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THEORETICAL STUDY OF SOME MIXED-LIGAND COMPLEXES OF SODIUM [5-(P-NITRO PHENYL)-4-PHENYL-1, 2, 4-TRAIZOLE-3-DITHIOCARBAMATO HYDRAZIDE] AND 1, 10 PHENANTHROLINE WITH FE (III) AND MN (II) IONS

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ABSTRACT

A new mixed ligand complexes have been prepared by reaction of Sodium [5-(p-nitro phenyl)-4/-phenyl-1, 2, 4-traizole-3-dithiocarbamato hydrazide] L1, and 1, 10 phenanthrolineL2with Fe (III) and Mn (II) ions. The newly prepared complexes were isolated and characterized by (FT-IR) and (UV-Vis) spectroscopy, elemental analysis, flame atomic absorption technique, in addition to magnetic susceptibility and conductivity measurements. The ligands and the newly prepared complexes were studied theoretically in the gas phase using two programs hyper chem.8 and Gaussian program (Gauss View Currently Available Versions (5.0.9) along with Gaussian 09 which is the latest in the Gaussian series of programs).

KEYWORDS: Hyper chem.8, Gaussian program, Sodium [5-(p-Nitro Phenyl)-4/-Phenyl-1, 2, 4-Traizole-3-Dithiocarbamato Hydrazide], Transition Metals

INTRODUCTION

Dithiocarbamate complexes are of great interest due to their chemical and biological properties and widely used in industries of agriculture, pharmaceutical, medicine and rubber [1, 2]. Dithiocarbamate complexes have been used as a precursor for the synthesis of metal sulfidenanoparticles [3,4].The dithiocarbamato derivative is good coordination ligand due to the fact that it consists of hard nitrogen atom as well as soft sulpher atom in the same structure[5,6]. Different metal-dithiocarbamato complexes have been designed that were expected to resemble the main features of cisplatin together with higher activity, improved selectivity and bioavailability, and lower side-effects [7].

The importance of preparing a dithiocarbamato ligand from its virility as starting materials for the synthesis of many complexes especially with some light and heavy transition metal ions due to the expected biological activity especially as therapeutic of the ligand and its complexes [8]. However, The TRZ.DTC ligand and co-ligand 1, 10-phenanthroline did not receive any attention in spite of well-defined applications of both the molecules. On the basis of the obtained encouraging achievements with other metals (such as gold and copper) we have decided to enlarge the studies to the complexes of Iron and Manganese using the same ligand TRZ.DTC. Hence, it was thought that it is worthwhile to study the complexation of TRZ.DTC as primary ligand along with 1, 10 phenthroline as secondary ligand theoretically with Fe (III) and Mn (II) metal as mixed ligand complexes [5].

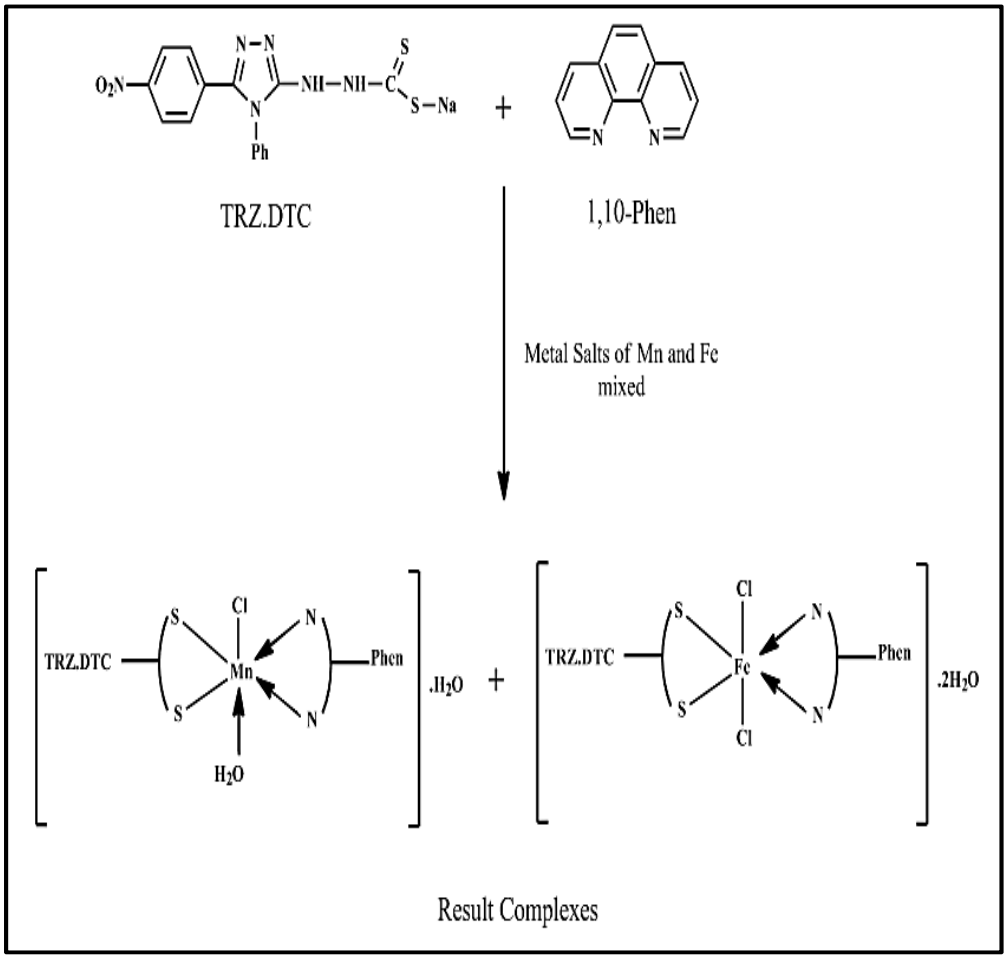
EXPERIMENTAL

Instrumentation

Two programs were used in this paper; hyper chem.8 and Gaussian program (Gauss View Currently Available Versions (5.0.9) along with Gaussian 09 which is the latest in the Gaussian series of programs).

