

Complexes with New Schiff base (N, N`Z, N`, NZ)-N,N-(5,5-dimethylcyclo hexane-1,3-diyldiene) dibenzothiazol-2-amine Synthesis, Spectral, Thermal and Theoretical Studies

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Abstract: The synthesis of new bidentate Schiff base (N, N`Z, N`, NZ)-N,N-(5,5-dimethylcyclo hexane-1,3-diyldiene) dibenzothiazol-2-amine (L), from condensation of 5,5-Dimethyl-cyclohexane-1,3-dione with Benzothiazol-2-ylamine. Synthesis of complexes with from reaction of Schiff base and metal ions [Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II)] are reported. The structures of new ligand, mode of bonding and overall geometry of the complexes were determined through ¹H-NMR UV-Vis, Mass and FT-IR spectral studies, TGA curve, magnetic moment measurements, elemental microanalyses (C.H.N.S.O.), chloride containing, Atomic absorption and conductance. These studies revealed tetrahedral geometries for all complexes. Complex formation studies via molar ratio and continuous variation methods in DMF solution were consistent to those found in the solid complexes with a ratio of (M : L) as (1 : 1). Hyper Chem-8 program has been used to predict structural geometries of compounds in gas phase, the heat of formation, binding energy, total energy and electronic energy) and dipole moment at 298 K.

Keywords: Benzothiazol-2-ylamine Theoretical Studies, Spectral studies, Schiff base Complexes.

1. Introduction

The coordination chemistry of metal ions with ligands from the 5, 5- dimethyl cyclohexane-1,3- dione has been of interest due to different bonding modes show by these ligands with both electron rich and electron poor metals [1, 2]. Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions. The presence of donor atoms in the ligand will play in important role in the formation of a stable chelated ring and this situation facilitates the complexation process [3]. Schiff base derivatives attract a significant interest and occupy an important role in the development of coordination chemistry [4]. Moreover, Schiff base complexes containing metal ions have been studied in several research areas such as structural chemistry [4]. Metal complex with Schiff bases are important class of ligands due to their synthetic flexibility, selectivity and sensitivity towards the central metal atom, structural similarities with natural biological substances, and also, due to presence of azomethine group which imports in elucidating the mechanism of transformation and racemisation reaction in biological system [5,6] also have been studied for their application in clinical, analytical and pharmacological areas [7].

2. Experimental

Instrumentation and Materials

Thermal analysis studies of the compounds were performed on Perkin-Elmer Pyris Diamond DTA/TG. (FT-IR) the spectra were recorded in the range (4000-400) cm⁻¹ on a Shimadzu 3800, spectrometer. ¹H-NMR spectra were recorded using Bruker 400 MHz spectrometer Elemental

(C.H.N.S.O) analyses were carried out on a Perkin-Elmer automatic equipment model 240.B. Electronic absorption spectra were recorded in the range (200-1100) nm on a Shimadzu 160 Spectrophotometer and Mass spectra were obtained by LC-Mass 100P Shimadzu. Metals were identified using a Shimadzu (F.A.A) 680 G atomic absorption Spectrometer. Conductivity measurements were made with DMSO solutions using a Jenway 4071 digital conductivity meter at room temperature, 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

The following chemicals were commercially available products of analytical reagent grade. Benzothiazol-2-ylamine, 5 ,5-Dimethyl-cyclohexane-1,3-dione, DMSO, pure ethanol, methanol, CaCl₂, CoCl₂.6H₂O, NiCl₂.6H₂O, CuCl₂, ZnCl₂ 2H₂O, CdCl₂.H₂O and HgCl₂ were obtained from Fluka, Aldrich.

a) Synthesis of Ligand: (N, N`Z, N`, NZ)-N,N-(5,5-dimethylcyclo hexane-1,3-diyldiene) dibenzothiazol-2-amine: An ethanolic solution (15 ml) of 5,5-Dimethyl-cyclohexane-1,3-dione (1.4 g, 0.01mol) was added to a mixture containing an neutral ethanolic solution by (NaOH + glacial acetic acid) (15 ml) of Benzothiazol-2-ylamine(3 g, 0.02mol). The resulting mixture was refluxed for 3 hours with stirring. A pall page crystals glossy was formed and then re-crystallized from ethanol. The product was dried over anhydrous CaCl₂ in vacuum. Yield: 59.4% (2.4 g), mp170-171 °C.

