SYNTHESIS AND CHARACTERIZATION OF SOME NEW METAL COMPLEXES WITH *B*IS[4-PHENYL-2-DIBUTYL AMINOMETHYL-1,2,4-TRIAZOLE-3-THION-5YL]METHANE AND THEORETICAL STUDY

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Abstract

A new Mannich base bis[4-phenyl-2-dibutyl aminomethyl-1,2,4-triazole-3-thion-5yl]methane , formed by the condensation of formaldehyde and appropriate dibutyl amine,with bis triazole ,and its complexes(Cu^{II},Co^{II},VO^{IV},Pd^{II}, Pt^{IV}) have been synthesized . Their structures have been elucidated on the basis of analytical, magnetic susceptibility, electrical conductivity and spectra study as well as metal analysis.

Structural geometries of complexes were suggested in solid state and in gas phase by using theoretical treatments,using the hyperchem-6program for the molecular mechanics and semi-empirical calculations.The heat of forma- tion(ΔHf^{o})and binding energy(ΔE_b)for the free ligand and its metal complexes were calculated by PM3,ZINDOandAMBERmethods,PM3was used to evaluate the vibration spectra of Mannich base and to compare the theoretically calculated wave numbers with experimental values by using bis (4-phenyl-3-thio-1,2,4-triazole-5yl) methane as authentic compound. The theoretically obtained frequencies a greed calculation helped to assign unambiguously the most diagnostic bands.

Introduction

The biological activity of many aromatic triazoles and their derivatives especially of 3-thio-1,2,4- triazole is now fairly documented [1,2].These compounds were described with variety of pharmacological actions,as fungicidal ,bactericidal and hypoglycemic agents[1,3].

In a previous work [4, 5], the synthesis and characterization of Mannich bases derived from 2-thio-1,3,4- oxadiazole and 3- thio-1,2,4-triazole with different cyclic aliphatic amines were described along with a number of their transition metal complexes.

The elements of medical important Pd,Pt, Cu,Co and Au offer the potential for design of novel therapeutic and diagnostic agents [6].

Recent reviews[6,7]cover the current states of metal therapeutic drugs,where a wide applications involving metal complexes ,which either used or close to being used clinically as antitumer drugs especially Platinium are scribed .Some drugs have increased activeity when administrated as metal complexes,this attributed to the synergetic effect between the metal and the ligand [8].

The present paper describes the preparation of new Mannich base,in an attempt to introdu-ce the methylamine moiety in the structure of mercapto traizole ring ,which is known to pos- ses therapeutic applications.Investigation of the coordination behavior of the prepared new ligand compound towards some transition metal ions will also be included.

Theoretical study in the gas phase by using semi-emprirical method in order to show the most stable conformation.The study aims to calculating the heat of formation,and binding energy for all the probable geometries,and to find the most active sites of the Mannich base by using the electrostatic potential calculations.

Calculation of the vibrational frequencies of the bis(4-phenyl-1,2,4-triazole-5yl)methane and Mannich base ligand have also been carried out in order to compare the results with the experimental vibrational frequencies to make a certain assignment of the most diagnostic bands .

Experimental

A-Materials and Methods:

The chemicals used in this work were obtained fromB.D.H.and they were all pure grade reagents . Flame atomic absorption of elemental analyzer, Shimadzu AA-670 was used for

metal determination . FT- IR spectra were recorded using Shimadza-8300.

Spectrophotometer,for the range of 4000-200 cm^{-1}. Electronic spectra were recordered using Shimadzu U.V. Visible. Spectrophotometer Type160.Electrical conductivity was measured by WTWconductmeter and magnetic susceptibility was measured by Bruker Magnetic using Faraday method.

B- Preparation of Ligands:

The method that was used to prepare the bis(4-phenyl-1,2,4-triazole-5yl)methane(BTRZ) was reported elsewhere[9] .The acid dihydrazides were synthesized by refluxing diethylmalonate with hydrazine hydrate.Treating the dihydrzides with phenylisothiocyanide in alkaline medium gave a BTRZ as solid mass.The Mannich base (L) was prepared according to the following: BTRZ (0.364g)was dissolved in a minimum quantity of ethanol and kept in an ice bathand treated with formaldehyde (0.6g, 40%),to this mixture ,an ethanol solution of butyl amine(2.56g)was added slowly with stirring for an hour,then,left over night in a refrigerator.A crystalline solid precipited was formed which was filtered off,washed with cold ethanol,dried and recrystallized from aqueous ethanol .The physical properties of Mannich base are list in Table (1).

C-Preparation of complexes:

One general procedure was a doped,as follows:

The salts of (VOSO$_4$.H$_2$O, CoCl$_2$.6H$_2$O, CuCl$_2$.2H$_2$O,PdCl$_2$(PhCN)$_2$ and H$_2$PtCl$_6$.6H$_2$O) were dissolved in ethanol and added to an ethanol solution of Mannich base in(2:1)mol ratio res- pectively with stirring.The mixture was heated under reflux for three hours.During this period the precipitation was completed from.The pre- cipitation was then collected by filtration, washed with ethnol and dried under vacuum for four hours.

All these complexes were analyzed by using different available techniques, the physical properties of these compounds are listed in Table (1).

