

## Synthesis and Chracterization of 1,3,4- oxadiazole derivatives with some new transition metal complexes

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### Abstract:

A new ligands N-[(1E)-(2-bromo phenyl)methylene]-5-hydrazino-1,3,4-oxadiazol-2-amine (L1) and ethanedial{5-[(2-bromobenzylidene)amino]-1,3,4-oxadiazol-2-yl}hydrazone (L2) and its Co(II), Ni(II) and Cu(II) complexes were synthesized. The authenticity of the ligands (L1, L2). This complexes were established by elemental analysis, conductance and magnetic susceptibility measurements, as well as spectroscopic (FTIR, mass, uv-visible,). The FTIR and mass spectra were corresponding as it is expected. The (L1) acts as a bidentate ligand coordinating through the oxygen atom of the oxadiazole ring and the nitrogen atom of amino group. This view is further supported by the appearance of a band corresponding to the metal-nitrogen and metal-oxygen stretching vibration at  $454\text{--}688\text{ cm}^{-1}$  and  $314\text{--}466\text{ cm}^{-1}$  in the complexes respectively. The (L2) acts as a tridentate ligand coordinating through the two oxygen atoms of the oxadiazole ring and [C=O] group and the nitrogen atom of Schiff base [C=N]. The magnetic studies suggest an tetrahedral and octahedral geometry of the complexes. The complex of Co(III) for the (L1) have shown octahedral geometry, the complex of Cu(II) has shown tetrahedral geometry with (L1). The complexes of [Ni(II), Cu(II)] for the (L2) have shown tetrahedral geometry.

**Keywords :** 1,3,4-oxadiazol, transition metal complexes, IR spectra, mass spectra, electronic spectra.

### الخلاصة:-

تم في هذا البحث تحضير ليكاندين لمشتقات من 1,3,4-او كسادايازول وهي:

1- N-[(1E)-(2-bromophenyl)methylene]-5-hydrazino-1,3,4-oxadiazol-2-amine (L1)

2- ethanedial{5-[(2-bromobenzylidene)amino]-1,3,4-oxadiazol-2-yl}hydrazone (L2)

وكذلك تم تحضير بعض معقدات العناصر الانتقالية Co(II), Cu(II) مع (L1) و Ni(II), Cu(II) مع (L2) وشخصت الصيغ التركيبية لليكاندين ومعقداتهما باستخدام تقنية تحليل العناصر والحساسية المغناطيسية والتوصيل المولاري بالإضافة إلى استخدام أطياف الأشعة تحت الحمراء وطيف الكتلة والأطياف الالكترونية. وتم الاستنتاج بان الليكاند (L1) هو ثنائي السن ويحصل التناسق من خلال ذرة الاوكسجين لحلقة الاوكسادايازول وذرة النيتروجين لمجموعة الامين والليكاند (L2) ثلاثي السن ويحصل التناسق من خلال ذرة الاوكسجين لحلقة الاوكسادايازول وذرة الاوكسجين لمجموعة [C=O] وذرة النيتروجين لمجموعة [C=N] وهذا الاستنتاج يؤكد من خلال تشخيص حزم امتصاص عند  $454\text{--}688\text{ cm}^{-1}$  و  $314\text{--}466\text{ cm}^{-1}$  عائدة إلى تناسق الذرة المركزية مع ذرة النيتروجين والاكسجين على التوالي لكلا الليكاندين. دراسة الخواص المغناطيسية و الاطياف الالكترونية ساهمت في تأكيد الهيئة الفراغية للمعقدات المحضرة حيث وجد ان معقد الكوبلت الثلاثي يمتلك شكل ثنائي السطوح مع (L1) اما معقد النحاس الثنائي فيمتلك شكل رباعي السطوح مع (L1). اما معقدات النيكل الثنائي والنحاس الثنائي فقد امتلكا شكل رباعي السطوح مع (L2).

### 1.Introduction

1, 3, 4-Oxadiazole derivatives are the heterocyclic that have received considerable attention during the last two decades, They found in number of pharmaceutical applications [1-4] several compounds are known as antimicrobial agents [5-7], Some of these compounds have also analgesic, anti-inflammatory, anticancer, anti-HIV agent, antiparkinsonian and antiproliferative agent [8,9,10,11,12]. Some material applications of 1,3,4-oxadiazole derivatives lie in the field of liquid crystals [13], PVC stabilizers [14-16]. 1,3,4-Oxadiazole derivatives are also among the most widely employed electron conducting and hole blocking (ECHB) materials in organic light-emitting diodes (LEDs).. Although some types of metal complexes have found to be good emitters and or excellent electron transporters with excellent thermal properties.

## 2.1 Instrumentation

Elemental C, H and N analysis were carried out on a Thermofinigan flash analyzer, the FTIR spectra in the range (4000-200) cm<sup>-1</sup> were recorded as CsI discs using a Shimadzu FTIR spectrophotometer, molar conductance measurements were made in anhydrous DMSO at 25 °C using Inolabcond 720. The electronic spectra of ligand and their metal complexes have been recorded in the range of (200-900)nm by using T60 U Spectrometer the concentration of solutions 10<sup>-3</sup> M using DMSO as solvent. Melting points were determined in open capillary tubes using an electro thermal melting point /SMP3I apparatus. Mass spectra were recorded in the range (0-800) m/e on a 5973 network mass selective detector .

