PREPARATION, CHARACTERIZATION AND THEORETICAL STUDY OF SOME METAL COMPLEXES OF NEW N[4-BIS(5-THION-1,3,4-OXADIAZOLE-2YL) METHANE) METHYL] DIBENZYL AMINE OF POSSIBLE BIOLOGICAL ACTIVITY

S. S. Hassan, F. M. Abdul-Hameed and M. F. Alias

College of Science for Women, University of Baghdad.

Abstract

A new Mannich base N[4-bis(5-thion-1,3,4-oxadiazole-2yl)methane)methyl] dibenzyl amine (L), have been prepared and characterized by (FTIR) spectroscopy. (L) has been used as a chelating ligand to prepare a number of metal complexes were isolated and characterized by (FTIR) (UV-Vis) spectroscopy, and Flame atomic absorption technique,in addition to magnetic susceptibility, and conductivity measurement. The study of the nature of the complexes formed in ethanolic solution following the mole ratio method, gave results which were compared successfully 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, *pseudomonas aeruginosa* and *Bacillus subtilis*, the antibiotics Ampicillin has been chosen to compare their activity with those of the new compounds. Theoretical treatment of the formation of the complexes in the gas phase, this was done using the HyperChem-6 program for the semi-empirical and molecular mechanics calculations. The heat of formation (ΔHf^o) and binding energy (ΔE_b) at 298K for the free ligand and their complexes were calculated by PM3 and AMBER. Furthermore the electrostatic potential of the free ligand was calculated to investigate the reactive sites of the molecule.PM3 was used to evaluate the vibrational spectra of the base(L) and compare the theoretically calculated wave number with the experimental values by using bis (5-thion-1,3,4-oxadiazole-2yl) methane, as authonetic compound. The theoretically obtained frequencies a gree with those values experimentally found, in addition, the calculation helped to assign unambiguously the most diagnostic bands.

Introduction

The biological activity of many thiooxadiazole derivatives is now fairly documented [1-3]. These compounds were described as fungicial, bactericidal and hypoglycemic agents [4, 5]. Mannich base compounds have been studied intersively mainly because of their application of organic synthesis especially for preparing dyse [6], Industrial [7], pharmaceutical [8], and polymer chemistry [9, 10].

In pharmacology fields, it is found that the intering of (-CH_2-NR_2) group through amine group connected with tetracycline, molecule that will give teteracyclic derivatives, exhibits a good medical property [11].

Recentally, agreat attention has been given to the synthesis and biological evolution of mannich bases compounds containing heterocyclic ring [12, 13] .A new inhibitor of ceramide trafficking from endoplasmic reticulum to the site of sphingomyerin, synthesis has been synthesized efficiently using the present Mannich-type reaction as key steps [14].

Metal complexes of Mannich bases have been studied extensively in recent years due to the selectivity and sensitivity of ligands towards various metal ions[15-17] Rai etal [18], prepared mannich bases complexes were screend for fungicial activity against helmin those porium oryzae, thy indicated that the dilute solution of the complexes was more active than for ligands.

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

Theoretical study in the gas phase was done by using semi-empricial 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 (5-thion-1, 3, 4-oxadiazole-2yl) 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- Material and Methods

The chemicals used in this work were obtained from B.D.H. and they were all pure grade reagents. Flam 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 were recorded using shimadza UV-Visible spectrophotometer Type 160A. Electrical conductivity was measured by corning ductivity meter 220, and magnetic susceptibility was measured by BM6 using Faraday method.

B-Preparation of ligande

The method that was used to prepare the bis (5-thion-1, 3, 4-oxadiazole-2yl) methane (BTOM) was prepared elsewhere [19].The Mannich base(L) was prepared according to the following :-

BTOM (2.16 gm) was dissolved in a minimum quantity of ethanol and kept in an ice bath and treated with formaldehyde (0.6g, 40%).To this mixture, an ethanol solution of dibenzyl amine (3.94gm) 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 [CoCl2.6H_2O, $CuCl_2$.2 H_2O, $VOSO_4$.H_2O,$PdCl_2(PhCN)_2$,andH_2PtCl_6.6H_2O] ,were dissolved in ethanol and added to an ethanol solution of mannich base in (2:1) mole ratio metal to ligand respectively with stirring. The mixture was heated under reflux for three hours, during this period the precipitation was completed form, and collected by filtration,then washed with ethanol and dried under vacuum for 4 hours.

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

D-Study of comple formation in solution

Complexes of Mannich base with metal ions were studied in solution using ethanol as a solvent, in order to determinded [M/L] ratio in the complex following molar ratio method [20,21]. A series of solutions were prepared having a constant concentration 10^3M of metal ion and ligand (L). The [M/L] ratio was determined from the relationship between 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 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 calcula-tions, Mechanic and dynamic.

HyperChem can plot orbital wave 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 in formation is useful in determining reactivity and correlating calculation results with experimental data.

2. Types of Calculation

- Single point calculation determines the molecular energy and properties for given fixed geometry.

