

PREPARATION AND CHARACTERISATION OF SOMETRANSATION METAL COMPLEXES OF NEW [BUTANAL (5-ETHYL-1, 3, 4-OXADIA- ZOL-2-YL) HYDRAZONE]

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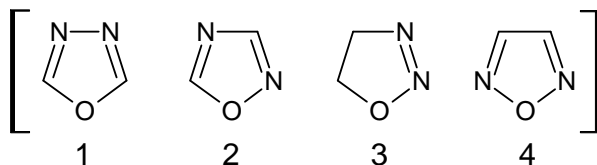
ABSTRACT

The solid complexes of Fe(II), Cr(III), Co(II), Ni(II), and Cu(II) with Synthesis of [Butanal(5-ethyl-1,3,4-oxadiazol-2-yl)hydrazone] have been synthesized and characterized by using the spectroscopic IR, ¹HNMR, Mass as well as by elemental analyses C,H,N and Molar conductance the were studied. It may be concluded that the ligand coordinate through Nitrogen atoms shown in Scheme (2). For all the complexes. The ligand acts as a didentate ligand coordinating through the oxadiazole nitrogen and the nitrogen of C=N group. This view is further supported by the appearance of a band corresponding to the metal–nitrogen stretching vibration at 513–540 cm⁻¹ in the complexes. The physicochemical data suggest the octahedral geometry for all complexes except for Ni and Cu complexes which were tetrahedral respectively.

KEYWORDS: PREPARATION. CHARACTERISATION. COMPLEXES. HYDRAZONE. ETHYL.

1. INTRODUCTION

1,3,4-Oxadiazole (1), is a heterocyclic compound containing an oxygen atom and two nitrogen atoms in a five-member ring. It is derived from furan by substitution of two methylene groups (=CH) with two pyridine type nitrogen (-N=). There are three known isomers: 1,2,4-oxadiazole (2), 1,2,3-oxadiazole (3) and 1,2,5-oxadiazole (4). However, 1,3,4-oxadiazole and 1,2,4-oxadiazole are better known, and more widely studied by researchers because of their many important chemical and biological properties [1].



Resistance to number of antimicrobial agents among a variety of clinically significant species of bacteria is becoming increasingly important global problem [2]. There are various problems arising with the use of antimicrobials such as local tissue irritation, interference with wound healing process, hypersensitivity reactions, systemic toxicity, narrow antimicrobial spectrum, emergence of resistance [3]. So the increasing clinical importance of drug-resistant microbial pathogens has lent additional urgency in microbiological and antifungal research. A wide

variety of heterocyclic systems have been explored for developing pharmaceutically important molecules. Among them the derivatives of oxadiazoles have been playing an important role in

the medicinal chemistry [4]. Oxadiazole moiety and its various derivatives studied frequently in the past few decades and found potent in various pharmacological and pathological conditions [5]

1, 3, 4-Oxadiazole is a highly privileged structure the derivatives of which exhibit a wide range of biological activities including insecticidal [6], antiperipheral vasomotility [7], CNS stimulant, anti-inflammatory [8], hypotensive [9], insecticidal [10], bactericidal [11], hypoglycemic [12], anticonvulsive

[13], analgesic [14], muscle relaxant [15,16], herbicidal [17] and fungicidal activity [18], anti-cancer [19], antitubercular [20], antimalarial [21]

The coordination chemistry of transition metal complexes of heterocyclic compounds, involving oxadiazole ligand have attracted much attention in recent years due to the fact that those ligands around central metal ions in natural systems are unsymmetrical. Generally the prepared complexes exhibited a greater activity and show good models of biological systems that compared to (L) . [22]

Najat Al- Obaidy, Khalil K. Abid, Yusra J. Al-Niami had been Synthesized Complexes of some transition metals with derivatives of-1,3,4- oxadiazole . They were concluded the metal complexes of 1,3,4-oxadiazole Ligand exhibited biological activity and medical uses as drugs , greater activity 1,3,4-oxadiazole . and this encourage searchers to prepare new derivatives and complexes and to study their biological activity . [23]

2. EXPERIMENTAL WORK

2.1 PREPARATION OF LIGAND

FIRST STEP: SYNTHESIS OF PROPANEHYDRAZIDE

A mixture of 0.1 mole (10.2 gm) of Ethyl propanoate and 0.2 mole (10ml) Hydrazine hydrate were refluxed in 150 ml of absolute ethanol for 5hr. The resultant mixture [A] was concentrated, cooled, The resultant is Colorless liquid , The purity of the compound was followed by TLC. Yield: 85.3 %, B.p. 134-136. [24]

SECOND STEP: SYNTHESIS OF 5-ETHYL-1,3,4-OXADIAZOLE-2-THIOL :

A mixture of [A] (8.8 gm, 0.1 mole), KOH (5.6 gm, 0.1mole) and CS₂ (12 ml, 0.2 mole) was refluxed in absolute ethanol (200 ml) for 23 hours or until evolution of hydrogen sulfide ceases. The excess of solvent was removed under vacuum and the residue was mixed with ice and poured onto ice water containing hydrochloric acid. The Pale yellow precipitate which separated was filtered and recrystallized from ethanol to give 5-ethyl-1,3,4-oxadiazole-2-thiol [B] , The purity of the compound was followed by TLC .Yield: 82.7 %, m. p. 197-199C . [25]

THIRD STEP: SYNTHESIS OF 2-HYDRAZINO-5-ETHYL-1,3,4-OXADIAZOLE

A mixture of [B] (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 H₂S ceased , then allowed to cool , the pale yellow precipitate was filtered , dried and recrystallized from ethanol to give 2-hydrazino-5-ethyl-1,3,4-oxadiazole [C]. The purity of the compound was followed by TLC .Yield(1.59g,82%) , m.p. 167C .

