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

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ABSTRACT

The new Schiff base bidentate H_2L 6-(4-Amino-2-phenyl-2,4-dihydro-pyrazol-3-ylideneamino)-pyrimidine-2,4-diol. Has been synthesized from condensation of 6-Amino-pyrimidine-2,4-diol with 4-Amino-2-phenyl-2,4-dihydro-pyrazol-3-one. Monomeric complexes with the general formula= $[M (H_2L) Cl_2]$ where $M(II)$ = Co, Ni, Cu, Zn, Cd and Hg are reported. New Schiff base the of structures mode of bonding and overall structure geometry of the complexes were determined through by the 1H -NMR, FT-IR, Mass and UV-Vis, spectral studies, TGA curve, magnetic moment measurements, elemental microanalyses (C. H. N and O.), chloride containing, Atomic absorption and conductance. These studies revealed tetrahedral geometries for all complexes. Complexes formation studies via molar ratio and continuous variation methods in (N, N'-dimethyl formamide) solution were consistent to those found in the solid complexes with a ratio of (Metal: Ligand) (1 : 1). A theoretical study was carried out using program Hyper Chem-8 of new compounds that were prepared in this research. It identified the most stable geometric shapes, as well as the total energy, the heat of formation, bonding energy and dipol moment. Study the effect of compounds prepared against different types of bacteria and fungus

Keywords: 6-Amino-pyrimidine-2,4-diol, Schiff base Complexes, theoretical treatment, bioactive

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INTRODUCTION

The coordination chemistry of metal ions with ligands from the 4-Amino-2-phenyl-2,4-dihydro-pyrazol-3-one has been of interest due to different bonding modes for amine and carbonyl groups, show by these with starting material and ligands (Schiff base) by synthesized from condensation the Primary and secondary maine and carbonyl with both electron poor metals and electron rich and Play an important role in inorganic chemistry because be it is complexes Highly stable with most ions [1-3]. Because attract a significant interest and occupy an important role in the development of coordination chemistry [4]. The presence of donor atoms in the ligand (phenol, carbonyl, amine,) will play in important role in the formation of a stable chelatering and this situation facilitates the complexation process [5]. Moreover, complexes containing metal ions have been studied in several research areas such as structural chemistry [6]. Organic compounds container on the azumethine group of a distinctive type and important for its ability to bond and composition of organic compounds because of their artificial elasticity and their sensitivity and sensitivity to the direction of metal ions, structural similarities with natural biological substances, and also, due to presence of azomethine, phenol and amine groups, which imports in elucidating the mechanism of transformation and racemisation reaction in bio activity system [7, 8] also have been studied for their application in clinical, analytical and pharmacological areas [9].

EXPERIMENTAL

Instrumentation

¹H-NMR spectra were recorded using Bruker 400 MHz spectrometer, FT-IR spectra were recorded using Shimadzu 3800, UV-Vis electronic absorption spectra were recorded Shimadzu 160, (C.H.N. and O) elemental microanalysis were recorded Perkin- Elmer omdel 240 B spectrophotometer. Conductivity measurements were made in (1×10⁻³)M with (DMSO) solvent using a Jenway 4071 digital. Mass spectra were obtained by LC-Mass 100P Shimadzu, Metals were identified using a Shimadzu (F.A.A) 680 G atomic absorption Spectrometer. chlorine content. Magnetic properties were measured using (Balance magnetic susceptibility model MSR-MKi). Melting points were obtained on a Buchi SMP-20 capillary melting point apparatus and are uncorrected.

Materials

The following chemicals were commercially available products of analytical reagent grade. 6-Amino-pyrimidine-2,4-diol, 4-Amino-2-phenyl-2,4-dihydro-pyrazol-3-one, DMSO, pure ethanol, methanol, NaOH, NiCl₂ 6H₂O, CoCl₂ 6H₂O, CuCl₂ ZnCl₂ 2H₂O, CdCl₂.H₂O and HgCl₂ were obtained from Fluka and Aldrich.

Synthesis of Ligand (H₂L): 6-(4-Amino-2-phenyl-2,4-dihydro-pyrazol-3-ylideneamino)-pyrimidine-2, 4-diol

(15 ml) Methanolic solution of 4-Amino-2-phenyl-2,4-dihydro-pyrazol-3-one (1.4 g, 0.008 mol) was added to a mixture containing an neutral solvent methanolic by (sodium hydroxide + glacial acetic acid) (10 ml) of 6-Amino-pyrimidine-2,4-diol (1.0168 g, 0.008mol). The resulting mixture was refluxed for 15 hours with stirring. A light red crystals glossy was formed and then re-crystallized mixture (ethanol: water) (1: 1). The product, Yield: 78%, M.p= (179-181 °C), Scheme (1) Synthesis of Ligand (H₂L).

