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

Moslem Hassan Mohamed AL-saadi
Dept. of chemistry , college of Education , AL-Qadisiya university

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 – bromobenzoldehyde [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 heterocyelic 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[1 – 4] 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 [3,5] . 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 . [6]

2 – Program package HyperChem 7.52 [7]

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 :

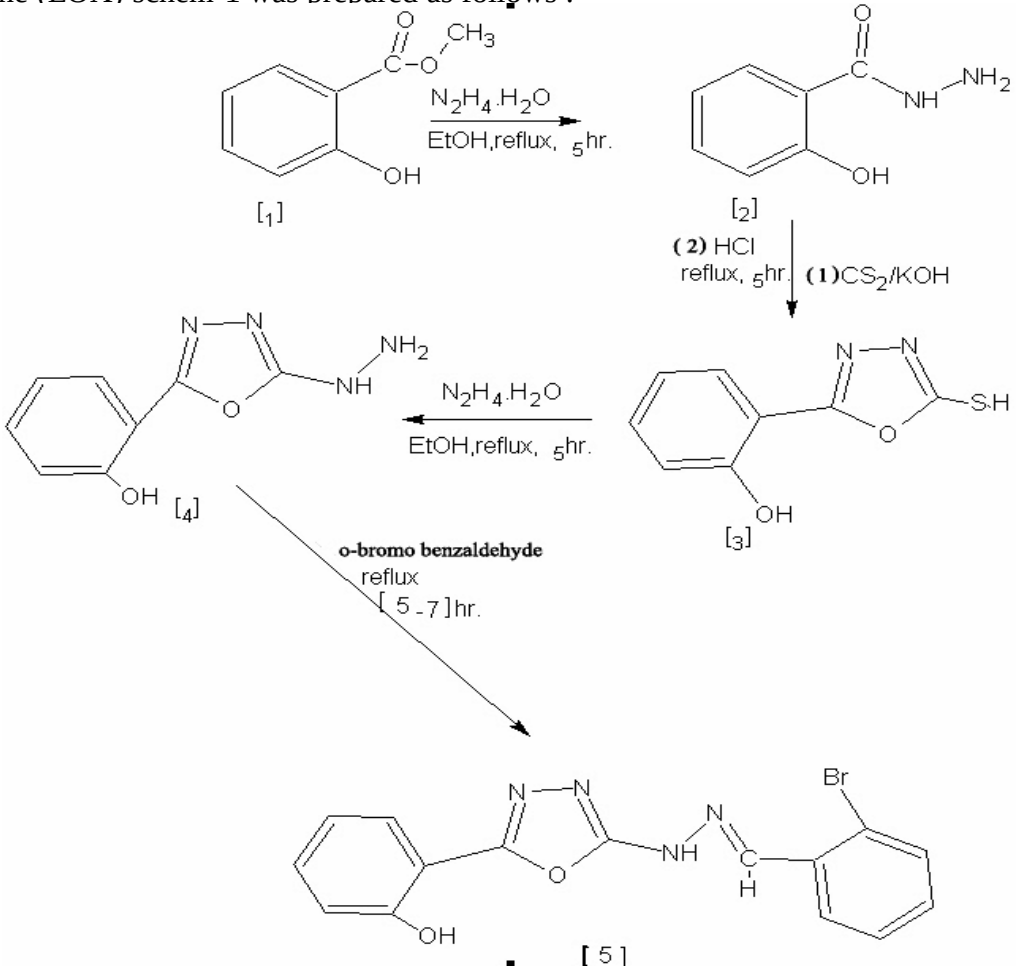
All chemical are supplied of (B.D.H , Fluka and Aldrich) . The FTIR spectra in the range (4000 – 200 cm^{-1}) were recorded as cesium iodide disc FTIR – 8300 shimadzu spectrophotometer .

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] [8,9] .

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_2 (12 mL , 0.2 mole) was refluxed on a water bath for 5 hours , until the evolution of H_2S 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 [10] . 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_2S 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 [8] .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 [11] . 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	Yieled %	μ_{eff} (B.M)	M%	
						CalC.	Found
LOX	$C_{15}H_{11}BrN_4O_2$	Yellow	158-160	80.2	-	-	-
1	[$Mn(LOX)_2Cl_2$]	Pale Brown	174 - 176	75.5	5.90	6.51	(6.42)
2	[Fe (LOX)$_2$ Cl_2]	Yellow	203 - 205	71.8	5.35	6.61	(6.46)
3	[Co (LOX)$_2$ Cl_2]	Gray	186 - 188	78.0	4.48	6.95	(6.86)
4	[Ni (LOX)$_2$] Cl_2	Pale blue	210 - 212	85	3.42	6.92	(6.81)
5	[Cu (LOX)$_2$ Cl_2]	Dark Brown	193 - 195	80.6	1.70	7.45	(7.25)

μ_{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 $\upsilon(C=N)$, υ (C = C) and other bands originate due to phenyl , oxadiazole ring and azomethene group appeared in the region below 1650 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 cm^{-1} due to υ(O – H) phenolic [12] . A moderately strong band at (3010) cm^{-1} appeared in the ligand spectrum , this band is due to υ(N – H) group [13] , two weak bands had been observed at (2940) and 2900 cm^{-1} in the ligand spectrum which are due to υ(C – H) aromatic and aliphatic respectively [14] . These band are stable in position in both ligand and metal complexes . A strong band in the region of (1615) and (1590) cm^{-1} in the ligands is characteristics of υ(C = N) ring group . Upon complexation , one band is located almost at the original position at 1616 cm^{-1} due to uncoordinated υ(C = N) and other is shifted to lower frequency (10 – 40) cm^{-1} arising from the coordinated
C = N mode [6,15] .

