Sys Rev Pharm 2020;11(12):747-753
A multifaceted review journal in the field of pharmacy

Synthesis and Characterization of Some Metal Complexes with New Ligand($C_{15}H_{10}N_4O_7SCl$) & Theoretical Treatment

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ABSTRACT

The current work deals with the VO(II), Cr (III) , Mn(II) complexes which have been made by a new ligand , To classify the three complexes, infrared spectroscopy was used. FTIR, UV SPectroscopy and AtomiC AbSorption Spectrometry were also used to detect the ratio of carbon, hydrogen and nitrogen synthesized and precise materials. There was also a study of the physical properties like Temperature, Color, Electrlcal Conductivity, and Magnetic characteristics. The ligand preparation was 2: 1, besides, all the synthesized complexes were 8 slanted façades. A theoretic treatment for structural of the (L) and its complexes in gas phase was conducted by using Hyper Chem. 8 program. PM3 Method used calculating the electrostatic potential (EP) and Molecular Orbital Surfaces of the (L). The Heatof Formation (ΔHf), Binding Energy (ΔEb), Total energy (ΔET), Vibration Spectra, and Electronic Spectra for the Ligand (L) and its metal complexes were calculated by PM3 and ZINDO/1 methods .

Keywords: metal complexes; new ligand; theoretical studies

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INTRODUCTION

Amide Bond Formation is a well-known transformation in Organic and Medicinal Chemistry.1 An smart procedure is the synthesis beginning from esters, for their stability and abundance in nature.2 A three-step arrangement of hydrolysis, initiation and handling with an amine is typically required to get the matching amide. Direct transformation has been used extensively in an effort to avoid the three-step technique,.

The biological activity of compounds essentially relies on their molecular construction. Heterocyclic moieties may be found in a great amount of compounds which show great deal of biological activities. Thiadiazole is a multipurpose moiety that displays a varied diversity of activity because of the existence of N=C-S moiety in the ring. These come to be an essential section of Heterocycles of unlimited concentration of researches for their expansive sorts of biological activity. Several drugs that contain 1,3,4-Thiadiazole Nucleus similar to Acetazolamide(1), Butazolamide(2) Sulfamethazole(3) are accessible in marketplace. Furthermore extra analogues were employed as dye, pesticides, lubricants and conducting polymers(1).

Metal Bound Organic Compounds are known to have possible activities in the zones of microbial, biological, insecticidal, clinical, catalytic, analytical, antibiotic, tumor inhibitor, cell division, growth factors, food additive, etc. That is because of whichever the unexploited coordination sites existing on ligand systems ,the metal and, or by reason of the selective Oxidation state of the complexed metal ions present within the coordination sphere [1]. Generally, the value of metal chelates in many divisions of Theoretical and Applied Chemistry is now commonly known.

Row transition metal elements have significant part in the life of humans [2] and chemists are concerned with th3 co-ordination compounds for the usage in synthetic and industrial and practices, like chemical, Biological,

Environmental, Ion Exchange Catalysis, Photochemistry, and Biological Applications .Likewise their spectral, microscopic ,thermal, spectral, microscopic and many further features have also been inspected [3-10]. Metal Carboxylates Constitute are main division of compounds and in receipt of boundless attention as a result of their inclusive range of applications in the aspects of biomedicine along with catalysis during the latest years[11].

Experimental

Whole of both the solvents and the chemicals and which were used for the synthesis were achieved from Fluka Company but the $VOSO_4.H_2O$, $Cr(NO_3)_3.9H_2O$ and $Mn(NO_3)_2.4H_2O$ Salts were from BDH. The melting point apparatus of Gallencamp MF.B-600.01 was used. Shimadzu Uv-Vis 1600 A Ultraviolet Spectrophotometer in the range (190-1100) nm has finished the Ultraviolet The ligand 's visible spectrum with its metal complexes. The Molar Conductivity was used by the Coring Conductivity Meter 220 to measure the conductivity of fully complexes at room temperature in a newly prepared 1 * 10^{-3} M in absolute ethanol. On the Euro EA 3000 Elemental Analyzer, elemental analysis methods were transcribed. Using the Perkin Elmer 5000 atomic absorption spectrophotometer, measuring the m of the complex content of the complexes. With the KBr disk using FTIR spectrophotometer shimadzu model 8400 in the range (4000-400) cm-1, IR Spectra for the Ligand and its Metal Complexes were recognized. Measurement of magnetic susceptibility has been defined using the Johuson matting Catalytic Device division 's magnetic vulnerability balance at Room Temperature.