- Geometry optimization calculations employ energy minimization olgorithms to locate stable structures
- Vibrational frequency calculations find the normal vibrational modes of anoptimized structure. The vibrational spectrum can be displayed and the vibrational motions associated with specific transitions can be animated [22].

3-Computational methods

a- semi-empirical quantum Mechanics:

i-Hyperchm offers ten semi-empirical molecular orbital methods, with options for organic and main group Compounds, for transition metal complexes and for spectral simulation [23].

ii-Choose from zerner's, INDO method (ZINDO/I) and parameterization model, version3(PM3),[including transition metals], [24]. PM3 were used for the calculation of heat of formation and binding energy for all metal complexes except V(IV) and Pt(IV).

b- Molecular Mechanics

It has three, important concepts, functional form, atoms types and parameter sets.Each molecular mechanics method have its own functional from (assisted model building and energy refinement), AMBER is based on a force field [23]. AMBER was use for the calculations of the heat formation and binding energy of V (IV) and Pt (IV) complexes.

F-Study of biological activity for Mannich base and their complexes

The biological activity of the prepared new ligand and their complexes were studied against selected types of bacteria which included *pseudomonas aeruginosa* as agram negative and *Bacillus Subtilis* as agram positive tobe cultivated in brain hart broth agar media, which is used DMF as a solvent and as a control for the disc sensitivity test [25], this method involves the exposure of the zone of inhibition toward the diffusion of micro-oranism on a gar plate. The plates were incubated for 24 hr. at 37C^o, the zone of inhibition of bacterial growth around the disc was observed.

Result and discussion

A-Elemental Analyses:

The physical and analytical data of the ligand and their metal complexes are given in Table (1).

The results obtained from elemental analysis a333re 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 spectra of (L) and its complexes with their respective assignments are shown in Table (2). (L) exhibited the diagnosis ν (CH_2-N) at (2923, 2846), ν (C=S) at (1280), ν (NCS) at (1141, 1049), ν (N-N) at (1450) and ν (NCN) at (1380) cm^{-1} vibrations. Most of the following changes were noticed in spectra of complexes:

- The bands due to ν (CH_2-N) were shifted to higher frequencies around (12-10), (10-8) cm^{-1} and change in the ligand, except vanadium complex, the second frequency of this band was shifted to a lower frequency by (7)cm^{-1} . The inspection of the bands due to (N-N) and (NCN) stretching frequencies showed small relative changes in the position accompanied by reduction in the intensity especially for the band (N-N) frequency, for all complexes, which rule out the coordination through donor nitrogen atoms of oxadiazole ringes .The bands of (C=S) stretching underwent a blue shift by (16) cm^{-1} in the case of (Co,Cu,Pt) complexes while (ν,Pd) complexes underwent red shift about (10-8) cm^{-1}, as well as the bands of the band ν (NCS) which one of them underwent blue shift about (23-13) cm^{-1} in the case (Co,Cu,Pt) complexes, while (ν,Pd) complexes of this band undergo red shift by (8) cm^{-1}, but the second band of ν (NCS) was shifted to a lower frequency around (23-15) cm^{-1} for all complexes except (Cu) complex, spectra was found a shifting to a higher frequency (10) cm^{-1} .Therefore, the ligand behaved as tetradentate tetra basic nature with metal ion, through the four donor atoms (two nitrogen of amino methyl and two atoms of thio group) can be suggested.

- The bonds attributed to (M-N), (M-S) and (M-X) were observed in the region (548-540), (488-484) and (385-378) cm^{-1} respectively in all complexes and the band of (V-O) for the (F_3) complex was observed in (550) cm^{-1}.
- The FT-IR spectrum of (F_3) complex displayed, a(V=O) stretching vibration as a strong band at (979) cm^{-1}[26,27] and aband related to sulfate anion was observed at (1211) cm^{-1}, which indicated a bidentate behavior [28].
- A broad band was observed around (3417-3379) cm^{-1} in the spectra of all complexes, assigned to (O-H) stretching which suggested the presence of water or ethanal molecules in the crystall lattic of the complexes.[29,30].

C-Electronic Spectroscopic Study:

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

F_1: For (F_1) complex, the measured magnetic moment was (4.78)BM this show the cobalt ion in it's greenish-blue complex to be paramagnetic with d^7 configuration [31,32].The spectra of this complex shows three bands at 15267,15798 and 16447 cm^{-1} can be assigned to ν_3 split transition $^4A_2 \rightarrow {}^4T_{1(P)}$ [33].for this bands and the color of it 's which indicate tetrahedral environment around Co(II) ion [31,32]. In infrared region we look for ν_1 and its found as a weak band at 3379 Cm^{-1}, due to transition $^4A_2 \rightarrow {}^4T_2$, on the basis of these assignments it was possible to calculate ν_2,B$^-$,β and 10Dq by fitting the ratio of ν_3/ν_1 to Tanaba-Sugano diagram d^7 taking ν_3 as the average value of three splilts, as are described in Table (3). The value of β signifies a fair amount of covalent character in metal to nitrogen and sulphur bands [34, 35]. As well as the value of spin-orbit coupling (λ^1)Which has been calculated to be (-200.9) cm^{-1}, this value fit with the value for distortion Td [36, 37].The conductivity measurement showed that the complex was non-electrolyte.

