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Baghdad Science Journal **Vol.12(3)2015**

Microwave Assisted Synthesis, Solution State, Spectral Studies and Theoretical Treatment of Pd(II) , Pt(IV) and Au(III) ions Complexes Containing 2-Benzamide Benzothiazole

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Received 23, June, 2014
Accepted 23, July, 2014

Abstract:

2-benzamide benzothiazole complexes of Pd(II) , Pt(IV) and Au(III) ions were prepared by microwave assisted radiation. The ligand and the complexes were isolated and characterized in solid state by using FT-IR, UV-Vis spectroscopy, flame atomic absorption, elemental analysis CHNS , magnetic susceptibility measurements , melting points and conductivity measurements. The nature of complexes in liquid state was studied by following the molar ratio method which gave results approximately identical to those obtained from isolated solid state; also, stability constant of the prepared complexes were studied and found that they were stable in molar ratio 1:1.The complexes have a sequar planner geometry except Pt(IV) complex has octahedral . A theoretical treatment of ligand and its metal complexes in gas phase were studied using HyperChem-8 program, moreover, ligand in gas phase also has been studied using Gaussian program(GaussView Currently Available Version (5.0.9) along with Gaussian 09 which was the latest in the Gaussian series of programs).

Key words: Green chemistry, Microwave irradiation, benzothiazole, Theoretical treatment.

Introduction:

Green chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous materials. One of the principles of green chemistry involves use of microwave to carry out the reaction [1].

The applications of microwave irradiation are used for carrying out chemical transformations, which are pollution free, eco-friendly, low cost and offer high yields together with simplicity in processing and handling. The salient features of microwave approach are shorter reaction times, simple reaction conditions and enhancements in yields [2,3].

Benzothiazole is a heterocyclic compound, having varied biological activities and still of great scientific interest now a days [4]. They are widely found in bio-organic and medicinal chemistry with application in drug discovery [5].

Benzothiazole moiety is found to be very important in the field of pharmacy as well as to develop newer anticancer agent in recent year,especially in the case of complexes with heavy metals due to the good response as an anticancer agent[6]. In the present work the main interest is to emphasize the various synthetic molecules developed to promote the benzothiazole moiety in the modern era of anticancer agent [7].

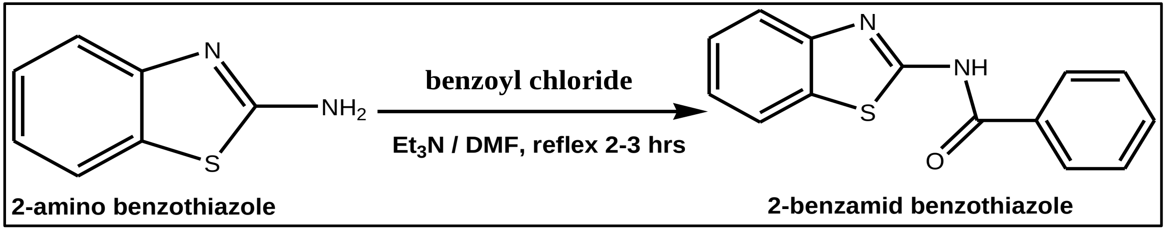
Material and Methods:

1- Instrumentation:

Elemental CHNS analysis were carried out on a EM-017.mth instrument, 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. The magnetic susceptibility values of the prepared complexes were obtained at room temperature using Magnetic Susceptibility Balance of Johanson mattey catalytic system division. Atomic absorption measurements of the prepared complexes were obtained using Shimadzu Atomic Absorption 680 Flame Spectrophotometer. The conductivity values of the prepared complexes were measured using 10^{-3}M DMF as a solvent, (WTW) Conductometer. The metal complexes were prepared by using Microwave Oven, MH6548FRR, Max. 2200W, LG Electronics Inc.

