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Synthesis, Characterization And Computational Studies Of Mannich Base Ligands And Their Metal Complexes Vo(II),Co(II),Ni(II) AndCu(II).

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ABSTRACT

Mannich base derivatives of Benzimidazole were prepared through the condensation reaction of benzimidazole derivative with formaldehyde and pyrazine amide and morpholine moieties respectively. Also Vindyl(II) ,Chromium(III), cobalt(II), nickel(II) and copper(II) complexes of these ligands have been synthesized. All the compounds were fully characterized by, elemental analyses, Uv-Vis ,FT-IR, mass spectra, ,magnetic moment determination and molar conductivity measurements. The nature of complexes in liquid state was studied using molar ratio method and give results similar approximately to those obtained from solid state; also, stability constant of the prepared complexes were studied and found that molar ratio 1:2 is more stable than the other complexes. Experimental results showed that metal complexes act as bi-dentate ligands towards divalent metal ions via CH_2-N ,S and N of morpholine .In this work, the heat of formation (ΔH°_{f}), binding energy (ΔE_{b}) and dipole moment (μ) for free ligands and their metal complexes studies . A comparison was made between spectra in theoretical and experimental results of FT-IR ,Uv-Vis spectra .HOMO and LUMO were also calculated in 2D and 3D. All these theoretical results have been calculated using two programs Hyper chem.-8 and Gussian 09 .

Keywords: Mannich bases, Benzamidazole derived, solution study, Computational study

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INTRODUCTION

Mannich reaction is a nucleophilic addition reaction which involves the condensation of a compound with active hydrogen with an amine (primary or secondary) and formaldehyde(any aldehyde)[1]. Mannich reaction is one of the most significant C-C bond forming reaction and has been used as a classical method for the preparation of Beta amino ketones and aldehydes which are called'Mannich Bases'[1,2]. Mannich bases are synthetic building blocks, which can easily be converted into a range of useful and valuable derivatives[2]. Pyrazine amide itself evinces unique physicochemical and chemical properties and its small molecule is exceedingly suitable for modifications. Alkylamino substitution of the pyrazine ring in positions 5- and 6- is quite well known and often results in good antimycobacterial activities[3]. A number of morpholine derivatives have been shown to possess strong bactericidal properties [4]. Benzimidazoles are very useful intermediates for the development of Molecules of biological interest. Substituted benzimidazole derivatives have found applications in antifungals, anticancers and antiulcers etc[5,6]. From the survey of existing literature, it appears that metal complexes of mannich bases played a vital role in the development of coordination chemistry and their analytical utility in the determination of both transition and non transition metal ions is well established[7,8].

EXPERIMENTAL

Instruments

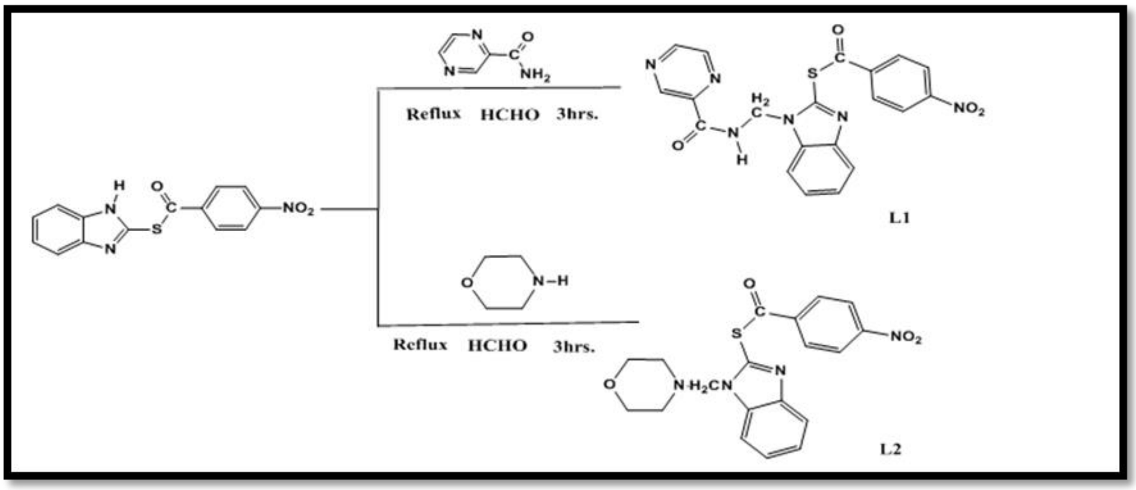
All chemical and reagents are of an analytical grade and used as supplied without any further purification BDH, Sigma-Aldrich ,and Fluka. elemental data were measured by EuroEA 3000 elemental analyzer. Metal contents were carried out by using shimadzu atomic absorption 680 Flam spectrophotometer. Conductance data were obtained in 10^{-3}M in DMF solution of the complexes using WTW conduct meter at 25°C. IR spectra were recorded using Shimadzu and Perkin Elmer FT-IR spectrophotometer using CsI pellets. Absorbance in Uv-Visible region was recorded in ethanol solution using Uv-Vis.1800 PC Shimadzu Spectrophotometer.. The mass spectra Mass spectra of the all ligands were measured by 5975VL MSD with tripe-Axis Detector , ion source (Electron impact 70eV).The room temperature magnetic susceptibility measurements of the complexes were made by using Balance of Johnson Mattey catalytic system division. Melting point apparatus of Gallenkamp M.F.B-60 was used to measure the melting points of all prepared compounds

Preparation of starting material as 2-mercaptobenzimidazole and 2-(p- nitrobenzoyl) thiobenzimidazole

These starting compounds was prepared according to the literature [9,10]

Synthesis of S- (1-((pyrazine-2-carboxamido)methyl)- 1-H-benzoimidaz- ole-2-yl)4- nitrobenzothioate(L_1) and S-(1-Morpholinomethyl)-1-benzoimidazol-2- yl)4-nitrobenzothio- ate (L_2)[11]

The organic compounds were synthesized by Mannich condensation reaction between 2-(p-Nitrobenzoyl) Thiobenzimidazole (0.01 mol) and (0.01mol), pyrazinamide, morpholine sequentially. The mixture dissolved in methanol (30 ml) in a beaker under ice-cold condition and with constant stirring. In the same solution, formaldehyde (0.01 mol) was added gradually and heated to reflux for (3 hrs) , then kept overnight in the freezer. Pale yellow and off white solid masses was obtained and it was washed then recrystallized from ethanol, the yield and melting point for these compounds obtained in 63& 66% , 104-106°C and 180-182°C respectively, and summarized in **Scheme** (1).