The singlet signal observed at (δ=2.743 ppm, 2.992 ppm, 6H, s) in the spectrum of free ligand [L], was assigned to the

methyl group (-C-CH₃), singlet signal showed at (δ=3.393 ppm, 3.439 ppm, 2H, s), was attributed to the (-C-H), multiple a ranged between (δ=7.008 – 7.908 ppm, 8H, m) were assigned to the aromatic protons. The singlet signal appeared at (δ=2.50 ppm) can be assigned to the solvent

(DMSO). The molecular ion peak for the free Schiff base show Figure 1, was observed at m/z = 404 (M) (relative abundance is 70%) for C₂₂H₂₀N₄S₂ which is in excellent agreement with the (404.55) theoretical value [1,8].

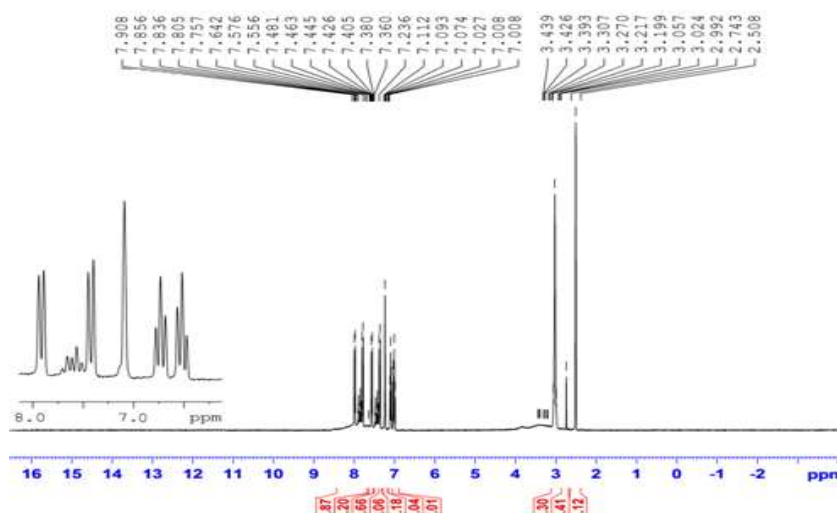
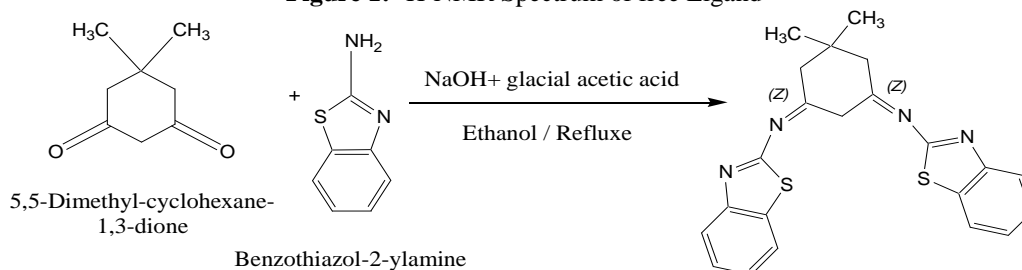
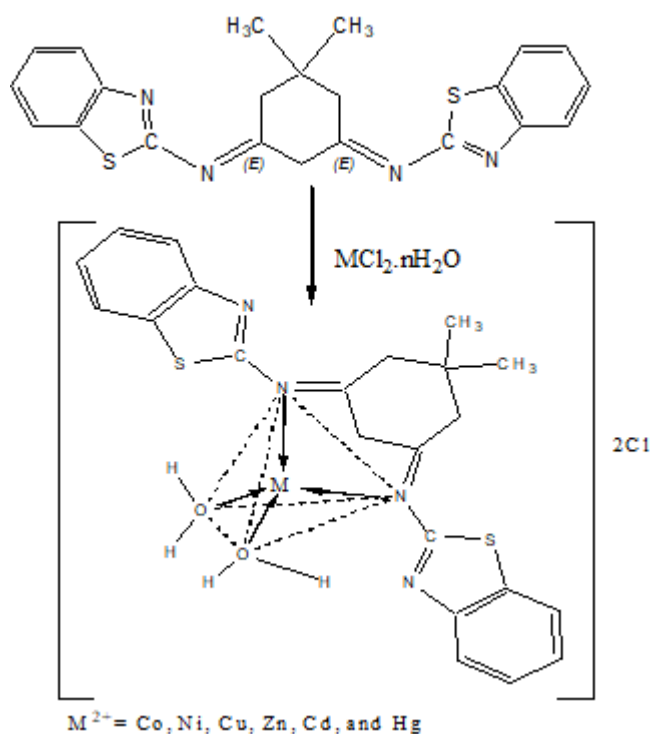


