Journal of Al-Nahrain University Vol.11(2), August, 2008, pp.24-36 Science

PREPARATION, CHARACTERISATION AND BIOLOGICAL ACTIVITIES OF SOME METAL COMPLEXES OF NEW N [4-BI(5-THION-1,3,4-OXADIAZOLE-2YL)METHANE)METYL] DIBUTYL AMINE AND THEORETICAL STUDY

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Abstract

A new Mannih base N[4-bi(5-thion-1,3,4-oxadiazole-2yl)methane)metyl] dibutyl amine (L), have been prepared and characterized by (FTIR) spectroscopy. (L) have been used as a chelating ligand to prepare a number of metal complexes with Co(III), Cu(II), Pd(II), V(IV) and Pt(IV). The complexes were isolated and characterized by (FTIR), UV-Vis spectrophotometer and flame atomic absorption techniques in addition to magnetic susceptibility, and conductivity measurement. The study of the nature of the complexes formed in absolute ethanol following the mole ratio method, gave results which were agreed with those obtained from isolated solid state studies.The antibacterial activity for the ligand and their metal complexes were studied against two selected micro-organisms *Bacillus subtilis* and *Pseudomonas aeruginosa*, the antibiotic Ampicillin has been chosen to compare their activity with those of the new compounds. Theoretical treatment of the formation of complexes in the gas phase, this was done by using the HyperChem-6 program for the Molecular mechanics and semi- empirical calculations. The heat of formation (ΔH°_{f}) and binding energy (ΔE_{b}) at 298K for the free ligand and their metal complexes were calculated by (PM3, ZINDO/1 and AMBER) methods. Furthermore, the electrostatic potential of the free ligand was calculated to investigate the reactive sites of the molecules. PM3 was used to evaluate the vibrational spectra of the base(L) and compare the theoretically calculated wave numbers with the experimental values by using bis(5- thion-1,3,4-oxadiazole-2yl) methane as authonetic compound. The theoretically obtained frequencies agreed with those values experimentally found, in addition, the calculation helped to assign unambiguously the most diagnostic bands.

Introduction

Interest in substituted of bis ring of 1,3,4-oxadiazole derivatives as a potential antibacterial and antiviral agents has continued, because of their activity against different micro-organisms [1,2]. A number of metal complexes of certain derivatives oxadiazole and bis-oxadiazole nuclei have been reported [3-5], many of these metal complexes have been shown to exhibit the expected syergic effect of activity. This is expected since the impact of metal ion in the structure of certain active organic molecules have proved to increase their activities [6-8].

Recently, agreat attention has been given to the synthesis and biological evaluation of Mannich bases compounds containing heterocyclic ring . pandeya and Co-workers [9,10] ,have been able to synthesize an antimicrobial evaluation of Schiff and Mannich base for isatin and it's derivatives with pyrimidine, oxadiazole and triazole ring respectively, they found that these compounds have a highly significaut activity against microbs.

Several intermediates for the synthesis of biologically important compounds were prepared using this novel catalytic asymmetric Mannich–type reaction, and at the same time, absolute and relative stereochemical assignments were made [11]. A new inhibitor of ceramide trafficking from endoplasmic reticulum to the site of sphingomyerin (SM) synthesis has been synthesized efficiently using the present, Mannich–type reaction as a key step [11].

Metal complexes of Mannich bases have been studied [12-15], extensively in recent years due to the selectivity and sensitivity of these ligands towards various metal ions. The metal complexes of a new Mannich bases, N-(1-morpholinobenzyl) semicarbazide was synthesized and their structural elucidated on the basis of analytical physically [16]. The biological activity of some new complexes of N,N- di (3(5-phenyl 2-thion-1,3,4- oxadiazale) methyl cyclohexyl amine) and cyclopentyl amine , showed a various effect against some bacterial [12] .

In present work we synthesis a new ligand derives from the oxadiazole heterocyclic ring and dibutyl amine, was described in an attempt to introduce the amino methyl moiety in the structure of mercaptooxadiazole ring to investigate the coordination behaviour of the new ligand toward some transition metal complexes, and to compare the biological activity of the ligand and their complexes with the main ring structure.

Theoretical study in the gas phase was done by using semi- empirical 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 electro static potential calculations. Calculation of the vibrational frequencies of the Bis (5-thiol-1,3,4-oxadiazole–2yl) methan 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 from B.D.H. and they were all pure grade reagents. Flame atomic absorption of elemental analyzer, shimadzu AA-670 was used for metal determination. FTIR spectra were recorded using shimadza-8000 spectrophotometer, for the range of 4000-200 cm^{-1} Electronic spectra of the complexes were obtained using, Shimadzu UV-Vis 160A. Electrical conductivity was measured by corning Conductivity Meter 220, and magnetic susceptibility was measured by BM6 using Faraday method.