Scheme (1): Main steps of preparation the Mannich bases ligands L_1,and L_2.

Synthesis of the Complexes

The Mannich bases reaction occurs in ethanol with metal ion salts , $VOSO_4.H_2O$, ,$Co(NO_3)_3.6H_2O$,$Ni(NO_3)_2.6H_2O$ and $Cu(NO_3)_2.3H_2O$ 1:1 and 1:2 molar ratio for all ligands respectively. The mixture was then refluxed for (3 hrs.); the color solid complexes were formed after evaporation the liquid, and then filtered, washed with ethanol and dried in desiccators Some physical properties can be display in **Table**(1).

Table (1): Some analytical and physical data of ligands (L_1, L_2) and their metal complexes.

Compounds	*m.p^{0}C*	*Color*	*Yield%*	*Elemental analysis Found (Calc.)*				*Metal% Found (Calc.)*
				C	*H*	*N*	*S*	
$C_{20}H_{14}N_6O_4S(L_1)$ 434.43 *g.mol^{-1}*	**104-106**	**Yellow**	**63**	**55.24 (54.93)**	**3.22 (4.17)**	**19.33 18.45)(**	**7.36 (7.61)**	**-----**
$[VOLSO_4]$. H_2O.0.5 C_2H_5OH 638.33 *g.mol^{-1}*	**158-160**	**Olive**	**81**	**39.47 39.97)(**	**2.97 (3.78)**	**13.15 (12.99)**	**10.02 (10.76)**	**7.97 7.45)(**
$[Co\ L(ONO_2)_2(H_2O)_2].H_2O$ 671.33 *g.mol^{-1}*	**64-66**	**Light brown**	**68**	**35.77 (35.94)**	**2.97 (2.99)**	**16.69 (15.73)**	**4.76 4.23)(**	**8.77 9.72)(**
$[Ni\ L(ONO_2)_2(H_2O)_2].0.5C_2H_5OH$ 676.03 *g.mol^{-1}*	**122-124**	**Greenish yellow**	**77**	**37.30 (38.21)**	**3.10 3.01)(**	**16.57 (17.22)**	**4.73 (4.08)**	**8.67 8.98)(**
$[Cu\ L\ (H_2O)_2\ (\ NO_3)_2].0.5H_2O$ 666.93 *g.mol^{-1}*	**220d**	**Greenish yellow**	**69**	**36.00 36.56)(**	**2.85 (2.99)**	**16.08 (16.57)**	**4.80 (5.13)**	**9.52 (8.95)**
$C_{19}H_{18}N_4O_4S(L_2)$ 398.44 *g.mol^{-1}*	**180-182**	**Pale yellow**	**66**	**57.22 58.03)(**	**4.51 5.18)(**	**14.05 14.91)(**	**8.03 8.50)(**	**-----**
$[CoL_2].2NO_3.H_2O$ 997.78 *g.mol-1*	**111-113**	**Greenish blue**	**81**	**45.70 46.11)(**	**3.80 4.01)(**	**14.03 (15.02)**	**6.41 5.99)(**	**5.90 6.78)(**
$[Ni\ L_2(ONO_2)_2]$. H_2O 997.48 *g.mol^{-1}*	**107-109**	**Greenish yellow**	**65**	**45.71 46.27)(**	**3.80 (3.97)**	**14.03 (14.55)**	**6.41 (7.09)**	**5.87 6.11)(**
$[Cu\ L_2(ONO_2)_2]$. H_2O 1002.38 *g.mol^{-1}*	**122-124**	**Pale Green**	**71**	**45.49 (46.09)**	**3.99 3.33)(**	**13.96 (14.09)**	**6.38 (7.00)**	**6.33 (5.98)**

d= decomposition degree

Formation of Ligands Complexes in Solution State

The molar ratio method was used in order to determine [M:L] ratio of the complexes by adding an excess amount of ligands (0.25-5.0 ml) of the concentration 10^{-3} M to (1ml) of the concentration 10^{-3} M of each metal ions in ethanol. Absorbance measurements were made with prepared blank for each concentration of chelating agents at λ_{max} of the formed complex. The absorbance (As & Am) of the solution was measured at λ_{max} of maximum absorption. From these results the stability constant of all complexes (K) has been calculated from following equation.

$$\mathrm{K} = \frac{(1-\alpha)}{\alpha^2 \mathrm{C}} \quad \textbf{When M:L was (1:1)} \; \ldots\ldots\ldots(1)$$

$$\mathrm{K} = \frac{(1-\alpha)}{4\alpha^3 \mathrm{C2}} \quad \textbf{When M:L was (1:2)} \ldots\ldots(2)$$

Given $\alpha = \frac{\mathrm{Am}-\mathrm{As}}{\mathrm{Am}}$. . . . (2-1)

$\mathbf{A_m = \epsilon_{max}\, b\, c}$. . . . (2-2) **when**

$\mathbf{A_m}$ =Absorbance of the solution containing an excess amount of ligand.
$\mathbf{A_s}$ = Absorbance of the solution containing stoichiometric amount of ligand metal ion.

Computational Details

Gaussian 09 and Hyper chem-8 programs was used to perform geometry optimizations of ligands and metal complexes, optimization energy, HOMO and LUMO , electrostatic potential (E.P),dipole moment ,Uv-Vis and FT-IR spectra for ligands can be calculated in two programs consequently.

RESUIT AND DISCUSSION

The physical and analytical data of the ligands ($\mathbf{L_1,L_2}$) and their metal complexes are summarized 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 moment. The ligand**s** are soluble in common organic solvents, whereas the new complexes of all prepared ligands are coloured crystalline solids, soluble in ethanol, DMF and DMSO.

Fourier transform infrared spectra of ligands and their metal complexes

The characteristic frequencies of free ligands and their metal complexes were readily assigned based on comparison with literature values.