Figure 1: ¹H-NMR Spectrum of free Ligand



Scheme 1: Preparation of the Ligand

b) Synthesis of Complexes: A solution of the Schiff base (2 mol) in methanol (35 ml), and (1+1) methanol+ water solution (40 ml) of the metal salt (2 mol) (CoCl₂.6H₂O, NiCl₂.6H₂O, CuCl₂, ZnCl₂ 2H₂O, CdCl₂.H₂O and HgCl₂) was then added drop wise. The resulting mixture was refluxed 8 hrs in (40-50) °C, resulting in the formation of a solid mass which was washed several times with hot ethanol and dried under vacuum. Physical properties for the complexes are given in Table 1.



M²⁺ = Co, Ni, Cu, Zn, Cd, and Hg

Scheme 2: synthesis of the Complexes

c) Programs used in Theoretical Calculation: Hyper Chem-8 program is a sophisticated molecular modeler, editor and powerful computational package that are known

for its quality, flexibility and ease of use, uniting 2D visualization and animation with quantum chemical calculations, 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 [9].

3. Results and Discussion

Bidentate complexes were obtained upon reaction between metal ions and Schiff base with molar ratio (1:1) (M:L). The synthesized ligand and its metals complexes are very stable at room temperature in the solid state. The ligand and its

metals complexes are generally soluble in hot DMF and DMSO. The yields, melting/decomposition points, elemental microanalyses of ligand and 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. ligand was decomposed at temperatures higher than 375°C, while all complexes were decomposed at temperatures higher than (287-333) °C. The ligand and its metal complexes have dye character due to the high molar extinction constant. Molar conductance values were found in the range (128-147.5) S. cm² mol⁻¹ for all complexes which indicate that they are electrolytes [1:2] [10, 11]. These were determined in (DMSO) solution (10⁻³M). Physical properties and elemental microanalysis are listed in Table 1.

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

Sam.	Molecular Formula =M _{wt}	m.p. °C	Element analysis % Calcu (Found)					
			M	C	H	N	Cl	S
L	C ₂₂ H ₂₀ N ₄ S ₂ 505.55	170-171		65.32 (64.97)	4.98 (5.01)	13.85 (12.01)		15.85 (14.56)
LC ₁	C ₂₂ H ₂₄ N ₄ O ₂ S ₂ Cl ₂ Co 570.42	309 d	10.33 (9.91)	46.32 (46.11)	4.24 (4.21)	9.82 (10.07)	12.43 (11.32)	11.24 (12.01)
LC ₂	C ₂₂ H ₂₄ N ₄ O ₂ S ₂ Cl ₂ Ni 570.18	297 d	10.29 (10.08)	46.34 (46.16)	4.24 (4.91)	9.83 (10.07)	12.44 (12.32)	11.25 (11.01)
LC ₃	C ₂₂ H ₂₄ N ₄ O ₂ S ₂ Cl ₂ Cu 575.04	287 d	11.05 (11.98)	45.95 (46.51)	4.21 (4.81)	9.74 (10.48)	12.33 (11.32)	11.15 (12.01)
LC ₄	C ₂₂ H ₂₄ N ₄ O ₂ S ₂ Cl ₂ Zn 576.88	295 d	11.34 (12.01)	45.80 (46.01)	4.19 (4.49)	9.71 (10.23)	12.29 (11.32)	11.12 (12.01)
LC ₅	C ₂₂ H ₂₄ N ₄ O ₂ S ₂ Cl ₂ Cd 623.90	333 d	18.02 (19.01)	42.35 (41.51)	3.88 (4.21)	8.98 (10.07)	11.36 (11.32)	10.28 (11.01)
LC ₆	C ₂₂ H ₂₄ N ₄ O ₂ S ₂ Cl ₂ Hg 712.08	322 d	28.17 (27.54)	37.11 (38.11)	3.40 (4.01)	7.87 (9.07)	9.96 (10.32)	9.01 (10.01)

d = decompose

a. Mass spectra for complexes

The LC-Mass spectra of complexes [LC₃, LC₅] Figures 2 and 3 showed the parent ion peaks at (M/Z=575) and (M/Z=624) correspond to (M= C₂₂H₂₄N₄O₂S₂Cl₂Cu) and (M= C₂₂H₂₄N₄O₂S₂Cl₂Cd) respectively. The fragmentation pattern is shown in Table 2.