The bands due to υ(C – O – C) in ligand appear at 1270 cm^{-1} (symmetric) and 1315 cm^{-1} (asymmetric) [6,16,17] .

The position of infrared bands due to heterocyclic oxadiazole ring does not change in the complexes indicating the noncoordination of oxygen (oxadiazole ring)[6] . A bands at (1430 – 1340) cm^{-1} and 645 cm^{-1} have also been appeared in the ligand spectrum , these bands is due to (OH) bending and υ(C – Br) stretching respectively [18,19] . 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 cm^{-1}) region these bands did not present in the spectrum ligand may be attributed to υ(M – N) and υ(M – Cl)[6,20] .

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 [21] . (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 μ_{eff} values reported for some complexes are slightly higher than spin – free value due to orbital contribution [22] .

The Mn(II) complex has a μ_{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[23] . A magnetic moment value of 3.42 B.M. is observed for the Ni(II) complex expected for tetrahedral geometry [23] .

Table (2) comparision between the experimental and (theoretical) vibrational frequencies for (LOX) and its metal complexes (υ cm^{-1})

No	Compound	υ OH phenotic cm^{-1}	υ NH cm^{-1}	υ (C = H) cm^{-1}	υ (C – O – C) cm^{-1}	υ M – N cm^{-1}	υ M – Cl cm^{-1}
LOX	$C_{15}H_{11}BrN_4O_2$	3420 wbr. (3440) P	3010 (s) (3043)p	1616 (vs) , 1590 (s) (1620) p , (1577)p	1315 (Asy) , 1270 (Sy) [1334(Asy) , 1277(sy)] p	-	-
1	[Mn (LOX)2 Cl_2]	3400 br. (3433)p	3010 w (305)p	1615 (vs) , 1550 (s) (1625)p , (1529)p	1315(Asy) , 1270(sy) [1340(Asy) , 1284(sy)]p	460 w (478)p	352 w (370)p
2	[Fe$(LOX)_2$ Cl_2]	3360 br. (3433)p	3010 (s) (3040)p	1615 (vs) , (1580 (s) (1630)p (1560)p	1315(Asy) , 1270(sy) [1358(Asy) , 1295(sy)]p	465 w (485)p	323 w (335)p
3	[Co$(LOX)_2Cl_2$]	3400 br. (3429)p	3000 w (3023)p	1615 (vs) , 1555(s) (1636)p , (1552)p	1315(Asy) , 1270(Sy) [1327(Asy) , 1258(Sy)]p	425 w (441)p	340 w (364)p
4	[Ni$(LOX)_2$] Cl_2	3400 br. (3451)p	3001 w (3023)p	1616 (sh) , 1555 (m) (1622)p , (1581)p	1315(Asy),(1270(Sy) [1345(Asy) , (1268(Sy)]p	459m (480)p	- -
5	[Cu$(LOX)_2Cl_2$]	3410 br. (3435)p	3007 w (3017)p	1616(vs) , 1560(S) (1640)p (1575)p	1315(Asy) , 1270(Sy) [1333(Asy) , 1280(Sy)]p	439 m (448)p	255 w (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 cm^{-1}) and (300 nm) (33333 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 $\pi \to \pi^*$ and $n \to \pi^*$ transition of either $N = C - O$ group or π electrons of aromatic 1,3,4– oxidiazole ring [24] . Whilst the peak at (385 nm) (25974 cm^{-1}) was assigned to charge transfer [25].

The $Mn(LOX)_2Cl_2$ complex four absorption peaks at (380 nm) (26316 cm^{-1}) assigned to charge transfer . Whilst the peaks at (424 nm) (23585 cm^{-1}) , (529 nm) (18904 cm^{-1}) and (610 nm) (16393cm^{-1}) assigned to $^6A_1g \to {}^4Eg(G)$, $^6A_1g \to {}^4T_2g(G)$ *and* $^6Ag \to {}^4T_1g(G)$ ransitions respectively . The position of the bands suggested confirmed the octahedral geometry of Mn(II) complex [22].

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

Abroad band at (830 nm) (12048) due to $^5T_2g \to {}^5Eg$ transition suggested the octahedral geometry of Fe(II) complex [26] .

The (UV – Vis) spectrum of the complex [$Co(LOX)_2Cl_2$] display absorption bands at (230 nm) (43478 cm^{-1}) and (328 nm) (30488 cm^{-1}) which are assigned to ligand field . The bands at (456 nm) (21930 cm^{-1}) , (560 nm) (17857 cm^{-1}) and (847 nm) (11806 cm^{-1}) pertaining to $^4T_1g(F) \to {}^4A_2g(F)(\upsilon_3), {}^4T_1g(F) \to {}^4T_1g(P)(\upsilon_2)$ *and* $^4T_1g(F) \to {}^4T_2g(F)(\upsilon_1)$ transitions respectively . These electronic spectral data were consistent with high – spin octahedral configuration around Co(II) ion [27, 28] .

