

# SOME TRANSITION METAL COMPLEXES WITH A NEW TETRADENDATE LIGAND BIS [4-PHENYL 2-DIPROPYL AMINO METHYL 1, 2, 4 -TRIAZOLE 3-THION-5 YL] METHANE

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## Abstract

The ligand bis[4-phenyl 2-dipropyl amino methyl 1,2,4-triazole 3-thion-5 yl] methane and its metal complexes, Ni(II), Zn(II), Hg(II), were synthesized. The prepared complexes were identified and their structural geometries were suggested by using flame atomic absorption technique, FT-IR and Uv-Vis spectrophotometry in addition to magnetic susceptibility and conductivity measurements. The stoichiometry of the complexes formed in ethanol solution were determined using the mole ratio method, gave result which were compared successfully with those obtained from isolated solid state studied.

Structural geometries of compounds were also suggested in gas phase by using theoretical treatments via HyperChem-6 program for the molecular mechanics and semi-empirical calculations. The heat of formation ( $\Delta H^{\circ}_f$ ) and binding energy ( $\Delta E_b$ ) for the free ligand and its metal complexes were calculated by PM3 to evaluate the vibration spectra of mannich base and to compare the theoretically calculated wave numbers with experimental values by using (4-phenyl-1,2,4-triazole-5 yl) methane as authentic compound. The theoretically obtained frequencies agreed calculation helped to assign unambiguously the most diagnostic bands.

## Introduction

Compounds having triazole nucleus have been reported as antibacterial, fungicidal, antiviral, anti-inflammatory and analgesic [1,2], some new derivatives of triazole have been synthesized to inhibit tumor proliferation, invasion and metastasis [3]. The nucleus of triazole, which incorporates an NCS linkage exhibit a large number of biological activities [4]. Mannich bases and metal complexes have received a great deal of attention during the last years to prepare new sets of these bases and their transition metal complexes. These complexes have proven to be anti-tumor and have carcinostatic activity [5].

Some drugs have increased activity when administered as metal complexes, this attributed to the synergetic effect between the metal and the ligand [6]. These results promoted us to continue our work, and we synthesized a new mannich base derivative of this heterocyclic ring and investigation of the coordination behavior of the prepared new ligand towards some divalent metal ions. Theoretical study in the gas phase by using semi-empirical method also done in order to show most stable conformation and to calculate the heat formation and binding energy for all the probable geometries. In

addition, we found the most active sites of ligand by using the electrostatic potential calculations, calculation of vibrational frequencies for the main molecule and mannich base have been also carried out in order to compare the result in the experimental vibrational frequencies values.

## Experimental

All chemicals were of highest purity and were used as received

### 1-Physical measurements and analysis

Melting points were recorded on Gallenkamp melting point apparatus and were uncorrected. IR spectra were recorded using IR 8400 shimadzu in the range of (4000-200)  $\text{cm}^{-1}$  and samples were measured as CsI disc. Electronic spectra were obtained using (UV-160) shimadzu spectrophotometer at room temperature. The metal content was estimated by using atomic absorption shimadzu (AA670) spectrophotometer. The conductivity measurements were measured using corning conductivity meter (WTW), these measurement were obtained in DMF solvent using concentration of  $10^{-3}\text{M}$  at  $25^{\circ}\text{C}$ . Magnetic susceptibility measurements were obtained at  $25^{\circ}\text{C}$  on the solid state applying faraday's method using Brukes BM6 instrument.

## 2-Preparation the ligand and its metal complexes

### A-Preparation of the ligand

The method that was used to prepare the bis(4-phenyl -1,2,4-triazole-5-yl) methane (BTM) as described in previous work[7], starting from the acid dihydrazied. The new ligand (L) was prepared from dissolving (0.36 g) BTM in ethanol and kept in an ice bath and treated with (0.6g,40%),formaline,To this mixture, an ethanolic solution of dipropyl amine was added slowly with stirring for half an hour, and the left over night in refrigerator. A Crystalline solid precipitated was formed which was filtered and washed with cold ethanol. The physical properties of the base are listed in Table (1).