2- Preparation of 2-Benzamide benzothiazole[8]

In a round bottom flask equipped with a magnetic bar stirrer, a mixture of benzoyl chloride 0.06 mole and 0.06 mole of 2-amino benzothiazole was placed with 2ml of triethylamine (Et_3N) in 25ml of (DMF) and refluxed for (2-3hrs). After cooling, the excess of solvent was removed under vacuum and the separated solid was filtered and purified by dissolving in DMF and reprecipitating from water. The pale yellow crystal has a m.p (166-167^{o}C) and yield (70 %).



Scheme(1): Preparation of 2-Benzamide benzothiazole

3- Preperation of ligand complexes by microwave irradiation

The ligand 2-benzamid benzothiazole (0.25g) and the metal salt 1 mmole [$PdCl_2$ (0.17g) ; $H_2PtCl_6.6H_2O$ (0.51g) and $HAuCl_4.H_2O$ (0.35g)] were mixed in 1:1 (M:L) ratio in a grinder. The reaction mixture was then irradiated in the microwave oven using few drops from solvent. The reaction was completed in a short time (1.0-2.30) min. The resulting product washed several times with ethanol and finally recrystalized by ether- ethanol mixture then dried using a desiccator.

4- Formation Complexes in Solution

The molar ratio plot was obtained in order to determine [M:L] ratio of the complexes by adding an increased amount of ligand (0.25-5.0 ml) of 10^{-3}M to a constant amount of matel ion 1ml of 10^{-3}M [$PdCl_2$;$H_2PtCl_6.6H_2O$ and $HAuCl_4.H_2O$] in a volumetric flask of 10 ml absolute ethanol. Absorbance measurements were made against blank prepared for each concentration of chelating agents at a λ_{max} of the formation complex.

Results and Discussion:

The analytical data together with some physical properties of the complexes are summarized in (Table 1). The isolated solid complexes are stable at room temperature and soluble in DMF and DMSO. The formation and their geometry were further confirmed by spectroscopy and magnetic studies, (Tables 2 and 3).

Table (1): Some analytical and physical data of the ligand and its metal complexes.

Compd. / **Colour**	**Reaction period**	**Yield %**	**M. p. ºC**	**M. Wt g.mol⁻**	**% Elemental analysis / Found (Calc.)**				**Metal% Found (Calc.)**
					C	***H***	***N***	***S***	
$C_{14}H_{10}ON_2S$ Pale yellow	3.00 hr.	70	166-167	254.00	65.28 (66.14)	3.80 (3.93)	12.31 (11.02)	13.11 (12.59)	---------
$[PdLCl_2].1/2EtOH$ Brown	2.30 min.	93	200d	454.32	38.96 (39.61)	2.65 (2.86)	6.87 (6.16)	6.43 (7.04)	24.98 (23.42)
$[PtLOH_2Cl_3]Cl.EtOH$ Yellowish orange	2.30 min.	81	157-159	654.80	29.13 (29.30)	3.55 (2.74)	4.02 (4.27)	5.76 (4.88)	28.96 (29.78)
$[AuLOH_2Cl]Cl_2.EtOH$ Yellowish orange	1.30 min.	93	146	581.25	32.89 (33.00)	3.07 (3.00)	4.65 (4.81)	5.23 (5.50)	32.92 (33.87)

Where: d = decomposition degree, hr. = hour , min. = minute.

FT-IR Spectra:

(Table 2) shows tentative assignments of the IR peaks for the ligand L.The spectrum of ligand is complicated due to a large number of groups which have overlapping regions. However , a few bands have been selected in order to observe of complexation .The most significant vibration bands of free ligand and its metal complexes.The spectrum stretching frequency of ν(N-H) amide at 3290 cm^{-1},another bands exhibits at 1670,1446 and 1253cm^{-1} which assigned to stretching / bending frequency of amide (I),amide (II) and amide (III) respectively [8].The spectra of metal complexes, the band related the stretching frequency of amide (I) was shifted to the lower frequency in these complex PtL_1 about (~19cm^{-1}) and higher frequency in PdL_1 and AuL_1 about (~15-23 cm^{-1}).This change indicates that the uncharged amide oxygen participation in the coordination, more evidence a new bands appeared in the spectra of these complexes corresponding to stretching frequency of ν(M-O) band in the range (559-586 cm^{-1})[9,10]. Also the stretching frequency of ν(C=N) was shifted to the lower frequencies about (4-20 cm^{-1}) as expected , more evidence new bands displayed in the lower frequencies at (455-493 cm^{-1}) which assigned to ν(M-N) bond[9,10], this indicate that this ligand coordinate to the metal ions as a bidenetate ligand through (cyclic N and amide O) atoms [11].The shifting frequencies about (~4-23 cm^{-1}) due to stretching frequency of amide (II).The stretching frequency of ν(NH) for all complexes shows some changes in shifting due to the possible hydrogen bonding interaction between (C=O) and (N-H) moiety [12]. The spectra of PdL_1; PtL_1; and AuL_1 exhibited bands at 3348; 3398 and 3387 cm^{-1} respectivily referred to presence of ethanol molecules.. Also another weak bands appeared at 311;328 and 325 cm^{-1} attributed to coordination between metal ions and chloride ions as M-Cl for PdL_1; PtL_1 and AuL_1 complexes respectively [12]. A broad band appeared in the range (~ 3387-3414cm^{-1}) due to presence of water molecules as coordinate water in some of these prepared complexes.

Table (2): The most diagnostic FTIR of the ligand L and its metal complexes in (cm^{-1}).

Compound	***L***	***[PdLCl$_2$].1/2EtOH***	***[PtLOH$_2$Cl$_3$]Cl.EtOH***	***[AuLOH$_2$Cl]Cl$_2$.EtOH***
Aimde(I)	1670	1685	1651	1693
ν(N-H)	3290	3288	3288	3302
Amide(II)	1446	1469	1450	1458
ν(C=N)	1651	1647	1631	1635
ν(C-S)	752	748	752	748
ν(C-H)$_{arom.}$	3055	3062	3055	3080
δ(C-H)$_{oop}$	848, 794, 752	844, 794, 748	844, 794, 752	844, 794, 748
δ(C-H)$_{ip}$	1276,125, 1165,118, 1018	1288, 1253, 1157, 1107, 1064, 1018	1276, 1253, 1157, 1114, 1068, 1018	1257, 1230, 1157, 1103, 1056, 1018
ν(M-O)	-------	559	582	586
ν(M-N)	-------	455	493	474
Others	--------	νEtOH = 3398 ν PdCl =311	νEtOH = 3348 δH$_2$O = 864 ν PtCl =328	νEtOH = 3387 δH$_2$O = 883 ν AuCl =325

Where oop= out of plane , ip= in plane

Electronic spectral and Magnetic moment studies:

The electronic spectrum of ligand generally exhibited in the three main bands .The first absorption band appeared at 238nm (42016 cm^{-1}) due to intera ligand ($\pi \rightarrow \pi^*$) transition located on the C=O group. The second absorption band appeared at 276nm (36231cm^{-1}) also arises from ($\pi \rightarrow \pi^*$) transition ,but within the –N=C- group. The third absorption band attributed to ($n \rightarrow \pi^*$) electronic transition may be located on the nitrogen atom of the -C=N- or Oxygen atom of the –C=O group which appeared at 307nm (32051cm^{-1}) [8], as shown in (Table 3).

Pd(II)L: The spectrum of brown Pd(II) complex shows bands in the range 26109.6 and 29316.9cm^{-1} which assigned to $^1A_1g \rightarrow {}^1B_1g$ and $^1A_1g \rightarrow {}^1E_1g$ transition [13] and a band appearing at 36483 and 38744.6 cm^{-1} which can be assigned to L→PdCT transition due to charge transfer transition [14], This is further supported by diamagnetic behavior of Pd(II) complex [15] (Table 3). From these obtained data which are in fairly good agreement and suggest that Pd(II) complex have square planer environments of ligands.