The Ni(II) complex , $[Ni(LOX)_2]Cl_2$, displays an electronic absorption spectrum assignable to tetrahedral environment with a band at (620 nm) (16129 cm^{-1}) assigned to $^3T_1(F) \to {}^3T_1(P)$ while the $^3T_1(F) \to {}^3T_2(F)$ transition is not being observed because the limited spectral rang [29] . The band at (235 nm) (42553 cm^{-1}) assigned to ligand field . Since the band at (350 nm) (28571 cm^{-1}) was assigned to change transfer . The electronic spectra of Cu(II) complex one a broad absorption band appeared in the visible region around (660 nm) (15152 cm^{-1}) was assigned to the transition $^2Eg \to {}^2T_2g$ of distorted octahedral , whilst the peaks at (390 nm) (25641 cm^{-1}) was assigned to change transfer [30] . 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) Ω^{-1}. $Cm^2.mol^-$ (table 3) in DMSO at room temperature indicating nonionic structure of these complexes . The value of conductivity for the Ni(II) complex (77.4) Ω^{-1}. $Cm^2.mol^{-1}$) indicating that the complex is (1:2) ionic structure [31] .

4.5. Metal : Ligand Ratios :

The metal : ligand ratios of complexes were determined by the method continous variation in DMSO , suggest that the metal to ligand stoichiometry is 1:2 for all complexes [32] .

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)	ΛM^* $(\Omega^{-1}.cm^2.mol^-)$	Ratio	Geometry
LOX	**$C_{15}H_{11}BrN_4O_2$**	(237)p ,227 (318)p ,300 (409)p ,385	-	-	C_1
1	**[Mn (LOX)$_2$ Cl_2]**	(379)p ,380 (435)p ,424 (550)p ,529 (669)p ,610	15.2	Neutral	Octahedral
2	**[Fe(LOX)$_2$ Cl_2]**	(259)p ,255 (313)p ,(305) (523)p ,500 (838)p ,830	9.9	Neutral	Octahedral
3	**[Co(LOX)$_2$$Cl_2$]**	(243)p ,230 (330)p ,328 (465)p ,456 (581)p ,560 (875)p ,847	12.6	Neutral	Octahedral
4	**[Ni(LOX)$_2$] Cl_2**	(255)p ,235 (351)p ,350 (650)p ,620	77.4	1:2	Tetrahedral
5	**[Cu(LOX)$_2$$Cl_2$]**	(385)p ,390 (668)p ,660	13.0	Neutral	Octahedral

ΛM^*: 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[33,34] 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 relactive 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 [35]. 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 [36] .

The Ni(II) complex tetrahedral geometry is less stable than the coordination compound of octahedral geometry [25] .

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

No	Compound	Semi-Empirical (PM3)(K cal.mol^{-})			Geometry	Symmetry
		ΔE Total energy	ΔH_f°	ΔE Binding		
LOX	$C_{15}H_{11}BrN_4O_2$	-81465.464	-75.134	-3659.195	-	C1
1	[Mn (LOX)2 Cl_2]	-186552.059	-81.150	-7513.189	Octahedral	C1
2	[Fe(LOX)$_2$ Cl_2]	-189878.497	-102.389	-7728.329	Octahedral	C1
3	[Co(LOX)$_2$$Cl_2$]	-195842.217	-131.074	-7760.114	Octahedral	C1
4	[Ni(LOX)$_2$] Cl_2	-186601.999	-79.589	-7191.870	Tetrahedral	C1
5	[Cu(LOX)$_2$$Cl_2$]	-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 nuclephiles in terms of the properties of frontier orbitals HOMO (highest occupied moleculer orbital) and LUMO (lowest unoccupied molecules orbital) .

Overlap between the HOMO and LUMO is a governing factor in many reactions [37] . (See figure – 6 -) .