Preparation of Ligand and Its Complexes

(TRZ.DTC) ligand and its complexes were prepared accordring to the literature [9].



Scheme 1: Preparation of Complexes

Programs Used in Theoretical Calculations

Computational chemistry techniques were used only by experienced experts in using tools that were for the most part difficult to understand and apply.Hyperchem-8 program is the most powerful and sophisticated molecular modeling environment it's known for its quality, flexibility, and ease of use, it offers ten semi empirical methods [10,11].Some of them have been devised specifically for the description of inorganic chemistry as well and generally good for predicting molecular geometry and energetic. They can be used for prediction vibrational modes and transition structures [11], while Gaussian is the most powerful computational chemistry environment a monolithic ab initio program. Gaussian probably incorporates the widest range of functionality of any ab initio code complex program [12].Gaussian has seen the widest use in modeling organic molecules. However, there are also options for handling many of the difficulties that can be

encountered in modeling inorganic systems. Nonetheless, inorganic modeling generally requires additional technical sophistication on the part of the user [12].

In present Zerner's, INDO and parameterization method3 (PM3) were used for the calculation of heat of formation, binding energy and dipole moment for all prepared metal complexes. Also ZINDO/S was used to calculate electronic transition for the primary and secondary ligands .PM3 is more popular than other semi empirical methods due to the availability of algorithms and more accurate than other methods [12].

RESULTS AND DISCUSSIONS

Some physical properties and analytical data of the ligands (L1) and (L2) with their metal complexes were showed in literature [9].

Theoretical Studies

The heat of formation (ΔH^{o}_{f}), binding energy (ΔE_b) and dipole moment (μ) for the free ligands and their metal complexes were calculated using ZINDO/I, PM3 and AMBER methods at 298 K. It was found that the complexes are more stable than their ligands **Table 1**; PM3 was used to evaluate the vibrational spectra of free ligands, and these obtained frequencies agreed well with those values experimentally found, in addition, the calculation helped to assign unambiguously the most diagnostic bands **Table 3**, **Figure 1**. Electronic spectra measurements for the ligands were calculated theoretically by using ZINDO/S method and comparing it with the experimental results. It was found that the results were close between the theoretical and experimental spectra, **Table (4**, **Figure 4,5**; Furthermore, the electrostatic potential for free ligands was calculated to investigate the reactive site of the molecules **Figure 8.**While Gaussian program semi-empirical (PM3) method was used to calculate, the geometry optimization, dipole moment (μ) and total energy **Table 2**. Electrostatic potential, E_{LUMO} and E_{HOMO} was obtained **Figure 9**; evaluate the vibrational spectra of free ligands, and these obtained frequencies agreed well with those values experimentally found **Table 3**, **Figure 2,3**. Electronic spectra measurements for the ligands were calculated theoretically by using the job type: Single point energy (SP) along with ZINDO method and also the job type Frequency used along with CIS method (3-21G) and compare both methods with the experimental results **Table 4**, **Figure 7**. It was found that there was a close agreement between the theoretical and experimental spectra.

Table 1: Conformation Energetic in (Kcal.mol^{-1}) and Dipole Moment (in Debye) for Ligands (L_1, L_2) and their Metal Complexes using Hyperchem-8 Program

Compound	*PM3*			*ZINDO/1*		
	ΔH°_{f}	ΔE_b	μ	ΔH°_{f}	ΔE_b	μ
L_1	265.55	-3852.93	7.55	-7857.81	-11976.31	7.76
L_2	-71.30	-2622.19	2.99	-5301.00	-7994.50	3.93
MnL_1L_2	--------	--------	------	-13147.35	-20142.91	19.8
FeL_1L_2	--------	---------	------	-13426.52	-20505.78	18.81

Table 2: Conformation Energetic in (Kcal.mol^{-1}) and Dipole Moment (in Debye) for Ligands (L_1, L_2) using Gaussian Program

