane-1,3-dione for convenient 6-Amino-pyrimidine-2,4-diol at ethanol solution was performed. Prepared ligand was characterized by $^1\text{H-NMR}$, FTIR, Mass, TG curve, elemental analysis and UV-Vis spectra.

Metal chelates were produced through immediate reaction from alcoholic solution to the ligand for aqueous solution from the metal ions in the ideal pH and at a M:L ratio from 1:1. Datum elemental analysis and metal content for compounds were at good agreements for calculated values, datum recorded in Table 2.

The complexes in (1×10^{-3} M) at (DMSO) solution have low molar conductance value ($14.1-16.8 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$) indicating their non-electrolyte nature [9, 10].



Scheme 1: Synthesis of metal complexes with Ligand (H₄L)

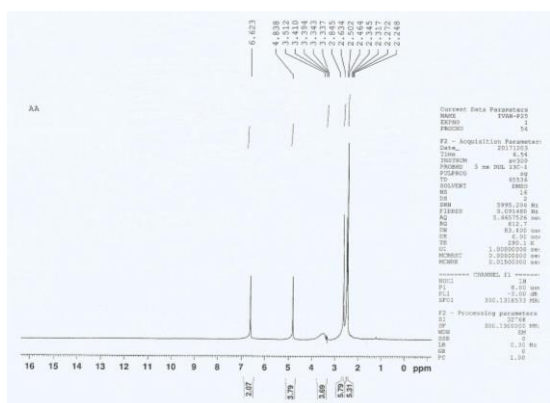


Figure 1: ¹H-NMR Spectrum of free Ligand (H₄L)

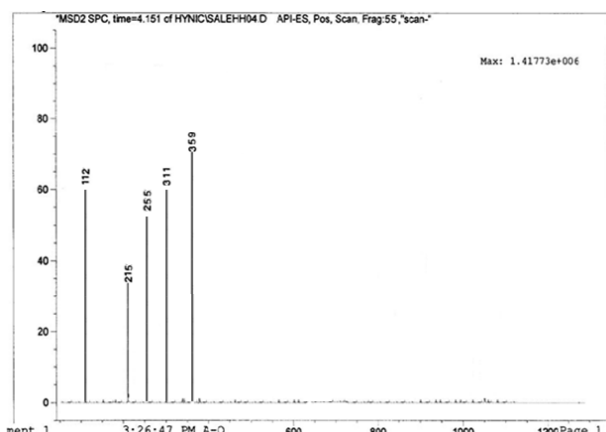


Figure 2: LC-Mass Spectrum of ligand

Stoichiometry of Complexes: Mole ratio and job methods writing of complexes done in solutions has been permanent. In two positions outcomes disclose 1:1 metal into ligand ratio. Choice chart is exemplified at (Fig. 3). (Table 3) outlines the results acquired, other than, conditions to the preparation for compounds.

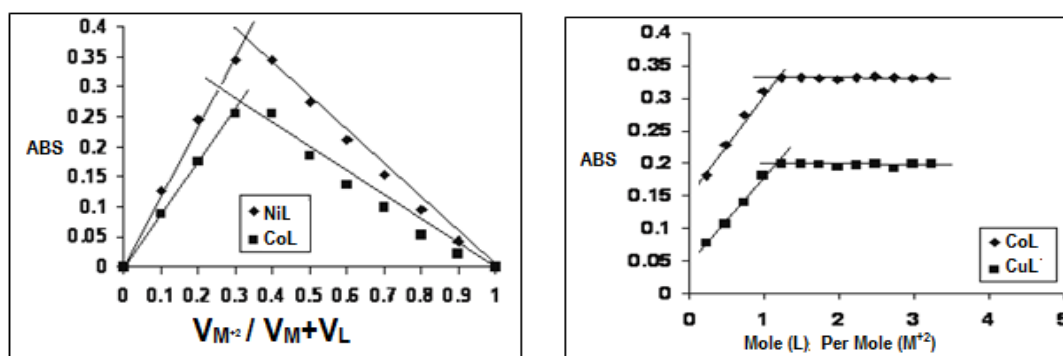


Figure 3: Mole ratio and Job methods to the compounds solutions.