F_2 : The electronic spectrum of this complex showed a broad band at 13020 Cm^{-1} which can be attributed to $^2Eg \rightarrow {}^2T_2g$ transition and other bands at higher than 25000 cm^{-1} can be assigned as a charge transfer. Also the effective magnetic moment of this complex was to be (1.23) BM, this value referred to squar planer suggestion structure [31]. The conductivity measurement showed that the complex was non ionic, Table (3).From these information about brown complex, we can suggested a square planer geometry around Cu (II) ion.

F_3: The prepared olive oxavanadium (IV) complex exhibited three main absorption bands which can be assigned to d-d transition, the first one at 13351 Cm^{-1} as a broad band, and the second at 23529 Cm^{-1} as shoulder band, to the third that appear at 27624 Cm^{-1}, which were assigned to the transition $^2B_2g \rightarrow {}^2Eg(n_1), {}^2B_2g \rightarrow {}^2B_1g(n_2)$ and $^2B_2g \rightarrow {}^2A_1g(n_3)$ respectively [32,33]. The magnetic moment at room temperature was found to be (1.89) BM, and the conductivity measurement showed the complex as non-ionic, Table (3) ,so from these data was made for the square pyramidel geometry of this complex.

F_4: The spectrum of this complex exhibited three absorption bands, the first and second bands appeared as a shoulder at 23529 and 27772 cm^{-1} and the third was more intense band at 28998 cm^{-1} .These bands can be assigned to the following transition $^1A_1g \rightarrow {}^1B_1g(n_1)$ which was equal to 10D$_q$, $^1A_1g \rightarrow {}^1Eg(n_2)$ and $L \rightarrow PdCT(n_3)$ respectively for spin-paired d^8 squar planer configuration, and come in a good agreement with the published data [38]. Measurement of magnetic susceptibility provides another evidence for squar planer stereochemistry supporting the assessments of low spin diamagnetic complex (0.92) BM .Conductivity measurement showed that the complex was non-conductance.

F_5: The prepared orange complex Pt(IV) showed three bands at 23529, 27777 and 29585 cm^{-1}, which indicate an octahedral geometry [31,39] .Magnetic moment of solid complex was found to be (0.85)BM, showed a higher orbital contribution [34]. Conductivity in DMF showed that the complex was non-ionic,as are describe in 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 those obtained from isolated solid state study, Table (1).

E-Theoretical Study:

(i) The program HyperChem-6 was used for the semi-empirical and molecular mechanics calculation at optimized geometries energies, the result of PM3 and AMBER methods of calculation in gas phase for the heat formation (ΔH_f^o) and binding energy (ΔE_b) for the ligand and their complexes were calculation and tabulated in Table (4).Also PM3 was used for evaluation the vibration 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 calculation and are described in Table (5) and (2), and Figs.(1, 2).

(ii) Electrostatic potential (E.P):Electron distribution governs the electrostatic potential of molecules, and describes the interaction of energy of the molecular system with a positive point charge, so it 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 attach [40,41].E.P of free ligand was calculated and plotted as 2D contour to investigate the reactive sites of the molecule Fig.(3), and one can interpret the stereochemistry and rates of many reaction involving (soft) electrophiles and nucleophiles interims of the properties of frontier orbital HOMO and LUMO. Overlap between the HOMO and LUMO is a governing factor in many reactions. The HOMO and LUMO values were plotted as 2D contour to get more information about these molecules.The result of calculation showed that the LUMO of transition metal ions prefer to react with HOMO of sulfur and nitrogen atoms of Mannich base ligand.

(iii) Optimized geometries and energy of metal cpmplexes for Mannich base. All theoretically probable structures of metal complexes with ligand have been calculated to search for the most probable model building structure, these shapes Fig.(4), show the calculation optima geometries for (L) and their complexes. The results of PM3 method of calculation in gas phase for the binding energies and heat formation of Co(II), Cu(II), Pd(II), while AMBER method was used to calculated the binding energies which is equal to the heat formation for the V(IV) and Pt(IV) complexes, 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 following points were concluded :

1-The results of antibacterial activity study for the Mannich base indicated that the new compound exhibited antibacterial activity against the studied bacteria at low and high concentration.

2-The result reflected that the starting material BTOM exhibited more inhibition than the prepared new donor base toward *Bacillus Subtilis*, at higher and lower concentration.

3-The study of antibacterial activities revealed that the (L) exhibited a greater activity a against the studied bacteria *a pseudomonas eruginosa*.

Compared to that BTOM, when we use low concentration.

This indicates that introductions of the amino methyl group on the oxadiazole derivatives ring raised the killing zone.

4-Generally, the results of prepared complexes exhibited antibacterial activity toward *pseudomonas* bacteria was more than the complexes inhibition on *Bacillus* bacteria.

5-The study of the antibacterial activities revealed that the complexes of Mannich base toward G^-ve bacteria at 10mM had no mentioned results except cobalt complex causes inhibition against G^-ve bacteria at lower and higher concentration.