Pt(IV)L: The electronic spectrum of prepared yellowish orange Pt(IV) complex shows five bands in the ultraviolet and visible region at11013; 13642; 23753; 31645 and 44444 cm^{-1} which assigned to the transitions :$^1A_1g \rightarrow {}^3T_1g$; $^1A_1g \rightarrow {}^1T_1g$; $^1A_1g \rightarrow {}^1T_2g$ and the others bands due to charge transfer from the donor atoms of ligand to the platinum ion , L→PtCT [16] as in (Table 3).The complex has diamagnetic behavior, an octahedral geometry around Pt(IV) can be suggested.

Au(III)L: The electronic spectrum of the diamagnetic yellowish orange Au(III)L$_1$ complex, showed three bands one at 16666 cm^{-1} which refers to the forbidden $^1A_1g_{\rightarrow}{}^3B_1g$ transition, the second at 27322 cm^{-1} which assigned to $^1A_1g_{\rightarrow}{}^1B_1g$ and the other appeared at 30769 cm^{-1} which refers to $^1A_1g \rightarrow {}^1Eg$ transition in square planner geometry [8].The bands which appeared at 33333 and 37594 cm^{-1} may be due to charge transfer, (Table 3).

Conductivity:

The molar conductance value of all the complexes has been measured in DMF as a solvent at concentration of $(10^{-3}M)$ at room temperature, indicate the conductance for Pt(IV) and Au(III) complexes while Pd(II) was non-ionic.

According to these data in addition to spectroscopic and analytical data, the following structures can be suggested in (Figure 1).

Table (3): Electronic spectra, Conductance in DMF solvent and magnetic moment (B.M) for the ligand and its metal complexes.

Compound	***L***	***[PdLCl₂].1/2EtOH***	***[PtLOH₂Cl₃]Cl .EtOH***	***[AuLOH₂Cl]Cl₂.EtOH***
Absorption Bands(cm⁻¹)	32051 36231 42016	26109 29316 36483 38744	11013 13642 23753 31645 44444	16666 27322 30769 33333 37594
Assignments	$n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	$^1A_1g\rightarrow{}^1B_1g$ $^1A_1g\rightarrow{}^1Eg$ L→PdCT L→PdCT	$^1A_1g\rightarrow{}^3T_1g$ $^1A_1g\rightarrow{}^1T_1g$ $^1A_1g\rightarrow{}^1T_2g$ L→PtCT L→PtCT	$^1A_1g_{\rightarrow}{}^3B_1g$ $^1A_1g_{\rightarrow}{}^1B_1g$ $^1A_1g\rightarrow{}^1Eg$ L →AuCT L →AuCT
μ_{eff} (B.M.)		diamagnetic	diamagnetic	diamagnetic
$\mu s.cm^{-1}$		31.3	66.2	96.7
Suggested geometry		D_4h	Oh	D_4h

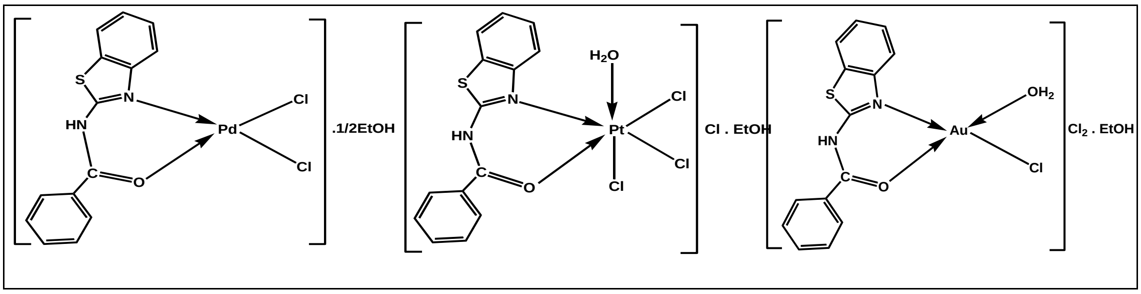


Fig. (1): Suggested structure of the prepared complexes.