Table 1: physical properties and elemental analysis for compounds

Comp.	Formula M _w t	m.p °C	Element microanalysis% Calau (Found)					
			M	C	H	N	O	Cl
Ligand	C ₁₆ H ₁₈ N ₆ O ₄ 358.35	197-200	-	53.63 (52.97)	5.06 (5.01)	23.45 (23.01)	17.86 (16.21)	-
[Co(H ₄ L)Cl ₂]	C ₁₆ H ₁₈ N ₆ O ₄ Cl ₂ Co 488.19	256 d	12.07 (13.01)	39.36 (38.97)	3.72 (4.01)	17.21 (18.01)	13.11 (14.21)	14.52 (13.11)
[Ni(H ₄ L)Cl ₂]	C ₁₆ H ₁₈ N ₆ O ₄ Cl ₂ Ni 478.95	307 d	12.03 (13.21)	39.38 (38.77)	3.72 (3.01)	17.22 (19.01)	13.12 (13.21)	14.53 (14.11)
[Cu(H ₄ L)Cl ₂]	C ₁₆ H ₁₈ N ₆ O ₄ Cl ₂ Cu 492.80	275 d	12.89 (12.01)	39.00 (38.47)	3.68 (4.31)	17.05 (18.34)	12.99 (13.21)	14.39 (14.11)
[Zn(H ₄ L)Cl ₂]	C ₁₆ H ₁₈ N ₆ O ₄ Cl ₂ Zn 494.65	229 d	13.22 (13.54)	38.85 (38.65)	3.67 (3.45)	16.99 (17.01)	12.94 (12.78)	14.33 (13.11)
[Cd(H ₄ L)Cl ₂]	C ₁₆ H ₁₈ N ₆ O ₄ Cl ₂ Cd 541.67	245 d	20.75 (21.01)	35.48 (34.97)	3.35 (4.32)	15.52 (16.21)	11.81 (10.21)	13.09 (13.56)
[Hg(H ₄ L)Cl ₂]	C ₁₆ H ₁₈ N ₆ O ₄ Cl ₂ Hg 629.51	246 d	31.85 (32.01)	30.81 (30.97)	2.88 (3.24)	13.34 (13.89)	10.16 (11.13)	11.26 (12.11)

d = decompose

Electronic spectra: The UV-Vis spectra of the produced ligand and metal chelates melted in DMSO (10^{-3} M) were recorded and the datum assigned in Table 2. The electronic spectrum of ligand (Fig. 4) show peaks in (238 and 374) nm due to ($\pi \rightarrow \pi^*$) electronic transition [11].

The electronic spectrum of Cu(II) complex showed one low energy weak band assigned to ${}^2T_2 \rightarrow {}^2E$ transition at 980 nm [12], The spectrum of Co(II) complex display peaks at (240 and 381) nm consequent to ligand field, else three peaks in (781, 890 and 978) nm related to electronic transition type ${}^4A_{2(F)} \rightarrow {}^4T_{1(P)}$, ${}^4A_{2(F)} \rightarrow {}^4T_{1(F)}$ and ${}^4A_{2(F)} \rightarrow {}^4T_{2(F)}$ continually show (Fig. 5) [12,13] . The spectrum of Ni(II) complex show peaks at (263 and 388) nm lead to ligand field, two peaks at (874 and 980) nm described to electronic transition ${}^3T_{1(F)} \rightarrow {}^3T_{1(P)}$ and ${}^3T_{1(F)} \rightarrow {}^3T_{2(F)}$ gradually [12-14]. The electronic spectra of [Zn(II), Cd(II) and Hg(II)] complexes do show the charge transfer due to (d-d) are not probable hence electronic spectra did not give each prolific information, actually this outcome is a good deal for previous work to the tetrahedral geometry [12,14,15].

Magnetic estates (Table 2) of the produced complexes have been happened to a paramagnetic that was accounted for tetrahedral structure [13, 15].

Table 2: Electronic Spectral Data of the Metal Complexes with Ligand and Magnetic Moments,

Compounds	ABS	(λ_{max}) nm	ϵ_{max} (L.mol ⁻¹ .cm ⁻¹)	Λ_m (S.cm ² .mol ⁻¹) at Absolute DMSO	μ_{eff} (B.M)
Ligand	238 374	1.002 1.975	1002 1975	-	-
[Co(H ₄ L)Cl ₂]	240 381 781 890 978	0.794 1.260 0.035 0.041 0.043	794 1260 35 41 43	14.1	4.15
[Ni(H ₄ L)Cl ₂]	263 388 874 980	0.667 1.218 0.006 0.042	667 1218 6 42	16.8	3.84
[Cu(H ₄ L)Cl ₂]	277 393 980	0.512 0.937 0.034	512 937 34	13	2.18
[Zn(H ₄ L)Cl ₂]	268 391	0.634 2.037	634 2037	14.9	Dia.