FORTH STEP: SYNTHESIS OF BUTANAL(5-ETHYL-1,3,4-OXADIAZOL-2-YL)HYDRAZONE

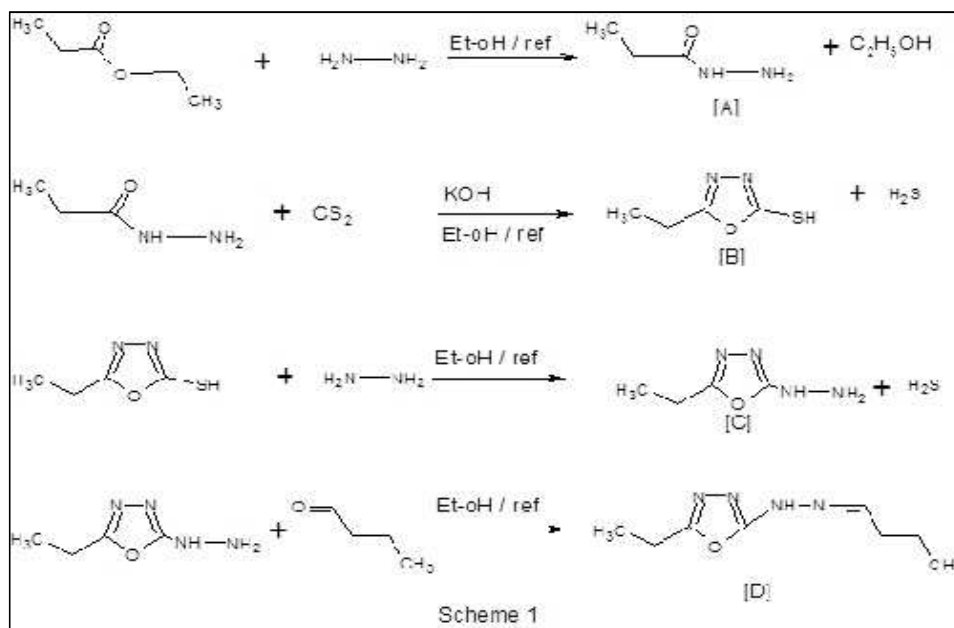
A mixture of [C] (1.92 g , 0.01 mol) and Butanal(1.849 g,0.01mol) was refluxed in absolute ethanol (35 mL) for (7) hours The bright yellow precipitate butanal(5-ethyl-1,3,4-Oxadiazol-2-yl)hydrazone [D] was filtered , dried and recrystallized from ethanol . The purity of the compound was followed by TLC. Yield(1.54 g , 80.2%) , m.p. 158 – 160 C . [26]

2.2 PREPARATION OF COMPLEXES

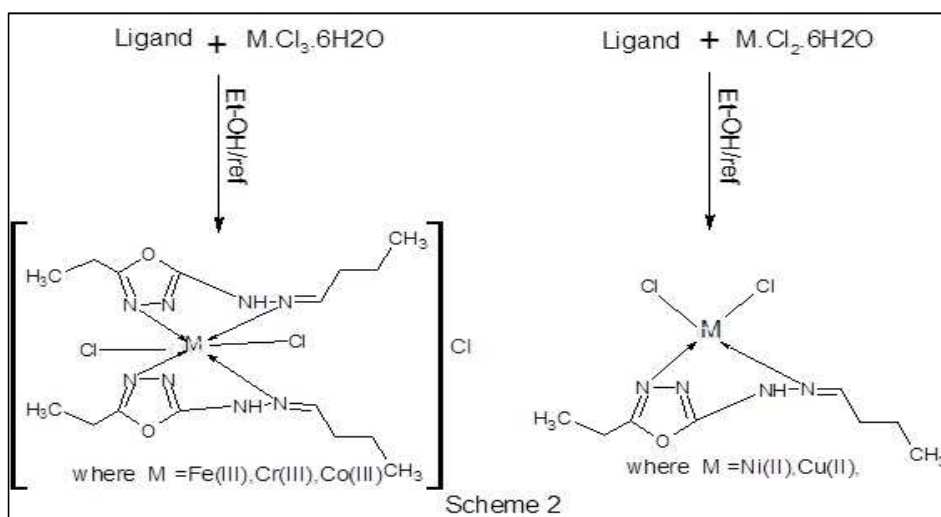
The hydrated metal chloride salts of The Fe(III), Cr(III), Co(III), Ni(II) and Cu(II) (0.01 mol) was added to solution of the ligand 2.21gm (0.01mol) in hot absolute ethanol (40 mL) and the mixture was refluxed on a water bath for 2 hours and the solvent was evaporated in vacuum to half of the original volume and then cooled. The isolated complexes were filtered off, washed several times with ethanol and finally dried in air. [27]

3. PRECENT WORK

3.1 PREPARATION OF LIGAND



3.2 PREPARATION OF COMPLEXES



4. RESULTS & DISCUSSION

The purity of the ligand and its complexes were checked by TLC . Molecular formula, physical properties and Molecular weight and molar conductance data of the ligand and its complexes tabulated in Table (1) and (2) elemental analysis and Mass Spectra Figure (5,6,7,8,9,10) , Infra-Red Spectroscopy tabulated in Table(3),(4) and (5). The calculated values were in a good agreement with the experimental values.