## 2.2 Preparation of the ligands

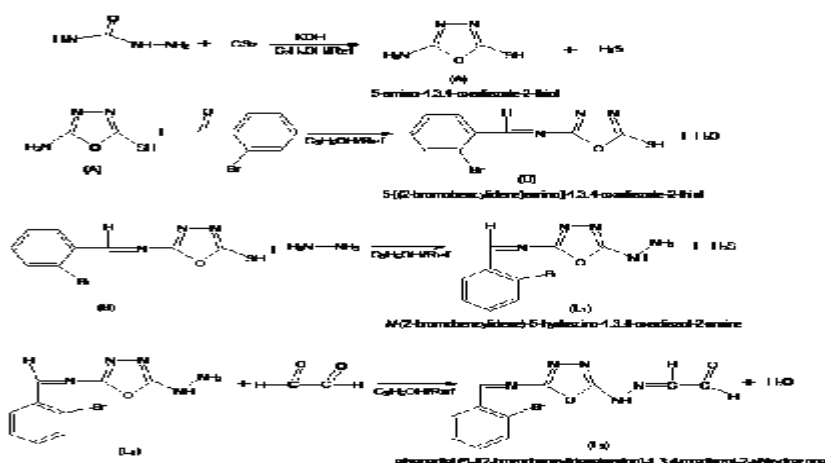
The new ligands N-[(1E)-(2-bromophenyl)methylene]-5-hydrazino-1,3,4-oxadiazol-2-amine (L1) and ethanedial{5-[(2-bromobenzylidene)amino]-1,3,4-oxadiazol-2-yl}hydrazone (L2) (Scheme 1) were prepared as follows:

A mixture of Semicarbazide (7.5g, 0.1mol) and Potassium hydroxide (5.6g, 0.1mol) and CS<sub>2</sub> (7.6 g,0.1 mol) in ethanol absolute (100mL)[14] was refluxed in a water bath for 5 hr or H<sub>2</sub>S gas is cease. The resultant mixture[A] was concentrated by distillation and acidified with dilute hydrochloric acid (0.1 mol) and the white solid which separated was filtered and recrystallised from ethanol. The purity of the compound was followed by TLC on precoated silica gel. Yield: 80 %, m.p. 222-224°C.

A mixture of [A](2.34g,0.02mol) , 2-bromo benzaldehyde (3.7g,0.02mol) in 100ml ethanol was refluxed in a water bath for 8 hr. The resultant mixture[B] yellow solid which separated was filtered and recrystallised from ethanol. The purity of the compound was followed by TLC on precoated silica gel. Yield: 80 %, m.p. 228-230 °C.

A mixture[B] (5.68g,0.02mol) and hydrazine hydrate (1gm,0.02mol) dissolved in ethanol (50mL) was refluxed on a water bath for 6 hr ,until the evolution of H<sub>2</sub>S gas ceased[17-18]. The resultant mixture[L1] was concentrated and separated then filtered and recrystallised from ethanol. The purity of the compound was followed by TLC on precoated silica gel. Yield: 73 %, m.p.217-219°C.

A mixture[L1] (2.82g,0.01mol) and glyoxal (0.58g,0.01mol) dissolved in ethanol (50mL) was refluxed on a water bath for 3 hr, . The resultant mixture[L2] was concentrated and the yellow solid which separated was filtered and recrystallised from ethanol. The purity of the compound was followed by TLC on precoated silica gel. Yield: 76 %, m.p.218°C.



Scheme (1): Synthesis of L1 and L2

## 2.3 Preparation of complexes

### 2.3.1 preparation of L1complexes

The Co(III), Cu(II) complexes were prepared by refluxing the respective hydrated metal chloride (2.73 g,0.01 mol) and (1.7 g,0.01 mol) in 15 ml ethanol with 50 ml of an ethanolic solution of the [L1]( 2.82g,0.01mol) for 4 hr. The resultant solids which separated were filtered, washed with ethanol and dried in air.

### 2.3.2 preparation of L2complexes

The Ni(II), Cu(II) complexes were prepared by refluxing the respective hydrated metal chloride (2.37 g,0.01 mol) and (1.7 g,0.01 mol) in 15 ml ethanol with 50 ml of an ethanolic solution of the [L2]( 3.22g,0.01mol) for 4 hr. The resultant solids which separated were filtered, washed with ethanol and dried in air.

## 3. RESULTS & DISCUSSION

The purity of the ligands and its complexes were checked by TLC using silica gel-G as adsorbent., elemental analysis tabulated in Table (1), Melting point ,magnetic susceptibility, physical properties and molar conductance of all the compounds studied are tabulated in Table (2).. The calculated values were in a good agreement with the experimental values.

Table 1.Analitical data for the (L1,L2)

NO.	Experimental			Theoretical		
	C%	H%	N%	C%	H%	N%
L1	38.25	2.77	24.79	38.32	2.86	24.83
L2	41.40	2.48	21.72	41.02	2.50	21.74

Table 2. conductance, physical properties and magnetic data of the (L1,L2) and its complexes

No	Compound	Molecular formula	Molecular Weight	$\Lambda$ Scm <sup>2</sup> mol <sup>-1</sup>	Melting point	$\mu_{\text{eff}}$ MB
1	L1	C <sub>9</sub> H <sub>8</sub> N <sub>5</sub> OBr	282	-----	217-219	-----
2	[Co(L1) <sub>2</sub> Cl <sub>2</sub> ]	CoC <sub>9</sub> H <sub>8</sub> N <sub>5</sub> OBrCl <sub>2</sub>	692	5.3	128	3.9
3	[Cu (L1) Cl <sub>2</sub> ]	CuC <sub>9</sub> H <sub>8</sub> N <sub>5</sub> OBrCl <sub>2</sub>	415	3.5	209-210	1.6
4	L2	C <sub>11</sub> H <sub>8</sub> N <sub>5</sub> O <sub>2</sub> Br	322	-----	218	-----
5	[Ni (L2) Cl]Cl	NiC <sub>11</sub> H <sub>8</sub> N <sub>5</sub> O <sub>2</sub> Br Cl <sub>2</sub>	416	34	170	2.9
6	[Cu (L2) Cl]Cl	CuC <sub>11</sub> H <sub>8</sub> N <sub>5</sub> O <sub>2</sub> Br Cl <sub>2</sub>	420	53	207-208	1.6

### 3.1 Infra-Red Spectroscopy

The FTIR spectrum for L1 shows a characteristic stretching absorption bands at 3294cm<sup>-1</sup>, 1612 cm<sup>-1</sup>, 1312 cm<sup>-1</sup> and 1425 assigned to  $\nu$ (N-H) group ,C=N of the oxadiazole ring, asymmetrical C-O-C, symmetrical C-O-C stretching respectively[19-20]. The FTIR spectrum for L2 shows a characteristic stretching absorption bands at 3226cm<sup>-1</sup>, 1616 cm<sup>-1</sup>, 1309 cm<sup>-1</sup> and 1448 assigned to  $\nu$ (N-H) group ,C=N of the oxadiazole ring, asymmetrical C-O-C, symmetrical C-O-C stretching respectively.