[Cd(H ₄ L)Cl ₂]	277 388	0.512 1.218	512 1218	15.1	Dia.
[Hg(H ₄ L)Cl ₂]	268 391	0.666 2.056	666 2056	14.9	Dia.

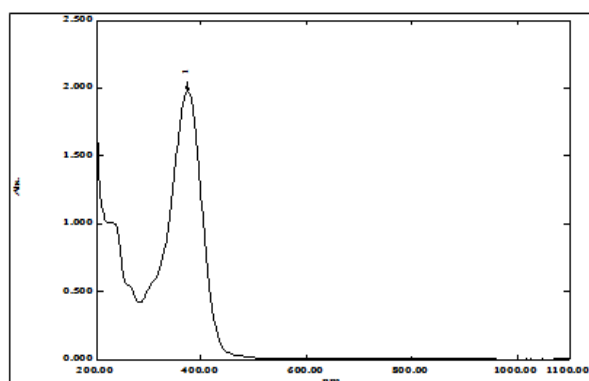


Figure 4:- UV-Vis spectrum to the ligand complex.

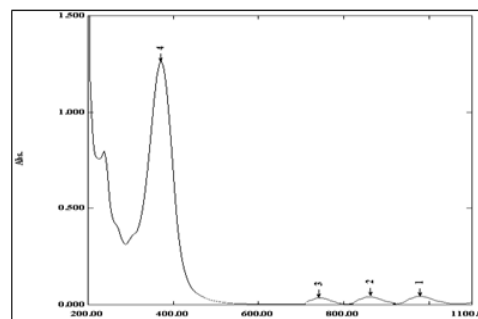


Figure 5:- UV-Vis spectrum to the [Co(H₄L)₂Cl₂]

IR spectra: The characteristic stretching vibration modes concerning Schiff base (H₄L) and its metal complexes are described in Table 3. The ligand (H₄L) exhibited a strong high intensity bands appeared at [(1624) cm⁻¹ and (1677) cm⁻¹] and weak absorption of [(3098) cm⁻¹ and (2975) cm⁻¹] which were ascribed to the stretching mode of $\nu(\text{C}=\text{N})$ ring, $\nu(\text{C}=\text{N})$ azomethen group $\nu(\text{C}-\text{H})$ aromatic and $\nu(\text{C}-\text{H})$ aliphatic, as show in (Table 3), respectively. Pertaining to the complexes, the ligand behaved as a bi dentate, which were been coordinating with the nitrogen of the azomethene group. The mentioned coordination was confirmed by shifting the bands $\nu(\text{C}=\text{N})$ to lower frequencies about (10- 23) cm⁻¹, respectively [16, 17]. These observations were further indicated by the appearance of $\nu(\text{M}-\text{N})$. the spectra showed new bands at [540, 487, 475, 489, 506, 514] cm⁻¹ can be refer to $\nu(\text{M}-\text{N})$ for complexes with metals Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II), respectively [16, 18].

Table 3: Infrared Spectra Data of the Free Ligand (H₄L) and its Complexes in (cm⁻¹)

Comp.	$\nu\text{C}=\text{N}$	$\nu\text{C}=\text{N}$ ring	$\nu\text{M}-\text{N}$	Other bands
H ₄ L	1677	1624		ν C-H arom =3098 ν C-H aliph=2975
[Co(H ₄ L)Cl ₂]	1649	1632	540	ν C-H arom =3087 ν C-H aliph=2959
[Ni(H ₄ L)Cl ₂]	1654	1622	487	ν C-H arom =3046 ν C-H aliph=2987
[Cu(H ₄ L)Cl ₂]	1657	1617	475	ν C-H arom =3079 ν C-H aliph=2971
[Zn(H ₄ L)Cl ₂]	1667	1619	489	ν C-H arom =3045 ν C-H aliph=2959
[Cd(H ₄ L)Cl ₂]	1663	1618	506	ν C-H arom =3044 ν C-H aliph=2977
[Hg(H ₄ L)Cl ₂]	1660	1623	514	ν C-H arom =3087 ν C-H aliph=2977

