

**Synthesis and Theoretical Study of  
New 2- Bromobenzaldehyde [ 5-(2-hydroxyphenyl ) – 1,3,4–oxadiazol  
–2–yl ] hydrazone and some of their Transition Metal complexes**

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**الخلاصة :**

في هذا البحث تم تحضير الليكاند

[2-bromobenzaldehyde[5-(2-hydroxyphenyl)-1,3,4-oxadiazole -2-yl ] hydrazone

وقد استخدم هذا الليكاند للتعقيد مع بعض املاح العناصر الانتقالية والتي تشمل :

( Mn(II), Fe(II), Co(II), Ni (II) and Cu(II) )

وتم دراسة المعقدات المحضرة باستخدام تقنية الامتصاص الذري ، طيف الاشعة تحت الحمراء ، طيف الاشعة فوق البنفسجية والمرئية ، الخواص المغناطيسية ، طرائق المتغيرات المستمرة ، التوصيل المولاري وباستخدام طريقة Semi – Empirical / PM3 لدراسة الشكل الفراغي بالاضافة لحساب الطاقة الكلية ، طاقة الاواصر وكذلك حرارة التكوين واطوال الاواصر واطياف الاشعة تحت الحمراء والاشعة فوق البنفسجية والمرئية ومقارنة هذه النتائج مع النتائج العملية لاثبات الصيغ التركيبية المقترحة للمعقدات .

**Abstract :**

A new derivative of 2 – bromobenzaldehyde [ 5 – ( 2 – hydroxyphenyl )–1,3,4–oxadiazole–2–yl] hydrazone was prepared , which was used as ligand to prepare a number of metal complexes with following transition metal salts Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) .

The structure elucidation of the prepared complexes was atomic absorption technique also the IR , UV as well as the molar conductance and the magnetic susceptibility were studied . The molar ratio metal : ligand was determined by continuous variation . The Semi – Empirical ( PM3 ) was used to study of the geometry of free ligand and complexes as well as to calculate total energy , binding energy , heat of formation , bond length , theoretical IR and UV spectra . The results are compared with the experimental data , probable structures of the complexes have been assigned .

**1 – Introduction :**

Oxadiazole derivatives , which belong to an important group of heterocyclic compounds , have been the subject of extensive study in the recent past . Numerous reports have highlighted their chemistry and use Diverse biological activities , such as anti–tuberculosis , anti-inflammatory , analgesic , antipyretic , anticonvulsant , antibacterial , antifungal , antimalarial and insecticidal agents have been found to be associated with oxadiazole derivations . Activities when properly substituted in 2– and 5- positions<sup>(1-4)</sup> for this reason to synthesize various 1,3,4–oxadiazol–2–thione derivative to make notable contributain to this class of heterocyclic compound . A number of commercially available hydrazides were treated with different carboxylic acids in the presence of phosphorous oxychloride to afford 2,5–disubstituted –1,3,4– oxadiazoles<sup>(3,5)</sup> . The heterocyclic molecule contains nitrogen and oxygen with free electron pairs on the five – member rings could provide active potential coordination site for metal ions , metal complexes showed biological application .<sup>(6)</sup>

**2 – Program package HyperChem 7.52 <sup>(7)</sup>**

HyperChem can use quantum mechanical methods to calculate several other properties . HyperChem Offers Semi – Empirical / PM3 molecular orbital methods , with options for organic and main group compounds for transition metal complexes , are use in the electronic part of the calculation to obtain total electron density , electrostatic potential , heat of formation , orbital energy levels , vibrational normal modes and frequencies , infrared spectrum ( IR ) , ultraviolet – visible spectrum frequencies , bond length , binding energy , and the complexation energy .

The Semi–Empirical / PM3 can calculate geometry optimization of free ligand and their complexes .

**3- Experimental :**

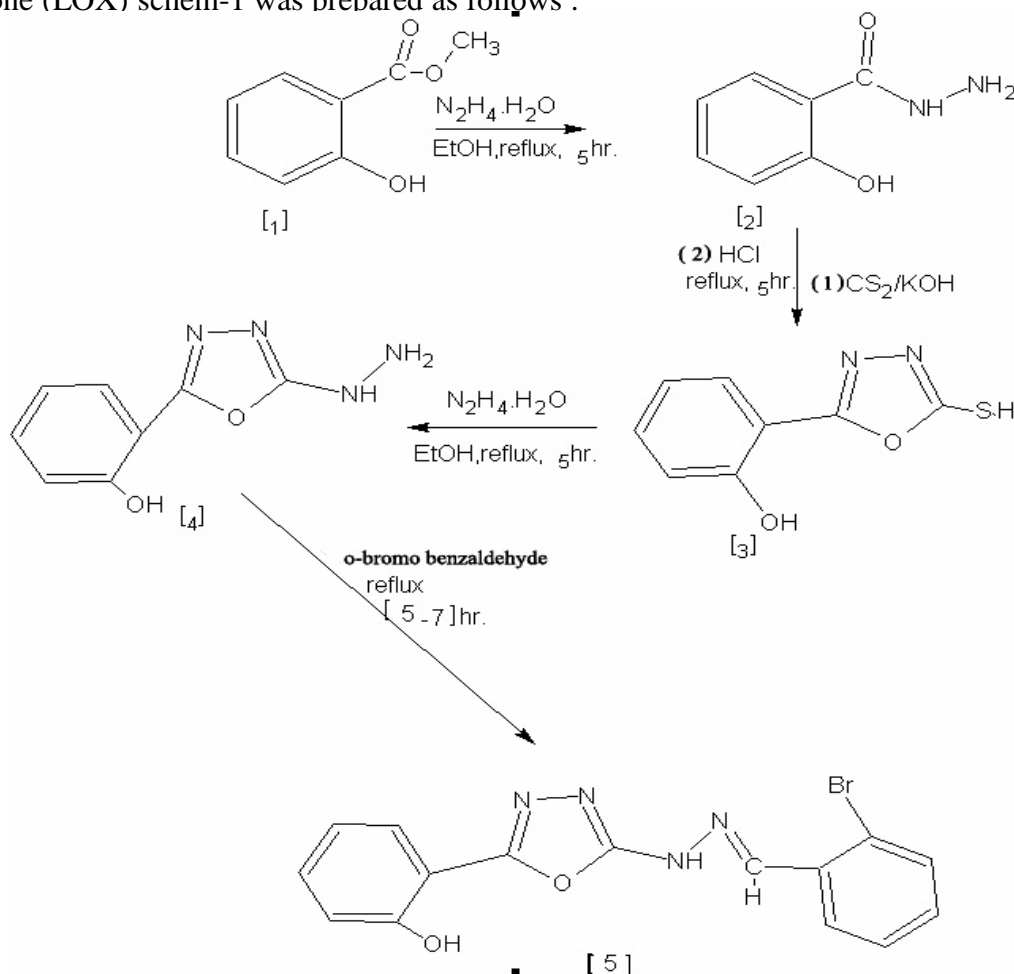
All chemical are supplied of ( B.D.H , Fluka and Aldrich ) . The FTIR spectra in the range ( 4000 – 200  $\text{cm}^{-1}$  ) were recorded as cesium iodide disc FTIR – 8300 shimadzu spectrophotometer .

