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Synthesis, Characterization, Theoretical Studies and Bioactivity of Pd(II), Rh(III), Ru(III) and Pt(IV) Complexes with 1,8-Naphthalimide Derivative

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Abstract

A New Mannich base [N-(4-morpholinomethyl)-1,8-naphthalimide] (L), was synthesized and characterized by C.H.N analysis, FTIR, UV-Vis and ^{1}HNMR spectral analysis. Metal ion complexes of (L) with Pt(IV), Rh(III), Ru(III) and Pd(II) ions were prepared and characterized by FT-IR, and UV-Vis spectroscopy, elemental analysis (C.H.N), flame atomic absorption techniques as well as magnetic susceptibility and conductivity measurements. The results showed that metal ion complexes for all complexes were found in [1:2] [M:L] ratio except for Pd(II) complex which was found in [1:1] [M:L] ratio. Hyperchem-8 program has been used to predict structural geometries of the (L) and it's complexes in gas phase. The electrostatic potential (E_P) of the (L) was calculated. Furthermore, the heat of formation (ΔHf^{o}), binding energy (ΔEb), vibration spectra, electronic spectra and bond length for the ligand (L) and its metal ion complexes were calculated by PM3 methods. The antimicrobial activity of (L) and its complexes has been extensively studied against pathogenic bacteria such as ***(Pseudonomous aerugionosa)*** as gram negative and ***(Bacillus Subtilis)*** as gram positive and fungi ***(Candida albicans)*** and ***(Aspergillus flavus)*** by agar-well diffusion technique.

Keywords: 1, 8-Naphthalimide/Mannich base/Morpholin/ Antimicrobial activity/Theoretical treatment/ Spectroscopic studies

تحضير وتشخيص ودراسة نظرية وفعالية بايولوجية لمعقدات الايونات Pt(IV), Rh(III), Ru(III) , Pd(II) مع مشتق1 ,8 – نفثال ايمايد

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الخلاصة

تم تحضير قاعدة مانخ الجديدة [N-(4- مورفولينومثيل)-1,8- نفثال ايمايد] (L) والتي شخصت باستخدام التحليل الدقيق للعناصر (C.H.N) وطيف الاشعة تحت الحمراء (FT-IR) وطيف الرنين النووي المغناطيسي (^{1}H.NMR). حضرت معقدات الليكاند (L) مع ايونات العناصر [Pd(II), Ru(III), Rh(III) Pt(IV)] والتي شخصت باستخدام اطياف الاشعة تحت الحمراء وفوق البنفسجية – المرئية والتحليل الدقيق

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للعناصر (C.H.N) والامتصاص الذري اللهبي بالاضافة الى قياسات التوصيلية الكهربائية والحساسية المغناطيسية . اظهرت النتائج ان المعقدات المحضرة كانت بنسبة [2:1] [L:M] مع [Ru(III), Rh(III), Pt(IV)] ماعدا مع [Pd(II)] كانت النسبة [1:1] [L:M]. استخدم برنامج (8−Hyperchem) لاستنتاج التراكيب الهندسية لكل من الليكاند (L) ومعقداته في الطور الغازي . تم حساب الجهد الالكتروستاتيكي (Ep) لليكاند (L) , بالاضافة الى ذلك تم حساب حرارة التكوين ($\Delta Hf°$) وطاقة التاصر (ΔEb) والتردد الاهتزازي والاطياف الالكترونية واطوال الاواصر لليكاند (L) ومعقداته باستخدام الدالة (PM3) و تم تقيم الفعالية لليكاند (L) ومعقداته ضد البكتريا (*Pseudonomous aerugionosa*) السالبة لصبغة كرام و (*Bacillus Subtilis*) الموجبة لصبغة كرام و الفعالية المضادة للفطريات باستخدام النوعين (*Candida albicans*) و *(Aspergillus flavus)* باستخدام تقنية التنافذ .

Introduction

1, 8-naphthalimide derivatives were among the various heterocyclic compounds that have been useful for a variety of applications owing to their strong fluorescence , electroactivity and photostability [1-4]. Owing to the high flouresence quantum yields 1, 8-naphthalimides are used as laser dyes [5]. Most of the substitution have been carried out at the (N) of nitrogen imide ring [6]. The synthesis and characterization of the Mannich bases derived from heterocyclic rings and different aliphatic amines were described along with a number of their transition metal complexes [7, 8]. From the survy of existing literature, it appears that chemistry of Mannich bases and their metal complexes possess several biological properties and pharmaceutical applications [7-10]. Cyclic imide compounds possess a structural feature (-CO-N(R)-CO-) and an imide ring received much attention due to their antibacterial, antifungal, analgesic, antitumour, anxiolytic and anti HIV-1 activities [11-13]. When phthalimide is subjected to Mannich condensation, it yields Mannich bases which may display more potent biological activites [12, 13]. The present paper describes the synthesis of a new Mannich base, in an attempt to introduce the amino methyl moiety in the structure of 1, 8-naphthalimide compound to investigate the coordination behavior of the new derivative toward Pd(II), Ru(III), Rh(III) and Pt(IV) ions by preparing new complexes and to compare the biological activity of the Mannich base and their complexes with the main 1,8-naphthalimide structure.

Experimental

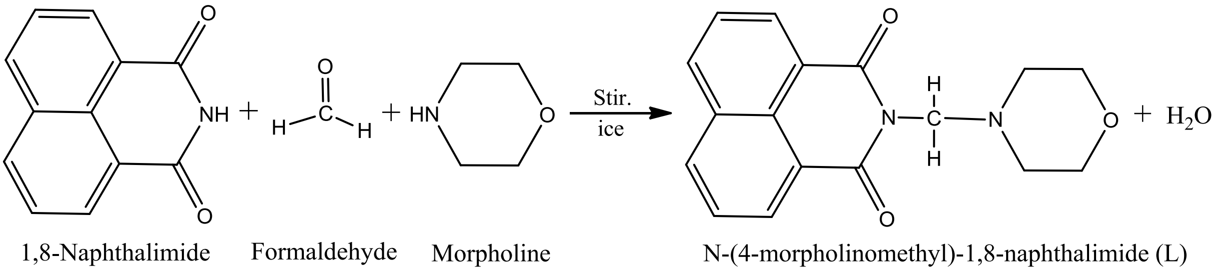
All chemicals were of highest purity and were used as received. Reagents were purchased from Fluka, BDH and Redial-Dehenge chemical companies.

Physical Measurements and Analysis

FT-IR spectra were recorded using FT-IR 8300 Shimadzu in the range of (4000-200)cm^{-1} for complexes with CsI disc and JASCO FT-IR (Fourier transform infrared spectrometer)-4200 for polymer film. Melting points were recorded on Gallen Kamp melting point apparatus. Electronic spectra were obtained using UV-1650 PC Shimadzu spectrophotometer at room temperature. Micro analytical data for C.H.N were obtained using EA-034 mth.^{1}HNMR measurements were taken (^{1}HNMR 300 MHz) using DMSO-d$_6$ as solvent. Conductivity measurements were obtained using corning conductivity meter 220. These measurements were obtained in (DMF) as a solvent using concentration of 10^{-3}M at 25^{o}C. Magnetic susceptibility measurements of metal complexes were obtained in the solid state applying Farady'a method using Bruker BM$_6$ instrument.

Preparation of Mannich Base Ligand (L)

Mannich base (L) has been synthesized Scheme-1 by condensation of (1,8-naphthalimide) aqueous formaldehyde(37%) and morpholine in (1:1:1 mol ratio) [7,13]. Ethanolic solution of 1,8-naphthalimide (19.7 g, 0.1 mol) was mixed with formaldehyde (15 mL, 0.1 mol) followed by adding morpholine (8.7 g, 0.1 mol) with stirring under ice – cold condition. A bright yellow solid mass was obtained and filtered, washed with ethanol several times and dried. The product was recrystallized from ethanol. The percentage yield of the compound was 85%. Some of the physical and chemical properties of the prepared ligand are listed in Table-1.