The C=N and N-H stretching vibrations are important to predict the bonding mode of the ligand ,these bands were shifted to the high or low frequencies in the spectra of complexes compare with ligand, observed changes are the evidences of complexation had happened . The IR data of the complexes are shown in Table (3) and figure(8-11). lists the stretching frequency ( $\nu$ ) for some of the characteristics groups exhibited by the (L1,L2) and complexes.

Table 3: Characteristic absorption bands of (L1,L2) and its complexes

NO	Compound	$\nu$ N-H	$\nu$ C=N	$\nu$ C-O- C asy.	$\nu$ C-O- C sy.	$\nu$ M-N	$\nu$ M-O	$\nu$ M- Cl
1	L1	3294	1612	1315	1425			
2	[Co(L1) <sub>2</sub> Cl <sub>2</sub> ]	3324	1687	1311	1406	688	466	322
3	[Cu (L1) Cl <sub>2</sub> ]	3272	1614	1321	1418	571	422	336
4	L2	3226	1616	1309	1448			
5	[Ni (L2) Cl]Cl	3232	1623	1382	1402	686	314	279
6	[Cu (L2) Cl]Cl	3236	1618	1362	1434	454	365	324

### 3.2 Electronic spectra

The electronic spectra of the ligands (L1) and (L2) under study exhibit three absorption bands due to  $n \rightarrow \pi^*$ ,  $\pi \rightarrow \pi^*$  and  $n \rightarrow \sigma^*$  transitions in the (422-445)nm, (265-275)nm and (245-263)nm respectively[21]. The Co(III) complex exhibits bands at (14814) $\text{cm}^{-1}$  and (24154) $\text{cm}^{-1}$ , assigned to  $^1A_{1g} \rightarrow ^1T_{1g}(P)$  and  $^1A_{1g} \rightarrow ^1T_{2g}(P)$ , in an octahedral field [22]. The Ni(II) complex exhibits bands at (17035) $\text{cm}^{-1}$ , (23094) $\text{cm}^{-1}$  and (37735) $\text{cm}^{-1}$ , assigned to  $^4A_{2g}(F) \rightarrow ^4T_{2g}(F)$ ,  $^4A_{2g}(F) \rightarrow ^4T_{1g}(F)$  and  $^4A_{2g}(F) \rightarrow ^4T_{1g}(P)$  respectively, in a tetrahedral field [23]. These bands supported the octahedral geometry of Co(III) with ligand (L1) and tetrahedral geometry of Cu(II) with ligand (L1).The Ni(II) and Cu (II) complexes with ligand (L2) have shown tetrahedral geometry, as shown in( Table 4) and figures(12-15).

Table 4: Electronic Spectra of (L1,L2) and its Metal Complexes

compound	Band (1)		Band (2)		Band (3)		Charge Transfer		$V_2/V_1$	Geometry
	$\lambda_{\max}$ nm	$\nu\text{cm}^{-1}$	$\lambda_{\max}$ nm	$\nu\text{cm}^{-1}$	$\lambda_{\max}$ nm	$\nu\text{cm}^{-1}$	$\lambda_{\max}$ nm	$\nu\text{cm}^{-1}$		
L1	422	23696	265	37735	245	40816	-----	-----	-----	-----
[Co(L1) <sub>2</sub> Cl <sub>2</sub> ]	675	14814	414	24154	278	35971	254	45045	1.63	Octahedral
[Cu (L1) Cl <sub>2</sub> ]	420	23809	-----	-----	266	37594	233	42918	-----	Tetrahedral
L2	445	22471	275	36363	263	38022	-----	-----	-----	
[Ni (L2) Cl]Cl	587	17035	433	23094	265	37735	251	39840	1.35	Tetrahedral
[Cu(L2) Cl]Cl	-----	-----	-----	-----	-----	-----	218	45871	-----	Tetrahedral

### 3.3 Mass spectra

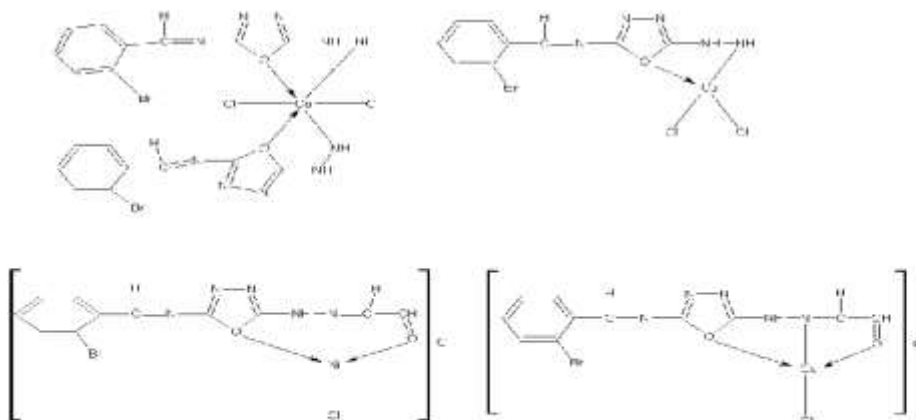
The mass spectrum of the complex [Co(L1)<sub>2</sub>Cl<sub>2</sub>] exhibits a molecular ion peak (M)<sup>+</sup> at m/z 692,the complex spectra shows fragment ion peak at m/z 621 due to (C<sub>18</sub>H<sub>16</sub>N<sub>10</sub>O<sub>2</sub>Br<sub>2</sub>Co)<sup>+</sup>, the spectra shows another peaks at m/z (128,183 and 311) due to (C<sub>2</sub>N<sub>2</sub>OCo)<sup>+</sup>, (C<sub>7</sub>H<sub>5</sub>BrN)<sup>+</sup> and (C<sub>9</sub>H<sub>5</sub>N<sub>3</sub>OBrCo)<sup>+</sup> respectively as shown in(Fig.16).