6-The results reflected for the complexes of donor base, that there was no effect on G^+ve bacteria at a low concentration except vanadium complex, while the antibacterial activity of the complexes toward the same bacteria became less when we used the high concentration except cobalt which had no effect in inhibiting bacteria.

Table (1)
Phyical data of ligand (L) and their metal complex.

Symb.	**Color**	**Crystallization solvent**	**M.P. °C or decomp.**	**Yield %**	**M:L Ratio**	**Suggested Formula for isolated precipitate**	**Metal analyses calc.(found)**
L	Pale yellow	hot ethanol	126 - 128	91%	2:1	$C_{35}H_{34}N_6S_2O_2$	_
F_1	Greenish- blue	Washing with hot ethanol and cold water	292 D	74%	1.9:1	$[Co_2LCl_4].5H_2O$	11.04 (11.99)
F_2	Brown	Washing with hot ethanol and cold water	277 D	88%	2:0.95	$[Cu_2LCl_4]$ .H_2 O	13.51 (13.78)
F_3	Darg Olive	Washing with hot ethanol and cold water	190 D	61%	2:1	$[(VO)_2L(SO_4)_2].H_2O$	(13.74)
F_4	Brown-reddnish	Washing with hot ethanol and cold water	296 D	72%	1.9:1	$[Pd_2LCl_4]$. 3EtOH	18.98 (18.88)
F_5	Orange	Washing with hot ethanol and cold water	267 D	70%	2:1	$[Pt_2LCl_8]$. 4EtOH	26.88 (26.13)

Table (2)
The most diagnostic FTIR bands of L and their metal complexes.

Sym.	υ 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	1280	1049 1141	1450	2846 2923	1380	-	-	-	-
F1	1296	1072	1455	2856 2930	1378	484	548	-	378
F2	1296	1072 1150	1450	2854 2923	1380	486	545	-	385
F3	1270	1041 1118	1455	2854 2916	1380	488	540	550	-
F4	1272	1049 1126	1455	2854 2931	1378	485	547	-	385.7
F5	1296	1064 1118	1455	2854 2931	1380	486	540	-	385.7

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

Symb.	Absorption Bands,cm^{-1}	Transitions	B	B¢	b	10Dq	Dq/B¢	15B¢	meff BM	Molar condictivity ms.cm^{-1}	Suggested structure
F_1	**3379** **5100** **15820**	$^4A_2\rightarrow{}^4T_2$ $^4A_2\rightarrow{}^4T_1$ $^4A_2\rightarrow{}^4T_1$	1128	718096	0.736	3520	0.49	107844	4.78	9	Tetrahedral
F_2	**13020** **27100** **28735**	$^2Eg\rightarrow{}^2T_2g$ **C.T** **C.T**	–	–	–	–	–	–	1.23	41	Square planar
F_3	**13351** **23529** **27624**	$^2B_2g\rightarrow{}^2Eg$ $^2B_2g\rightarrow{}^2B_1g$ $^2B_2g\rightarrow{}^2A_1g$	–	–	–	–	–	–	1.89	36	Square Pyramide
F_4	**23529** **27772** **28998**	$^1A_1g\rightarrow{}^1B_1g$ $^1A_1g\rightarrow{}^1Eg$ **L→ Pd**	–	–	–	–	–	–	0.92	10	Square planar
F_5	**23529** **27777** **29585**	$^1A_1g\rightarrow{}^1T_1g$ $^1A_1g\rightarrow{}^1T_2g$ **L→Pt(C.T)**	–	–	–	–	–	–	0.85	33	Octahedral

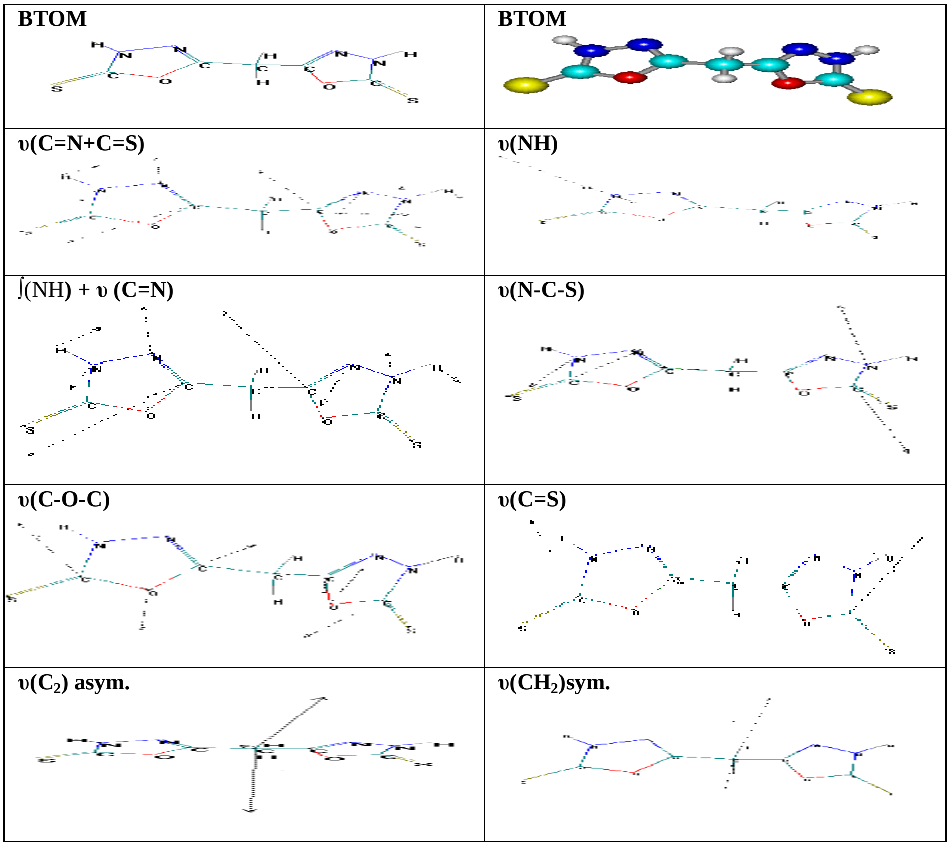
Table (4)
Conformation energetic (in $KJ.Mol^{-1}$) for Mannich base and their metal complexes.

