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Theoretical Treatment, Synthesis and Characterization of Some New Schiff Base Transition Metal Complexes.

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ABSTRACT

The complexes Schiff base (6-[2-Hydroxy - benzylidene)-amino]-pyrimidine-2,4-diol) (L) with Cu(II), Zn(II), Cd(II) and Hg(II) were prepared. The Schiff base and complexes have been characterized by FT-IR, ^{1}H-NMR UV-Vis, Mass spectra, magnetic moment, elemental microanalyses (C.H.N.), and molar conductance. The work also include a theoretical treatment of the formed complexes in the gas phase, this was done using the (hyperchem-8) program for the molecular mechanics and semi-empirical calculations. The electrostatic potential of the free ligands were calculated to investigate the reactive sites of the molecules .The heat of formation(ΔHf°) and binding energy(ΔEb) at 298K for the free ligands and its metal complexes were calculated by using PM3 method.

Keywords: Theoretical treatment, Schiff base, complex, (PM3) method

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INTRODUCTION

Schiff bases sustain azomethine or imine (–C=N) unit. This is the primary condensation of amines with carbonyl compounds and have been reported by Hugo Schiff [1-3]. Schiff bases have a wide variety of applications in different areas such as biological chemistry, organic and inorganic chemistry. The medicinal uses and applications Schiff bases and their metal complexes are of increasing clinical and commercial importance. Schiff bases have picked up significance in medicinal and pharmaceutical field because of an expansive range of biological activities like anti-inflammatory [4-7], analgesic [5-8], antimicrobial and antispasmodic [9,10].

The stability of the Schiff base complexes depends onthe strength of the C=N bond, basicity of the imino group andsteric factors. The presence of a second functional group with a replaceable hydrogen atom, preferably a hydroxyl group very near to the imine group allows the ligand to form a fairly stable four, five, or six membered ring on chelation to the metal atom. The role of the metal ions in these complexes seems to involve both stabilization and trapping of the Schiff base, and in addition it also ensures the planarity of the system [9] .

Experimental

Materials and Methods

The following chemicals were commercially available and were used without further purification: 4-Amino-2,6-dihydroxypyrimidin and 4-Di methyl amino benzaldehyde DMSO, pure ethanol, methanol from Fluka, acetic acid glacier from Riedel, $CuCl_2.2H_2O$, diethyl ether, $CaCl_2$, $ZnCl_2$, $CdCl_2.2H_2O$ and $HgCl_2$Aldrich.

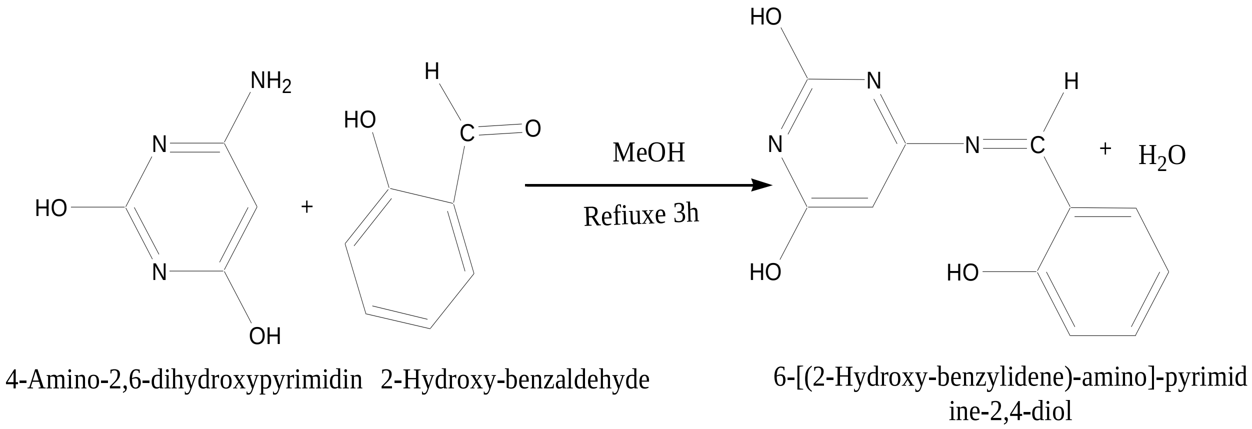
Instrumentation

Elemental (C.H.N) analyses were carried out on a Perkin-Elmer automatic equipment model 240.B. Mass spectra were obtained by using Mass 100P Shimadzu. Metal ratios were identified using a Shimadzu (A.A) 680G atomic absorption Spectrometer. Electronic absorption spectra were recorded in the range (200-900) nm for solution in DMSO ($1×10^{-3}$) on a Shimadzu 160 Spectrophotometer. FT-IR spectra were recorded in the range (4000-400) cm^{-1} on a Shimadzu 3800, spectrometer. ^{1}H-NMR spectra were acquired in DMSO -d_6 solution using Brucker AMX 300 MHz spectrometer. Melting points were obtained on a Buchi SMP-20 capillary melting point apparatus and are uncorrected. Conductivity measurements were measured for solution in DMSO ($1×10^{-3}$) using a Jenway 4071 digital conductivity meter at room temperature. Magnetic properties were measured using (Magnetic susceptibility balance model MSR-MKi).