Ligands spectra which are summarized in **Table(2)** . A potential ligand L_1 and L_2 Infrared spectra of the free ligands observed bands at (2904, 2954) and (2931, 2889) cm^{-1} which attributed to the frequencies νCH_2-N [12].In the complexes, the frequency of nitrogen amino methylene group suffered a positive and negative in the range (2839-2989),(2888-2800) and (2870-2978) and (2800-2877) cm^{-1}**,**for two bands of methylene group of two ligands L_1 and L_2 respectively[12,13]. The stretching vibration of ν(NH) that appeared at (3280)cm^{-1} undergoes a negative shift about (17,25) cm^{-1} in VL_1 and CuL_1 complexes and positive shift about(15,18) cm^{-1} in CoL_1 and NiL_1 complexes [12,13]. On the other hand, the bending vibration of δ(NH) at (1477) cm^{-1} exhibited a shift toward lower frequencies in all complexes about (15-39) cm^{-1} which also refers to coordination with central metal ion by this group[11], these results indicating that the nitrogen of methylene involved in chelating of ligand[11,12]. While a both shift with a reduce intensity were observed for other bands of (C-N) moiety in complexes[11]. The band appeared at 1111cm^{-1}which attributed to νCNC of morpholine moiety of the ligand L_2 shifted to lower frequencies in complexes suggests that the coordination is through nitrogen atom of morpholine[4,14]. In addition another bands appeared at (1180,740,1053,1153) and (1157,740,1068) which is attributed to νCSC, νCS& νNCS bands of L_1 and L_2 respectively . These bands is shifting of medium to high intensity towards higher or lower frequencies for all prepared complexes[11,15,16] ,indicating that the sulphur moiety is involved in coordination this support by the formation of νM-S band in the range (472-

451)cm^{-1}[17]. The bands of stretching vibrations carbonyl and nitro groups of ligand not suffered any change in their position and as the shape band in all complexes, indicating that these groups are not involved in coordination[18]. According to these results, the coordination made of this ligand is clearly predicted as a bidentate through N-CH_2 and sulphur Assignment of the proposed coordination sites is further supported by the appearance of medium bands at (543–578) and (567-586) cm^{-1} which could be attributed to νM–N and cm^{-1} νM–S (443-470),(489-497) cm^{-1} respectively for complexes with ligands L_1 and the L_2 [15,16]. Other bands can be showed in **Table** (2).

Table (2): Main FTIR bands cm^{-1} of ligands (L_1 and L_2) and its Complexes

Compounds									
Bands	**L_1**	**VL_1**	**CoL_1**	**NiL_1**	**CuL_1**	**L_2**	**CoL_2**	**NiL_2**	**CuL_2**
ν CH_2-N	2904 2854	2926 2819	2839 2800	2989 2877	2919 2888	2931 2889	2870 2800	2900 2877	2978 2866
ν NH	3280	3263	3295	3298	3255				
δ NH	1477	1462	1438	1462	1454				
ν C=O	1708 1685	1701 1685	1708 1685	1706 1681	1706 1686	1720	1720	1720	1716
ν CN	1356	1340	1342	1341	1341	1357	1341	1341	broadness
ν C=C	1523	1523	1524	1524	1523	1516	1516	1516	1517
ν CSC	1180	1199	1195	1199	1195	1157	1184	1176	1184
ν CS	740	758	760	764	760	740	764	760	761
ν CNC morph.						1111	1090	1090	1089
ν NCS	1053 1153	1041 1176	1041 1172	1072 1103	1014 1172	1068	1041	1041	1037
ν NCN	1377	1380	Broadness	Broad-ness	Broad-ness	1373	Broad-ness	1357	Broad-ness
ν M-N	---	574	543	578	570	---	567	582	586
ν M-S	---	470	443	462	447	---	489	493	497
Others	----	ν C_2H_5OH 3533 νH_2O 3410 SO_4 1118, 1138 V=O 987	ν H_2O 3460-3360 ν ONO_2 1380,1041, 1230 δ H_2O 825,871 Co-O 486	ν C_2H_5OH 3585 ν H_2O 3460-3360 δ H_2O 825,871 ν ONO_2, 1384, 1041, 1199 Ni-O 486	ν H_2O 3433 ν ONO_2 1381, 1014,972 δ H_2O 867 Cu-O 489	----	ν H_2O 3398 ν ONO_2 1041, 1222, 1341,972	ν H_2O 3400 ν ONO_2 1381,1010 , 1226 Ni-O 502	ν H_2O 3537-3387 Cu-O 516