B-Preparation of Ligands:

The method that was used to prepare the bis (5-thiol-1,3,4-oxadiazole -2yl) methane (BTOM) was reported elsewhere [17]. The Mannich base (L) was prepared according to the following :

BTOM (2.16gm) was dissolved in a minimum quantity of ethanol and kept in an ice bath and treated with formaldehyde (0.6gm, 40%). To this mixture, an ethanol solution of dibutyl amine (2.56gm) was added slowly with stirring for one hour, then, left over night in a refrigerator. A crystalline solid precipitate was formed which was filtered off, washed with cold ethanol, dried and recrystallized from aqueous ethanol. The physical data of Mannich base and their corresponding complexes are listed in Table (1).

C-Preparation of Complexes:

The salts of [$VOSO_4.H_2O$, $CoCl_2.6H_2O$, $CuCl_2.2H_2O$, $PdCl_2$. $(PhCN)_2$, H_2PtCl_6. $6H_2O$] were dissolved in ethanol and added to an ethanol solution of Mannich base in (2:1) (metal:ligand) mole ratio respectively with stirring. The mixture was heated under reflux for three hours. During this period the precipitation was completed form. The precipitation was then collected by filtration, washed with ethanol and dried under vacuum for 4 hours.

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

D- Study of Complexes Formation in the Solution:

Complex of Mannich base with metal ions were studied in solution using ethanal as a solvent, in order to determinded [M:L] ratio in the complex following molar ratio method [18,19]. Aseries of solutions were prepared having a constant concentration 10-3 M of the metal ion and ligand (L). The [M/L] ratio was determind from the relationship between the absorption of the absorbed light and the mole ratio of [M/L]. The results complexes formation in solution were listed in Table (1).

E-Programs Used in Theoretical Calculation:

1- HyperChem 6:

It is a sophisticaled molecular modeler, editor and powerful computional 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 were functions resulting from 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 information is useful in determining reactivity and correlating calculation results with experimental data.

2-Types of Calculation:-

- Single point calculation that determines the molecular energy and properties for a given fixed geometry.
- Geometry optimization calculations employ energy minimization algorithms to locate stable structures.
- Vibrational frequency calculations to 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[20].

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 spectral simulation [21].

ii- Choose from Zerner 's, INDO method (ZINDO/1) and parameterization model, version3(PM3), [including transition metals] [22]. PM3 were used for the calculation of heat of formation and binding energy for all metal complex except Pt(IV) complex, therefor (ZINDO/1) method was 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 functional form (Assisted Model Building and energy refinement) (AMBER) is based on a force field [23]. AMBER was used for the calculation of the binding energy and heat of formation of Pt (IV).

F-Study of Biological Activity for Mannich Base and their Metal Complexes :

The biological activity of the prepared Mannich and their respective complexes were studied against selected types of bacteria which included *Bacillus Subtilis* as Gram positive and *Pseudomonas aeruginosa* as a Gram negative to be cultivated in brain hart broth agar media, wich is used DMFas a solvent and as a control, for the Disc sensitivity test [24], this method involves the exposure of the zone of inhibition toward the diffusion of micro- organis on agar plate. The plates were incubated for 24hr at 37°C, the zone of inhibition of bacteried growth around the disc was observed.

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 values. The suggested molecular formula was also supported by spectral measurement as well as magnetic moments.

B- Infrared Spectroscopic Study :

The infrared spectrum of the ligand exhibited several bands at approximately (2923, 2846), (1288), (1141, 1049), (1450), and (1380) cm^{-1}, and were assigned to strectching mode of [υ CH_2-N, υ C=S, υ N-C=S, υ N-N and υ NCN] respectively. In all complexes (F_1–F_5) ligands behave as ateteradented coordinating with two metal ions through four-donor atoms (through two sulfur of thio carbonyl and two nitrogen of the methylene group); therefore, the bands due to υ (CH_2-N) were shifted to a higher frequency by (23-8, 11) cm^{-1}, and the band due to υ (C=S) was shifted to a lower frequency by (38-8) cm^{-1}. This red shift means a decrease in the double bond character, while for the bands of υ (NCS) one of was them shifted to higher frequency about (23-15) $cm^{-1}$and the others undergo red shifting about (16-15) cm^{-1}, Table (2). These observations were further indicated by the appearance of υ (M-N, M-S and M-X) respectively. The bands due to υ NCN and υ N-N showed a small relative change in the position accompanied by reduction in the intensity in the case of band υ N-N, which ruled out the possibility of bonding with metal ion. In addition, a strong band was observed at (979) cm^{-1} due to (V=O) stretching mode in (F_3) complexes [25,26] while the band related to sulfate anion was observed at (1203) cm^{-1}, which indicate abidentate behavior[27,28]. A broad band was observed a round (3433-3386) cm^{-1} in the spectra of all complexes assigned to a (O-H) stretching and suggested the presence of water or ethanol molecules in the crystall lattic of the complexes [29].

C-Electronic Spectroscopic Study :

The electronic spectra of the metal complexes were recorded for their solution in chloroform in the range (200-1100) nm.

F1: The electronic spectral bands of the prepared complex in the present work are presented in Table (3), along with their assigned transitions and the calculated values of 10 Dq, B`and β. Low spin Co(III) has the electronic configuration d^6, the ground term for which in Oh stereochemistry is ^1A_1g, two bands are expected to appear in the visible region due to the transition to the ^1T_1g and ^1T_2g states.