The Ligand (L) Synthesis :-

Using a round bottom flask melt (2gm) of aques sodioum acetat in (25 ml) acetic anhydride and then add (2gm) from acids N (-benzothiazole-2-yel compensator (3-nitrophthalmic) and ascending Mixture on a two-hour water bathwith stirring,Cool the mixture after the escalation is complete and pour over (100 ml) of Cold distilled water with stirring until amides is filtered, The precipitate was washed several times with cold water and after the precipitate has dried .It was re-crystallized using ethanol.

Preparation of Complexes:-

A common technique was employed for preparing new Metal complexes through reacting 1 mmole of metal salts of Co, Ni, and Cu which melted in 12 ml of Ethanol, then blended with 2 mmole of the prepared Ligand in the identical solvent. Reaction blend was then a subject of reflexing for three hrs. at R. temp. The precipitates was then filtered and washed with Ethanol and dried at 55 C° by an oven for 1:30 hr. The analytical and some characteristics are recorded in Table **(1).**

RESULTS AND DISCUSSION

The simple analysis shows (1:2) stoichiometry in Table (1) for all prepared complexes, certain physical properties, complex analytical results, and the proposed chemical formula.

They agree well with proposed formula $ML_2(X_2)$ Y. nH_2O, where M = VO^{II}, Cr^{III}, Mn^{II}, X= H_2O , $2H_2O$, $2NO_3$, Y= SO_4 , $3NO_3$, 0.0 , n= 1/2 H_2O, 1/2 H_2O, $3H_2O$. The complexes were insoluble in Organic solvents, but Soluble in DMF & DMSO.

Comp.	Color	μ scm^{-1}	Melting point (°C)	Elemental analysis found%, Calc.						Chemical Formula
				Yield %	C	H	N	S	M	
L	Off white	----	203-205	83%	42.35 (42.01)	3.04 (3.22)	19.78 (19.92)	10.32 (10.55)	--	$C_{15}H_{10}N_4O_7SCl$
VO L	Olive Green	110	219	76%	36.00 (36.69)	2.01 (2.24)	10.99 (11.41)	9.21 (9.78)	7.66 (8.80)	V $C_{30}H_{22}N_8O_{21}S_3Cl_2$
Cr L	Green	187	311	71%	33.92 (34.12)	1.94 (2.08)	15.00 (14.54)	5.89 (6.06)	8.96 (8.10)	Cr $C_{30}H_{22}N_{11}O_{24}S_2Cl_2$
Mn L	Light	55	195	79%	34.05	2.22	12.86	5.97	9.88	Mn $C_{30}H_{26}N_{10}O_{23}S_2Cl_2$

	Pink				**(34.98)**	**(2.52)**	**(13.60)**	**(6.21**	**(9.98)**	

Table 1 : Elemental micro-analysis and some of the physical properties of the complex.

The FTIR spectra of ligand [L] and its metal complexes:-

IR spectrum of this Ligand is very complex because of the big number of group which was overlying regions, yet few bands were designated in order to detect the special effects of complexion.

The Spectra of free ligand, shows four bands at 1681, 1647, 1492 and 1276 cm^{-1}, which corresponding to the amid (I) and C= N, amid (II) & (III) respectively. In the spectra complexes of the amide (I) and (C = N) bands, changes to lower frequencies (~ 47,39 & 77) cm-1 cm are seen. This adjustment stated that the uncharged amide Oxygen[12] and the C = N group were part of the coordination. More confirmation of the formation of complexes, the unveiling of new weak bands, in the Regions (551, 555) and (474, 483) cm-1, which were assigned to the υ(M-N) and the υ(M-O).All of the complexes showed a broad band in the area (3402) cm^{-1} which corresponding the presence of lattice out of coordination sphere, for the manganese complex, and abroad band at (3456,3414cm^{-1}) which supports to coordinated water,. Beside that there is two absorption bands in the (914,922) and (9871,880cm^{-1}) for rocking and wagging frequencies respectively for bending coordinated water[12], which appear in chromium and vanadium complexes. The bands of ionic sulphate, the mode of nitrate coordination and other band shown in Table (2).