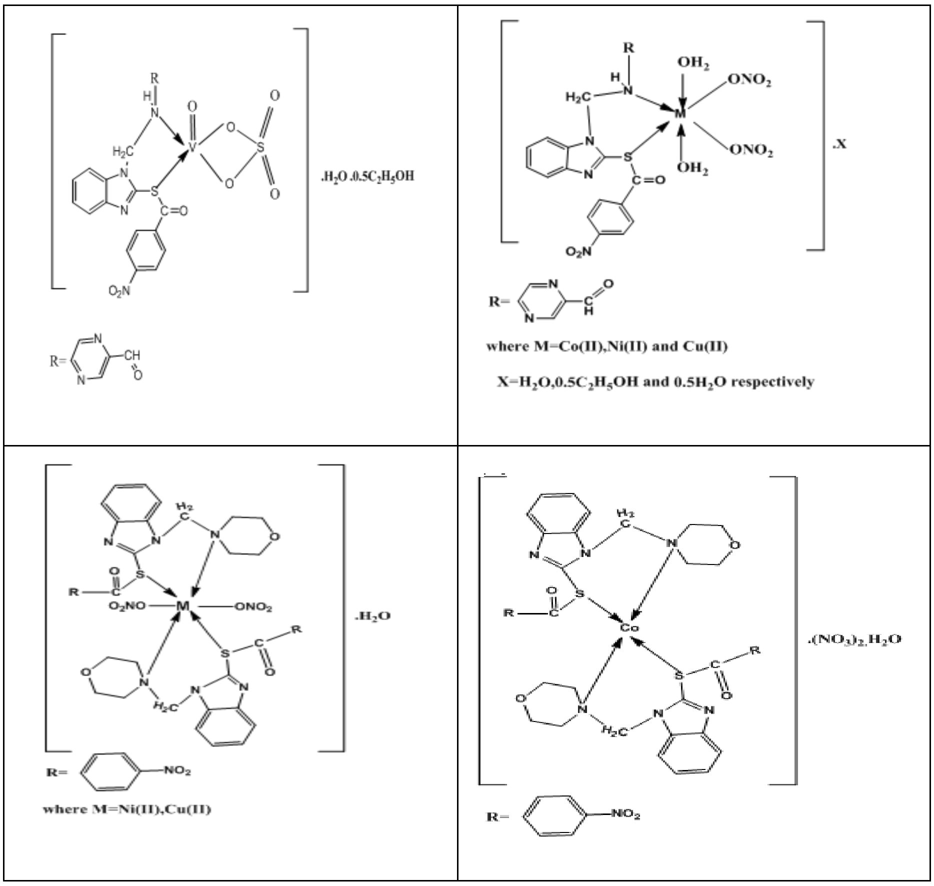
Electronic Spectra

The electronic spectrum of VL_1 complex, **Table (3),** shows prominent (d-d) absorption bands, the first one is a band at (12820) cm^{-1} and the second at (16949) cm^{-1} but the third bands appeared at (24509) cm^{-1}. These bands can be attributed to the following transitions; $^2B_2 \rightarrow {}^2E$, $^2B_2 \rightarrow {}^2B_1$, and $^2B_2 \rightarrow {}^2A_1$, respectively[19,20,21]. The magnetic moment (2.02) BM is higher than spin value of the vanadium ion only this indicates a higher orbital contribution[19]. These transitions and the magnetic moment value came in accordance with the published data for square pyramid vanadium complexes [19,20],**Figure(1)**. Conductivity measurement appeared that the complex was nonionic[20],**Table(3)** .The magnatic measurement of CoL_1

(4.20) B.M indicates that the light brown complex to be paramagnatic and is characteristic of high spin octahedral[19,22]. The electronic spectrum of this complex, **Table (3)**, shows prominent (d-d) absorption bands at 10050 and 19950 cm^{-1} which attributed to **$^4T_{1g} \rightarrow {}^4T_{2g}$** v1 and **$^4T_{1g} \rightarrow {}^4T_{1g(P)}$** v3[19,22,23] . The values of v2 calculated as well as all parameter β , **B** and 10Dq are all in good agreement with cobalt (II) octahedral complexes [19,22]. Conductivity measurement showed that the complex was nonionic[23] .While in CoL$_2$ revealed that the three bands at 15267, 15798 and 16999 cm^{-1} of the present complex can be assigned to υ_3 split, while υ_2 expected in the range 5000-6000 cm^{-1} (NIR) which is outside the scope of the device, υ_1 is appeared at 3470 cm^{-1}[19,24].

Table (3): Electronic spectra, Conductance in DMF solvent and magnetic moment (B.M.) for all prepared compounds

Comp.	**Absorption Bands(cm^{-1})**	**Assignments**	**B°**	**B′**	**ß**	**10Dq**	**15B′**	**μ_{eff} B.M.**	**µs. cm^{-1}**
L$_1$	32467,39840 43668	n→π* π→π						-----	-----
VL$_1$	12820 16949 24509 26737,32786 36363	$^2B_2 \rightarrow {}^2E$ $^2B_2 \rightarrow {}^2B_1$ $^2B_2 \rightarrow {}^2A_1$ L→ VCT L→ VCT						2.02 (1.73)	23
CoL$_1$	10050 23014(cal.) 19920 28653 41841	$^4T_1g \rightarrow {}^4T_2g$ $^4T_1g \rightarrow {}^4A_2g_{(F)}$ $^4T_1g \rightarrow {}^4T_1g_{(P)}$ L→Co CT L→Co CT	1128	852.3	0.755	10227	12784.5	4.20 (3.87)	46
NiL$_1$	10810 15873 27111(cal.) 29411,32786 41493	$^3A_2g \rightarrow {}^3T_2g$ $^3A_2g \rightarrow {}^3T_1g_{(F)}$ $^3A_2g \rightarrow {}^3T_1g_{(P)}$ L → Ni CT L → Ni CT	1035	703.6	0.67	9991.1	10554.0	3.40 (2.82)	33
CuL$_1$	19801 19630 30120,33112 35460,44843	$^2B_1g \rightarrow {}^2B_2g$ $^2B_1g \rightarrow {}^2Eg$ L →Cu CT L → Cu CT						1.82 (1.73)	50
L$_2$	35087,32154sh. 41322, 44444	n→π* π →π*						-----	-----
CoL$_2$	3470 5174 16181(cal.) 25641,27173 39370,43103	$^4A_2 \rightarrow {}^4T_2$ $^4A_2 \rightarrow {}^4T_1$ $^4A_2 \rightarrow {}^4T_{1\,(P)}$ L→Co CT L→Co CT	1128	729.6	0.64	3444	10945	4.79 (3.87)	36
NiL$_2$	12195 10204 16000 24813 25974,35460	$^3A_2g \rightarrow {}^1Eg$ $^3A_2g \rightarrow {}^3T_2g$ $^3A_2g \rightarrow {}^3T_1g_{(F)}$ $^3A_2g \rightarrow {}^3T_1g_{(P)}$ L→Ni CT	1035	680	0.65	10200	10220	3.21 (2.82)	14
CuL$_2$	148148 31645,35335 44843	$^2Eg \rightarrow {}^2T_2g$ L→Cu CT L→Cu CT						1.88 (1.78)	17



Figure(1): **Suggested Structures of Prepared Complexes**.

The solution spectra of the greenish yellow of NiL_1 and NiL_2 complexes in ethanol appeared bands at,(10810,15873) is assigned to $\mathbf{^3A_{2}g\rightarrow{}^3T_{2}g}$, $\mathbf{^3A_{2}g\rightarrow{}^3T_{1}g_{(F)}}$ transitions respectively and (10204,16000 and 24813) cm^{-1} is due to $\mathbf{^3A_{2}g\rightarrow{}^3T_{2}g}$, $\mathbf{^3A_{2}g\rightarrow{}^3T_{1}g_{(F)}}$ and $\mathbf{^3A_{2}g\rightarrow{}^3T_{1}g_{(p)}}$ transitions respectively, which indicate octahedral geometry of Ni(II)[19,24]. The absence of any band below 10000 cm^{-1} eliminates the possibility of tetrahedral environment in this complex. The different ligands field parameters B^-, β, $15B^-$ and 10Dq have been calculated using Tanabe-Sugano diagram for d^8 , The value of the calculated neuphelauxetic indicating that Ni**L** bond of all complexes is covalent. Magnetic moment, 3.40 and 3.21 B.M, of the solid complex showed a higher orbital contribution[24,25]. Conductivity measurement in DMF appeared that the complexes were nonionic[24],**Table(3),Figure(1)**.