Compound	Total Energy	μ
L_1	456.9776	6.53
L_2	78.6897	3.14

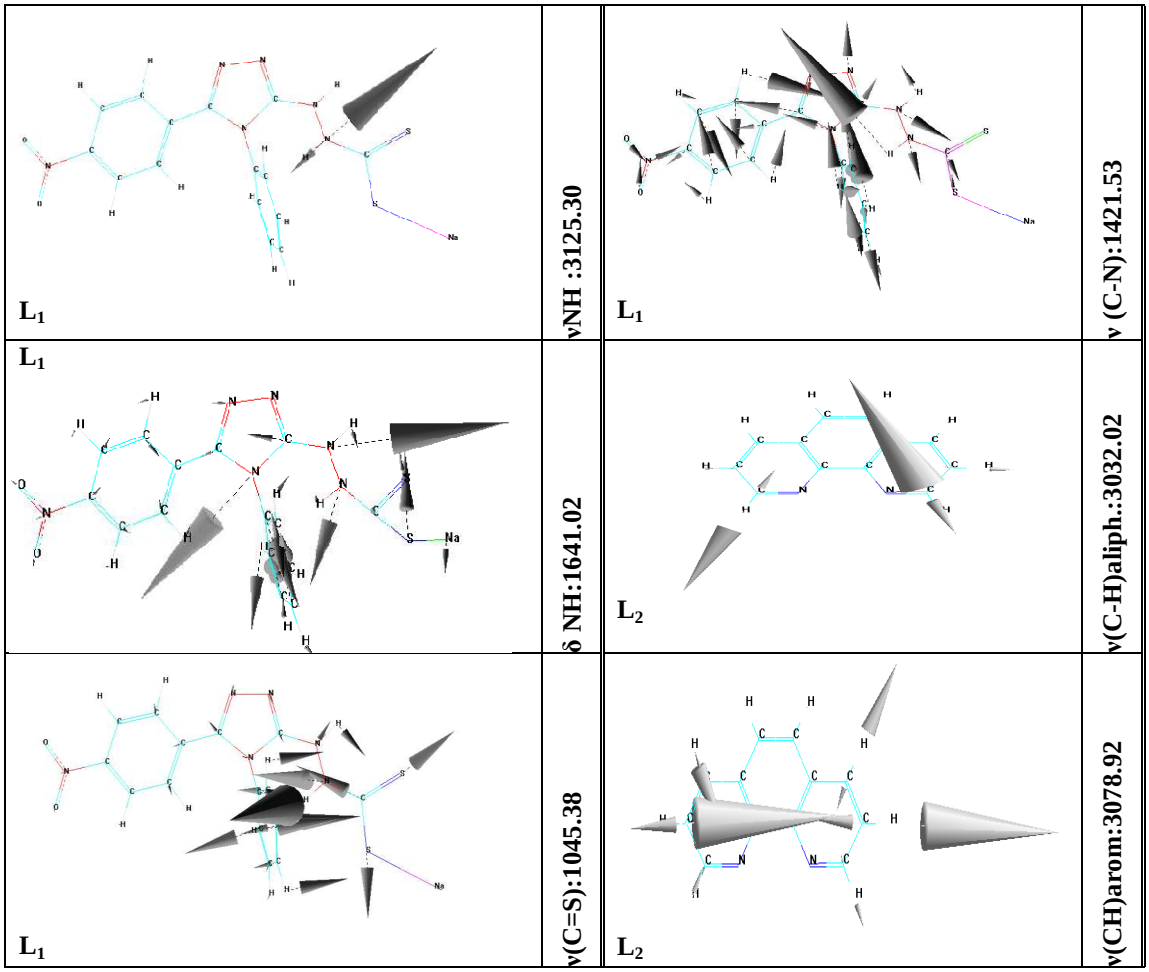
Table 3: Comparison of Experimental and Theoretical Main Vibration Frequencies for TRZ.DTC (L_1) and (L_2) using Hyperchem-8 and Gaussian Programs

Symb.		*vN-H*	*δNH*	*v (C=S)*	*v (C-S)*	*v N-N*	*v C-N*
L_1	**Exp.**	3380	1652	1041	995	1496	1438
	Hyper.	3125* (7.53)	1641* (0.66)	1045* (0.42)	934* (6.05)	1540* (2.94)	1421* (1.18)
	Gass.	3331* (1.44)	1613* (2.36)	1044* (0.28)	909* (8.54)	1490* (0.40)	1428* (0.69)
Symb.		*v(C=N+C=C)*	*v(C-H)aliph*		*v(C-H)arom.*		*δ(C-N)*
L_2	**Exp.**	1616	2981		3078		-----
	Hyper.	1616* (4.98)	3032* (1.71)		3078* (0.017)		1217*
	Gass.	1622* (0.37)	1807* (39.11)		3056* (0.71)		1218*

Experimental frequency

*Theoretical frequency

( ) Error % due to the main difference in the experimental measurements and theoretical treatment of vibrational spectrum



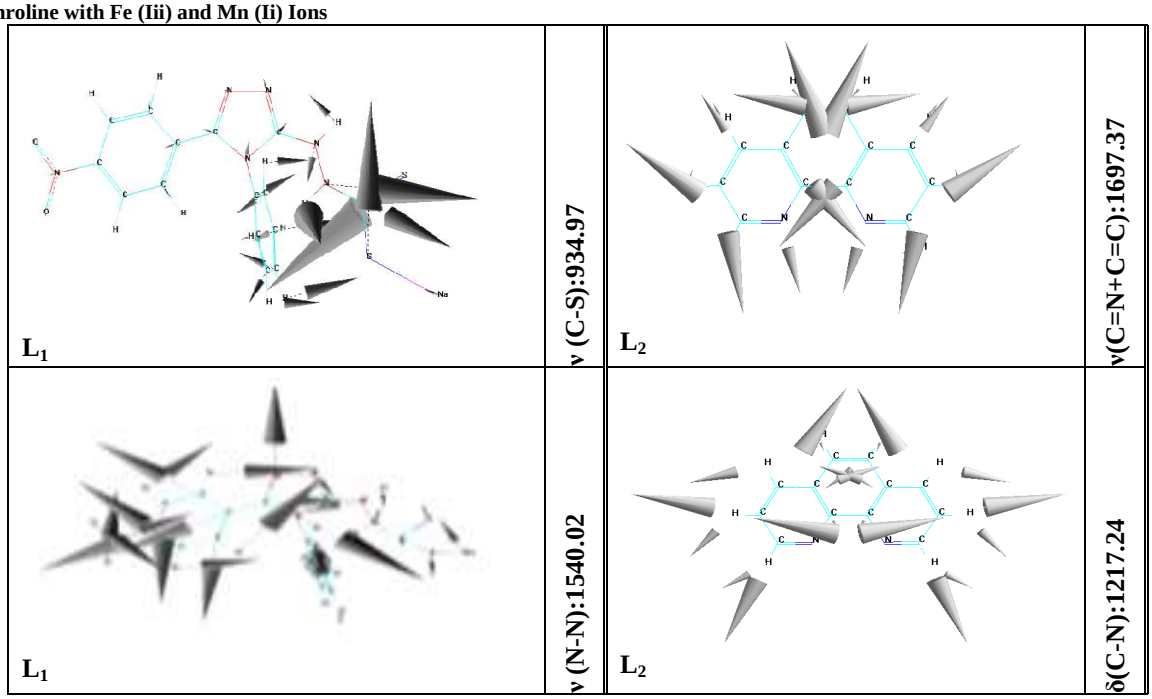


Figure 1: Calculated Some Main Vibrational Frequencies of L1and L2 Using Hyperchem-8 Program