These transition correspond to the electronic promotion $t_2g^6 \rightarrow t_2g^5\ eg^1$ with the promoted electron maintaining its spin unaltered. The orbital multiplicity of $t_2g^5 \rightarrow eg^1$ is 6 and so corresponds to two orbital triplet terms ^1T_1g and ^1T_2g[30,31]. In the spectrum of our complex , a weak band was observed at 12315 cm^{-1}, this band was attributed to the spin-forbiddn $^1A_1g \rightarrow {}^3T_1g$ transition which may occur when the promoted electron changes its spin and the two T terms be ^3T_1g and ^3T_2g The assignments are made by fitting the ratio of $υ_1/υ_2$ to Tanaba- sugano diagram, which produces the values of B`, β as well as 10 Dq. The magnetic susceptibility and molar conductivity measurements indicated that the complex to be diamagnetic (0.5 BM), and non conducting.

F2: The present green CuL complex had shown a limited solubility in some solvents, this suggests, to some extent, a polymerization of the product. The electronic spectrum of this complex showed a broad band at 12610 cm^{-1}; in addition, other bands appear at higher than 23200 cm^{-1}. The position of the bands as well as their intensities were not consistent with tetrahedral, distorted octahedral Cu(II) complexes . The band observed, i.e. 12610 cm^{-1} in the visible region, for the present complex was attributed to the transition $^2Eg \rightarrow {}^2T_2g$, the other bands can be assigned as charg transfer. The value of magnetic moment was found to be (1.32 BM), which agreed well with square planar geometry around Cu (II) ion, and the conductivity measurement showed that the complex was non ionic, Table (3).

F3: The olive colour of spectrum vanadyl (IV) complex, show three main absorption bands, Table (3), which are assigned to the $^2B_2 \rightarrow {}^2Eg$,$^2B_2 \rightarrow {}^2B_1g$ and$^2B_2 \rightarrow {}^2A_1$ respectively in a squar pyramidal geometry [30]. The magnetic moment (2.03) is higher than spin value of vanadium metal only; this result indicates a higher orbital contribution [32]. Conductivity measurement in DMF showed that the complex was non ionic.

F4: The brown palladium complex, show three absorption bands which were observed at (23529, 27173, and 30030) cm^{-1}. The spectrum was typical of squar planer Pd (II) complexes [33,34]. The measured magnetic moment (0.87) BM showed that the complex to be low-spin, and conductivity measurement showed that the complex was non electrolyte, Table (3).

F5: The prepared orang Pt(IV) complex showed three bands at (23255, 27397, and 31125)cm^{-1}, which indicate an octahedral geometry [35,36]. Magnetic moment of solid complex, was found to be (0.52) BM showed a higher orbital contribution [32]. Conductivity in DMF showed that the complex was non ionic, Table (3).

D-Solution Study :

Molar ratio method was followed to determined the M:L ratio. The results of complexes in ethanol solution, suggest that the metal to ligand ratio was (2:1) for all prepared compounds, which were comparable to these obtained from isolated solid state study Table (1).

E- Theoretical Study :

(i) The program hyperchem6 was used for the semi-empirical and molecular mechanic calculations, at optimized geometries energies, the result on PM3, ZINDO/1 and AMBER methods of calculation in gas phase for the heat of formantion (ΔH°_{f}) and binding energy (ΔE_{b}) for the ligands and their complexes were calculated and tabulated in Table (4). Also PM3 was used for evalution the vibrational spectra of the BTOM and Mannich base 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 Table (5) and (2), and the Figs. (1,2).

(ii) Electrostatic potential(E.P):- Electron distribution governs the electrostic potential of molecules and describes the interaction of energy of the molecular system with a postive 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 [37,38]. (E.P) of free ligand was calculated and plotted as 2D contour to investigate the reactive sites of the molecules Fig. (3), and one can interpret the stereochemistry and rates of many reactions involving soft electrophiles and nuclephiles in terms of the properties of frontier orbitals (HOMO and LUMO). Overlap between the HOMO and LUMO is a govering factor in many reactions. The HOMO and LUMO values were plotted as 2D contour to get more information about these molecules. The results of calculation showed that the LUMO of transition metal ion prefer to react with the HOMO of sulfur and nitrogen atoms of Mannich bases ligand.

(iii) Optimized Geometries Energy of Metal Complexes for Mannih Base:- All theoretically probable structures of metal complexes with Mannich base have been calculated to search for the most probable model building stable structure, these shapes Fig. (4), show the calculated optima geometries for (L) and their metal complexes. The results of PM3 and ZINDO/1 methods of calculation in gas phase for the binding energies and heat of formation of Co (III), Cu (II), Pd (II) and V(IV),while AMBER method was used to calculate the binding energies which is equal to heat formation of Pt (IV) complex, and are described in Table (4).

F- Biological Activity:-

As a result from the study of antimicrobial of prepared compounds and their metal complexes Fig(5,6),the follwing points were concluded:-

1) The results of antibacterial activity study for the Mannich base indicated that the new compounds exhibited antibacterial activity against the studied bacteria at low and high concentrations.

