Synthesis, Structural Study and Computational Treatment of Some Heavy Metals Complexes with Mixed Ligand Using Microwave and *Conventional* methods

Mahasin F. Alias* ***Basha'ar A. Stephan****
Farah S. Jaafer**

*Department of Chemistry/ College of Science for Woman/ University of Baghdad, Iraq.
**Cambridge International School Kurdistan, Erbil.
***University of Ibn Sina of Medical and Pharmaceutical Sciences, Iraq.
Email: alias_mahasin@yahoo.com

Received 21/6/2016
Accepted 27/11/2016

Abstract:

Some complexes were prepared by conventional and microwave methods using primary ligand 2-amino acetic acid-6- chloro benzothiazole (L) was prepared as a chelating ligand, which was treated with the Rh(III), Pd(II), Cd(II), Pt(IV) and Au(III) in ethanolic medium in order to prepare series of new metal complexes in presence co-ligand 1,10-phenanthroline (L"). The compounds were characterized by some techniques : FT-IR, UV-Visible, flame atomic absorption technique as well as elemental analysis, conductivity measurementsand μ_{eff}. Spectral done indicated thatthere was an octahedral geometry for all prepared complexes. A theoretical treatment of these compounds in gas phase was studied using Hyper Chem-8 program, Semi-empirical method was performed to evaluate heat of formation ΔH°_{f} and binding energy ΔE_b for ligands and complexes, also the vibration frequencies and electronic transitions were calculated for the ligands. Electrostatic potential, HOMO and LUMO energies for ligands were estimeted to determine the reactive positions for these ligands.

Keywords: Heterocyclics, mixed ligand, computational chemistry,transition metals

Introduction:

Many heterocyclic compounds and their derivatives are made to synthesize by large number of efforts are found to possess different antibiotics activities (antimicrobial, anticonvulsant and anthelmintic)[1],as well as benzothaizole group is very small but it possess many of biological activities and some of 2-aminobenzothiazoles have been studiedas central muscle relaxants[1,2]. Coordination chemistry of mixed different ligands complexes areconsideredimportant field because they can provide new materials with favorite properties such as magnetic exchange, photoluminescence, electricity, nonlinear optical properties and antibiotic activity[3], in addition to this,stabilities of mixed ligandshave great importance inbiological

systems where the metabolic and toxicological functions relies upon this stability[4]. Computational chemistry, sometimes called (theoretical chemistry) or (molecular modeling); can be defined as the science or art in which studying the molecular structure and function of atoms and molecules through computation and model building[5],computational chemistry helps to characterize and predict the structure of chemical systems and their stability, alsodeterminesdifference in energy, explain reaction routs and mechanisms at the atomic level[6].

Experimental

Instrumentation:

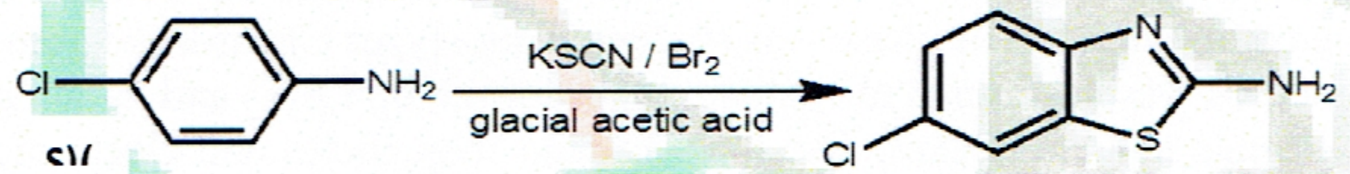
The metal complexes were prepared by using Microwave Oven, MH6548FRR, Max. 2200W, LG Electronics Inc.Products were analyzed by some techniqus; the FT-IR spectra in range (4000-200 cm^{-1}) were recorded as CsI disc on IR-Prestige-21, Single beam path Laser, Shimadzu Fourier Transform infrared Spectrophotometer, UV-Visible spectra were measured using UV-1650PC Shimadzu, in the range (200-1100 nm).Atomic absorption measurements of the prepared complexes were obtained using Shimadzu Atomic Absorption 680 Flame Spectrophotometer.Elemental C.H.N.S analysis were carried out on a EM-017.mth instrument.The conductivity values of the prepared complexes were measured using 10^{-3} M DMF as a solvent, (WTW) Conductometer. The magnatic susceptibility values of the prepared complexes were obtained at room temperature using Magnatic Succeptibility Balance of Johanson matter catalytic system division.

Material and methods:

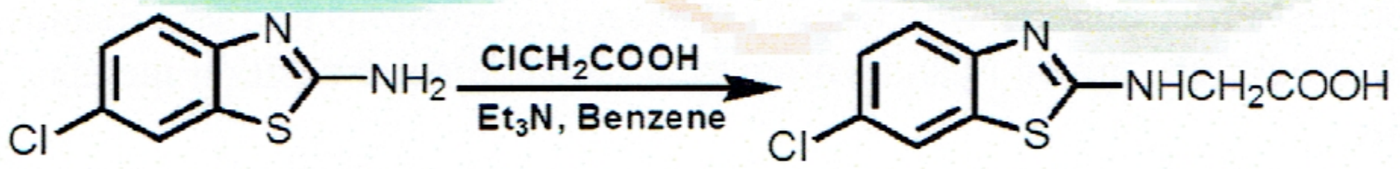
All materials were used without purification.

Preparation of 2-amino-6-chloro benzothiazole (S)[7a] and 2-amino acetic acid-6-chloro benzothiazole (L).

This ligand was prepared accordring to the literature **[7b]**:



.....1



.....2

Preperation of the complexes

a. Conventional Method

An ethanolic solution of (0.252 g) 2-amino acetic acid-6- chloro benzothiazole (L) as a primary ligand and mixed with (0.198 g) (1,10- Phenanthroline) (L") as a co-ligand which was added slowly, into warm ethanolic solution of heavy metal salts[$RhCl_3.H_2O$(0.227 g) , $PdCl_2$ (0.170 g), $Cd(NO_3)_2.4H_2O$ (0.300 g) , $H_2PtCl_6.6H_2O$ (0.518 g) and $HAuCl_4.H_2O$ (0.339 g)] with gently stirring. The resulting solution was refluxed for about (2-4) hrs on water bath. The colored precipitated was filtered, washed

several times with ethanol and dried under vacuum. Some physio-chemical properties are shown in Table (1).

b. Microwave Method

The primary ligand 2-amino acetic acid-6-chloro benzothiazole(L)(0.252 g) and the secondary ligand (1,10- Phenanthroline) (L") (0.198 g)and the heavy metal salts [$RhCl_3.H_2O$(0.227 g) , $PdCl_2$ (0.170 g), $Cd(NO_3)_2.4H_2O$ (0.300 g) , $H_2PtCl_6.6H_2O$ (0.518 g) and $HAuCl_4.H_2O$ (0.339 g)]were mixed in 1:1:1 (M: L: L") ratio in a grinder. The reaction mixture was then irradiated in the microwave oven using (5) drops of ethanol. The reaction was finished in a few minutes (2-3) min. The products was then recrystallized with ethanol and ether and finally dried under vacuum. Some analyticaland physicalproperties are shown in Table (1).