Table 2 : The Ligand and Its Metal Complexes' Diagnostic Vibration Bands (cm-1)

Comp.	υ(NH)	Amid I	υ(C=N)	Amid II	Amid III	υ (M-N)	υ(M-O)	υ(H_2O) ρ,w/H_2O	Others
L	**3230**	**1681**	**1647**	**1492**	**1276**	**----**	**---**	**---**	**υ(C-Cl)= 10 υ(C-NO_2)=1351,1535 υ(C-S)= 621**
VO L	**3297**	**1577**	**1600**	**1485**	**1262**	**551**	**474**	**3456 914,871**	**υSO_4=1345,1130,1083 V=O = 972 υ(C-Cl)= 1090 υ(C-NO_2)=1350,1525 υ(C-S)= 616**
Cr L	**3265**	**1581**	**1608**	**1480**	**1258**	**532**	**470**	**3440-3414 922,880**	**υ(C-Cl)= 1095 υ(C-NO_2)=1350,1535 υ(C-S)= 616 υ(NO_3)= 1384,1330, 1300 ,1072**
Mn L	**3282**	**1575**	**1597**	**1477**	**1248**	**555**	**483**	**3402**	**υ(C-Cl)= 1091 υ(C-NO_2)=1352,1535 υ(C-S)= 616 υ(NO_3)=1350,1110, 1012**

Electronic Spectra of Ligand [L] and Complexes:-

Two absorption bands ,shows medium and weak shape which corresponding to π-π* transition at 268 nm due to aromatic system ,and n-π* transition at 369 nm for oxygen atom of carbonyl groups in addition to other donors (nitrogen atom in the C=N, N=N, [13].

VO L:- The Electronic Spectrum of this olive green complex display a single absorption Band in the area 16949 cm^{-1} which refer to an octahedral system [14]. Others two prominent (d-d) absorption bands at (12422 and 23809 cm^{-1}) that correspond to ($^2B_2 \rightarrow {}^2E$) and

$^2B_2 \rightarrow {}^2A_1$transitions respectively

These three bands are assigned to ligand field transitions :dxy → (dxz, dyz),

dxy → (dx^2-y^2 and dxy-dz^2) respectively [15,16].

These transitions align with the suggested V/(IV) complex geometry of Oh. The calculation of conductivity for this complex in DMF solvent at room temperature is a proof that it is ionic table (1) and that the complex's magnetic moment is equal to (1.81B.M) in expectation.Cr L:- The electronic spectrum of green complex shows three absorption bands in the region 16694, 24691 and 36100 cm-1 which attributed to $^4A_2g \rightarrow {}^4T_2g$, $^4A_2g \rightarrow {}^4T_1g$,

$^4A_2g \rightarrow {}^4T_1g(p)$ transitions respectively . This indication with published data for octahedral geometry [17]. The value of the racah parameter B^- where calculated from this equation $15B^- = \upsilon 3 + \upsilon 2 - 3\upsilon 1$, which equal to 715 cm^{-1} and nephelauxetic factor β which equal to 0.78 after taking β^o of free ion to be 918 cm^{-1}.

The magnetic behavior of Oh of Cr(II) is independent of the field strength of the ligand [18], so the Magnetic moment for this complex was 3.79 BM. This value is in agree with that reported for Oh geometry [5]. From conductivity measurement in DMF solvent show this complex is non-electrolyte, and this is further evidence can be made for geometry of this proposed complex .

Mn L:- Mn(II) complex showed three bands which results at the region 10989,20833 and 26315 cm^{-1} which refer to to $^6A_1g \quad {}^4T_1g_{(G)}$, $^6A_1g \quad {}^4T_2g_{(G)}$, and $^6A_1g \quad {}^4A_2g + {}^4Eg_{(G)}$.

The values of the Racah parameter B^- equal to 800 cm^{-1} and nephelauxetic factor β 0.93 are high, this is in keeping with general opinion that manganese (II) complex was high ionic [19,20]. The electronic spectrum coupled with magnetic 4.88 BM and conductivity measurement showed that the complex was nonionic indicate the proposed Oh geometry around Mn (II).