Scheme 1: Synthesis of Mannich base (L)

Synthesis of Mannich Base Complexes [PtL_2, RhL_2, RuL_2 and PdL]

Ethanolic solution of each of the following metal ion salts (1mmol) [$H_2PtCl_6.9H_2O$, $RuCl_3.5H_2O$ and $RhCl_3.3H_2O$] was added to an ethanolic solution of (0.580g, 2mmol) of (L) with stirring. The mixture was heated under reflux for 3 hrs. During this time a precipitate was formed and the product was isolated by filtration, washed several times with water and hot ethanol and then dried under vacuum. Pd^{2+} complex was prepared as follows: Mannich base (L) (0.367g, 1.25 mmol) was refluxed with $PdCl_2$ (0.29g, 1.25 mmol) in ethanol (in 1:1 ratio) for about 2hrs. During this time, a deep brown precipitate was formed. The product was filtered, washed with hot ethanol and dried under vacuum.

Theoretical treatment

Hyperchem is a sophisticated molecular modeler, editor and powerful computational package, that is known for its' quality, flexibility and ease of use [14-17]. It can plot orbital wave functions resulting from semi-empirical quantum mechanical calculations, as well as the electrostatic potential, the total charge density or the total spin density can also be determined during semi-empirical calculation, this information is useful in determining reactivity and correlating calculation results with experimental data. The types of prediction possible of molecules are:

Geometry optimization calculations employ energy minimization algorithms to locate stable structures, bond distances, molecular dynamics which provide the thermodynamic calculations and dynamic behavior of molecules, plot the electrostatic potential field (HOMO and LUMO), vibrational spectrum (I.R and Raman spectra) and electronic spectrum (U.V- Visible spectra) [16,17].

Biological activities

The *in vitro* biological screening effects of the investigated compounds were tested against selected types of bacteria which include ***Pseudonomous aerugionosa*** as Gram negative and ***Bacillus Subtilis*** as Gram positive and the fungs, ***Candida albicans*** and ***Aspergillus niger*** by the well diffusion method using agar nutrient as the medium. Stock solutions (10^{-3}M) were prepared by dissolving the compounds in DMSO. In a typical procedure, a well was made on the agar medium inoculated with microorganisms [18,19]. The well was filled with the test solution using a micropipette and the plate was incubated at 35°C for 72 hours. During this period, the test solution diffused and the growth of the inoculated microorganisms was affected.

Results and Discussion

Elemental analysis

The analytical data of Mannich base ligand (L) and its metal ion complexes (PtL_2, RhL_2, RuL_2 and PdL) are given in Table 1, and are in a satisfactory agreement with the calculated values. The suggested molecular structure is formulated and characterized by subsequent spectral and molar ratio as well as magnetic moment. The new (PtL_2, RhL_2, RuL_2 and PdL) complexes are colored crystalline solids soluble in (CH_2Cl_2, $CHCl_3$, DMF and DMSO). They are thermally stable and unaffected by atmospheric oxygen and moisture.

Table 1- Some physical data for Mannich base ligand (L) and its metal ion complexes

Comp. No.	Color	M.wt	Meltig point	Molar ratio inethaol	Yied %	Metal analysis found (Calc.)				Suggested formula
						C%	H%	N%	M%	
(L)	Bright Yellow	294	200	-	88	70.03 (68.92)	5.95 (5.41)	9.66 (9.46)	-	($C_{17}H_{16}N_2O_3$)
[PdL]	Deep brown	470.42	136 d	1:1	82	44.02 (43.18)	3.65 (3.39)	5.99 (5.93)	22.87 (22.53)	[Pd($C_{17}H_{16}N_2O_3$) Cl_2]
[RhL₂]	Deep Orange	795.9	159 d	1:2	80	51.77 (51.13)	4.16 (4.01)	7.86 (7.02)	13.11 (12.89)	[Rh($C_{17}H_{16}N_2O_3$)$_2$ Cl_2] Cl
[RuL₂]	Black Red	794	161 d	1:2	86	51.90 (51.26)	4.23 (4.02)	7.11 (7.04)	11.89 (12.69)	[Ru($C_{17}H_{16}N_2O_3$)$_2$ Cl_2] Cl
[PtL₂]	Dark Red	923	173 d	1:2	79	44.68 (44.01)	3.88 (3.45)	7.00 (6.04)	22.01 (21.04)	[Pt($C_{17}H_{16}N_2O_3$)$_2$ Cl_2] Cl_2

^{1}H-NMR Spectra

Evidence for the bonding mode of the ligand (L) is also provided by the ^{1}H-NMR spectra. The ^{1}H-NMR spectra of L displayed the following signals: a multiplet at 7.09-7.24 δ (Ar-H), 4.18 δ (S, 2H, -CH_2-), 3.5 δ (morpholine-OCH_2) and 2.8 δ (morpholine N-CH_2), Figure-1.

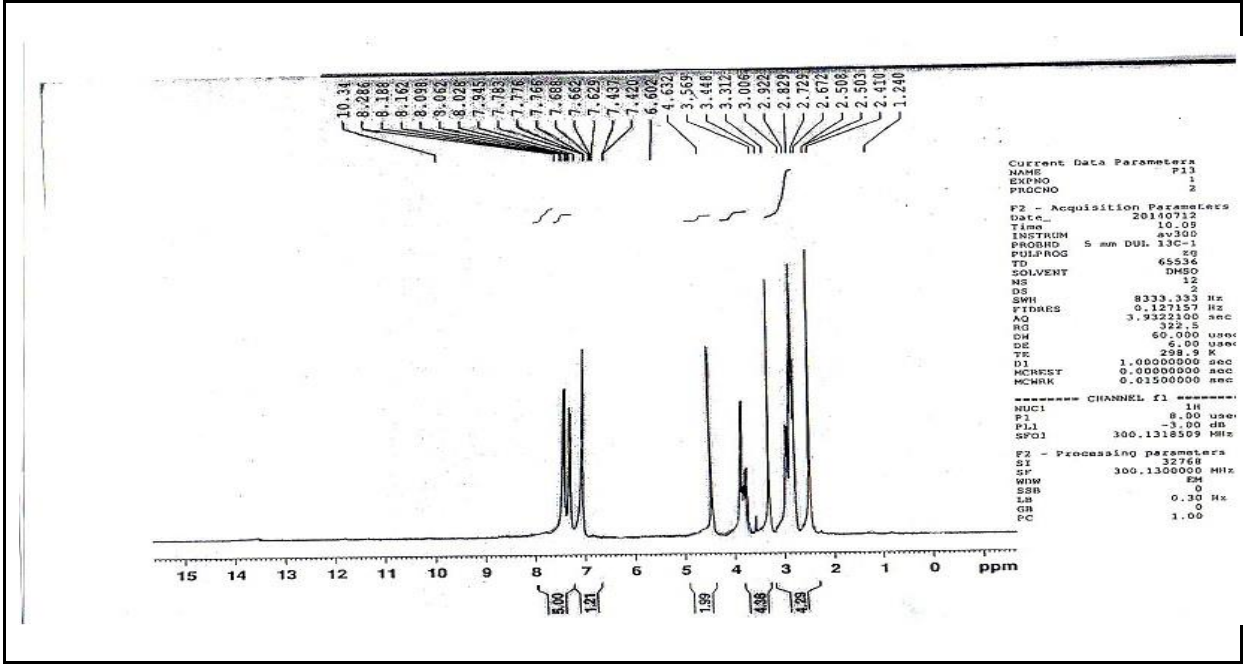


Figure 1- The 1H-NMR spectrum of the ligand (L)