The mass spectrum of the complex [Cu (L1) Cl<sub>2</sub>] shows a molecular ion peak at m/z [M+1] 416. the complex spectra shows fragment ion peak at m/z 399 and 384 due to (C<sub>9</sub>H<sub>6</sub>BrN<sub>4</sub>OCuCl<sub>2</sub>)<sup>+</sup> and (C<sub>9</sub>H<sub>5</sub>BrN<sub>3</sub>OCuCl<sub>2</sub>)<sup>+</sup> respectively. the complex spectra shows fragment ion peak with loss two chlorine atom at m/z (349,313) due to (C<sub>9</sub>H<sub>5</sub>BrN<sub>3</sub>OCuCl)<sup>+</sup> and (C<sub>9</sub>H<sub>5</sub>BrN<sub>3</sub>OCu)<sup>+</sup> respectively. the spectra shows another peaks at m/z (70, 83 and 183) due to (C<sub>2</sub>N<sub>2</sub>O)<sup>+</sup>, (C<sub>2</sub>N<sub>3</sub>O)<sup>+</sup> and (C<sub>7</sub>H<sub>5</sub>BrN)<sup>+</sup> respectively as shown in(Fig.17).

The mass spectrum of the complex  $[\text{Ni}(\text{L2})\text{Cl}]\text{Cl}$  shows a molecular ion peak at  $m/z (\text{M})^+ 415$ , the complex spectra shows fragment ion peak at  $m/z 387$  and  $374$  due to  $(\text{C}_{10}\text{H}_7\text{BrN}_5\text{ONiCl})^+$  and  $(\text{C}_9\text{H}_4\text{BrN}_5\text{ONiCl})^+$  Respectively. The spectrum shows another peaks at  $m/z 70, 84, 111, 183$  and  $211$  due to  $(\text{C}_2\text{N}_2\text{O})^+$ ,  $(\text{C}_2\text{HN}_3\text{O})^+$ ,  $(\text{C}_3\text{HN}_4\text{O})^+$ ,  $(\text{C}_7\text{H}_5\text{BrN})^+$  and  $(\text{C}_8\text{H}_6\text{BrN}_2)^+$  respectively as shown in(Fig.18).

The mass spectrum of the complex  $[\text{Cu}(\text{L2})\text{Cl}]\text{Cl}$  shows a molecular ion peak at  $m/z (\text{M})^+ 420$ , This complex shows another a fragment ion peak with loss of chlorine atom at  $m/z 384$ , the spectrum shows another peaks at  $m/z 111$  and  $183$  due to  $(\text{C}_3\text{HN}_4\text{O})^+$  and  $(\text{C}_7\text{H}_5\text{BrN})^+$  respectively as shown in(Fig.19).

On the basis of the preceding discussion, the structure of the complexes suggested as follows in scheme(2)below .



Scheme(2): Shows proposed structures of complexes

Analytical and spectra data (IR, mass spectra ) of all synthesized compounds were in full agreement with the proposed structure

#### 4. conclusion

The ligands N-[(1E)-(2-bromo phenyl)methylene]-5-hydrazino-1,3,4-oxadiazol-2-amine (L1) and 5-[(2-bromo benzylidene)amino]-1,3,4-oxadiazol-2-amine (L2) were successfully synthesized. The ligands were treated to different transition metal salt to afford the corresponding complexes. It may be concluded that the ligands coordinate through Nitrogen atom and oxygen atom as shown in figures ( 5-6). This view is further supported by the appearance of a bands corresponding to the metal-nitrogen and metal- oxygen stretching vibrations at  $454\text{--}688\text{ cm}^{-1}$  and  $314\text{--}466\text{ cm}^{-1}$  in the complexes respectively [24]. the Co atom leading to the formation octahedral geometry with the (L1) and Cu atom leading the formation tetrahedral geometry with the (L1). tetrahedral geometry was proposed for the (Ni (II) and Cu(II) prepared complexes with the (L2).