Table 2: The Fragmentation Pattern data for Complexes

Complex	Peaks
LC ₃ = C ₂₂ H ₂₄ N ₄ O ₂ S ₂ Cl ₂ Cu	575, 212, 158, 138, 96, 67
LC ₅ = C ₂₂ H ₂₄ N ₄ O ₂ S ₂ Cl ₂ Cd	624, 430, 429, 205, 204, 79.5, 36

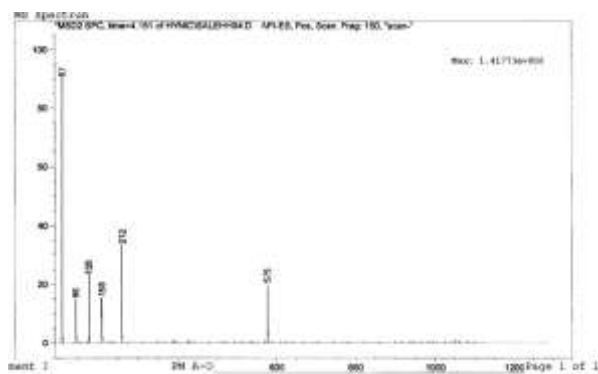


Figure 2: LC-Mass Spectrum of LC₃

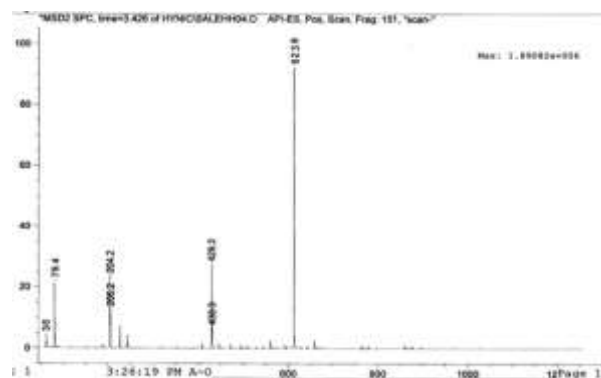


Figure 3: LC-Mass Spectrum of LC₅

b. IR spectra

IR spectral data for the ligand and prepared complexes were listed in Table 3. The IR spectrum for ligand displayed band at (1685) cm⁻¹ whose referred to ν(C=N) of azomethen group in the free ligand were shifted to lower frequency and appeared at [1624,1618, 1643, 1653, 1622, 1649] cm⁻¹ for complexes Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II), respectively. The shift to lower frequency may be due to delocalization of metal electron density into the ligand π-system (HOMO→LUMO), (where HOMO: Highest Occupied Molecular Orbital, LUMO: Lowest Unoccupied Molecular Orbital), the shift in ν(C=N) confirming the coordination of the ligand through nitrogen atom azomethen group to the metal ion [12,13]. The spectra showed new

bands at [(530, 503), (567, 498), (501, 490), (577, 558), (580, 542) and (567, 490)] cm^{-1} can be refer to $\nu(\text{M-N})$ for complexes with metals Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II), respectively. A broad band was observed round (3365, 3297, 3290, 3410, 3440 and 3388) cm^{-1} and (723,

746, 727, 746, 752 and 748) cm^{-1} in each of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes spectra respectively, which is assigned to the $\nu(\text{O-H})$ and $\delta(\text{H}_2\text{O})$. The results led to a suggestion for the presence of water molecules [14-17].

Table 3 Infrared spectra data of the free ligand and its complexes in (cm^{-1})

Comp.	$\nu\text{C}=\text{N}$	$\nu(\text{OH}_2)$, $\delta(\text{OH}_2)$	$\nu\text{M-N}$	$\nu\text{M-O}$	$\nu\text{S}=\text{CN}$	Other bands
L	1685				951	$\nu\text{C-H arom}=3068$, $\nu\text{C-H aliph}=2957$
LC ₁	1624	3365, 723	530, 503	488, 436	901	$\nu\text{C-H arom}=3010$, $\nu\text{C-H aliph}=2961$
LC ₂	1618	3297, 746	567, 498	467, 432	941	$\nu\text{C-H arom}=3063$, $\nu\text{C-H aliph}=2959$
LC ₃	1643	3290, 727	501, 490	478, 436	943	$\nu\text{C-H arom}=3065$, $\nu\text{C-H aliph}=2974$
LC ₄	1653	3410, 746	577, 558	471, 438	928	$\nu\text{C-H arom}=3096$, $\nu\text{C-H aliph}=2957$
LC ₅	1622	3440, 752	580, 542	467, 426	962	$\nu\text{C-H arom}=3089$, $\nu\text{C-H aliph}=2957$
LC ₆	1649	3388, 748	567, 490	476, 426	927	$\nu\text{C-H arom}=3055$, $\nu\text{C-H aliph}=2957$

c. UV-Vis Spectra, Magnetic Moments:

The electronic spectrum of LC₁ Co(II) complex, displayed four new absorption peak. The first peak at (274) nm attributed to the (L. F.), and the second peak at (392) nm attributed to the (C.T.) and third peak at (857) nm due to (d-d) electronic transitions type $^4\text{A}_2 \rightarrow ^4\text{T}_1(\text{p})$ which are a good evidence for tetrahedral geometry. The electronic spectrum of LC₂ Ni(II) complex displayed third new absorption peaks. The first peak at (406) nm attributed to the (C. T), and the second peak at (508) nm due to (d-d) electronic transitions type $^3\text{T}_1 \rightarrow ^3\text{T}_1(\text{p})$, which are a good evidence for tetrahedral geometry. The electronic spectrum of LC₃ Cu(II) complex displayed second new absorption peaks. The first peak at (389) nm attributed to the (C. T), and the second peak at (508) nm due to (d-d) electronic transitions type $^2\text{T}_2 \rightarrow ^2\text{E}$ which are a good evidence for tetrahedral geometry [18-20].

The electronic spectrum of LC₄ Zn(II) displayed first new absorption peak. The first peak at (399) nm attributed to the (C. T) which are a good evidence for tetrahedral geometry. The electronic spectrum of LC₅ Cd (II) complex displayed first new absorption peak. The first peak at (391) nm attributed to the (C. T) which is a good evidence for tetrahedral geometry. The electronic spectrum of LC₆ Hg(II) complex displayed first new absorption peak. The first peak at (400) nm attributed to the (C. T) which is a good evidence for tetrahedral geometry [16-17].

A similar method to that mentioned in measurement the magnetic susceptibility and μ_{eff} of ligand complexes. The μ_{eff} values were listed in Table 4. LC₁= 4.06) B.M, LC₂= 4.00) B.M, LC₃=1.63) B.M, but LC₄, LC₅ and LC₆] diamagnetic [23].

Table 4: Electronic Spectral Data of the Metal Complexes with Ligand and Magnetic Moments

Complexes	λ nm	ABS	ϵ L. $\text{mol}^{-1}\text{cm}^{-1}$	Assignment	Λ $\text{S.cm}^2\text{mol}^{-1}$	μ_{eff} B.M
LC ₁	274	2.030	2030	L.F	128	4.06
	392	0.115	115	C.T		
	857	0.058	58	$^4\text{A}_2 \rightarrow ^4\text{T}_1(\text{p})$		
LC ₂	283	0.936	936	L.F	135	4.00
	341	1.226	1226	L.F		
	406	1.687	1687	C.T		
	508	0.235	235	$^3\text{T}_1 \rightarrow ^3\text{T}_1(\text{p})$		
LC ₃	275	0.916	916	L.F	147.5	1.63
	331	1.206	1206	L.F		
	389	1.228	1228	C.T		
	508	0.233	233	$^2\text{T}_2 \rightarrow ^2\text{E}$		
LC ₄	285	1.460	1460	L.F	144	dia
	326	1.192	1192	L.F.		
	399	1.689	1689	C.T		
LC ₅	288	1.323	1323	L.F	147.5	dia
	332	1.505	15016	L.F.		
	391	1.663	1663	C.T		
LC ₆	287	1.003	1003	L.F	142.2	dia
	340	1.212	1212	L.F.		
	400	1.302	1302	C.T		

d. Thermal Gravimetric Analyses TGA

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

The TG curve of L show relatively rapid decomposition in the first (34.6 – 123.7 °C), second (125.1 – 431) and third (462.3 - 694°C) steps with T_{DTG} peaks at 69.5°C, 370 °C and 650°C. The very large and strongly sharp T_{DTG} peak observed for the first step at 370 °C is preceded with a sharp peak. 4.94%, 22.72% and 69.34% mass losses in the first, second and third steps correspond to the release of (CH₃),

(C₄H₆N) and (C₁₆H₁₁N₃S₂) fragments (cal. 5.27 %, 22.82% and 70.09 %, respectively). The TG curve of L show relatively rapid decomposition in the first (34.6 – 123.7 °C), second (125.1 – 431) and third (462.3 - 694°C) steps with T_{DTG} peaks at 69.5°C, 370 °C and 650°C. The very large and strongly sharp T_{DTG} peak observed for the first step at 370 °C is preceded with a sharp peak. 4.94%, 22.72% and 69.34% mass losses in the first, second and third steps correspond to the release of (CH₃), (C₄H₆N) and (C₁₆H₁₁N₃S₂) fragments (cal. 5.27 %, 22.82% and 70.09 %, respectively), [1].