### B-Preparation of Complexes

The salts of  $[\text{NiCl}_2 \cdot 6\text{H}_2\text{O}, \text{HgCl}_2$  and  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$  (0.237,0.271,0.2195) gm respectively were dissolved in ethanol and added to an ethanol solution of (1 mmol L) with stirring. The mixture was heated under reflux for three hours .During this period the precipitation was completed from. The precipitate was then collected by filtration washed with cold ethanol and then dried under vacuum for four hours. The physical properties of these compounds are listed in Table (1).

All these complexes were analyzed via different techniques, FT-IR, UV-Vis. spectrophotometer, flame atomic absorptions spectrometry, magnetic susceptibility and conductivity measurements.

## 3-Theoretical studied

### 1-Programs Used in Theoretical Calculation

#### HyperChem-6

It 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. [8]

HyperChem-6 can plot orbital 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 [9].

### 3-Computational Methods

#### Semi-empirical Quantum Mechanics

HyperChem-6 offers ten semi-empirical molecular orbital methods, with options for organic and main group compounds, for transition metal complexes and spectral simulation [10, 11]. PM3 were used for the calculation of heat of formation and binding energy for all metal complexes.

### Results and Discussion

The reaction of appropriate metal salts with mannich base has shown to give the new compounds of the general formula  $(\text{M}_2\text{LX}_4) \cdot \text{Y}$ , where  $\text{M}=\text{Ni}$  (II),  $\text{Hg}$  (II) and  $\text{Zn}$  (II) and  $\text{X}=\text{Cl}$ ,  $\text{Cl}$ ,  $\text{OAC}$  respectively, while  $\text{Y}=\text{O}$ ,  $\text{O}$ ,  $\text{H}_2\text{O}$  respectively

The results obtained from metal analysis, which was satisfactory, agreement with the calculated values .All the physical and analytical data of the compounds were given in Table (1). The suggested molecular formula was also supported by spectroscopic measurements besides magnetic moments.

#### A-Infrared spectroscopic study

- The ligand behaves as tetradentate chelating agent in all complexes, and the coordinating were from the nitrogen of methylene group and sulfur atom of the triazole ring.
- The prepared complexes exhibit a considerable lowering in the stretching band of  $\text{C}=\text{S}$  and  $\text{NCS}$ , due to decrease in double bond character of the sulfur to carbon bond.
- The behavior of new complexes were further indicated by appearance of stretching bands frequencies of  $\text{M-N}$ ,  $\text{M-S}$ ,  $\text{M-O}$  and  $\text{M-Cl}$  respectively [12].

•The assignment of the  $\pi$  C-N bond was not easy, due to the presence of four (C-N) bonds at different position, also the assignment of  $\pi$  (N-N) was not well resolved and was found to be overlapped with another peaks in the same range.

### B-Electronic spectra,magnetic susceptibility and conductivity measurements

Another structural tool, electronic spectral magnetic and conductivity measurements have been used to confirm the geometry of the complexes.

Square planner nickel (II) complexes commonly orange or red, but green examples are known [13,14]. The yellowish-green color of the present Ni(II) chelate is therefore not inconsistent with our postulation of a square planner structure. Furthermore the color of ethanolic solution complex was noticed to change gradually from yellow-green then to yellow during dissolving of the solid compound.