Synthesis of metal ions Complexes

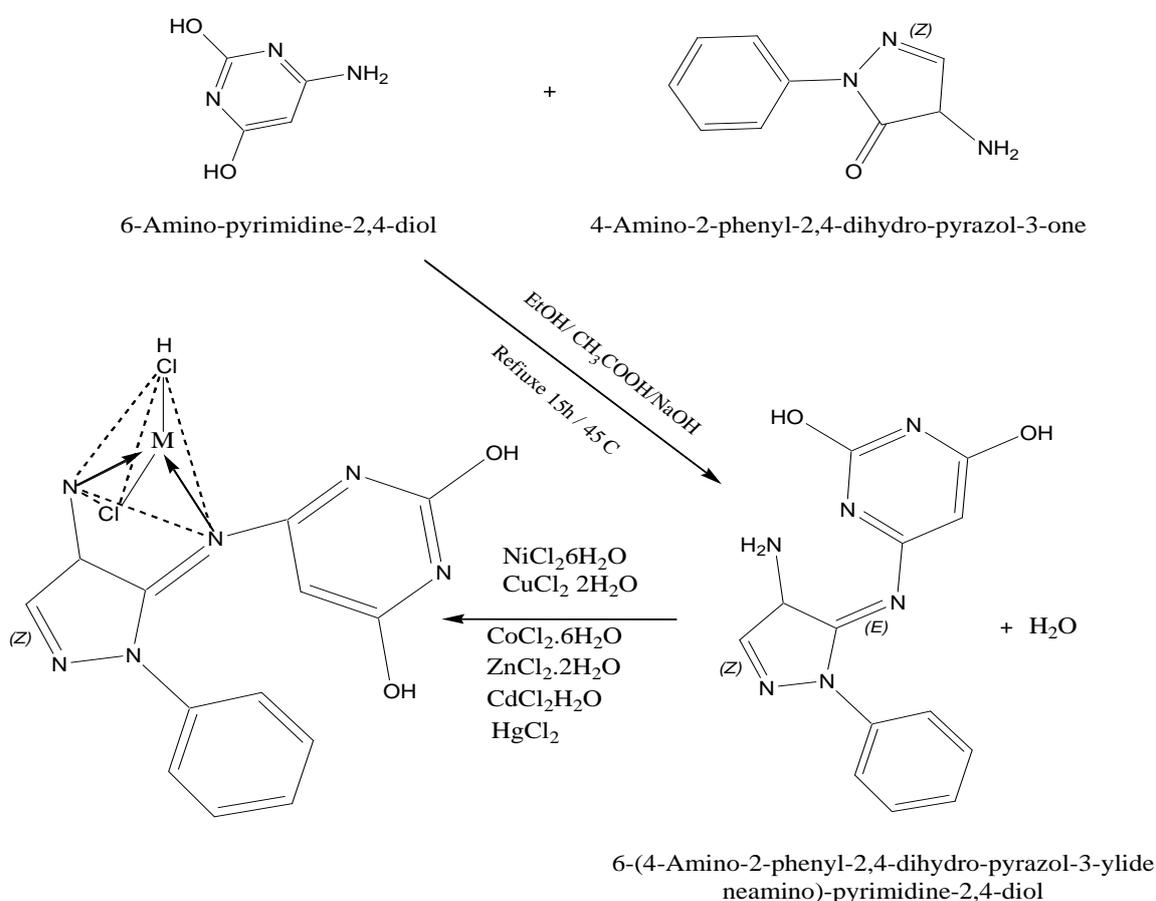
A solution of ligand (H₂L) 6-(4-Amino-2-phenyl-2,4-dihydro-pyrazol-3-ylideneamino)-pyrimidine-2, 4-diol (2.5 g, 0.0088 mole) in hot ethanol was added with stirring to (0.0088 mole) of [HgCl₂, CdCl₂H₂O, ZnCl₂2H₂O, CuCl₂, NiCl₂6H₂O and CoCl₂.6H₂O] respectively. The reaction mixture was allowed to reflux, and the solid was collected by filtration re-crystallized from (hot methanol and water) (1: 1). Scheme (1) Synthesis of metal complexes with Ligand (H₂L). Table (1) Given in elemental analysis and physical properties for the new compounds.

Study of Bioactivity:

All compounds 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 dimethyl salfoxide, the concentration of the compounds in this exposure was (1×10^{-3} M) by using disc sensitivity test literature [10].

Programs used in Theoretical Calculation

A study of the compounds that were prepared using Hyper Chem-8 program to determine the most stable geometric shapes uniting 3D visualization and animation with quantum chemical calculation , molecular mechanics and dynamic (PM3) and (AMBER) are more popular than other semi-empirical methods due to the availability of algorithms and more accurate than with other methods. It has parameterized primarily for organic molecules and selected transition metals [11].