Infrared Spectroscopic Study

The IR spectra of the Mannich base ligand (L) and its complexes are recorded in the solid state using CsI. As expected, FT-IR gave a good information about the complexation behavior of the ligand with various metal ions. In the spectrum of (L), the infrared bands observed at (2930 and 2866), (1768 and 1713) 1120 and 1160 cm^{-1} have been assigned to ***υ***C-H (of amino methyl), ***υ***C=O (imide), ***υ***C-O-C and ***υ***C-N-C of morpholine groups respectively [7, 20, 21]. In FT-IR spectra of all the complexes, the two bands due to (***υ***CO) of naphthalimide moiety, one shifted at higher position and another at a lower position, indicating the coordination of one of the two carbonyl oxygens to the metal ions. A band due to ***υ***C-N-C stretching vibration of the morpholine ring appeared at 1160 cm^{-1} in the Mannich base , is shifted to (1139-1148) cm^{-1} in the metal complexes , suggesting the involvement of the nitrogen atom from the morpholine ring to the central metal ion . The new bands at (530-535) cm^{-1} (442-446) and (390-396) cm^{-1} in the spectra of the metal complexes were assigned to ***υ***M-O, ***υ***M-N and ***υ***M-Cl stretching vibrations [7, 22, 23], Figures -2and3.

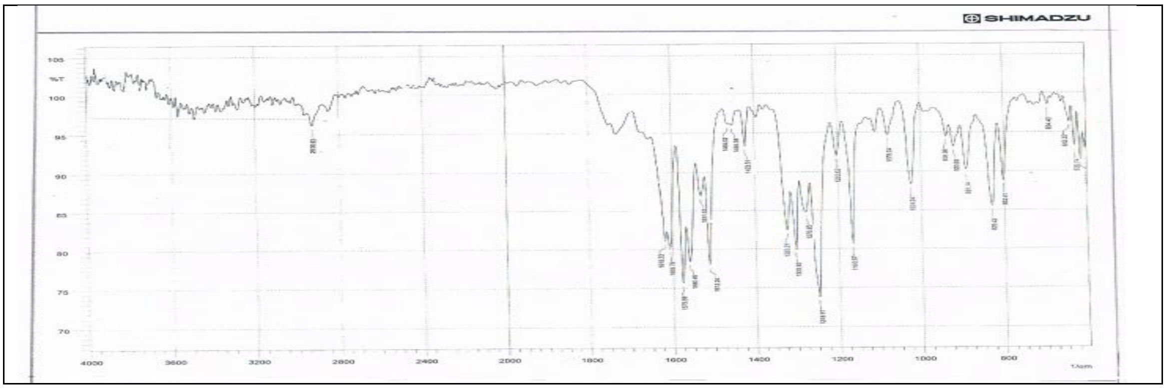


Figure 2- The FTIR Spectrum of the ligand (L)

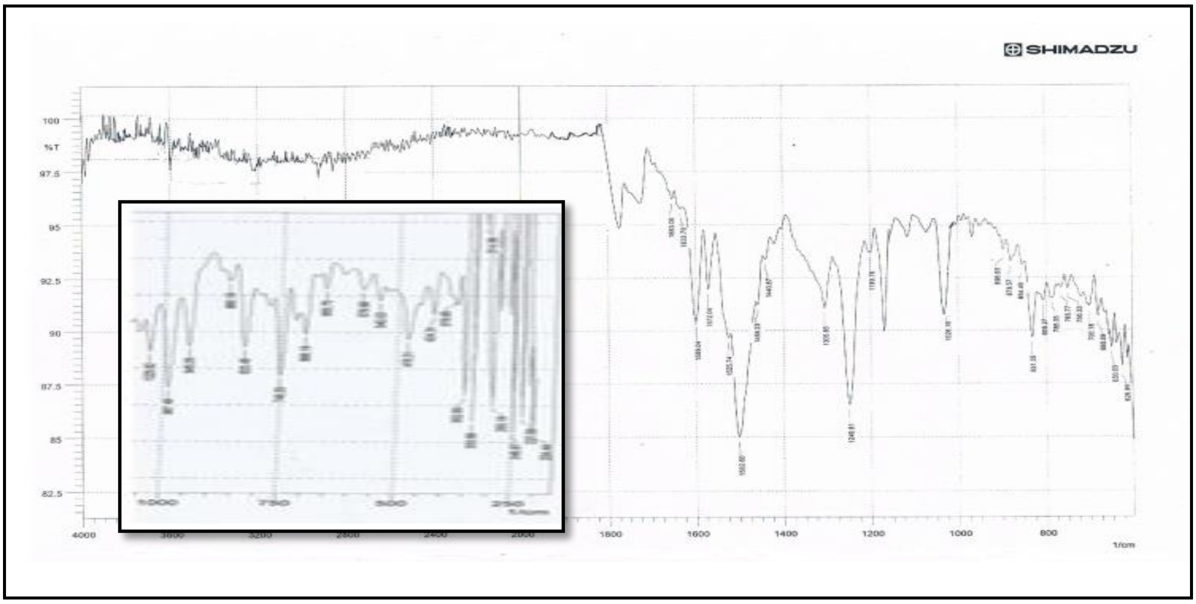


Figure 3- The FTIR Spectrum of the (RuL_2) complex

Table2- Stretching vibrational frequencies (cm^{-1}) located in the FT-IR spectra of (L)and its complexes

Comp. No.	υ_{CH}	$\upsilon_{C=O}$	$\upsilon_{C\text{-}N\text{-}C}$	$\upsilon_{C\text{-}O\text{-}C}$	$\upsilon_{M\text{-}O}$	$\upsilon_{M\text{-}N}$	$\upsilon_{M\text{-}Cl}$
(L)	2930 2866	1768 1713	1160	1120	-	-	-
[PdL]	2958 2860	1774 1690	1148	1118	535	446	392
[RhL_2]	2960 2855	1773 1691	1139	1121	533	445	390
[RuL_2]	2960 2859	1777 1688	1145	1118	530	442	395
[PtL_2]	2958 2852	1775 1689	1145	1122	530	442	396

Electronic spectra, Magnetic susceptibility and Conductivity measurements

Table -3 gives the electronic spectra of the metal ion complexes which were recorded for their solution in chloroform, in the range (200-1100) nm and magnetic moments at room temperature as well as the molar conductance values of the complexes in (DMF). The ligand **(L)** exhibited two bands around 35000 and 30000 cm^{-1}, these bands are due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively

[20,24]. Complexation of (L) with metal ions caused bathochromic shift with the appearance of new bands in the visible and near I.R regions. These bands were attributed to M – L charge transfer and to ligand field transitions [25], Table- 3.

[PdL] : The electronic spectrum of light brown palladium ion complex gave three absorption bands appeared at 21052, 25322 and 29409cm^{-1} due to $^1A_1g\rightarrow{}^1B_1g$, $^1A_1g\rightarrow{}^1E_1g$ and L→Pd (C.T), respectively, the position of these bands are in good agreement with that reported for square planer geometry [26,27]. In addition the measured magnetic moment for this complex was found to be 0.0 B.M, while the conductance measurements indicate that the complex was to be non ionic .

[RhL$_2$] : The electronic spectrum of Rh(III) complex in dichloromethane solution , exhibited four main absorption bands Table-3 , which are assigned to the four transitions: $^1A_1g \rightarrow {}^3T_1g$, $^1A_1g \rightarrow {}^3T_2g$, $^1A_1g \rightarrow {}^1T_1g$ and $^1A_1g \rightarrow {}^1T_2g$ respectively in an octahedral geometry[27-29]. Magnetic moment of solid complex, Table -3 , showed diamagnetic behaviour [30]. Conductivity measurement showed that the complex was to be ionic.

[RuL$_2$]: Three absorption bands of Ru(III) complex at (16086,18260 and 26811) cm^{-1} ,which indicate an octahedral geometry[27,31-33]. The complex was low spin[27,30], conductivity measurement in DMF showed that the complex was ionic.