Solution State:

(Figure 2) shows the change in optical density of the observed light with the L / M^{+n} at λ_{max} for each complex. The result of M:L is approximately (1:1) , ratio obtained from this study came in accordance with those obtained isolated from solid state , as shown in Table(4).

Table (4): Stability constant and molar absorptivity of prepared L complexes at room temperature.

Compound	A_s	A_m	α	K L.mol⁻	λ_{max} nm
[PdLCl₂].1/2EtOH	0.3	0.348	0.137	4.598×10^4	325
[PtLOH₂Cl]Cl. EtOH	0.038	0.060	0.366	4.73×10^3	363
[AuLOH₂Cl]Cl.EtOH	0.035	0.038	0.078	1.51×10^4	385

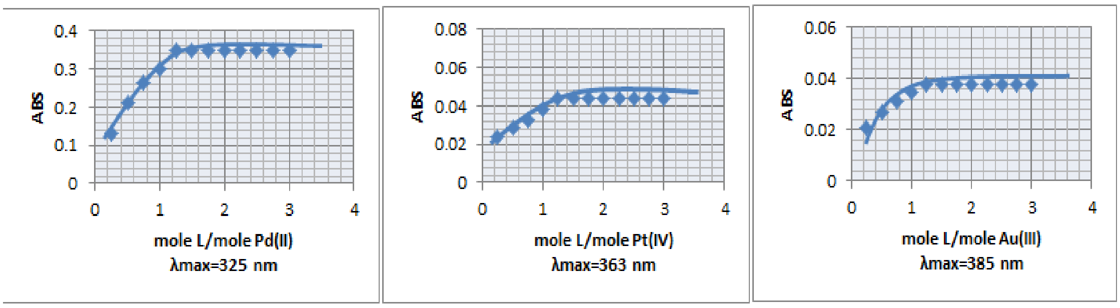


Fig. (2): Molar ratio plot of ligand and its complexes

Theoretical Studies:

In this work, Hyperchem-8 program was used to calculate the heat of formation (ΔH^{o}_{f}), binding energy (ΔE_b) and dipole moment (μ) for the free ligand and its metal complexes using semi-empirical (ZINDO/I & PM3) and molecular mechanics (AMPER) methods at 298K. It was found that the complexes are more stable than the ligand (Table5). Furthermore, the electrostatic potential for free ligand was calculated to investigate the reactive site of the molecules (Figure 3),PM3 was used to evaluate the vibrational spectrum of free ligand. It has been found that these obtained frequencies agree well with experimental results ; in addition , the calculation helped to assign unambiguously the most diagnostic bands, (Table 7). Electronic spectra measurements for the ligand was calculated theoretically by using ZINDO/S method and comparing it with experimental results. It was found that it was a close agreement between the theoretical calculation and experimental results (Table 8). While Gaussian program semi-empirical (PM3) method was used to calculate, the geometry optimization , dipole moment (μ) and total energy as shown as in (Table 6), electrostatic potential,E_{LUMO} and E_{HOMO} was obtained (Figure 3) and evaluate the vibrational spectra of free ligand and these obtained frequencies agree well with experimental results (Table 7).Electronic spectra measurements for the ligand was calculated theoretically by using the job type : Single point energy (SP) along with ZINDO method and also along with CIS method (3-21G) (Table 9).

Table (5): Conformation energetic (in K.J.mol^{-1}) and dipole moment (in Debye) for ligand (L) and it's metal complexes using HyperChem-8 program.

