

PREPARATION AND CHARACTERISATION OF SOME TRANSITION METAL COMPLEXES OF NEW 4-[(5- ETHYL-1,3,4-OXADIAZOL-2-YL)SULFANYL]ANILINE

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Abstract

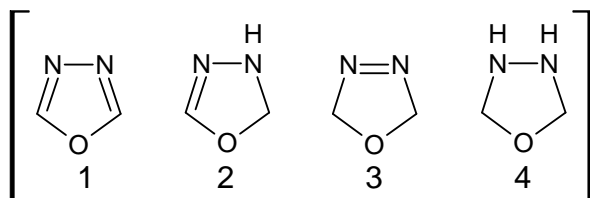
1,3,4-oxadiazoles are important because of its versatile biological actions such as antimicrobial, anti-malarial, anticonvulsant, hypoglycemic, also analgesic, anti-inflammatory, anticancer, anti-HIV agent. In the present study the solid complexes of Fe(II), Cr(III), Co(II), Ni(II), and Cu(II) with Synthesis of 4-[(5-ethyl-1,3,4-oxadiazol-2-yl)sulfanyl]aniline have been synthesized and characterized by using the spectroscopic IR, ¹HNMR, Mass as well as by elemental analyses C, H, N and Molar conductance they were studied. It may be concluded that the ligands coordinate through Nitrogen and Sulfur as atoms shown in Scheme (2). For all the complexes. The ligand acts as a didentate ligand coordinating through the oxadiazole nitrogen and the Sulfur atom of 2-sulfanyl. This view is further supported by the appearance of a band corresponding to the metal–nitrogen and the metal–Sulfur stretching vibration at 503–553 cm⁻¹ and 474–484 cm⁻¹ in the complexes. The physicochemical data suggest the octahedral geometry for all complexes except for Ni and Ca complexes which were tetrahedral respectively.

KEYWORDS: PREPARATION. CHARACTERISATION. TRANSITION. METAL. SULFANYL.

1. INTRODUCTION

1,3,4-Oxadiazole is a heterocyclic molecule with oxygen atom at 1 and two nitrogen atoms at 3 and 4 position. They have been known for about 80 years, it is only in the last decade that investigations in this field have been intensified. This is because of large number of applications of 1,3,4-oxadiazoles in the most diverse areas.

It also contains broad range of therapeutic activity Oxadiazoles belong to an important group of heterocyclic compounds having –N=C-O- linkage [1]. 1,3,4-Oxadiazole (1) is thermally stable aromatic heterocyclic and exists in two partially reduced form (2); 2,3,-dihydro 1,3,4-Oxadiazole and (3) 2,5-dihydro-1,3,4-Oxadiazole depending on the position of the double bond. The completely reduced form of 1,3,4-Oxadiazole is designated as 2,3,4,5-tetrahydro-1,3,4-Oxadiazole (4) [2].



Due to the interesting activity of 2, 5-disubstituted 1,3, 4-oxadiazole as biological agent's considerable attention has been focused on this class. The pharmaceutical importance of these compounds lies in the fact that they can be effectively utilizing as antibacterial, anti-tubercular and insecticidal agents. Some of these compounds have also analgesic, anti-inflammatory, anticancer, anti-HIV agent, anti-Parkinsonism and anti-proliferative agent. In addition, 1,3,4-oxadiazole have played a crucial part in the development of theory in heterocyclic chemistry and also used extensively in organic synthesis [3].

1,3,4-Oxadiazole is a versatile lead molecule for designing potential bioactive agents. The 1,3,4-oxadiazole derivatives have been found to exhibit diverse biological activities such as antimicrobial, anti-malarial, analgesic, anticonvulsant, hypoglycemic [4].

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).

Mahmoud Najim Al-Jibori, Sinan AL-Bayati and Majeed Rasheed had synthesized complexes of 1,3,4 oxadiazole. All complexes have been screened biologically against +ve and -ve Grams bacteria and fungi, it is found that most newly complexes showed remarkable activity against the tested microorganisms in comparison with standard Tetracycline and Amphertoriaine drugs [5].

S.K. Ibrahim, F.M. Abdul-Hammed and M.F. Alias. They were concluded the metal complexes of 1,3,4-oxadiazole Ligand exhibited a greater activity against the studied bacteria *Pseudomonas aeruginosa* and micro-organisms *Bacillus subtilis*, compared to (L) [6].