Synthesis of Schiff base Ligand: 6-[2-Hydroxy - benzylidene)-amino]-pyrimidine-2,4-diol (L):

A solution of 2-Hydroxy-benzaldehyde (0.960 g, 7.867 mmol) in methanol (15 ml) was mixed with a solution of 4-amino-2,6-dihydroxypyrimidine (1 g, 7.867 mmol). The reaction was reflux for 3hrs. A dark yellow precipitated formed which was washed with diethyl ether and recrystallized from methanol: water (1:1) mixture. The product was dried via anhydrous $CaCl_2$ in vacuum as shown in Scheme (1).

The yield is 89.8%, mp.198-199°C. ^{1}H-NMR (DMSO-d_6, ppm):5.06 (s, 3H, O-H phenol), 7.57- 8.06 (m, 5H, arom-CH), 8.98(s, 1H, N=C-H azomethine), Figure (1).



Scheme 1: Preparation of the Ligand (L)

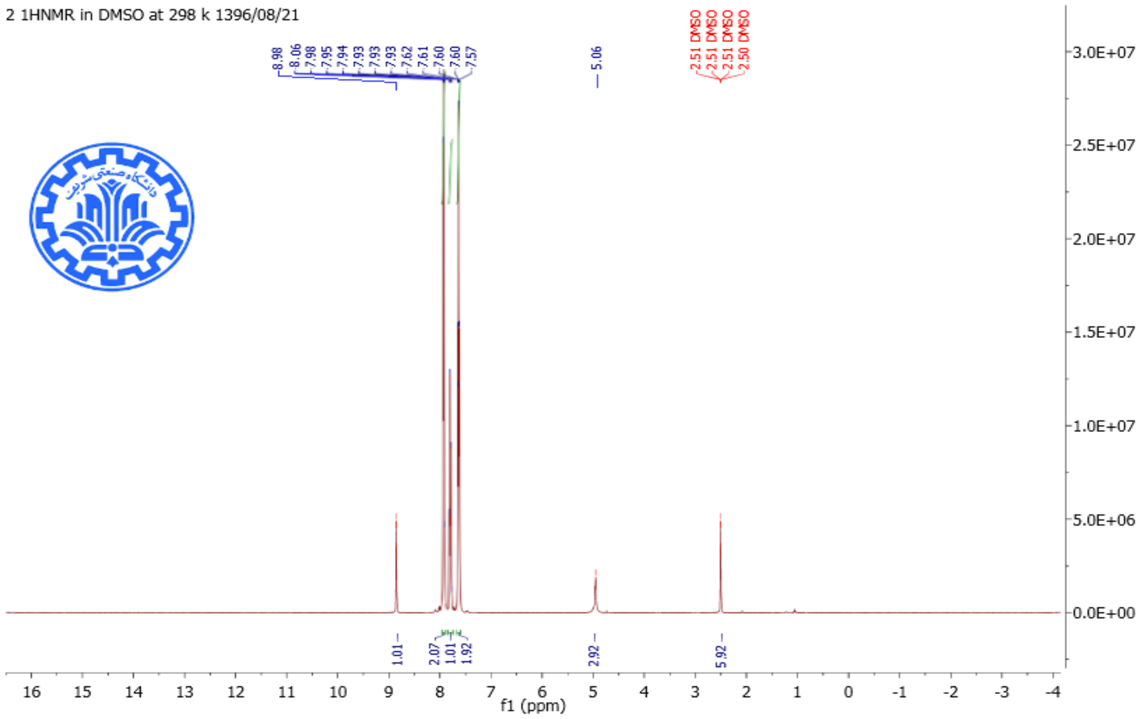
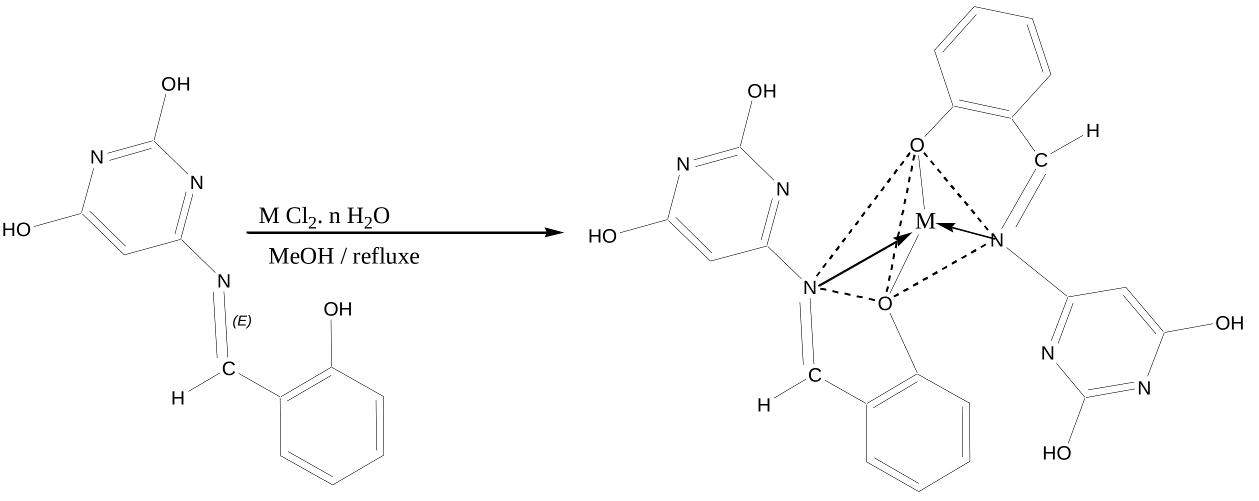