The UV spectra were measured in DMSO using Hitachi UV – 2000 spectrophotometer in the range (200–900)nm . Magnetic susceptibility measurements for the complexes were obtained at room temperature using the susceptibility balance model MSB – MKI . Gallen – Kamp MFB – 600 melting point apparatus was used to measure the melting points of all prepared compounds .

Flame atomic absorption data were obtained using shimadzu AA- 670 . Conductivity measurements were done by using electrolytic conductivity measuring set model ( CRB3 ) using platinum electrode with cell constant (1cm) concentration (  $10^{-3}$  M ) in DMSO as solvent .

**3 . 1 Preparation of the ligand :**

The new ligand 2–Bromobenzaldehyde [5–(2–hydroxy– phenyl )–1,3,4 – oxadiazol –2–yl ] hydrazone (LOX) schem-1 was prepared as follows :



**Schem – 1 preparation of the ligand ( LOX)**

( 10 g , 0.4 mol ) of hydrazine hydrate ( 99% ) in ( 25mL ) absolute ethanol was added to an ethanolic solution of methyl salicylate (1) (30.4 g , 0.2 mol) in (25 mL) . The mixture was refluxed on a water bath for 5 hours then allowed to cool . The separated white precipitate (2) was filtered , dried and recrystallized from ethanol to give [2-hydroxy- benzohydrazide] <sup>(8,9)</sup> .

Yield ( 23 g , 75.6% ) , m.p. 148 – 150°C .

A mixture of (2) (15.2 g , 0.1 mol) dissolved in ethanol ( 50 mL ) , KOH ( 5.6 g , 0.1 mol in ( 60 mL ) ethanol and CS<sub>2</sub> ( 12 mL , 0.2 mole ) was refluxed on a water bath for 5 hours , until the evolution of H<sub>2</sub>S gas ceased .

The excess of solvent was removed under reduced pressure . The content were poured onto crushed ice and acidified with dilute HCl and the white solid which separated was filtered and recrystallized from ethanol to give (3) 2-(5-mercapto -1,3,4- oxadiazol -2-yl ) phenol <sup>(10)</sup> . Yield ( 10.8 g , 71% ) , m.p. 200°C .

A mixture of (3) ( 1.94 g , 0.01 mol ) and hydrazine hydrate ( 6 mL ) was refluxed in absolute ethanol ( 35 mL ) for 5 hours , or until evolution of H<sub>2</sub>S ceased ,then allowed to cool , the pale yellow precipitate was filtered , dried and recrystallized from ethanol to give (4) 2-[5-Hydrazino -1,3,4 - oxadiazol - 2-yl ] phenol <sup>(8)</sup> .Yield ( 1.59 g , 82% ) , m.p. 167°C .

A mixture of ( 4 ) ( 1.92 g , 0.01 mol ) and 2 - Bromo-benzaldehyde ( 1.849 g , 0.01 mol ) was refluxed in absolute ethanol ( 35 mL for ( 5 – 7 ) hours .

The bright yellow precipitate (5) 2-Bromoloenzaldehyde [ 5- (2- Hydroxy phenyl ) -1,3,4- oxadiazol -2-yl ] hydrazone ( LOX ) was filtered , dried and recrystallized from ethanol <sup>(11)</sup> . Yield ( 1.54 g , 80.2% ) , m.p. 158 – 160 °C .

### 3.2. Preparation of complexes :

The metal salts (1 mmol) was dissolved in hot absolute ethanol (15 mL) was added to solution of the ligand (LOX) ( 0.717 g , 2 mmol ) in hot absolute ethanol (10 mL) and the mixture was refluxed on a water bath for 2 hours and the solvent was evaporated in vacuum to half of the original volume and then cooled . The isolated complexes were filtered off , washed several times with ethanol and final in vacuum over anhydrous calcium chloride ( table – 1 ) .

**Table ( 1 ) : Physical properties , Formula of ligand ( LOX ) and its metal complexes .**

| No. | Formula and names   | Color      | m.p. °C   | Yielded % | $\mu_{eff}$ (B.M) | M%    |        |
|-----|---|------------|-----------|-----------|-------------------|-------|--------|
|     |   |            |           |           |                   | CalC. | Found  |
| LOX | C <sub>15</sub> H <sub>11</sub> BrN <sub>4</sub> O <sub>2</sub> | Yellow     | 158-160   | 80.2      | -                 | -     | -      |
| 1   | [ Mn(LOX) <sub>2</sub> Cl <sub>2</sub> ]                        | Pale Brown | 174 - 176 | 75.5      | 5.90              | 6.51  | (6.42) |
| 2   | [ Fe ( LOX ) <sub>2</sub> Cl <sub>2</sub> ]                     | Yellow     | 203 - 205 | 71.8      | 5.35              | 6.61  | (6.46) |
| 3   | [ Co ( LOX ) <sub>2</sub> Cl <sub>2</sub> ]                     | Gray       | 186 - 188 | 78.0      | 4.48              | 6.95  | (6.86) |
| 4   | [ Ni ( LOX ) <sub>2</sub> ] Cl <sub>2</sub>                     | Pale blue  | 210 - 212 | 85        | 3.42              | 6.92  | (6.81) |
| 5   | [ Cu ( LOX ) <sub>2</sub> Cl <sub>2</sub> ]                     | Dark Brown | 193 - 195 | 80.6      | 1.70              | 7.45  | (7.25) |

$\mu_{eff}$  : Magnetic Moment in Bohr Magneton .

CalC : calculation .

M% : The percentage of the metal by atomic absorption technique .

#### **4. Results and Discussion :**

##### **4.1. Characterization of the complexes : infrared studies .**

The infrared spectroscopic data of (LOX) and their complexes are summarized in table (2) .