Therefore it was postulated that two  $C_2H_5OH$  molecules coordinates through the axial positions of the square planner change it to distorted octahedral. The electronic spectral data of this solution was provided further evidence in favor of distorted octahedral structure. The ground term for spin-free  $d^8$  configuration is  $^3F$ , in octahedral stereochemistry the triplet term of  $d^8$  ion is the  $^3A_2g$ , the possible spin-allowed transition can be assigned as shown in Table (3) with their respective values. The value of  $v_1$  which is equal to  $10Dq$ , The Racah interelectronic repulsion parameter  $B$  and their nephelauxetic factor  $\beta$  where calculated by fitting the ratio  $v_2/v_3$  0.68 fit the diagram at  $1.9 Dq/B'$ , therefore from  $v_2/B' = 29.2, B$  will be  $560 \text{ cm}^{-1}$  and  $B = 1035 \text{ cm}^{-1}$  (taking  $B$  for the free ion to be  $1035 \text{ cm}^{-1}$ ) [15]. The Transition observed at  $13,200 \text{ cm}^{-1}$  was assigned to be spin-forbidden transition  $^3A_2g \rightarrow ^1Eg$  [16].

The assigned value of transition and the calculated parameter are all in good agreement with nickel (II) complexes having similar donor atom groups [17]. The magnetic measurements have shown that the nickel ion to be paramagnetic in distorted octahedral environment [18]. Conductivity measurement

was showed that the complex to be none conducting.

Generally, Zinc, Cadmium and Mercury ions behave similarly with respect to their coordination number, which may be 2, 4, 4 and 6, and the most probable is the 4 and 6 coordination number [17,18]. The prepared complexes are colorless and diamagnetic which is expected for  $d^{10}$  ion. The UV-Vis spectra of the compounds show relative change in the band position compared to that of the ligand alone. The conductivity measurement was indicated that the non conducting behavior of the complexes, Table (3).

### C-Theoretical study of Mannich base and their metal complexes in gas phase.

(i) The program HyperChem-6 was used for the semi-empirical and molecular mechanic calculations, at optimized geometries energies, the result on PM3 method of calculation in gas phase for the heat of formation ( $\Delta H^o_f$ ) and binding energy ( $\Delta E_b$ ) for the ligands and their complexes were calculated and tabulated in Table (4).

Also PM3 was used for evaluation the vibrational spectra of the BTM and mannich base to compare the theoretically calculated wave numbers with the experimental values. Theoretically calculated wave numbers for these ligand showed that some deviations from the experimental values, these deviations were generally acceptable in theoretical calculations and were described in Table (2) and (5) and the Figs.(1) (2).

#### (ii) Electrostatic Potential (E.P.):

Electrostatic Potential 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 nucleophiles in terms of the properties of frontier orbital's (HOMO and LUMO). Overlap between the HOMO and LUMO a governing 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 Schiff base ligand.

### (iii) Optimized Geometries 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 stable structure. These shapes

Fig.(4), show the calculated optima geometries for (L) and their metal complexes. The results of PM3 method of calculation in gas phase for the binding energies and heat of formation of Ni(II), Zn(II), Hg(II), can be found in Table (4).

**Table (1)**  
*Physical data for the new ligand and its metal complexes.*

Comp.	Color	m.p.C	Yield%	Metal analysis found (Cal)	Metal to ligand ratio	Suggest Molecular formula
L	Whit	142-138	85	-	-	C <sub>31</sub> H <sub>42</sub> N <sub>8</sub> S <sub>2</sub>
NiL	Yellowish-green	200d	72	13.83(14.39)	2:1	[Ni <sub>2</sub> LCl <sub>4</sub> ].H <sub>2</sub> O
ZnL	White	184d	87	13.652(14.48)	2:1	Zn <sub>2</sub> L(OAC) <sub>4</sub>
HgL	White	196	80	-	2:1	[Hg <sub>2</sub> LCl <sub>4</sub> ]

d: decomposed point.  
OAC=acetate.