The TG curve of Ni complexes with L₃ show relatively rapid decomposition in the first (42.5 - 141.7°C), second (144.5 – 227.6°C), third (227.6 – 370 °C) and fourth (375- 598 °C) steps with T_{DTG} peaks at 87.8°C, 183.3°C, 281°C and 463°C. The very large and strongly sharp T_{DTG} peak observed for the second step at 281°C is preceded with a sharp peak. 2.18%, 11.18%, 23.53% and 54.15% mass losses in the first, second third and fourth steps correspond to the release of (2H₂O), (Cl₂+ C₃H₄N), (C₆H₈) and (C₁₃H₈N₃S₂) fragments and final product (Ni) (cal. 2.66%, 10.13%, 22.65% and 55.5%, respectively). The tentative decomposition reaction

of LC₂ is shown in Table 5. The TG curve of Cu complexes with L show relatively rapid decomposition in the first (60.61- 180°C), second (180-415.12°C) and third (415.12-599.6°C) steps with T_{DTG} peaks at 110.5°C, 283.3°C and 529.3°C. The very large and strongly sharp T_{DTG} peak observed for the first step at 283.3°C is preceded with a sharp peak. 1.98 %, 50.35% and 41.77% mass losses in the first, second and third steps correspond to the release of (2H₂O), (C₆H₅N₂S +Cl₂) and (C₁₆H₁₅N₂S) fragments and final product (Cu) (cal. 2.31%, 50.95% and 42.03%, respectively). The tentative decomposition reaction of LC₃ is shown in Table 5. The TG curve of Cd complexes with L show relatively rapid decomposition in the first (48.3-113.5°C), second (113.5-410.4°C) and third (419-599.6°C) steps with T_{DTG} peaks at 90.7°C, 250.6°C and 520.3°C. The very large and strongly sharp T_{DTG} peak observed for the first step at 250.6°C is preceded with a sharp peak. 4.14 %, 36.63% and 48.88% mass losses in the first, second and third steps correspond to the release of (2H₂O), (C₆H₅S +Cl₂) and (C₁₆H₁₅N₄) fragments and final product (Cd) (cal. 4.96%, 38.01% and 47.77%, respectively). The tentative decomposition reaction of LC₅ is shown in Table 5, Figure 4 [1, 16, 23].

Table 5: 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	
L	34.6-123.7 125.1-431 462.3-694	69.5 370 650	4.94 (5.27) 22.72(22.82) 69.34 (70.09)	(98.2) 97.00	-CH ₃ -C ₄ NH ₆ -C ₁₆ H ₁₁ N ₃ S ₂ C
LC ₂	42.5-141.7 144.7-227.6 227.6-370 370.8-598	87.8 183.3 281 463	(2.66) 2.18 (10.13) 11.18 (22.65) 23.53 (55.5) 54.15	91.04 (90.94)	2H ₂ O 2Cl + C ₃ H ₄ N C ₆ H ₈ C ₁₃ H ₈ N ₃ S ₂ Ni
LC ₃	60.61-180 180-415.12 415.12-599.6	110.5 283.3 529.3	(2.31) 1.98 (50.35) 50.95 (42.03) 41.77	94.1 (95.29)	2H ₂ O 2Cl + C ₆ H ₅ SN ₂ C ₁₆ H ₁₅ N ₂ S Cu
LC ₅	48.3-113.5 113.5-410.4 419-599.6	90.7 250.6 520.3	(4.96) 4.14 (38.01) 38.63 (47.77) 48.88	89.65 (90.74)	2H ₂ O 2Cl + C ₆ H ₅ S C ₁₆ H ₁₅ N ₄ S Cd