Figure 1: ^{1}H-NMR spectrum for Ligand

Preparation of Complexes:

A solution of ligand (6-[Hydroxy - benzylidene)-amino]-pyrimidine-2,4-diol) (1.5 g, 6.487 mmole) in methanol was added gradually with stirring to (12.974 mmol) of $CuCl_2.2H_2O$, $ZnCl_2$, $CdCl_2.2H_2O$ and $HgCl_2$, respectively. The reaction mixture was allowed to reflux and the solid was collected by filtration recrystallized from ethanol and dried at room temperature, shown in Scheme (2). Physical properties and elemental microanalysis for the complexes are given in Table (1).



M(II)= Cu, n= 2; Zn, n= 0 ; Cd, n= 2; and Hg, n= 0.

Scheme 2: Preparation of the Complexes

RESULTS AND DISCUSSION

Complexes were obtained upon reaction between metal ions and bidentate ligand (6-[Hydroxy-benzylidene)-amino]-pyrimidine-2,4-diol) with molar ratio (1:2) (M:L). The synthesized ligand and its complexes are very stable at room temperature in the solid state. The compounds are generally soluble in hot DMF and DMSO. The yields, melting/decomposition points, elemental micro analyses of Schiff base and its metals 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. Schiff base was melting point at temperatures normal than 198-199ºC. Molar conductance values were found in the range (9-21) S. cm^2 mol^{-1} for all complexes which indicate that they are non-electrolytes. These were determined in (DMSO) solution (1 ×10^{-3}M). Physical properties and elemental microanalysis are listed in Table 1.

Table 1: Microanalysis results and some physical properties of the Ligand and its complexes

Symb.	Molecular Formula =M_{Wt}	m.p. °C	Element analysis % Calcu. (Found)			
			M	C	H	N
L	$C_{11}H_9N_3O_3$ 231.21	198 -199		57.14 (56.89)	3.92 (3.81)	18.17 (19.78)
LCu	$C_{22}H_{16}N_6O_6Cu$ 523.95	323d	12.13 (11.89)	50.43 (51.09)	3.08 (4.01)	16.04 (15.18)
LZn	$C_{22}H_{16}N_6O_6Zn$ 525.79	344 d	12.44 (12.99)	50.25 (49.79)	3.07 (3.11)	15.98 (15.18)
LCd	$C_{22}H_{16}N_6O_6Cd$ 572.81	298 d	19.62 (18.99)	46.13 (45.89)	2.82 (3.11)	14.67 (15.18)
LHg	$C_{22}H_{16}N_6O_6Hg$ 660.99	309 d	30.35 (29.99)	39.98 (39.09)	2.44 (2.09)	12.71 (13.28)

d = decompose

Mass spectra for complexes

The LC-Mass spectra of complexes [L, LCu and LCd] (Figure 2, Figure 3) showed the parent ion peaks at (m/z=231.4), (m/z = 523.95) and (m/z=572.81) correspond to (M= $C_{11}H_9N_3O_3$), (M= $C_{22}H_{16}N_6O_6Cu$) and (M= $C_{22}H_{16}N_6O_6Cd$) respectively. The fragmentation pattern is shown in Table(2) .

Table 2: The Fragmentation Pattern data for ligand and it is metal Complexes

Compounds	Peaks
L = $C_{11}H_9N_3O_3$ = 231.21	231.1, 207
LCu = $C_{22}H_{16}N_6O_6Cu$= 523.95	524, 515.2, 282.2, 164.2
LCd =$C_{22}H_{16}N_6O_6Cd$= 572.81	573.1, 563.4, 548.4, 513.2, 491, 451,429,….

