GLOBAL JOURNAL OF BIOLOGY, AGRICULTURE & HEALTH SCIENCES
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Synthesis and Spectral Identification of Some Transition Metal Complexes with New Derivative Of of *N*-(5-Sulfanyl-1,3,4-Thiadiazol-2-yl) Benzene Sulfonamidem Ligand

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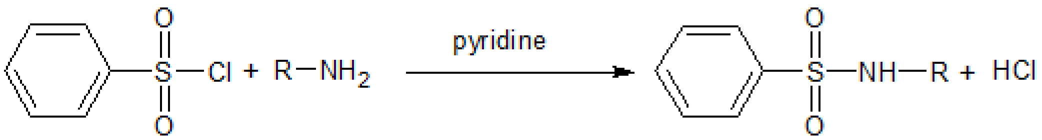
ABSTRACT

1, 3, 4-thiadiazole –benzenesulfonamide compounds are important due to these are have versatile pharmacological activity such as gonorrhea, scarlet fever, blood poisoning ,tonsillitis ,sinus infection ,urinary tract infection, antimicrobial , Antibacterial, Anti- thyroid, Anticancer ,Anti-tumor, Diuretic. anti-inflammatory .antiviral, antifungal, anti malarial, anti-HIV, Anticancer . In our present study Some Transition Metal Complexes which are Co(III), Fe(III), Cr(III), Cu(II), Ni(II) with New Ligand of *N*-(5-Sulfanyl-1,3,4-Thiadiazol-2-yl)Benzene Sulfonamide have been synthesized and identify by using the spectral methods of 1HNMR , Mass ,IR, as well as Molar conductance and C,H,N . It may be concluded for all the synthesized complexes ligand acts as a bidentate and coordinated through thiadiazole nitrogen and sulfonamide oxygen atoms. Its supported by the appearance of a band corresponding to the metal–nitrogen and the metal–Oxygen stretching vibration at 600–608 cm–1 and 485-488 cm–1 in the complexes. The physical and chemical data suggested the octahedral geometry for all complexes except for Cu and Ni complexes which where tetrahedral consequently .

Keywords: - Identification .complexes. Sulphonamide .Synthesis.thiadiazole .

Introduction

The history of discovery and development of sulphonamide is very interesting.in 1908 Ghlemo has successfully prepared (Sulpha drug) .1935 Sulphonamide was established by G. Dhomagk as antimicrobial drugs compounds . he has been suggested that the biological activity of sulphonamide is due to its metabolic product 4-aminobenzene sulphonamide. These were containing sulphonamido group (-SO_2NH_2-) which was responsible for the higher activity of Sulphonamide drugs [1] .



Scheme (1)

The antimicrobial activity of Sulphonamide extends to treatment of infections caused by gram (+) and gram (-) microorganisms ccoci and bacilli ,fungi, mycobacteria ,some large viruses and protozoa .these were the first effective chemo therapeutic agents of antibacterial drugs has been used for treatment of bacterial infection of human Furthermore used in the treatment of many disease like gonorrhea, scarlet fever, blood poisoning ,tonsillitis ,sinus infection ,urinary tract infection [2] .There are several Authors reports on the synthesis of Sulpha drug.
Gomathi vellaiswamy has been synthesized sulfa drug as pharmacological agents with a wide variety of biological activity such as antimicrobial , Antibacterial, Anti- thyroid, Anticancer,Anti-tumor,Diuretic.[3]anti-inflammatory.[4].antiviral, antifungal,antimalarial,anti-Hiv,Anticancer [5] .

The most common method used for synthesis of sulfa compound is by the reaction between alkyl or aryl sulfonyl halide, with amines. In present basic medium [6].
However, in present work we synthesized *N*-(5-sulfanyl-1, 3,4-thiadiazol-2-yl)benzenesulfonamide Ligand with some transition metal complexes of Cu(II), Ni(II) ,Co(III), Fe(III), Cr(III),Which are expected to be highly pharmacological activity of these Complexes compared to it ligand [7]

2. Material

1) hydrazinecarbothioamide 2) methanedithione CS2
3) ethanol 4) anhydrous sodium carbonate Na2CO3 5) hydrochloric acid HCl 6) pyridine 7) benzenesulphonyl chloride.