Scheme 1: Synthesis of metal complexes with Ligand (H₂L)

RESULTS AND DISCUSSION

New Tetra dentate metal ions complexes were obtained upon reaction between metal salts all with [M (II)= Co, Ni, Cu, Zn, Cd and Hg] and ligand with molar ratio (1:1) (Metal :Ligand). The ligand synthesized and metal inos complexes are stable in the solid state. The ligand and its metal ions complexes are generally soluble in N,N-dimethyl forammaide (DMF) and The yields, elemental microanalyses of ligand and its metal ions complexes are presented in Table (1). It is found that the analytical data are in a good agreement with the proposed stoichiometry of the complexes. These were determined in dimethyl sulfuxied (DMSO) solution (1×10^{-3} M). Table (1). Physical properties and element analysis and conductivity measurements in (1×10^{-3} M) N,N-dimethyl forammaide for all complexes this attributed non-electrolyte nature [12].

Table 1: Physical properties, Element analysis of new all compounds

Sam.	Molecular Formula =M _w t	m.p. °C	Element microanalysis % Calculated (Found)					Cl
			M	C	H	N	O	
H ₂ L	C ₁₃ H ₁₂ N ₆ O ₂ 284.27	179-181		54.93 (53.88)	4.25 (5.01)	29.56 (3.88)	11.26 (11.56)	-
H ₂ LC ₁	C ₁₃ H ₁₂ N ₆ O ₂ CoCl ₂ 414.11	320 d	14.23 (13.99)	37.70 (38.09)	2.92 (4.11)	20.29 (22.18)	7.73 (8.77)	17.12 (18.14)
H ₂ LC ₂	C ₁₃ H ₁₂ N ₆ O ₂ NiCl ₂ 413.87	334 d	14.18 (15.19)	37.73 (36.79)	2.92 (3.11)	20.31 (21.18)	7.73 (8.11)	17.13 (18.11)
H ₂ LC ₃	C ₁₃ H ₁₂ N ₆ O ₂ CuCl ₂ 418.73	267 d	15.18 (14.99)	37.29 (38.09)	2.89 (3.11)	20.07 (21.18)	7.64 (7.09)	16.93 (15.87)
H ₂ LC ₄	C ₁₃ H ₁₂ N ₆ O ₂ ZnCl ₂ 420.57	295 d	15.55 (14.99)	37.13 (36.09)	2.88 (2.11)	19.98 (20.28)	7.61 (8.88)	16.86 (15.91)
H ₂ LC ₅	C ₁₃ H ₁₂ N ₆ O ₂ CdCl ₂ 467.59	297 d	24.04 (55.99)	33.39 (33.09)	2.59 (3.11)	17.97 (18.28)	6.84 (7.01)	15.16 (14.97)
H ₂ LC ₆	C ₁₃ H ₁₂ N ₆ O ₂ HgCl ₂ 555.77	288 d	36.09 (35.99)	28.09 (29.09)	2.18 (1.11)	15.12 (16.18)	5.76 (6.01)	12.76 (13.11)

d = decompose

Mass spectra for ligand

The mass spectrum of ligand (H₂L) 6-(4-Amino-2-phenyl-2,4-dihydro-pyrazol-3-ylideneamino)-pyrimidine-2,4-diol [(C₁₃H₁₂N₆O₂) = 284.27] confirms the probable formula by showing a peak at 284 m/z, corresponding to Schiff base [(C₁₃H₁₂N₆O₂), calculated atomic mass 284.27]. The series of peaks in the range of [250, 200 and 143 m/z] may be assigned to various fragments, show Figure 1.

Mass spectra for some complexes

The mass spectrum of [H₂LC₂] = Ni- complex [(C₁₃H₁₂N₆O₂NiCl₂) = 413.87] confirms the probable formula by showing a peak at 414 m/z, corresponding to complex moiety [(C₁₃H₁₂N₆O₂NiCl₂), calculated atomic mass 413.87]. The series of peaks in the range of [345, 306, 205, 204, 176, 76.5 and 60 m/z] may be assigned to various fragments.

The mass spectrum of [H₂LC₅] = Cd-complex [(C₁₃H₁₂N₆O₂CdCl₂) = 467.59] confirms the probable formula by showing peak at 467.6 m/z, to complex formula, calculated atomic mass 467.59. The series of peaks the 336.5, 300, 204, 80 and 76.5 m/z may be assigned to various fragments. Show in Figure 2.

The mass spectrum of [H₂LC₄] = Zn-complex [(C₁₃H₁₂N₆O₂ZnCl₂) = 420.6] confirms the probable formula by showing a peak at 420.57 m/z, corresponding to complex formula, Calculated atomic mass 420.6. The series peaks 336, 300, 205, 204, 79.2 and 36 m/z may be assigned to various fragments, show figure 3.