These spectra are complicated owing to the extensive overlap of a number of band arising due to  $\nu(C=N)$ ,  $\nu(C=C)$  and other bands originate due to phenyl , oxadiazole ring and azomethene group appeared in the region below  $1650\text{ cm}^{-1}$  , the shifts in the positions or change in shape of the complexes bands due to free ligand suggest the probable modes of bonding in the complexes . The spectrum of ligand shows a very broad and weak absorption band around  $3420\text{ cm}^{-1}$  due to  $\nu(O-H)$  phenolic <sup>(12)</sup> . A moderately strong band at  $(3010)\text{ cm}^{-1}$  appeared in the ligand spectrum , this band is due to  $\nu(N-H)$  group <sup>(13)</sup> , two weak bands had been observed at  $(2940)$  and  $2900\text{ cm}^{-1}$  in the ligand spectrum which are due to  $\nu(C-H)$  aromatic and aliphatic respectively <sup>(14)</sup> . These band are stable in position in both ligand and metal complexes . A strong band in the region of  $(1615)$  and  $(1590)\text{ cm}^{-1}$  in the ligands is characteristics of  $\nu(C=N)$  ring group . Upon complexation , one band is located almost at the original position at  $1616\text{ cm}^{-1}$  due to uncoordinated  $\nu(C=N)$  and other is shifted to lower frequency  $(10-40)\text{ cm}^{-1}$  arising from the coordinated

$C=N$  mode <sup>(6,15)</sup> .

The bands due to  $\nu(C-O-C)$  in ligand appear at  $1270\text{ cm}^{-1}$  ( symmetric ) and  $1315\text{ cm}^{-1}$  ( asymmetric ) <sup>(6,16,17)</sup> .

The position of infrared bands due to heterocyclic oxadiazole ring does not change in the complexes indicating the noncoordination of oxygen (oxadiazole ring)<sup>(6)</sup> . A bands at  $(1430-1340)\text{ cm}^{-1}$  and  $645\text{ cm}^{-1}$  have also been appeared in the ligand spectrum , these bands is due to (OH) bending and  $\nu(C-Br)$  stretching respectively <sup>(18,19)</sup> . the fixed position of these bands in ligand and all metal complexes means that the (OH) phenolic group and bromine atom does not participate in coordination . ( See figure 1 and 2 ) .

Complexes spectra show new weak bands in the  $(465-255\text{ cm}^{-1})$  region these bands did not present in the spectrum ligand may be attributed to  $\nu(M-N)$  and  $\nu(M-Cl)$ <sup>(6,20)</sup> .

Theoretical vibrational and electronic spectra of the free ligand ( LOX ) and its metal complexes calculated using the Semi - Empirical ( PM3 ) methods are given in table ( 2 ) and ( 3 ) .

The agreement between the experimental and theoretical calculated was generally satisfactory .

The theoretically calculated wave numbers for this ligand and its metal complexes showed some deviations from the experimental values . These deviations are generally acceptable in theoretical calculation . The deviations that occur in the calculated frequencies are due to ( Hartree - Fock Theory ) ( HFT ) is a single point approximation , and therefore can not adequately treat the correlated motion of electron that occurs due to electron - electron interaction .

Neglected of electron correlation has been blamed for systematic HF errors such as underestimated bond lengths and overestimated vibrational frequencies and electronic spectra <sup>(21)</sup> . ( See figure 3 and 4 ) .

**4.2. Magnetic properties :**

The magnetic moment data of these complexes calculated from the corrected magnetic susceptibilities determined at room temperature are given in table ( 1 ) .

The  $\mu_{eff}$  values reported for some complexes are slightly higher than spin – free value due to orbital contribution <sup>(22)</sup> .

The Mn(II) complex has a  $\mu_{eff}$  value of 5.90 B.M. which suggests a spin – free complex . The Fe(II) , Co(II) and Cu(II) have a magnetic moment of 5.35 , 4.48 and 1.70 respectively , which are typical of ions in an octahedral environment<sup>(23)</sup> . A magnetic moment value of 3.42 B.M. is observed for the Ni(II) complex expected for tetrahedral geometry <sup>(23)</sup> .

*Table ( 2 ) comparison between the experimental and ( theoretical ) vibrational frequencies for ( LOX ) and its metal complexes (  $\nu$   $\text{cm}^{-1}$  )*

| No  | Compound   | $\nu$ OH phenotic $\text{cm}^{-1}$ | $\nu$ NH $\text{cm}^{-1}$ | $\nu$ ( C = H ) $\text{cm}^{-1}$                    | $\nu$ ( C – O – C ) $\text{cm}^{-1}$                    | $\nu$ M – N $\text{cm}^{-1}$ | $\nu$ M – Cl $\text{cm}^{-1}$ |
|---|--|------------------------------------|---------------------------|---|---|------------------------------|-------------------------------|
| LOX   | $\text{C}_{15}\text{H}_{11}\text{BrN}_4\text{O}_2$ | 3420 wbr.<br>( 3440 ) P            | 3010 ( s )<br>( 3043 ) p  | 1616 ( vs ) , 1590 ( s )<br>( 1620 ) p , ( 1577 ) p | 1315 ( Asy ) , 1270 ( Sy )<br>[1334(Asy) , 1277(sy) ] p | -                            | -                             |
| 1   | [ Mn ( LOX) <sub>2</sub> Cl <sub>2</sub> ]         | 3400 br.<br>( 3433 ) p             | 3010 w<br>( 305 ) p       | 1615 ( vs ) , 1550 ( s )<br>( 1625 ) p , ( 1529 ) p | 1315(Asy) , 1270(sy)<br>[1340(Asy) , 1284(sy)]p         | 460 w<br>( 478 ) p           | 352 w<br>( 370 ) p            |
| 2   | [ Fe(LOX) <sub>2</sub> Cl <sub>2</sub> ]           | 3360 br.<br>( 3433 ) p             | 3010 ( s )<br>( 3040 ) p  | 1615 ( vs ) , ( 1580 ( s )<br>( 1630 ) p ( 1560 ) p | 1315(Asy) , 1270(sy)<br>[1358(Asy) , 1295(sy)]p         | 465 w<br>( 485 ) p           | 323 w<br>( 335 ) p            |
| 3   | [ Co(LOX) <sub>2</sub> Cl <sub>2</sub> ]           | 3400 br.<br>( 3429 ) p             | 3000 w<br>( 3023 ) p      | 1615 ( vs ) , 1555 ( s )<br>( 1636 ) p , ( 1552 ) p | 1315(Asy) , 1270(Sy)<br>[1327(Asy) , 1258(Sy)]p         | 425 w<br>( 441 ) p           | 340 w<br>( 364 ) p            |
| 4   | [ Ni(LOX) <sub>2</sub> ] Cl <sub>2</sub>           | 3400 br.<br>( 3451 ) p             | 3001 w<br>( 3023 ) p      | 1616 ( sh ) , 1555 ( m )<br>( 1622 ) p , ( 1581 ) p | 1315(Asy),(1270(Sy)<br>[1345(Asy) , (1268(Sy)]p         | 459m<br>( 480 ) p            | -<br>-                        |
| 5   | [ Cu(LOX) <sub>2</sub> Cl <sub>2</sub> ]           | 3410 br.<br>( 3435 ) p             | 3007 w<br>( 3017 ) p      | 1616(vs) , 1560(S)<br>( 1640 ) p ( 1575 ) p         | 1315(Asy) , 1270(Sy)<br>[1333(Asy) , 1280(Sy)]p         | 439 m<br>( 448 ) p           | 255 w<br>( 265 ) p            |
| Sy = Symmetrical , Asy = Asymmetrical vibration , p = Semi – Empirical ( PM3) |  |                                    |                           |   |   |                              |                               |

### **3.4. Electronic Spectra :**

Ultra violet Spectra of (LOX) show absorption bands (227 nm) ( $44053\text{ cm}^{-1}$ ) and (300 nm) ( $33333\text{ cm}^{-1}$ ) . These bands are shifted to higher wave lengths in the spectra of complexes , indicating the coordination between ligand and metal ions . This absorption was assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transition of either  $N=C-O$  group or  $\pi$  electrons of aromatic 1,3,4- oxidiazole ring <sup>(24)</sup> . Whilst the peak at (385 nm) ( $25974\text{ cm}^{-1}$ ) was assigned to charge transfer <sup>(25)</sup> .