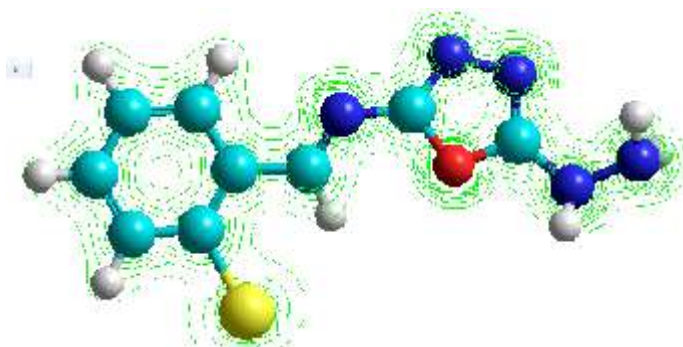


Fig.1. Total charge density of L1

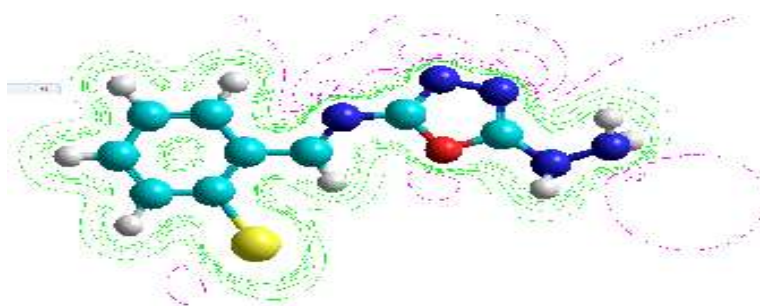


Fig.2. Electrostatic potential of L1



Fig. 3. Total charge density of L2

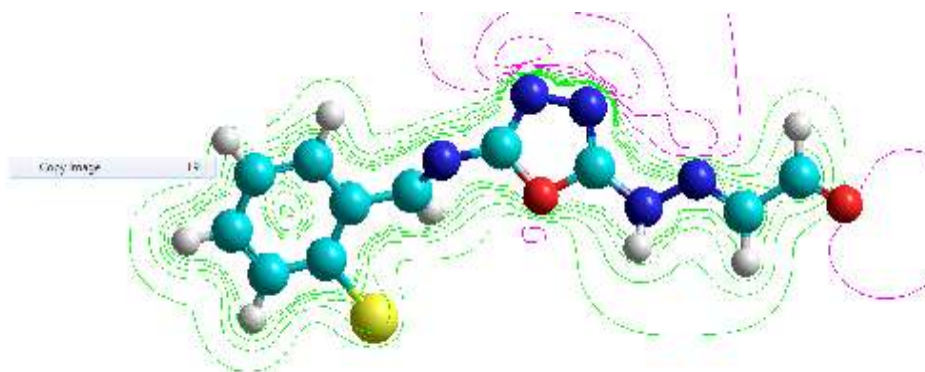


Fig.4. Electrostatic potential of L2

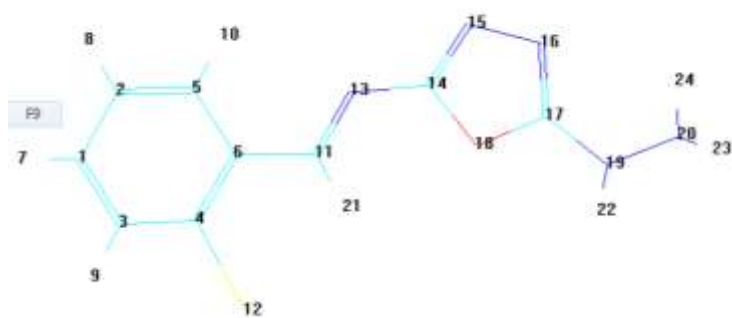


Fig.5. L

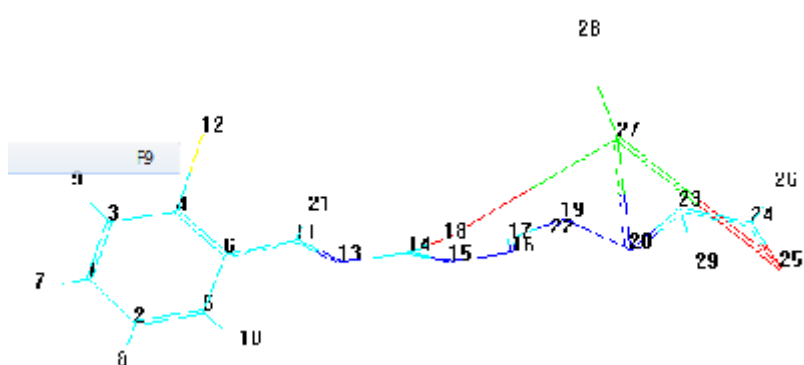


Fig.6. L2-Ni

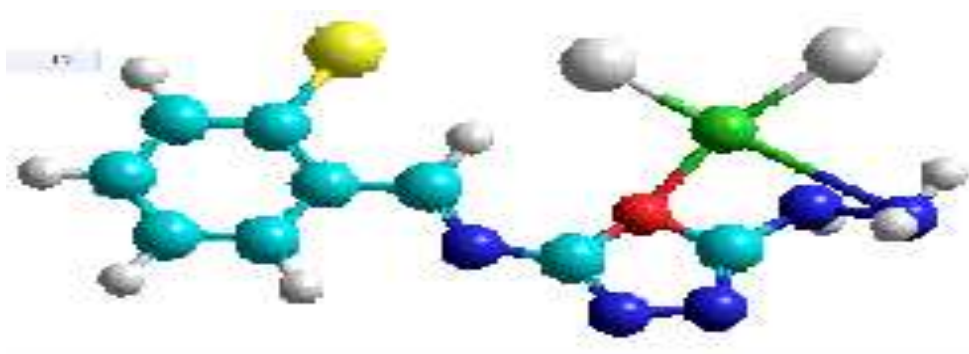


Fig.7. L1-Cu



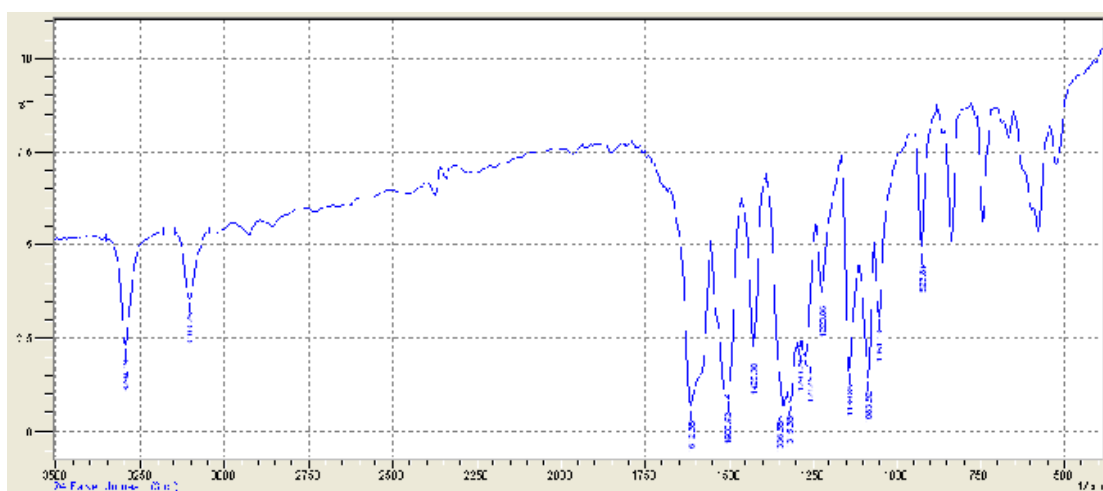


Fig.8. FTIR spectrum of the (L1)