Comp.	PM3			ZINDO/1			AMPER
	ΔH^{o}_{f}	ΔE_b	μ	ΔH^{o}_{f}	ΔE_b	μ	$\Delta H^{\circ}_{f} = \Delta E_b$
L	223.75	-13438.84	3.86	-26582.68	-40245.28	3.16	----------
PdL	---------	---------	-----	---------	----------	-----	125.43
PtL	---------	---------	-----	---------	---------	-----	815.18
AuL	---------	---------	-----	---------	--------	-----	130.43

Table (6): Conformation energetic in (in K.J.mol^{-1}) and dipole moment (in Debye) for ligand (L) using Gaussian program.

Comp.	Total energy	μ
L	207.44	2.9889

Table (7):Comparison of experimental and theoretical vibrational frequencies for benzothiazole derevative ligand by HyperChem and Gaussian programs.

Symb.		νN-H	νC=O	νC=N	νAmideII	νC-H aromatic	νC-S	ν C-H aliphatic
L	**Exp.**	3290.56*	1670.35*	1651.07*	1446.61*	3055.24*	752.24*	--------
	Hyper.	3314.98 (3.06)	1894.30 (11.8)	1649.17 (-0.11)	1439.19 (-0.5)	3077.07 (0.7)	796.98 (5.6)	--------
	Gass.	3344.24 (1.6)	1717.32 (2.7)	1673.31 (1.3)	1311.66 (-10.2)	3258.97 (6.2)	747.53 (-0.6)	--------

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

Table (8): Ultra violet spectrum of ligand from ZINDO/S calculation and experiment by HyperChem program.

Symb.	Transition	Experimental	Theoretical (ZINDO/S)
L	n→π* π→π* π→π*	307.00 276.00 238.00	296.38 250.00 235.00

Table (9): Comparison of experimental and theoretical electronic transition for ligand from CIS and ZINDO calculation and Experiment method using Gaussian program.

Symb.	Transition	Experimental	Theoretical	
			CIS	ZINDO
L	n→π* π→π* π→π*	307.00 276.00 238.00	181.07	341.39