Table 3: Ligand [L] and Complexes' Electronic Spectra

Compounds	Absorption Bands (cm^{-1})	Assigned transitions	B^-	B^o	B	B.M
L	**37313** **27100**	**π-π*** **n-π***	---	----	----	----
VO L	**12422** **16393** **23809**	$^2B_2 \rightarrow {}^2E$ $^2B_2 \rightarrow {}^2B_1$ $^2B_2 \rightarrow {}^2A_1$	**----**	**----**	**----**	**1.81**
Cr L	**16694** **24691** **36100**	$^4A_2g \rightarrow {}^4T_2g$, $^4A_2g \rightarrow {}^4T_1g$, $^4A_2g \rightarrow {}^4T_1g(p)$	**715**	**918**	**0.78**	**3.79**
Mn L	**10989** **18652** **26315**	$^6A_1g \rightarrow {}^4T_1g_{(G)}$, $^6A_1g \rightarrow {}^4T_2g_{(G)}$ $^6A_1g \rightarrow {}^4A_2g + {}^4Eg_{(G)}$.	**800**	**860**	**0.93**	**4.88**

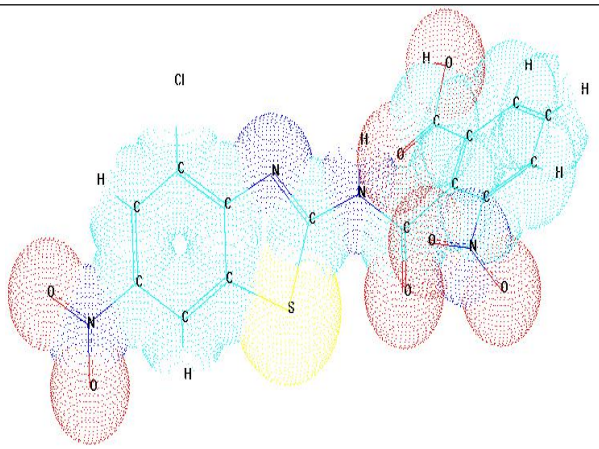
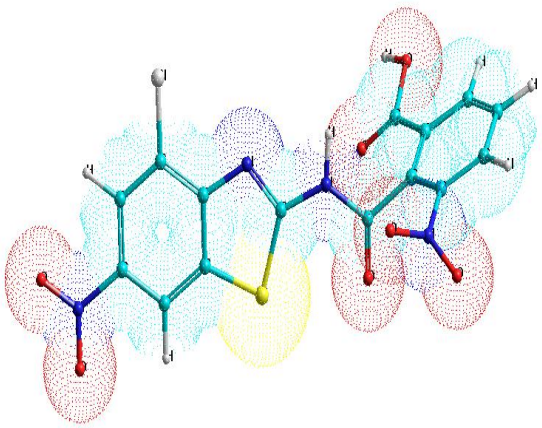
Theoretical Treatment:

I) geometries and energies for Ligand and complexes: As seen in Figure (1), hyperChem-8 is used for semi analytical measurements of optimized-geometries and energies for Ligand and its metal complexes. The findings of the PM3 and ZINDO/1 methods performed for these compounds in the gas phase at 0 ° K for approximate formation heat (ΔHf), binding energy (ΔEb) and total energy (ΔET) as tabulated in Table (4).

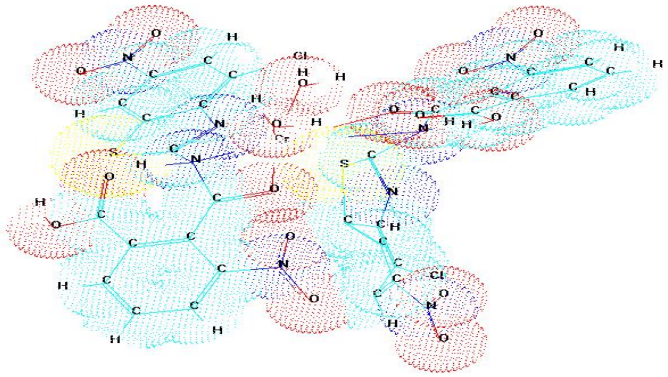
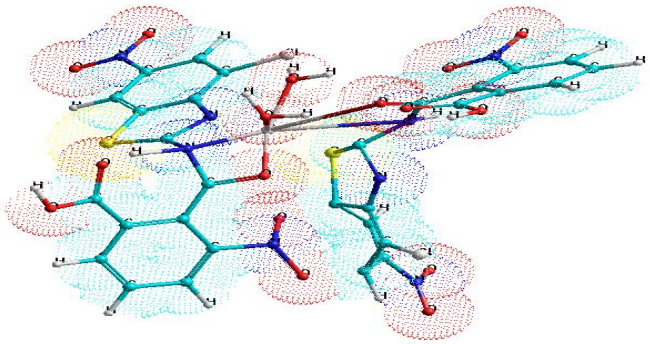
Table (4) : For The Ligand and its Metal Complexes, Conformation Energetic (KJ.mol-1)