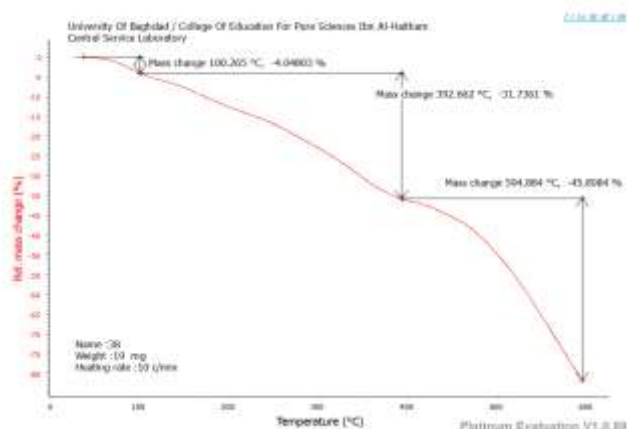


Figure 4: TGA and DTA Curve of LC₅ complex

e. 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) [24]. The (E.P) of the free ligand was calculated and plotted as 2D contour to investigate the reactive sites of the molecules, Figure 5. 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 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 carbonyl and nitrogen of azomethen group for free ligand, Figure 6.

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 6. [13, 22].

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)	Isolated Atomic Energy
L	-90717.384	-5255.9933	130.42669	-768303.3297	2.369	-85461.3909
LC ₁	-154545.90	-6513.5828	511.65318	-1162035.5455	6.776	-148032.3179
LC ₂	-121719.08306	-3938.6922	836.0137	-795252.202	16.679	-117780.3908
LC ₃	-99276.08233	-39975.56348	12.288	-710242.29	11.86	-132567.654
LC ₄	-106342.206	-5698.3059	46.810061	-872892.254	2.763	-100643.90
LC ₅	-98276.08233	-3775.56348	923.0625	-658069.98019	5.959	-94500.5188
LC ₆	-98525.0378	-3875.7755	810.820474	-730242.29	13.037	-94649.2623

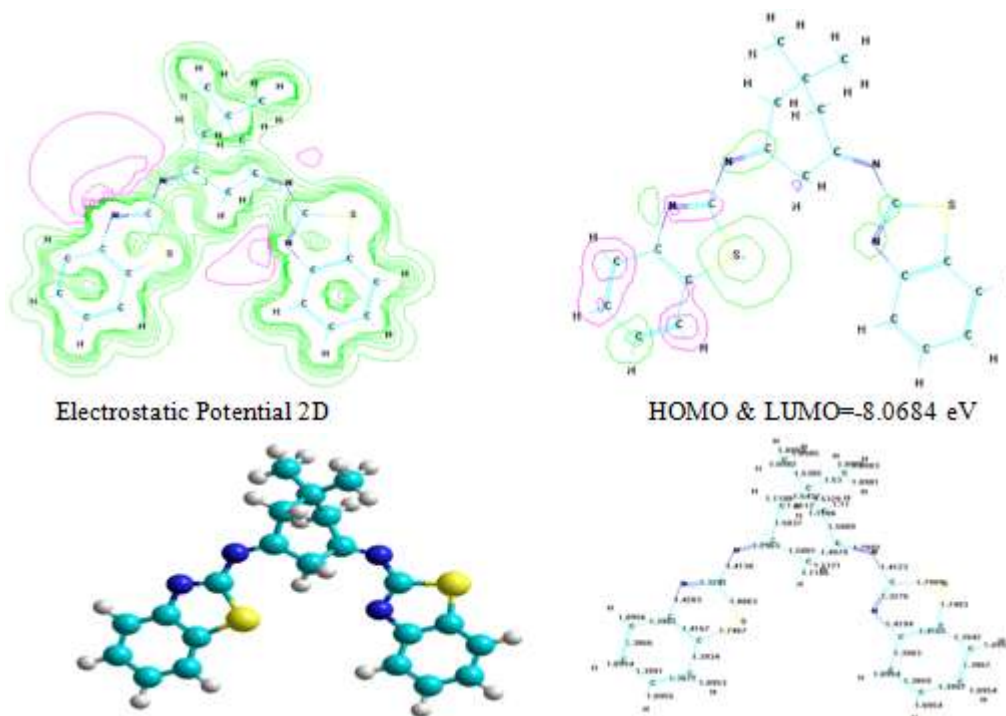
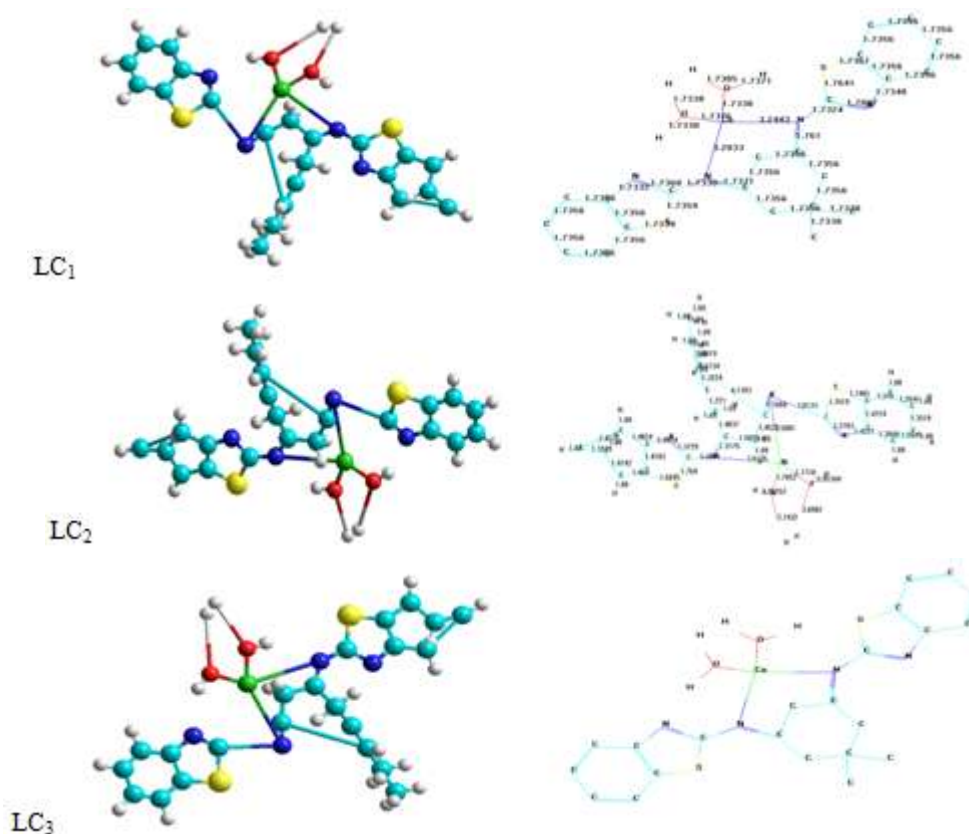