[PtL$_2$] : Electronic spectrum of the prepared dark red Pt (IV) complex showed three bands at (19013, 24699 and 28580) cm^{-1} which are assigned to the transitions :-$^1A_1g \rightarrow {}^3T_1g$, $^1A_1g \rightarrow {}^3T_2g$ and (L) → Pt (C.T) respectively[27,29,30] Figure- 4. The magnetic moment of the present complex is (0.0 B.M) of the present Pt(IV) complex (d^6) configuration agree with octahedral configuration[27,28], this result indicates a diamagnetic behaviour. The conductivity measurement in DMF showed that the complex was a higher conducting, Table 3, Figure -5, therefore the two (Cl$^-$) ions are located out side the coordination zone.

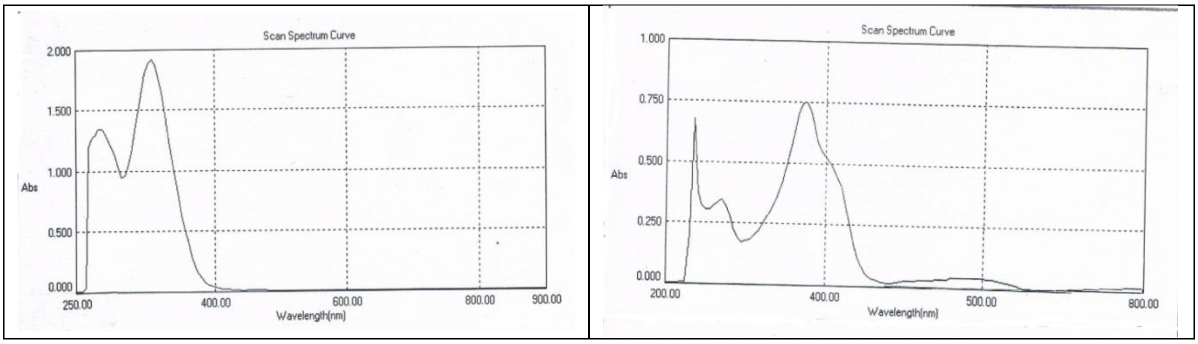


Figure 4- The UV-Vis. Spectra of the ligand (L) and (PtL$_2$) complex

Table 3- Electronic spectral data (in $CHCl_3$) (10^{-3} M), electrical conductivities (in DMF 10^{-3} M), magnetic susceptibilities (μeff,B.M) and suggested geometries for metal complexes of (L)

Comp. No.	**Maximum absorption $\upsilon_{max}(cm^{-1})$ and (nm)**	**Band assignment**	**Molar Cond. $S.cm^2.mol^{-1}$**	**μeff. B.M**	**Suggested geometry**
[L]	35000(286) 30000(333)	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-	-
[PdL]	21049(475) 25316(395) 29409(340)	$^1A_1g \rightarrow ^1B_1g$ $^1A_1g \rightarrow ^1E_1g$ $[L] \rightarrow Pd_{(C.T)}$	16.42	0.0	Square planer
[RhL_2]	18175(550) 21016(476) 23012(435) 24388(410)	$^1A_1g \rightarrow ^3T_1g$ $^1A_1g \rightarrow ^3T_2g$ $^1A_1g \rightarrow ^1T_1g$ $^1A_1g \rightarrow ^1T_2g$	69.11	0.0	Octahedral
[RuL_2]	16086(622) 18260(548) 26811(373)	$^2T_2g \rightarrow ^4T_1g$ $^2T_2g \rightarrow ^4T_2g$ $^2T_2g \rightarrow ^2Eg$	66.34	1.95	Octahedral
[PtL_2]	19013(526) 24699(405) 28580(350)	$^1A_1g \rightarrow ^3T_1g$ $^1A_1g \rightarrow ^3T_2g$ $[L] \rightarrow Pt_{(C.T)}$	168	0.0	Octahedral

General Proposed Stereo Chemistry Structure of Complexes

According to the results obtained from the elemental analysis, spectral studies, magnetic and conductivity measurements, the general structure of the above mentioned complexes can be illustrated as follows in Figure-5.