Electronic spectra of greenish yellow and pale green complexes of CuL_1 and CuL_2 displayed bands in the range of 30120–44843 cm^{-1} which can be attributed to charge transfer for two complexes as well as the spectra showed d–d electronic transition at 19801and19630 cm^{-1} in CuL_1 complex and 148148 cm^{-1} in CuL_2 complex which is due to $\mathbf{^2B_{1}g\rightarrow{}^2B_{2}g}$, $\mathbf{^2B_{1}g\rightarrow{}^2Eg}$ and $\mathbf{^2Eg\rightarrow{}^2T_{2}g}$ transitions, the broadness of the band is due to the ligand field and the Jahn–Teller effect, these absorptions prefer the distorted octahedral geometry for the Cu(II) ion[19,26]. Moreover, the magnetic moment for the Cu(II) complexes are 1.82 and 1.88 B.M. suggesting a monomeric structure. Furthermore, the complex is non-electrolyte as the molar conductance was found to be non ionic[26], **Table(3), (Figure 1)**.

Mass spectra of two Mannich base ligands L_1 and L_2

The mass spectrum of **-(1-((pyrazine-2-carboxamido)methyl)-1-H-benzoimidazole-2-yl)4-nitrobenzothioate (L_1) and S-(1-Morpholinomethyl)-1-benzoimidazol-2-yl)4- nitrobenzothioate (L_2)** is depicted in **Figure(),** which displayed a weak intensity peak at m\z=434,398 due to the molecular ion of the empirical formula ($C_{20}H_{14}N_6O_4S$) and ($C_{19}H_{18}SN_4O_4$) and the other peaks around 298m\z [$(C_6H_4N_2CSCOC_6H_4NO_2)^+$,80)] , 77 m\z [$(C_6H_5)^+$,47)], 136m\z [$(C_4N_2H_3CONHCH_2)^+$,55] , 79 m\z [$(C_4H_3N_2)^+$,48)], 52 m\z [$(C_3H_2N)^+$,20)] ,51m\z [$(C_3HN)^+$,14)],50m\z[$(C_3N)^+$], 26 m\z [$(CN^+$,32)] and 298, 122,100 , 86 ,77, 70, 42 m\z are resulted from the breaking of [($C_6H_4N_2CSCOC_6H_4NO_2$)$^+$,80)], [($C_6H_4NO_2$)$^+$,61)] ,[($C_4H_8NOCH_2$)$^+$,76),] ,[(C_4H_8NO)$^+$, 19] , [(C_6H_5)$^+$,47)], [(C_4H_8N)$^+$,15] ,[(C_3H_6)$^+$,5)] for L_1 and L_2 respectively . The peak at m\z =150 of base peak (100% intensity) confirms the presence of the molecular ion [($COC_6H_4NO_2$)$^+$,100)], in two ligands consequently[27,28].

Solution study

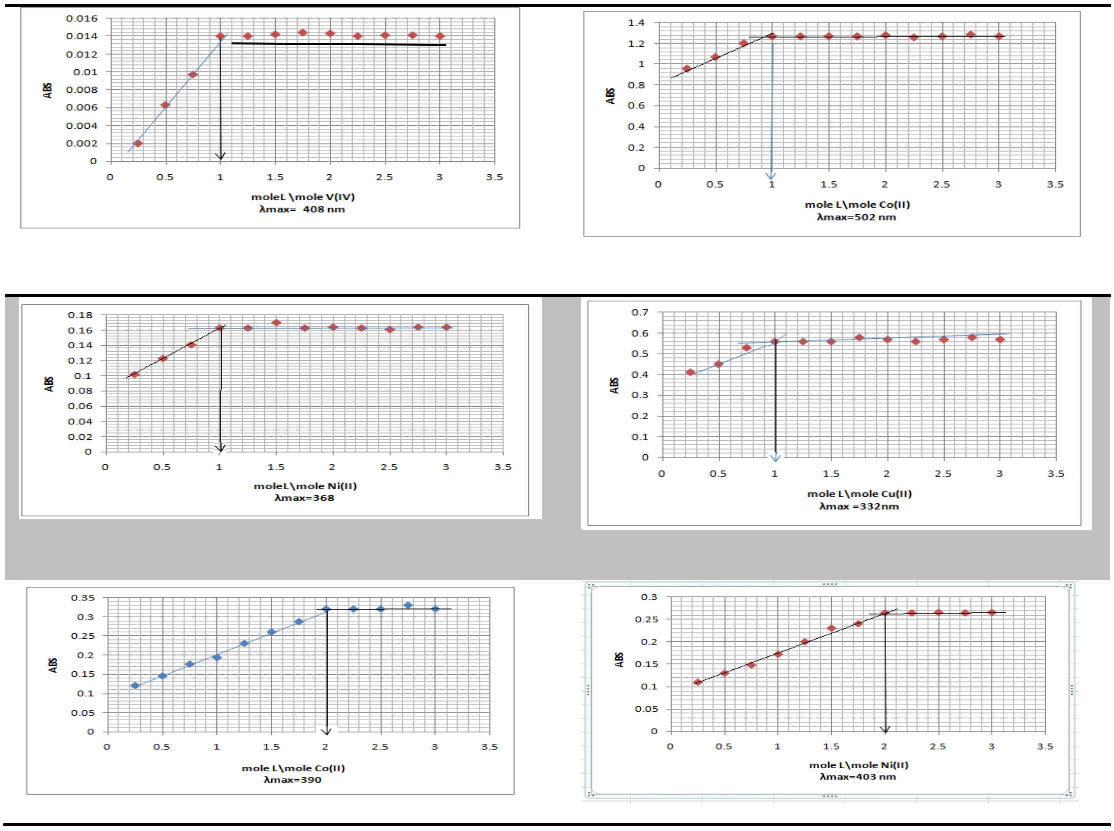
(1)- Molar ratio and Continuous variation methods

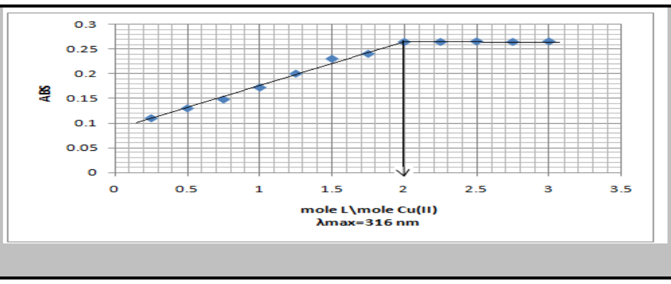
The Molar ratio method was followed to determine the M:L ratio. The results of complexes in ethanol solvent, suggest that the metal to ligand ratio was (1:1) for L_1, while (1:2) for L_2, which were comparable to those obtained from solid state study **Table(4) ,Figure(2)**.