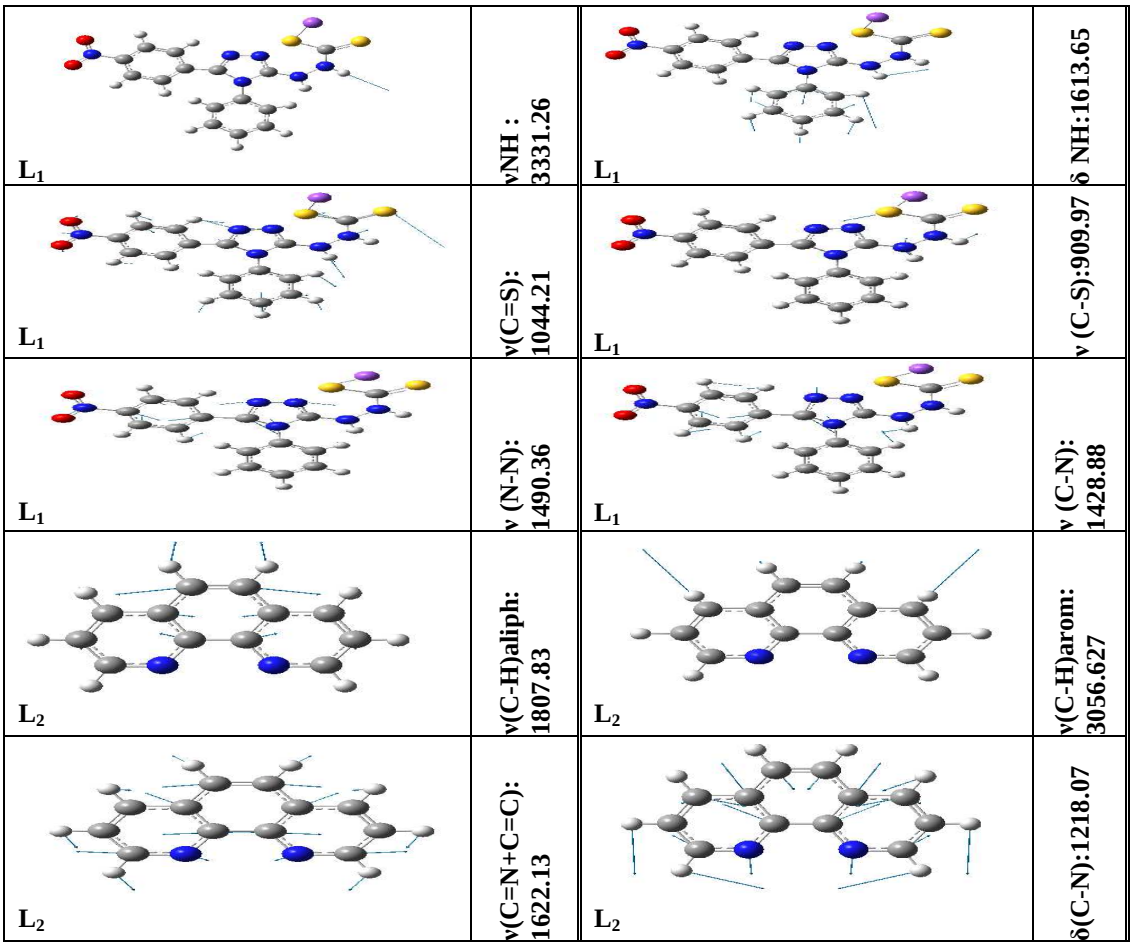


Figure 2: Calculated Some Main Vibrational Frequencies of L_1 and L_2 using Gaussian Program

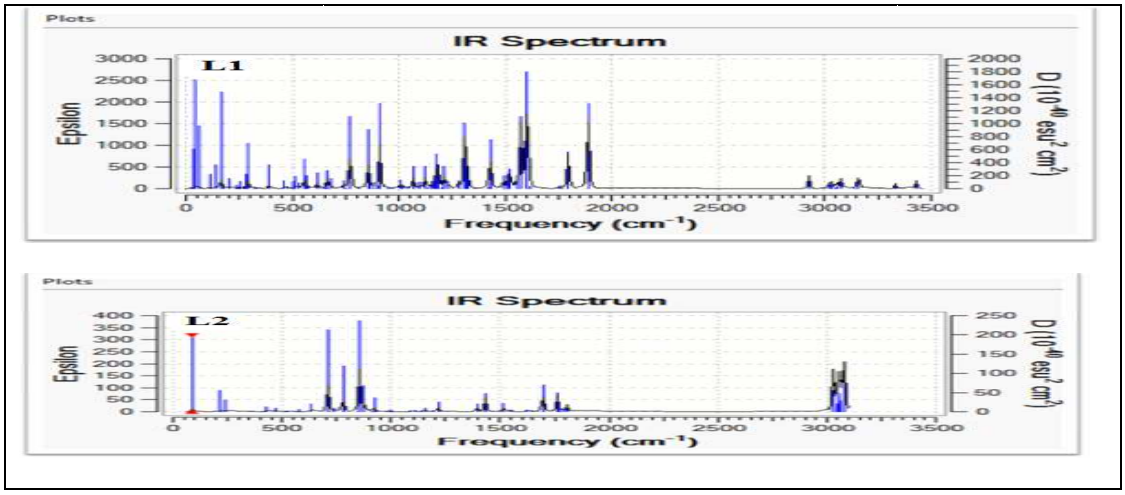


Figure 3: IR Spectrum of L_1 and L_2 using Gaussian Program

Table 4: Compression of Experimental and Theoretical Electronic Transition for Ligands From ZINDO/S Calculation and Experiment Method using Hyper Chem-8 and Gaussian Program