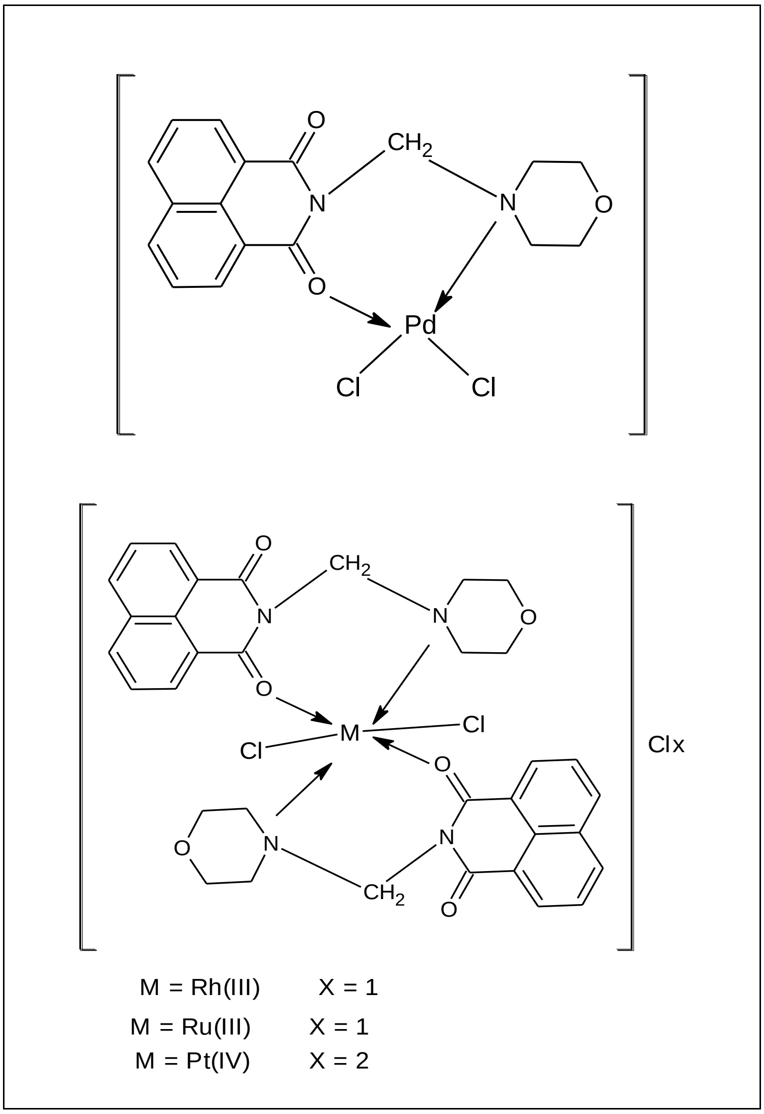


Figure 5- Proposed structures of Mannich base metal ion complexes

Theoretical studies of the ligand (L) and its metal ion complexes

1) Optimized geometries and energies

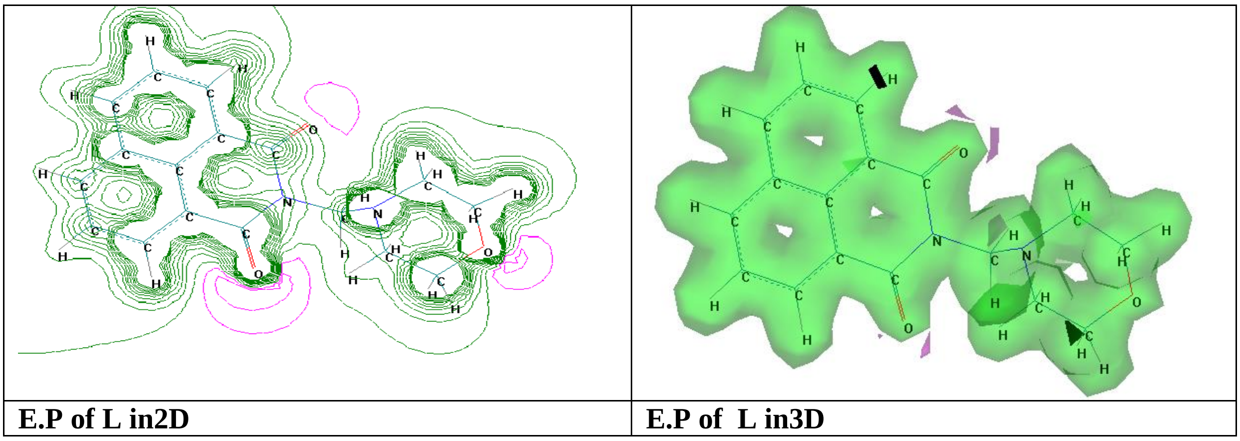
The program hyperchem-8 was used for the semi-empirical and molecular mechanic calculations in gas phase to estimate the binding energy (ΔEb) , heat of formation (ΔHf°) and total energy (ΔET) for the ligand (L) and its metal ion complexes, were calculated by PM3, ZINDO1 and AMBER methods at 298 K and at a value of geometry optimization constant (0.01 $KJ.mol^{-1}$) as tabulated inTable- 4.

Table 4- Conformation energetic (in $KJ.mol^{-1}$) for the Ligand (L) and its metal ion complexes

Comp.	**PM3**		**AMBER**	**ZINDO1**	
	ΔH°*f*	**ΔEb**	**ΔET**	**ΔH°*f***	**ΔEb**
L	-293.139	-17629.288			
[PdL]	-380.990	-18336.296			
[RhL_2]	-1091.563	-36562.888			
[RuL_2]				-72897.011	-108483.42
[PtL_2]			-103785.89		

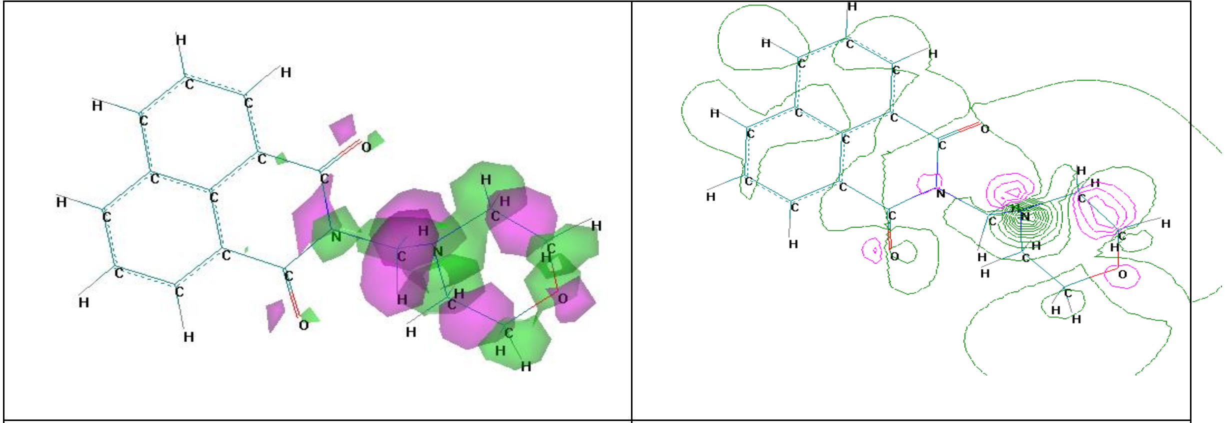
2) Electrostatic potential (E.P.)

It designates the interaction of energy of the molecular system with a positive charge point, that is the reason why it is practical for finding sites of reaction in molecule positive charge species. They tend to attack a molecule wherever the E.P is powerfully negative electrophilic attach. The E.P of the free ligand (L) is measured and plotted as 2D and 3D contour to inspect the reactive sites of the molecules shown in Figure-3. The results of calculation illustrate that the LUMO of transition metal ion choose to react with the HOMO of donor atoms in the ligand [17], as shown in Figures- 6 and 7. via adopting Hyperchem-8 program.



E.P of L in2D **E.P of L in3D**

Figure 6- Electrostatic Potential as 2D&3D counters for the ligand

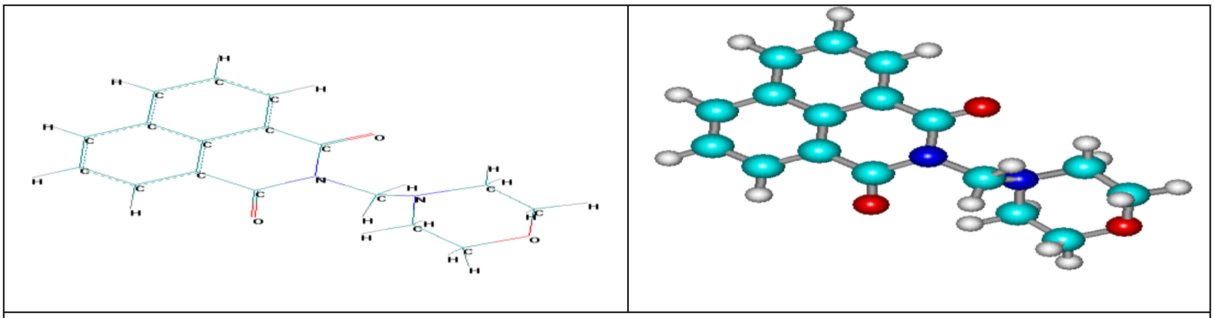


HOMO and LUMO in 3D for L **HOMO and LUMO in 2D for L**

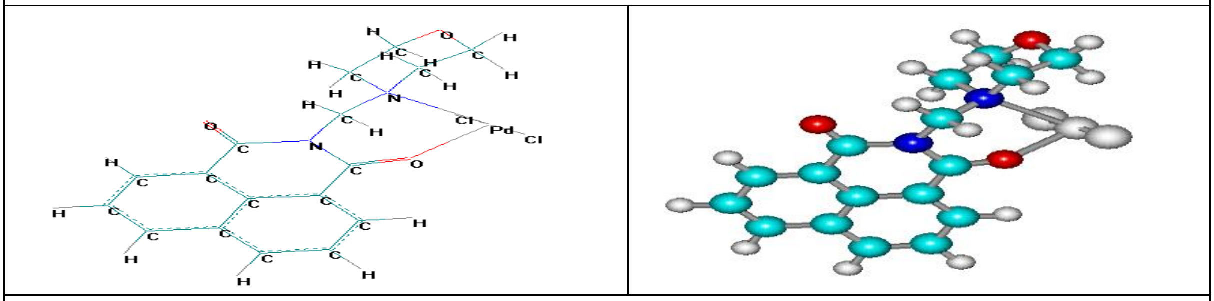
Figure7- HOMO and LUMO sites for the ligand

3) Optimized geometries of ligand (L) and its metal ion complexes

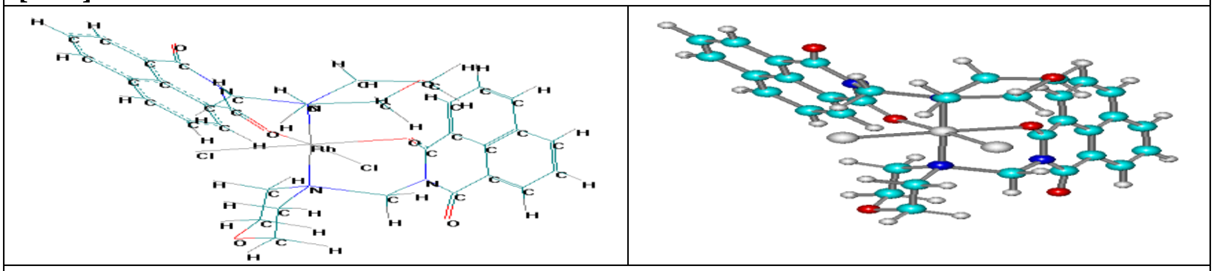
Theoretically probable structures of metal complexes with the ligand have been calculated to find the most possible model building stable structure. The shapes appearing in Figure -8 indicate the calculation optima geometries for the ligand (L) and its metal complexes are shown in Figure- 8.



