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Synthesis and Spectroscopic Characterization for Some Metal ion Complexes with 2-Hydroxy-3-((5-Mercapto-1,3,4-Thiadiazol-2-yl)Diazenyl)-1-Naphthaldehyde

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Abstract

New metal ion complexes were synthesized with the general formula; K[PtLCl$_4$], [ReLCl$_4$] and K[ML(Cl)$_2$] where M = Pd(II), Cd(II), Zn(II) and Hg(II), from the Azo ligand (HL) [2-Hydroxy-3-((5-mercapto-1,3,4-thiadiazol-2-yl)diazenyl)-1-naphth aldehyde] (HL) the ligand was synthesized from (2-hydroxy-1-naphthaldehyde) and (5-amino-1,3,4-thiadiazole-2-thiol). The ligand and its metal complexes are characterized by phisco- chemical spectroscopic techniques (FT.IR, UV-Vis and Mass spectra, elemental analysis, molar conductivity, Atomic Absorption, Chloride contain and magnetic susceptibility). The spectral data suggest that the (HL) behaves as a bidentate ligand in all complexes. These studies revealed tetrahedral geometries for all metal complexes, except square planar for Pd(II) complex and except octahedral geometry for Pt(IV) and Re(V) complexes. The study of complexes formation via molar ratio of (M:L) as (1:1). Theoretical treatment of this ligand and its metal complexes in gas phase using Hyper chem.8 was preformed.

Key words: Bidentate Ligand; Azo Ligand, Azo Complexes, Theoretical Treatment.

Introduction

The coordination chemistry of transition metals with dervied from the 5-amino-1,3,4-thiadiazole-2-thiol, 2-hydroxy-1-naphthaldehyde (aromatic heterocyclic components) are of interest due to different bonding modes shown by these ligands with both electron rich and electron poor metals[1]. Furthermore, they have been studied widely because of their excellent thermal and optical properties in applications such as optical recording medium [2-4], toner [5,6], ink-jet printing [7,8], and oil-soluble lightfast dyes [9]. Several ligands containing 1,2,4-triazole are well known as drugs. For vorozole, letrozole, and anastrozole are non-steroidal drugs used for the treatment of cancer [10], while loreclezole is used as anticonvulsant

[11] and fluconazole is used as an antimicrobial drug [12,13]. In this report the preparation of ligand and spectroscopic studies of complexes with Zn(II), Pd(II), Cd(II), Re(V), Pt(IV) and Hg(II) were done.

Materials and Methods:

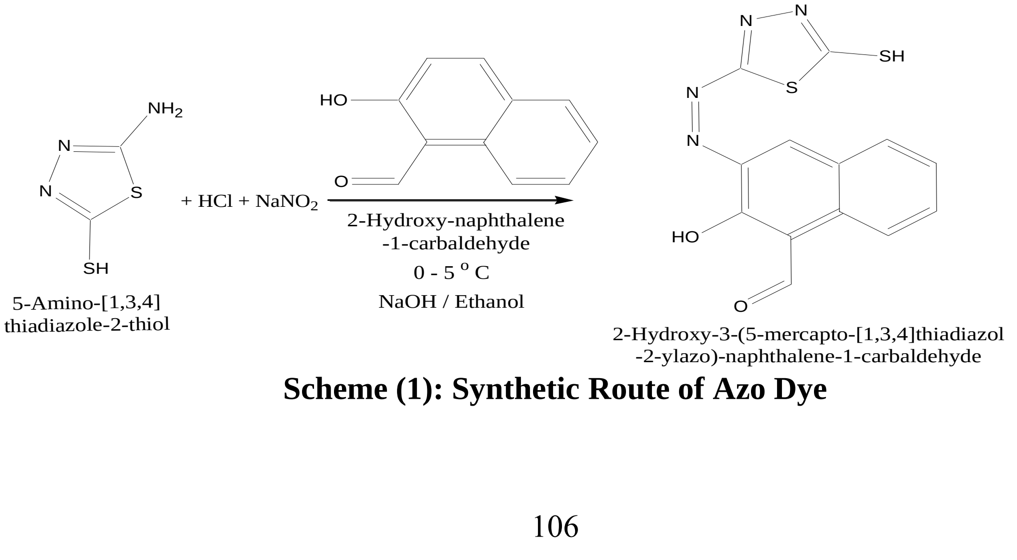
The following chemicals were commercially available products of analytical reagent grade. 2-hydroxy-1-naphthaldehyde, 5-amino-1,3,4-thiadiazole-2-thiol, DMSO, pure ethanol, methanol, $CaCl_2$, $ZnCl_2$, $PdCl_2$, $CdCl_2$ $ReCl_5$, $H_2PtCl_6.6H_2O$ and $HgCl_2$ were obtained from Fluka, Aldrich.