3. Measurements

The FTIR spectra in the range (4000-200) cm-1 were recorded as CsI discs using a Shimadzu FTIR spectrophotometer . Mass spectra were recorded in the range (0-900) m/z on a 5973 network mass selective detector **.** Elemental analysis C , H , N were carried out on a Thermo finigan flash analyzer, , molar conductance measurements were made in anhydrous DMSO at 25oC using Inolabcond 720 professional benchtop meter ,.The 1H nuclear magnetic resonance spectra were recorded on a Mercury-300BB NMR 300 spectrometer, DOSO-d6 used as solvent. Melting points were determined in Melting points apparatus U.k .

4. Experimental Work

4.1 Preparation of Ligand

1) Synthesis of 5-amino -1, 3, 4-thiadiazole-2-thiol :- A

hydrazinecarbothioamide (,0.045 mole) was suspended in absolute ethanol (50ml) in (R.B.F) round bottom flask (500ml), with Na_2CO_3 anhydrous sodium carbonate (0.025mole) and CS2 (0.131mole) were then added respectively with continues stirring. The reactant mixture was refluxed for 6 hours; the reaction mixture was then allowed to cool at room temperature and filtered. The filtrate was evaporated under vacuum then added cold distilled water (90 ml) , finally acidification with concentrated HCl drop by drop, white –yellowish precipitate was formed, the white-yellowish precipitate was collected by filtration, and washed with distilled water, re-crystallized by using hot distilled water. The percentage of yield (82 %), melting point m.p. 234 – 236 C , [8] **.**

2) Synthesis of *N*-(5-sulfanyl-1,3,4-thiadiazol-2-yl) benzenesulfonamide :- B

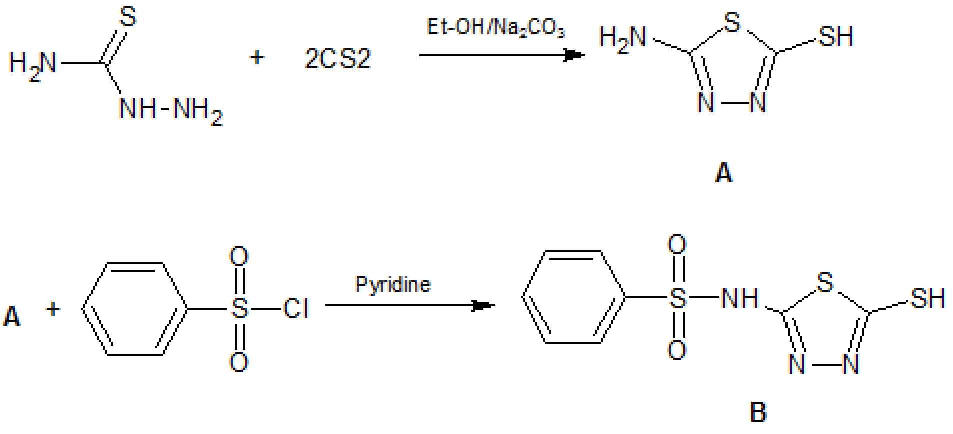
N-(5-sulfanyl-1,3,4-thiadiazol-2-yl)Benzenesulfonamide synthesized by Refluxing the mixture of 2 gm of the Synthesis of 5-amino -1, 3, 4-thiadiazole-2- thiol with 6 gm of benzenesulphoyl chloride and 10 ml of pyridine for 45 min. pour the reaction mixture into 20 ml of cold distilled water and stirrer until the wanted product crystallizes .then filter of the solid and recystallize it from ethanol. percentage of yield (62 %), melting point m.p. 228 – 230 C [9] .

4.2 Preparation of complexes

By the reaction between the The hydrated metal chloride salts of Ni(II) , Cu(II) ,Cr(III), Fe(III), Co(III), (0.02 mol) was added to solution of the *N*-(5-sulfanyl-1,3,4-thiadiazol-2-yl)Benzenesulfonamide (0.02mol) in hot absolute ethanol (75 ml) and the mixture was refluxed on a water bath for 3 hours and the solvent was evaporated by concentrated the mixture to half of the original volume and then cooled . The isolated complexes were filtered and washed several times with ethanol and finally dried in air. The physical appearance, percentage of yield, melting point was listed in tablet 1 [10]**.**