Table 1. Molecular formula, physical properties and Molecular weight data of the ligand and its complexes.

NO	Formula	M.Wt	Color	M.P C	Yield %
L	C ₈ H ₁₄ N ₄ O	182	Pale yellow	141-143	82.7
1	[Fe(L) ₂ Cl ₂]Cl	526	Brown	177-179	87.1
2	[Cr(L) ₂ Cl ₂]Cl	522	Deep brown	154-156	82.5
3	[Co(L) ₂ Cl ₂]Cl	529	Deep blue	167-169	79.2
4	[Cu(L)Cl ₂]	316	Pale green	159-161	85.5
5	[Ni(L)Cl ₂]	311	Pale Brown	134-136	86.8

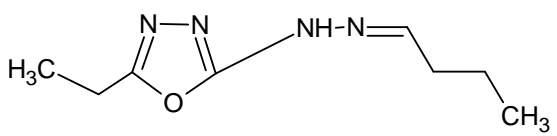
Table 2. Molar conductance data of all complexes measurements were made in anhydrous DMSO at 25°C ,Concentration 10⁻⁴ at 298K .

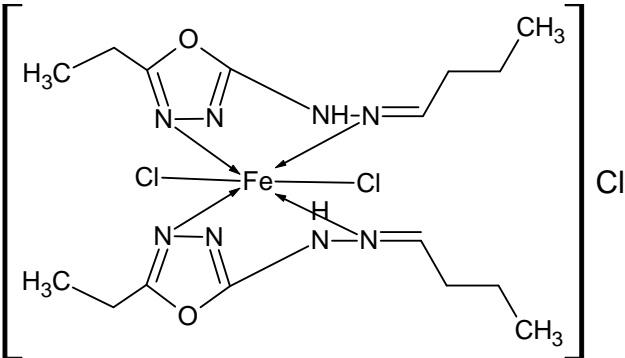
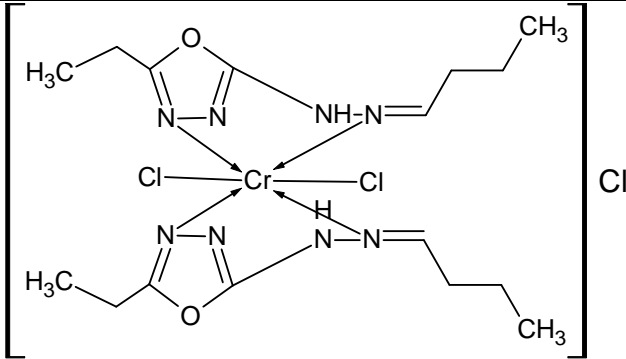
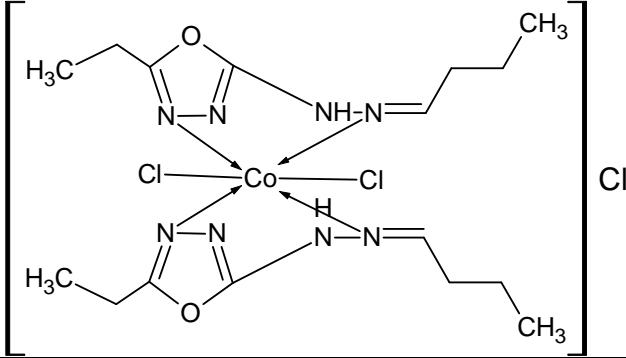
NO	Formula	$\Lambda_M(S.cm^2.mol^{-1})$	Electrolyte Type
1	[Fe(L) ₂ Cl ₂]Cl	24	1:1
2	[Cr(L) ₂ Cl ₂]Cl	28	1:1
3	[Co(L) ₂ Cl ₂]Cl	27	1:1
4	[Cu(L)Cl ₂]	19	Non Electrolyte
5	[Ni(L)Cl ₂]	18	Non Electrolyte

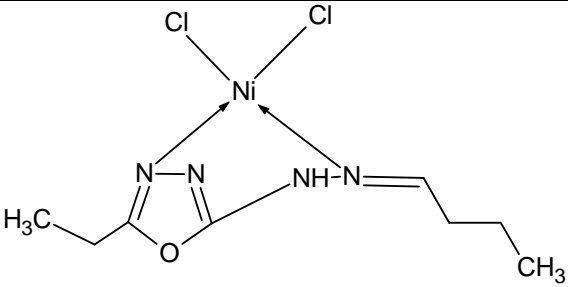
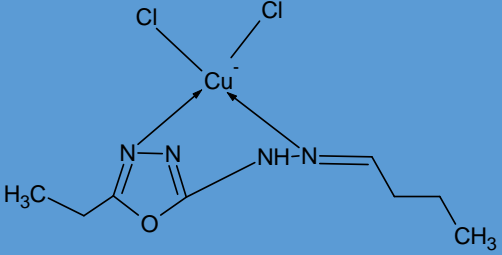
Table3. elemental analysis data for the ligand

Experimental			Theoretical		
C%	H%	N%	C%	H%	N%
52.34	7.88	30.11	52.73	7.74	30.75

Table 4. The mass spectrum of ligand and its complexes

Ion	Structure	Molecular Ion
L		182
[C ₆ H ₉ N ₄ O] ⁺		153
[C ₅ H ₇ N ₄ O] ⁺		139
[C ₅ H ₉ N ₃ O] ⁺		127
[C ₄ H ₆ N ₃ O] ⁺		111
[C ₄ H ₅ N ₂ O] ⁺		97
[C ₂ H ₂ N ₃ O] ⁺		84
[C ₄ H ₈ N] ⁺		69
[C ₂ N ₂ O] ⁺		68
[CH ₂ N ₂ O] ⁺		57
[C ₃ H ₅ N] ⁺		55