¹H-NMR spectral studies

The new ligand (H₂L) of compound in the NMR (nuclear magnetic resonance) spectrum showed multiple chemical shifts DMSO-d₆ gives the following signals: phenyl as multiple at (7.008 -8.084 ppm), (7.008 - 8.084 ppm), peaks at (5.008 and 4.493 ppm) are attributable to the phenolic -OH group and amine -NH₂ group, respectively, peak at (9.108 ppm) is attributable to the (-N=C-H) group, The singlet signal appeared at (2.50 ppm) can be assigned to the solvent (DMSO) of the free ligand [13], show Figure 4. Moreover, Hg complex (H₂LC₆) in DMSO-d₆ gives the following signals: phenyl as multiple at (7.063-8.056 ppm), ,N=C-H at (9.112 ppm), peak at (4.503 ppm) is attributable to the primary amine -NH₂ group, peak at (5.63 ppm) is attributable to the phenolic -OH groups present in complex, show Figure 5

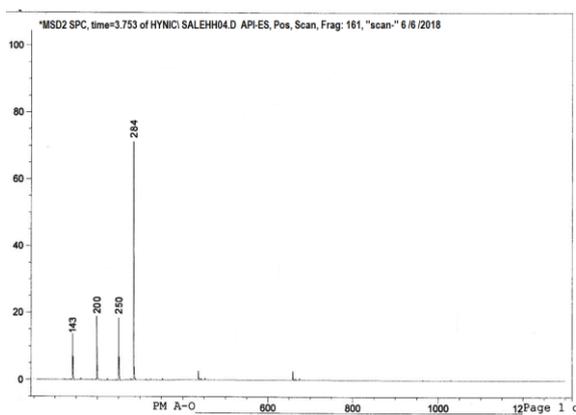


Figure 1: LC-Mass Spectrum of Schiff base Ligand

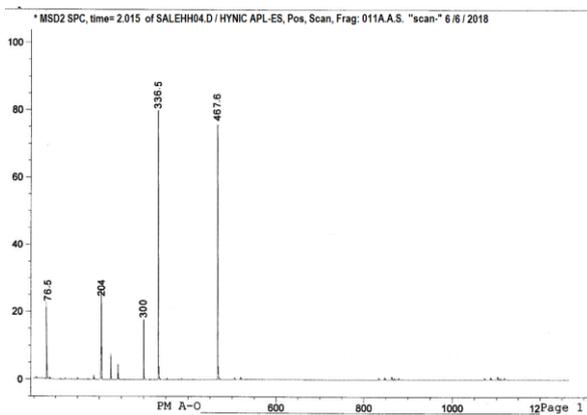


Figure 2: LC- Mass Spectrum of Cd-complex

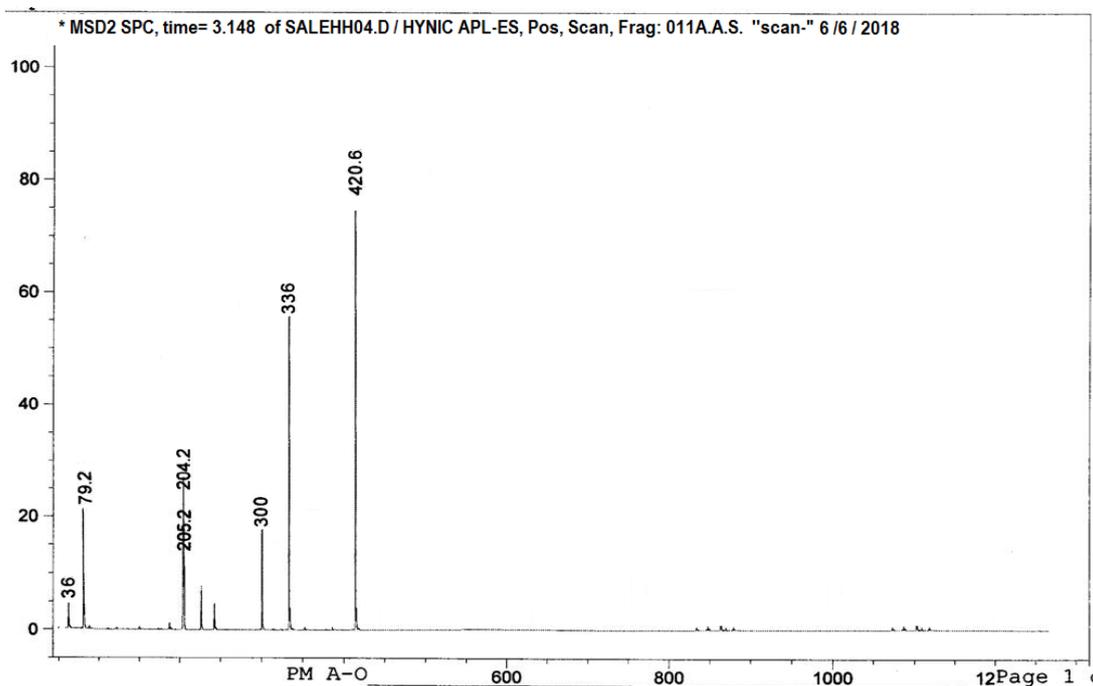


Figure 3: LC-Mass Spectrum of Zn-complex

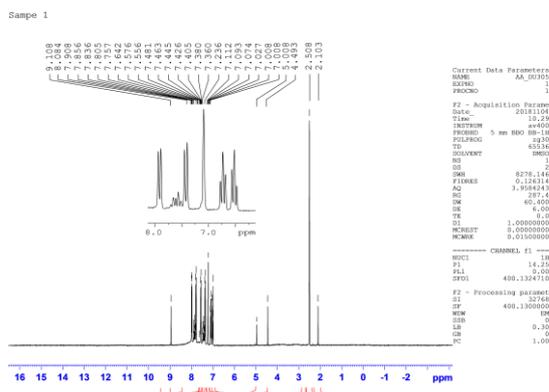


Figure 4: ¹H-NMR Spectrum of free Ligand (H₂L)

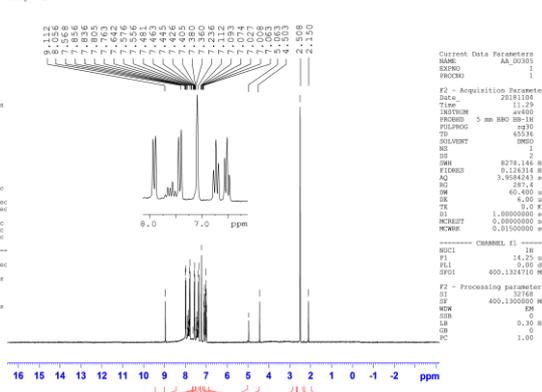


Figure 5: ¹H-NMR Spectrum of Hg-complex

IR spectra

The Infrared (FT-IR) spectrum of the free ligand (H₂L) exhibited a strong high intensity bands appeared at (3312) cm⁻¹, (3288, 3125) cm⁻¹, (1620) and (1589) cm⁻¹ which were ascribed mode of $\nu(\text{O}-\text{H})$ phenol, $\nu(\text{N}-\text{H}_2)$ amine, $\nu(\text{NH}_2)$ amine, $\nu(\text{C}=\text{N})$ azomethen groups and $\nu(\text{C}=\text{N})$ ring, as show in Table 2, respectively. The weak absorption bands appeared at (3029) and (2965) cm⁻¹ were assigned to $\nu(\text{C}-\text{H})$ aromatic and aliphatic, respectively to the complexes, the