Results and Discussion:

The elemental analysis and atomic absorption show 1:1 (metal:ligand) stoichiometry for the prepared complexes. The analytical data together with some physical properties of the complexes are shown in Table (1). The isolated complexes are stable at room temperature and insoluble in most organic solvents, but soluble in dimethyl formamide and dimethyl sulfoxide. The conductance values of the compounds indicating that all complexes are ionic except Pd complex, Table (3). The formation and their geometry were further confirmed by IR, UV-Vis and magnetic studies.

Table (1): The different results of thermall and microwave methods, analytical data of primary ligand (L), co-ligand (L") and their metal complexes.

Compounds Colour	Reaction period TM (MI) hr min	Yield % TM (MI)	M. P. °C TM (MI)	M. Wt g.mol⁻	Elemental analysis / Found (Calc.) C	H	N	S	Metal % Found (Calc.)
$C_9H_5N_2O_2SCl$ (L) Pale yellow	——	76	150 – 152	242.5	44.05 (44.53)	3.12 (2.88)	10.97 (11.54)	13.32 (13.19)	——
$C_{12}H_8N_2.H_2O$ (L") White	——	——	100 - 102	198.0	——	——	——	——	——
[Rh L L" Cl]$Cl_2.H_2O$ Light yellow	4.0 (2.5)	82 (95)	240 d (238 d)	650.0	38.23 (38.76)	3.00 (2.61)	8.79 (8.61)	5.03 (4.92)	15.00 (15.83)
[Pd L L" Cl].$2H_2O$ Brownish gray	4.0 (2.5)	80 (93)	240 d (242 d)	599.4	41.87 (42.04)	2.88 (3.00)	10.15 (9.34)	4.83 (5.33)	17.27 (17.75)
[Cd L L" H_2O]$NO_3.3H_2O$ Light beige	4.0 (2.0)	81 (90)	113 d (112 d)	667.9	36.92 (37.73)	2.94 (3.29)	9.98 (10.48)	4.11 (4.79)	17.05 (16.82)
[Pt L L"Cl]$Cl_2.0.5EtOH$ Orange	4.0 (2.5)	79 (96)	210 d (208 d)	746.1	35.03 (35.38)	2.93 (2.27)	6.98 (7.50)	4.41 (4.28)	25.77 (26.14)
[Au L L" Cl]Cl.EtOH Dark brown	4.0 (2.5)	63 (90)	113 d (115 d)	735.5	37.24 (37.52)	2.46 (2.71)	7.71 (7.61)	4.97 (4.35)	26.09 (26.78)

Where: d = decomposition degree, TM = Thermal or Conventional Method, MI = Microwave Irradiation.

FT-IR Spectra

Table (2) shows thetentative assignments of IR peaks for the ligand L together with 1,10-phenanthroline. The IR spectrum of L,Fig.(1), shows a typical broad band in the range (2400-3500 cm^{-1}) with its maximum at (3286 cm^{-1}) that refers to stretching frequency of ν(OH) band of carboxylic acid[8]. Strong and sharp absorption band at 1635 cm^{-1} is due to the stretching frequency of carbonyl band of carboxylic acid[8]. This band undergo a slight shift in (RhLL") complex that indicates incomplete deprotonation of the ligand in this complex. Furthermore, the presence of bands in the region about (910-937 cm^{-1}) in this complex more confirms the incomplete deprotonation[8,9]. The spectrum also displays medium bands at (1712 and 1400 cm^{-1}) due to asymmetric and symmetric stretching vibration of carboxylategroup, the asymmetric band records a significant increased in all complexes except $AuL_1L"$ complex, while symmetric band exhibits a significant decrease in all complexes.The difference of the values between asymmetric and symmetric stretching vibration of COO^- in complexes was compared according to the equation [$\Delta\nu = \nu(COO^-)_{asym.} - \nu(COO^-)_{sym.}$] and the values displayed a greater than 200 cm^{-1} for all complexes, indicating the monodentate coordination of the carboxylate group[8-10],also band appeares at (1249 cm^{-1}) which assigns to ν(C-O) and increases in all complexes. The sharp band at 1465 cm^{-1} can refere toδ(N-H + C-N) changes in shape and location in all complexes about 8-11 cm^{-1}; another absorption bands which shows at (810 and 775 cm^{-1}) related to stretching frequencies of ν(C-Cl) and ν(C-S) bands respectively.Table (2), other bands undergo a very slight shift in compounds which verify that these groups areuncoordinating with metal ions. According to these results, the coordination mode of this ligand with heavy metal ions as a tridentate through the carboxylate group and two amino groups for the complexes, more evidence new bands in the range (424-470cm^{-1}) and (516-567 cm^{-1}) due to the stretching frequency of (M-O) and (M-N) bonds appeare. The Infrared spectrum of 1,10-phenanthroline, shows the main bands which refer to the stretching vibrations of ν(C=N)+(C=C) which appearat (1616-1423cm^{-1}) and (1616-1419 cm^{-1}) respectively[8,9]. All bands shift towards higher and other to lower wave numbers in spectra of complexes compared to the spectrum of the free ligands, thus indicating the coordination to metals through the two sp^2 hybridized nitrogen atoms[11]. Also new band appears in the range (260-274 cm^{-1}) and has been appeared in all complexes indicating two N atomof co-ligands which coordinate with metal ion[8]. Bands which appear almost at (1384, 1180 and 945) $cm^{-1}$with some higher or lower frequencies comparable with this range in most complexes aredue to nitrate ionic group. Other bandsat in the range (3260-3460) cm^{-1} in the spectra of metal compounds, which are characterized to the ν(OH) for water or ethanol molecules.Figure (2) shows IR spectrum of Pd complex.