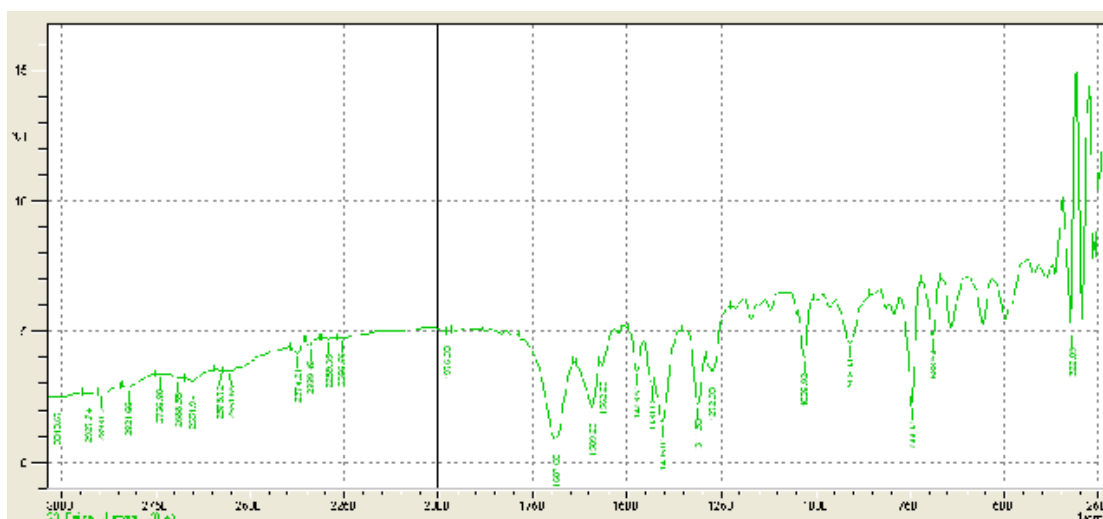


Fig. 9. FTIR spectrum of the complex  $[Co(L1)_2Cl_2]$

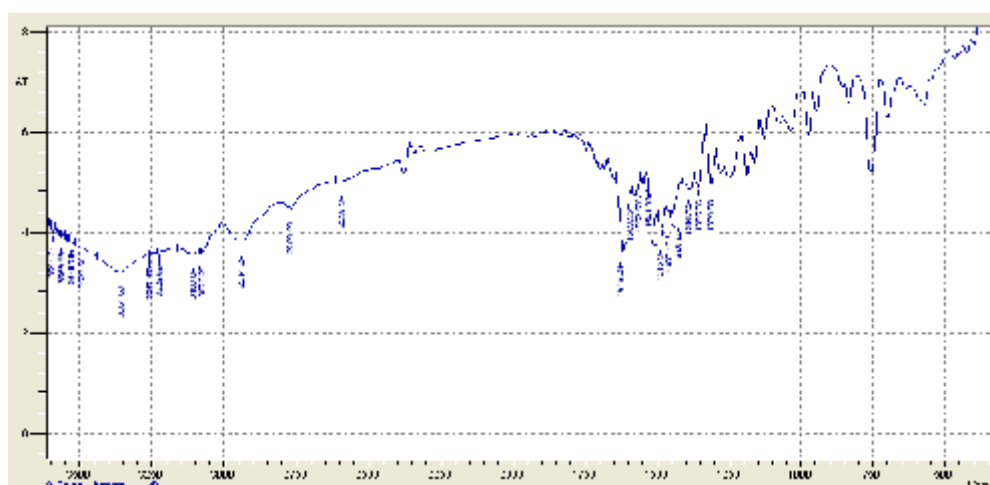


Fig. 10. FTIR spectrum of the (L2)



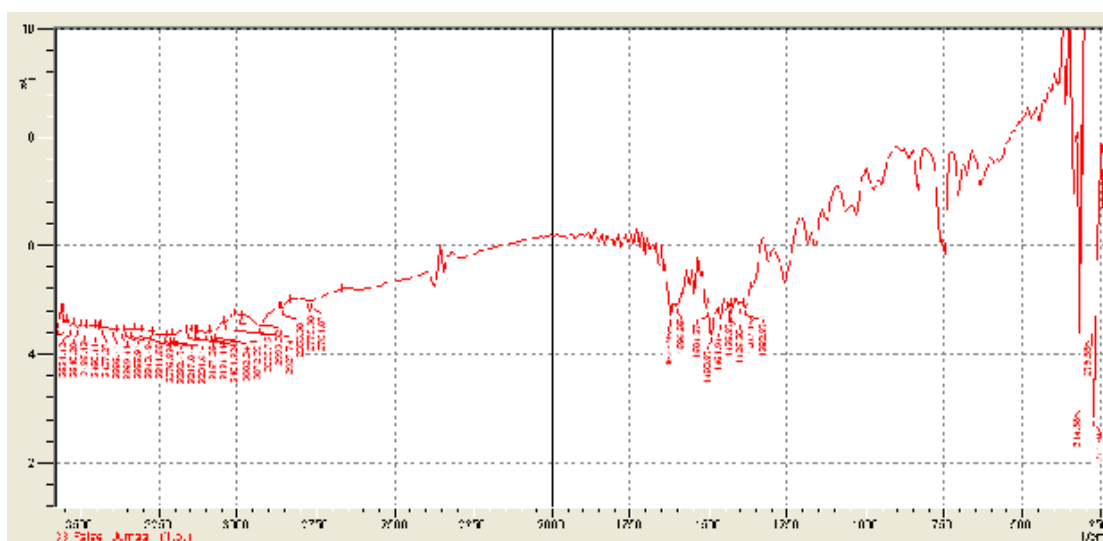


Fig. 11. FTIR spectrum of the complex  $[\text{Ni} (\text{L2}) \text{Cl}]\text{Cl}$

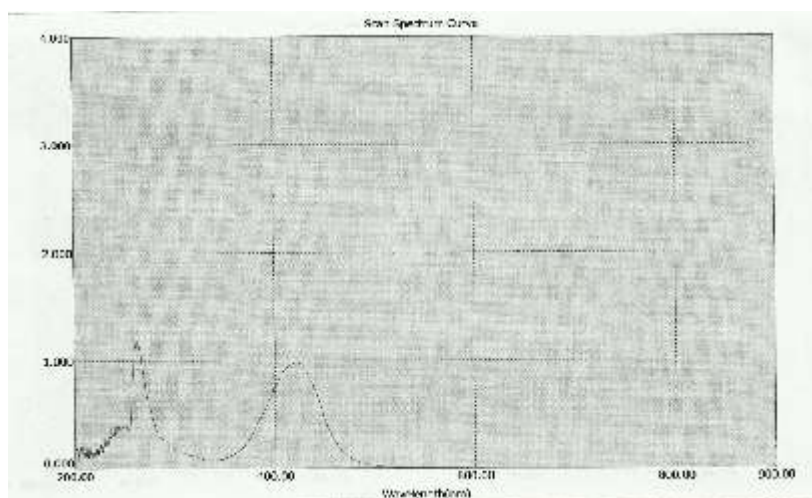


Fig.12. UV-visible spectrum of the (L1)