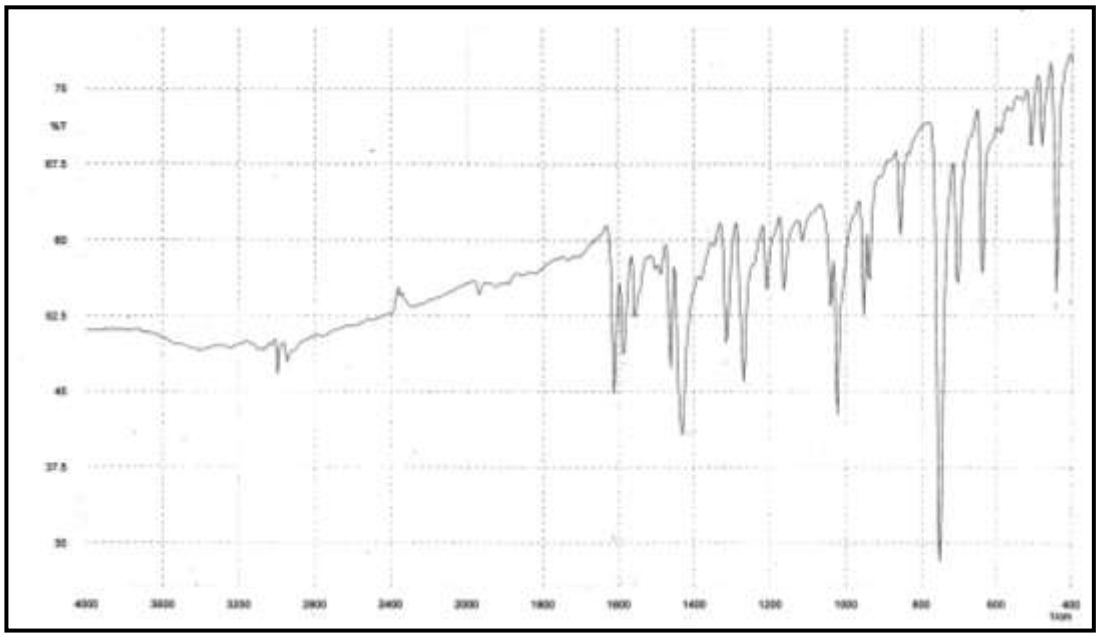
The calculated bond lengths of the compounds are in good agreement with the experimental data [38] . (See figure - 7-) .

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 .

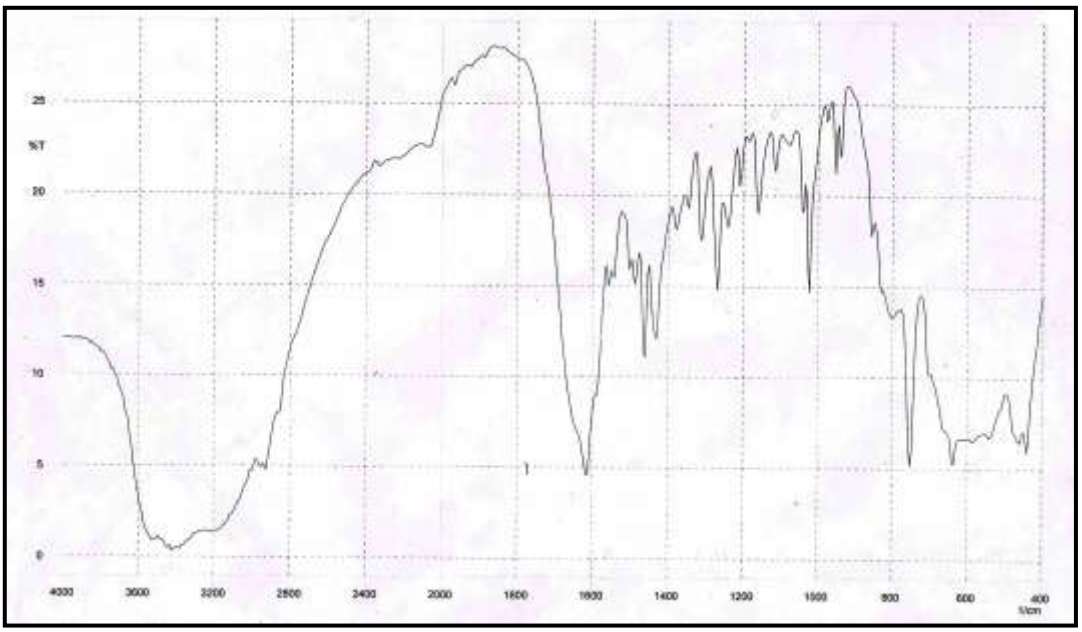
Table (5) : Selected Bond length (A°) for ligand and its metal complexes

No.	Compound	C=N(oxa)	C=N(azo)	M-N(oxa)	M-N(azo)	M-Cl
LOX	**$C_{15}H_{11}BrN_4O_2$**	1.2902	1.2858	-	-	-
1	**[Mn (LOX)$_2$ Cl$_2$]**	1.3329	1.3582	1.8448	1.9445	2.1938
2	**[Fe(LOX)$_2$ Cl$_2$]**	1.3334	1.3542	1.8691	1.9233	2.1905
3	**[Co(LOX)$_2$Cl$_2$]**	1.3353	1.3564	1.8603	1.9069	2.1835
4	**[Ni(LOX)$_2$] Cl$_2$**	1.3328	1.3522	1.8079	1.8542	-
5	**[Cu(LOX)$_2$Cl$_2$]**	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 [$Ni(LOX)_2]Cl_2$