Compounds	PM3			ZINDO/1		
	ΔHf	ΔEb	ΔET	ΔHf	ΔEb	ΔET
L	-220.30	-16516.86	-491016.79	---	----	----
VOL	-68784.57	-102827.26	-1630531.22	---	----	----
CrL	---	---	---	-3927.12	-103201.86	-1643525.23

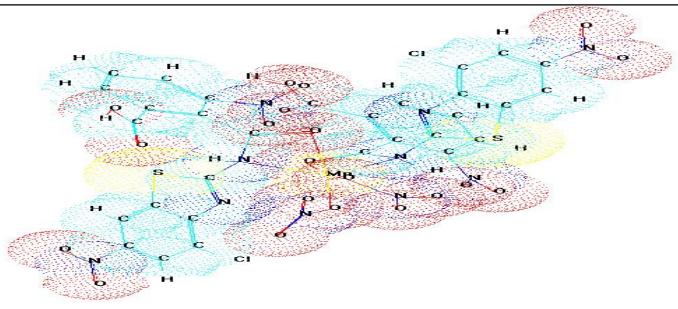
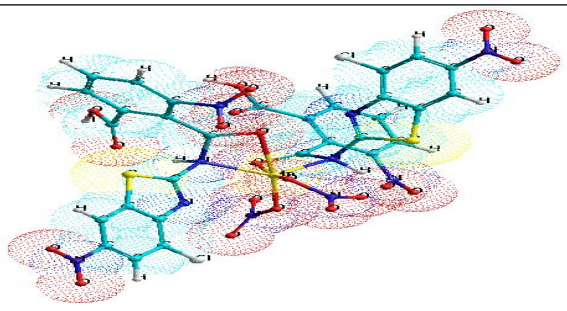
MnL	----	---	----	-74506.70	-109825.65	-18887681.58