Mass spectra for complexes: The mass spectra of Hg and Zn complexes the parent ion peaks at ($m/z=629.5$) and ($m/z=494.65$) correspond to ($M= \text{C}_{16}\text{H}_{18}\text{N}_6\text{O}_4\text{Cl}_2\text{Hg}$) and ($M= \text{C}_{16}\text{H}_{18}\text{N}_6\text{O}_4\text{Cl}_2\text{Zn}$) respectively, the fragmentation pattern are peaks (629,355,216 and 67) m/z for Hg complex and (494, 359,247,212 and 67) m/z for Zn complex

Thermal Gravimetric Analyses TGA: To understand the thermal decomposition processes of the studied compounds, the Schiff base ligand and its metal complexes were examined by thermo gravimetric analysis in the temperature range of 30–700 °C.

TG curve of (H₄L) show relatively rapid decomposition in the first (39.2- 128.7 °C), second (128.7- 429) and third (450.3 - 689°C) steps with T_{DTG} peaks at 68.7°C, 368 °C and 654°C. The very large and strongly sharp T_{DTG} peak observed for the first step at 368 °C is preceded with a sharp peak. 5.27%, 28.82% and 64.09% mass losses in the first, second and third steps correspond to the release of 2(OH), (C₇H₉O₂) and (C₈H₇N₆) fragments (cal. 4.756 %, 28.788% and 64.352 %, respectively), Show the (Table 4) Characterization Parameters of thermal decomposition (10°C min⁻¹) of ligand [3,19,20].

The TG curve of Cu(II) complexes with H₄L show relatively rapid decomposition in the first (135.200°C) and second (100.599.6°C) steps with T_{DTG} peaks at 180°C and 318°C. The very large and strongly sharp T_{DTG} peak observed for the first step at 318°C is preceded with a sharp peak. 12.24 % and 86.49% mass losses in the first and second steps correspond to the release of (2Cl) and (C₁₆H₁₈N₆O₃) fragments and final product (CuO) (cal. 2.31%, 50.95% and 42.03%, respectively). The tentative decomposition reaction of Cu-complex is shown in (Table 4). The TG curve of Hg (II) complex with H₄L show relatively rapid decomposition in the first (180-245°C) and second (255-520°C) steps with T_{DTG} peaks at 165°C and 401°C. The very large and strongly sharp T_{DTG} peak observed for the first step at 301°C is preceded with a sharp peak. 10.23 % and 78.39% mass losses in the first and second steps correspond to the release of (Cl) and (C₁₆H₁₈N₆O₃Cl) fragments and final product (HgO) (cal. 11.09% and 79.68%, respectively). The tentative decomposition reaction of Hg-complex is shown in (Table 4). [3,20].

Table 4: Characterization Parameters of Thermal Decomposition (10°C min⁻¹) for Metal Complexes of Ligand

Com	TG range (°C)	DTG _{max} (°C)	%Estimated (calculated)		Assignment
			Mass Loss	Total mass Loss	
H ₄ L	39.2-128.7	68.7	4.756 (5.27)	(98.188)	-2OH
	128.7-429	368	28.788(28.82)	97.896	-C ₇ H ₉ O ₂
	450.3-689	654	64.352 (64.09)		-C ₈ H ₇ N ₆ C
[Cu(H ₄ L)Cl ₂]	135-200	180	(13.08) 12.24	98.73	2Cl
	200-599	318	(85.07) 86.49	(98.15)	C ₁₆ H ₁₈ N ₆ O ₃ CuO
[Hg(H ₄ L)Cl ₂]	180-245	165	(11.09) 10.23	88.62	Cl
	255-520	401	(79.68) 78.39	(90.77)	C ₁₆ H ₁₈ N ₆ O ₃ Cl HgO

Theoretical study: In this part, ligand and their metal complexes were studied in two types of two programs Hyperchem-8 and Gaussian computation which calculated the following data. Heat of formation (ΔH[°]_f), binding energy (ΔE_b), dipole moment (μ), spectroscopic study, vibration frequency, electronic transitions and molecular orbital energy (E_{HOMO}-E_{LUMO})