The  $\text{Mn(LOX)}_2\text{Cl}_2$  complex four absorption peaks at ( 380 nm ) (  $26316\text{ cm}^{-1}$  ) assigned to charge transfer . Whilst the peaks at (424 nm) ( $23585\text{ cm}^{-1}$ ) , (529 nm) ( $18904\text{ cm}^{-1}$ ) and (610 nm) ( $16393\text{ cm}^{-1}$ ) assigned to  ${}^6A_{1g} \rightarrow {}^4E_g(G)$  ,

${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$  and  ${}^6A_g \rightarrow {}^4T_{1g}(G)$  transitions respectively . The position of the bands suggested confirmed the octahedral geometry of Mn(II) complex <sup>(22)</sup> .

The spectra of Fe(II) complex showed absorption peak at (255 nm) ( $39216\text{ cm}^{-1}$ ) and (305 nm) ( $32787\text{ cm}^{-1}$ ) assigned to ligand field . The peak at (500 nm) ( $20000\text{ cm}^{-1}$ ) was assigned to charge transfer .

A broad band at (830 nm) (12048) due to  ${}^5T_{2g} \rightarrow {}^5E_g$  transition suggested the octahedral geometry of Fe(II) complex <sup>(26)</sup> .

The ( UV – Vis ) spectrum of the complex [  $\text{Co(LOX)}_2\text{Cl}_2$  ] display absorption bands at ( 230 nm ) (  $43478\text{ cm}^{-1}$  ) and (328 nm) (  $30488\text{ cm}^{-1}$  ) which are assigned to ligand field . The bands at ( 456 nm ) (  $21930\text{ cm}^{-1}$  ) , ( 560 nm ) (  $17857\text{ cm}^{-1}$  ) and (847 nm) (  $11806\text{ cm}^{-1}$  ) pertaining to

${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(\nu_3)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_2)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$  transitions respectively . These electronic spectral data were consistent with high – spin octahedral configuration around Co(II) ion <sup>(27, 28)</sup> .

The Ni(II) complex ,  $[\text{Ni(LOX)}_2]\text{Cl}_2$  , displays an electronic absorption spectrum assignable to tetrahedral environment with a band at (620 nm) ( $16129\text{ cm}^{-1}$ ) assigned to  ${}^3T_1(F) \rightarrow {}^3T_1(P)$  while the  ${}^3T_1(F) \rightarrow {}^3T_2(F)$  transition is not being observed because the limited spectral rang <sup>(29)</sup> . The band at (235 nm) ( $42553\text{ cm}^{-1}$ ) assigned to ligand field . Since the band at (350 nm) ( $28571\text{ cm}^{-1}$ ) was assigned to charge transfer . The electronic spectra of Cu(II) complex one a broad absorption band appeared in the visible region around (660 nm) ( $15152\text{ cm}^{-1}$ ) was assigned to the transition  ${}^2E_g \rightarrow {}^2T_{2g}$  of distorted octahedral , whilst the peaks at (390 nm) ( $25641\text{ cm}^{-1}$ ) was assigned to charge transfer <sup>(30)</sup> . The UV absorption and the positions of d – d bands and their assignments are given in table ( 3 ) .

### **4 . 4 . Conductivity Measurements :**

All complexes except of Ni(II) complex show the conductivity measurement values ranging between (9.9 – 15.2)  $\Omega^{-1} . \text{Cm}^2 . \text{mol}^{-1}$  (table 3) in DMSO at room temperature indicating nonionic structure of these complexes . The value of conductivity for the Ni(II) complex (77.4)  $\Omega^{-1} . \text{Cm}^2 . \text{mol}^{-1}$ ) indicating that the complex is (1:2) ionic structure <sup>(31)</sup> .

**4.5. Metal : Ligand Ratios :**

The metal : ligand ratios of complexes were determined by the method continuous variation in DMSO , suggest that the metal to ligand stoichiometry is 1:2 for all complexes <sup>(32)</sup> .

According to these results ( Experimental and theoretical ) structural formula of prepared complexes in the work may be proposed in figure ( 5 ) .

**Table ( 3 ) : Comparison between the experimental and theoretical of the electronic spectra of ligand ( LOX ) and its metal**

| No  | Compound                                   | Band position (nm)  | $\Lambda M^*$<br>( $\Omega^{-1}.cm^2.mol^{-1}$ ) | Ratio   | Geometry    |
|-----|--|---|--|---------|-------------|
| LOX | $C_{15}H_{11}BrN_4O_2$                     | (237)p ,227<br>(318)p ,300<br>(409)p ,385                               | -  | -       | $C_1$       |
| 1   | [ Mn ( LOX) <sub>2</sub> Cl <sub>2</sub> ] | (379)p ,380<br>(435)p ,424<br>(550)p ,529<br>(669)p ,610                | 15.2   | Neutral | Octahedral  |
| 2   | [ Fe(LOX) <sub>2</sub> Cl <sub>2</sub> ]   | (259)p ,255<br>(313)p ,(305)<br>(523)p ,500<br>(838)p ,830              | 9.9  | Neutral | Octahedral  |
| 3   | [ Co(LOX) <sub>2</sub> Cl <sub>2</sub> ]   | (243)p ,230<br>(330)p ,328<br>(465)p ,456<br>(581)p ,560<br>(875)p ,847 | 12.6   | Neutral | Octahedral  |
| 4   | [ Ni(LOX) <sub>2</sub> ] Cl <sub>2</sub>   | (255)p ,235<br>(351)p ,350<br>(650)p ,620                               | 77.4   | 1:2     | Tetrahedral |
| 5   | [Cu(LOX) <sub>2</sub> Cl <sub>2</sub> ]    | (385)p ,390<br>(668)p ,660  | 13.0   | Neutral | Octahedral  |

$\Lambda M^*$  : Molar conductivities .