D-Programs used in Theoretical Calculation:
1. Hyperchem 6

Is a sophisticated molecular modeler,editor and powerful computational package, that is known for its quality, flexibility and ease of use. Uniting 3D visualization and animation with quantum chemical calculations, mechanic and dynamic.

Hyperchem can plot orbital wave functions resulting form semi- empirical quantum mechanical calculation, as well as the electrostatic potential, the total charge density or the total spin density can also be determined during a semi- empirical calculation this in formation is useful in determining reactivity and correlateing calculation results with experimental data.

2.Types of Calculation :

(i) single point calculation determine the molecular energy and properties for given fixed geometry **(ii)** Gerometry optimization calculations employ energy minimization algorithms to locate stable structures**(iii)** vibrational frequentcy calculations find the normal vibrational modes of an optimized structure.The vibrational spectrum can be displayed and the vibrational motions associated with specific transitions can be animated.

3. Computational Methods:
a-Semi – empirical quantum mechanics

(i) Hyperchem offers ten semi–empirical molecular orbital methods,with options for organic and main group compounds,for transition metal complexes and for spectral simulation **(ii)** choose from Zerner's, INDO method (ZINDO/1) and parameterization model,version 3(PM3),[incl- uding transition metals].PM3 were used for the calculation of heat of formation and binding energy for all metal complex except Pt(IV)com- plex, therefore (ZINDO/1) method were used for the calculation of the heat of formation and binding energy of V (IV) complex .

b. Molecular Mechanics :

It has three, important concepts, functional form, atoms types and parameter sets .Each molecular mechanics method has its own funct- ional from (assisted model building and energy refinement),AMBER is based on a force field.

AMBER was use for the calculations of heat formation and binding energy for Pt(IV)complex.

Result and Discussion

A-Elemental Analyses:

The physical and analytical data of the ligand and metal complexes are given in Table (1).The results obtained from elemental analysis are in satisfactory agreement with the calculated val- ues.The suggested molecular formula was also supported by spectral measurements as well as magnetic moments.

B-Infrared Spectroscopic Study:

The infrared spectrum of the ligand exhibited several absorption bands at approximately (1180),(1062, 1083)and (2864, 2955) cm^{-1}.

These bands have been assigned to the νc=s, νN-c=s andνCH$_2$-N respectively.The structural formula of the ligand may be suggested as follows:
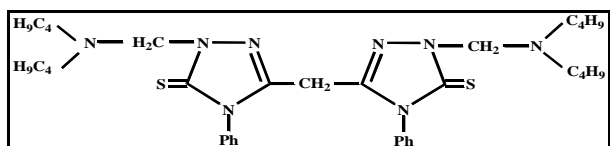
The important IR absorption peaks of the complexes were compared with pure ligand , which are given in Table (2).The ligand coord- intes to metal ions in two different ways,and they showed the followings :

1- All the complexes exhibit a considerable lowering in theνC=S and νN-C=S band exc- ept (M$_1$andM$_3$),due to decrease in double bond character of the sulfur to carbon bond .

2- In the case of (M$_1$) and (M$_3$),the ligand was suggested to coordinate with two metal ions through four–donor atoms (two nitrogens of the triazole ring, and two nitrogen of aminom- ethyl moiety),while in the complexes (M$_2$,M$_4$ and M$_5$),coordination took place through two thiol group and two nitrogen of methylene group.

3- These absorptions were further supported by the appearance νM-S,νM-N and νM- Cl respectively [10].

4- νV=O stretching mode in (M$_1$)was observed at 979cm^{-1}as a strong band .Coordination of sulfate ion in this complex as a bidentate beh- avior [10].

5- The assignment of theνC–N bands was not easy,due to the presence of four (C-N)bands at different positions also the assignment of the (N-N) was not well resolved and was found to be overlapped with another peaks in the same range.

6- A broad band was observed around(3400-3462) cm^{-1} in the spectra of (M$_2$-M$_5$) complexes ,assigned to a νO-H and suggested the presence of water or ethanol molecules in the crystal latt- ice of the complexes [11].

C- Electronic Spectra:

The electronic spectra of the metal complexes were done in chloroform in the range of 200-1100 nm.

(M$_1$): Vanadium complex showed two bands related to square pyramide vanadium complex [12, 13]. They were observed at 11220 (ν_1) and 23950 (ν_3) cm^{-1}and were assigned to $^2B_2g \rightarrow {}^2Eg$ and $^2B_2g \rightarrow {}^2A_1g$ transitions respectively [14-19].

The magnetic moment (2.04) BM is higher than spin only value, this due to orbital contribution [17,18]. Conductivity in DMF, showed that the complex was non ionic Table (3).

(M$_2$) : The blue cobalt(II)complex was showed a magnetic moment of(4.52)BM, which indicates a high-spin type complex. Electronic spectrum in chloroform solvent exhibited a splitted band in the range of(17550-15980)cm^{-1}.The blue color besided this splitted band,is typical of tetrahedral geometry around spin free Co(II) ion[19,20].

These bands can be assigned the transition $^4A_2 \rightarrow {}^4T_{1(P)}$ (ν_3).A broad band was observed at 3237cm^{-1} in infrared spectrum can be assigned to the $^4A_2 \rightarrow {}^4T_2$ $_{(F)}(\nu_1)$,while the transition of (ν_2)expected in the range(5000-6000)cm^{-1}(NIR) can not be measured.