2) The inhibition which is exhibited from L toward the bacteria used in this study, at higher and lower concentrations, is similar to the inhibition of Ampicilin compound at the same species of bacteria and concentration.

3) The results reflected that the starting material BTOM exhibited more inhibition than the prepared new donor bases toward *Bacillus Subtilis*, at higher and lower concentrations.

4) The study of antibacterial activities revealed that the(L), exhibited a greater activity against the studied bacteria *Pseudomonas aeruginosa*, compared to that (BTOM), when we use low concentration. This indicates that introductions of the aminomethyl group on the oxadiazole derivatives ring raised the killing zone.

5) Generally, the result of the prepared complexes exhibited antibacterial activity toward *Pseudomonas aeruginosa* bacteria was more than the complexes inhibition on *Bacillus Subtilis* bacteria.

6) The study of the antibacterial activities revealed that the complexes of (L) toward G^{-}ve bacteria showed a high activity at 10 mmole (except vanadium and platinum complex).

7) The results of the antibacterial activites of the new complexes of donor base, showed that there is no effect toward G^{+}ve bacteria when we use the two concentration, except copper and plutin complexes which they exhibit at the same bacteria only when we use high and low concentration resprctively.

Table (1)

Physical data of ligand (L) and their metal complexes.

Symb.	**Color**	**Crystallization solvent**	**M.P. °C or decomp.**	**Yield %**	**Metal analyses**	**Metal to ligand ratio**	**Suggest Molecular formula**
					Found (calc.)		
L	Pale yellow	hot ethanol	132 - 134	52%	_	_	$C_{23}H_{42}N_6S_2O_2$
F_1	Brick-red	Washing with hot ethanol and cold water	270 D	66%	11.04 (11.99)	2:1	$[Co_2LCl_4(OH)_2((H_2O))_2]. 4H_2O$
F_2	Green	Washing with hot ethanol and cold water	200 D	83%	13.51 (13.78)	2:1	$[Cu_2LCl_4]. 4EtOH$
F_3	Olive	Washing with hot ethanol and cold water	119 D	56%	(13.74)	2:1	$[(VO)_2\ L(SO_4)_2]\ .H_2O$
F_4	Brown	Washing with hot ethanol and cold water	218 D	64%	18.98 (18.88)	2:1	$[Pd_2LCl_4]. 4EtOH$
F_5	Light Orange	Washing with hot ethanol and cold water	189 D	70%	26.88 (26.13)	2:1	$[Pt_2LCl_8]. 5EtOH$

Table (2)

The most diagnostic FT-IR bands of L and its metal complexes.

Symb.	**$\upsilon_{C=S}$**	**υ_{NCS}**	**υ_{N-N}**	**υ_{CH2-N}**	**υ_{NCN}**	**υ_{M-S}**	**υ_{M-N}**	**υ_{M-O}**	**υ_{M-X}**
L	1288	1049 1141	1450	2846 2923	1380	-	-	-	-
F_1	1280	1072 1126	1455	2869 2931	1378	471	525	970	370
F_2	1280	1072 1126	1456	2854 2931	1378	478	530	-	390
F_3	1250	1064 1125	1450	2869 2931	1378	462	520	548	-
F_4	1272	1072 1126	1456	2854 2923	1378	470	555	-	347
F_5	1280	1064 1126	1450	2854 2923	1380	470	515	-	393

Table (3)
Electronic spectra, conductance and magnetic moment, for metal complexes of (L).

Symb.	Absorption Bands ,cm^{-1}	Transitions	B	B\`	β	10Dq	Dq/B\`	15B\`	μ eff BM	Molar condictivity μs.cm^{-1}	Suggested structure
F_1	12315 16393 22831 27922 28985	$^1A_1g \rightarrow {}^3T_1g(f)$ $^1A_1g \rightarrow {}^1T_1g(f)$ $^1A_1g \rightarrow {}^1T_2g(p)$ C.T or LIT C.T or LIT	1400	472	0.337	160047	3.4	106200	0.5	37	Octahedral
F_2	12610 23809 28985	$^2Eg \rightarrow {}^2T_2g$ C.T C.T	-	-	-	-	-	-	1.32	28	Square planar
F_3	12330 23148 27777	$^2B_2g \rightarrow {}^2Eg$ $^2B_2g \rightarrow {}^2B_1g$ $^2B_2g \rightarrow {}^2A_1g$	-	-	-	-	-	-	2.03	75	Square Pyramide
F_4	23529 27173 30030	$^1A_1g \rightarrow {}^1B_1g$ $^1A_1g \rightarrow {}^1Eg$ L → Pd(C.T)	-	-	-	-	-	-	0.87	32	Square planar
F_5	23255 27397 31125	$^1A_1g \rightarrow {}^1T_1g$ $^1A_1g \rightarrow {}^1T_2 g$ L→ Pt (C.T)	-	-	-	-	-	-	0.52	41	Octahedral

Table (4)
Conformation energetic (in KJ.Mol^{-1}) for L and their metal complexes.