P = Semi – Empirical ( PM3 )



**4.6. Semi – Empirical Quantum Mechanical ( PM3) Method :**

**Optimized Geometries and Energies :**

The conformation of the host and complexes obtained from ( Molecular Mechanics ) ( MM ) calculations of HyperChem<sup>(33,34)</sup> were fully re-optimized by using the PM3 method to estimate the binding energy and the enthalpies of formation for the complexes . The total electronic energy are directly connected for calculation of the complexation energy which can be calculated theoretically as follow .

$$\Delta E_{complexation} = E_{complex} - (E_{Ion} + E_{ligand})$$

(( Where  $\Delta E_{complexation}$  represents the theoretical complexation energy which refers to the ion selectivity )). Since the binding energy and the enthalpies of formation are directly connected for the calculation of complexation energy , the complexation energy (  $E_{complex} - ( E_{Ion} + E_{Ligand} )$  ) is exactly the same as the enthalpies of formation  $\Delta H_f = \Delta H_{complex} - (\Delta H_{Ion} + \Delta H_{Ligand})$  . Form the results obtained in table (4) , the relative stability of these complexed could be calculated from the total electronic energies . The smaller the result of total electronic energies (  $\Delta E_{complexation}$  ), the more stable complex . Thus , the trend of the stability of the complexes follows the order  $Cu > Co > Fe > Mn$ .

This order agrees with the conclusions reached by Irving and Williams <sup>(35)</sup> . The Cu(II) complex is the most stable of the studied complexes , probably the stability of complexes are increased with the increasing the of number of electrons of electrons in the outer sheel according to Irving – Williams series <sup>(36)</sup> .

The Ni(II) complex tetrahedral geometry is less stable than the coordination compound of octahedral geometry <sup>(25)</sup> .

**Table ( 4 ) : total energies (  $K cal.mol^{-1}$  ) , heat of formation in (  $K cal.mol^{-1}$  ) and binding energies for ( LOX ) and its metal complexes**

| No  | Compound  | Semi-Empirical ( PM3)(K cal.mol <sup>-1</sup> ) |                    |                      | Geometry    | Symmetry |
|-----|---|---|--------------------|----------------------|-------------|----------|
|     |   | $\Delta E_{Total\ energy}$                      | $\Delta H_f^\circ$ | $\Delta E_{Binding}$ |             |          |
| LOX | C <sub>15</sub> H <sub>11</sub> BrN <sub>4</sub> O <sub>2</sub> | -81465.464                                      | -75.134            | -3659.195            | -           | C1       |
| 1   | [ Mn ( LOX) <sub>2</sub> Cl <sub>2</sub> ]                      | -186552.059                                     | -81.150            | -7513.189            | Octahedral  | C1       |
| 2   | [ Fe(LOX) <sub>2</sub> Cl <sub>2</sub> ]                        | -189878.497                                     | -102.389           | -7728.329            | Octahedral  | C1       |
| 3   | [ Co(LOX) <sub>2</sub> Cl <sub>2</sub> ]                        | -195842.217                                     | -131.074           | -7760.114            | Octahedral  | C1       |
| 4   | [ Ni(LOX) <sub>2</sub> ] Cl <sub>2</sub>                        | -186601.999                                     | -79.589            | -7191.870            | Tetrahedral | C1       |
| 5   | [Cu(LOX) <sub>2</sub> Cl <sub>2</sub> ]                         | -204845.920                                     | -119.348           | -7487.991            | Octahedral  | C1       |

Electron distribution govern the electrostatic potential of the molecules . The electrostatic potential describes the interaction of energy of the molecular system with a positive point charge . The electrostatic potential is useful for finding sites of reaction in a molecule , positively charged species tend to attack a molecule where the electrostatic potentials is strongly negative ( electrophilic attack ) . The electrostatic potentials of free ligand was calculated and plotted as 2D contour to

investigate the reactive sites of molecule . We can interpret the stereochemistry and rates of many reactions involving electrophiles and nucleophiles in terms of the properties of frontier orbitals HOMO (highest occupied molecular orbital ) and LUMO ( lowest unoccupied molecules orbital ) .

Overlap between the HOMO and LUMO is a governing factor in many reactions <sup>(37)</sup> . ( See figure – 6 - ) .

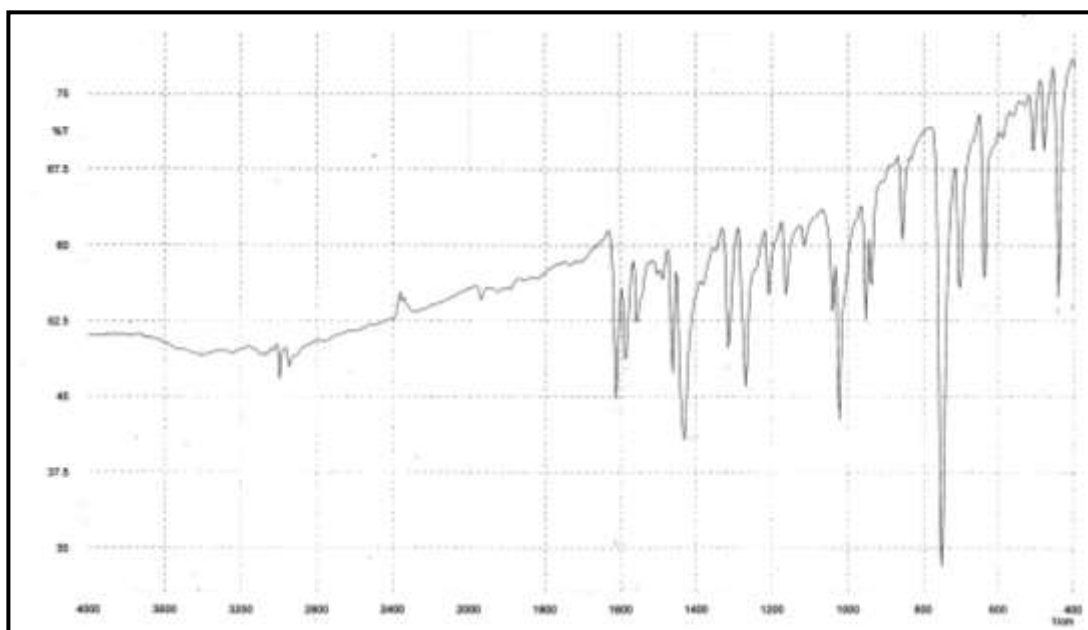
The calculated bond lengths of the compounds are in good agreement with the experimental data <sup>(38)</sup> . ( See figure - 7- ) .

The C = N band becomes too long when attached to the metal . The metal–nitrogen bond were shorter the metal–chloride (see table -5-) . The calculated geometries were in good agreement with our experimental evidences and may serve well for more complex arrangement of these ions .