Table(4):Stability constant of prepared all complexes at 25C^0

Comp.	As	Am	A	ε_{max} L.mol^{-1} cm $^{-1}$	K L.mol^{-1}	λ_{max}/nm	Molar ratio
VL_1	0.421	0.499	0.156	4990	3.71X10^4	408	1:1
CoL_1	1.266	1.496	0.153	14960	3.60X10^4	502	1:1
NiL_1	0.163	0.200	0.185	2000	2.38X10^4	368	1:1
CuL_1	0.536	0.621	0.136	6210	4.62X10^4	332	1:1
CoL_2	0.320	0.390	0.179	3900	4.10X10^8	390	1:2
NiL_2	0.264	0.403	0.344	4030	5.66X10^7	403	1:2
CuL_2	0.259	0.299	0.133	2990	9.20X10^8	316	1:2

Note: When the molar ratio (1:2) ,the stability constant unit is (L^2 mol^{-2}).





Figure(2):The molar ratio plot complexes between metal and ligand

(2)-Stability constant of the Mannich base complexes

The apparent stability constant of [Metal: Ligand] complexes ,were evaluated, at λmax absorption, furthermore molar absorptivity (εmax) and degree of dissociation for all complexes were calculated, **Table** (4).

The results indicate that mole ratio of (1:2) for L_2 complexes , yielded rather high stability constants in contrast to the other values obtained with (1:1) for L_1 complexes, may be due to the size of moiety[29], **Table(4)**.The most stable for Cu (II) complexes and this is due to Jahn- Teller distortion [30] .

Theoretical treatment

The conformations of the free ligands and its complexes obtained from the semi-empirical and molecular mechanics calculations that were fully re-optimized to estimate the heat of formation (ΔHf º) and binding energy (ΔE_b) by using the PM3,ZINDO\1,AMBER method for free ligands and their metal complexes. The heat of formation and binding energy values showed that the complexes is more stable than the ligands **,Table(5)**.

Table (5): Conformation energetic (in KJ.mol^{-1}) and dipole moment (in Debye) for ligands and their metal complexes using HyperChem-8 program

Comp.	PM3			ZINDO/1			AMPER	μ
	ΔH°_{f}	ΔE_b	μ	ΔH°_{f}	ΔE_b	μ	$\Delta H^{\circ}_{f} = \Delta E_b$	
L_1	89.7233204	-5300.650	4.11	-9878.599	-15008.463	4.268	----------	
VL_1							708.023	4.0
CoL_1	-458.891	-6862.545	10.62	183. 9-1795	-19428.878	9.78		
NiL_1	363.800-	-6767.854	11.44	-13154.648	-19558.702	11.26		
CuL_1	-246.945	-6628.899	15.21	13358.751-	-19740.701	14.89		
L_2	280.965	-4283.796	4.443	-9717.032	-14698.578	5.56	----------	
CoL_2	-277.799	-10262.963	15.77	-20315.526	30300.690-	17.79		
NiL_2	-151.409	-10720.327	11.34	-170619.538	-19660.124	9.76		
CuL_2	-90.680	273757.82-	16.99	83331.127-	-272480.463	16.09		

The total energy and dipole moment μ for two prepared ligands can be calculated using (Gaussian.0.9) program by semi-empirical (PM3) method as shown in **Table (6)**.

Table (6): Conformation energetic in (in KJ.mol^{-1}) and dipole moment (in Debye) for organic molecules using Gaussian program.

Comp.	Total energy	μ
L$_1$	0.43676366	4.6038
L$_2$	0.20817067	4.6307

Theoretical Computation Vibration Frequencies of Ligands

Vibration spectra of the prepared ligands L$_1$ and L$_2$ were calculated using PM3 method due to this method is Very compatible with experimental data than others, for both program **Tables (7) and Table (8)** .The theoretical frequencies for the prepared ligands display some deviations from the experimental values **[31]**. The deviations or errors occur in the calculated frequencies are due to several factors, such as there are coupling between vibrational modes, anharmonicity of large amplitude vibrational modes and approximation that each normal mode of vibration interact independently with IR beam**[32].**

Table (7): shows the data vibrational of frequencies experimental and theoretical of L$_1$ using Gaussian program.

Symb.	vC=N+ C=C	δC-N	vC=O	v N-H	vCH$_2$-N	vNCS	vNCN	vCS
Hyper.	1688 *1608-1523 (-7.82)	1389 *1357 (-2.35)	1800 *1708 (-5.38)	3180 *3280 (3.04)	2972 *2904 (-2.34) 2867 *2854 (-0.45)	1003-1144 *1053-1153 (4.74)	1292 *1377 (6.57)	685 *740 (7.43)
Gass.	1645 *1608 -1523 (-5.07)	1233 *1357 (9.08)	1843 *1708 (-7.90)	3346 *3280 (-2.01)	2927 *2904 (-0.79) 2810 *2854 (1.54)	1033-1112 *1053-1153 (1.89-3.55)	1268 *1377 (7.85)	691.81 *740 (6.63)

Table(8): shows the data vibrational of frequencies experimental and theoretical of L$_2$ using Gaussian program

Symb.	vC=N+ C=C	δC-N	vC=O	vNCN	*v* C-O-C	vCS	vCSC	vCNC morph.
Hyp.	1651 *1627-1516 (1.45-8.17)	1322 *1357 (-2.64)	1700 *1720 (-1.17)	1395 *1373 (1.57)	1259 *1215 (3.49)	789 *740 (6.21)	1183 *1157 (2.19)	1132 *1111 (0.188)
Gass.	1644 *1627-1516 (1.03-7.78)	1234 *1357 (-9.96)	1758 *1720 (2.16)	1402 *1373 (2.00)	1162 *1215 (-4.50)	774 *740 (4.39)	1152 *1157 (-0.43)	1135.01 *1111 (2.11)