Theoretical Energies and Dipole Moment: Energy is one of the maximum useful principles in science. The analysis of energies can help inside the prediction of which molecular processes likely arise, or able to occur. All computational chemistry techniques energy such that the machine with the bottom energy is the maximum strong. For that reason, the form of a molecule corresponds to the form with the bottom strength [3,14,17]. The molecular dipole moment is possibly the only experimental degree of price density in a molecule. The accuracy of the general distribution of electrons in a molecule is tough to quantify because it entails all the multi-dipole moments. In this work, the heat of formation (ΔH[°]_f), binding energy (ΔE_b) and dipole moment (μ) of ligand and their metallic complexes had been studied by using PM3, AMBER& ZINDO/1 techniques [21]. The results showed that the complexes have a higher stability than the ligand as noted in the table below, (Table - 5) by using of hyper-chem software

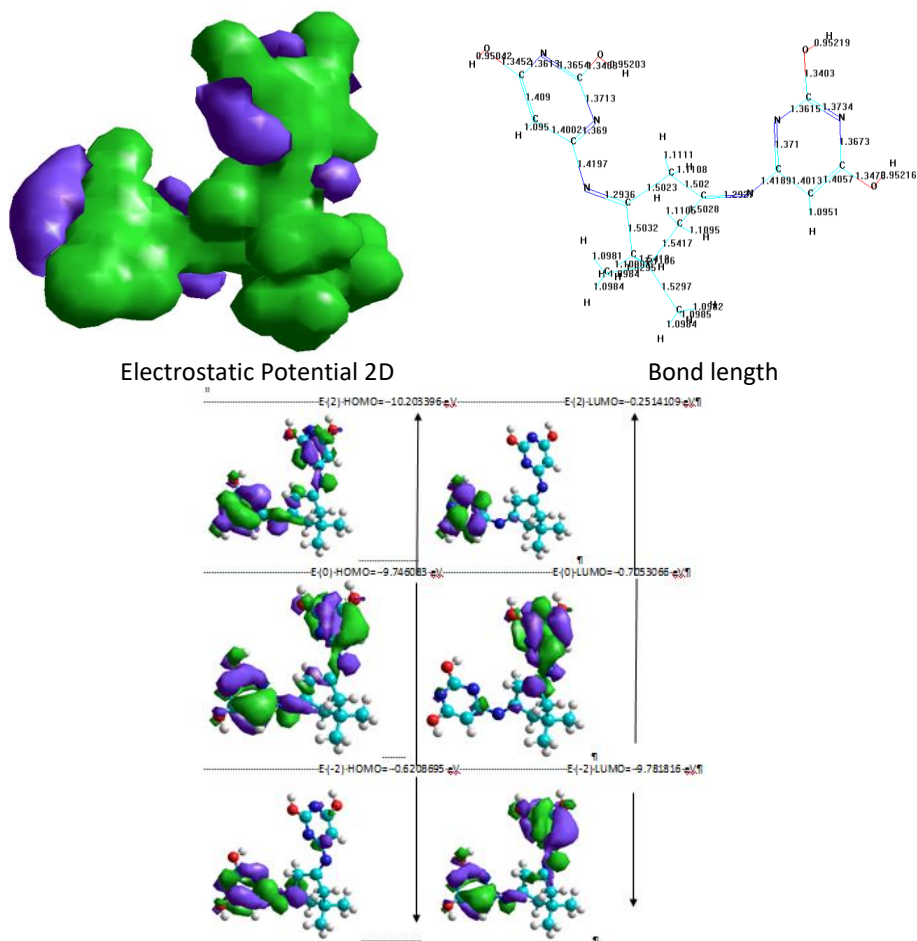
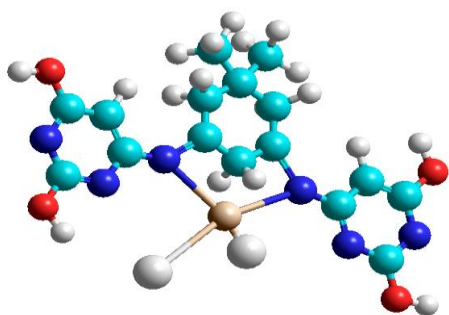
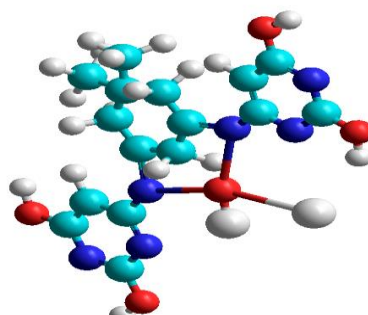