[Fe(L) ₂ Cl ₂]Cl		526
[Fe(L) ₂ Cl ₂] ⁺		491
[Fe(L) ₂ Cl] ⁺		455
[Fe(L) ₂] ⁺		420
[Cr(L) ₂ Cl ₂]Cl		522
[Cr(L) ₂ Cl ₂] ⁺		487
[Cr(L) ₂ Cl] ⁺		451
[Cr(L) ₂] ⁺		416
[Co(L) ₂ Cl ₂]Cl		529
[Co(L) ₂ Cl ₂] ⁺		494
[Co(L) ₂ Cl] ⁺		458
[Co(L) ₂] ⁺		423

[Ni(L)Cl ₂]		311
[Ni(L)Cl] ⁺		276
[Ni(L)] ⁺		240
[Cu(L)Cl ₂]		316
[Cu(L)Cl] ⁺		281
[Cu(L)] ⁺		245

4.1 Infra-Red Spectroscopy:

The FTIR spectrum for L shows a characteristic stretching absorption bands. 3051cm⁻¹, 1653cm⁻¹, 1624cm⁻¹, 1373cm⁻¹, 1431cm⁻¹ assigned, ν C-H Aliphatic=N of the oxadiazole ring, C=N of Azomethen group, asymmetrical C-O-C and symmetrical C-O-C stretching respectively. The C=N stretching vibrations are important to predict the bonding mode of the ligand, these bands shift lower wavelength in the spectra of complexes compare with ligand, observed changes are the evidences of complexation had happened [28]. The IR data of the complexes are shown in Table (5) and figure(1,2,3,4). The Table lists the stretching

Frequency (ν) for some of the characteristics groups exhibited by the ligand and complexes.

Table5. Infra-Red Spectroscopy absorption bands of ligand and its complexes								
NO	Compound	ν C-H Ali-phatic	ν C=N of ring	ν C=N out ring	ν C-O-C Asy	ν C-O-C, Sy	ν M-N	ν M-Cl
1	C ₈ H ₁₄ N ₄ O	2964	1643	1600	1379	1440	-----	-----
2	[Fe(L) ₂ Cl ₂]Cl	2931	1650	1591	1373	1435	540	354
3	[Cr(L) ₂ Cl ₂]Cl	2955	1653	1624	1373	1431	539	356
4	[Co(L) ₂ Cl ₂]Cl	2930	1644	1590	1375	1433	535	355

5	[Cu(L)Cl ₂]	2931	1640	1562	1330	1435	513	347
6	[Ni(L)Cl ₂]	2929	1639	1565	1332	1434	516	348

4.2 ¹H-NMR SPECTRA:

The spectral data for the free ligand in DMSO-solution was reported along with the possible assignments in experimental. The proton nuclear magnetic resonance spectral data gave additional support for the composition of the ligand, All the protons are at their expected region. The CH₃, CH₂, CH₂-C=N of Oxadiazole ring and CH₂ next to Azomethen, NH and CH=N- signals, are shown in the regions of 1.3, 1.6, 2.7, 5.7 and 8.9 ppm, respectively, The number of protons calculated from integration curves and the recorded chemical shifts in figure (5)[29].

5. CONCLUSION

In the present work, a series of Fe(III), Cr(III), Co(III), Ni(II), Cu(II) complexes with new ligand (L), have been prepared and characterized on the basis of IR, ¹H NMR, Mass spectroscopic as well as by elemental analyses C, H, N and Molar conductance.

According to all the physicochemical measurements as the prepared complexes, we can suggest the chemical configuration for the complexes. The ligand Butanal[(5-ethyl-1,3,4-Oxadiazol-2-yl)hydrazono] was successfully synthesized. The ligand was treated to different transition metal salt to form the corresponding complexes as shown in the scheme (2). It may be concluded that the ligand coordinates through Nitrogen atoms. This view is further supported by the appearance of a band corresponding to the metal–nitrogen stretching vibration at 513–540 cm⁻¹ in the complexes. (Cr(III), Fe(III) and Co(III)) leading to the formation of octahedral geometry complexes, while the Cu and Ni atoms lead to the formation of tetrahedral geometry complexes.