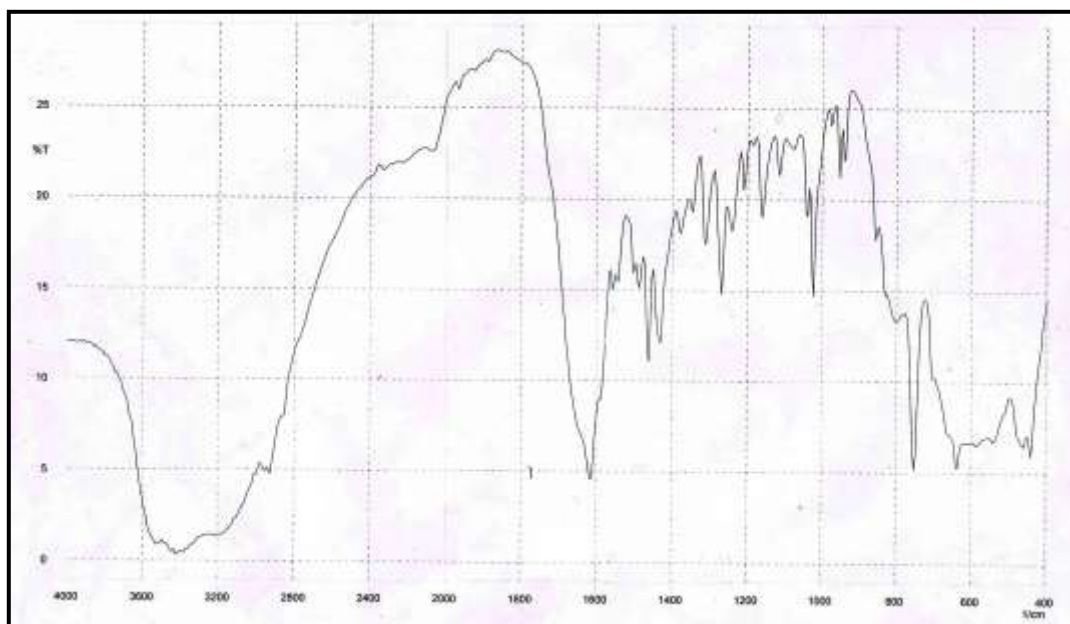
**Table ( 5 ) : Selected Bond length ( Å ° ) for ligand and its metal complexes**

| No.        | Compound  | C=N(oxa) | C=N(azo) | M-N(oxa) | M-N(azo) | M-Cl   |
|------------|---|----------|----------|----------|----------|--------|
| <b>LOX</b> | <b>C<sub>15</sub>H<sub>11</sub>BrN<sub>4</sub>O<sub>2</sub></b> | 1.2902   | 1.2858   | -        | -        | -      |
|            | <b>[ Mn ( LOX)<sub>2</sub> Cl<sub>2</sub> ]</b>                 | 1.3329   | 1.3582   | 1.8448   | 1.9445   | 2.1938 |
|            | <b>[ Fe(LOX)<sub>2</sub> Cl<sub>2</sub> ]</b>                   | 1.3334   | 1.3542   | 1.8691   | 1.9233   | 2.1905 |
|            | <b>[ Co(LOX)<sub>2</sub>Cl<sub>2</sub>]</b>                     | 1.3353   | 1.3564   | 1.8603   | 1.9069   | 2.1835 |
|            | <b>[ Ni(LOX)<sub>2</sub>] Cl<sub>2</sub></b>                    | 1.3328   | 1.3522   | 1.8079   | 1.8542   | -      |
|            | <b>[Cu(LOX)<sub>2</sub>Cl<sub>2</sub>]</b>                      | 1.3352   | 1.3515   | 1.8696   | 1.9143   | 2.1957 |

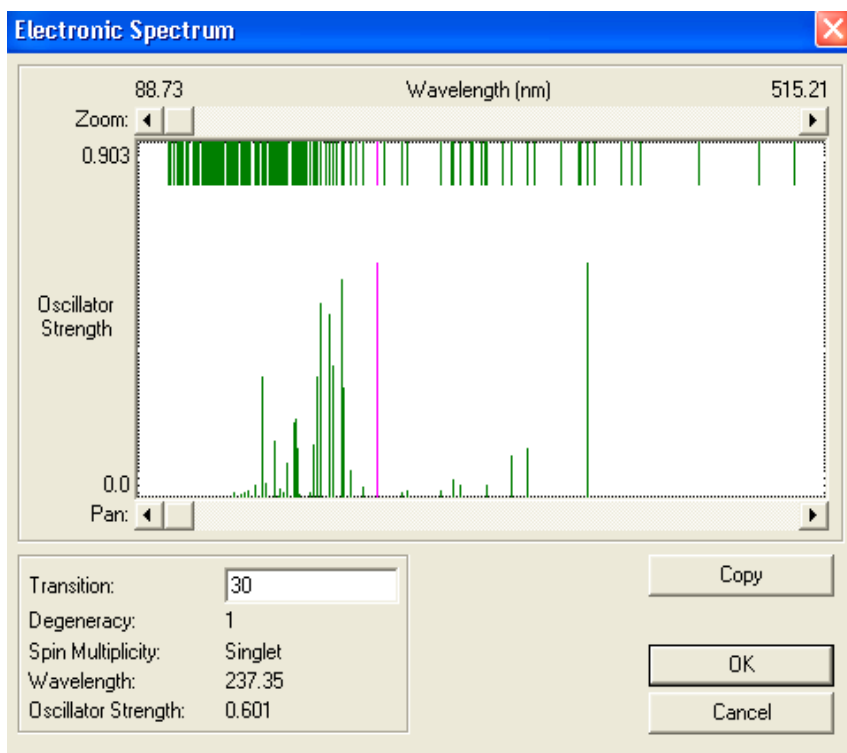
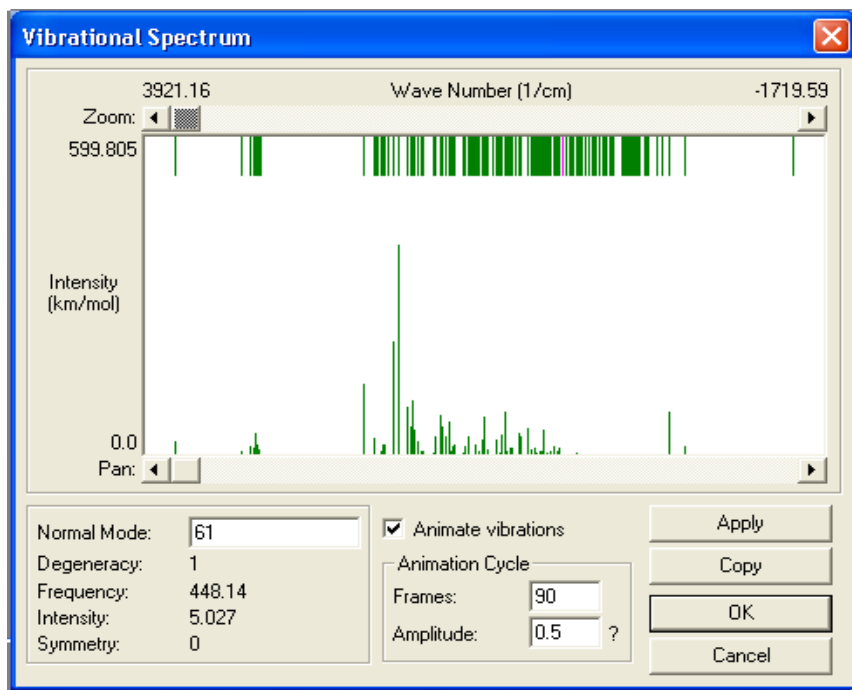
*Oxa = oxadiazole ring , azo = azomethene group*