Figure 6: Electrostatic Potential, Bond length and level (HOMO and LUMO) for Ligand

 Table 6: Conformation Energetic in (K J.Mol⁻¹) for the Ligand and Complexes

Comp.	Total energy	Binding energy	Heat of formation	Electronic energy	Dipole (Debyes)
Ligand	-111149.7794	-6775.99042	19.919	-112169.745	7.87
[Co(H ₄ L)Cl ₂]	-136804.6161	-69381.3179	19.288	-156303.654	4.45
[Ni(H ₄ L)Cl ₂]	-154545.90	-6513.5828	51.65318	-162035.545	6.776
[Cu(H ₄ L)Cl ₂]	-136545.6468	-9644.4574	92.6685	-106928.336	6.115
[Zn(H ₄ L)Cl ₂]	-131804.6161	-6938.3179	15.288	-126303.654	3.46
[Cd(H ₄ L)Cl ₂]	-131361.8681	-6609.42211	39.73388	-105209.29	8.43
[Hg(H ₄ L)Cl ₂]	-131545.6468	-6644.4574	92.6685	-106928.336	6.15


 [Co(H₂L)Cl₂]

 [Ni(H₂L)Cl₂]

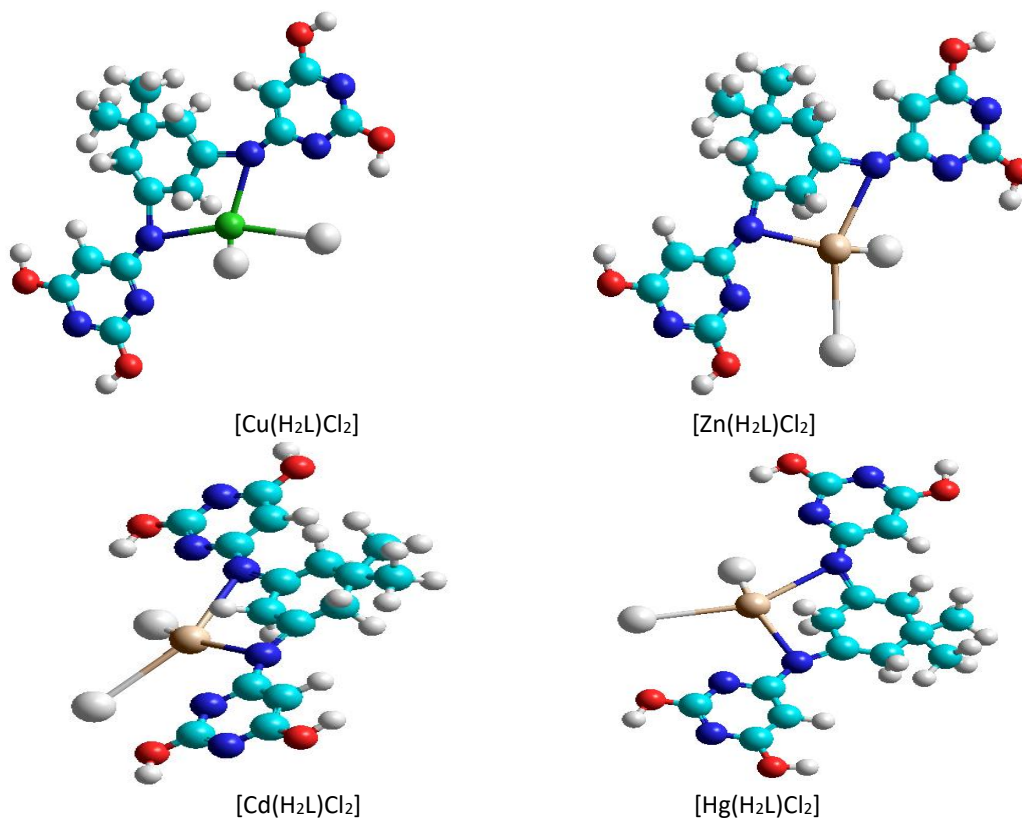


Figure 7: Conformational Structure of metal complexes

ACKNOWLEDGMENTS

Thanks are due to the College of Sciences of women, University of Baghdad and

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