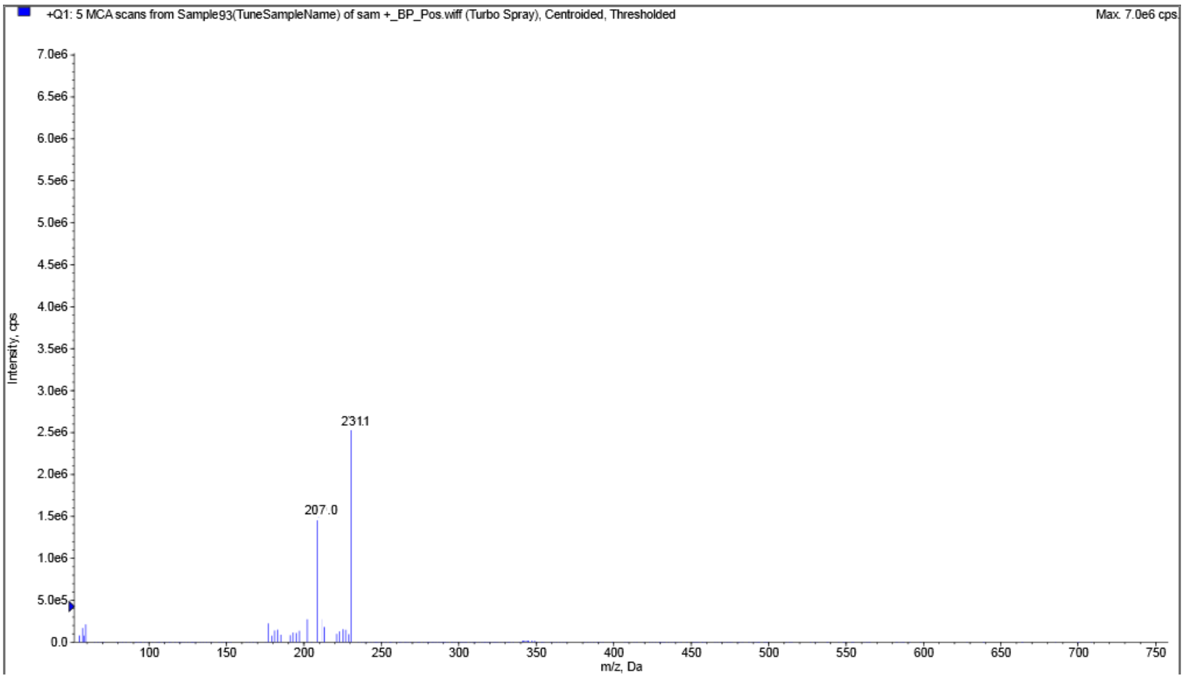


Figure 2: Mass Spectrum of ligand

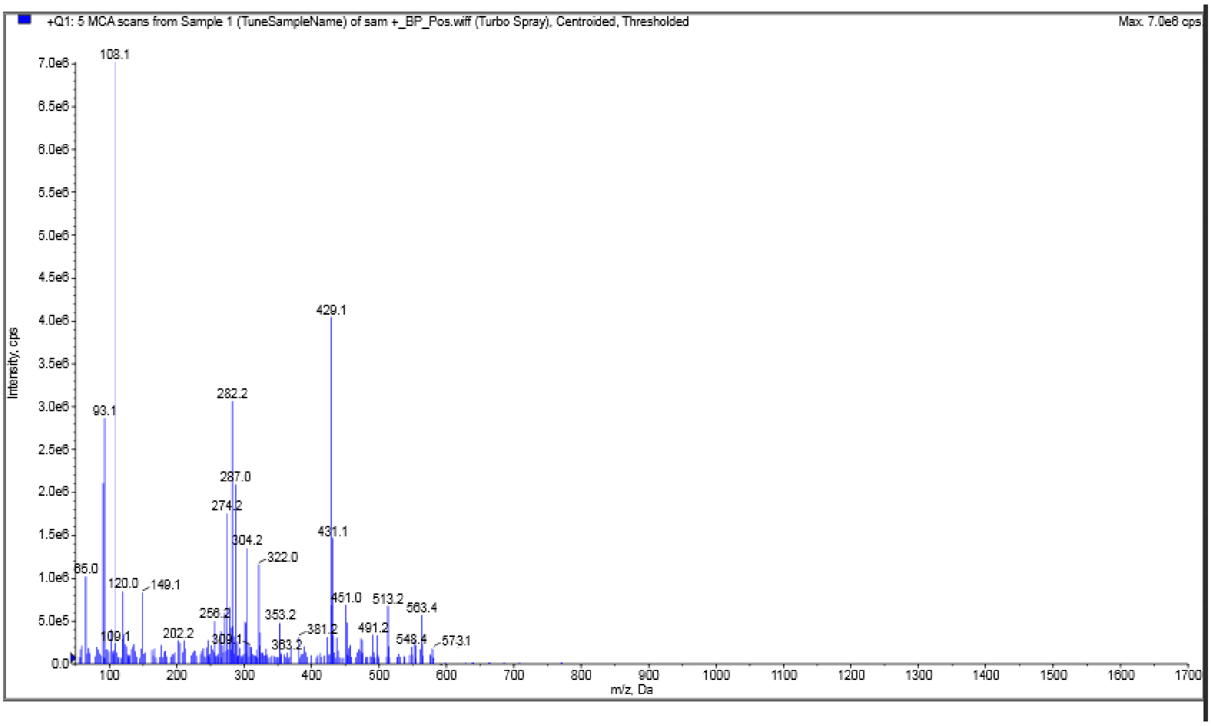


Figure 3: Mass Spectrum of [Cd (L)$_2$]

IR Spectra

The IR spectra bands of the ligand (L) and its complexes were characterized at 3058 and 3047 cm^{-1} due to the ν(CH) aromatic, 2984, 2989 cm^{-1} ν(CH) aldehyde, 3512 cm^{-1}ν(O-H) phenol,1655, 1608 cm^{-1} υ(C=C) and 1713 cm^{-1} υ(C=N) azomethine, functional groups, respectively, for the ligand [10].