2. OBJECTIVES

1. Preparation of new 1,3,4 oxadiazole derivative 4-[(5-ethyl-1,3,4-oxadiazol-2-yl)sulfanyl]aniline Preparation of some transition metal complexes $[Fe(L)_2Cl_2]Cl$, $[Cr(L)_2Cl_2]Cl$, $[Co(L)_2Cl_2]Cl$, $[Cu(L)Cl_2]$, $[Ni(L)Cl_2]$.
2. Identification of synthesized Ligand and Complexes by IR, ¹HNMR Spectra, Mass spectroscopic as well as by elemental analyses C, H, N and Molar conductance.
3. Prepared complexes has greater activity and good models of biological activity systems comparable to Ligand.

3. MATERIAL

1) Ethyl propionate 2) Hydrazine hydrate 3) absolute ethanol 4) KOH 5) CS₂ 6) hydrochloric acid
7) 4-bromoaniline 8) pyridine.

4. EXPERIMENTAL WORK

4.1 PREPARATION OF LIGAND

First step: Synthesis of propanehydrazide :

A mixture of 0.1 mole (10.2 gm) of Ethyl propionate and 0.2 mole (10ml) Hydrazine hydrate were refluxed in 150 ml of absolute ethanol for 5 hr. 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. [7]

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. [8]

Third step: Synthesis of 4-[(5-ethyl-1,3,4-oxadiazol-2-yl)sulfanyl]aniline:

A mixture of (0.65gm, 0.005mol) of 5-ethyl-1,3,4-oxadiazole-2-thiol and (0.005mol) of 4-bromoaniline were refluxed in 25 ml of pyridine solution for 3.5 hrs. The resultant mixture was cooled and poured into crushed ice. The Brownish yellow [C]

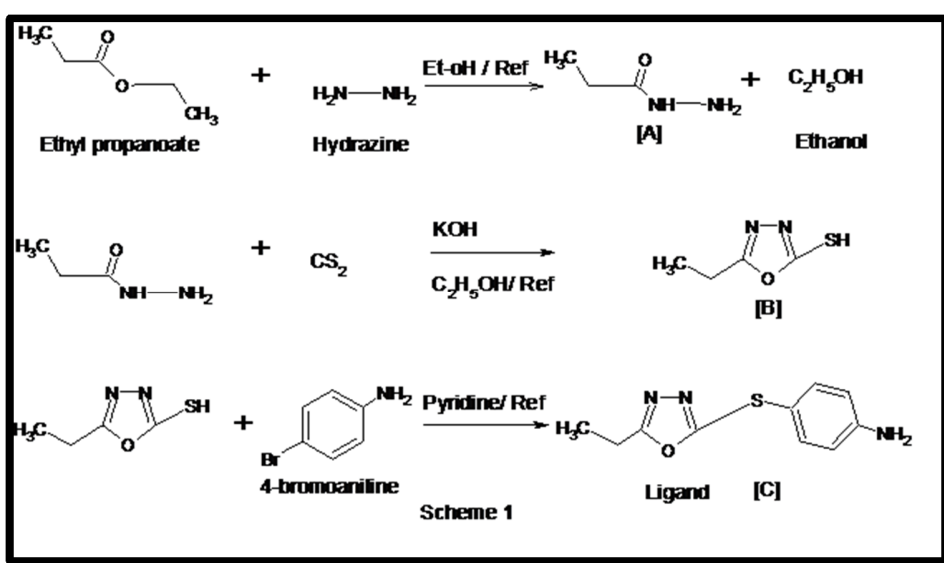
mass is thus separated out was dried and recrystallized from ethanol. The purity of the compound was followed by TLC .Yield: 74.8 %, m. p. 137-139C .[9]