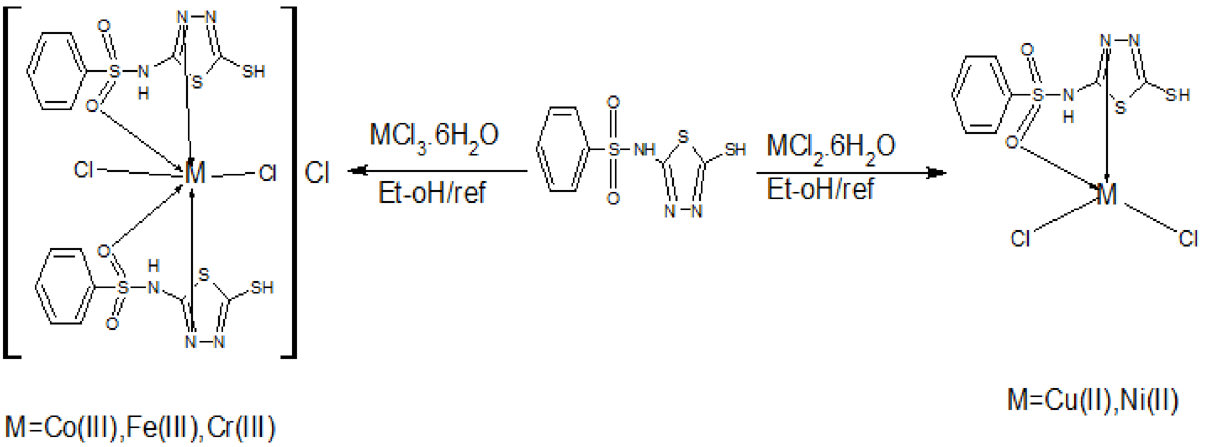
5. Present Work

5.1 Preparation of Ligand



Scheme (2)

5.2 Preparation of Complexes:-



Scheme (3)

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

No	Formula	M.Wt	Colour	M.P °C	% Yield
1	[$C_8H_7N_3O_2S_3$]	273	Yellowish white	228	62%
2	[Ni(L)Cl_2]	403	Deep Green	240	65%
3	[Cu(L)Cl_2]	408	Blue	238	68%
4	[Cr$(L)_2Cl_2$]Cl	705	Green	251	70%
5	[Fe$(L)_2Cl_2$]Cl	709	Pale brown	256	72%
6	[Co$(L)_2Cl_2$]Cl	712	Deep brown	254	67%

6. Results & Discussion

1H-NMR Spectra data of the free ligand reported in figure (1). The physical properties, Molecular weight, Molecular formula, and and molar conductance data and elemental analysis of the ligand and its complexes tabulated in table (1) and table (2) and (3)

The Mass Spectra as shown in a figure (2,3,4) tabulated in table (4) . While the Infra-Red Spectroscopy as shown in a figure (5,6) tabulated in table (5).

the Analytical and spectra data (mass spectra,1H NMR,IR, elemental analyses C,H,N and Molar conductance of all synthesized Ligand and it complexes were appeared a good agreement between the The calculated values and experimental values and appeared full agreement with the proposed structure .

Table 2. molar conductance data of all complexes measurements were made in anhydrous DMSO at 25^{o}C ,Concentration 10^{-} at 298K .

NO	**Formula**	**Λ_M(S.cm^2.mol^{-1})**	**Electrolyte Type**
1	$[Ni(L)Cl_2]$	11.9	Non Electrolyte
2	$[Cu(L)Cl_2]$	13.5	Non Electrolyte
3	$[Cr(L)_2Cl_2]Cl$	22.1	1:1
4	$[Fe(L)_2Cl_2]Cl$	27.8	1:1
5	$[Co(L)_2Cl_2]Cl$	24.2	1:1

Table 3 . Elemental analysis of Ligand : C H N

Theoretical Data		
C	**H**	**N**
35.15%	2.58%	15.37%
Experimental Data		
C	**H**	**N**
35.28%	2.64%	15.25%

6.1 1H-NMR

The ¹H-NMR of the synthesized Ligand the following peaks appeared: at 3.621 (Singlet, 1H, SH), and 5.7 (Singlet ,1H, NH) and 7.520–8.036 (multiplet , 5H, Ar-H).