**Table (2)**  
*The most diagnostic FT-IR bands for the L and its metal complexes.*

Comp.	$\nu$ C=S	$\nu$ NCS	$\nu$ CH <sub>2</sub> -N	$\nu$ N-N	$\nu$ N-CN	$\nu$ M-S	$\nu$ M-N	$\nu$ M-O	$\nu$ M-Cl	$\nu$ OAC
L	1184	1068,1095	2931,2862	1458	1408	-	-	-	-	-
NiL	1168	1063,1018	2924,2854	1438	1400	424	547	-	362,355	-
ZnL	1170	1072,1014	2924,2854	1435	1392	424	520	451	-	1550,1025
HgL	1172	1072,1010	2924,2870	1431	1396	462	559	-	450,369	-

**Table (3)**  
*Electronic spectral data and their probable assignments, conductivity, and magnetic moment data of the new prepared complexes.*

Comp.	Band (cm <sup>-1</sup> )	Assignment	B cm <sup>-1</sup>	Dq/B <sup>-1</sup>	B'	$\beta$	10 Dq	$\mu_{\text{eff}}$ B.M	$\mu_{\text{s}}$ cm <sup>-1</sup>
NiL	13,200	<sup>3</sup> A <sub>2g</sub> → <sup>1</sup> E <sub>g</sub>	1035	1.9	560	0.541	10640	3.11	16
	10,672(cal.)	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>2g(F)</sub>							
	17,090	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g(F)</sub>							
	23995	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g(P)</sub>							
ZnL	30303	CT.I.L.	-	-	-	-	-	0.0	22
HgL	29985	CT.I.L.	-	-	-	-	-	0.0	38

Table (4)

Conformation Energetic (in KJ.Mol<sup>-1</sup>) for L and its metal complexes.

Conformation	PM3	
	$\Delta H_f^\circ$	$\Delta E_b$
BTM	171.8663	-4273.4916
L	146.3230	-8480.5550
NiL	-105.6786	-9054.116
ZnL	-149.5828	-11307.6168
HgL	-236912	-8795.9100

Table (5)

Comparison of experimental and theoretical vibrational frequencies.

Comp.	$\nu_{\text{N-H}}$	$\nu_{\text{(NH+C=N+C-C)}}$	$\nu_{\text{(C=N+C=S)}}$	$\nu_{\text{NCS}}$	$\nu_{\text{NCN}}$	$\nu_{\text{N-N}}$	$\nu_{\text{C=S}}$	$\nu_{\text{CH}_2\text{-N}}$
BTM	(3110)*	(1589)*	(1550)*	(970)*	-	(1440)*	(1250)*	-
	(3404.4)**	(1610.6)**	(1530)**	(989.3)**	-	(1432)**	(1215.2)**	-
	(-9.4)***	(1.3)***	(-1.3)***	(-1.9)***	-	(0.5)***	(2.7)***	-
L	-	-	-	(1068,1095)*	(1408)*	(1458)*	(1184)*	(2931,2858)**
	-	-	-	(1068,1074)**	(1392)**	(1466)**	(1280.58)**	(2926,2858)**
	-	-	-	(-0.04,1.9)***	(1.1)***	(-0.5)***	(-8.1)***	(0.17,0.14)***

Where:

\*: Experimental frequency

\*\*: Theoretical frequency

\*\*\*: Error % due to main difference in the experimental measurements and theoretical treatments of vibrational spectrum.