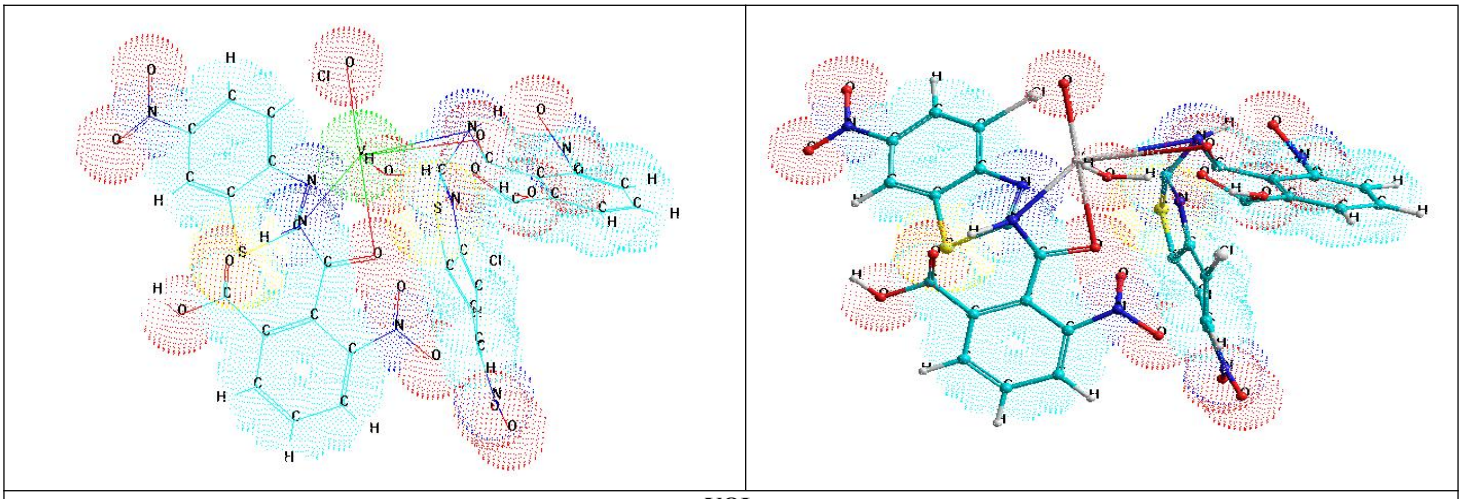
L

CrL

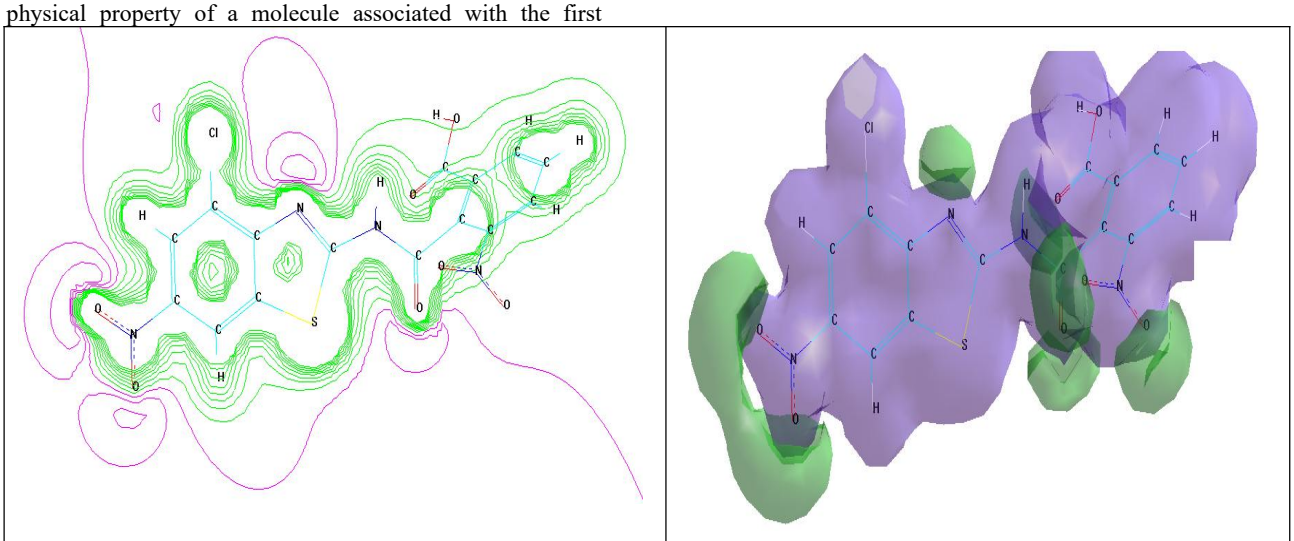
MnL



VOL

Figure (1) : Ligand and its metal complexes' conformation arrangement using HyperChem-88