The various ligand field parameters have been calculated, by reference to Tanaba-sugano diagram for d^7 configuration [21], and are described in Table (3).

The calculation of the spin-orbit coupling constant (λ) was calculated using the following equation:

$$[\ \mu_{obs} = \ \mu_{S0} - 15.59 \ \lambda` \ | \ 10 \ Dq]$$

where : μ_{obs} = The oberved effective magnetic.

$\mu_{S\cdot0}$ = the electronic spin only magnetic moment.

The resulting value ($\lambda` = -196.2$) shows the present complex to be distorted tetrahredal [14,22]. The nephelauxetic factor β was calculated and found to be(0.61) indicating

high degree of covalence in bonding of ligand donor atoms with cobalt(II)ion .The molar conductance showed that the complex was nonelectrolyte.

(M$_3$): This complex was readily soluble in chloroform giving dark green solution,it's electronic spectrum gave four absorption bands at 10890(ν_1), 13994(ν_2), 18850(ν_3) and 23820 cm-^{1}.

The position of these bands are in a good agreement with that reported for highly distorted octahedral geometry[23,24],and were assigned to $^2B_1g{\rightarrow}^2A_1g(\nu_1)$ $^2B_1g{\rightarrow}^2B_2g(\nu_2)$, $^2B_1g{\rightarrow}^2Eg(\nu_3)$ and L$\rightarrow$cu(CT) transition respectively.

The implies that the proposed square planner configuration has changed in chloroform to distorted octahedral structure[25,26].

This behavior was further indicated by the addition of stronger ligand like DMSO, to the chloroform solution where a blue shift was noticed by (272) nm.

The colure change from dark green to greenish-yellow so the structure can be assumed to change from square planer to distorted octahedral (tetragonal).

The effective magnetic moment was found to be (2.12)BM ,which agree with square planner geometry around Cu(II) complex [24,27].

Conductivity measurement showed that the complex was non ionic, Table (3).

(M$_4$): The electronic spectrum of octahedral Pd (II) consists of three absorption bands [15]. In the present complex the first energy band (ν_1) may be assigned as (10Dq) absorption is not observed because of the instrument range limitation, but the second spin-allowed abound $^3A_2g \rightarrow {}^3T_1g_{(F)}$was centered around 18200cm^{-1} and other band spin–allowed$^3A_2g{\rightarrow}^3T_1g_{(p)}$ was in the range 25000cm^{-1}[12,28].

The magnetic value (1.3)BM, of palladium (II) observed for d^{8}configuration agree with octahedral geometry around Pd (II)ion [14, 29].The conductance measurement indicates the nonelectrolytic behavior of the complex, Table (3).

(M$_5$): The prepared red Pt (IV) complex showed three bands at18880 (ν_1), 25570 (ν_2) and 28330 (ν_3) cm^{-1}, and were assigned to : $^1A_1g{\rightarrow}^3T_1g$, $^1A_1g{\rightarrow}^3T_2g$ and (CT) transition respectively [12,14].

The observed magnetic value(2.51) BM of the present platinum (IV) complex (d^6) configuration agree with octahedral geometry around metal ion. This result indicates higher orbital contribution [21, 30]. The conductivity measurement Table (3) showed that the complex was non ionic.

D-Theoretical Study of Mannich Base Derived from BTRZ and Their Metal Complexes in Gas Phase:

∗ The program hyper chem6 was used for the semi-empirical and molecular mechanics calcul-ation at optimized geometries energies, the result of PM3, ZINDO/1 and AMBER methods of calc-ulation in gas phase for the heat of formation ($\Delta Hf°$) and binding energy (ΔE_b) for ligand and their metal complexes were calculated and tabul-ated in Table (4). Also PM3 was used for evaluat- ation the vibrational spectra of the (BTRZ) and Mannich base (L) to compare the theoretically calculated wave numbers with the experimental values. Theoretically calculated wave numbers for these ligands showed that some deviations from the experimental values, these deviations are generally acceptable in theoretical calculations and are described in Tables (2) and (5) and Figs.(1) and (2).

∗∗ Electrostatic potentials (E.P) :Electron distrib-ution governs the electrostatic potential of mole-cules,and describes the interaction of energy of the molecular system with a positive point charge, so it is useful for finding sites of reaction in a molecule positive charged species tend to attack a molecule where the E.P is strongly negative electrophilic attack [31, 32]. E.P of free ligand was calculated and plotted as 2D contour to investig-ate the reactive sites of the molecule Fig.(3), and one can interpret the sterochemistry & rates of many reactions involving (Soft) electrophiles & nucleophiles interems of the properties of fronti-er orbitals (HOMO) & (LUMO). Overlap between the HOMO and LUMO is a governing factor in many reactions. The HOMO and LUMO value were plotted as 2D contour to get more informat- ion about these molecules.The results of calcula- tion showed that the LUMO of transition metal ions prefer react with the HOMO of sulfur and nitrogen atoms of mannich base Ligand.

*** Optimized geometries and energy of metal complexes for mannich base. All theoretically probable structures of metal complexes with mannich base have been calculated to search for the most probable model building structure ,these shapes Fig.(4), show the calculated optima geometries for (L)and their metal complexes. The results of PM3and ZINDO/ I methods of calculation in gas phase for the binding energies and heat of formation of Co(II), Cu(II), Pd(II), V(IV), while AMBER method was used to calculate the binding energies which is equal to heat of formation of Pt(IV), and are described in Table (4).