Symb.	PM3		ZINDO/1		AMBER
	ΔH°$_f$	ΔE$_b$	ΔH°$_f$	ΔE$_b$	ΔH°$_f$=ΔE$_b$
BTOM	69.7183003	-1697.057	-	-	-
L	6.5228923	-7O42.14910	-	-	-
F$_1$	-802.3427	-98722.6227	-	-	-
F$_2$	-89.76092	-7415.7929	-	-	-
F$_3$	-	-	15456.51939	23479.51939	-
F$_4$	-207.0964	-9551.728	-	-	-
F$_5$	-	-	-	-	363.711670

Table (5)
Comparison of experimental and theoreticl vibrational frequencies.

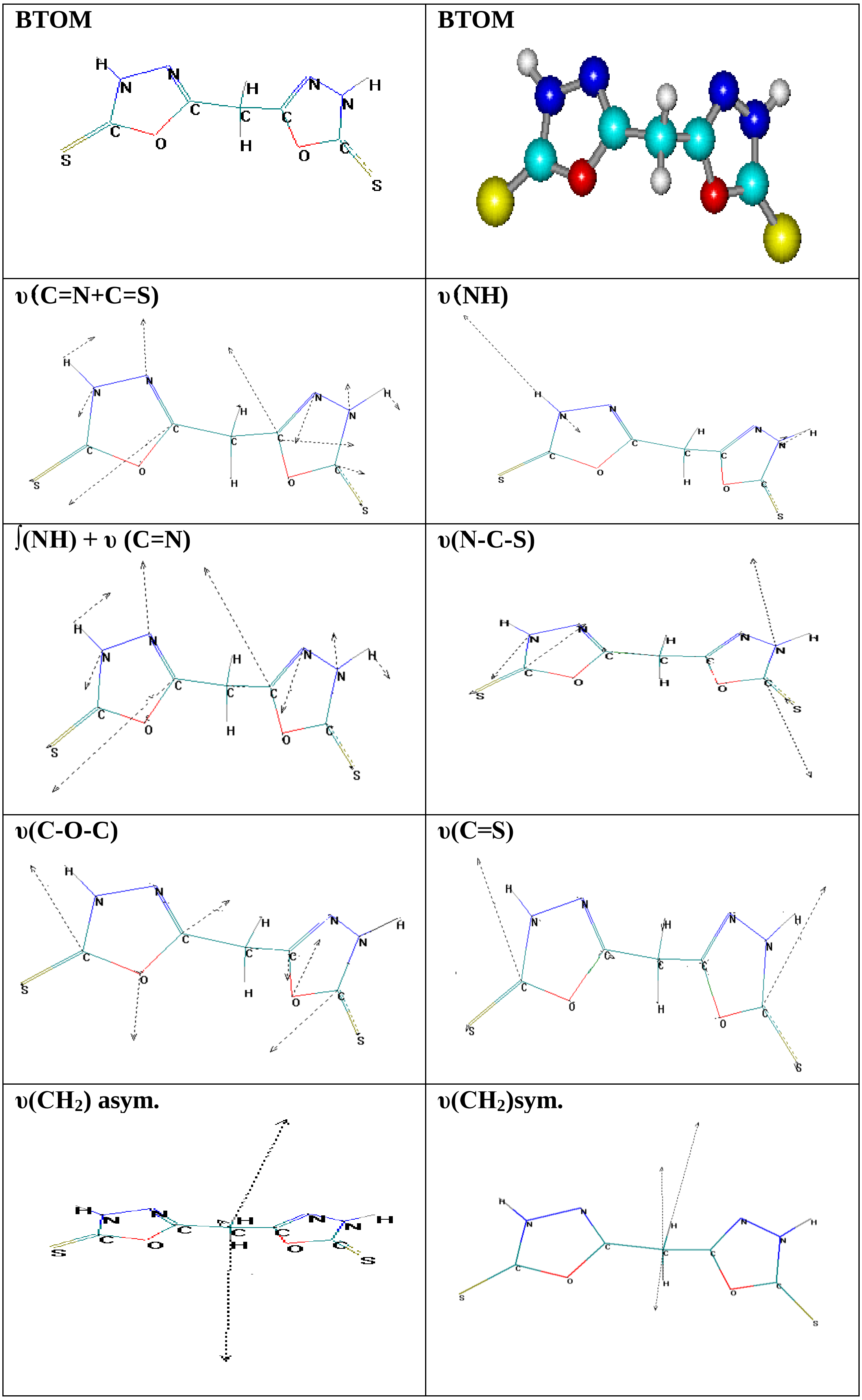
Symb.	υ NH	δ NH + υ C=N +C=S	υ C=N + C=S	υ NCS	υ N-N	υ C=S	υ NCN	υ CH2-alph.	υ CH2-N
BTOM	(3285)* (3403)** (-3.5)***	(1643,1620)* (1445.9)** (11,9,10.8)***	(1396.3)* (1381)** (1.1)***	(985,998)* (979.9)** (0.51,1.81)***	(1056)* (1021)** (3.31)***	(1272)* (1233.2)** (3.05)***	-	(2916,2839)* (2998,2938)** (-2.81, -3.49)***	-
L	-	-	-	(1049,1141)* (1049,1039)** (3.3,8.9)***	(1450)* (1386.9)** (4.3)***	(1288)* (1234)** (4.2)***	(1380)* (1347)** (2.4)***	(2923,2846)* (2970,2894)** (-1.6,1.68)***	(2846,2923)* (2853.9,2899)** (-0.27,0.82)***