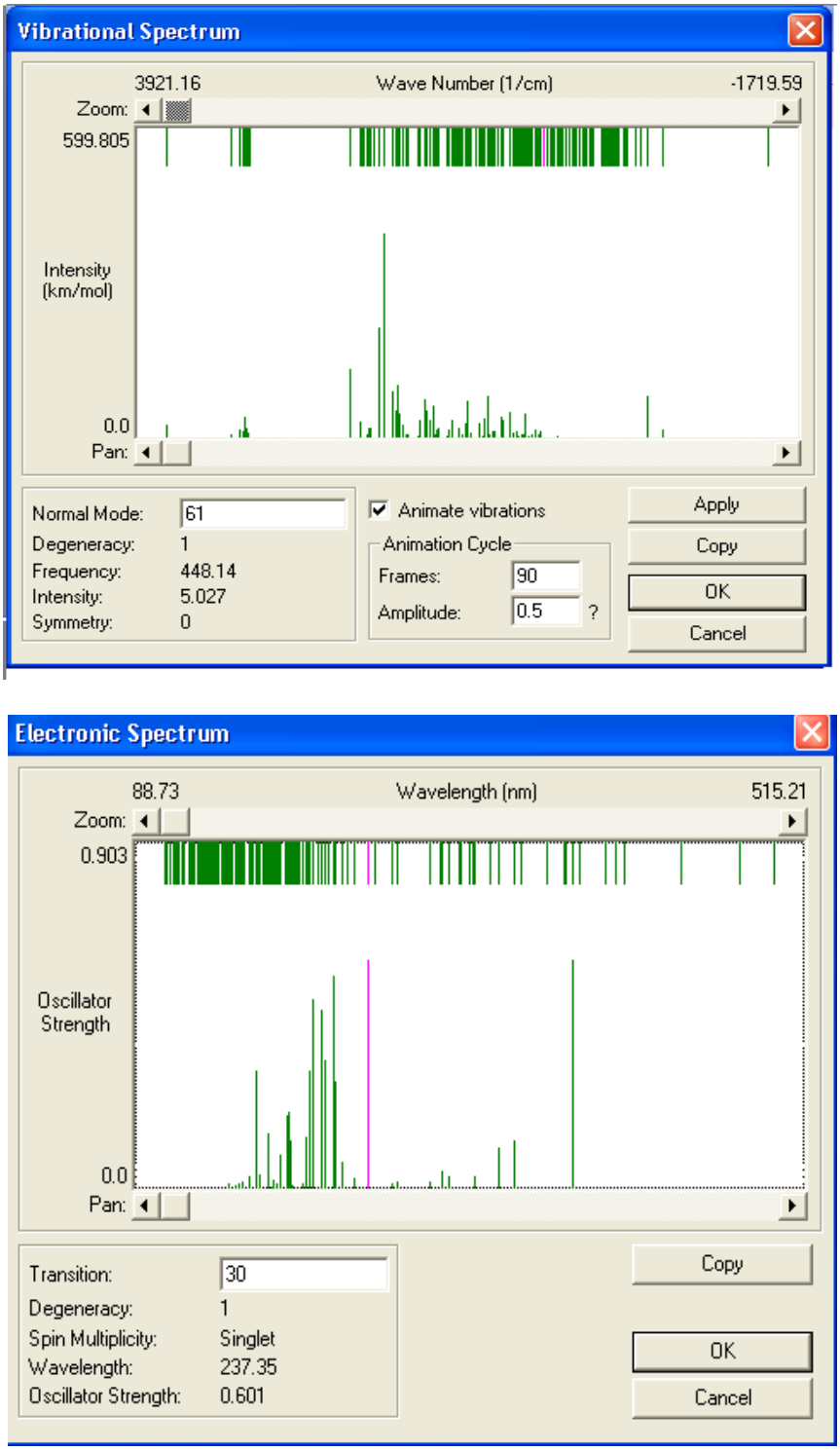
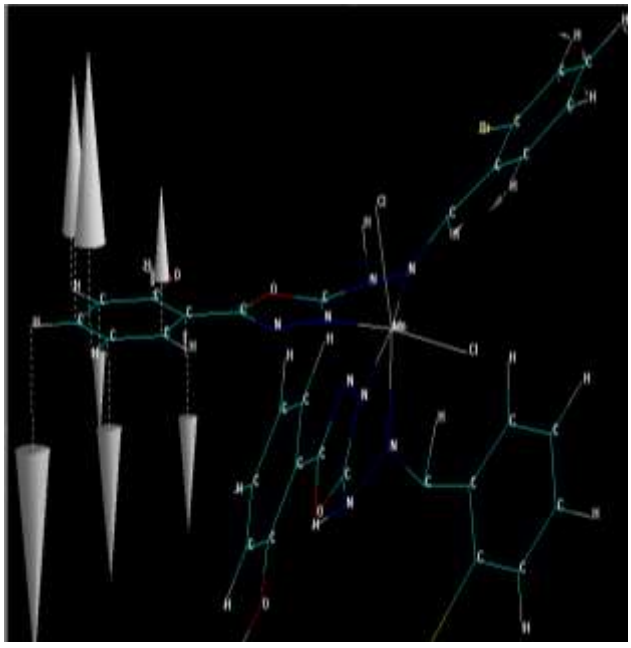
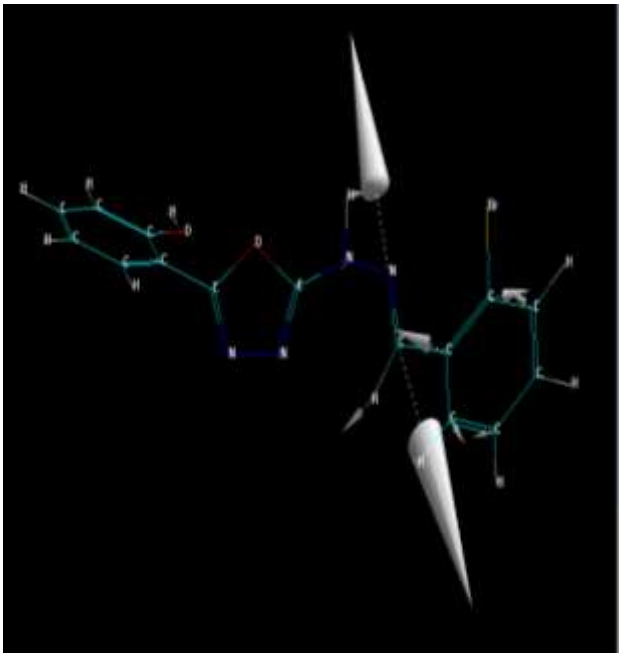