Table (1)
Physical date for the Ligand (L) and it's metal complexes.

Compound	Colour	Melting point C	Yield %	M% Found	M% Calc.	Suggested formula
L	White	138-140	92	-	-	$C_{35}H_{50}N_8S_2$
M_1	Greenish blue	220	59	9.52	10.49	$[(VO)_2L (SO_4)_2]$
M_2	Blue	198	78	12.20	12.51	$[Co_2LCl_4]. 2H_2O$
M_3	Green	201	82	14.31	13.61	$[Cu_2LCl_4].H_2O$
M_4	Brown	233	90	16.86	17.23	$[Pd_2L (EtOH)_4 Cl_4]. C_2H_5OH$
M_5	Deep red	248	72	25.58	26.74	$[Pt_2LCl_8].3C_2 H_5OH$

Table (2)
Characteristic stretching vibration Frequencies located in the FTIR of the ligand and their metal complexes in Cm^{-1} Units.

Compounds	ν c=s	ν N-c=s	ν CHz 0020 2- N	ν N-N	ν N-C-N	ν M-S	ν M-N	ν M-Cl	ν SO4^{-2} Band
L	1180	1062,1083	2864-2955	1455	1410	—	—	—	—
M_1	1162	1060,1080	2855-2935	1450-1435	1400	—	526	—	1504,1015
M_2	1168	1032,1074	2860-2925	1450	1408	451	500	330	—
M_3	1160	1059,1080	2852-2920	1450 1431	1380	—	513	360	—
M_4	1162	1025,1074	2860-2929	1449	1410	422	520	320 360	—
M_5	1175	1028,1076	2860-2932	1450	1408	462	530	360 400	—

Table (3)
Electronic spectra, conductivity and magnetic moment data of the prepared complexes.

Compound No.	Bands(Cm^{-1})	Assignment	IODq Cm^{-1}	µeff(BM)	µscm^{-1}
M$_1$	11220 23950	$^2B_2g \rightarrow {}^2Eg$ $^2B_2g \rightarrow {}^2A_1 g$		2.04	10.5
M$_2$	3237 5450(cal) 16517(av.)	$^4A_2 \rightarrow {}^4T_{2\,(F)}$ $^4A_2 \rightarrow {}^4T_{1\,(F)}$ $^4A_2 \rightarrow {}^4T_{1\,(P)}$	3288	4.52	14.8
M$_3$	10890 13994 18850 23820	$^2B_1g \rightarrow {}^2A_1g$ $^2B_1g \rightarrow {}^2A_2g$ $^2B_1g \rightarrow {}^2Eg$ $L \rightarrow Cu$ (CT)	11020	2.12	27.2
M$_4$	18200 25000	$^3A_2g \rightarrow {}^3T_1g_{(F)}$ $^3A_2g \rightarrow {}^3T_1g_{(P)}$		1.30	23.5
M$_5$	18880 25570 28330	$^1A_1g \rightarrow {}^3T_1g$ $^1A_1g \rightarrow {}^3T_2g$ $L \rightarrow Pt$ (CT)		2.50	12.6

Table (4)
Conformation energetic (KJ /mol^{-1}) for Mannich base andtheir metal complexes.

Conformation	PM3		ZINDO		AMBER
	ΔHf^o	ΔE_b	ΔH_f^o	ΔE_b	$\Delta H_f^o = \Delta E_b$
L	131.273	-9595.98	–	–	–
[M$_1$]			-20987.25	-31688.69	–
[M$_2$]	-147.217	-10034.85	–	–	–
[M$_3$]	465.994	-9938.62	–	–	–
[M$_4$]	339.716	-11194.960	–	–	–
[M$_5$]	-	-	–	–	425.732

Table (5)
Comparison of experimental and theoretical vibration frequencies for (BTRZ) and (L) using semi- empirical method.

Compound	ν N-H	(νN-H + ν C= N + ν C=C)	(ν C=N+ ν C=S)	ν (N-C=S)	ν (N-C-N)	ν (N-N)	ν (C=S)	ν C-Halph.
BTRZ	(3406)[*]	(1810,1734.4)[*]	(1468)[*]	(1005)[*]	-	(1262)[*]	(1214)[*]	(2938,2990)[*]
	(3110)[**]	(1589)[**]	(1550)[**]	(970)[**]	-	(1440)[**]	(1250)[**]	(2839,2916.17)[**]
	[-9.51][***]	[-13.40,-9.155][***]	[5.29][***]	[-3.60][***]	-	[12.36][***]	[2.88][***]	(-3.49,-2.8)[***]
L	-	-	-	(1068.67,1066.43)[*]	(1442)[*]	(1440.16)[*]	(1134.05)[*]	(2888.51,2962.14)[*]
				(1062,1083)[**]	(1596)[**]	(1455)[**]	(1180)[**]	(2864,2955)[**]
				[-0.628,1.528][***]	[9.639][***]	[1.0194][***]	[3.892][***]	[-0.504,0.2416][***]