Where :

*** : Experimental frequency**

****: Thoretical frequency**

*****: Error % due to main difference in yhe experimental measurements and theoretical treatment of vibrational spectrum.**



BTOM

BTOM

υ(C=N+C=S)

υ(NH)

∫(NH) + υ (C=N)

υ(N-C-S)

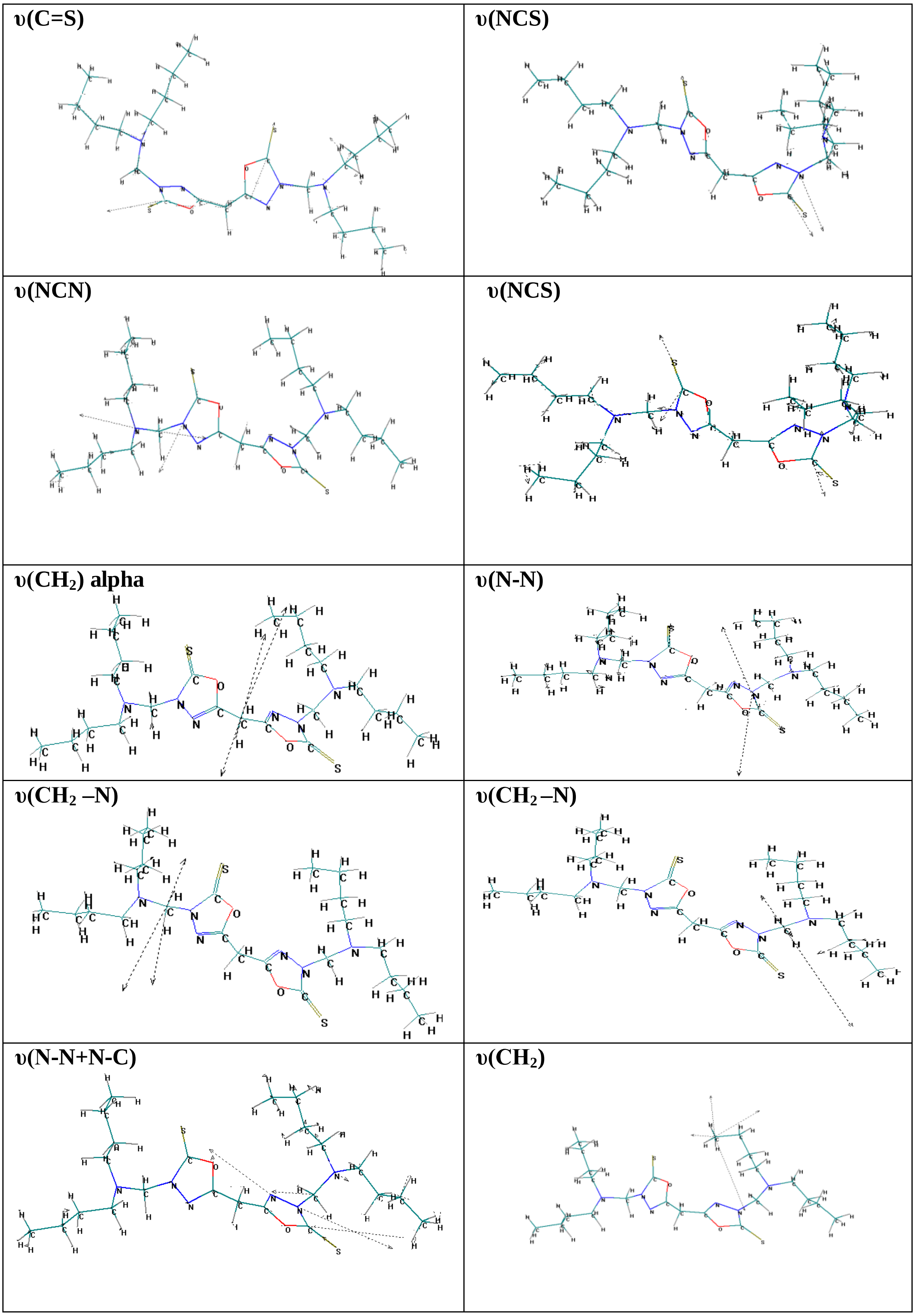
υ(C-O-C)

υ(C=S)

υ(CH_2) asym.

υ(CH_2)sym.

Fig. (1) : The Calculated vibrational frecuencies of BTOM.



υ(C=S)

υ(NCS)

υ(NCN)

υ(NCS)

υ(CH_2) alpha

υ(N-N)

υ(CH_2 –N)

υ(CH_2–N)

υ(N-N+N-C)

υ(CH_2)

Fig. (2) : The Calculated vibrational frecuencies of Mannich base L.