ligand behaved as a bi dentate ligand, which were been coordinating with the metal via nitrogen of amine group and nitrogen of the azomethene group [14]. The mentioned coordination was confirmed by shifting the bands $\nu(\text{NH}_2)$ and $\nu(\text{C}=\text{N})$ to lower frequencies about (11-18) cm⁻¹ and (15-21) cm⁻¹, respectively [14, 15]. These observations were further indicated by the appearance of $\nu(\text{M}-\text{N})$. The spectra showed new bands at [(563), (578), (513), (575,559), (561) and (569, 519)] cm⁻¹ can be refer to $\nu(\text{M}-\text{N})$ for complexes with metals [M(II) = Co, Ni, Cu, Zn, Cd and Hg, respectively].

Table 2 Infrared Spectra Data of the Free Ligand (H₂L) and its Complexes in (cm⁻¹)

Compounds	$\nu \text{O}-\text{H}$	νNH_2	$\nu\text{C}=\text{N}$	$\nu\text{C}=\text{N}$ ring	$\nu\text{M}-\text{N}$	$\nu(\text{C}-\text{H})$ aromatic	$\nu(\text{C}-\text{H})$ aliphatic
H ₂ L	3312	3288 3125	1620	1589	-	3029	2965
H ₂ LC ₁	3309	3270 3116	1605	1588	563	3087	2983
H ₂ LC ₂	3297	3279 3120	1600	1584	578	3046	2987
H ₂ LC ₃	3321	3281 3120	1599	1586	513	3068	2971
H ₂ LC ₄	3321	3278 3118	1604	1581	575 559	3087	2959
H ₂ LC ₅	3325	3278 3119	1601	1587	561	3077	2957
H ₂ LC ₆	3299	3281 3118	1599	1580	569 519	3029	2986

Electronic Spectral of Compounds

The electronic spectra of the ligand H₂L exhibit intense absorption at (265) and (315) nm for H₂L attributed to ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transitions respectively [16, 17]. The electronic spectra of the Cobalt complex with H₂L ligand exhibit one absorption band at 677 nm which are attributed to ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1\text{P}$. Furthermore, the magnetic moment of the cobalt (II) (d7), was found to be 4.1 B.M., All the above mentioned data correspond to an tetrahedral geometry [17].