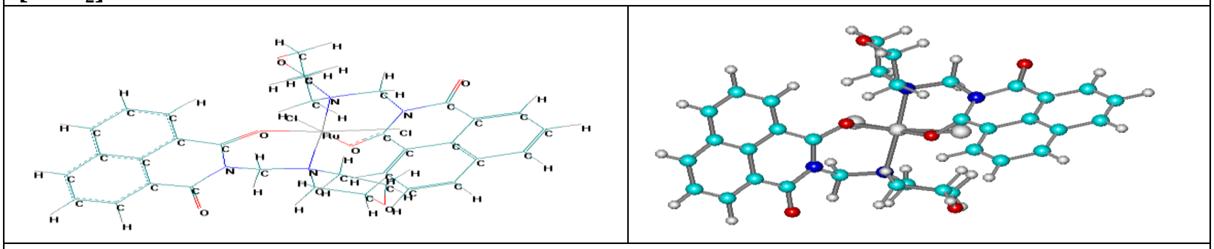
L



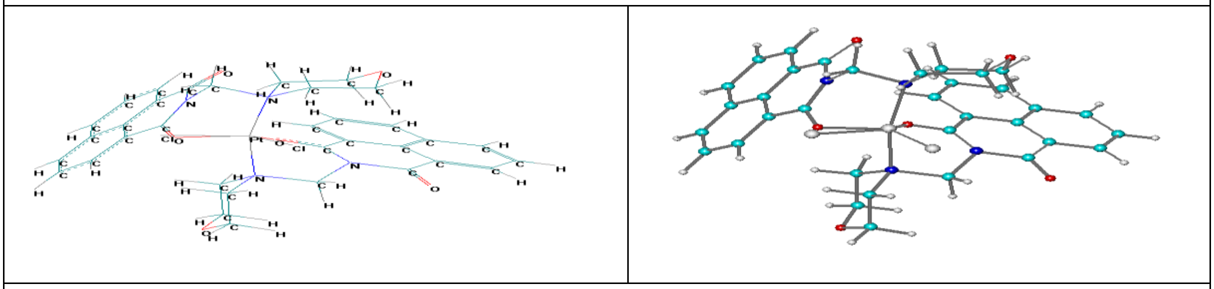
[PdL]



[RhL$_2$]



[RuL$_2$]

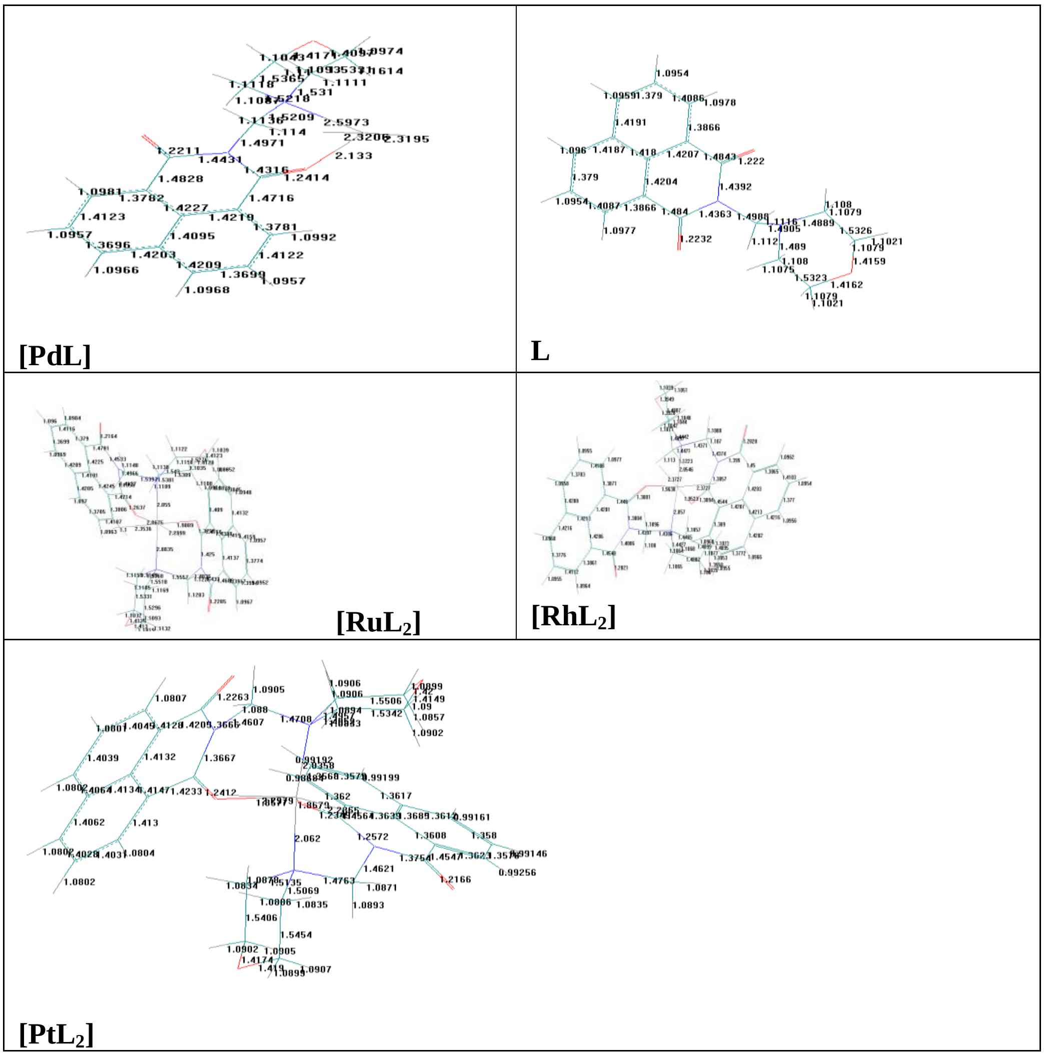


[PtL$_2$]

Figure 8- Conformation structure of the Ligand (L) and its metal ion complexes using Hyperchem-8 Program

4) Bond lengths measurements for the ligand (L) and its metal ion complexes

The Gaussian suite of software was employed throughout this study optimizations were carried out for the model systems represented in Figure-9 . The initial state for structure didn't give bond lengths naturally so that the geometry optimization was used for correct bond lengths, calculation parameters were optimized of bond lengths for the free ligand and its metal ion complexes by using the semi-empirical (PM3) method at geometry optimization (0.001 Kcal / mol), to give excellent agreement with the experimental data[15,17].