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APPENDICES

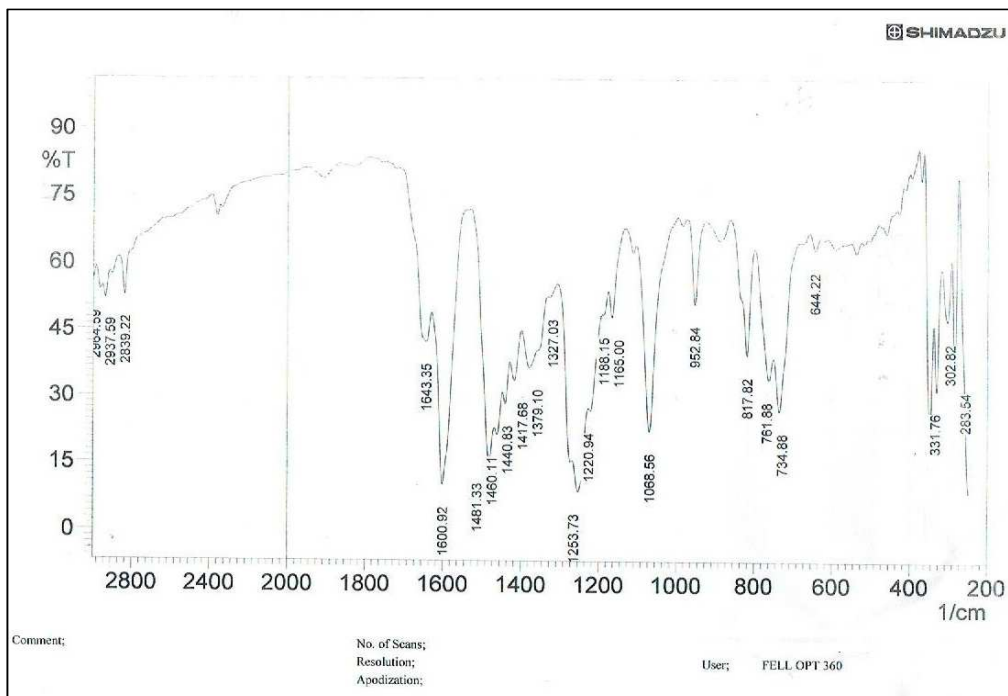


Figure (1) IR spectrum of the ligand cm-1

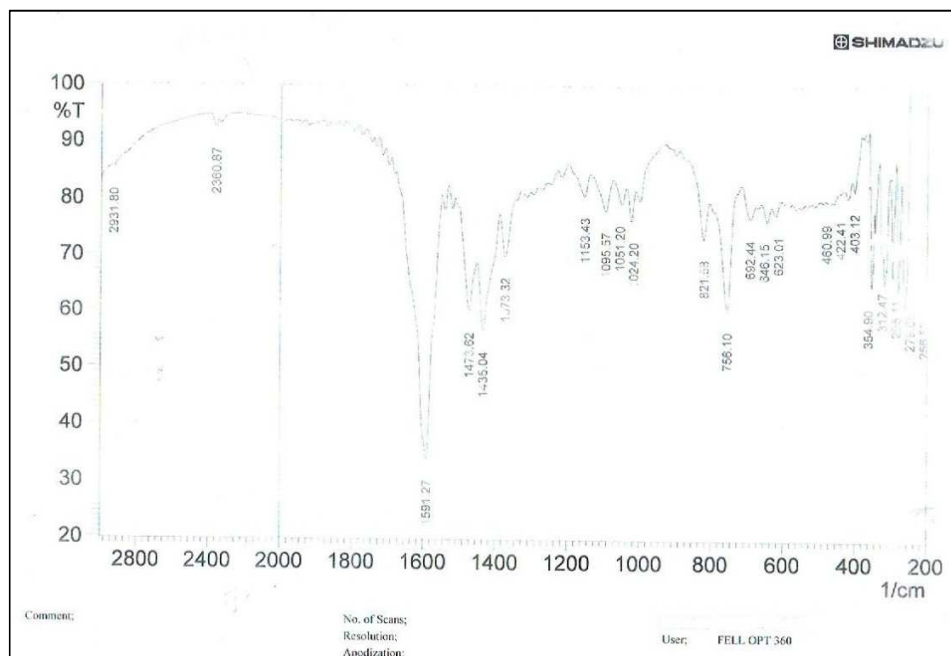


Figure (2) IR spectrum of the $[Fe(L)_2Cl_2]Cl$ cm-1

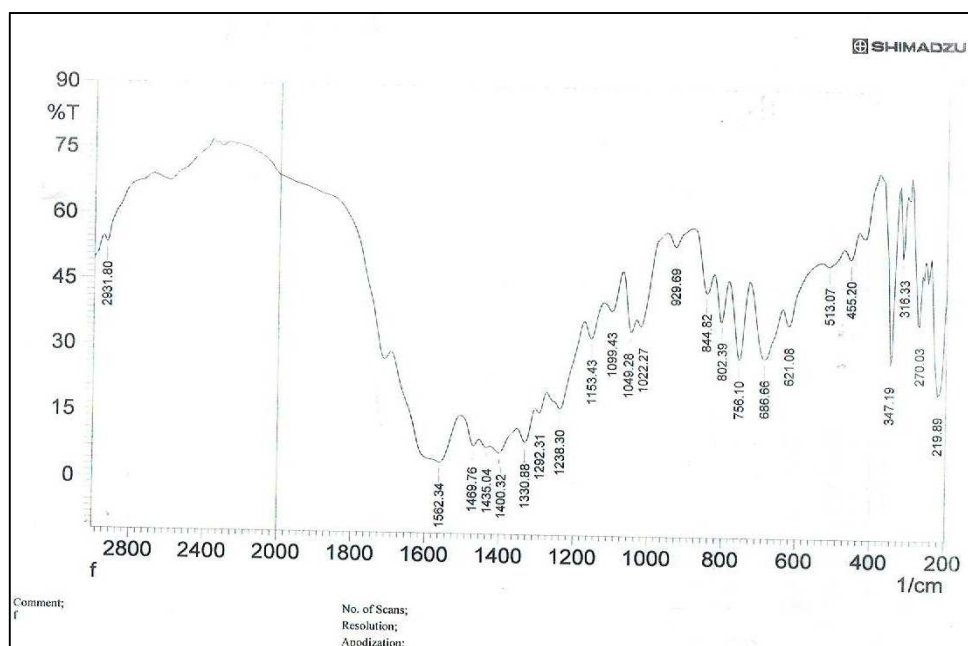