IR spectra were obtained by using KBr discs on Perkin –Elmer FT-IR spectrometer. The electronic spectra were carried out using a Cary 50 Conc. Elemental microanalyses (C.H.N.) were performed by using a flash E A 1112 Series Elemental Analyzer. Chloride ion content is determined by using potentiometric titration method on a 686-Titro processor – 665 Dosimat Metrohm Swiss. Conductivity measurements were made in DMSO by using a Jenway 4071 digital conductivity meter. The magnetic properties are measured by using Jonson Mattey Catalytic were Division. Melting points were measured by using a Buchi SMP -20 capillary melting point apparatus, LC-Mass spectra by using (LC-Mass 100 P Shimadzu). Metals were identified using a Shimadzu (A.A) 680 G atomic absorption Spectrometer

Preparation of the Ligand 2-Hydroxy-3-((5-mercapto-1,3,4-thiadiazol-2-yl)diazenyl)-1-Naphth Aldehyde (HL) [14]:

5-Amino-1,3,4-thiadiazole-2-thiol (1g, 9.17 mmol) was dissolved in a mixture of (2 ml) hydrochloric acid, (20 ml) ethanolic solution, and diazotized at 5^oC with sodium nitrite solution. The diazonium salt solution was added dropwise with stirring to a cooled ethanolic solution of (1.5g, 9.17 mmol) of (2-hydroxy-1-naphthaldehyde) (25 ml) of (1 M) NaOH solution is added to the orange colored mixture. The precipitate is filtered off and washed several times with (1:1) ethanol: water, mixture then left to dry. The product precipitated (65%) yielding (1.875g), m. p. (145ºC). The reaction illustrated in Scheme (1).

IR (KBr) for HL: ▶(azo -N=N-) = 1520-1430, ▶(O-H) = 3566, ▶(C-OH) = 1096, ▶(Ar-CH) = 3067, ▶(aldehyde C-H) = 2889, ▶(aldehyde C=O) = 1645, ▶(S-H) = 2597, ▶(C-S) = 660-653 and ▶(C=N) = 1635 and 1575 cm^{-1}. The GC-Mass for L (316m/ z) with ($C_{13}H_8N_4O_2S_2$), (315m/ z) with ($C_{13}H_7N_4O_2S_2$), (289 m/ z) with ($C_{11}H_5N_4O_2S_2$), (253 m/ z) with ($C_{11}HN_4O_2S$), (237 m/ z) with ($C_{11}HN_4OS$), (209 m/ z) with ($C_{11}HN_2OS$), (195 m/ z) with ($C_{11}HNOS$), (145 m/ z) with ($C_{11}NOS$), (50 m/ z) with (C_7NOS) and (39 m/ z) with (C_6NOS).



Scheme (1): Synthetic Route of Azo Dye

Preparation of Metal Complexes with Ligand:

An ethanolic solution of the ligand (1g, 3.164 mmol) HL was added gradually with stirring to (0.235g, 0.421g, 0.313g, 0.376g, 0.363g and 0.212g) (3.164 mmol), of $PdCl_2$, $ZnCl_2$, $HgCl_2$, $H_2PtCl_6.6H_2O$, $ReCl_5$ and $CdCl_2$ respectively, was added gradually with stirring to KOH (0.117g, 3.164 mmol). The solid was collected by filtration recrystallized from methanol dried at room temperature. Elemental micro analysis data color and yield for the compounds are given in Table (1).

The LC-Mass for PdL ($C_{13}H_7Cl_2KN_4O_2PdS_2$) (531.78 m/ z). The LC-Mass for ZnL ($C_{13}H_7Cl_2KN_4O_2S_2Zn$) (490.75 m/ z). The LC-Mass for CdL ($C_{13}H_7CdCl_2KN_4O_2S_2$) (537.77 m/z). The LC-Mass for HgL (626 m/ z). The LC-Mass for PtL ($C_{13}H_7Cl_4KN_4O_2PtS_2$) (691 m/ z). The LC-Mass for ReL ($C_{13}H_7Cl_4N_4O_2ReS_2$) (643.4 m/ z)

Results and Discussion:

Elemental microanalysis and some physical properties of the (L) and its prepared complexes are shown in Table (1).