4.2 PREPARATION OF COMPLEXES

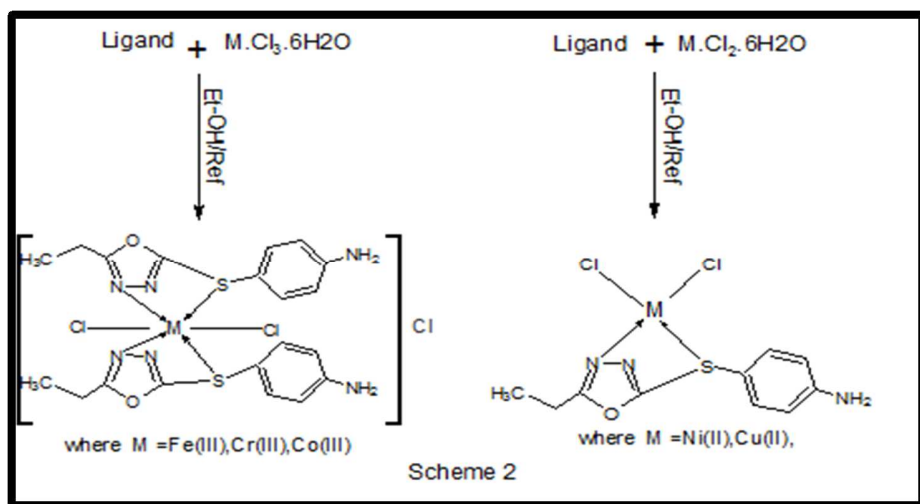
The hydrated metal chloride salts of The Fe(III), Cr(III), Co(III), Ni(II) and Cu(II) (0.01 mol) was added to solution of the ligand 2.21gm (0.01mol) in hot absolute ethanol (40 mL) and the mixture was refluxed on a water bath for 2 hours and the solvent was evaporated in vacuum to half of the original volume and then cooled . The isolated complexes were filtered off , washed several times with ethanol and finally dried in air [10] .

5. PRECENT WORK

5.1 PREPARATION OF LIGAND



5.2 PREPARATION OF COMPLEXES



6. RESULTS AND 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, Infra-Red Spectroscopy as shown in a figure (1,2,3) tabulated in table (3) and (4). The spectral data of ¹H-NMR Spectra for the free ligand reported in figure (4) while The Mass Spectra shown in a figure (5,6,7,8,9,10) and tabulated in Table(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 ₁₀ H ₁₁ N ₃ OS	221	Brownish yellow	137-139	74.8
1	[Fe(L) ₂ Cl ₂]Cl	604	Brown	170-168	83.3
2	[Cr(L) ₂ Cl ₂]Cl	600	Pale Brown	163-165	89.1
3	[Co(L) ₂ Cl ₂]Cl	607	Green	177-179	77.8
4	[Cu(L)Cl ₂]	355	Pale green	153-151	75.5
5	[Ni(L)Cl ₂]	350	Pale brown	143-145	78.3

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	27,7	1:1
2	[Cr(L) ₂ Cl ₂]Cl	33.4	1:1
3	[Co(L) ₂ Cl ₂]Cl	32.2	1:1
4	[Cu(L)Cl ₂]	17.5	Non Electrolyte
5	[Ni(L)Cl ₂]	20.3	Non Electrolyte

Table3. elemental analysis data for the ligand

Experimental			Theoretical		
C%	H%	N%	C%	H%	N%
54.56	4.95	19.2	54.28	5.01	18.99

6.1 INFRA-RED SPECTROSCOPY

The FTIR spectrum for L shows a characteristic stretching absorption bands . 3300 cm⁻¹, 3065 cm⁻¹, 2943 cm⁻¹, 1581 cm⁻¹, 1419 cm⁻¹, 1321 cm⁻¹ assigned to ν N-H group , ν C-H Aromatic C-H Aliphatic , C=N of the oxadiazole ring, symmetrical C-O-C, asymmetrical 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 [11]. The IR data of the complexes are shown in Table (4) and figures (1,2,3). The Table lists the stretching frequency (ν) for some of the characteristics groups exhibited by the ligand and complexes.

6.2 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 Ar-H, NH₂ and CH₃, CH₂-C=N proton signals, are shown in the regions of 7.5-8.0, 5.3, 1.3, 2.8 and ppm, respectively, The number of protons calculated from integration curves and the recorded chemical shifts in figure (4)[12] .