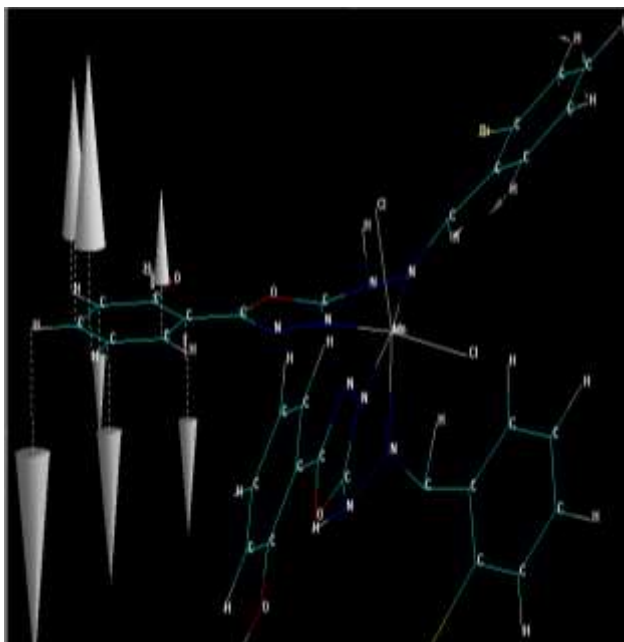
***Figure(1):FTIR Spectrum of (LOX) Ligand***



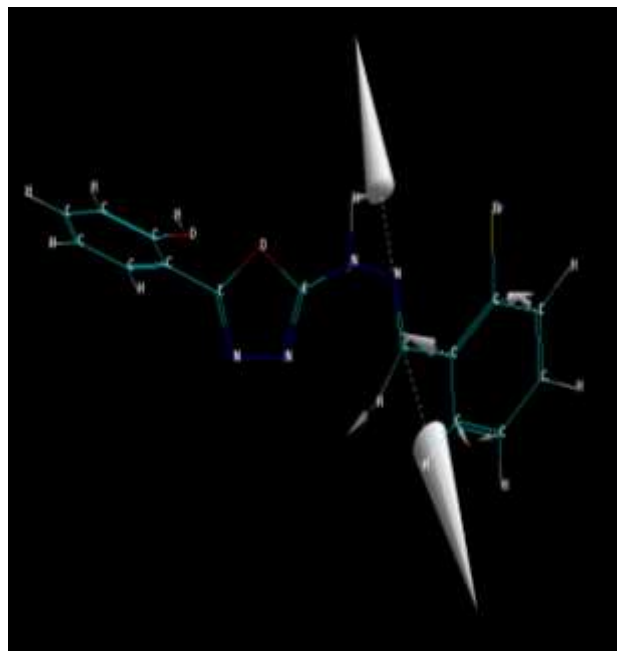
***Figure(2): FTIR Spectrum of [ Ni(LOX)<sub>2</sub>]Cl<sub>2</sub>***



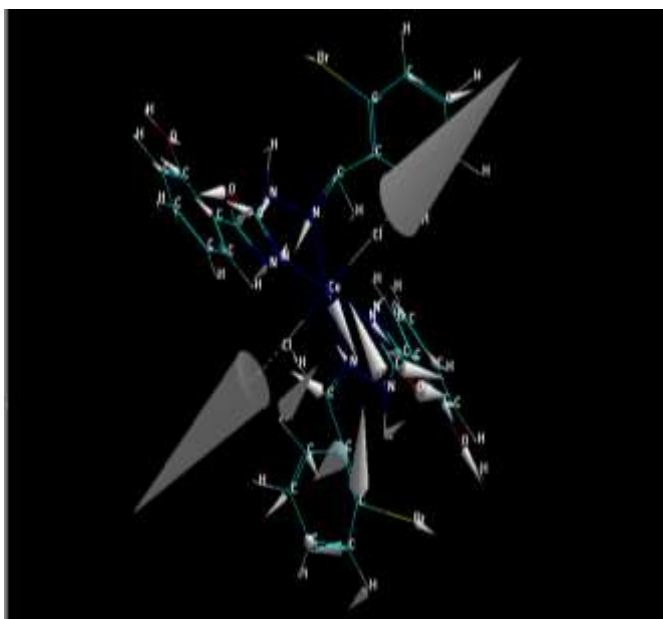
**Figure (3): Theoretical IR and UV Spectra**



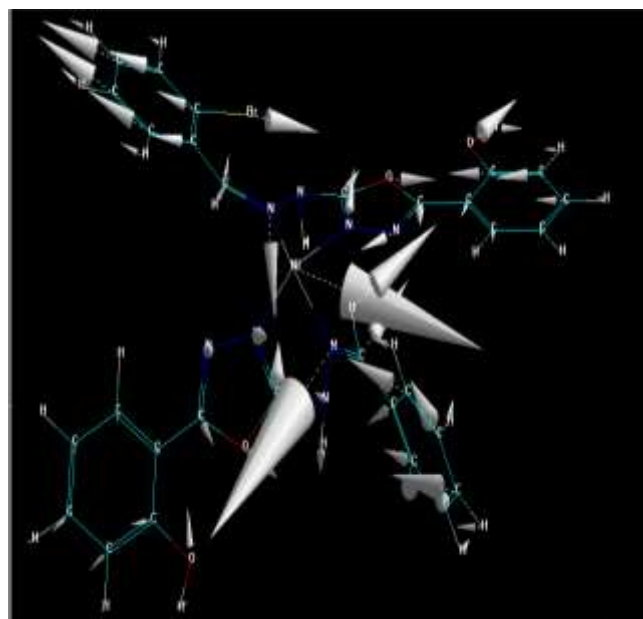
*$\nu(\text{C—H})$  out of plane in Mn-complex*