When:

* : Experimental frequencies.,
:Without star represented theoretical frequencies
( ): Error % due to main different in the experimental measurements and theoretical treatment of vibrational spectrum

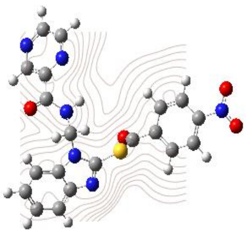
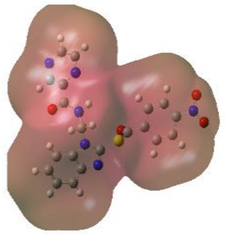
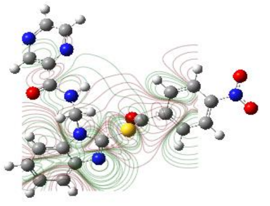
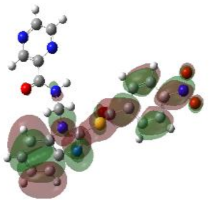
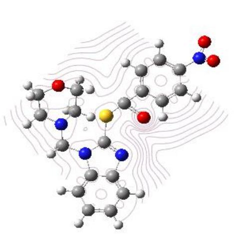
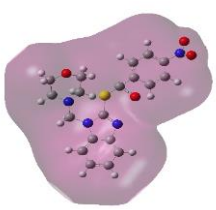
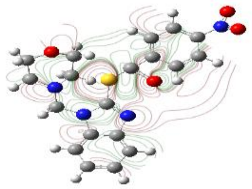
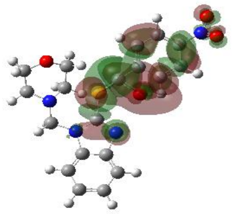
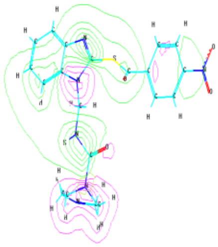
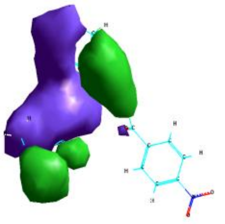
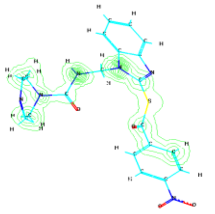
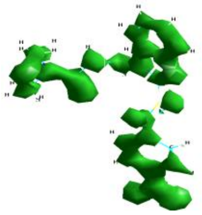
Theoretical Computation for Electronic Spectra of Ligands

The theoretical Uv-spectra of ligands was calculated using PM3 method in Hyper chem. -8, while Gaussian program can provide (λ_{max}) using job type single point energy (SP) along with ZINDO , TD-SCF method for ligands and by using job type frequency (Freq.) along with CIS method (basis set 3-21G) as in **Table (9)**.showed some deviations from the experimental values ,these deviations are generally acceptable in theoretical calculations.

Table (9): Comparison of experimental and theoretical electronic transition for two ligands from CIS, TD-SCF and ZINDO calculation using Gaussian program and PM3 method using Hyper Chem-8

Symb.	Transition	Experimental	Theoretical\ *Gaussian* program			Theoretical\Hyper Chem-8 program
			CIS	TD-SCF	ZINDO	PM3
L_1	n→π* π→π*	32467,39840 43668	29568	23121	25641	35606 , 44523377653 35211 ,
L_2	n→π* π→π*	35087,32154sh. 41322,44444	34211	29411	26364	3610134722 , ,42735,4291847846

The **HOMO** and **LUMO** and electrostatic energy **E.P** value were plotted can be calculated using two programs in 2D and 3D. The results appear that the **LUMO** of transition metal ion prefers to react with HOMO of donor atoms in prepared ligands. The electrostatic potential (**E.P**) describes the interaction of energy of the molecular system with a positive point charge. The **E.P** of ligands **L_1 and L_2** appear that S atom and **N** are more reactive than other atoms [32,33].The **HOMO** and **LUMO** represented in **Figure(3).** The geometry optimization of ligands and metal complexes can be represented in **Figure(4).**

E.P (L_1) in 2D 	**E.P (L_1) in 3D** 	**HOMO & LUMO (L_1) in 2D** 	**HOMO & LUMO (L_1) in 3D** 
E.P (L_1) in 2D 	**E.P (L_2) in 3D** 	**HOMO & LUMO (L_2) in 2D** 	**HOMO & LUMO (L_2) in 3D** 
E.P (L_2) in 2D 	**E.P (L_2) in 3D** 	**HOMO & LUMO (L_2) in 2D** 	**HOMO & LUMO (L_2) in 3D** 