6.3 MASS SPECTRA

The mass spectrum of the ligand shows a molecular ion peak [M/e] at 221, the ligand spectra shows fragment ion peak at m/e (205, 192, 166, 124, 97, 92, 77 and 65 due to [C₁₀H₉N₂OS]⁺, [C₈H₆N₃OS]⁺, [C₇H₆N₂OS]⁺, [C₆H₆NS]⁺, [C₄H₅N₂O]⁺, [C₆H₆N]⁺, [C₆H₅]⁺, [C₅H₅]⁺ , respectively as shown in Figure(5) . The mass spectrum of the complex [Fe(L)₂.Cl₂]Cl shows a molecular ion peak at m/z 604 which is equivalent to molecular mass of the complex. This complex shows another a fragment ion peak with loss of chlorine atom at m/z 569. the ligand spectra shows fragment ion peak with loss two chlorine atom at m/e (533, 498) due to [Fe(L)₂Cl]⁺ and [Fe(L)₂]⁺ . Respectively as shown in Figure(6).

The mass spectrum of the complex [Cr(L)₂.Cl₂]Cl shows a molecular ion peak at m/z 600 which is equivalent to molecular mass of the complex. This complex shows another a fragment ion peak with loss of chlorine atom at m/z 565. The ligand spectra shows fragment ion peak with loss two chlorine atom at m/z (530, 494) due to [Cr(L)₂Cl]⁺ And [Cr(L)₂]⁺ . Respectively as shown in Figure (7). The mass spectrum of the complex [Co(L)₂.Cl₂]Cl shows a molecular ion peak at m/z 607 which is equivalent to molecular mass of the complex. This complex shows another a fragment ion peak with loss of chlorine atom at m/z 572. the ligand spectra shows fragment ion peak with loss two chlorine atom at m/z (536, 501) due to [Co(L)₂Cl]⁺ and [Co(L)₂]⁺ . Respectively as shown in Figure(8). The mass spectrum of the complex [Ni(L)Cl₂]⁺ shows a molecular ion peak at m/z 350 , This complex shows another a fragment ion peak with loss two chlorine atom at m/z 315, 279 due to [Ni(L)Cl]⁺ , [Ni(L)]⁺ . Respectively as shown in Figure (9).

The mass spectrum of the complex [Cu(L)Cl₂]⁺ shows a molecular ion peak at m/z 355 , This complex shows another a fragment ion peak with loss two chlorine atom at m/z 320, 284 due to [Cu(L)Cl]⁺ , [Cu(L)]⁺ . Respectively as shown in Figure (10).

7. CONCLUSIONS

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 and physiochemical measurements as the prepared complexes, we can suggested the chemical configuration for the complexes. The ligand (4-[(5-ethyl-1,3,4-oxadiazol-2-yl)sulfanyl]aniline) was successfully synthesized as shown in the scheme (1). 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 coordinate through Nitrogen and Sulfur atoms . This view is further supported by the appearance of a band corresponding to the metal-nitrogen and the metal-Sulfur stretching Vibration at 503–553 cm⁻¹, 474–484 cm⁻¹ respectively in the complexes . (Cr(III), Fe(III) and Co(III) leading to the formation Octahedral geometry complexes . while the Cu and Ni atoms leading to the formation tetrahedral geometry complexes.

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APPENDAGES

Table4. Infra-Red Spectroscopy absorption bands of ligand and its complexes

NO	Compound	ν C-H Ali-phatic Aromatic	ν N-H	ν C=N	ν C-O-C Asy,Sy	ν C-S	ν M-N	ν M-S	ν M-Cl
1	C ₁₀ H ₁₁ N ₃ OS	2943 Ali 3065 Aro	3300	1581	1419 Sy 1321 Asy	771	----	----	----
2	[Fe(L) ₂ Cl ₂]Cl	2939 3020	3298	1637	1421 1317	763	503	474	355
3	[Cr(L) ₂ Cl ₂]Cl	2945 3050	3295	1629	1412 1313	765	511	477	360
4	[CO(L) ₂ Cl ₂]Cl	2935 3045	3296	1620	1405 1310	769	521	483	367
5	[Ni(L)Cl ₂]	2925 3030	3302	1618	1400 1306	770	536	480	374
6	[Cu(L)Cl ₂]	2941 3011	3304	1612	1396 1301	771	553	484	387