Infrared Spectral Studies of the ligand and the Complexes

The main vibrational bands of the FTIR spectrum were assigned to the functional groups of the ligand HL. The spectrum of the HL shows strong bands at 1520- 1430, 3566 and 1096 cm^{-1} that assigned to the ν(N=N) and ν(O-H) phenolic and ν(C-OH) respectively [15,16]. On complex formation, the bands of ν(N=N) are shifted to lower frequencies by (56-53 to 16-3) cm^{-1}, these shifts confirm the coordination of the L through the oxygen of the phenol group and nitrogen of azo group with the metal ions. [17-19]. Characteristic vibrations and assignments of these complexes are reported in Table (2).

Electronic Spectral, Magnetic Moments and Conductivity Measurements

The electronic spectra of the ligand L exhibits intense absorption at (265) and (315, 357, 420) nm attributed to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions for functional groups with azo dye respectively [19,20]. The diamagnetic of Zn(II), Cd(II) and Hg(II) complexes exhibited absorption bands at 405, 390 and 540 nm due to the charge transfer M→L (C.T) as the electronic configuration respectively. Moreover, the spectrum of the complexes also shows the absence of any d-d transition [21, 22]. The Pd(II) complex exhibited absorption bands at 515 and 645 nm due to $^1A_1g\rightarrow {}^1B_1g$ and $^1A_1g\rightarrow {}^1A_2g$ The Pt(IV) complex exhibited absorption bands at 696 and 850 nm due to $^1A_1g \rightarrow {}^1T_2g$ and $^1A_1g \rightarrow {}^1T_1g$. The Re(V) complex exhibited absorption bands at 535, 645 and 905 nm due to $^3T_1g \rightarrow {}^3A_2g$, $^3T_1g \rightarrow {}^3T_1g_{(P)}$ and $^3T_1g \rightarrow {}^3T_2g_{(F)}$. All the data of the magnetic susceptibility and electronic spectra of the ligand and its complexes are listed in Table (3). The molar conductance values Table (3) of 32.5-45 $ohm^{-1}\ cm^2\ mol^{-1}$ in (1×10^{-3}M) DMSO medium indicate that the metal complexes are electrolytes (1:1) and Re(V) complex value 18 $ohm^{-1}cm^2\ mol^{-1}$ is non electrolyte. The proposed structure for the complexes are shown in Figure (1).

Table (1): Analytical and some Physical Data of the Ligand and its Complexes

Compounds	Formula M. wt.	Color	M. P. °C	Yield %	Elemental analysis, Calc. (found) %				
					C	H	N	M	Cl
HL	$C_{13}H_8N_4O_2S_2$ 316.36	Orange	145	65	49.36 (50.12)	2.55 (3.07)	17.71 (17.67)	-	-
$K[PdL(Cl)_2]$	$C_{13}H_7Cl_2KN_4O_2PdS_2$ 529.81	Dark orange	270 d	63	29.36 (30.12)	1.33 (1.10)	10.54 (11.20)	20.01 (20.65)	13.33 (14.05)
$K[ZnL(Cl)_2]$	$C_{13}H_7Cl_2KN_4O_2S_2Zn$ 487.83	Yellow	310 d	72	31.82 (31.97)	1.44 (2.09)	11.42 (10.98)	13.33 (13.13)	14.45 (15.10)
$K[CdL(Cl)_2]$	$C_{13}H_7CdCl_2KN_4O_2S_2$ 537.81	Dark yellow	330 d	81	29.03 (30.1)	1.31 (1.13)	10.42 (11.09)	20.90 (21.71)	13.19 (13.68)
$K[HgL(Cl)_2]$	$C_{13}H_7Cl_2HgKN_4O_2S_2$ 625.87	Dark yellow	290 d	66	24.94 (25.13)	1.13 (1.61)	8.95 (9.18)	32.05 (32.78)	11.33 (10.78)
$K[PtLCl_4]$	$C_{13}H_7Cl_4KN_4O_2PtS_2$ 688.80	Reddish orange	305 d	81	22.59 (23.12)	1.02 (0.98)	8.10 (7.97)	28.22 (29.10)	20.51 (21.11)
$K[PtLCl_4]$	$C_{13}H_7Cl_4N_4O_2ReS_2$ 641.83	Dark reddish orange	290 d	78	24.27 (24.57)	1.10 (1.11)	8.71 (9.12)	-	22.04 (22.24)

d=decomposetion

Table (2): FTIR Spectral Data for the ligand and the Complexes (cm^{-1})