Symb.	PM3		AMBER
	ΔH°_{f}	ΔE_{b}	$\Delta H^{\circ}_{f}=\Delta E_{b}$
BTOM	69.7183003	-1697.057	-
L	183.1533959	-6499.3826	-
F_1	-453.08263	-9456.37863	-
F_2	774292.0001	765332.1	-
F_3	-	-	382.248627
F_4	-11.3119283	-8989.8079	-
F_5	-	-	380.752808

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

Symb.	u NH	δ NH + υ C=N +C=S	υ C=N + C=S	u NCS	u N-N	u C=S	u NCN	u CH_2-alph	u CH_2-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)* (1023,1128)** (2.4, 1.1)***	(1450)* (1229)** (15.24)***	(1280)* (1249.5)** (2.38)***	(1272)* (1233.2)** (3.05)***	(2846,2923)* (2932,2998)** (-3.02, -2.56)***	(2846,2923)* (2865,2878)** (0.66,1.53)***

Where :
* : Experimental frequency
** : Theoretical 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)

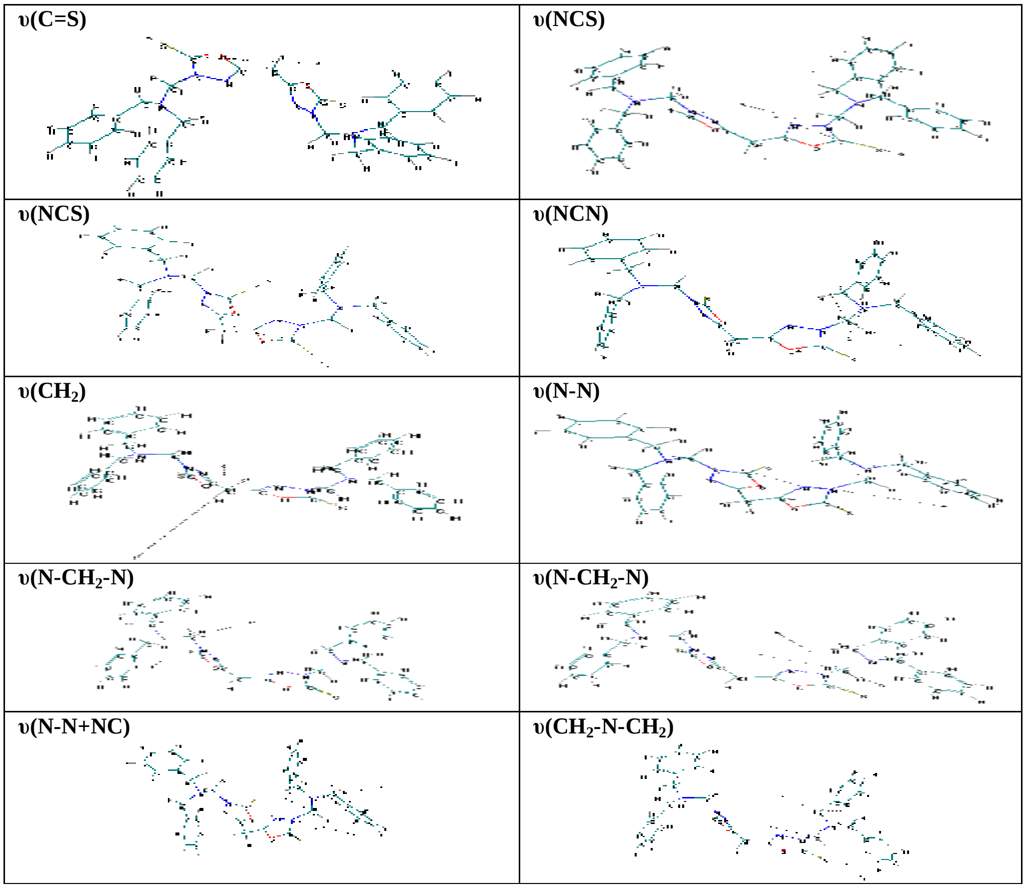
υ(C-O-C)

υ(C=S)

υ(C_2) asym.