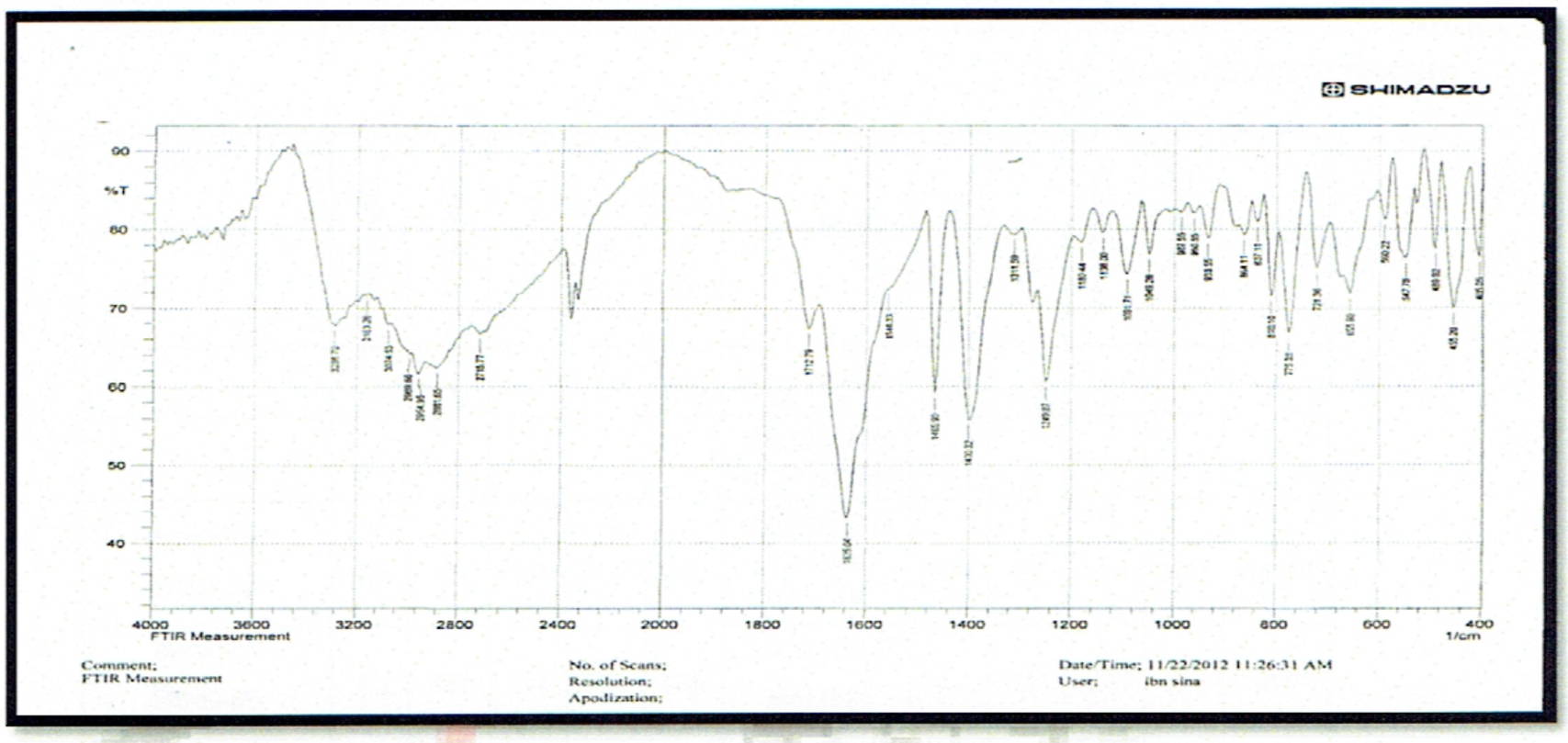


Figure (1) : FTIR spectrum of 2-amino-6-chloro benzothiazole (L).

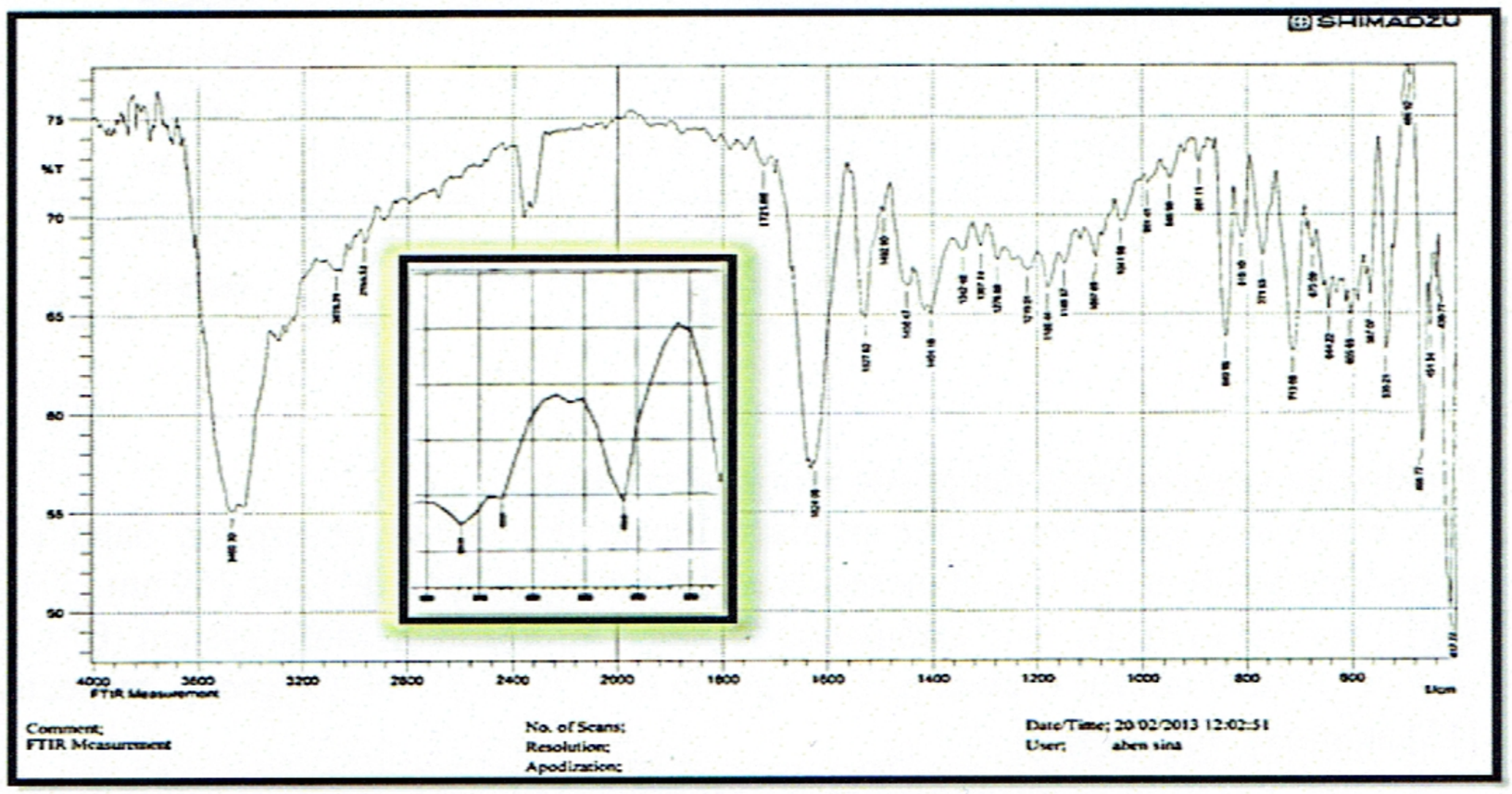


Figure (2) : FTIR spectrum of Pd complex.

Table (2): The most diagnostic FTIR of the ligand L, co-ligand L" and their metalcomplexes in (cm^{-1}).