Figure (3) IR spectrum of the $[Cu(L)_2Cl_2]$ cm⁻¹

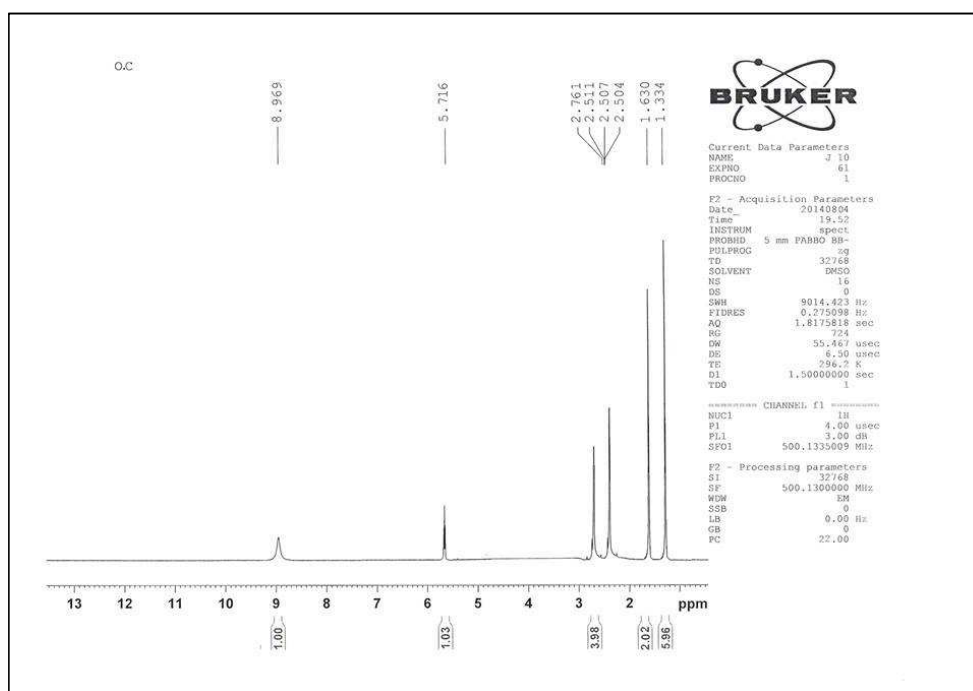


Figure (4) NMR spectra of the ligand

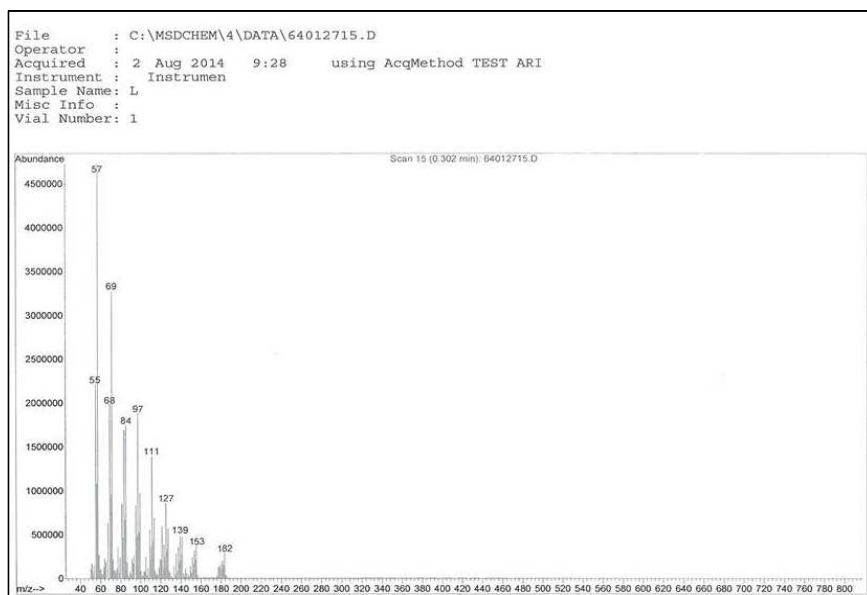


Figure (5) mass spectra of ligand

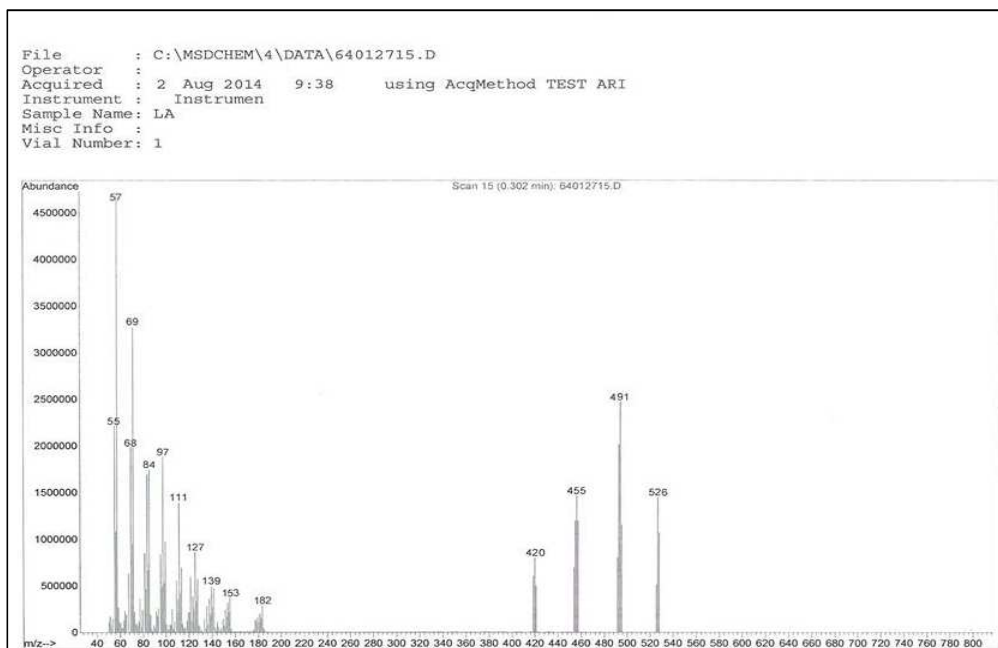