The IR spectra of the complexes exhibited ligand bands with the appropriate shifts due complexes formation [10,11].This indicates that the ligand was coordinated with the metal ions through the nitrogen azomethine group, oxygen phenol group. At lower frequency the complexes exhibited new bands around (455-418), and (529-459) cm^{-1} assigned to the υ(M-O)and υ(M-N), respectively [12,13].

Table 2: FT-IR spectral data (wave number υ^{-}) cm^{-1} for the ligand and its complexes

Compounds	υ (O-H) phenol	υ (C-H) aromatic	υ (C-H) aldehyde	C=C	C=N	M-N	M-O
L	3512	3058 3047	2984, 2989	1655 1608	1713	-	-
LCu	3517	3055	2824	1605	1673	459 497	418
LZn	3611	3055	2879 2886	1627 1604	1677	479 520	448 420
LCd	3623	3043 3049	2824 2845	1650, 1611	1665	470 512	428
LHg	3516	3044	2852 2841	1643 1611	1640	498 529	424 455

Electronic spectral, magnetic moments:

The electronic spectra of the free ligand L, Figure 4 shows electronic transitions π→π* and n→π* at 262 and 340 460 nm respectively. Finally, the diamagnetic of Zn(II), Cd(II) and Hg(II) complexes exhibited absorption bands at 276, 277 and 280 nm due to π→π*. Appearance of these band are due to n→π* transition associated with azomethine linkage and M→L (C.T) charge transfer transition. Moreover, the absorption bands at 276, 277 and 280 nm due to π→π*. Moreover, the spectrum of the complexes also shows bands at 410, 421 and 424 nm due to the charge transfer as the electronic configuration of these complexes Zn (II), Cd (II) and Hg (II) respectively. The electronic spectrum of Cu$^{(II)}$ complex showed four broad peaks at 289 nm, 401 nm, 571 and 668 nm assigned to π →π*, n →π* and C.T , $^{2}B_{1g}$→$^{2}A_{1g}$ and $^{2}B_{1g}$→$^{2}E_{1g}$ respectively, suggesting a tetrahedral geometry [14,15].

In this case the magnetic moment for Zn$^{(II)}$, Cd$^{(II)}$ and Hg $^{(II)}$ complexes are diamagnetic, but Cu(II) complex 1.67 B.M which confirmed the tetrahedral geometry for complexes [16]. All the absorption bands were fully assigned in Table (3).

Table 3: Electronic data magnetic moment and molar conductivity for ligand and its complexes

compounds	λ_{max} nm	ϒ cm^{-1}	Assignment	μ_{eff} M.B.
L	**460**	**21739.13**	**n→π***	**-**
	340	**29411.76**	**n→π***	
	262	**38167.93**	**π →π***	
LCu	**289**	**34602.07**	**π→π***	**1.67**
	401	**24937.65**	**n→π* and C.T**	
	571	**17513.13**	**$^{2}B_{1g}$→$^{2}A_{1g}$**	
	668	**14970.05**	**$^{2}B_{1g}$→$^{2}A_{1g}$**	
LZn	**410**	**24390.24**	**C.T and n→π***	**diamagnetic**
	276	**36231.88**	**π→π***	
LCd	**421**	**23752.97**	**C.T and n→π***	**diamagnetic**
	277	**36101.08**	**π→π***	

LHg	**424** **280**	**23584.9** **35714.28**	**C.T and n→π*** **π→π***	**diamagnetic**

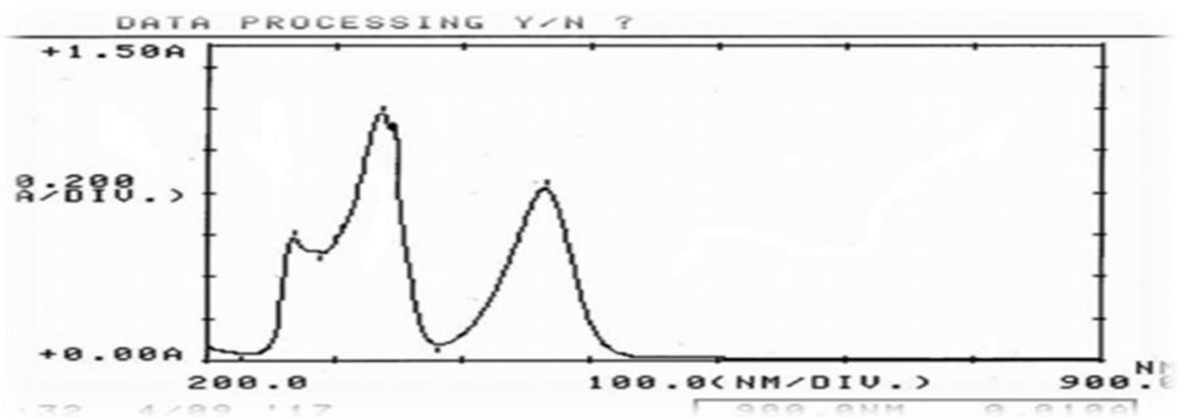


Figure 4: UV-Vis Spectrum of Ligand L

Theoretical studies in Gas State

Electrostatic Potentials:

Electron distribution governs the electrostatic potential of the molecules. The electrostatic potential (E.P) describes the interaction of energy of the molecular system with a positive point charge. (E.P) is useful for finding sites of reaction in a molecule; positively charged species tend to attack a molecule where the electro static potential is strongly negative (electrophonic attack) [16]. The (E.P) of the free ligand (L) was calculated and plotted as 2D contour to investigate the reactive sites of the molecules, figure 6. Also one can interpret the stereochemistry and rates of many reactions involving “soft” electrophiles and nucleophiles in terms of the properties of frontier orbital (HOMO, highest occupied molecular orbital) and (LUMO, lowest unoccupied molecules). The results of calculations show that the LUMO of metal ions prefer to react with the HOMO of two-donor atoms with nitrogen of azomethane and oxygen of the hydroxyl group for free ligand (L).

Optimized energies:

The program Hyperchem-8 was used for the semi-empirical and molecular mechanics calculations. The heat of formation (ΔH_f^o) and binding energy (ΔE_b) for free ligand and their metal complexes were calculated, table(4).

Optimized vibrational spectra for ligand (L):

The vibrational spectra of the free ligand and their metal complexes have been calculated, table 5. The theoretically calculated wave numbers for this ligand showed that some deviations from the experimental values, these deviations are generally acceptable in theoretical calculations [17]. The most diagnostic calculated vibrational frequencies were chosen for the assignment of ligand (L) and metal complexes which are included in table (5) and their respective experimental vibrational modes are shown in the same table (2). The results obtained for the theoretical calculations of the frequencies agreed well with those obtained for the experimental values, tables (2).

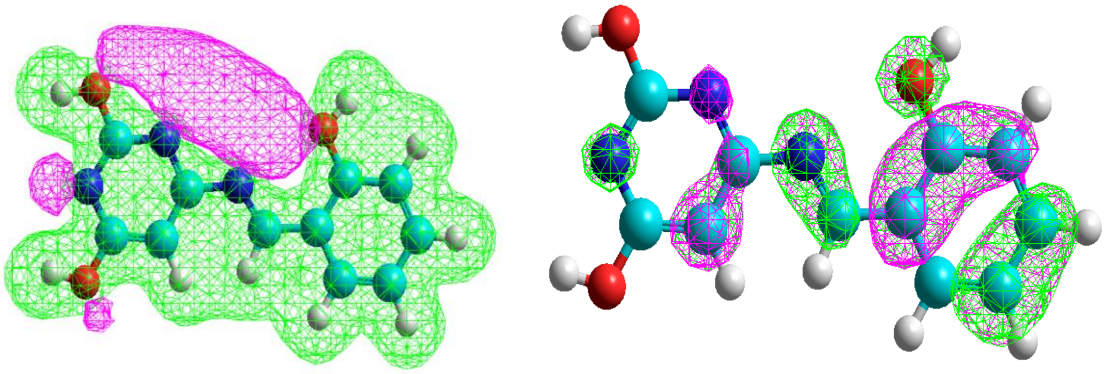


Figure 5: Electrostatic potential and (HOMO & LUMO) as 3D contours for (L).

Bond length measurements for the (H_2L) and their metal complexes:

Calculation of parameters has been optimized bond lengths of the free ligand (H_2L) and their metal complexes by applying the Semi-empirical (PM3) at Geometry Optimization (0.001 $K.Cal.mol^{-1}$), which to give excellent agreement with the experimental data [18,19] as shown in table (5) .

Table 4: Conformation energetic (in $KJ. mol^{-1}$) for naringin and its metal complexes

Compounds	ΔE_{tot}	ΔH^o_f	ΔE_b	Dipole (Debyes)
L	-64769.9765	-52.7211748	-2919.1061	2.6892
LCu	-156578.4393	-208.83966	-5970.20766	10.284
LZn	-1212.65785	-167.3495	-5687.46879	8.214
LCd	-1478.341587	-201.54781	-1346.4628	5.147
LHg	-1241.15974	-209.24861	-4620.15974	7.357

Table 5: Comparison between the experimental and theoretical vibational frequencies (cm^{-1}) for free ligand (L) metal complexes

Com.	υ (O-H) phenol		C=N		M-N		M-O	
L	3512**	3577*	1688*	1713**	-			
LCu	3517**	3455*	1546*	1673**	469*	459** 497**	501*	418**
LZn	3611**	3550*	1557*	1677**	510* 611*	479** 520**	514* 557*	448** 420**
LCd	3623**	3555*	1549*	1665**	510*	470** 512**	510*	428**
LHg	3516**	3540*	1597*	1640**	542* 588*	498** 529**	506* 587*	424** 455**