Symbol	*Transition*	*Experimental*	*Hyp.*	*Gauss.*	
			(ZINDO/S)	*CIS*	*ZINDO*
L_1	n→ π* π→π* π→π*	353 312 266	333.16 272.97 226.00	$(311.59)_{max}$	$(360.07)_{max}$
L_2	n→π* n→π* π →π*	324 263 228	278.32 234.55 210.32	$(235.54)_{max}$	$(309.54)_{max}$

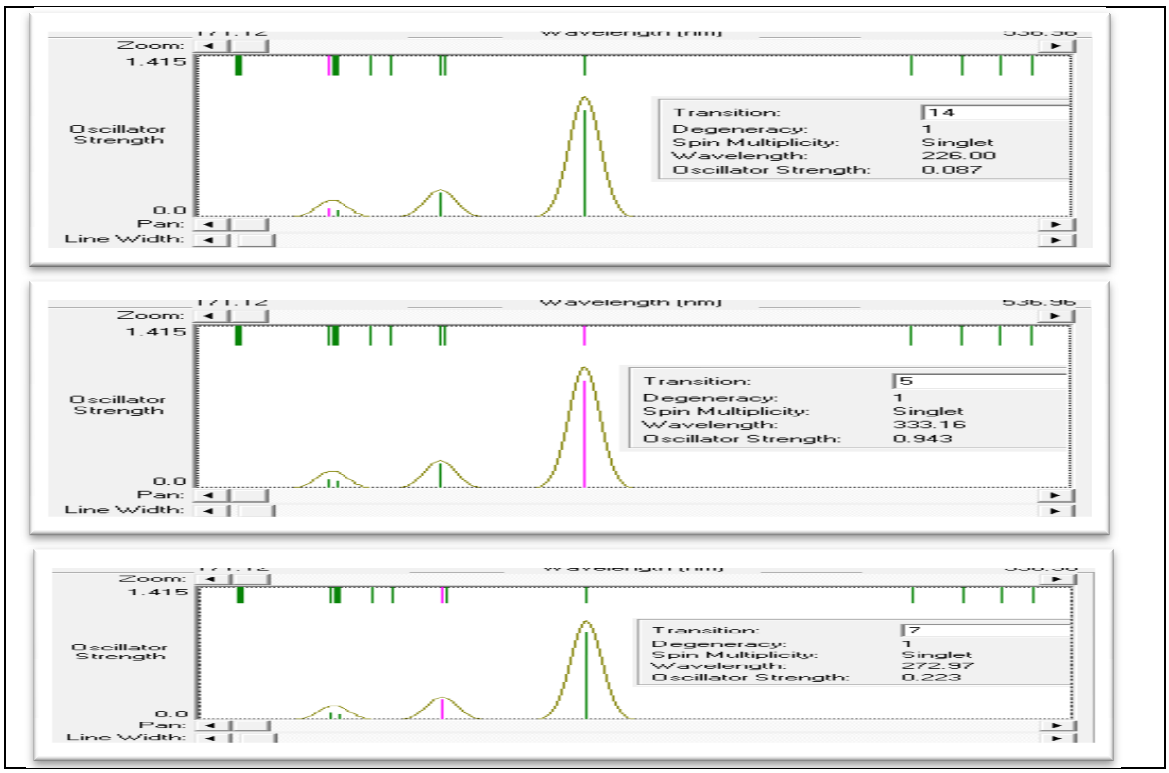


Figure 4: Electronic Spectrum of L_1 using ZINDO/S Method by Hyper CHEM.-8 Program