υ(CH_2)sym.

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


υ(C=S)

υ(NCS)

υ(NCS)

υ(NCN)

υ(CH_2)

υ(N-N)

υ(N-CH_2-N)

υ(N-CH_2-N)

υ(N-N+NC)

υ(CH_2-N-CH_2)

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

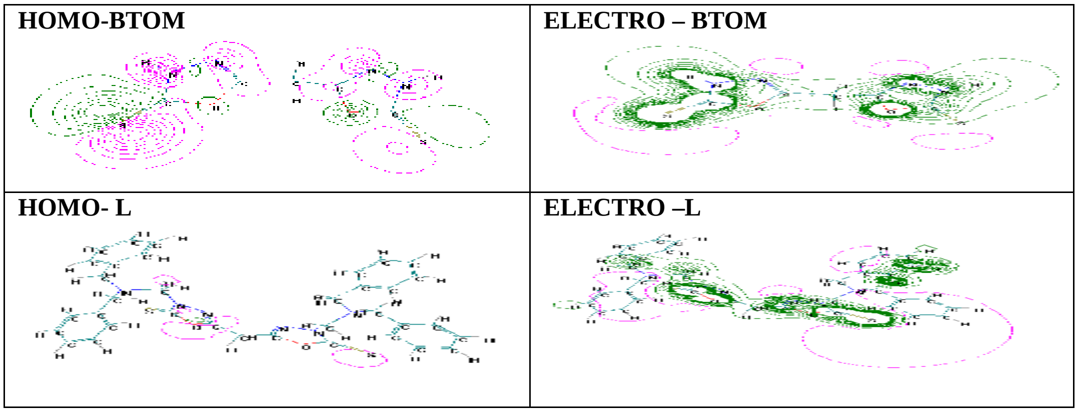


Fig.(3) : HOMO and Electrostatic Potential as 2D Contours for Starting material and Mannich bas.