Comp.	$\nu_{asy.}COO^-$	$\nu_{sym.}COO^-$	Δν	νC=O	νC=N+C=C	ν C-O	δN-H+ C-N	νM-O	$(\nu M-N)_L$	$(\nu M-N)_{L''}$	Others
L	—	—	—	1635	1540,1465,1400	1249	1465	—	—	—	—
L"	—	—	—	—	1616,1589,1558, 1504,1446,1419	—	—	—	—	—	—
RhLL"	1728	1346	382	1639	1620,1535,1519, 1496, 1455, 1427, 1408	1280	1455	447	532	262	νOH=3406 νRh-Cl=308
PdLL"	1725	1342	383	—	1624,1527,1492, 1450,1404	1276	1450	451	567	273	νOH=3460 νPd-Cl=320
CdLL"	1705	1388	317	—	1620, 1598, 1519, 1473, 1429	1276	1473	462	528	274	νOH=3452 δH_2O=852 νNO_3=1307,1180, 979
PtLL"	1722	1342	380	—	1620,1597,1519, 1470, 1429	1276	1470	451	524	270	νOH=3406 νPt-Cl=304
AuLL"	1701	1377	324	—	1620,1535,1508, 1450, 1411	1276	1454	470	528	262	νOH=3410 νAu-Cl=324

Electronic spectral and magnatic moment studies.

The electronic spectrum of the primary ligand (L) shows absorption band in the ultraviolet position, the two main bands at 236 nm (42372.8 cm^{-1}) and 269 nm (37174.7 cm^{-1}), are due to the ($\pi \rightarrow \pi^*$) transition for the intra ligand aromatic system (C=C) and ($n \rightarrow \pi^*$) transition for O atom of C=O group or N atom of –N=C– group, respectively **[12]**,as shown in Fig(3).

Electronic spectrum of the co-ligand 1,10-phenanthroline (L"), shows a strong band in the UV. region, the three main bands at 228 nm (43859.6 cm^{-1}), 263 nm (38022.8 cm^{-1}) and 324 nm (30864 cm^{-1}). The first absorption is due to the ($\pi \rightarrow \pi^*$) transition for the intra ligand aromatic system (C=C). The second and third absorption are due to the ($n \rightarrow \pi^*$) transition of imine group (C=N), respectively [9].

RhLL" complex: The main bands oflight yellowRhcomplex in the present work are shown in Table (3) along with their assignable transitions. Low-spin Rhodium (III) has the electronic configuration d^6. The ground term for which in octahedral stereochemistry is ^1A_1g. Two bands are expected to appear in visible region due to the transition ^1T_1g and ^1T_2g levels.

These transitions correspond to the electronic promotion $t_2g^6 \rightarrow t_2g^5eg^1$ with promoted electron maintaining its spin unaltered. The orbital multiplicity of $t_2g^5eg^1$ is 6 and

corresponds to two orbital triplet term ^1T_1g and ^1T_2g[13]. In the spectrum of Rh(III) complex, a weak band appears at (11627 cm^{-1}),which refers to the spin-forbidden $^1A_1g \rightarrow {}^3T_1g$ transition which may occur when the promoted electron changes its spin and the two T terms be ^3T_1g and ^3T_2g. These transitions are indeed observed in some cases in the region of (10000-14000 cm^{-1})[14].Values of all ligand field parameters Dq/B', B' and $\beta$are calculated using Tanabe-Sugano diagram for d^6 system by fitting ratio of the frequencies ($\upsilon_2/\ \upsilon_1$) of the observed spin-allowed bands, where it is found (B =720 cm^{-1},B' = 605cm^{-1}, 15B' = 9075cm^{-1},10Dq = 17400$cm^{-}$and^{1}Dq/B' = 2.89).The value of factor β which is (0.84) refers to ionic feature of bonding between the rhodium and the donation atom of the ligands[13,14]. Rhodium (III) complex is diamagnetic andconductivity measurement shows that the complex is an electrolyte,

Pd L L'' complex: The ground term for d^8 configuration in octahedral stereochemistry is ^3A_2g state, consequently. The possible spin-allowed transition can be assigned as in **Table (3)** with their respective values.The electronic spectrumof the showed complex, weakly band is observed at (9823) cm^{-1}, which refers to the spin-forbidden ($^3A_2g \rightarrow {}^1Eg$) transition[15]. In addition, the other three bands at (23255, 28011 and 29239 cm^{-1}) are assignable to ($^3A_2g \rightarrow {}^3T_2g$), ($^3A_2g \rightarrow {}^3T_1g$) and ($^3A_2g \rightarrow {}^3T_1g_{(P)}$) transitions, respectively. The sites of these bands are in agreement with that reported for octahedral configuration[15]. The $\mu_{eff}$for this complex was found to be (2.31 B.M.). The conductance for this complex in DMF solvent at room temperature shows to be non-electrolyte.Fig(4) shows the uv-vis. spectrum.

Cd L L'' complex: The coordination number of cadmium may be 2, 4, 5 and 6, and the most probable are 4 and 6 coordination number[13,14].The electronic spectrum of thiscomplexexhibit three bands at (32258, 36900 and 41493 cm^{-1}) shows relative change in the bands site compared to that of the alone ligands that is due to charge transfer as listed in **Table (3)**. Thus, the octahedral shape has been suggested for these complexes came in accordance with the publisher data for octahedral shape[16]. The prepared complexdiamagnetic and this is expected for d^{10} ion[17]. The conductance isdone for this complex in dimethylformamide solvent at room temperature shows to be ionic character.

Pt L L'' complex: The platinum complex is zero bormagneton as expected[18], the ground state proposed spin-paired octahedral geometry. The atomic ground state is ^5D. The low spin ground state in an octahedral field is ^1A_1g referring to ^6t_2g configuration, which gives rise to two principle spin allowed transitions whose band envelopes are very sensitive towards certain types of distortion.Excitation of an electron to eg orbital yields the configuration $t_2g^5eg^1$ which spins $^3T_1g+{}^1T_1g+{}^1T_2g+{}^3T_2g$ with the spin-triplet state lying at lower energy than the singlet[19].Two principle spin-allow absorption bands are to be expected belong to the transitions ($^1A_1g \rightarrow {}^1T_1g$ and $^1A_1g \rightarrow {}^1T_2g$) , also two bands assignable to the spin forbidden singlet-triplet transition may be exhibitedat lower energies than the spin-allowed transition**[18]**.The electronic spectrum of prepared orange **(Pt L L'')** compound, emerges three bands in the visible region which assignable to the transitions ($^1A_1g \rightarrow {}^1T_1g$),($^1A_1g \rightarrow {}^1T_2g$) and (L→PtCT). These transitions come in

accordance with the published data for octahedral geometry[19], **Table (3)**.The conductivity measurement for the prepared complex in DMF solvent at room temperature shows to be electrolyte.

Au L L" complex: Gold(III) complex is in high crystal filed effect due to the large size of gold(III) ion, being in the third transition series in addition to the high oxidation state of this ion [12]. The electronic spectrum of this complex exhibits three bands at (28248, 32573 and 39525 cm^{-1}) which assigned to ($^3A_2g \rightarrow {}^3T_2g$), ($^3A_2g \rightarrow {}^3T_1g$) and third transition L→AuCTwhich were in agreement with reported octahedral environment[15], The magnetic moment of this complex (2.81 B.M.), the conductance measurement for this complex at room temperature shows to be electrolyte.
According to these data in addition to spectroscopic and analytical data, the following structures can be suggested in Fig. (1).