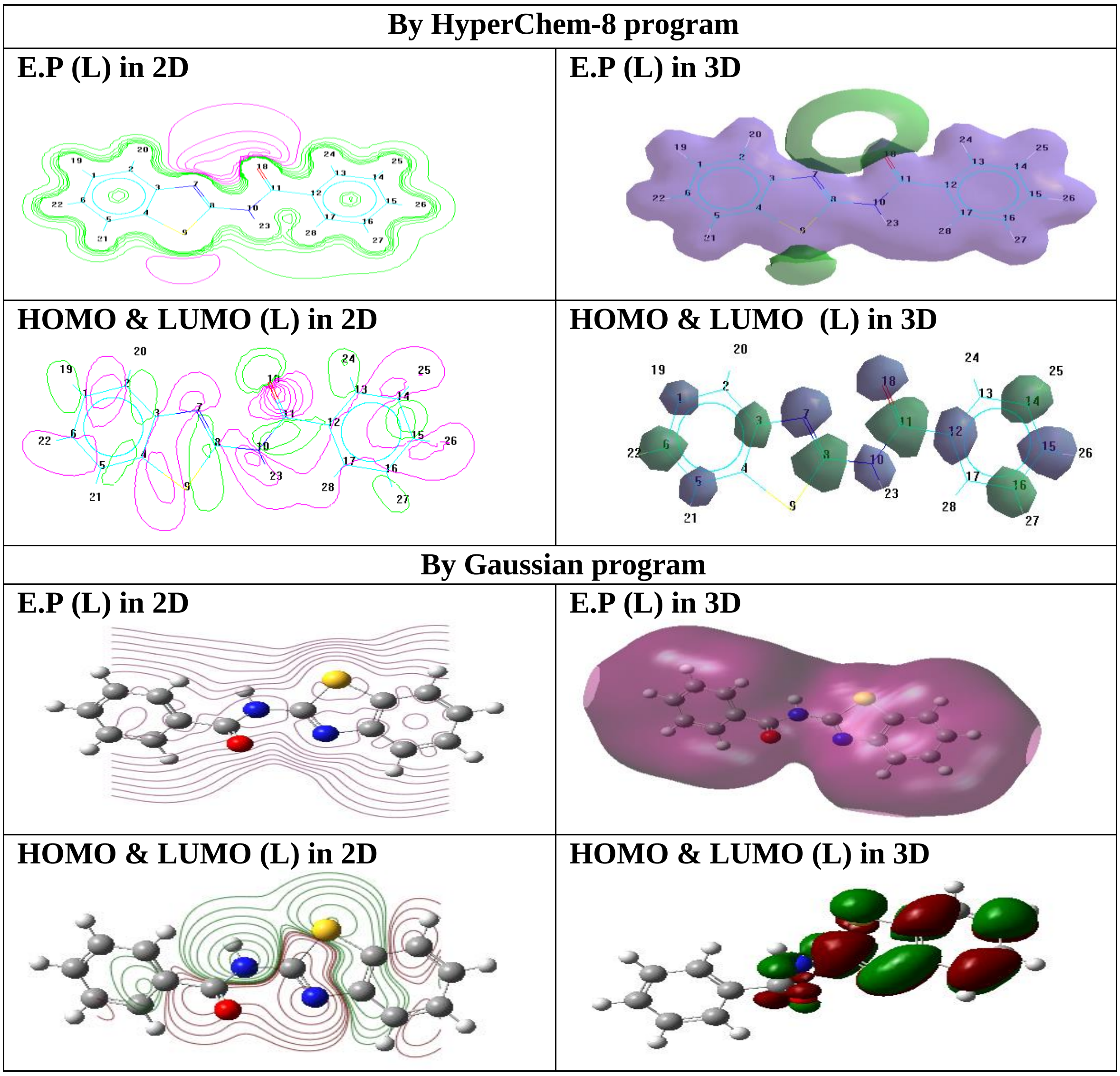


Fig. (3):HOMO, LOMO & Electrostatic potential as 2&3D counters for Ligand L

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التحضير بمساعدة المايكرويف، الحالة السائلة، الدراسة الطيفية والمعالجه النظرية لمعقدات الايونات Pd(II) ، Pt(IV) و Au(III) الحاويه على 2- بنزاميد بنزوثايزول

محاسن فيصل الياس **فرح سعدون جعفر**

قسم الكيمياء، كلية العلوم للبنات، جامعة بغداد، بغداد- العراق

الخـلاصــه:

تم تحضير معقدات 2ـ بنزاميد بنزوثايزول لايونات العناصر البلاديوم الثنائي ، البلاتين الرباعي و الذهب الثلاثي بمساعدة اشعة المايكرويف .عزلت و شخصت المركبات المحضرة بواسطة تقنيات الاشعة تحت الحمراء والاشعة فوق البنفسجيةـالمرئية والحساسية المغناطيسية والامتصاص الذري اللهبي وكذلك التحليل الدقيق للعناصر والتوصيلية الكهربائية. تم دراسة طبيعة بعض معقدات الليكاند في الحالة السائله باتباع طريقة النسبة المولية ، وقد أعطت هذه الدراسة نتائج متطابقة تقريباً مع تلك الدراسة التي تم الحصول عليها بالحالة الصلبة المعزولة و درست ثوابت الاستقرار للمعقدات المحضرة ووجد بأنها مستقرة عند النسب المولية 1:1. اجريت المعالجه النظريه لليكاند والمعقدات المحضره في الطور الغازي باستخدام برنامج Hyper chem.-8 ، ولليكاند فقط باستخدام برنامج Gaussian (GaussView (5.0.9) Gaussian 09) .

الكلمات المفتاحية: الكيمياء الخضراء، اشعة المايكرويف، بنزوثايزول، المعالجة النظرية.