Compounds	OH Phen.	S-H	C=O ald	C=N Triazol azo	N=N	C-H arom.	C-H ald.	C-S	M-N	M-O
HL	3566	2597	1645	1635 1575	1520 1430	3076	2889	660 653	-	-
$K[PdL(Cl)_2]$	-	2590	1642	1638	1490 1405	3089	2888	665 659	540	441
$K[ZnL(Cl)_2]$	-	2600	1648	1630	1488 1410	3070	2895	670 660	510	448
$K[CdL(Cl)_2]$	-	2601	1650	1631	1489 1408	3075	2878	667 651	505	481
$K[HgL(Cl)_2]$	-	2598	1645	1636	1491 1417	3080	2890	665 659	518	465
$K[PtLCl_4]$	-	2599	1647	1635	1489 1415	3098	2880	667 659	527	471 423
$[ReLCl_4]$	-	2588	1641	1640	1499 1409	3089	2800	671 650	590	485

Phen.= phenol; ald. = aldehyde; arom. = aromatic

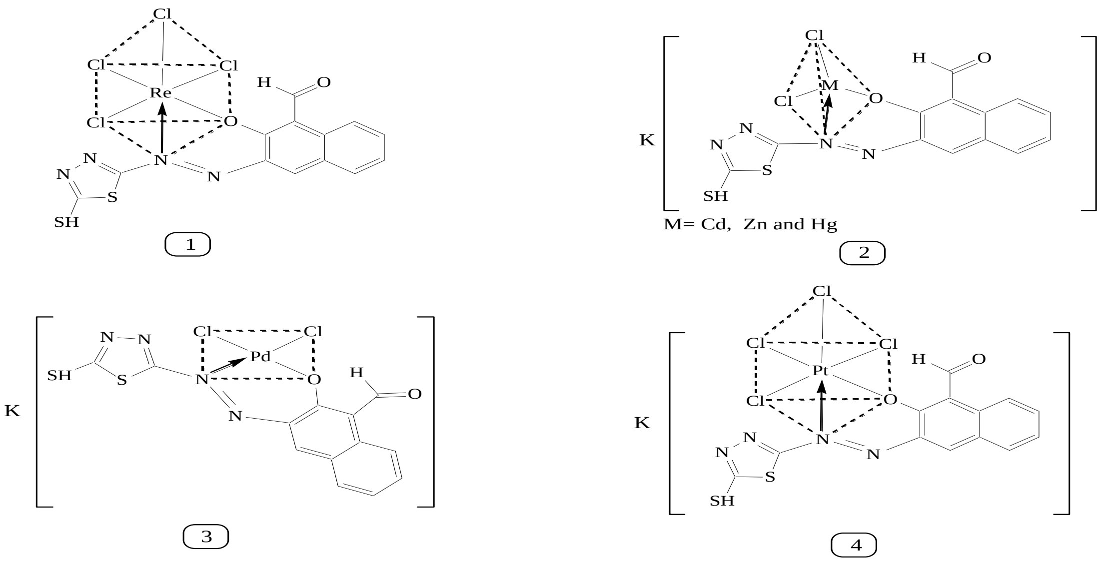


Fig. (1): The proposed Structure of the prepared Complexes

Table (3): Electronic Data, μ_{eff} and Molar Conductivity for the ligand and its Complexes