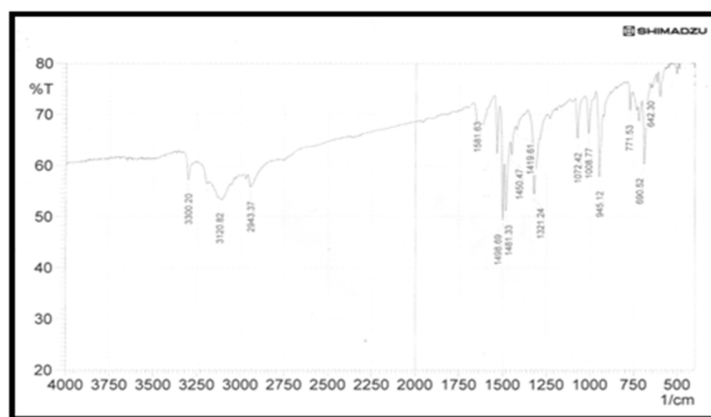


Figure (1) IR spectrum of the ligand cm-1

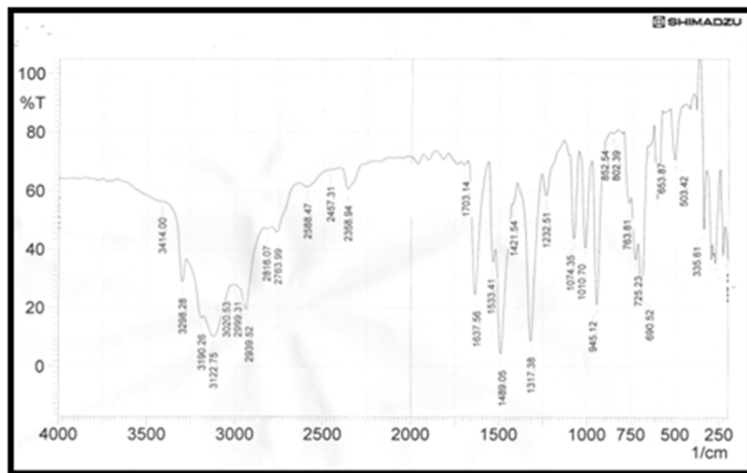


Figure (2) IR spectrum of the $[Fe(L)_2Cl_2]Cl$ cm-1

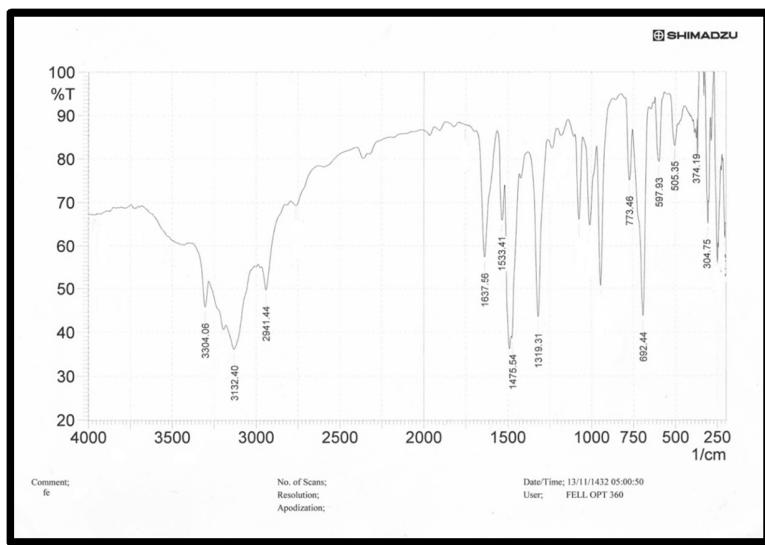


Figure (3) IR spectrum of the $[Cu(L)_2Cl_2]$ cm-1

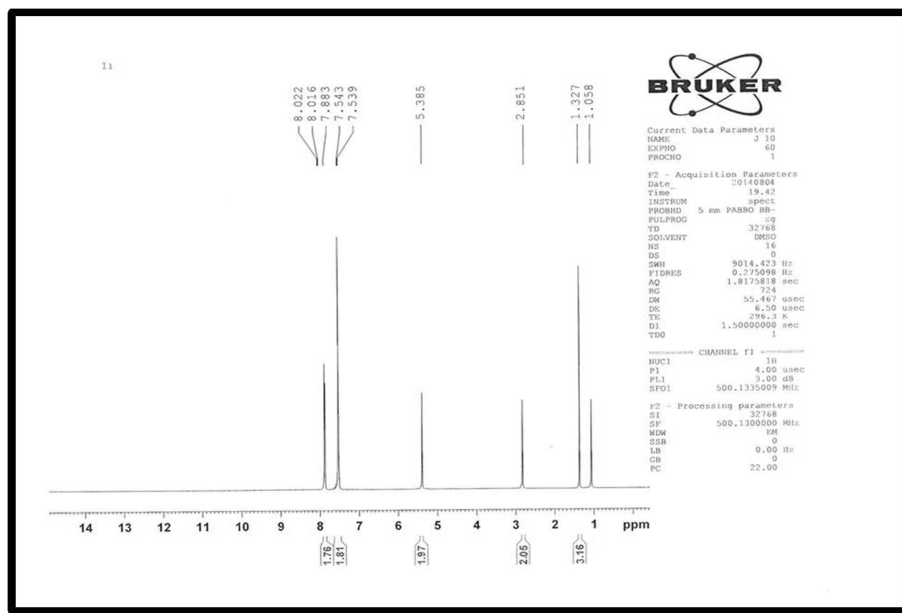
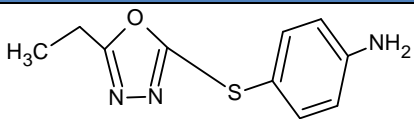
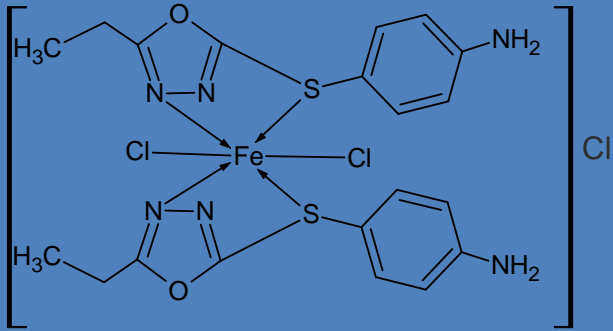