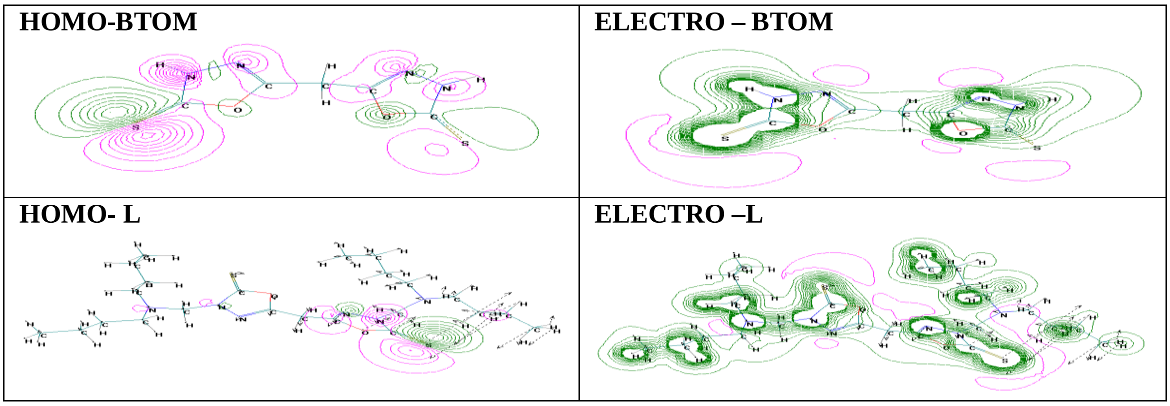

HOMO-BTOM
ELECTRO – BTOM
HOMO- L
ELECTRO –L

Fig. (3) : HOMO and Electrostatic Potential as 2D Contours for Starting material and L.

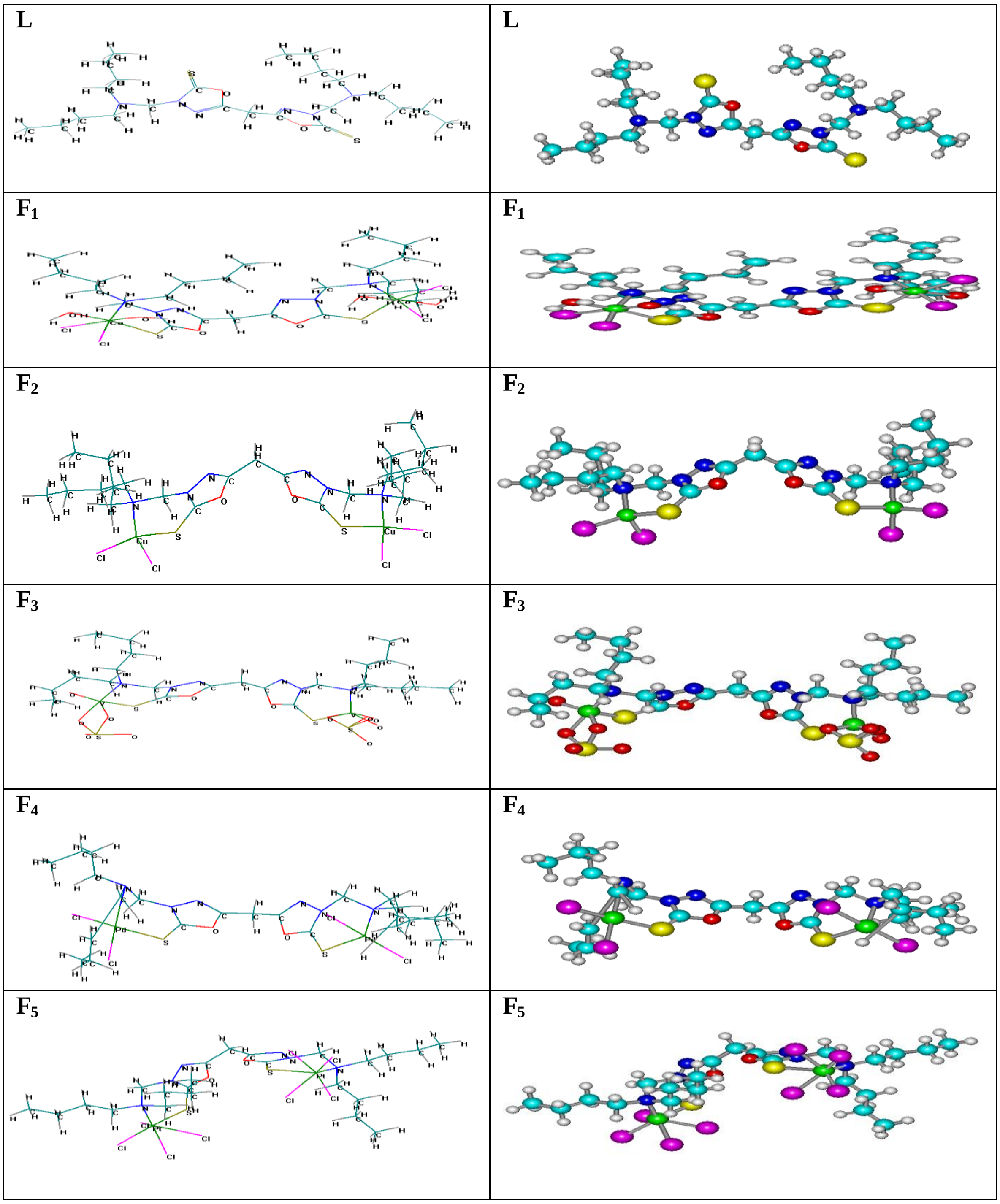

L
L
F_1
F_1
F_2
F_2
F_3
F_3
F_4
F_4
F_5
F_5

Fig. (4) : Conformational Structure of L and their metal Complex (F_1-F_5).