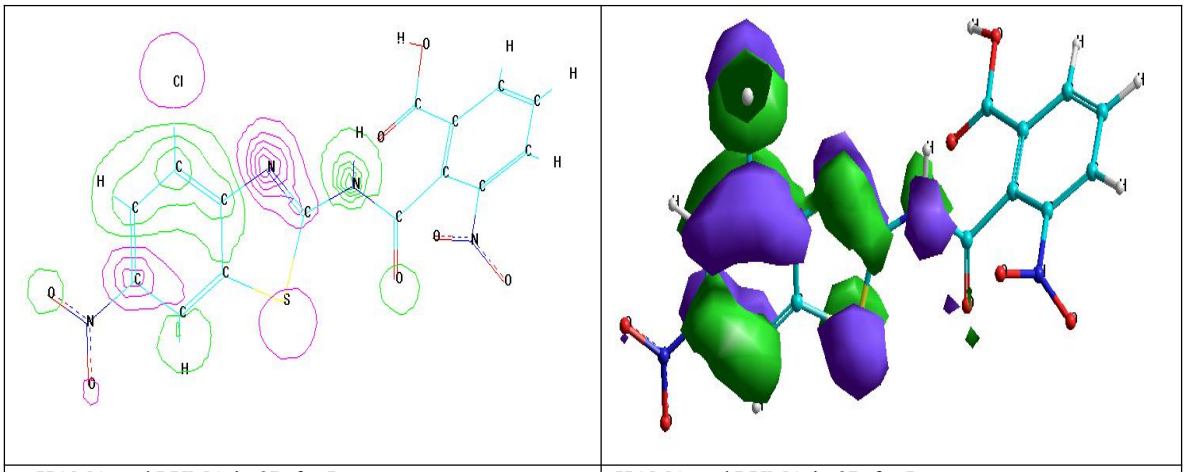
II) Electrostatic Potential: The Electric Charge Division produces energy that is possible in surrounding space. A positive electricity potential provides the expectation that a positive charge would be deterred in the space area in question. A negative electrical potential means that there would be a positive charge involved. A molecule is an electrical potential group of charges-usually referred to as the "electrostatic potential." The Electrostatic Potential is a physical property of a molecule associated with the first (seen) or (felt) alternate species of a molecule. Electrophilic attack is met with a proportion of a molecule with a negative electrostatic potential-the more negative, the greater. The use of electrostatic potential to predict nucleophilic attack[21] is not as straightforward. In order to analyze the reactive sites of the Ligand as in figure (2), the electrostatic potential of the free Ligand is determined and designed as a 2D and 3D curve.



Electrostatic Potential in 2D	Electrostatic Potential in 3D

Figure (2) : Electrostatic Potential as 2D and 3D counters for L

III) **Molecular Orbital Surfaces:** calculation results clarify that the LUMO of Transition Metal ion selects to have a reaction with the HOMO of donor atoms in ligand[22-26] as revealed in Figure (3) by means of adopting Hyperchem.-8.07 program.



HOMO and LUMO in 3D for L	HOMO and LUMO in 2D for L

Figure (3) HOMO and LUMO Sites for the L.

IV) Optimized Vibrational Spectra for ligand (L) and its metal complexes: The theoretical vibrational spectra of the free ligand (L) and its metal complexes were calculated by semi-empirical (PM3) and (ZINDO/I) techniques. The results frequencies agreed well with those values which obtained from experimentally as illustrated in Table (5).

Table 5. A Comparison of Experimental and Theoretical vibrational frequencies data for the Ligand and their Metal complexes (cm^{-1})

Comp.	υ(NH)	Amid I	υ(C=N)	Amid II	Amid III	υ (M-N)	υ(M-O)	υ(H_2O)
L	3230* 3345** 3.437***	1681* 1745** 3.667***	1647* 1608** -2.425***	1492* 1505** 0.863***	1276* 1261** -1.189***	----	---	---
VO L	3297* 3273** -0.733***	1577* 1548** -1.873***	1600* 1591** -0.565***	1485* 1486** 0.067***	1262* 1279** 1.329***	551* 542** -1.660***	474* 469** -1.066***	3456* 3273** -5.591***
Cr L	3265* 3262** -0.092***	1581* 1585** 0.252***	1608* 1677** 4.114***	1480* 1465** -1.023***	1258* 1240** -1.451***	532* 524** -1.526***	470* 445** -5.617***	3440* 3429** -0.320**
Mn L	3282* 3557** 7.73***	1575* 1548** -1.74***	1597* 1592** -0.314***	1477* 1465** -0.819***	1248* 1230** -1.463***	555* 568** 2.288***	483* 486** 0.617***	----

*experimental frequencies

**theoretical frequencies

***error

V) theoretical UV/Vis spectrum of ligand : The theoretical UV/Vis spectrum of Ligand was calculated by PM3 method and comparing with the approximately experimental . The results were compatible between the theoretical and experimental spectra data , Table (6)

Table (6). Compression of Experimental and Theoretical Electronic Transition of Ligand using PM3 method

Transition	Experimental Absorption bands (cm^{-1})	Theoretical (PM3) Absorption bands (cm^{-1})
π-π*	**37313**	**38910**
n-π*	**27100**	**30505**

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