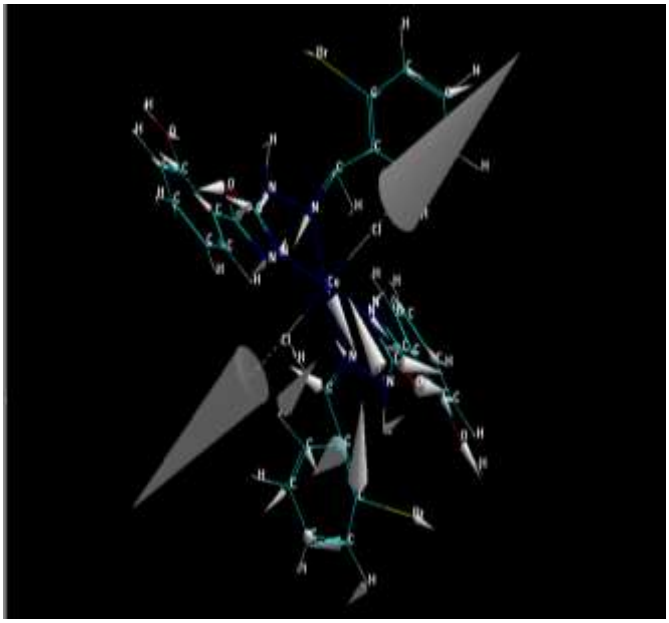
Figure (3): Theoretical IR and UV Spectra



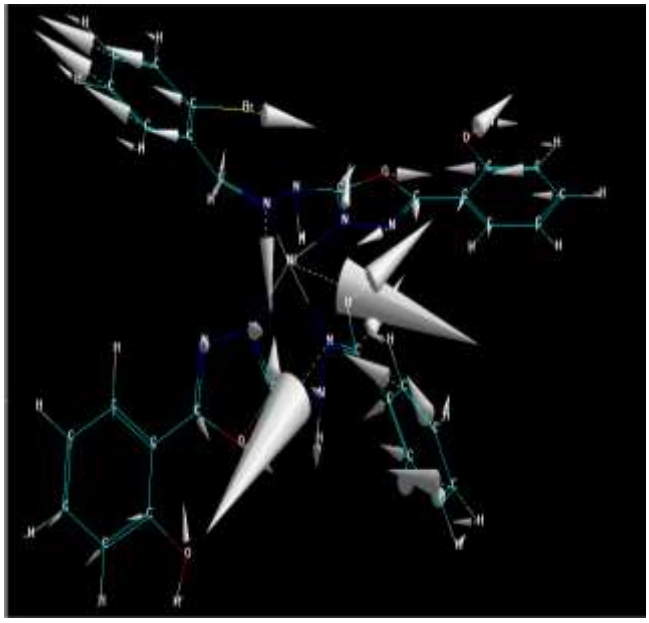
υ(C—H)out of plane in Mn-complex



υ(C=N) of free ligand(LOX)