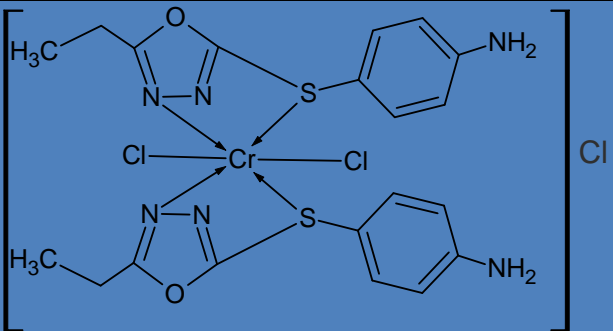
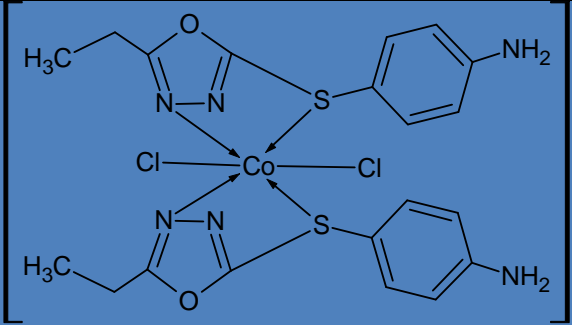
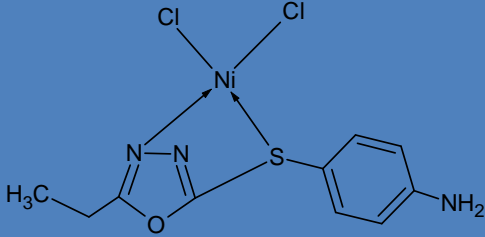
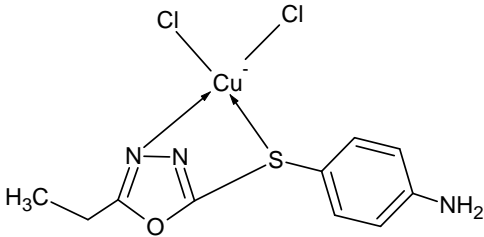


Figure (4) NMR spectra of the ligand

Table 5. The mass spectrum of ligand and its complexes		
Ion	Structure	Molecular Ion
L		221
$[C_{10}H_9N_2OS]^+$		205
$[C_8H_6N_3OS]^+$		192
$[C_7H_6N_2OS]^+$		166
$[C_6H_6NS]^+$		124
$[C_4H_5N_2O]^+$		97
$[C_6H_6N]^+$		92