Figure (6) mass spectra of $[\text{Fe}(\text{L})_2\text{Cl}_2]\text{Cl}$ cm-1

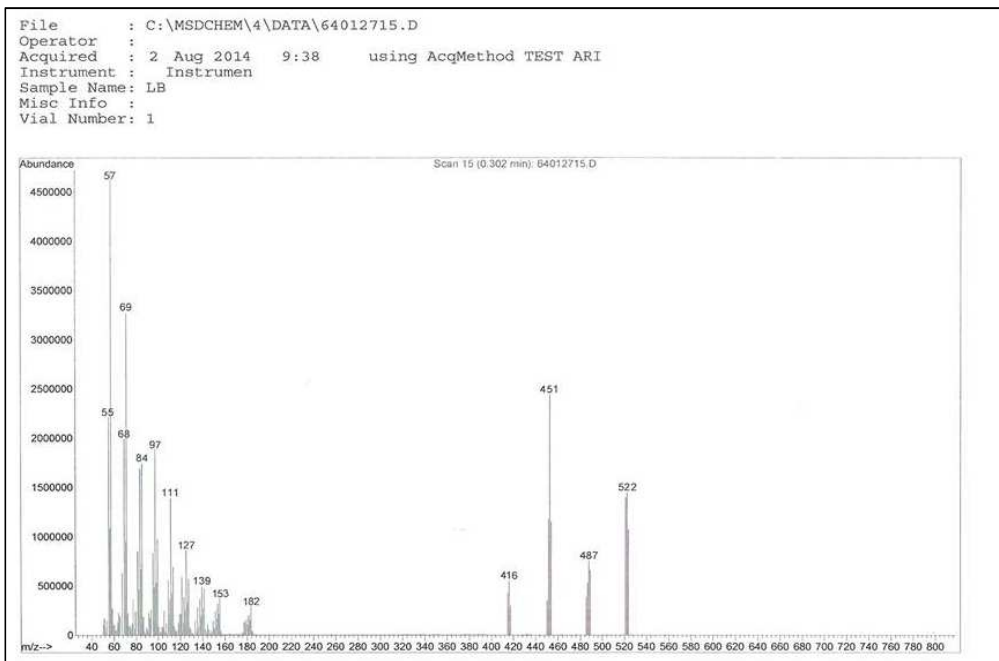


Figure (7) mass spectra of $[\text{Cr}(\text{L})_2\text{Cl}_2]\text{Cl}$ cm-1

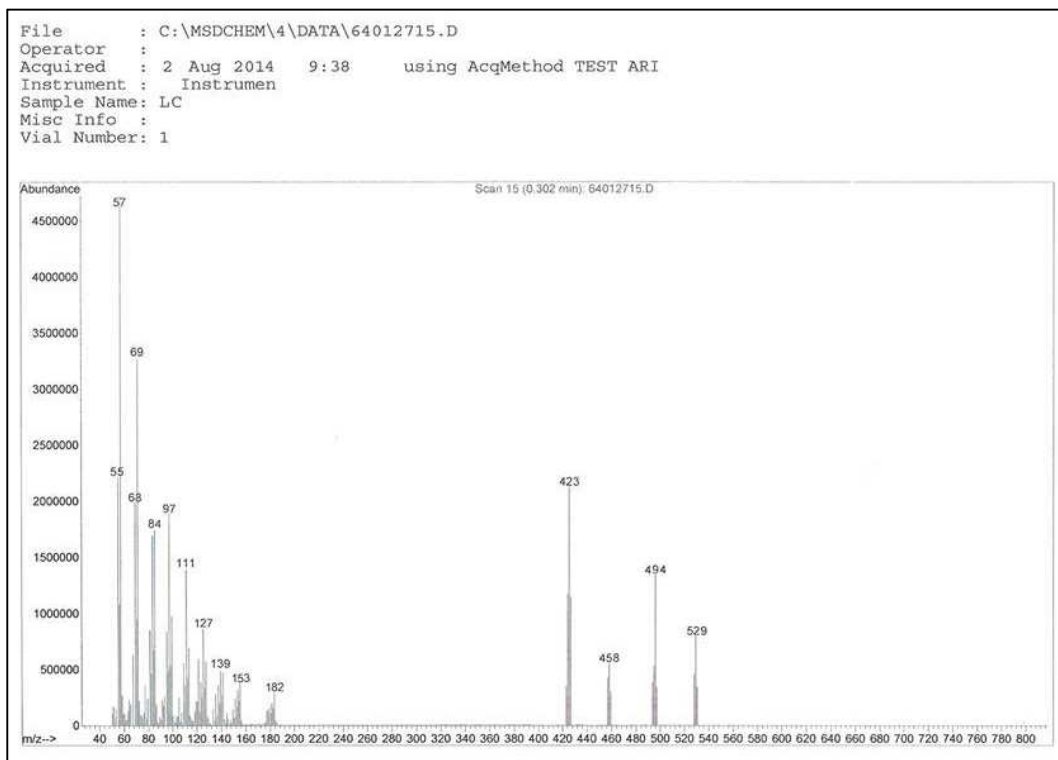