Where

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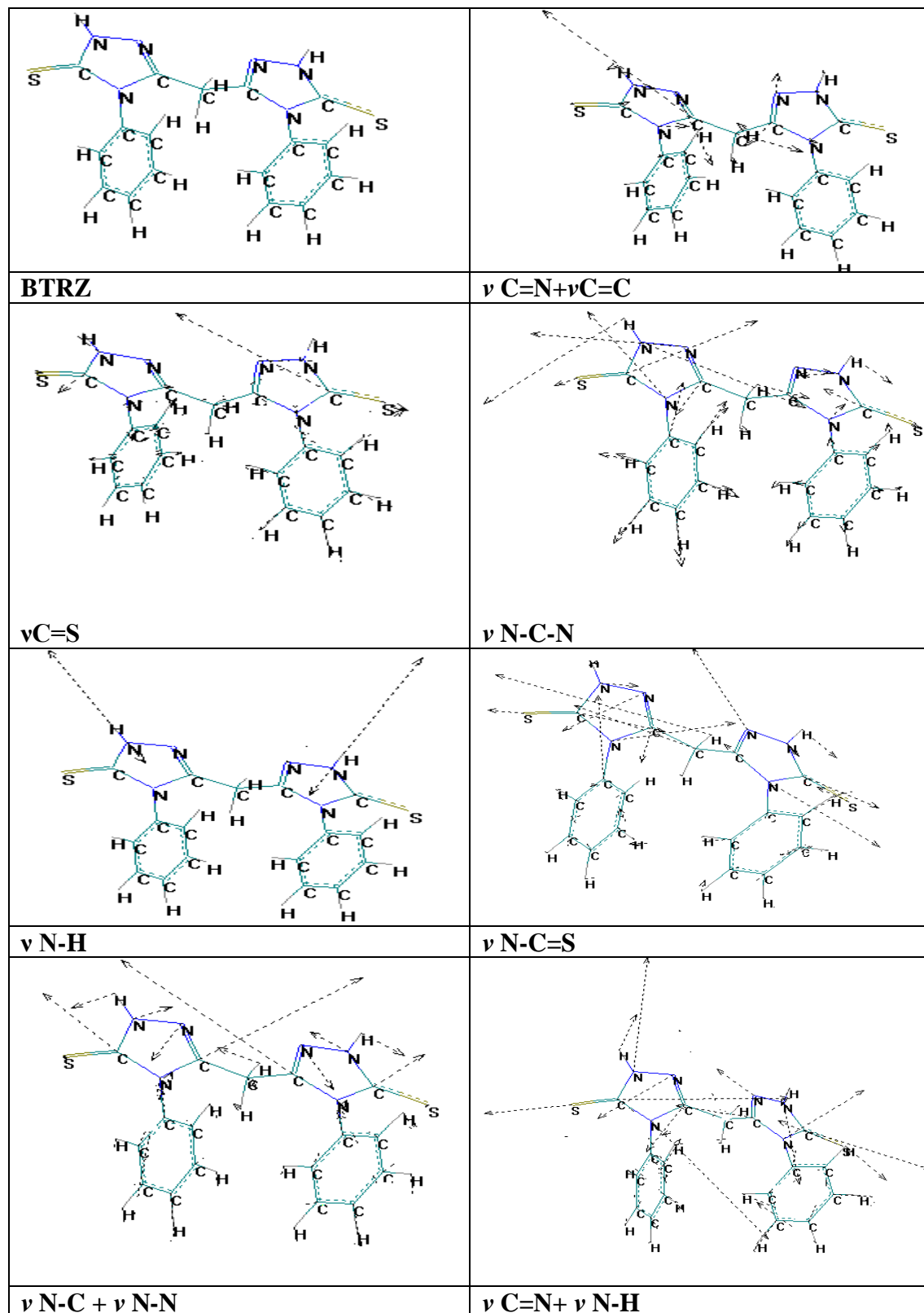*** = Error % due to main difference in the experimental measurements and theoretical treatment of vibration spectrum.