$[\text{C}_6\text{H}_5]^+$		77
$[\text{C}_5\text{H}_5]^+$		65
$[\text{Fe}(\text{L})_2\text{Cl}_2]\text{Cl}$		604
$[\text{Fe}(\text{L})_2\text{Cl}_2]^+$		569
$[\text{Fe}(\text{L})_2\text{Cl}]^+$		533
$[\text{Fe}(\text{L})_2]^+$		498
$[\text{Cr}(\text{L})_2\text{Cl}_2]\text{Cl}$		600
$[\text{Cr}(\text{L})_2\text{Cl}_2]^+$		565
$[\text{Cr}(\text{L})_2\text{Cl}]^+$		530
$[\text{Cr}(\text{L})_2]^+$		494

$[\text{Co}(\text{L})_2\text{Cl}_2]\text{Cl}$		607
$[\text{Co}(\text{L})_2\text{Cl}_2]^+$		572
$[\text{Co}(\text{L})_2\text{Cl}]^+$		536
$[\text{Co}(\text{L})_2]^+$		501
$[\text{Ni}(\text{L})\text{Cl}_2]$		350
$[\text{Ni}(\text{L})\text{Cl}]^+$		315
$[\text{Ni}(\text{L})]^+$		279
$[\text{Cu}(\text{L})\text{Cl}_2]$		355
$[\text{Cu}(\text{L})\text{Cl}]^+$		320
$[\text{Cu}(\text{L})]^+$		284