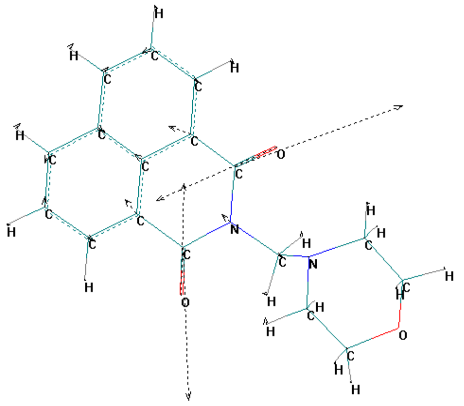
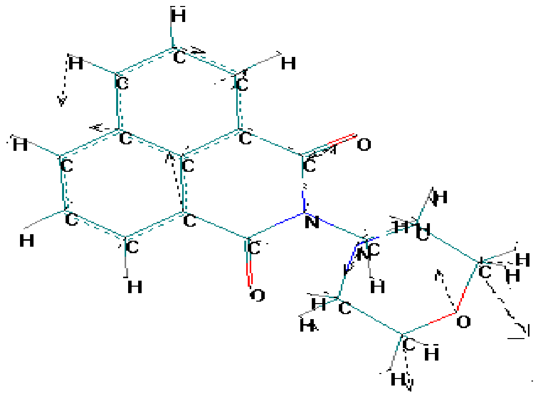
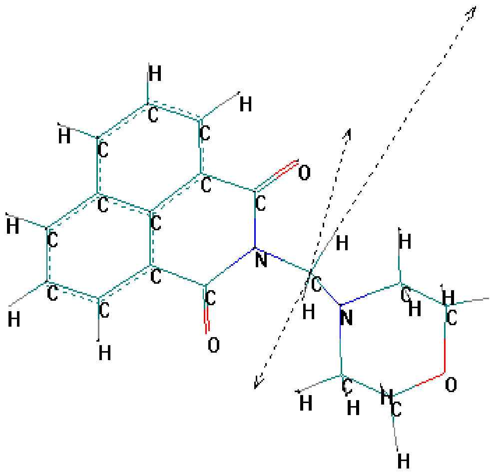
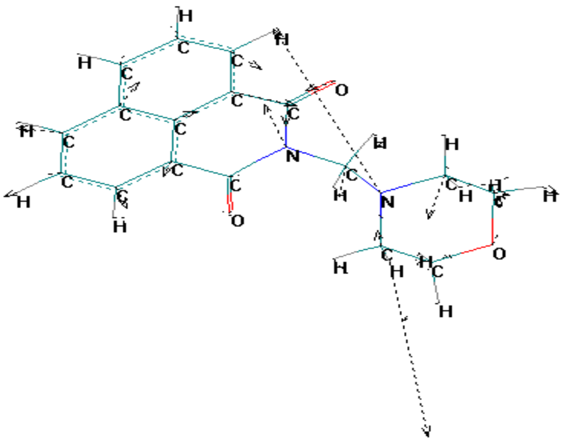
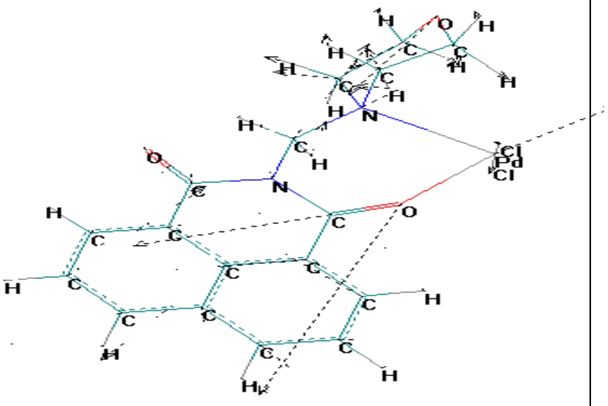
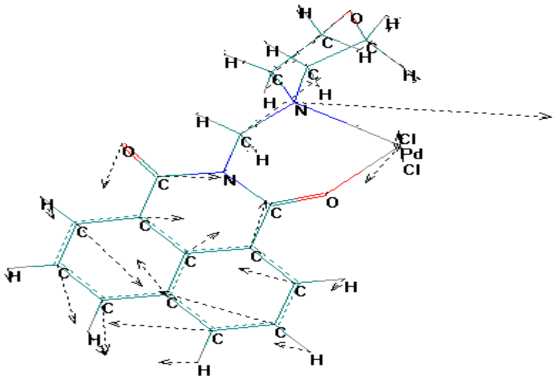


[PdL] L **[RuL_2]** **[RhL_2]** **[PtL_2]**

Figure 9- Bond length of the ligand and its metal ion complexes using Hyperchem-8 Program

5) Optimized vibrational spectra for the (L) and its complexes

The theoretical calculations of the frequencies of υC=O , υC-N-C , υC-O-C , υCH_2-N and υC-S for free ligand (L), Figure-10 their metal complexes as well as υM-O and υM-N have been calculated, Table-5. The theoretically calculated wave numbers for all compounds showed some deviations from the experimental values.These deviations are generally acceptable in theoretical calculations[15,16]. The most diagnostic calculated vibrational frequencies were chosen for the assignment of (L) and metal complexes which are included in Table-5 with their respective experimental vibrational Table-2 modes. The results obtained for the theoretical calculations of the frequencies for (L) and their metal complexes, agreed well with those obtained for the experimental values. .

	
υ C=O	**C-O-C**
	
CHof(N-CH$_2$-N)	**CNC**
	
Pd-O	**Pd-N**

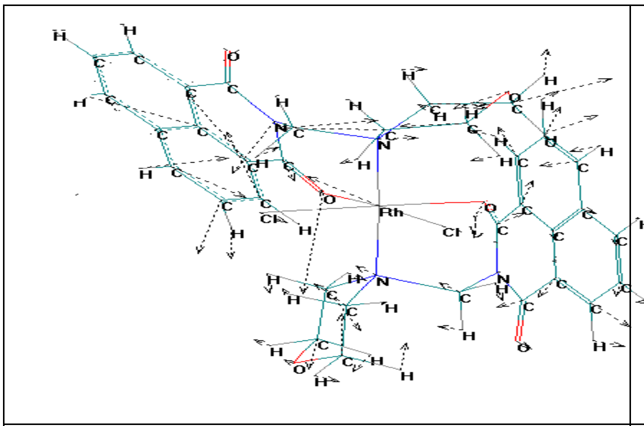
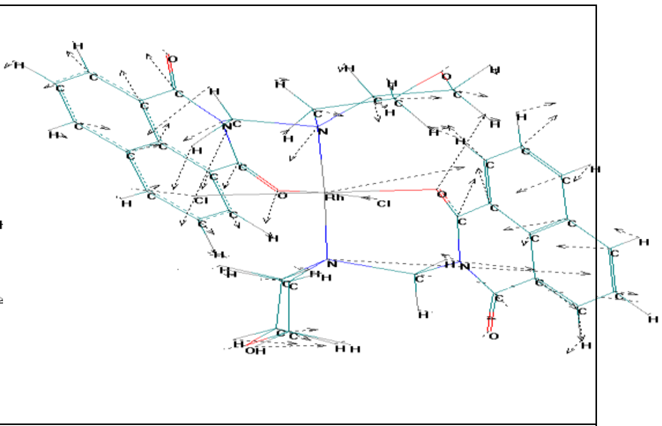
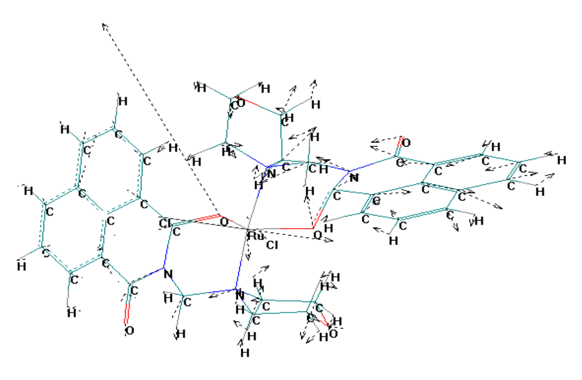
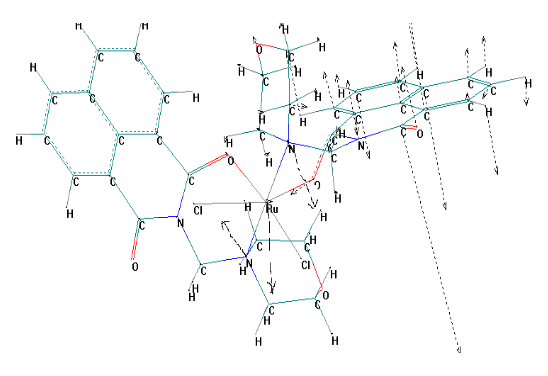
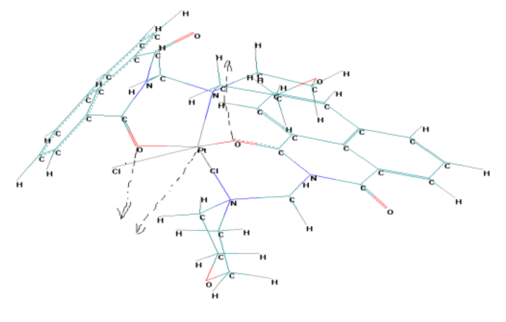
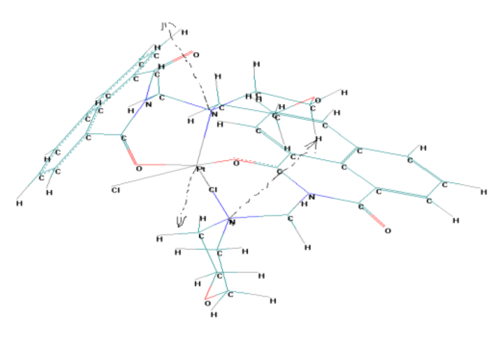
	