Complexes	ABS	λ nm	ῡ cm^{-1}	ε L. $mol^{-1}cm^{-1}$	Assignment	Ω Ohm^{-1} cm^2 mol^{-1}	μ_{eff} B.M	Suggested Formula
HL	1.150 1.271 0.980 0.460	265 315 357 420	37735,8 31746 28011.2 23809.5	1150 1271 980 460	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$ $n\rightarrow\pi^*$ $n\rightarrow\pi^*$	-	-	-
K[PdL(Cl)$_2$]	1.731 2.031 1.909 0.608 0.206 0.056	270 318 345 394 515 645	37037 31446.5 28985.5 25380.7 19417.4 155038	1731 2031 1909 608 206 65	L. F. L. F. L. F. L. F. $^1A_1g \rightarrow {}^1B_1g$ $^1A_1g \rightarrow {}^1A_2g$	32.5	Diamagnetic	Square Planer
K[ZnL(Cl)$_2$]	1.760 1.587 1.508 2.016	269 316 360 405	37174.7 31645.5 27777.7 24691.3	1760 1587 1508 2016	L. F. L. F. L. F. C. T.	37.13	Diamagnetic	Tetrahedral
K[CdL(Cl)$_2$]	1.744 1.482 1.507 2.216	269 325 337 390	37174.7 30769.2 29673.5 25461	1744 1482 1507 2216	L. F. L. F. L. F. C. T.	39.1	Diamagnetic	Tetrahedral
K[HgL(Cl)$_2$]	1.709 1.606 1.638 1.165 2.357	268 324 337 390 540	37313.4 30864.1 29673.5 25641 18518.5	1709 1606 1638 1165 2357	L. F. L. F. L. F. L. F. C. T.	40.9	Diamagnetic	Tetrahedral
K[PtLCl$_4$]	1.266 1.781 1.610 1.368 0.216 0.068	365 313 345 357 696 850	37735.8 31948.8 28985.5 28011.2 14367.8 11764.7	1266 1781 1610 1368 216 68	L. F. L. F. L. F. L. F+C.T $^1A_1g \rightarrow {}^1T_2g$ $^1A_1g \rightarrow {}^1T_1g$	45	Diamagnetic	Octahedral
[ReLCl$_4$]	1.352 1.585 1.659 0.248 0.064 0.056 0.008	266 314 346 415 535 645 905	37594 31847.1 28901.7 24096.3 18691.5 15503.8 11049.7	1352 1585 1659 248 64 56 8	L. F. L. F. L. F. L. F+C.T $^3T_1g \rightarrow {}^3A_2g$ $^3T_1g \rightarrow {}^3T_1g_{(p)}$ $^3T_1g \rightarrow {}^3T_2g_{(f)}$	18	3.9	Octaedral

Theoretical Study

The vibration spectra Azo dye ligand was calculated by using a Hyber chem.8 method. The results obtained for wave numbers are presented in Table (6), and the comparison with the experimental values indicates some deviations. These deviations may be due to the harmonic oscillator approximation and lack of electron correlation. It is reported [23] that frequencies coupled with (HFT) approximation and quantum harmonic oscillator approximations tend to be 10% too high. And structures of ligand are calculated to search for the most probable model building stable structure. These shapes show the calculated optima geometries for compounds prepared as shown in Figure (4). And the ΔE_b and ΔH_f for compounds in Table (7).

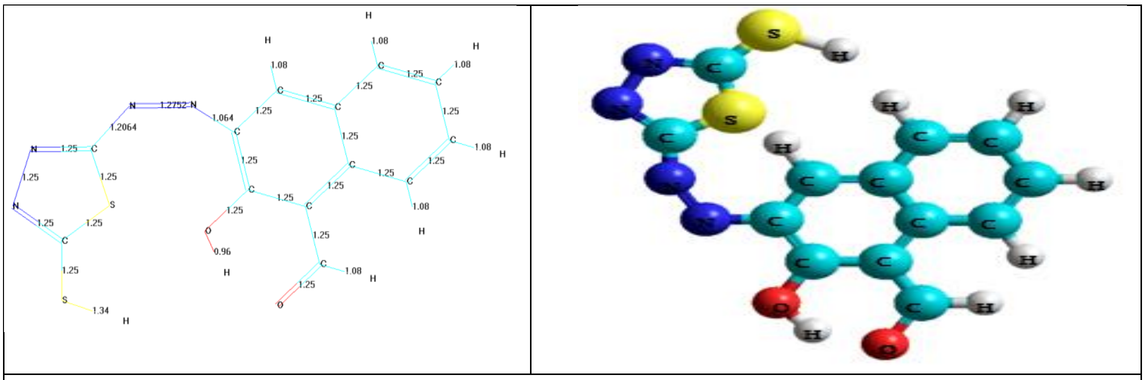
Table (6): Comparison of Experimental and Theoretical Vibration Frequencies for Ligand