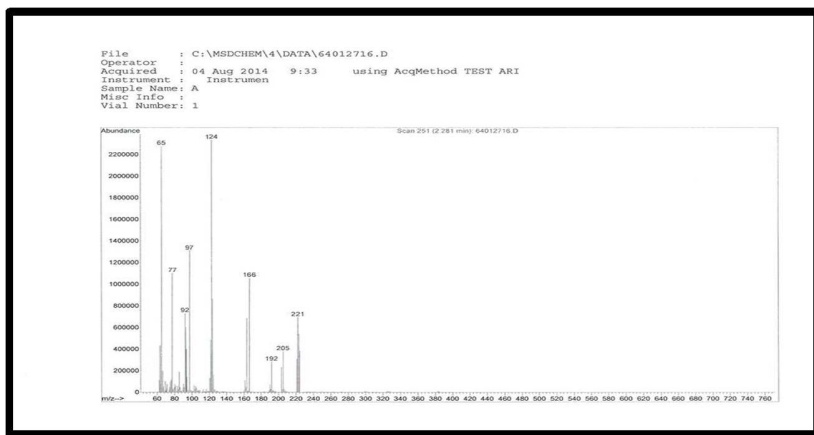


Figure (5) mass spectra of ligand

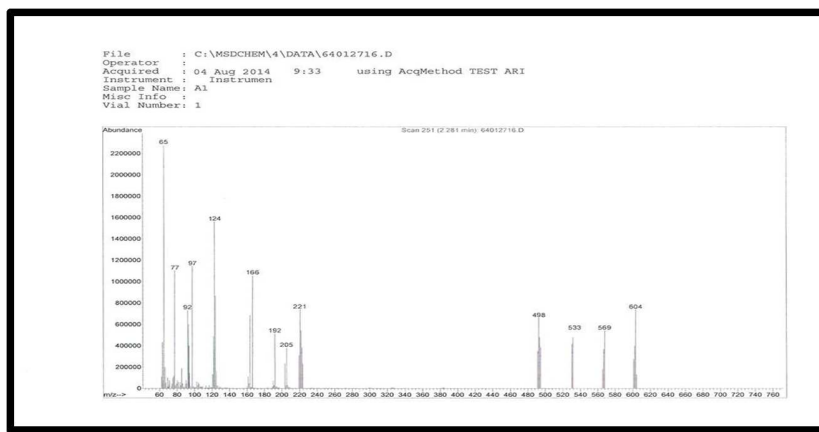


Figure (6) mass spectra of [Fe (L)2Cl2] Cl cm-1

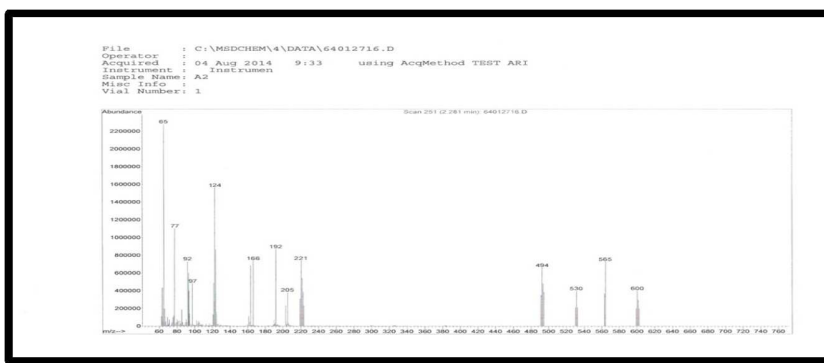


Figure (7) mass spectra of [Cr (L)2Cl2]Cl cm-1

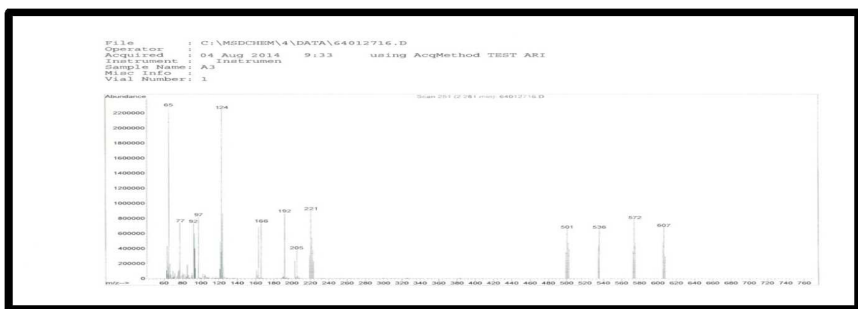


Figure (8) mass spectra of $[\text{Co}(\text{L})_2\text{Cl}_2]\text{Cl}$ cm-1

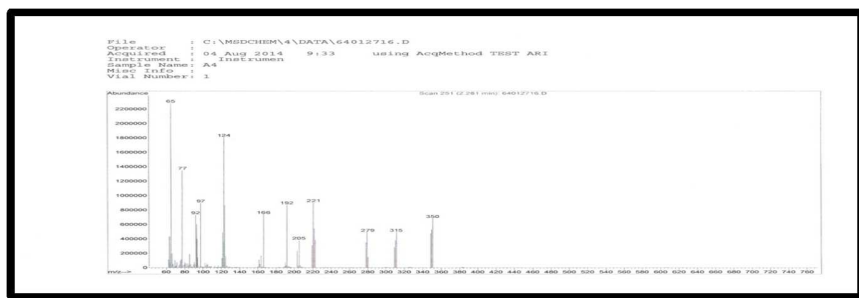


Figure (9) mass spectra of $[\text{Ni}(\text{L})_2\text{Cl}_2]$ cm-1

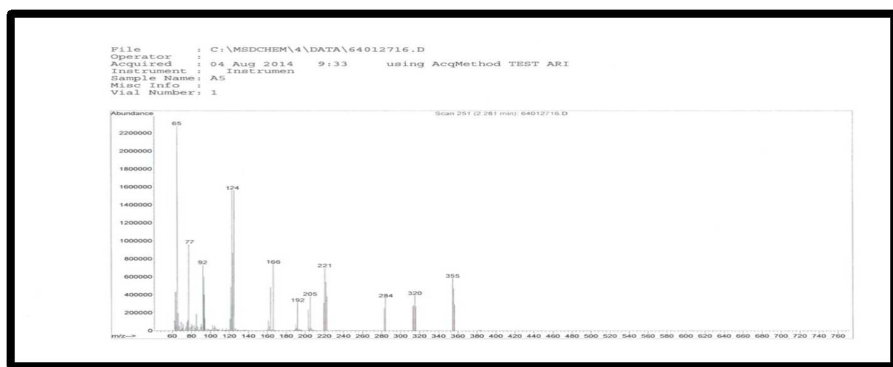


Figure (10) mass spectra of $[\text{Cu}(\text{L})_2\text{Cl}_2]$ cm-1

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