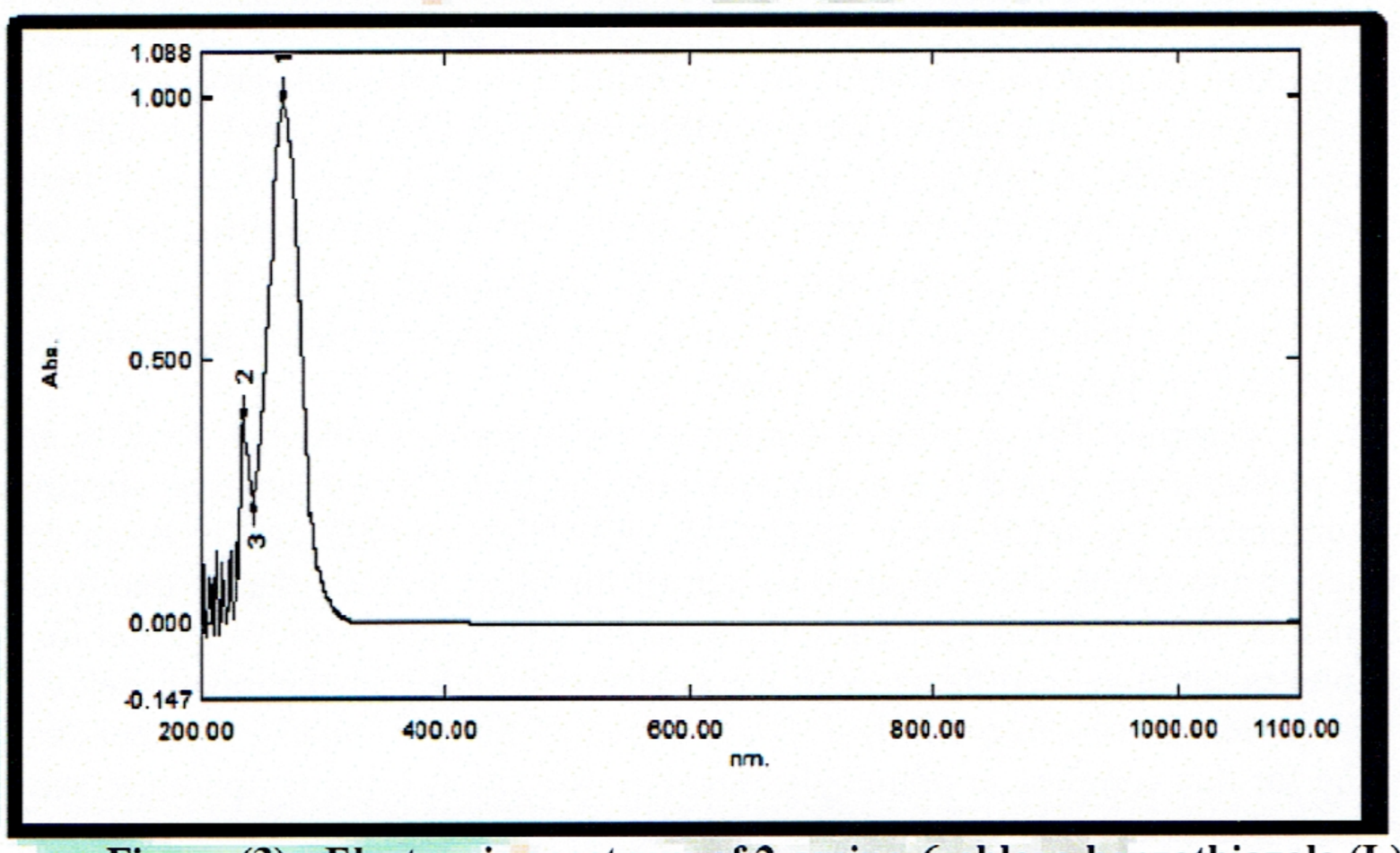


Figure (3) : Electronic spectrum of 2-amino-6-chloro benzothiazole (L).

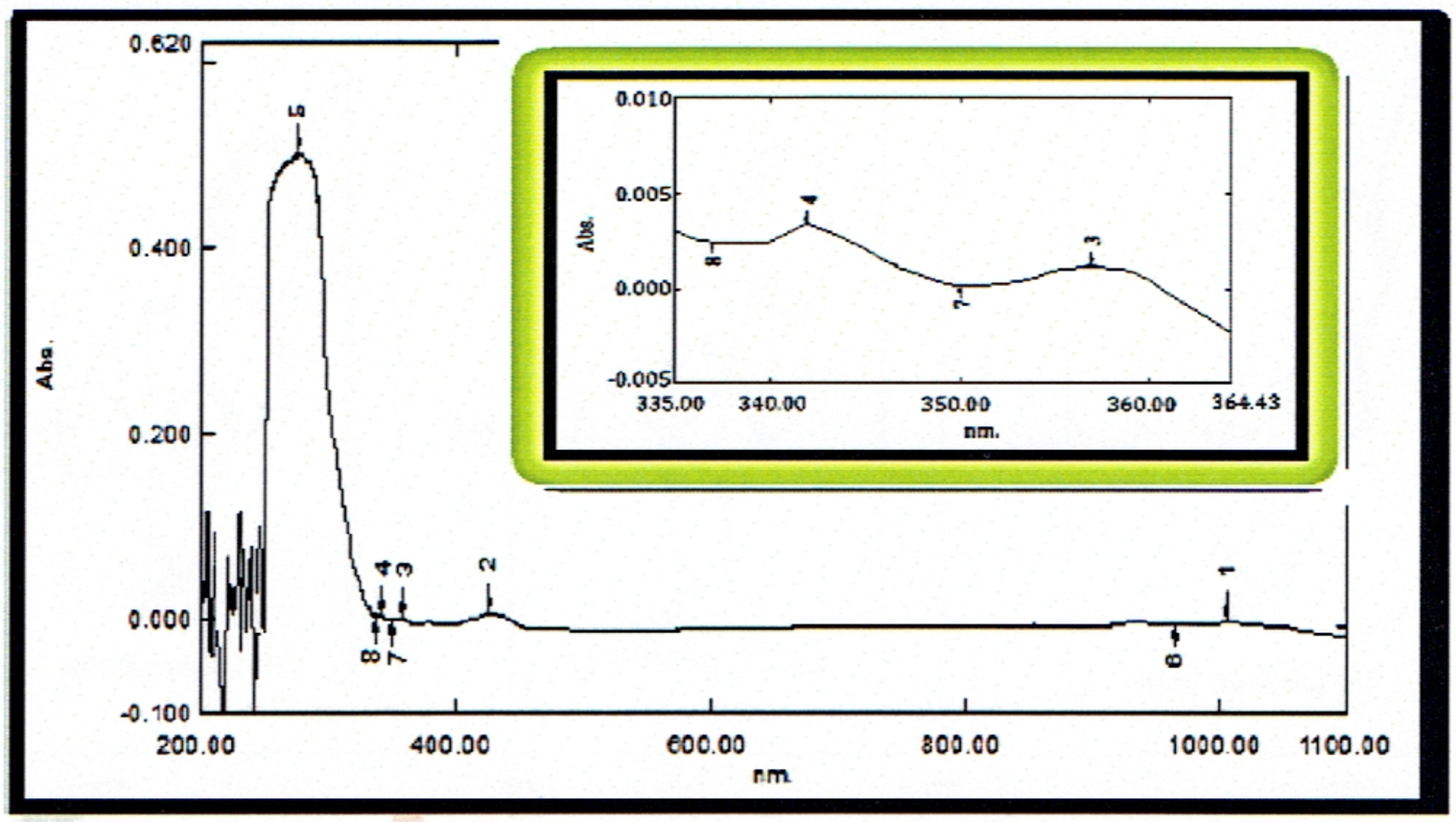


Figure (4) : Electronic spectrum of Pd complex.