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

Table 6: Selected bond lengths (A°) for (E) ligand and their metal complexes

Compounds	C=N	C-O	M-N	M-O
L	**1.2969**	**1.3582**		
LCu	**1.6095**	**0.91293**	**1.245**	**1.313**
LZn	**1.6095**	**0.91293**	**1.245**	**1.313**
LCd	**1.6095**	**0.91293**	**1.244**	**1.313**
LHg	**1.6095**	**0.91293**	**1.245**	**1.313**

Theoretical electronic spectra for the metal complexes

The electronic spectra of the metal complexes have been calculated and the wave number for these compounds showed some deviations from the experimental values as shown in table(7) . These deviations in theoretical calculation are generally acceptable due to couplings between the electronic spectra modes and the approximation that each normal mode of the electronic spectra inter acts independently electronic spectra beam [20-22]. The most diagnostic calculated electronic spectra were chosen for the assignment of the metal complexes. Experimental electronic modes are shown in table (3). All the theoretical electronic spectra of all compounds were calculated by using the semi-empirical (PM3) method at geometry optimization (0.01 K.Cal. Mol^{-1}) was used, and the comparison between of the experimental data and theoretical data of the electronic spectra for metal complexes in table (7).

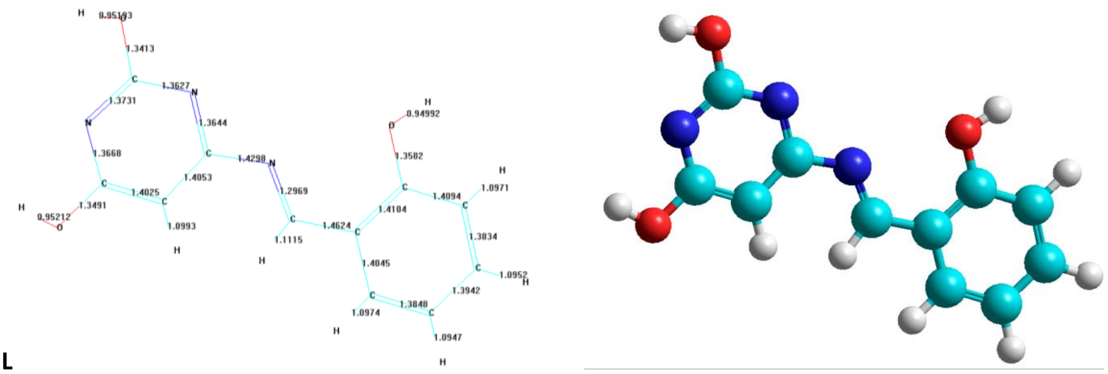
Table 7: Comparison between experimental and theoretical of the electronic spectra for complexes

Complexes	Maximum absorption (nm)		Band assignment	Suggested geometry
LCu	301*	289**	$\pi \rightarrow \pi^*$	Tetrahedral
	419*	401**	$n \rightarrow \pi^*$ and C.T	
	598*	571**	$^2B_{1g} \rightarrow ^2A_{1g}$	
	743*	668**	$^2B_{1g} \rightarrow ^2A_{1g}$	
LZn	501*	410**	C.T and $n \rightarrow \pi^*$	Tetrahedral
	312*	276**	$\pi \rightarrow \pi^*$	
LCd	510*	421**	C.T and $n \rightarrow \pi^*$	Tetrahedral
	312*	277**	$\pi \rightarrow \pi^*$	
LHg	512*	424**	C.T and $n \rightarrow \pi^*$	Tetrahedral
	315*	280**	$\pi \rightarrow \pi^*$	

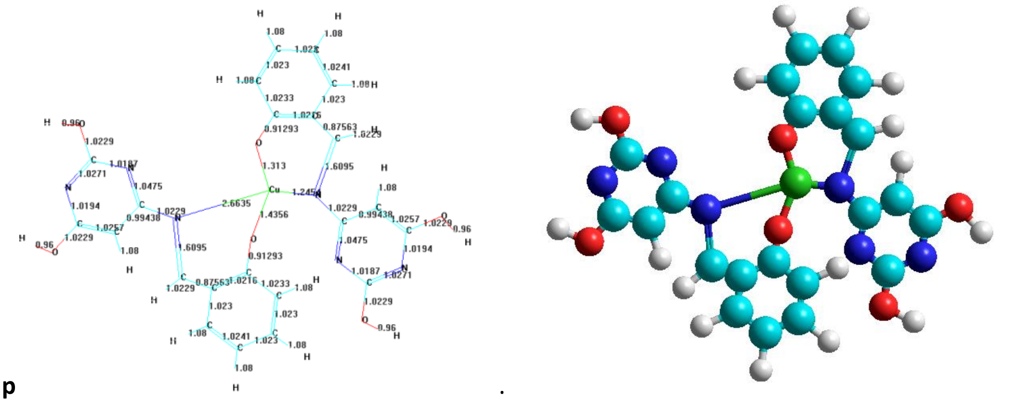
Where: *Theoretical frequency; **Experimental frequency

Optimized geometries of (L) and their complexes:

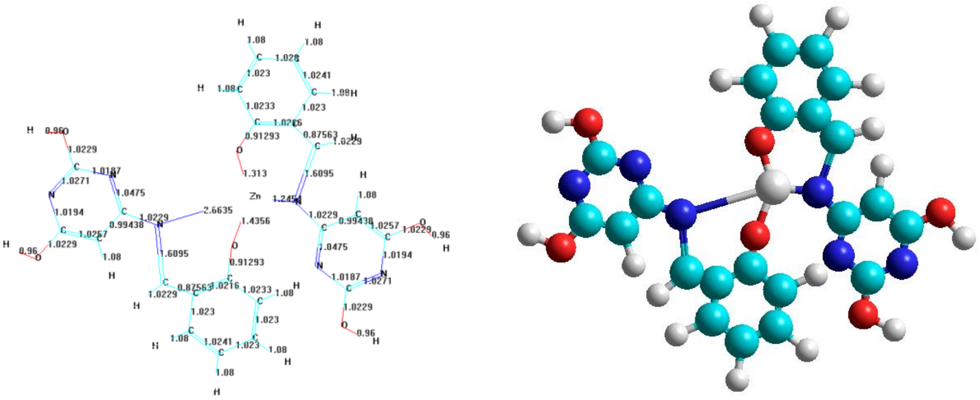
All theoretically probable structures of free ligand and their complexes have been calculated by (PM3) method in gas phase to search for the most probable model building stable structure, figure (4).



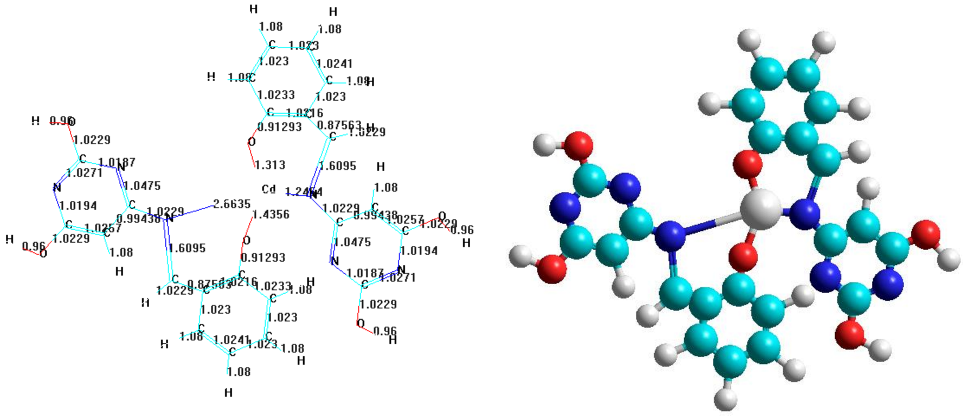
L



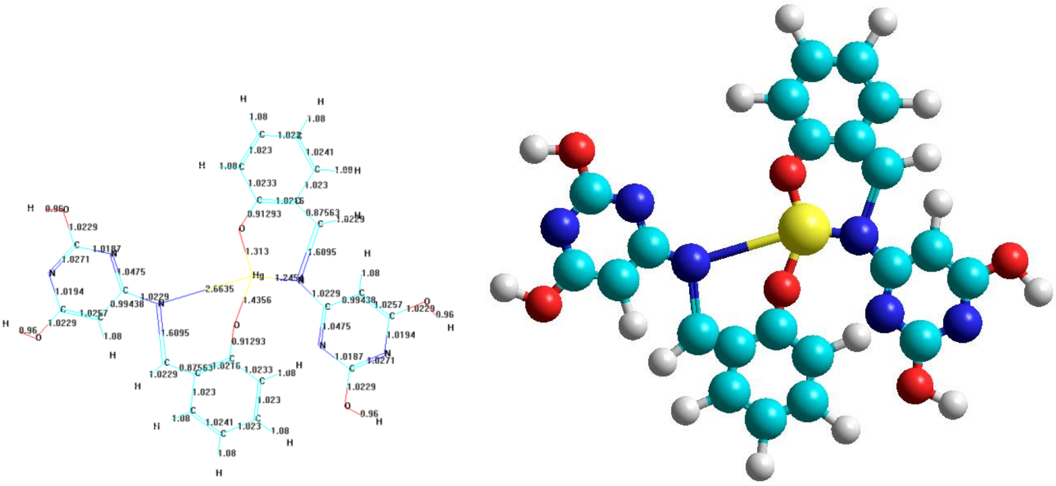
Cu Comp



Zn Comp.



Cd Comp.



Hg Comp

Figure 6: Conformational structure of (L) and their metal complexes

CONCLUSION

In this paper new Schiff Base ligands (L) complexes with the Cu(II), Zn(II), Cd(II) and Hg(II) were synthesized. the configurations were performed to coordinate the Schiff base through the nitrogen and oxygen atoms. Therefore, from the presented results the complexes have tetrahedral geometry**.** Theoretically probable structures of metal complexes with Schiff base have been calculated, These shapes shows the calculated optima geometries for (L) and its metal complexes.

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