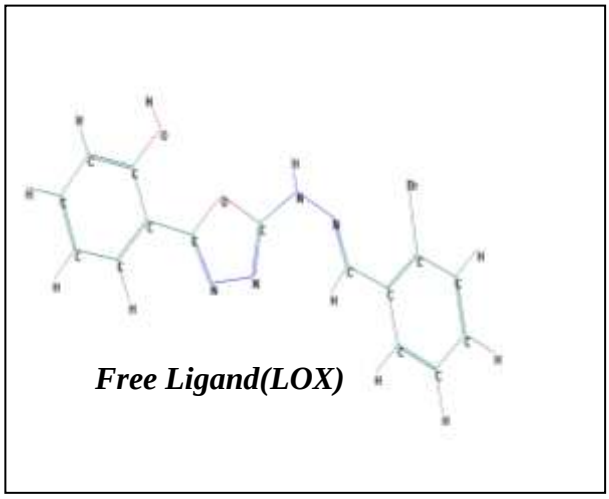


υ (M---Cl) in Co-complex



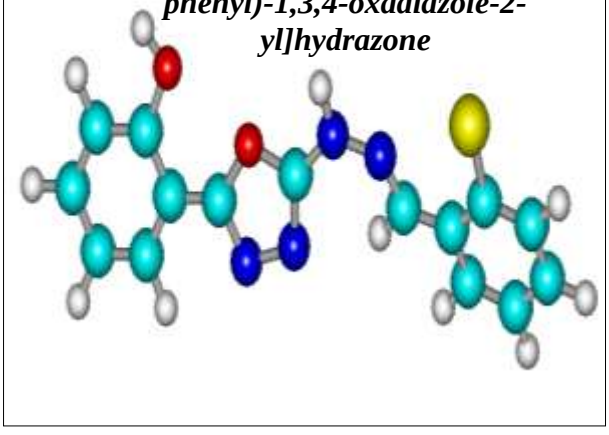
υ(M-N)in Ni-complex

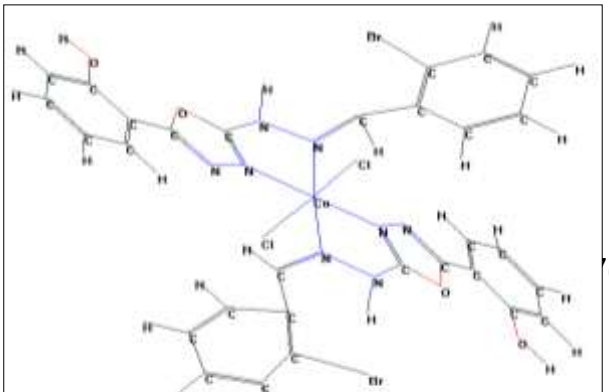
Figure(4) Some Frequencies of the (LOX) and its Complexe :

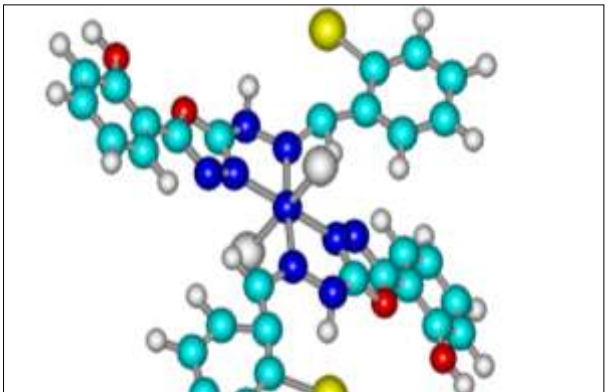


Free Ligand(LOX)

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

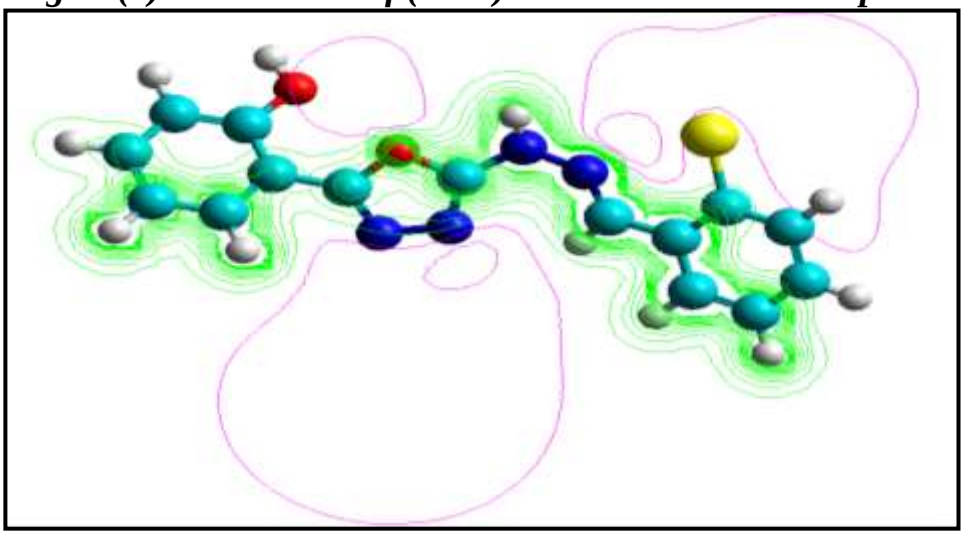




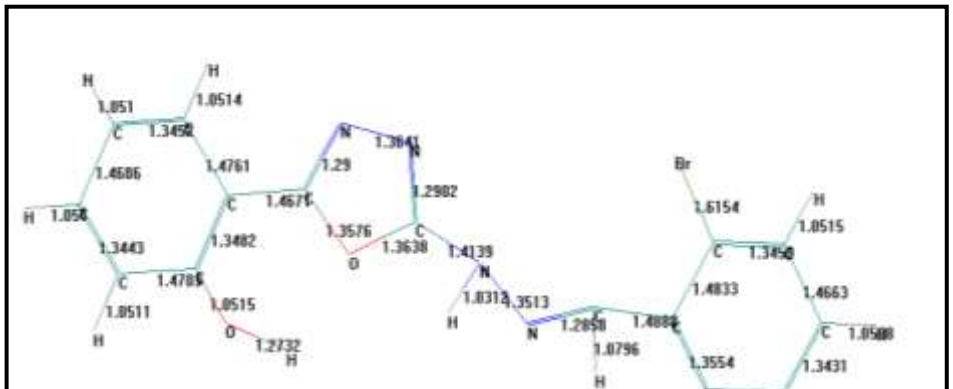


$[Cu(LOX)_2Cl_2]$

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

REFERENCES

1- K.Ladva *et al.*, **India Journal of Chemistry , 35**(**B**),1062-1066,(**1996**).