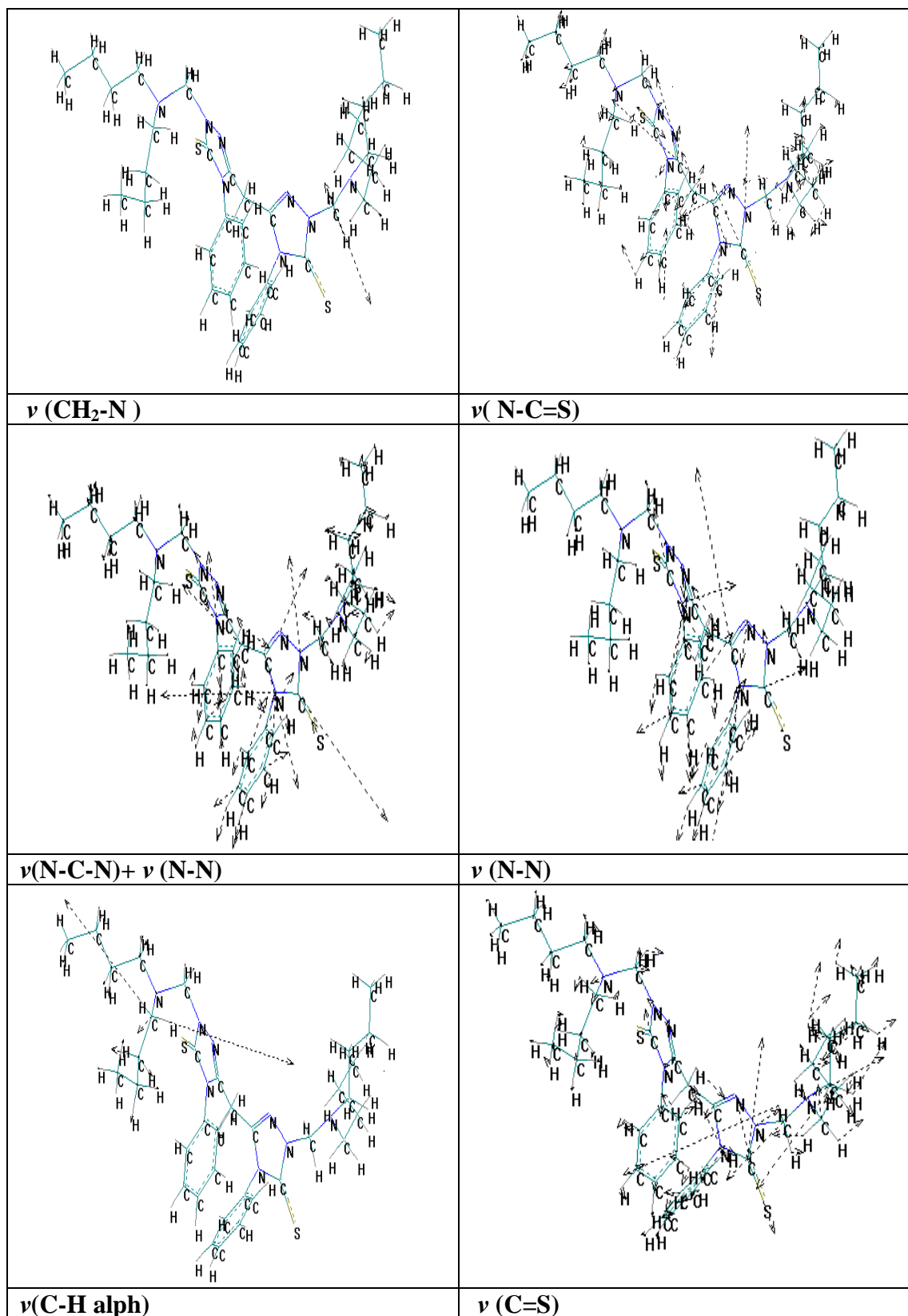|	
BTRZ	*ν* C=N+*ν*C=C
vC=S	*ν* N-C-N
ν N-H	*ν* N-C=S
ν N-C + *ν* N-N	*ν* C=N+ *ν* N-H

Fig.(1) : The calculated vibration frequencies of (BTRZ).

v (CH₂-N)	*v*(N-C=S)
v(N-C-N)+ *v* (N-N)	*v* (N-N)
v(C-H alph)	*v* (C=S)