Ligand	υ(OH)	υ(CH) aromatic	υ(CH) aleph	υ(C-H) aldehyde	υ (C-S)	υ (C=N)	υ (S-H)	υ(C=O) aldehyde	υ(C=O) ring	υ(N=N)
HL	*3566 **3600 ***-0.95	*3076 **3110 ***-1.10	-	*2889 **2800 ***3.17	*660*653 **680**621 ***-3.03***4.90	*1635*1575 **1643**1455 ***-0.4***7.61	*2597 **2553 ***1.69	*1645 **1656 ***-0.66	-	*1520*1430 **1400**1390 ***7.89***2.79

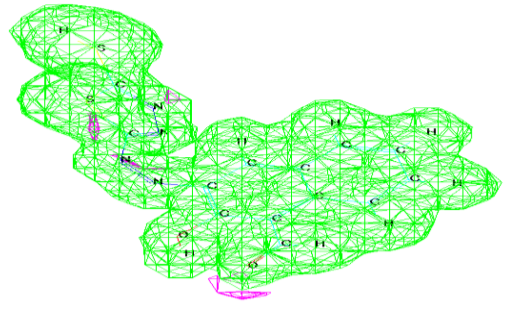
*Experimental frequency. ** Theoretical frequency. *** Error% due to main difference in the experimental measurements and theoretical treatments of vibration spectrum.

Table (7): Conformation Energies in (kJ mol^{-1}) for the Ligand and its Metal Complexes

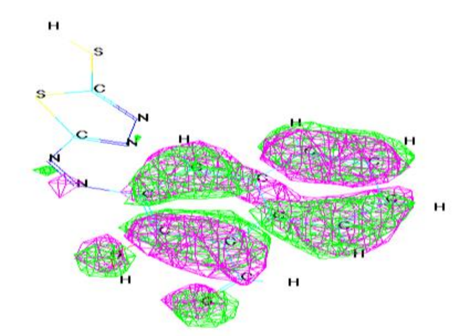
Compounds	PM3		
	ΔH_f°	ΔE_b	Dipole (Debyes)
HL	117.873	-3224.430	4.667
$K[CdL(Cl)_2]$	100.1090407	-3274.7929593	3.871
$K[ZnL(Cl)_2]$	101.0418074	-3278.3101926	8.418
$K[PdL(Cl)_2]$	-1081.1930865 (AMBER)		10.158
$K[PtL(Cl)_4]$	-1626.463316 (AMBER)		9.453
$K[HgL(Cl)_2]$	-2272.9972790 (AMBER)		10.084
$[ReLCl_4]$	-3357.82801 (AMBER)		10.44