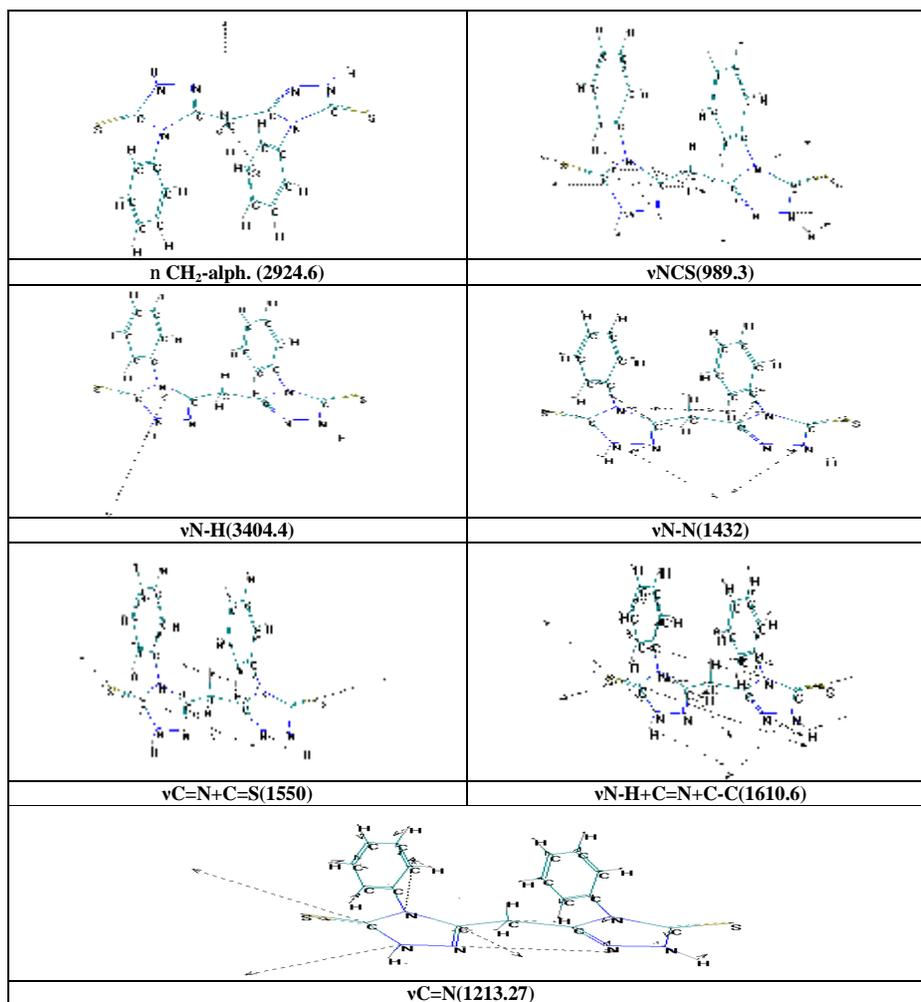
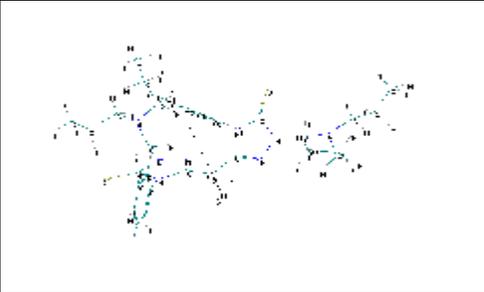
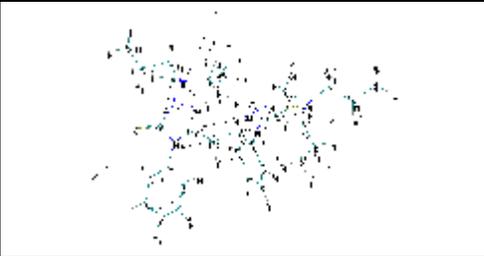
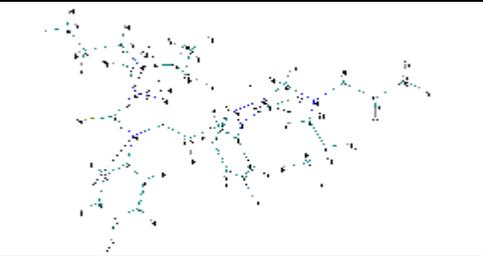
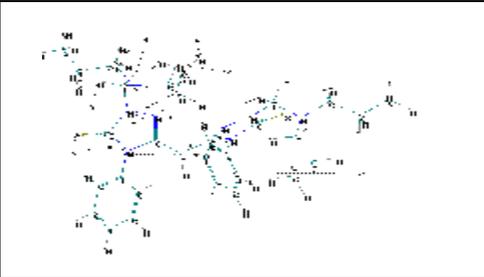
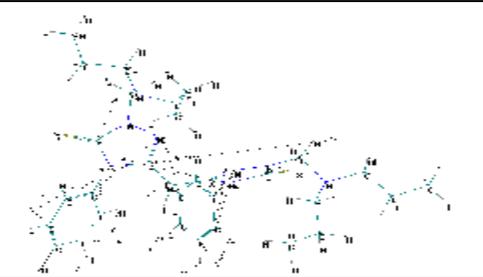
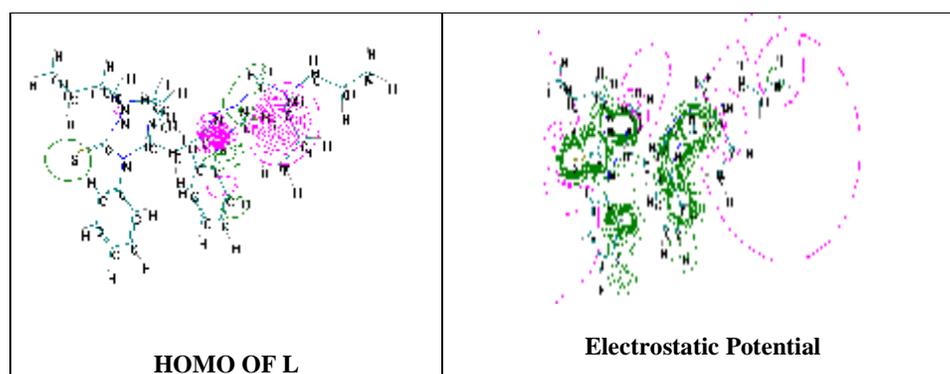