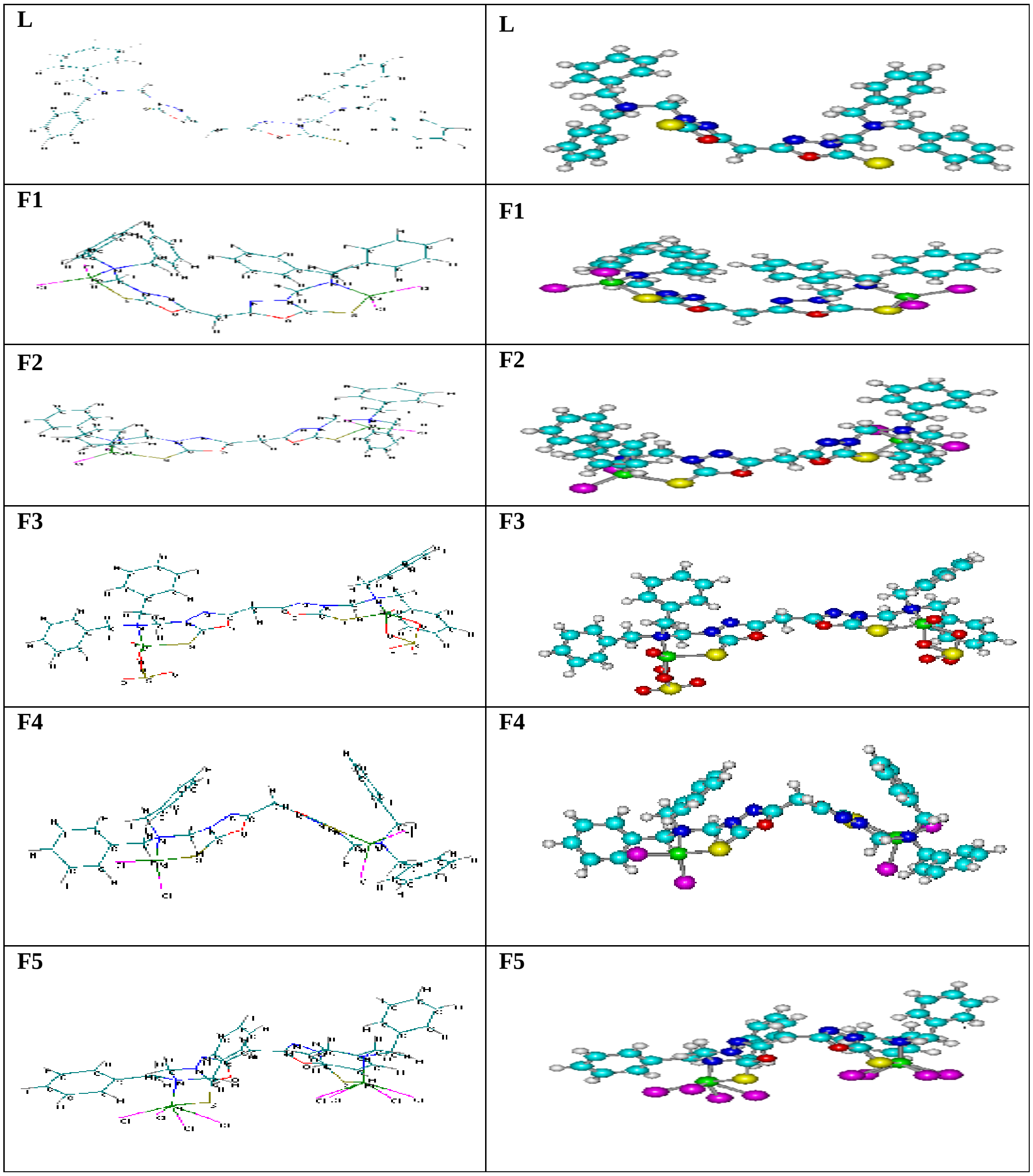


Fig. (4): Conformational Structure of L and their metal Complexes (F_1-F5).

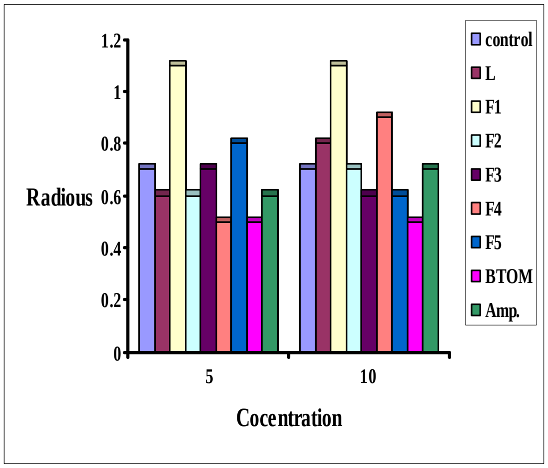


Fig. (5): Shows the effect of *Pseudomonas aeruginosa* bacterial toward complexes of L.

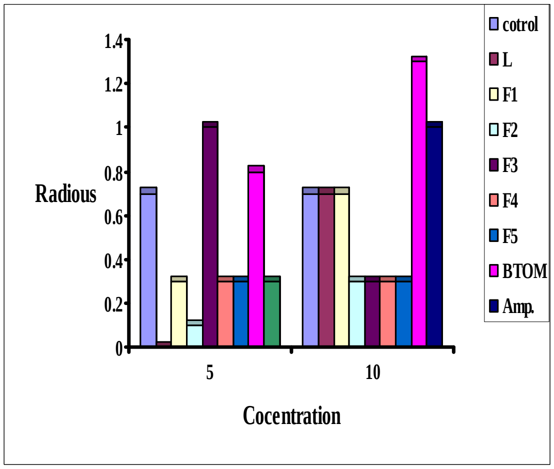


Fig.(6) : Shows the effect of *Bacillius Subtilis* bacterial toward complexes of L.

References

[1] T. Ramalingam; A. A. Dishmukh : P. B. Sattur; J. Indiun chem.soc. 58(3):269-271 (1981).

[2] B. Bcat; D. Dag. Rger offtes, 2 : 428, 204 (1975) c.A. 82 : 15632j (1975).

[3] M. E. Woifi Burgers "Medical chemistry" 4th ed. Part (11), (1975).

[4] H.Hazza, and R.M.Shafik, Pharma, J.Sci. 19:201-206(1980) cited in c. A. 95 : 62088 (1981).

[5] M. Y. Mhasalkev, M. H. Singh, and C. V. Deliwa, J. Med chem., 13 (14) : 672-673 (1970).

[6] W. E. Bachmann, J. R. Johson and H.R.Sngder,"Organic Reaction" 6th ed. Wiley 970). sonc.Inc. New York (1975).

[7] H.P.S.Ghawla; J.med.chem. 13 (1970).

[8] W.J.Gottstein and L.C.Chem., 13,480 (1970).

[9] S. P. Suman and S. C. Bahel; J. Ind. Chem. soc. LVI; (1979).

[10] E.Grech and A.szady polish; J.chem. 74; 717; (2000).

[11] M.A.Kap; an; Nature; 205:399 ;(1965).

[12] S.N.Pandeya, D.sriram and G.nath; Farmaco; 54(9); 624 ;(1999).

[13] S.N.Pandeya, D.sriram and G.nath; Arazneimittel fors Schung; 50 (1); 55; (2000).

[14] S. Kobayashi, R. Matsubara, Y. Nakamura, H. Kitagawa and M. Sugiura; J.Am.Chem.Soc. 125(9); (2003).

[15] A. P. Mishra and S. K. Srivastsvan; J.Ind.Council Chem.; 102 ;(1994).

[16] M.D.Deshmuck; Orent J.Chem.; 11; 185; (1995).

[17] R. S. Varma, N. Rastogi and A. P. Singh; Ind. J. Heterocyclic Chem.; 12; 159; (2002).

[18] R.A.Rai, V.Agarwala and Lakshmi; Ind.J.of Chem.; Vol.18A ;(1979).

[19] V. K. Mashra and S. C. Bahed; Ind. chem. soc. Lx (1983).