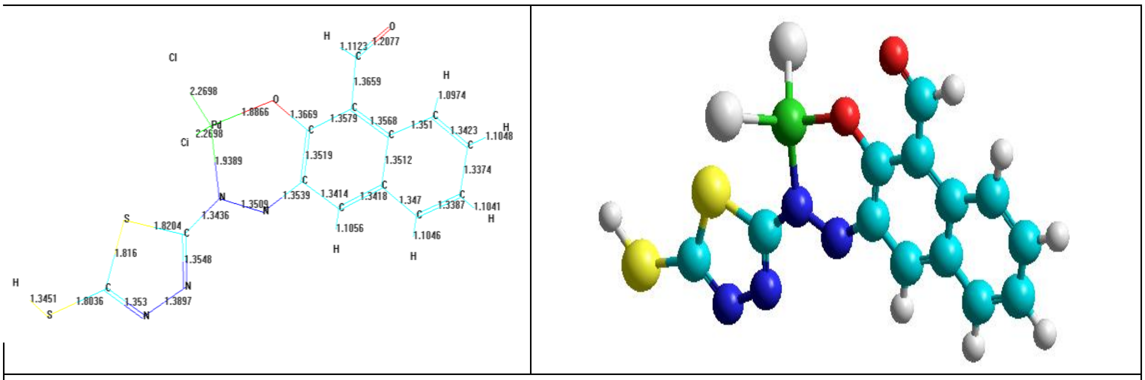
HL



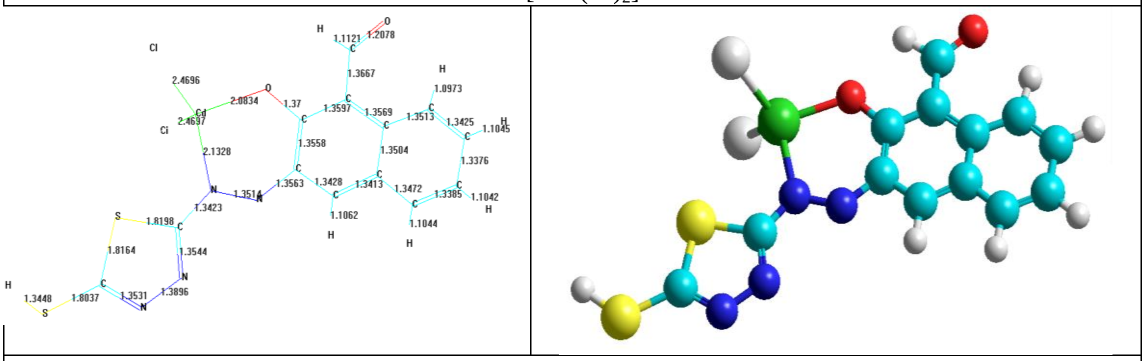
Electrostatic Potential



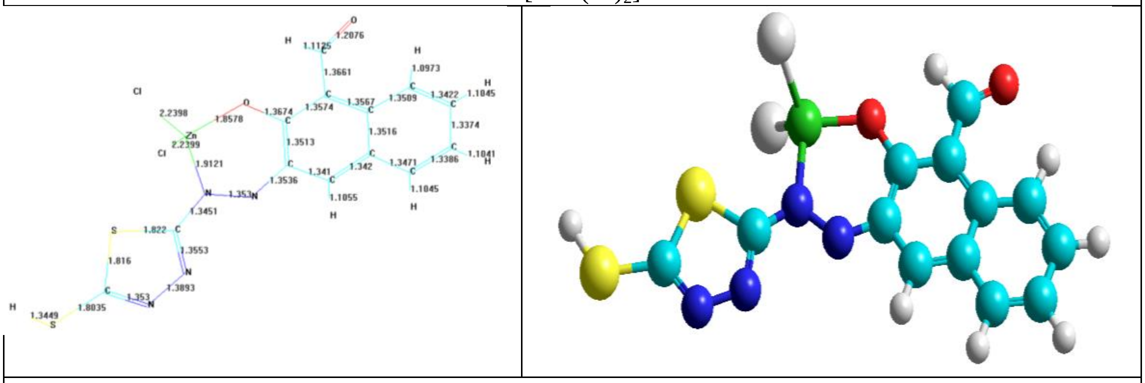
HOMO and LUMO



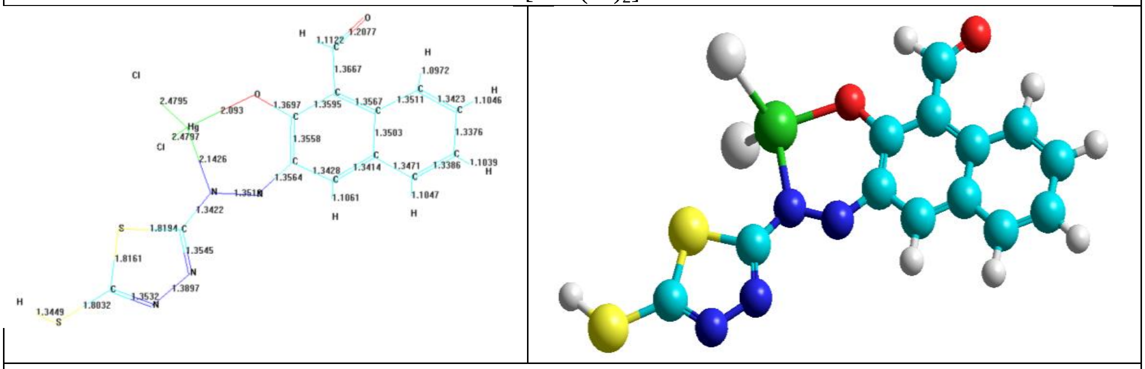
K[PdL(Cl)$_2$]