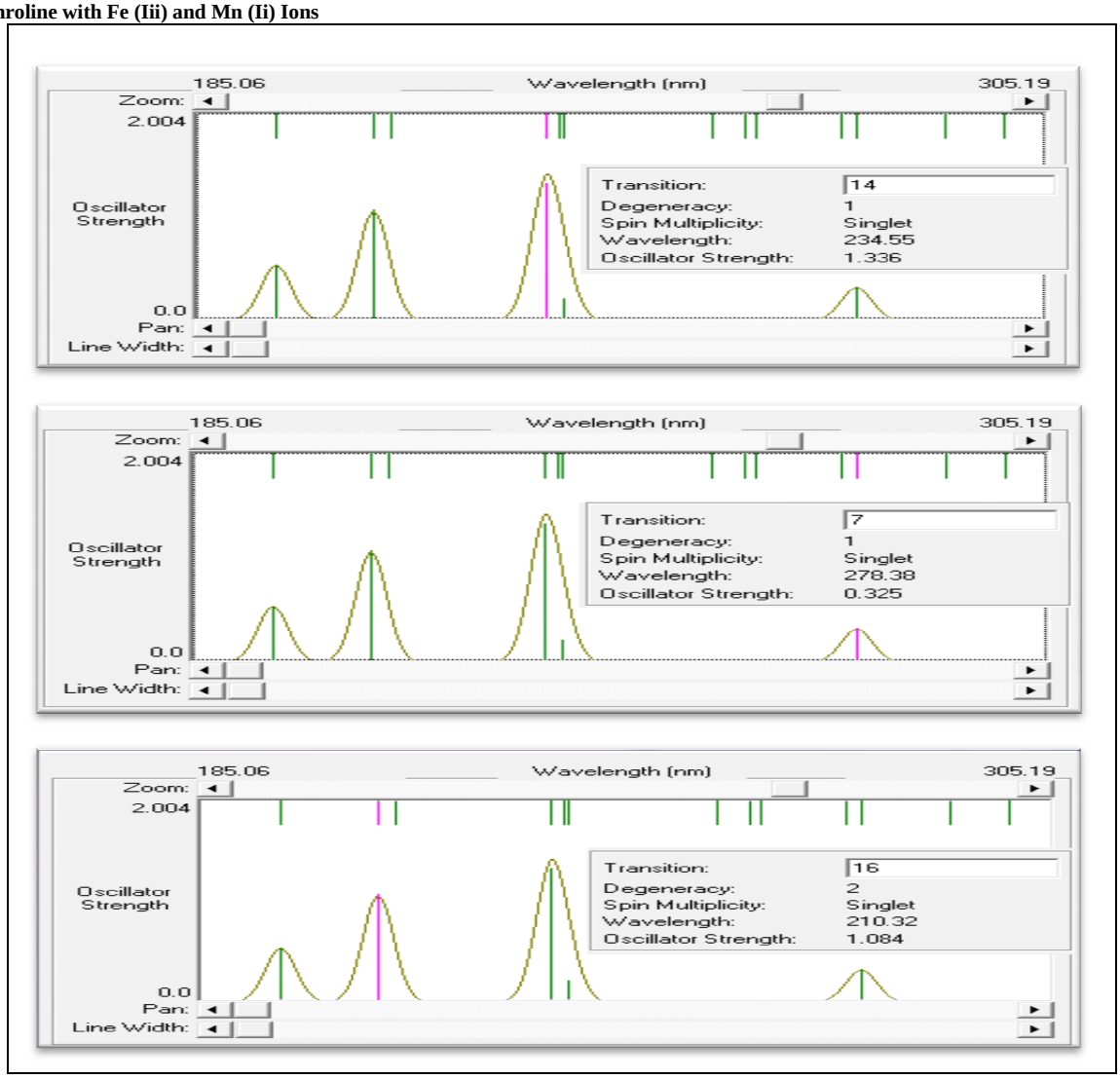


Figure 5: Electronic Spectrum of L_2 using ZINDO/S Method by Hyper Chem.-8. Program