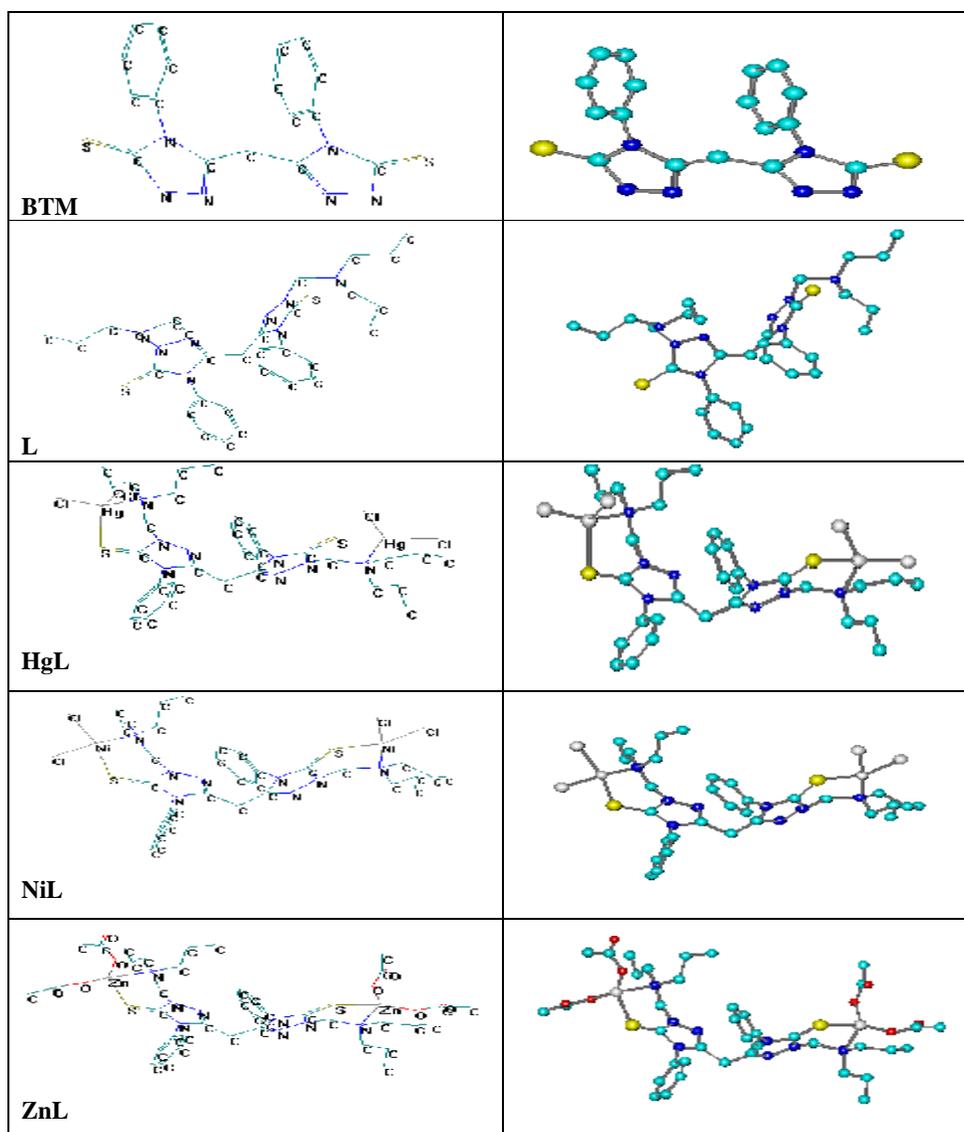
Fig. (1) : The Calculated Vibrational Frequencies of BTM Theoretically.