Fig.(2) : The calculated vibration frequencies of (L).
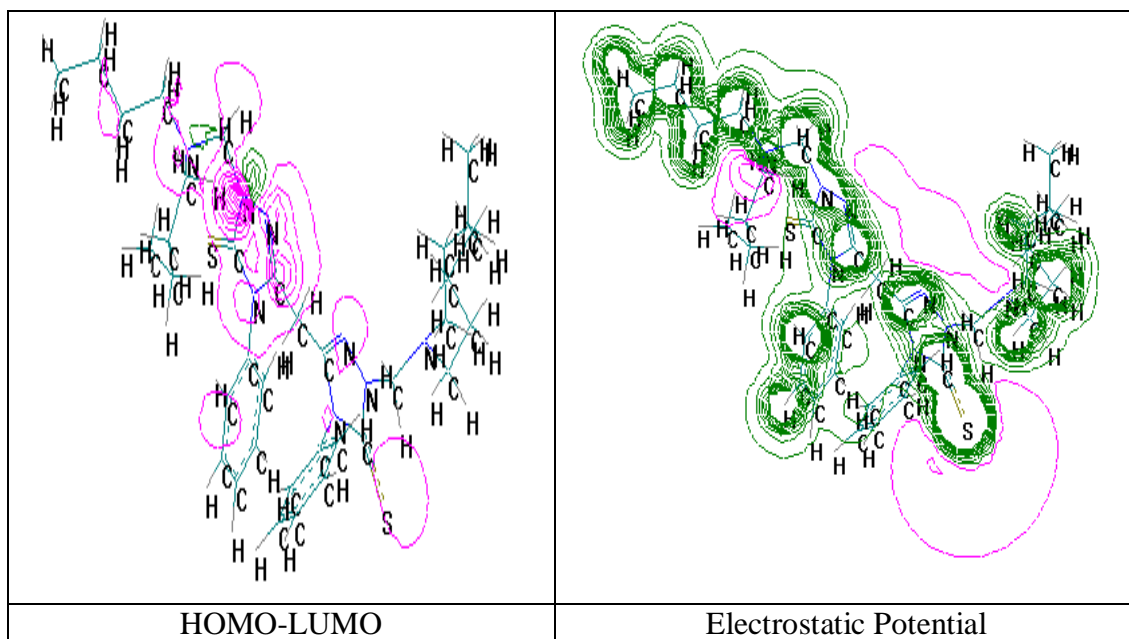
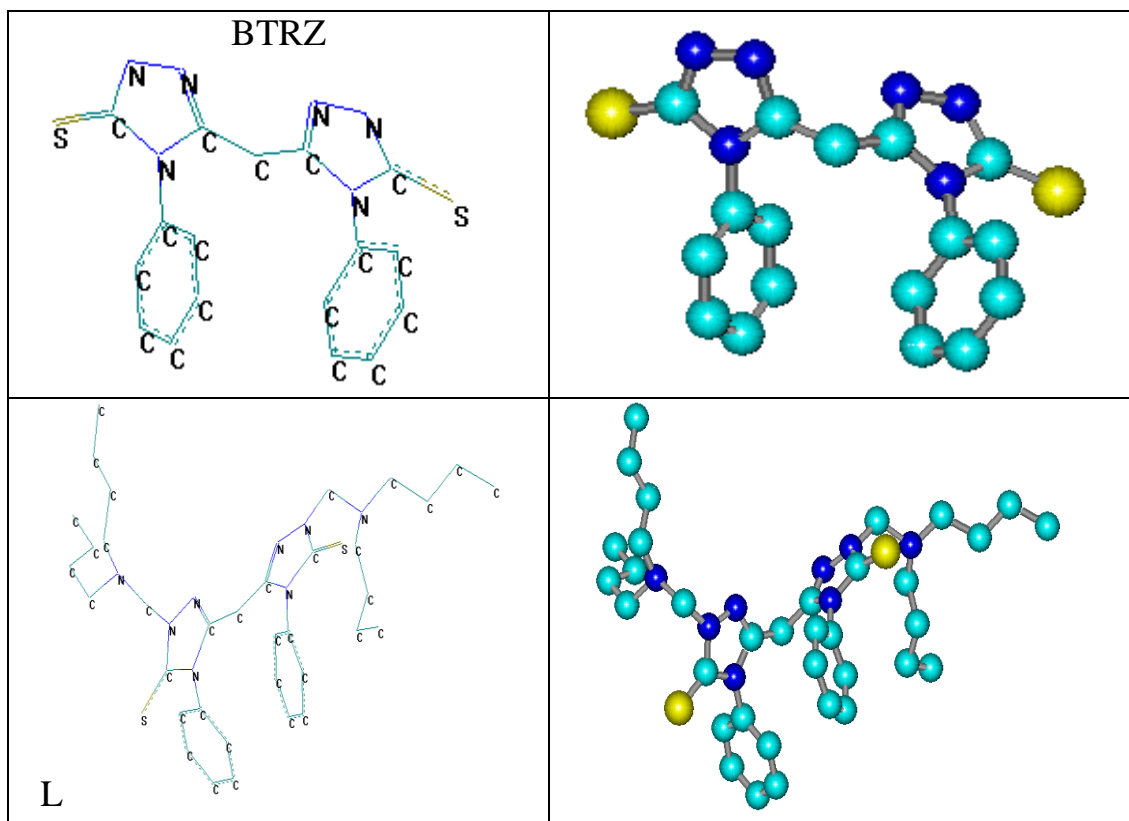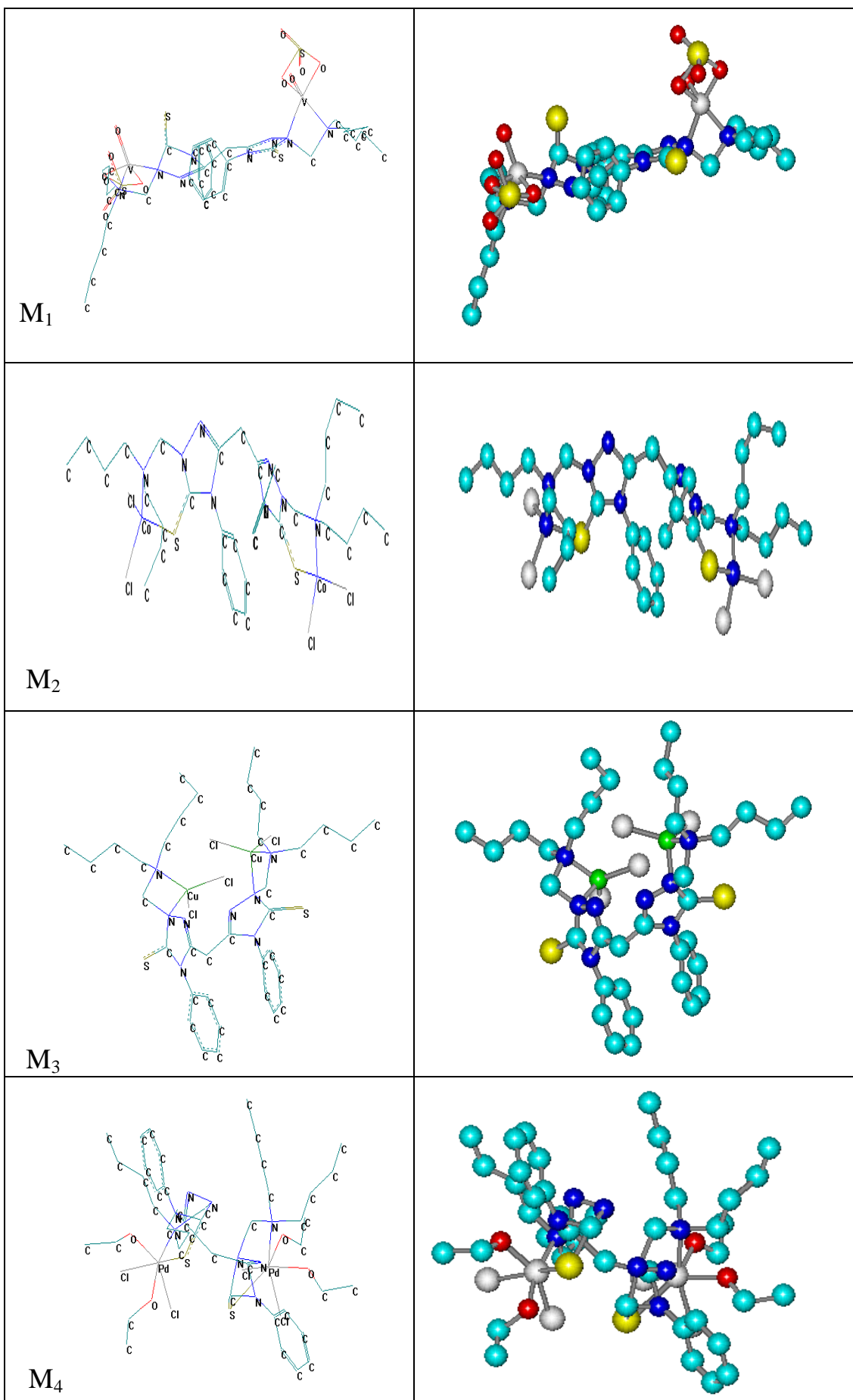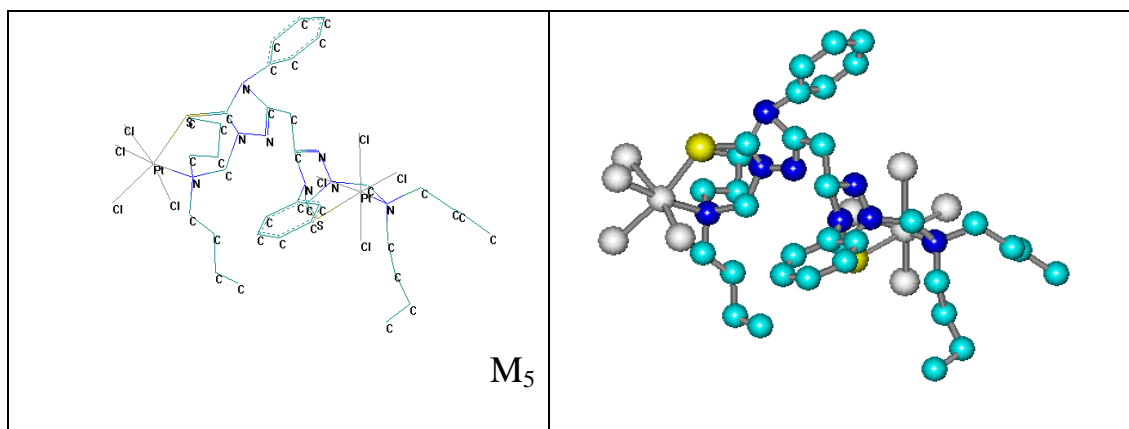| HOMO-LUMO | Electrostatic Potential |