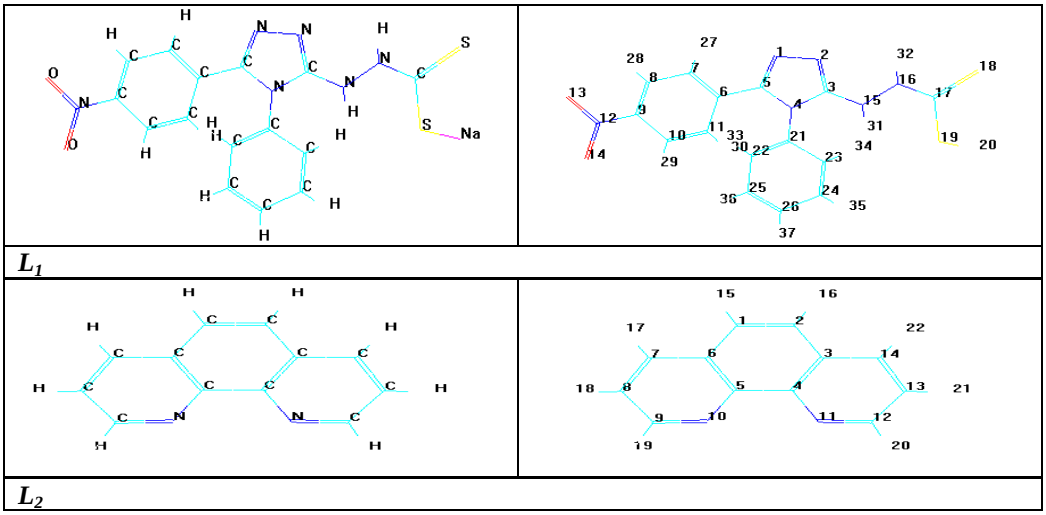


Figure 6: Serial Number of L_1 and L_2 using Hyper Chem.-8 Program

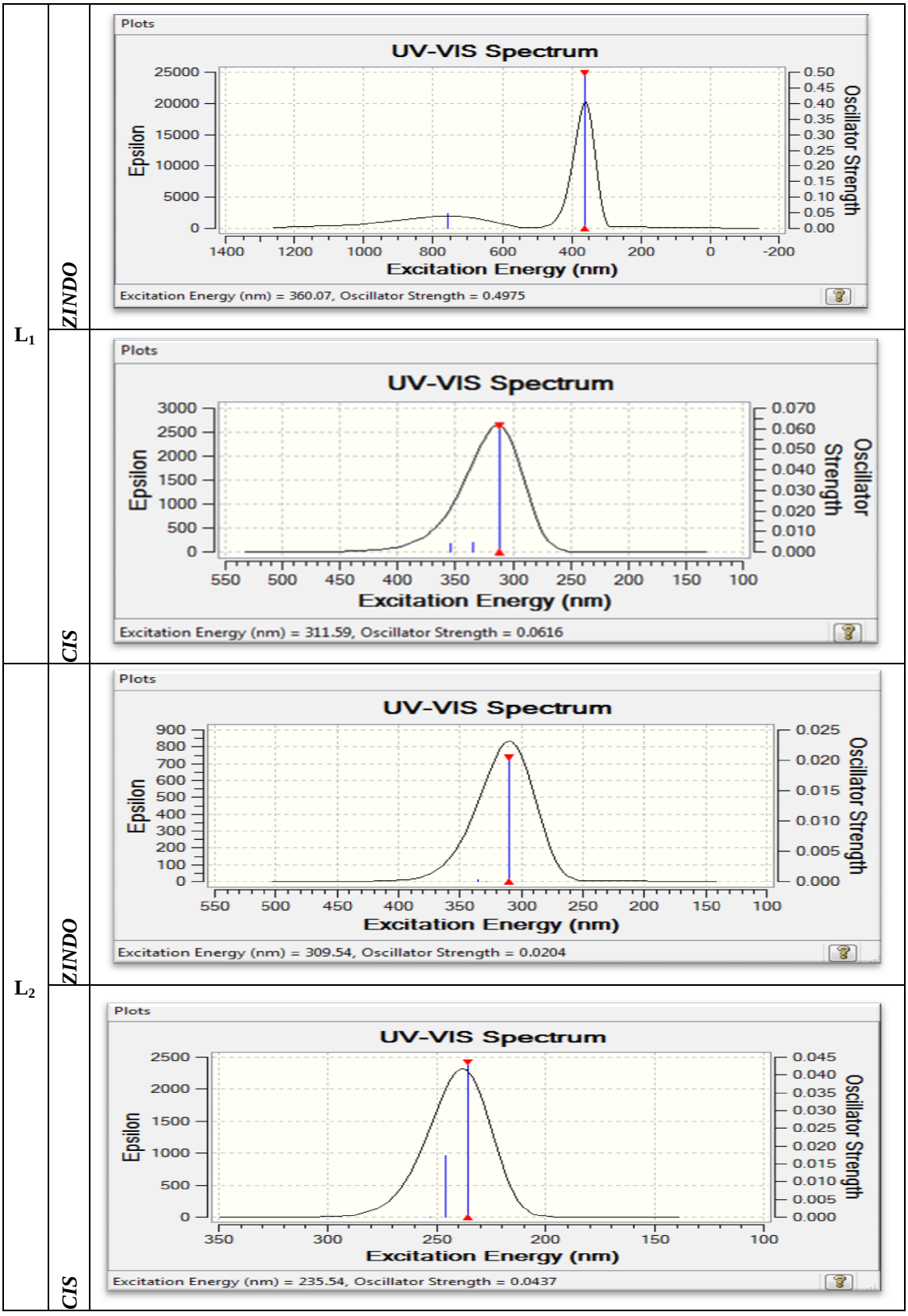


Figure 7: Electronic Spectrum of L_1 and L_2 using ZINDO and CIS Method by Gaussian Program

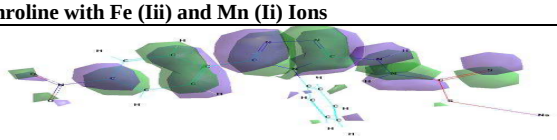
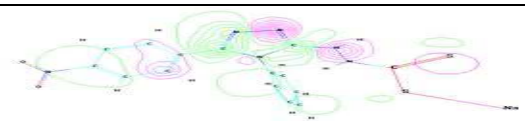
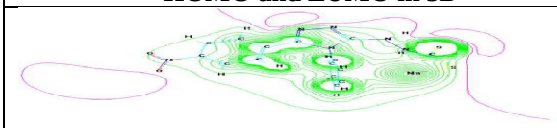
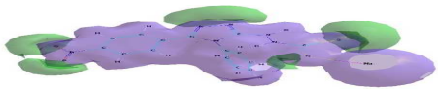
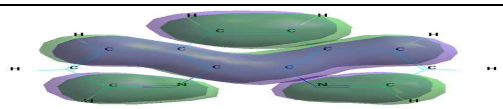
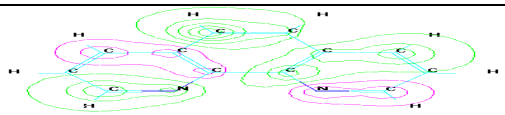
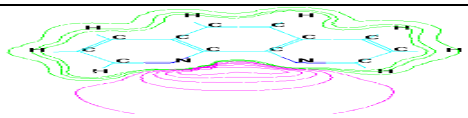
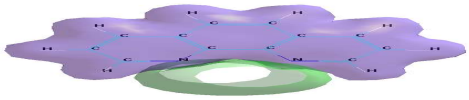
 L_1	 L_1
HOMO and LUMO in 3D	**HOMO and LUMO in 2D**
 L_1	 L_1
E.P in 2D	**E.P in 3D**
 L_2	 L_2
HOMO and LUMO in 3D	**HOMO and LUMO in 2D**
 L_2	 L_2
E.P in 2D	**E.P in 3D**

Figure 8: HOMO, LUMO & Electrostatic Potential as 2&3D Counters for L_1 and L_2 using Hyper Chem.-8 Program