The electronic spectra of the Nickel complexes with H₂L 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 Nickle (II) (d8) complexes is found to be 3.9 B.M., All the above mentioned data correspond to an tetrahedral geometry [17,18]. The electronic spectra of the Copper (II) complexes exhibit one absorption band with H₂L ligand at 953 nm which attributed to ${}^2\text{T}_2 \rightarrow {}^2\text{E}$. Furthermore, the magnetic moment of the Copper (II) (d9) complexes is found to be 2.01 B.M.

Finally, the diamagnetic of Zinc (II), Cadmium (II) and Mercury (II) complexes exhibited absorption bands at [258, 258 and 257 nm] respectively due to ($\pi \rightarrow \pi^*$), and [324, 309 and 310 nm] respectively due to ($n \rightarrow \pi^*$). Appearance of these band are due to ($n \rightarrow \pi^*$) transition associated with azomethine linkage and $\text{M} \rightarrow \text{L}$ (C.T) (metal \rightarrow ligand) charge transfer transition. Moreover, the spectrum of the complexes also shows bands at 345, 380 and 355 nm due to the charge transfer as the electronic configuration of these complexes Zinc (II), Cadmium (II) and Mercury (II) respectively, confirming the absence of any d-d transition [17,19].

Thermal Gravimetric Analyses TGA

To understand the thermal decomposition processes of the studied compounds, the ligand and its some metal complexes were examined by thermo gravimetric analysis in the temperature range of 30–700 °C. TG curve of ligand (H₂L) show relatively rapid decomposition in the first bending (110 - 572 °C), step with T_{DTG} peak at 287 °C. The very large and strongly sharp T_{DTG} peak observed for the step at 287 °C is preceded with a sharp peak. 83.419%, mass losses in the step correspond to the release of (C₁₂H₁₂N₆) fragments (cal. 84.426 %), fragments and final product (CO₂) (calculated. 15.573% and Estimated 16.581%), Show Figure 6 and the Table 3 Characterization Parameters of thermal decomposition (10°C min⁻¹) of ligand [20].

The TG curve of Co(II) complex with H₂L show relatively rapid decomposition in the first (230 - 337 °C) and second (340 – 595 °C) steps with T_{DTG} peaks at 293 °C and 472 °C. The very large and strongly sharp T_{DTG} peak observed for the first step at 472 °C is preceded with a sharp peak. 26.811 % and 54.831 % mass losses in the first and second steps correspond to the release of (Cl₂C₂H₃N) and (C₁₁H₉N₅O) fragments and final product metal oxide (CoO) (cal. 27.094 %, 55 011 % and 17.895%, respectively). The tentative decomposition reaction of (H₂LC₁), is shown in Table 3 and the Figure7.

The TG curve of Cu (II) complex with H₂L show relatively rapid decomposition in the first (157-231°C), second (231- 396°C) and third (396- 599.6°C) steps with T_{DTG} peaks at 203 °C, 349 °C and 486 °C. The very large and strongly sharp T_{DTG} peak observed for the first step at 349 °C is preceded with a sharp peak. 15.401 %, 20.449% and 41.811 % mass losses in the first, second and third steps correspond to the release of (Cl₂), (C₄H₅N₂) and (C₉H₇N₄) fragments and final product (CuO) (cal. 16.746 %, 19.378 %, 40.831 % and 23.045 respectively). The tentative decomposition reaction of (H₂LC₃), is shown in Table 3.

The TG curve of Hg (II) complex with H₂L show relatively rapid decomposition in the first (142 - 205 °C) and second (275 – 528 °C) steps with T_{DTG} peaks at 185 °C and 398 °C. The very large and strongly sharp T_{DTG} peak observed for the first step at 398 °C is preceded with a sharp peak. 13.084 % and 47.947 % mass losses in the first and second steps correspond to the release of (Cl₂) and (C₁₃H₁₂N₆O) fragments and final product (HgO) (cal. 12.595 %, 48.221%, 39.184 % and respectively). The tentative decomposition reaction of (H₂LC₆), is shown in Table 5. [7, 9, 22, 23].