2- R.R. Kamble, B.S. Sudha and D.G.Bhadregowda , **J. Serb .Chem. Soc., 73(**2), 131-138,(**2008**).

3- A.R.Katritzky *et al* ., **ARKIVOC** ,(**ix**), 62-68,(**2008**).

4- F.Aydogan , Z. Turgut , **Turk J. Chem**. , **26** , 159-68,(**2002**).

5- K.Mohammed Khan , M .Rani *et al* ., **Letters in Organic Chemistry** , **1**, 50-52,(**2004**).

6- S.Sinha,C.Mohan Tripathi and S.Kumar Sengupta, **Bioinorganic Chemistry and Applications** ,Article **ID** 87918, 1-9,(**2007**).

7- HyperChem , **Computational Chemistry** , user manual . Hypercube , inc. printed in Canada , **(1996)** .

8- O.S.Mostafa and T.I.El-Emary , **Bull Korean Chem.Soc.,23**(**4**),567-570, (**2002**).

9- G.Rama Roo,K.Mogilaiah and B.Sreenivasulu, **Indian J. Chem.,35**(**B**),339-344,(**1996**).

10- K.Gudasi,M.Patil,R.Vadavi,R.Shenoy and S. Patil, **J. Serb.Chem.Soc. 72**, (**4**), 357-366,(**2007**).

11- A.Syamal and M.R.Maurya , **Indian Journal of Chemistry, 25**(**A**),934-938,(**1986**).

12- M.Y.Muhamad , **Iraqi J.of Chem.,40**(**1**),1-13,(**1999**).

13- M.Koparir,A.Cansiz, **Molecules,10**,475-480,(**2005**).

14- I.F.Mustafa ,A.T.Atto and H.Y. Ahmed, **Iraqi J. of Chem.,27**(**3**),695-701,(**2001**).

15- N.Demirbas, **TurkJ.Chem.,29**,125-133,(**2005**).

16- M.Ashraf and M.Shaharyar, **Bioorganic and Medicinal Chem.Lett.,xxx**,1-3,(**2007**).

17- M.Belkadi and A.A.Othman, **ARKIVOC,(xi**),183-195,(**2006**).

18- K.J.Khallow, **Iraqi J. of Chem., 27**(**1**),157-163, (**2001**).

19- D.H Williams and I.Fleming **, Spectroscopic Methods in Organic chemistry 2nd Ed.** , England , P. 65 , **(1973)** .

20- N.H.Buttrus , O.M.Al-Ramadane, **National J. of Chem.,23**,344-351-,(**2006**).

21- J.P.Stewart, **Journal of Computational Chemistry ,10**(**2**),209-220,(**1989**).

22- N.David, **Complexes and First Row Transition Elements,** Translated by W.I.Azeez,123-147,(**1984**).

23- F.A.Cotton and G.Wilkinson, **Advanced Inorganic Chemistry, Interscience,** New York , 625 – 628 , (**1980**).

24- D.H.Williams and I.Fleming, **Spectroscopic Methods in Organic Chemistry,** 2nd Ed.,England, 1 – 33 , (**1973**).

25- M.Jaber Al- Jeboori , **National Journal of Chemistry** , **23** , 352 , **(2006)** .

26- C.B.Mahto, **J.Indian Chem.Soc., LV11**,485-489 ,(**1980**).

27- K.Gudasi *et al.*, **J. Serb.Chem.Soc.,72**(**4**),357-366 , (**2007**) .

28- B.Basavaraju *et al*., **Bioinorganic Chemistry and Application**, **ID**42587,6 pages, 1 – 6 , (**2007**) .

29- M.S.Masoud *et al*., **Canadian Journal of Analytical Sciences and Spectroscopy,50**(**4**),207-220,(**2005**).

30- P.Venkateswar Rao *et al*., **Indian Journal of Chemistry , 25**(**A**),482-484, (**1986**).

31- S.F.Akettle, **Coordination Compounds**, Thoms Nelson and Sons London, 186-212,(**1975**).

32- V.G.Cootes and D.Ridley,**J.Chem.Soc.,**166,(**1964**).

33- J.I.Choe ,S.K.Chang, M.Satoshi and S.Nanbu, **Bull.Korean Chem.Soc., 24**(**1**),75-80,(**2003**).

34- J.I.Choe and S.K.Chang, **Bull.Korean Chem.Soc., 23**(**1**),48-52,(**2002**).

35- H.M.Irving ,R.J.P.Williams, **J.Chem.Soc., 11** ,3192 , (**1953**).

36- S.S.Konstantinovic etal.,**J.Serb.Chem.Soc. ,72**(**10**) , 975-981 ,(**2007**).

37- T.Kubar and P.Benjamin, **J Phys.Chem.,B**(**112**),7937-7947,(**2008**).

38- H.Keypour,K.P.Wainwright and M.R.Taylor, **Journal of the Iranian Society, 191**,53-64,(**2004**).