	
<b>n CH2-alpha. (2907)</b>	<b>n CH2-N (2858)</b>
	
<b>nN-C-N(1392.5)</b>	<b>nasymNCS(1074.3)</b>
	
<b>nSym NCS(1068.5)</b>	<b>nN-N(1466)</b>

*Fig. (2) : The Calculated Vibrational Frequencies of L.*



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



*Fig. (4): Conformational Structure of BTM, L and its Complexes.*

### Conclusion

The ligand behave as atetradentate chelating with two metal ions through four donor atoms, and all prepared complexes have four coordination number as a tetrahedral or squera planer. The theoretically obtained frequencies agreed helped to assign unambiguously the most diagnostic bands.

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جرى تحضير الليكاند ثنائي (4-فنيل -2 ثاني بروبييل امين مثيل -4،1،2 -ترايزول -3-ثايون -5 كيل) ميثان ومعداته مع الايونات النيكل (II) والزنك (II) والزنك (II) وتم تشخيص وتعيين الشكل الهندسي للمركبات (II). المحضرة باستخدام الأجهزة الطيفية، الأشعة تحت الحمراء والأشعة فوق البنفسجية- المرئية بالإضافة الى قياس الحساسية المغناطيسية والتوصيل الكهربائي لها. درس طبيعة المعقد المتكون في المحاليل بأنتباع طريقة النسب المولية حيث اعطت نتائج مقارنة مع النتائج التي تم الحصول عليها بالحالة الصلبة المعزولة.

جرى معالجة تكوين المعقدات نظرياً في الطور الغازي باستخدام برنامج (HyperChem-6) بتطبيق الميكانيك الجزيئي والشبه التجريبي في الحساب وذلك باستخدام الدالة PM3 لحساب حرارة التكوين ( $\Delta H_f^\circ$ ) وطاقة الترابط ( $\Delta E_b$ ) عند درجة حرارة 298 كلفن لليكاند ومعداته المحضرة، كذلك تم حساب الجهد الألكتروستاتيكي لبيان المواقع الفعالة لقاعدة مانخ وجرى حساب التردد الاهتزازي نظرياً والدالة PM3 لقاعدة مانخ ومقارنتها مع القيم المقاسة عملياً باستخدام ثنائي (4-فنيل - 1،2،4 - ترايزول - كيل) ميثان كمركب قياسي ووجد بأن هناك توافقاً كبيراً بين القيم العملية والمحسوبة نظرياً مع زيادة امكانية تشخيص الحزم بشكل ادق.