Table (3): Electronic spectral data, their assignment as well as conductance and magnetic efffect for ligands and their complexes.

Comp.	Absorption Bands (cm^{-1})	Assignment	B.M.	μscm^{-1}	Proposal structure
L	42372.8 ; 37174.7	$\pi \rightarrow \pi^*$; $n \rightarrow \pi^*$	-	-	-
L"	43859.6 ; 38022.8 ; 30864.0	$\pi \rightarrow \pi^*$; $n \rightarrow \pi^*$; $n \rightarrow \pi^*$	-	-	-
RhLL"	11627; 13531; 37777	$^1A_1g \rightarrow {}^3T_1g$; $^1A_1g \rightarrow {}^1T_1g$; $^1A_1g \rightarrow {}^1T_2g$	dia	100.3	Distorted Oh
PdLL"	9823; 23255; 28011; 29239	$^3A_2g \rightarrow {}^1Eg$; $^3A_2g \rightarrow {}^3T_2g$; $^3A_2g \rightarrow {}^3T_1g$; $^3A_2g \rightarrow {}^3T_1g(P)$	2.31	15.7	Distorted Oh
CdLL"	32258; 36900 ; 41493	ILCT	dia	66.1	Distorted Oh
PtLL"	21321; 25773; 35773	$^1A_1g \rightarrow {}^1T_1g$; $^1A_1g \rightarrow {}^1T_2g$; ILCT	dia	95.2	Distorted Oh
AuLL"	28248 ; 32573 ; 39525	$^3A_2g \rightarrow {}^3T_2g$; $^3A_2g \rightarrow {}^3T_1g$; ILCT	2.81	74.2	Distorted Oh

Where **ILCT** is Internal Ligand Charge Transfer.

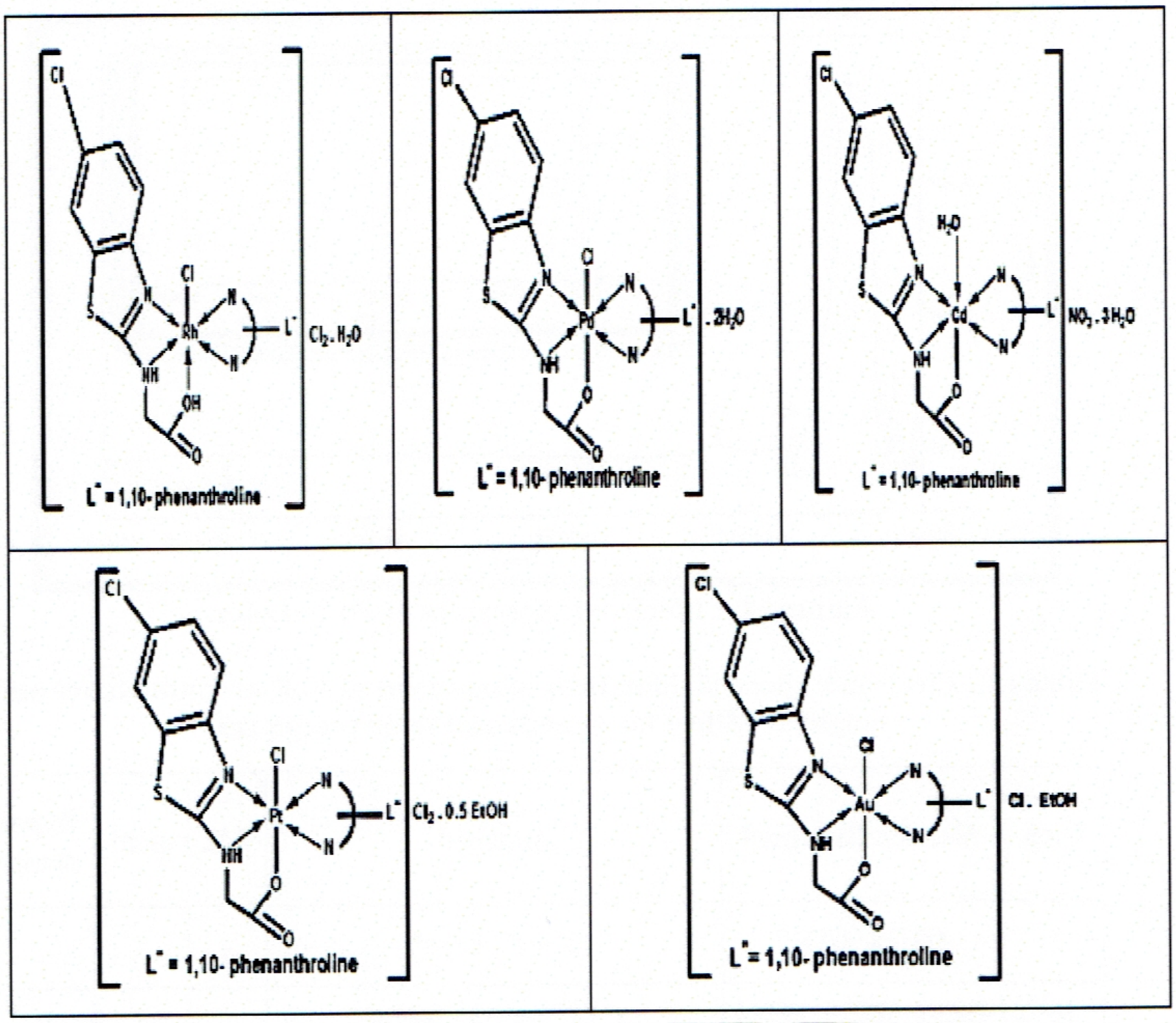


Figure (5): Formula structure may be assigned for the prepared complexes.

Computional Study:

Semi-empirical calculation by Hyperchem-8 program is used to calculate heat of formation ($\Delta H°_f$), binding energy (ΔE_b) and dipole moment (μ) for free ligands and the prepared metal complexes by PM3, ZINDO/1 and AMBER methods in addition to IR, UV spectra and molecular orbital energy (E_{HOMO}-E_{LUMO}) for free ligands.Table (4) shows heat of formation ($\Delta H°_f$), binding energy (ΔE_b) and dipole moment (μ) for free ligands and their metal complexes which were calculated by PM3, ZINDO/1 and AMPER methods. The results show that the prepeared compounds are more stable than the free ligands. PM3 was used for evaluating the vibration frequancies for the ligands and compared with the experimental frequencies, Table (5) and (6). ZINDO/S method is used to calculate electronic transitions for the ligands and compared with experimental transition, Table (7). Fig. (2), electrostatic potential of ligand L shows that the oxygen and nitrogen atoms are more reactive side than other atoms, while the result of ligand L" shows the nitrogen atoms are more reactive than other. Also the studyarises

that the LUMO of transition metal ion that much better to react with HOMO of donor atoms in both two ligands.