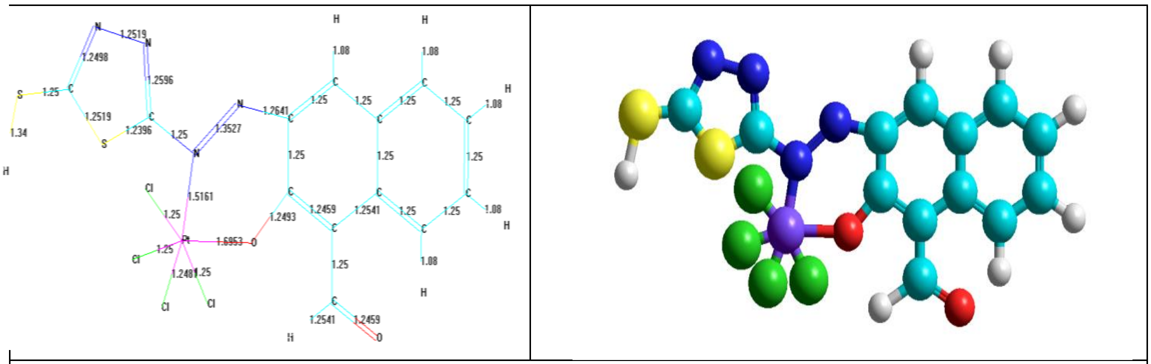
K[CdL(Cl)$_2$]



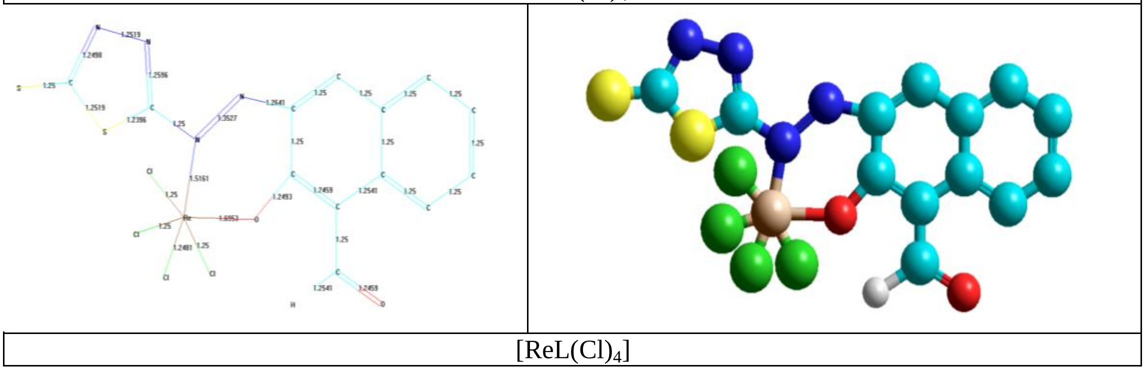
K[ZnL(Cl)$_2$]



K[HgL(Cl)$_2$]



K[PtL(Cl)4]



[ReL(Cl)4]

Fig. (2): Conformational Structures of Ligand and its Complexes

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تحضير وتشخيص طيفي لبعض معقدات ايونات المعادن مع 2-هايدروكسي-3-((5-ميركبتو-1،3،4-ثايادزايازول-2-يل) -ثنائي زينيل) -1-نفثالديهايد

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الخلاصة

حضرت المعقدات الجديدة بالصيغة العامة $K[PtLCl_4]$ ، $[ReLCl_4]$ و $K[ML(Cl)_2]$ حيث M = بلاديوم، كادميوم، خارصين وزئبق، إذ ان L = ليكاند الازو 2-هيدروكسي-3-((5-ميركبتو-1،3،4-ثايادايازول-2-يل) ثنائي زينيل)-1-نفثالديهايد المحضر من تفاعل 2-هايدروكسي-1-نفثالديهايد مع 5-امينو-1،3،4-ثايادايزول-2-ثايول.

شخصت المعقدات والليكاند المحضرة بالطرق الفيزيائية-الكيميائية (الاشعة تحت الحمراء، فوق البنفسجية – المرئية، الكتلة، التحليل الدقيق للعناصر، الامتصاص الذري، محتوى الكلور، التوصيلية المولارية والحساسية المغناطيسية). أظهرت نتائج الاطياف ان الليكاند يسلك ثنائي السن في كافة المعقدات .

كما اظهرت هذه الدراسة ان المعقدات ذات شكل رباعي السطوح بينما اعطى معقد البلاديوم شكل مربع مستوي ومعقدي الرينيوم والبلاتين ثماني السطوح ، علماً ان جميع المعقدات كانت بنسبة (1:1) (فلز: ليكاند) وكانت ايونية بنسبة (1:1) فقط معقد الرينيوم كان غير الكتروليتي. كما عولجت المركبات نظريا ببرنامج الهايبر كيم -8 في الحالة الغازية عند 298 كلفن.

الكلمات المفتاحية: ليكاندات ثنائية السن، ليكاندات آزو، معقدات الآزو، المعالجات النظرية.