Fig. (3): HOMO and Electrostatic Potential as 2D contours for Mannich base (L).

Fig.(4): Conformational structure of BTRZ,L and their metal complexes.

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الخلاصة

تم تحضيرقاعدة مانخ الجديدة (4–فنيل–2 ثاني بيوتيل امين مثيل –4,2,1–ترايازول–5يل) ميثان من تكاثف الفورمالديهايد مع نسبة من ثاني بيوتيل امين بوجود ثنائي الترايازول.

تم تحضيرعدد من معقداتة الفلزية مع النحاس (II)، الكوبلت(II)، البلاديوم (II)، الفناديوم (IV) والبلاتين (IV)، واقترح الشكل الهندسي للمعقدات المحضرة بالحالة الصلبة بأستخدام قياسات الحساسية المغناطسية ،التوصيلية الكهربائية والدراسة الطيفية بألأضافة الى تقنية الامتصاص الذري اللهبي للعناصر وبالحالة الغازية بأستخدام معالجة تكوين المعقدات نظرياً في الطور الغازي، بأستعمال برنامج (Hyperchem.6) وبتطبيق الميكانيك الجزيئي والشبة التجريبي في الحساب وذلك بأستخدام الدوال PM3، ZIND و AMBER لحساب حرارة تكوين ($\Delta Hf°$) وطاقة التآصر (ΔEb) بدرجة حرارة 298 كلفن الليكاندات والمعقدات.

جَرى حساب التردد الاه تزازي نظرياً وبأستخدام الدالة PM3 لقاعدة مانخ ومقارنتة مع القيم المقاسة عملياً بأستخدام ثنائي (4–فنيل –2 ثاني بيوتيل امين مثيل –4,2,1–ترايازول –5يل) ميثان كمركب قياسي ووجد توافقاً كبيراً بين القيم العملية والمحسوبة نظرياً مع زيادة امكانية تشخيص بعض الحزم بشكل أدق.