Figure (8) mass spectra of $[\text{Co}(\text{L})_2\text{Cl}_2]\text{Cl}$ cm-1

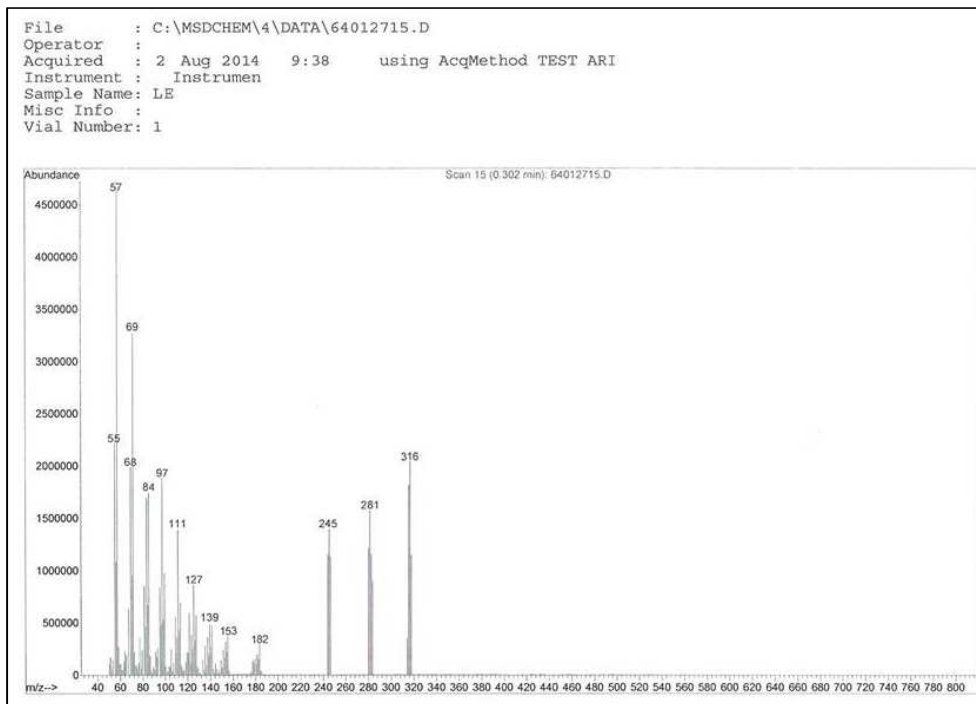


Figure (9) mass spectra of $[\text{Ni}(\text{L})_2\text{Cl}_2]$ cm-1

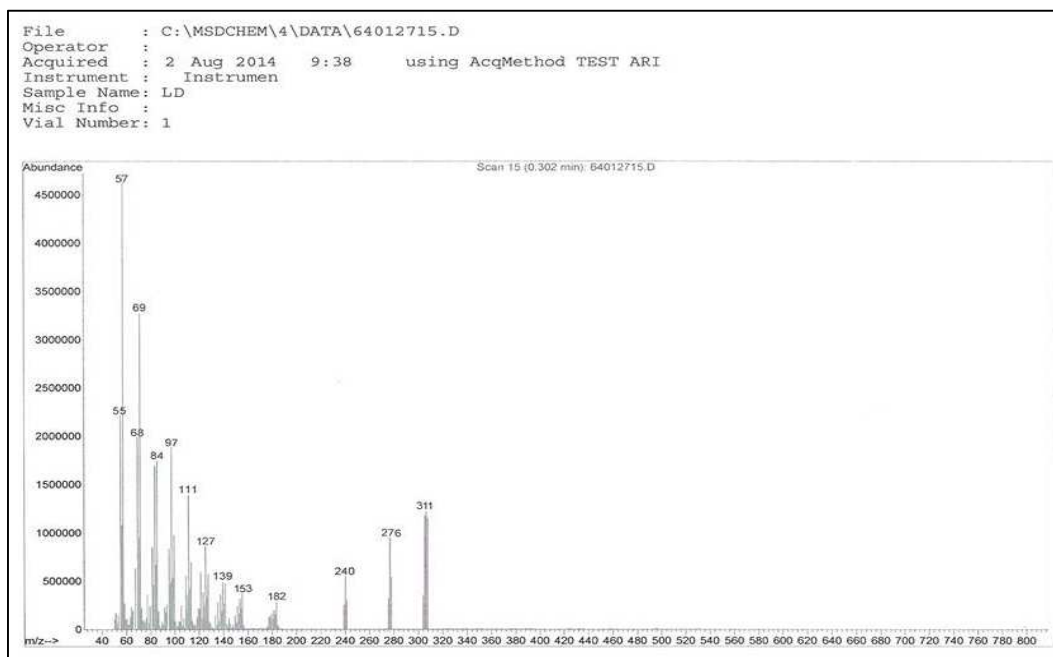


Figure (10) mass spectra of $[\text{Cu}(\text{L})_2\text{Cl}_2]$ cm-1