Table 3: 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 ₂ L	110-572	287	83.419(84.426)	83.419(84.426)	C ₁₂ H ₁₂ N ₆ CO ₂
H ₂ LC ₁	230-337	293	(26.811) 27.094	82.105	-Cl ₂ C ₂ H ₃ N -C ₁₁ H ₉ N ₅ O CoO
	340-595	472	(54.831) 55.011	(81.642)	
H ₂ LC ₃	157-231	203	(16.746)15.401	77.661	Cl ₂ C ₄ H ₅ N ₂ C ₉ H ₇ N ₄ CuO
	231-396	349	(19.378) 20.449	(76.955)	
	396-599	486	(40.831) 41.811		
H ₂ L	142-205	185	(12.595) 13.084	61.031	Cl ₂ C ₁₃ H ₁₂ N ₆ O HgO
	275-528	398	(48.221) 47.947	(60.816)	

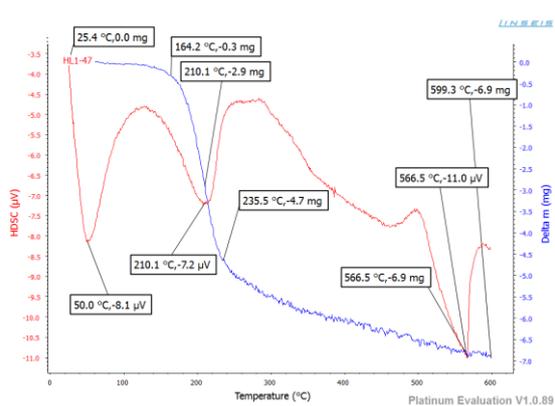
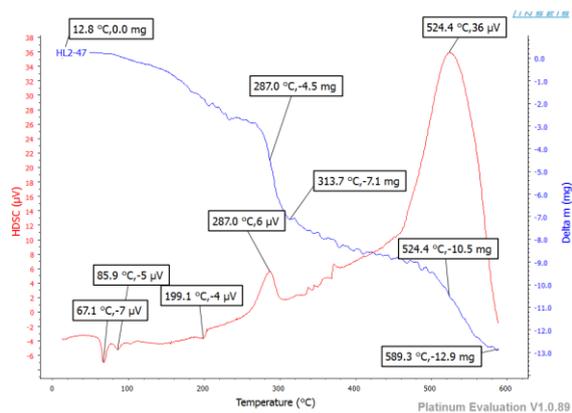
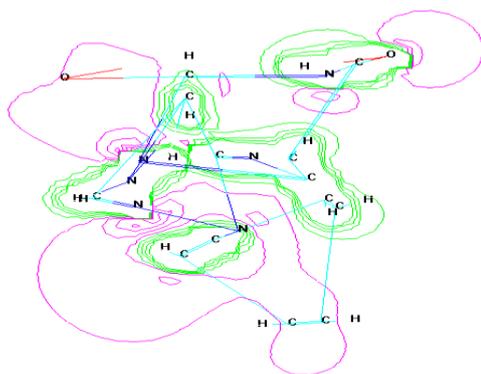

 Figure 6: TGA and DTA Curve of Ligand H₂L


Figure 7: TGA and DTA Curve of Co-Complex

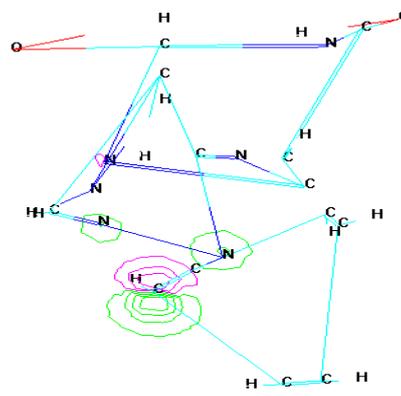
Electrostatic Potentials:

Electron distribution governs the electrostatic potential of the molecules. The (E.P) electrostatic potential 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 electro static potential is strongly negative (electrophonic attack) [22]. The (E.P) electrostatic potential of the free ligand was calculated and plotted as 3D contour to investigate the reactive sites of the molecules, Figure 8. Also one can interpret the stereochemistry and rates of many reactions involving “soft” nucleophiles and electrophiles in terms of the properties of frontier orbital HOMO and LUMO. The results of calculations show that the LUMO of transition metal ions prefer to react with the HOMO of three-donor atoms of two oxygen of phenol, nitrogen of amine and nitrogen of azomethen group for free ligand, Figure 9.

All theoretically probable structures of free ligand and their complexes have been calculated by (PM3) and (ZINDO/1) methods in gas phase to search for the most probable model building stable structure, Table 4. [23].