Rh-O	**Rh-N**
	
Ru-O	**Ru-N**
	
Pt-O	**Pt-N**

Figure 10- Some theoretical vibrational modes of the ligand (L) and its metal ion complexes

Table 5- A comparison between experimental and theoretical vibrational frequencies for the ligand and its metal ion complexes (cm^{-1})

Compo.	**C=O (sh)**	**C=O(s)**	**C-N-C**	**CH of(N-CH$_2$-N)**	**C-O-C**	**M-N**	**M-O**	**M-Cl**
L	1777* 1926** 7.7***	1708* 1708** 0. 0***	1160* 1168** 0.68***	(2930,2866)* (2948,2888)** (0.6,0.76)***	1120* 1125** 0.44***	-	-	-
PdL	1774* 1780** 0.33***	1690* 1694 ** 0.24***	1148* 1147** 0.09***	(2942,2875)* (2921,2870)** (0.71,0.17)***	1118* 1123** 0.44***	446* 450** 0.88***	535* 541** 1.11***	392* 389** 0.77***
RhL$_2$	1773* 1766** 0.39***	1691* 1693** 0.12***	1139* 1145** 0.52***	(2940,2875)* (2696,2663)** (9.05, 7.96)***	1121* 1125** 0.36***	445* 464** 4.09***	533* 527** 1.14***	390* 388** 0.52***
RuL$_2$	1777* 1769** 0.45***	1688* 1680** 0.48***	1145* 1149** 0.35***	(2940,2875)* (2696,2663)** (9.05, 7.96)***	1118* 1125** 0.62***	442* 446** 0.89***	530* 527** 0.57***	395* 389** 1.54***
PtL$_2$	1775* 1780** 0.28***	1689* 1674** 0.89***	1145* 1147** 0.17***	(2942,2875)* (2921,2870)** (0.71,0.17)***	1122* 1123** 0.08***	442* 459** 3.70***	530* 525** 0.95***	396* 401** 1.25***

Where:
***Experimental frequencies**
****Theoretical frequencies**
*****Error %**

6) Theoretical electronic spectra for the ligand (L) and its metal ion complexes

The electronic spectra of the free ligand (L) and its metal complexes have been calculated and the wave number for these compounds showed some deviations from the experimental values as shown in Table-3. 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 interacts independently electronic spectra beam[17,19]. The most diagnostic calculated electronic spectra were chosen for the assignment of the free ligand (L) and its metal complexes. 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 (L) ligand and its metal complexes showed that the percentage of error was in the range of (0.39 – 1.63), as is shown in Table -6.

Table 6- A comparison between experimental and theoretical electronic spectra for the ligand and its metal ion complexes (nm)

Comp. No.	**Maximum absorption (nm)**	**Band assignment**
[L]	285*,277**,2.88*** 333*,329**,1.22***	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
[PdL]	475*,470**,1.06*** 394*,388**,1.55*** 340*,338**,0.59***	$^1A_1g \rightarrow ^1B_1g$ $^1A_1g \rightarrow ^1E_1g$ $[L] \rightarrow Pd_{(C.T)}$
[RhL$_2$]	550*,548**,0.36*** 475*,470**,1.06*** 434*,430**,0.93*** 410*,404**,1.49***	$^1A_1g \rightarrow ^3T_1g$ $^1A_1g \rightarrow ^3T_2g$ $^1A_1g \rightarrow ^1T_1g$ $^1A_1g \rightarrow ^1T_2g$
[RuL$_2$]	621*,618**,0.49*** 547*,542**,0.92*** 372*,366**,1.63***	$^2T_2g \rightarrow ^4T_1g$ $^2T_2g \rightarrow ^4T_2g$ $^2T_2g \rightarrow ^2Eg$
[PtL$_2$]	525*,511**,2.74*** 404*,399**,1.25*** 349*,345**,1.16***	$^1A_1g \rightarrow ^3T_1g$ $^1A_1g \rightarrow ^3T_2g$ $[L] \rightarrow Pt_{(C.T)}$

Where:
***Experimental frequencies**
****Theoretical frequencies**
*****Error %**

Biological activity results

The new synthetic compounds were screened ***in vitro*** for their ability to inhibit the growth of representative ***Pseudonomous aerugionosa*** as Gram negative and ***Bacillus Subtilis*** as Gram positive. Also the study was done against ***Candida albicans*** and ***Aspergillus flavus*** fungus, in DMSO (10^{-3} M) as a solvent. The following points were concluded:

1) The study of antibacterial activities revealed that the Mannich base ligand, exhibited high activity against the studied bacteria ***Pseudonomous aerugionsa*** while against ***Bacillus Subtilis*** it was moderately active, Table- 7.

2) All complexes were found to be more toxic than the corresponding parent ligand **[L]** against all the types of the microorganisms Table-7. This was attributed to the synergetic effect [19,34] between the metal ion and the ligand.

3) The [PdL] complex showed moderate activity whereas [RhL$_2$, RuL$_2$ and PtL$_2$] complexes exhibited a great enhancement of activity against types of bacteria Table- 7. This difference may be attributed to that [RhL$_2$, RuL$_2$ and PtL$_2$] complexes are considered to be a hard metal ions making their complexes to be less lipophilic, on the other hand the [PdL] complex is considered to be soft metal ion, which render their complexes to be more lipophilic, this will facilitate the penetration the cell wall and affect the constituents of the cell [19,35].

4) Results of the antifungal activity of the new ligand and its metal complexes Table- 7 showed that the metal ion chelates have moderate antifungal activity compared with their parent ligand toward both fungi.

Table 7- Antimicrobial activities of free ligand (L) and its metal ion complexes at (10^{-3}mgm.ml^{-1})

Comp. No.	***Pseudonomous aerugionosa***	***Bacillus Subtilis***	***Candida albicans***	***Aspergillus flavus***
Control DMSO	-	-	-	-
(L)	6	0	28	33
[PdL]	10	6	18	24
[RhL$_2$]	16	12	22	18
[RuL$_2$]	12	10	18	22
[PtL$_2$]	18	12	11	16

Conclusions

The new Mannich base (L) ligand and its metal complexes were successfully synthesized and characterized. The mode of bonding and overall structure of the complexes was determined through physico-chemical and spectroscopic methods. Hyperchem-8 program has been used to predict structural geometries of all compounds in gas phase. The free ligand (L) and its metal complexes show significant antimicrobial activity.

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