[20] J. H. Yoe and A. I. Jones; Ind. Eng. Chem. Anal. Ed; 16; 11; (1944).

[21] P.Job; Ann, chim; 9. 113 (1923).

[22] J.Foresman and C.Frish "Exploring chemistry with electronic structure methods"2nded; Gaussian Inc.; Pittsburgh; PA. ;(1996).

[23] L.Fried, Howard and P.Souers; CHEETAH 2.0 Users Manual, Lawrence Livermore National Laboratory ;(1999).

[24] P. Atkins and R. Friedman; "Molecular Quantum Mechainics"; 3rd ed.; Newyork; Oxford University Press Inc.; NY.; (1997).

[25] M.R.Atlas, E.Alfres, Brown and C.Lawrence parks,"Laboratory Manual Experimental Microbiology"Mosby-year book, Inc.;(1995).

[26] M. C. Ganorkar and L. Nalada, Ind. J. Chem. 27 (6), 542, (1988).

[27] T.A.Bora and M.Devi, Ind.J.Chem. 27 (A), 705, (1988).

[28] K.Nakamoto, “Infrared of Inorganic and Coordination Compounds”, 6th ed., John Wiely, Inc., New York, (1997).

[29] R.M.Silversein, G.C.Bassler and T.G.Morrill, “Spectrometic Identification of organic compounds”, 4th ed. John-Wiley and Sons, (1981).

[30] M.M.Aly, Trans.Met.Chem. 15, 99, (1990).

[31] B.N.Figgis “Introduction to Ligand Field”, New York, (1966).

[32] D.Suttan, “Electronic Spectra of Transition Metal Complexes”, MC Graw-Hill ,Publishing, company litd, (1968).

[33] A.B.P.Lever,"Inorganic Electronic Spectroscopy"; Elsevier Publishing Company New York, London, (1968).

[34] K.Burgger, "Magneto Chemistry",2nd ed., publishers, Ltd., London, (1956).

[35] K.Jorgenson, "Absorption spectra and chemical Bonding in Complexes", pergamon press, (1964).

[36] B.B.Wayl and R.J.Fitzgerald and R.S.Drago; J.Amer.Chem.Soc; 88; 4600; (1966).

[37] R.Longhi and R.S.Drgo; Inorg.Chem; 4; 11; (1965).

[38] M.F.Alias, SH.Obed andA.H.Jassim, J.Um-Salama Sci.Vol.4 (1) ;(2007).

[39] R.C.Saxena, C.L.Jain and S.K.Sangal; J.Ind.chem.soc; LXII; 435; (1986).

[40] J.J.P.Steword, MOPA 2000vio for windows (single), Mo20-As-w, FUJITSU SYSTEM EUROPE.

[41] W. P. Anderson, P. Behm, and T. M. Glennon, J. Phys. chem., A; vol (101); (1997).

الخلاصة:

تم تحضير قاعدة مانخ الجديدة[N-(4-ثنائي (5-ثايون-4,3,1-اوكساديازول-2يل)ميثان)مثيل] ثاني بنزيل الامين (L), وشخصت بطريقة تحليل طيف الاشعة تحتالحمراء (FTIR).تم استخدام (L) كليكاند لتحضير عدد من المعقدات الجديدة مع ايونات عناصر الكوبلت (II)، والنحاس (II) ،والفناديوم (IV)، والبلاديوم (II)، والبلاتين (IV). تم عزل المعقدات الجديدة وتشخيصها باستخدام طيف الاشعة تحت الحمراء وطيف الاشعة فوق البنفسجية-المرئية وتقنية الامتصاص الذري اللهبي للعناصر فضلا عن قياسات الحساسية المغناطيسية والتوصيلية الكهربائية .تم كذلك دراسة طبيعة المعقد المتكون في محلول الايثانول باتباع طريقة النسبة المولية،وقد اعطت هذه الدراسة نتائج متطابقة مع تلك المعزولة في الحالة الصلبة. تم تقويم الفعالية المضادة للبكتريا لليكاند ومعقداته واختير نوعان من البكتريا

Bascillius Subtilis و *Pseudomonas aeruginosa*

كما اجريت مقارنة فعالية هذه المركبات المحضرة مع المضاد الحيوي (Ampicillin).

تم معالجة تكوين المعقدات نظريا في الطور الغازي وباستخدام برنامج (Hyperchem-6) وبتطبيق الميكانيك الجزيئي وشبه التجريبي في الحساب وباستعمال الدوال AMBER,PM3 لحساب حرارة التكوين (ΔH_f^o)وطاقة الترابط (ΔE_b) بدرجة 298 كلفن لليكاند ومعقداته المحضرة، كذلك تم حساب الجهد الالكتروستاتيكي لبيان المواقع الفعالة لقاعدة مانخ ،وتم حساب التردد الاهتزازي نظريا وباستخدام الدالة PM3 لليكاند ومقارنتها مع القيم المقاسة عمليا باستخدام ثنائي (5-ثايول-4,3,1 – اوكساديازول-2 يل) ميثان كمركب قياسي ووجد بانه هنالك توافقا بينهما مع زيادة امكانية تشخيص الحزم بشكل ادق.