Electrostatic Potential 2D



HOMO & LUMO = -8.0305 eV

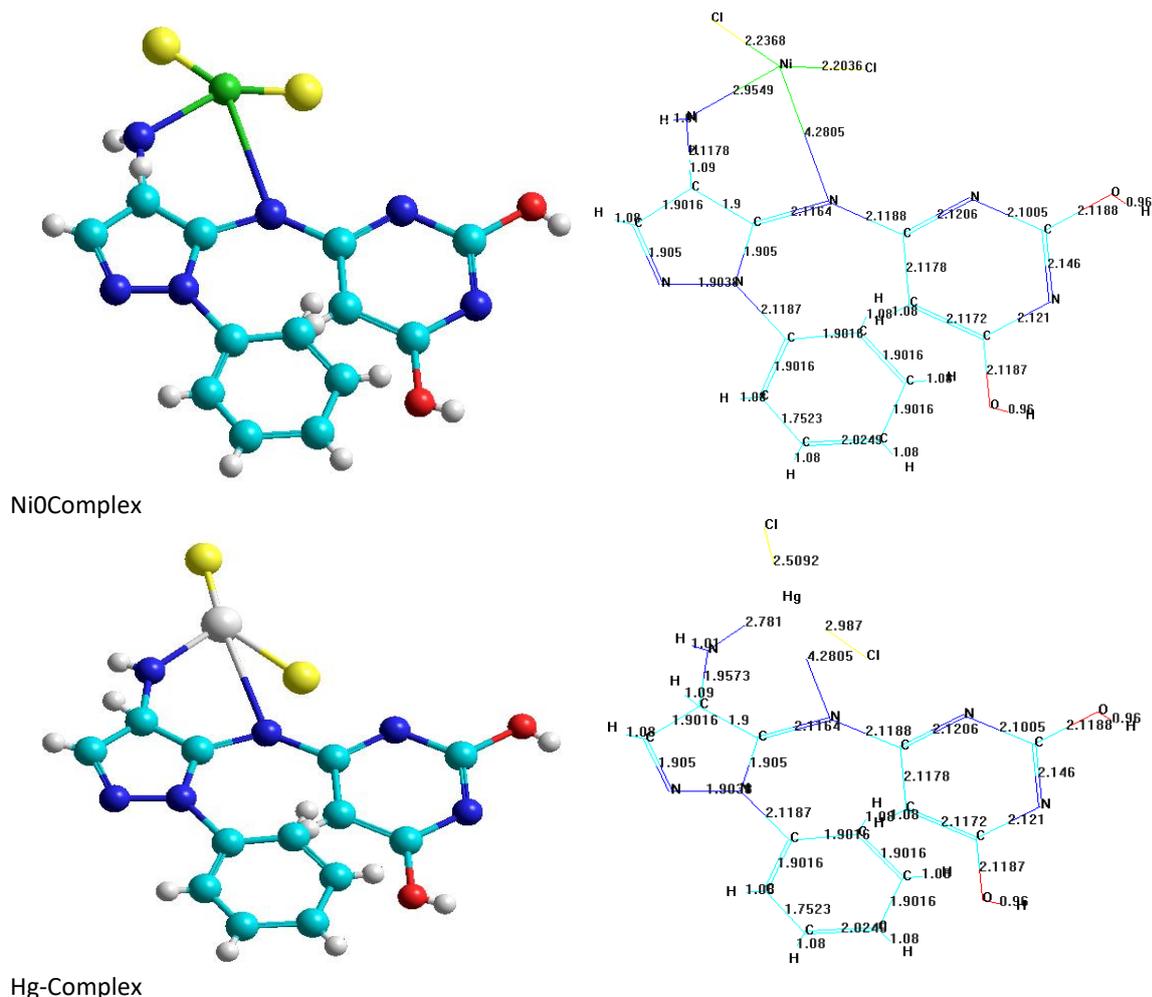


Figure 9: Conformational Structure of metal complexes

Bio activity of ligand and all complexes

Ligand and their complexes of metal ions were screened for antibacterial and antifungal activity. The entire tested compounds exhibited variable activity antifungal and antibacterial as shown in Table 5. Ligand activity exhibited antibacterial against *S. aureus* and *P. aeruginosa* but activity was to be lower than the metal complexes. Schiff base which did not exhibit have antifungal activity but exhibited activity was in some metal complexes as shown in, Table 5. 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, exhibited some complexes Prepared antifungal activity strong against *F. graminearum* and *M. phaseolina* as compared with the ligand which did not exhibit antimicrobial activity. From the data shown in the Table 5, a lot of compounds exhibited bio activity against 2 kinds of bacteria and 4 kinds of fungal.

Table 5: Antibacterial and antifungal activities for ligands, metal Salts and complexes.

Comp.	<i>Staphylococcus aureus</i> G(+)		<i>Pseudomonas aeruginosa</i> G(-)		<i>Penicillium expansum</i>		<i>Fusarium graminearum</i>		<i>Macrophomina phaseolina</i>		<i>Candida albicans</i>	
	A	B	A	B	A	B	A	B	A	B	A	B
H ₂ L	12	-	12	-	-	-	-	-	-	-	-	-
H ₂ LC ₁	20	-	12	-	-	-	-	-	-	-	-	-
H ₂ LC ₂	16	-	15	-	20	18	28	22	24	16	-	-
H ₂ LC ₃	20	-	15	-	13	-	-	-	25	16	-	-

H ₂ LC ₄	12	-	10	-	-	-	-	-	-	-	-	-
H ₂ LC ₅	24	-	14	10	-	-	-	-	20	15	-	-
H ₂ LC ₆	18	-	20	18	23	20	-	-	25	14	-	-

A=conc., B=dilu.

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