Table (4): Energy conformation (in K.J.mol^{-1}) and dipole moment (in Debye) for ligand (L), co-ligand (L") and their metal complexes.

Comp.	PM3			ZINDO/1			AMBER
	ΔH^o_f	ΔE_b	μ	ΔH^o_f	ΔE_b	μ	$\Delta H^o_f = \Delta E_b$
L_1	-171.80	-9975.88	2.103	-19120.97	-28925.05	3.675	———
L"	298.32	-10971.26	2.993	-22179.41	-33449.00	3.937	———
Rh LL"	———	———	———	———	———	———	1089.32
Pd LL"	———	———	———	———	———	———	1082.62
Cd LL"	682.31	-20947.3	12.73	———	———	———	———
Pt LL"	———	———	———	———	———	———	1078.92
Au LL"	———	———	———	———	———	———	1072.13

Table (5): Comparison of the main vibration frequencies in (cm^{-1}) for L between experimental and theoretical data.

Comp.	ν(C=O)	ν(C-O)	δ(AmideII)	ν(C-S)	ν(O-H)	ν (COC)
L	1635 * 1900.01 (16.2)	1249 * 1233.01 (-1.28)	1465 * 1423.09 (-2.86)	775 * 781.60 (0.85)	3286 * 3851.78 (17.2)	------

Table (6): Comparison of main vibration frequencies in (cm^{-1}) for L" between experimental and theoretical data.

Comp.	ν(C=N+C=C)	ν(C-H)arom.	δ(C-N)
L"	1616.35 * 1760.40 (8.91)	3059.10 * 3062.84 (0.12)	1419.61 * 1394.58 (-1.76)

* : Experimental frequency
: Theoretical frequency
( ) : Error % due to main different in the experimental data and theoretical treatment of vibrational frequency.

Table (7): Comparison of electronic transition for ligands between experimental and theoretical (ZINDO/S calculation)data.

Comp.	Transition	Experimental	Theoretical (ZINDO/S)
L	$n\rightarrow\pi^*$	269.00	282.70
	$\pi\rightarrow\pi^*$	236.00	210.50
L''	$n\rightarrow\pi^*$	324.00	309.70
	$n\rightarrow\pi^*$	263.00	282.90
	$\pi\rightarrow\pi^*$	228.00	245.00

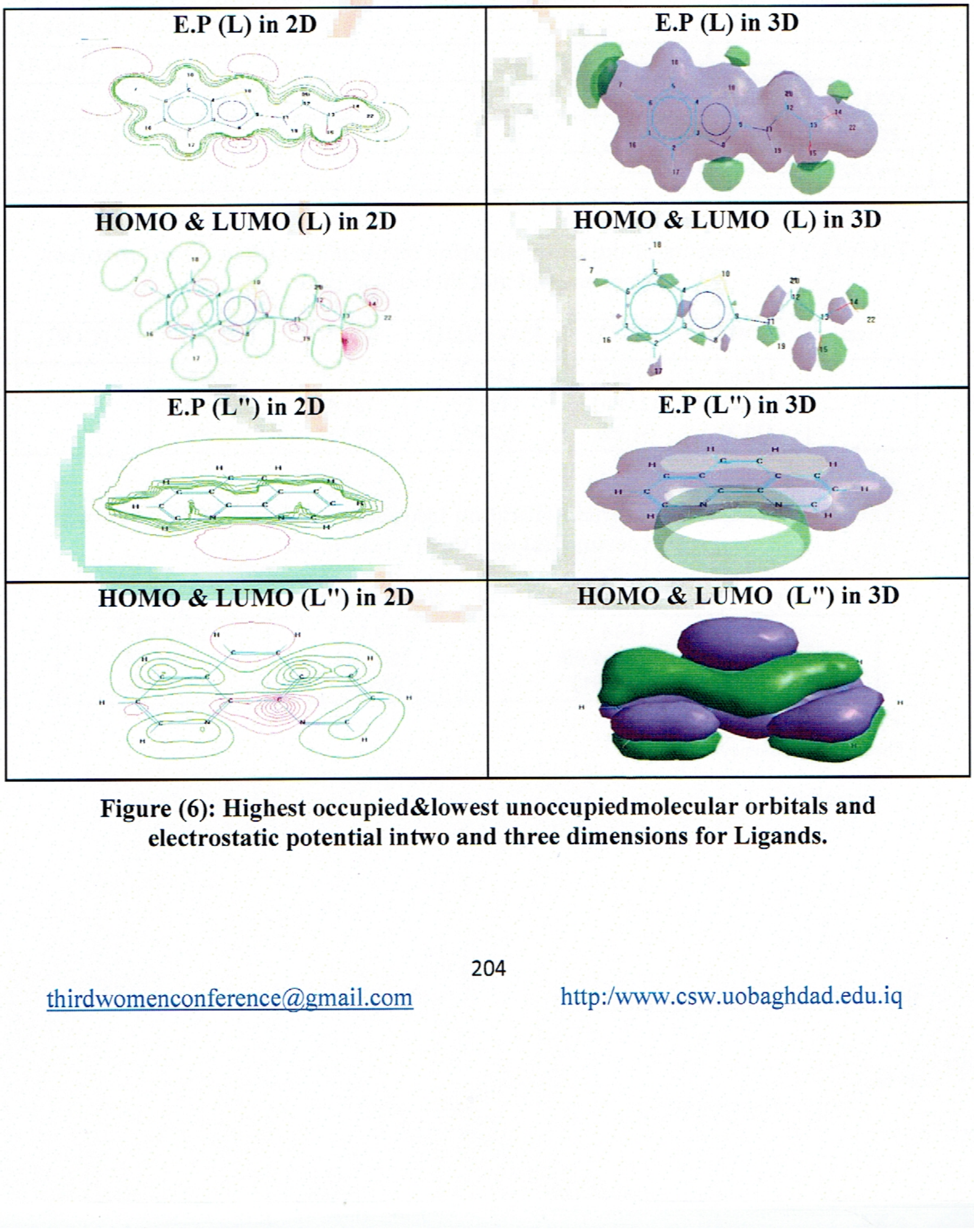


Figure (6): Highest occupied&lowest unoccupiedmolecular orbitals and electrostatic potential intwo and three dimensions for Ligands.

Conclusion:

The ligand 2-amino acetic acid-6- chloro benzothiazole complexesis successfully synthesized by microwave and conventional reaction. The ligand behaves as tridenetate ligand through (O, N, N) atoms. The FT-IR studyshowsthat all complexes have complete deprotonation except Rhinvestigate.The UV-Visible studyshow all complexes have Oh geometry. The conductivity results show that all prepared complexes are ionic except Pd. The computitional calculation data of wave number for the ligands aresimilar and support theinvestigat unambiguously the diagnognostic bands. Theoretical electronic transition helped to identify type of transition and the energy calculations that givesidea about the most stable conformation.

Reference:

[1]Chaudhary, P.; Sharma, P. K.; Sharma, A. and Varshney, J. 2010. Recent advances in pharmacological activity of benzothiazole derivatives, *Int. J. Curr. Pharm. Res.*,2 (4): 5-11.