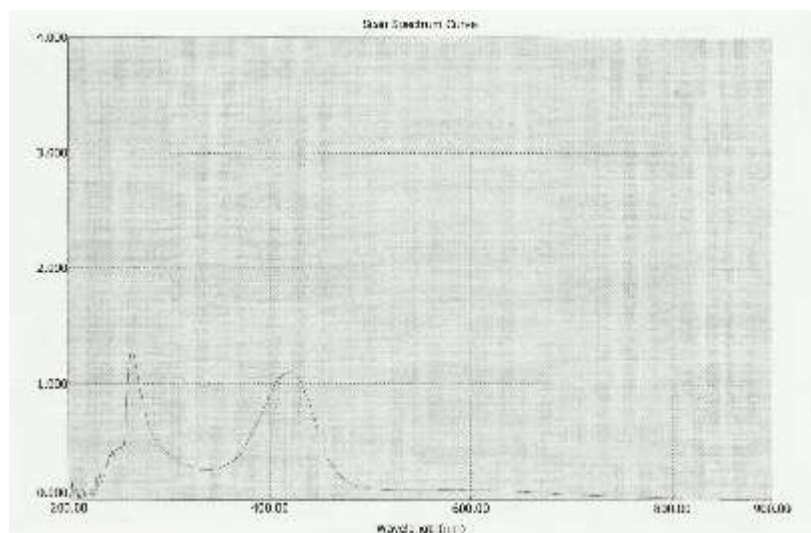


Fig. 13. UV-visible spectrum of the complex  $[Cu (L1) Cl_2]$

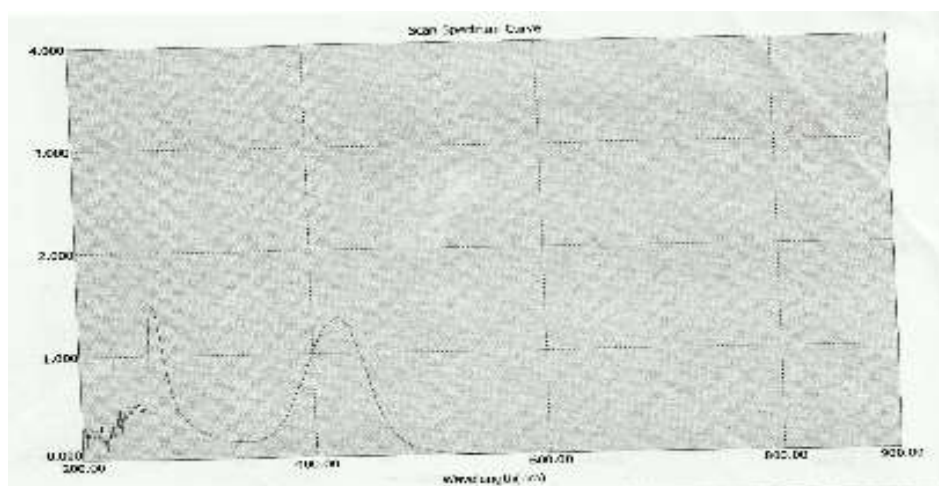


Fig.14. UV-visible spectrum of the (L2)