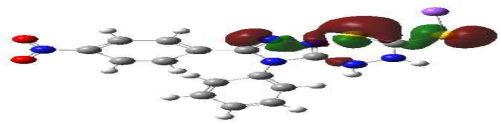
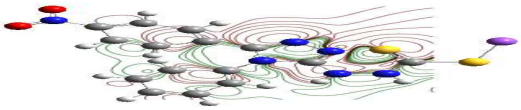
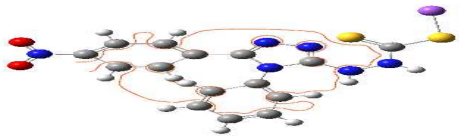
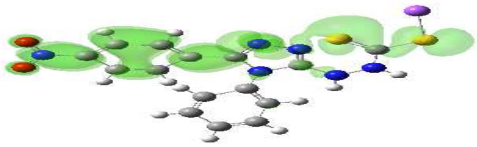
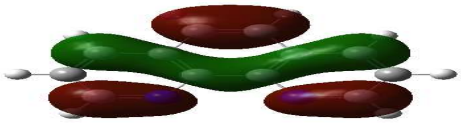
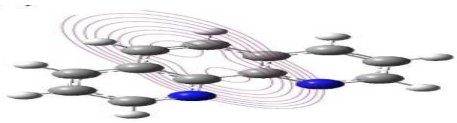
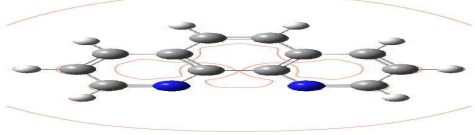
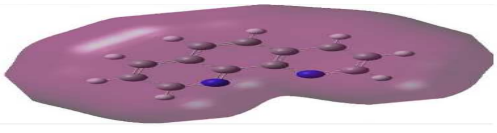
 L_1	 L_1
HOMO and LUMO in 3D	**HOMO and LUMO in 2D**
 L_1	 L_1
E.P in 2D	**E.P in 3D**
 L_2	 L_2
HOMO and LUMO in 3D	**HOMO and LUMO in 2D**
 L_2	 L_2
E.P in 2D	**E.P in 3D**

Figure 9: HOMO, LUMO & Electrostatic Potential as 2&3D Counters for L_1 and L_2 using Gaussian Program

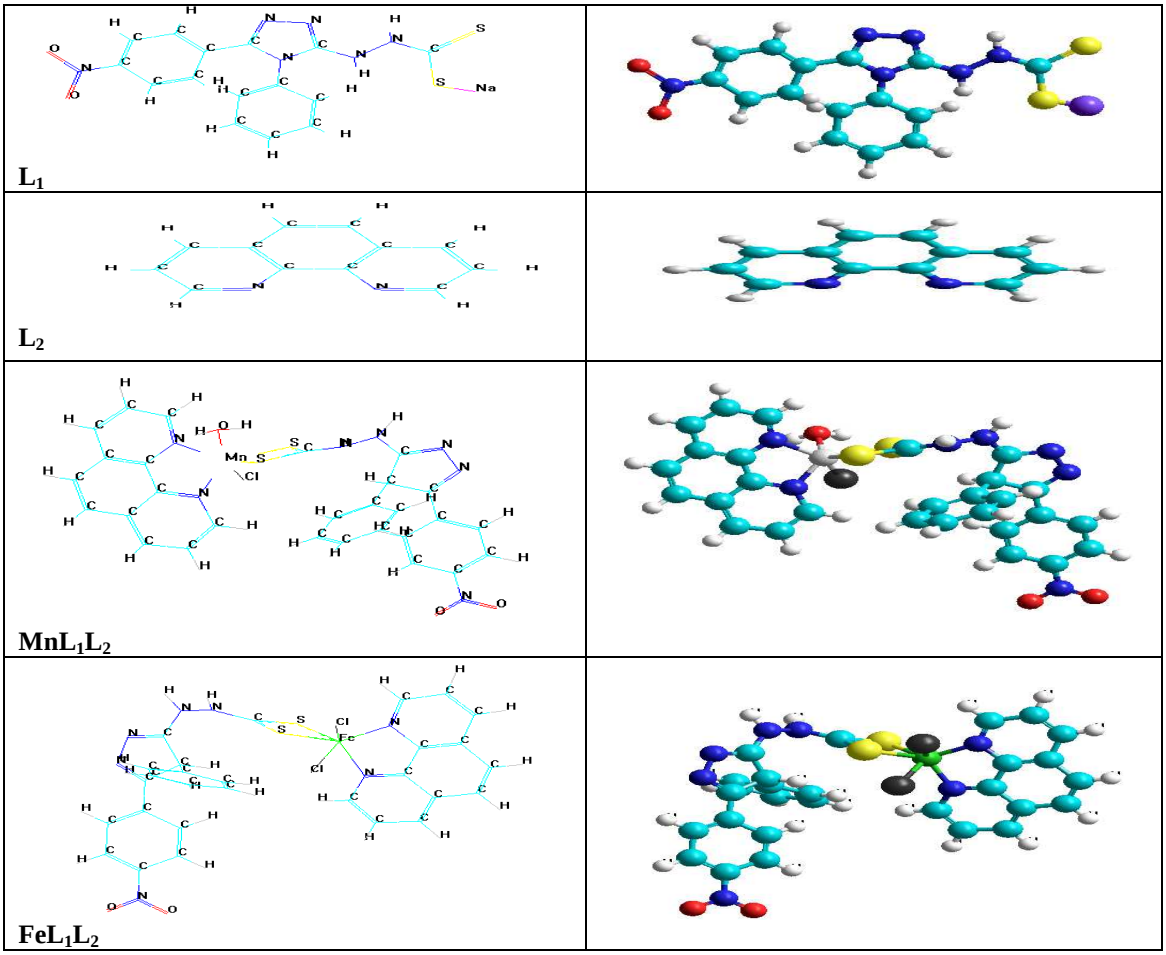


Figure 10: Conformation Structure of L_1, L_2 and Their Metal Complexes Using Hyper Chem.-8 Program

CONCLUSIONS

The results obtained from the compounds that isolated in the solid state were compared with the results obtained from the gas phase study by using Hyper Chem-8 and Gaussian programs which exhibited approximately results between these states.

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