Figure 5: Electrostatic Potential (HOMO and LUMO) Contours for Ligand



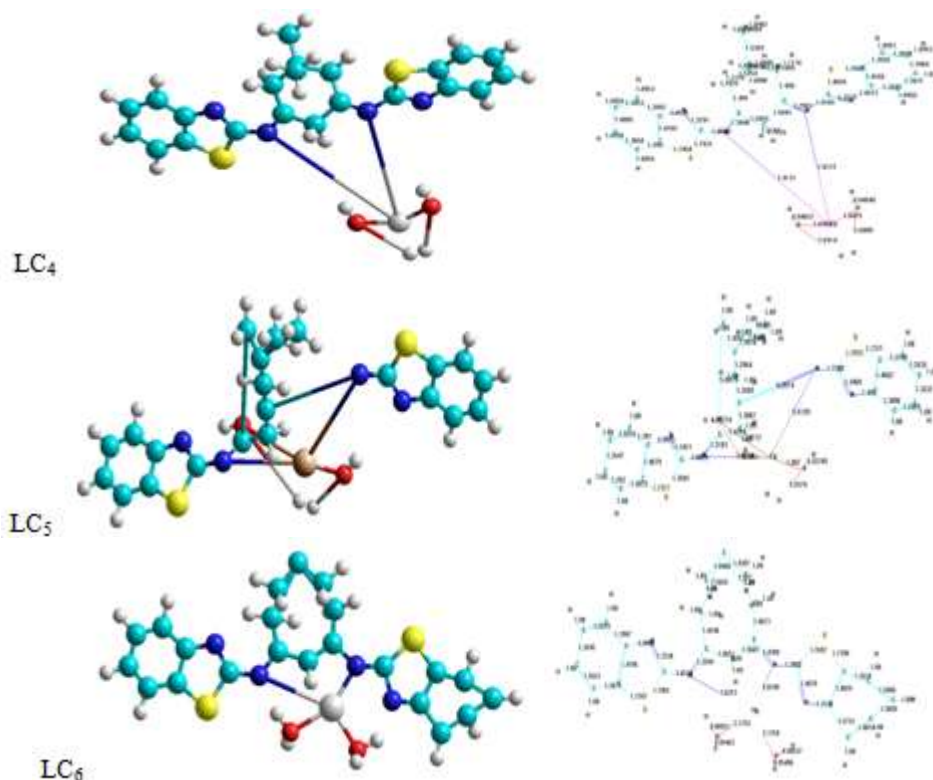


Figure 6: Conformational Structure of metal complexes

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