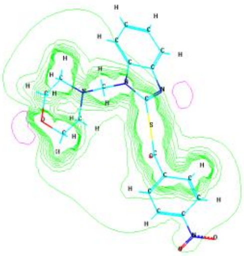
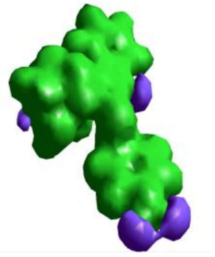
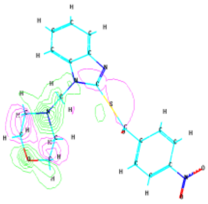
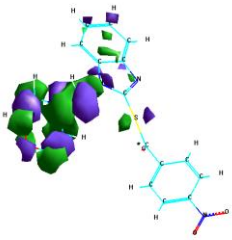
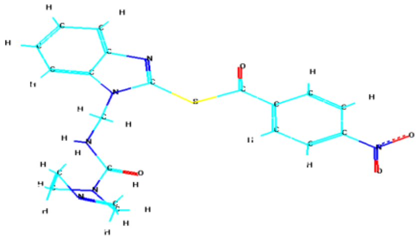
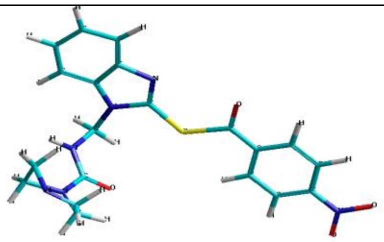
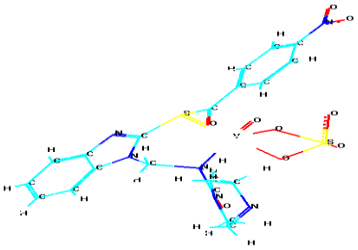
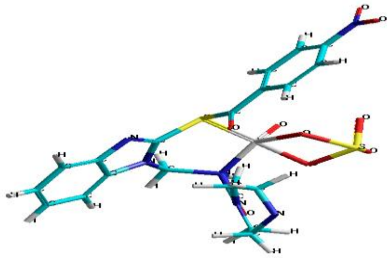
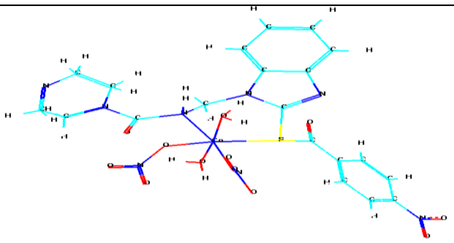
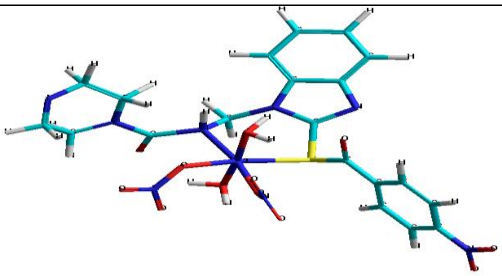
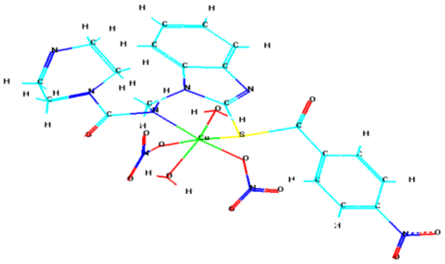
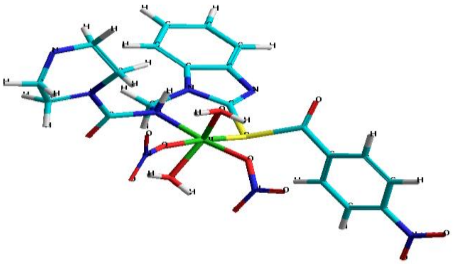
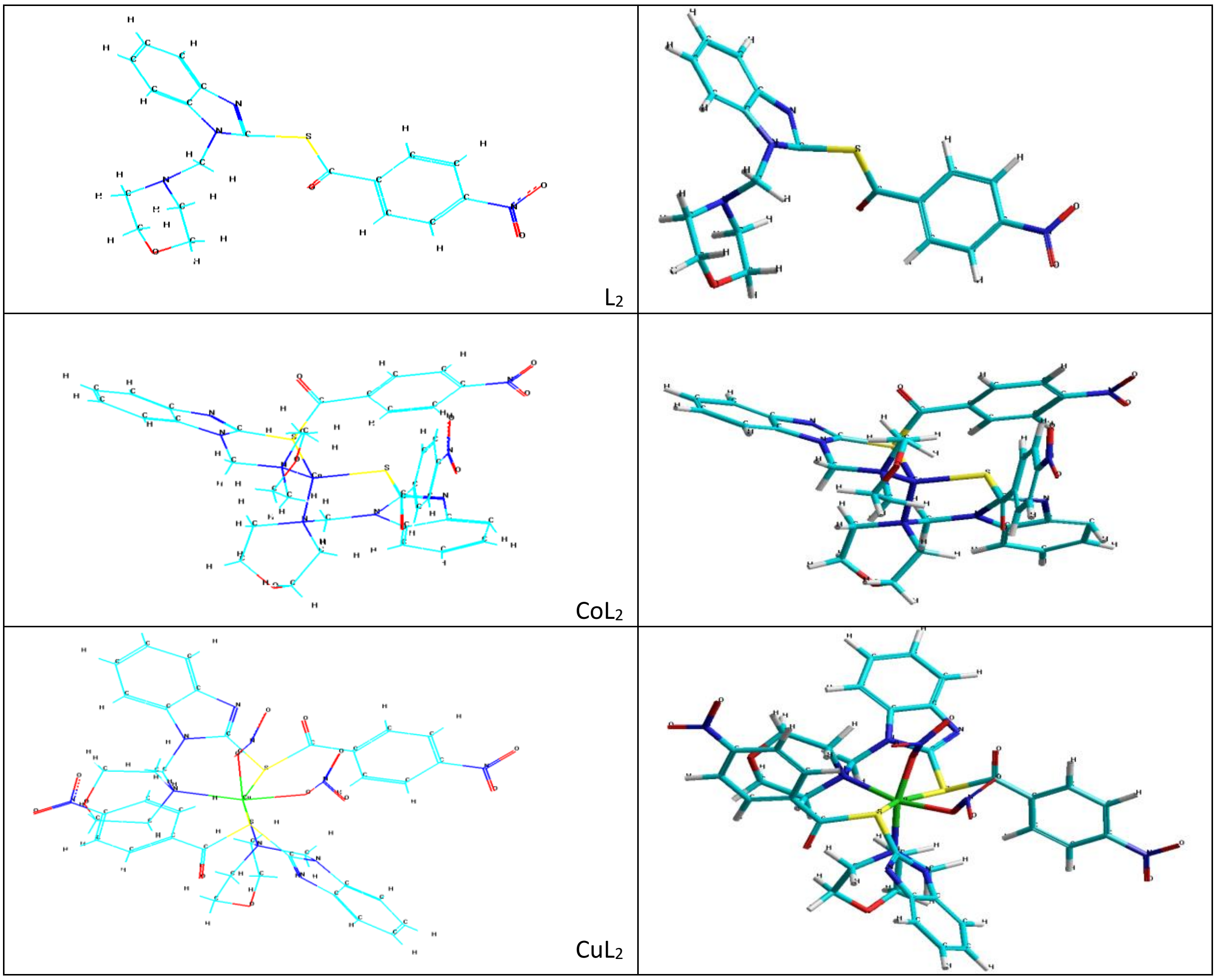
E.P (L_2) in 2D 	**E.P (L_2) in 3D** 	**HOMO & LUMO (L_2) in 2D** 	**HOMO & LUMO (L_2) in 3D** 

Figure (3): HOMO, LUMO & Electrostatic potential as 2&3D counters for Ligands using Gaussian and Hyper Chem-8 program.

 L_1	
 VL_1	
 CoL_1	
 CuL_1	



Figure(4):Conformation structure of ligands and their complexes using Hyper Chem.-8 program

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