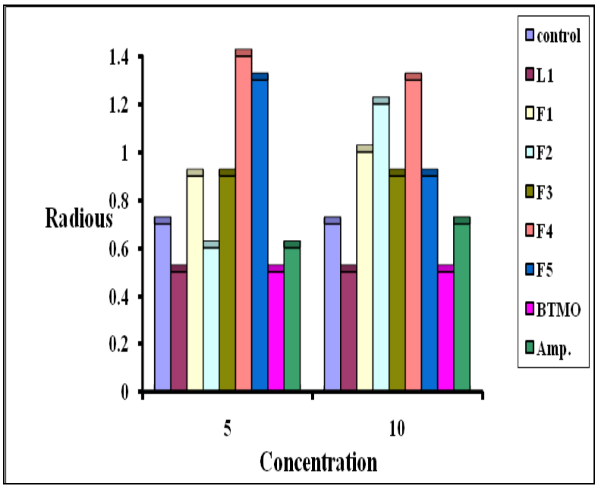


Fig.(5) : Shows the effect of Pseudomonas aeruginosa bacterial toward complexes of L.

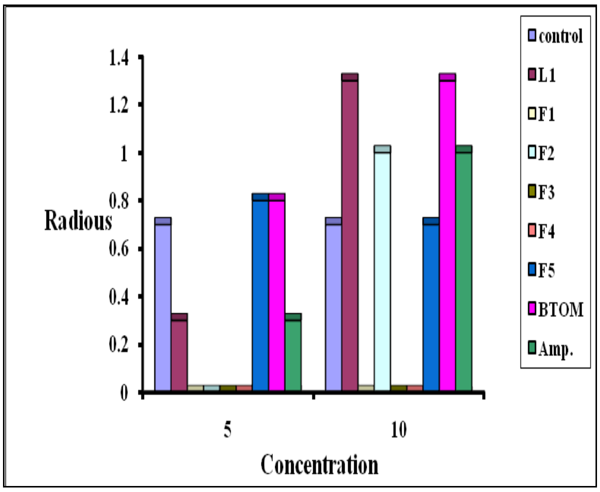


Fig.(6) : Shows the effect of *Bacillius Subtilis* bacterial toward complexes of L.

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الخلاصة

تم تحضير قاعدة مانخ الجديدة (N−(4− ثنائي(5− ثايون−4,3,1 − اوكساديازول −2يل) ميثان) مثيل) ثنائي بيوتيل امين(L)، وشخصت بطريقة تحليل طيف الاشعة تحت الحمراء . تم استخدام(L) كليكاند لتحضير عدد من المعقدات الجديدة مع ايونات عناصر الكوبلت (II) والنحاس(II) والفناديوم(VI) والبلاديوم(II) والبلاتين(VI). تم عزل المعقدات الجديدة وتشخيصها باستخدام طيف الاشعة تحت الحمراء وطيف الاشعة فوق البنفسجية−المرئية وقياسات التوصيلية المولارية الكهربائية والحساسية المغناطيسية ,اضافة الى قياسات الامتصاص الذري اللهبي للعناصر. تم كذلك دراسة طبيعة المعقد المتكون في الايثانول النقي باتباع طريقة النسبة المولية ، وقد اعطت هذه الدراسة نتائج متطابقة مع تلك المعزولة في الحالة الصلبة.

تم تقييم الفعالية المضادة للبكتريا لليكاند ومعقداته واختير نوعان من البكتريا *Bacillus subtilis* و*Pseudomonas aeruginosa*. كما تم مقارنة فعالية هذه المركبات المحضرة مع المضاد الحيوي (Ampicillin)

تم معالجة تكوين المعقدات نظريا في الطور الغازي وبأستخدام برنامج (HyperChem-6) وبتطبيق الميكانيك الجزيئي وشبه التجريبي في الحساب وباستخدام الدوال AMBER,ZINDO/1,PM3 لحساب حرارة التكوين (ΔH_f°) وطاقة الترابط (ΔE_b) وبدرجة حرارة 298 كلفن لليكاند ومعقداته المحضره , كذلك تم حساب الجهد الالكتروستاتيكي لبيان المواقع الفعالة لقاعدة مانخ وجرى حساب التردد الاهتزازي نظرياً وباستخدام الدالة PM3 لقاعدة مانخ ومقارنتها مع القيم المقاسه عملياً باستخدام ثنائي (5−ثايون−4,3,1− اوكساديازول− 2يل) ميثان كمركب قياسي ووجد بان هناك توافقا كبيرا بين القيم العمليه والمحسوبه نظرياً مع زياده امكانية تشخيص الحزم بشكل ادق.