[2]Shi, X.; Wang, Z.; Xia,Y.;Ye,T.; Deng, M.; You-Zhi, X. ; Yu-Quan, W. and Luo-Ting, Y. 2012. Synthesis and Biological Evaluation of Novel Benzothiazole-2-thiol Derivatives as Potential Anticancer Agents, *Molecules*,17: 3933-3944.

[3]Halli, M. B.; Patil,V. B.; Sumathi, R. B. and Mallikarjun, K. 2012. Synthesis, characterization and biological activity of mixed ligand metal (II) complexes derived from benzofuran-2-carbohydrazide schiff base and malonyldihydrazide ,*Der Pharma Chemica*, 4 (6): 2360-2367.

[4]Patil,S. S.;Thakur,G. A. and Patil,V. R. 2009. Synthesis, spectral and biological studies on some mixed ligand ni(ii) complexes , *Acta Poloniae Pharm. a- Drug Research*, 66 (3): 271-277.

[5]Schlick,T.2010. Molecular Modeling and Simulation An Inter-disciplinary Guide 2nd Ed. Springer.

[6]Cramer, C. J. 2004. Essentials of Computational Chemistry Theories and Models. 2nd Ed., John Wiley & Sons Ltd.

[7]a)Yadav, P. N.; Cheuhan, P. J.; Chauhan, S. and Jain, A. 2011. 2-Amino-N(7Substitu Benzo[d]2yl)benzamide: Synthesis and characterization of novel antibacterial compounds, *Der. Pharacia. Lett.*, 3(1): 208-213.

b)Alias, M. F. and Stephan, B. A. 2014. A Comparative Study of Microwave Assisted and Conventional Synthesis of Mixed Ligand Complexes with Cr(III), Co(II), Ni(II) Cu(II) and Cd(II), *Baghdad Sci. J.*, 11 (4): 1556-1566.

[8]a)Nakamoto,K. 2009.Infrared and Raman Spectra of Inorganic and coordination compounds., 6th Ed., John Wiley and Sons Ltd.

b) Stuart, B. 2004. Infrared Spectroscopy. John Wiley and sons Ltd, England.

[9]Silverstein, R . M.; Bassler, G. C. and Morill, T. C. 1981. SpectroChemitric Identificat ion of Organic Chemistry. John Wiley and Sons.

[10]Kini, S. G.; Choudhary, S. and Mubeen, M. 2012. Synthesis, docking study and anticancer activity of coumarin substituted derivatives of benzothiazole, *J. Comput. Met. Mole. Des.*, 2(1): 51-60.

[11]Li,F. H.;Zhao,G. H.;Wu,H. X.;Lin,H.;Wu,X. X.;Zhu,S. R. and Lin,H. K. 2006.Synthesis, characterization and biological activity of lanthanum(III) complexes containing 2-methylene-1,10-phenanthroline units bridged by aliphatic diamines.*J. Inorg. Biochem.*, 100 (1): 36-43.

[12]Figgis,B. N. and Hitchman,M. A. 2000. Ligand Field Theory and Its Applications. Wiley, New York.

[13]Cotton,F. A.;Wilkinson,G. and Gaus,P. L. 2004. Basic Inorganic Chemistry.3rd Ed., John Wiley and Sons, New York .

[14]Greenwood,N.N. and Earnshaw,A. 1998. Chemistry of Elements. 2nd Ed., Pergamum Press.

[15]Al-Hasani,R.A.;Al-Abodi A.K. and Kadem,S.A. 2009. Synthesis , structural study and antibacterial activity of Pd(II) , Ru(III) , Rh(III) , Au(III) and Pt(IV) complexes of 4-nitro-3-{[4-(4-hydroxyphenyl)-2-methyl-5-oxo-4,5-dihydro-1h-imidazol-1-yl]imino}-1,3-dihydro-2h-indol-2-one,*J. Al-Nahr. Uni.*, 12 (2): 35-45.

[16]Fayad,N.K.;Al-Noor, T.H. and Ghanim,F.H. 2012.Synthesis, characterization and antibacterial activity of mixed ligand complexes of some metals with 1-nitroso-2-naphthol and L-phenylalanine, *Chem. Mater. Res.*, 2(5): 18-29.

[17]Gray and Donaled 2010. "Inorganic Chemistry" 4th Ed., Preutic-Hall, Inc.

[18]Lever,A.B.P. 1986. Inorganic Electronic Spectroscopy. 2nd Ed., Elsevier New York.

[19]Shakir, C. and Alias, M. F. 2012. Synthesis, spectroscopic study of Pt (IV), Au (III), Rh(III),Co(II) and V (IV) complexes with sodium[5-(p-nitro phenyl) -/4-phenyl-1,2,4-triazole-3-dithiocarbamato hydrazide] and cytotoxicity assay on rhabdomyosarcoma cell line of heavy metals. *J. Baghdad .Sci.*, 9(4): 668-679

تحضيرات, دراسة تركيبية و معالجة حاسوبية لمعقدات بعض العناصر الثقيلة ممزوجة الليكاند بأستخدام طرق المايكروويف والتقليدية

محاسن فيصل آلياس* **بشائر عادل اسطيفان****

فرح سعدون جعفر***

*قسم الكيمياء, كلية العلوم للبنات, جامعة بغداد, بغداد, العراق.
**مدرسة كامبرج الدولية- كردستان, اربيل.
***جامعة ابن سينا للعلوم الطبية وانية, بغداد, العراق

الخلاصـــة :

حضرت بعض المعقدات بواسطة الطرق الاعتيادية و المايكروويفية باستخدام الليكاند الاولي 2- امينو اسيتيك اسيد-6-كلورو بنزوثايازول و الذي حضر كليكاند مخلبي و تم معاملته مع أيونات عناصر Rh(III) و Pd(II) و Cd(II) و Pt(IV) و Au(III) في وسط كحولي لتحضير سلسلة جديدة من المعقدات بوجود الليكاند مشارك 10,1- فينانثرولين. شخصت هذه المركبات بالتقنيات المتوفرة (الاشعة تحت الحمراء و الاشعة فوق البنفسجية – المرئية و الحساسية المغناطيسية و الامتصاص الذري اللهبي اضافة الى تحليل العناصر الدقيق و قياسات التوصيلية). و من خلال هذه الدراسات الطيفية اقترح الشكل الهندسي ثماني السطوح لجميع المعقدات المحضرة. درست المعالجة النظرية لهذه المركبات في الطور الغازي باستخدام برنامج Hyper Chem-8 و استخدمت الطرق التقريبية لتقدير حرارة التكوين ΔH°_{f} و طاقة التآصر ΔE_b و عزم ثنائي القطب (μ) لكل من الليكاندات ومعقداتهما المحضرة. ايضاً تم حساب الترددات الاهتزازية و الانتقالات الاليكترونية لليكاندات المستخدمة. الجهد الاليكتروستايتيكي و طاقات HOMO و LUMO تم حسابها لتحديد المواقع الفعالة في الليكاندات.

الكلمات المفتاحية: الحلقات غير المتجانسة, الليكاندات الممزوجة, الكيمياء الحسابية, عناصر انتقالية