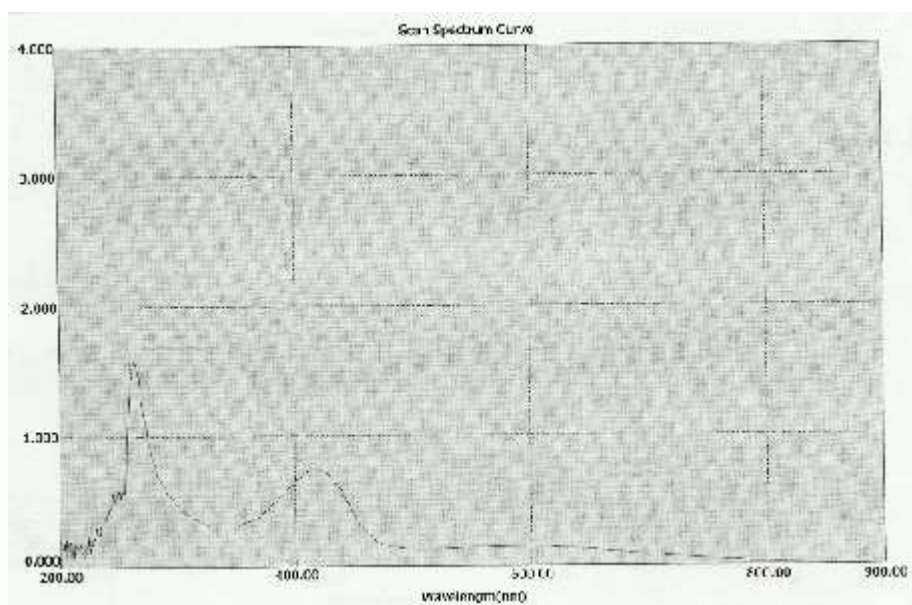


Fig. 15. UV-visible spectrum of the complex  $[Ni (L2) Cl]Cl$

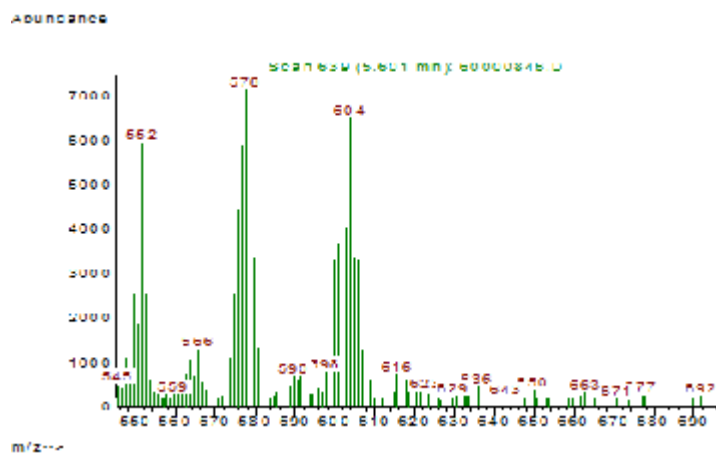


Fig. 16. Mass spectrum of the complex  $[\text{Co}(\text{L1})_2\text{Cl}_2]$

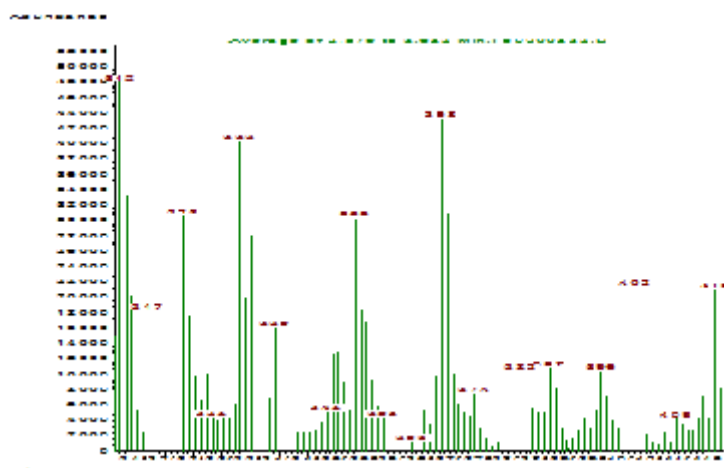


Fig. 17. Mass spectrum of the complex  $[\text{Cu}(\text{L1})\text{Cl}_2]$

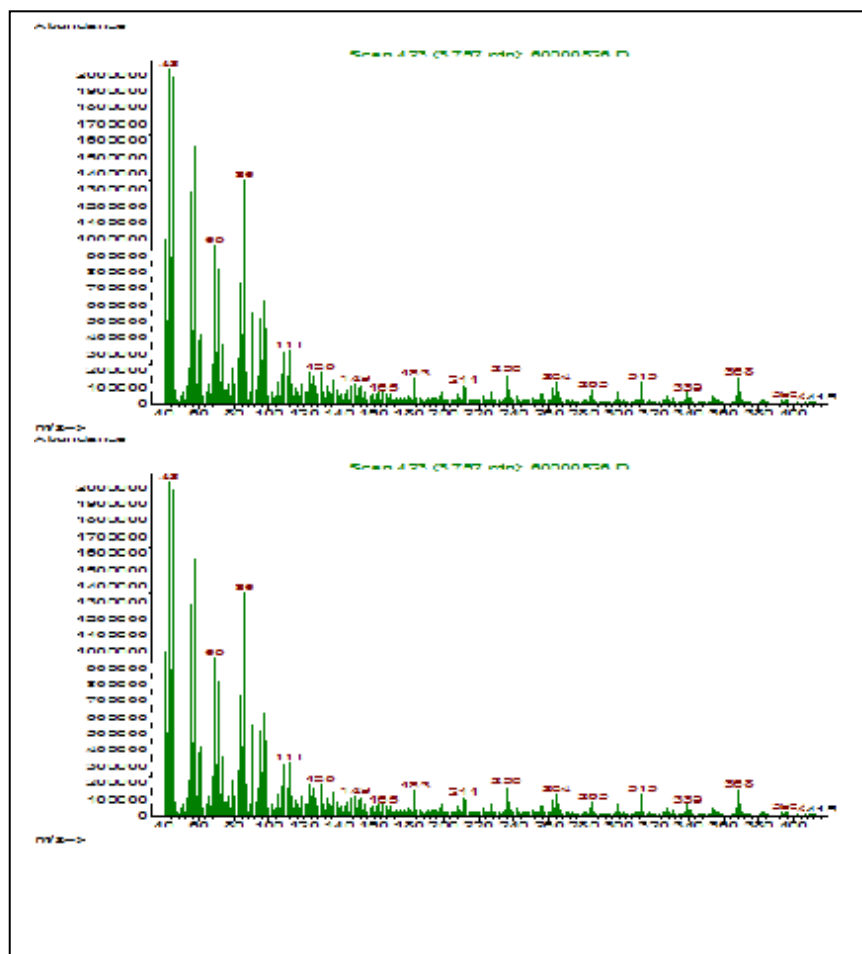


Fig. 18. Mass spectrum of the complex [Ni (L2)Cl]Cl

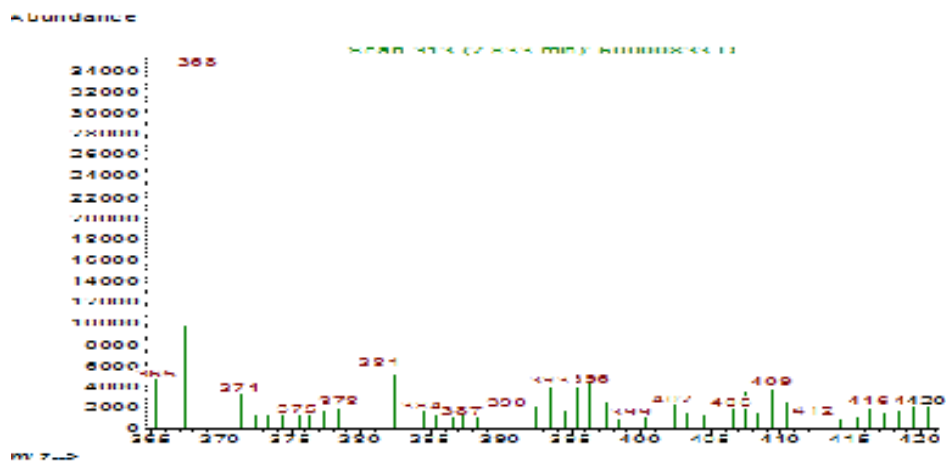


Fig. 19. Mass spectrum of the complex [Cu (L2) Cl]Cl

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