*$\nu(\text{C=N})$  of free ligand(LOX)*

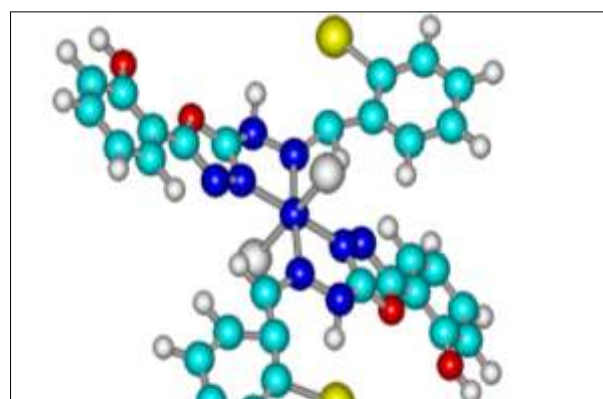
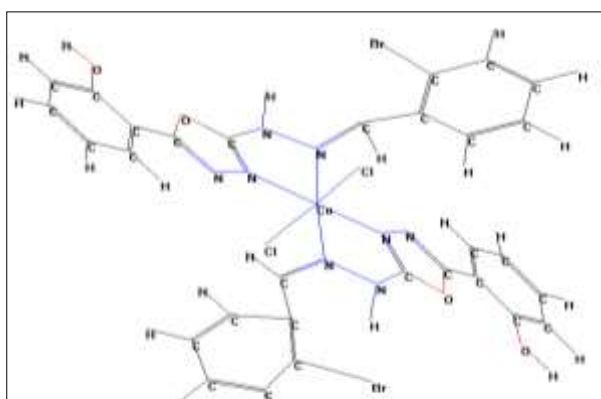
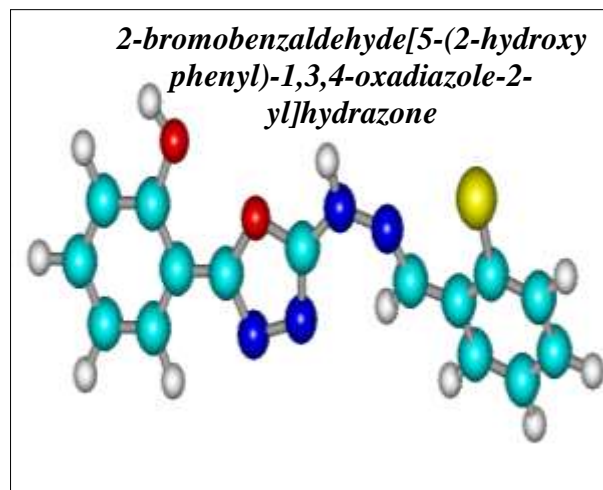
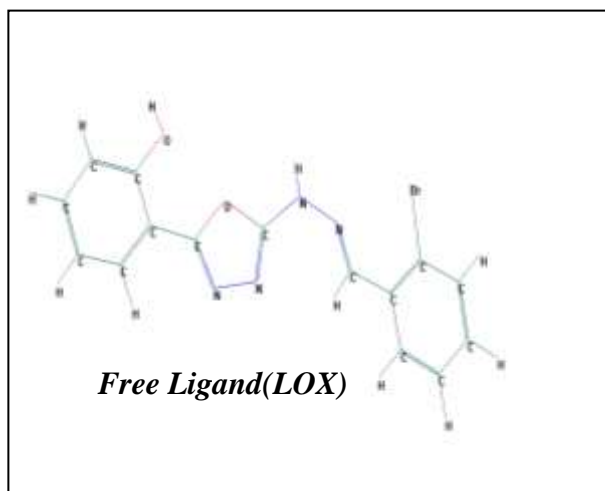


*$\nu(M-Cl)$  in Co-complex*



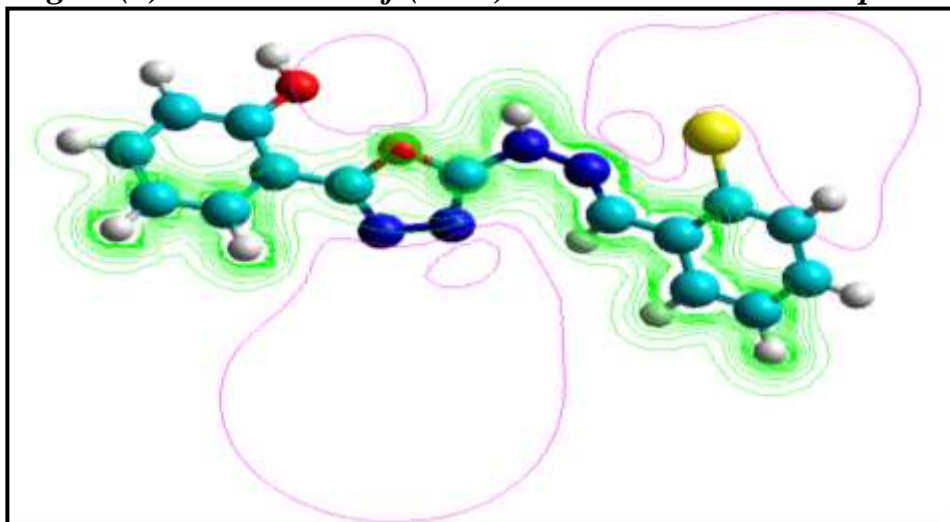
*$\nu(M-N)$  in Ni-complex*

**Figure(4) Some Frequencies of the (LOX) and its Complexes :**

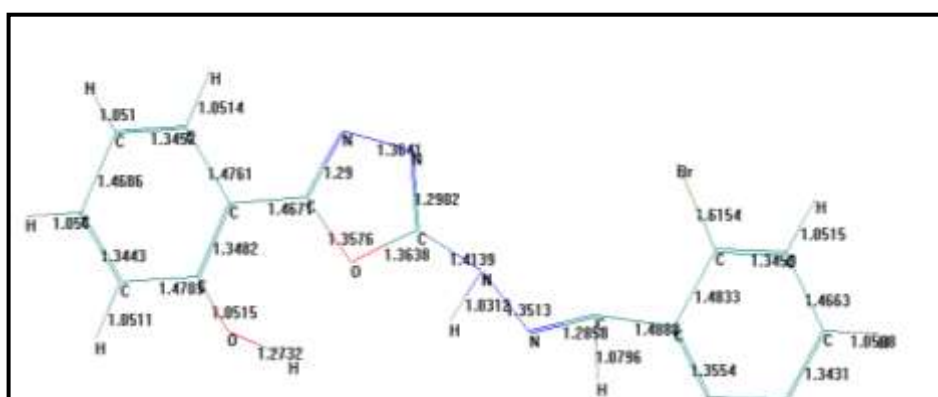




***Figure(5): Geometries of (LOX) and its metal ions complexes***



***Figure(6): HOMO Electrostatic Potential as 2D contour***



***Figure(7) Bond lengths(Å) For –a-(LOX) –b- Co-complex***

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