The NMR Spectra give strong support for the composition of the ligand ,so all the protons are at their expected region The number of protons calculated from integration curves and the recorded chemical shifts in figure (1)[11]

6.2 Mass spectra

The mass spectra of the ligand shows a molecular ion peak fragment [M/Z] at 273 ,200,215,197,182,141,90,77,65, and 59 due to fragments ion $[C_8H_7N_3O_2S_3]^{+\cdot}$,$[C_7H_6NO_2S_2]^{+\cdot}$, $[C_7H_6N_3O_2S]^{+\cdot}$,$[C_7H_6N_2O_2S]^{+\cdot}$, $[C_6H_5O_2S]^{+\cdot}$, $[C_6H_5]^{+\cdot}$ $[C_5H_5]^{+\cdot}$,$[CHNS]^{+\cdot}$., Consequently as showed in Figure(2).

The mass spectra of the complex [Cr(L)2.Cl2]Cl shows a molecular ion peak at m/z at 705,669,634,598 which is correspond to the fragment ion peak of [Cr(L)2Cl2] $^{+\cdot}$ Cl , [Cr(L)2Cl2] $^{+\cdot}$,[Cr(L)2Cl] $^{+\cdot}$, [Cr(L)2] $^{+\cdot}$ Consequently. As showed in Figure (3).The mass spectra of the complex [Co(L)2.Cl2]Cl shows a molecular ion peak at m/z at 712,677,641,606 which is correspond to the fragment ion peak of [Co(L)2Cl2]$^{+\cdot}$Cl ,[Co(L)2Cl2]$^{+\cdot}$ [Co(L)2Cl] $^{+\cdot}$, [Co(L)2]$^{+\cdot}$ Consequently.The mass spectra of the complex [Fe(L)2.Cl2]Cl shows a molecular ion peak at m/z 709,674,639,603 which is correspond to the fragment ion peak of [Fe(L)2Cl2]$^{+\cdot}$Cl ,[Fe(L)2Cl2]$^{+\cdot}$ [Fe(L)2Cl] $^{+\cdot}$, [Fe(L)2]$^{+\cdot}$ Consequently. The mass spectra of the complex [Ni(L)Cl2]$^{+\cdot}$ shows a molecular ion peak at m/z 403 , 367,332 correspond to the fragment ion peak of [Ni(L)2Cl2]$^{+\cdot}$,[Ni(L)2Cl]$^{+\cdot}$, [Ni(L)2] $^{+\cdot}$, Consequently. As showed in Figure (4).

The mass spectra of the complex [Cu(L)Cl2]$^{+\cdot}$ shows a molecular ion peak at m/z 403 , 367,332 correspond to the fragment ion peak of [Cu(L)2Cl2]$^{+\cdot}$,[Cu(L)2Cl]$^{+\cdot}$, [Cu(L)2]$^{+\cdot}$, Consequently.[12]

Table 4 . The mass spectrum of ligand and its Complexes

No	Ion	Molecular Ion
1	$[C_8H_7N_3O_2S_3]^{+\cdot}$	273
2	$[C_7H_6NO_2S_2]^{+\cdot}$	200
3	$[C_7H_6N_3O_2S]^{+\cdot}$	197
4	$[C_7H_6N_2O_2S]^{+\cdot}$	182
5	$[C_6H_5O_2S]^{+\cdot}$	141
6	$[C_6H_5]^{+\cdot}$	77
7	$[C_5H_5]^{+\cdot}$	65
8	$[CHNS]^{+\cdot}$	59
9	[Cr(L)2Cl2] $^{+\cdot}$ Cl	705
10	[Cr(L)2Cl2] $^{+\cdot}$	669
11	[Cr(L)2Cl] $^{+\cdot}$	634
12	[Cr(L)2] $^{+\cdot}$	598
13	[Fe(L)2Cl2] $^{+\cdot}$ Cl	709
14	[Fe (L)2Cl2] $^{+\cdot}$	674
15	[Fe (L)2Cl] $^{+\cdot}$	639
16	[Fe(L)2] $^{+\cdot}$	603
17	[Co(L)2Cl2] $^{+\cdot}$ Cl	712
18	[Co(L)2Cl2] $^{+\cdot}$	677
19	[Co(L)2Cl] $^{+\cdot}$	641
20	[Co(L)2] $^{+\cdot}$	606
21	[Cu(L)2Cl2] $^{+\cdot}$	408
22	[Cu(L)2Cl] $^{+\cdot}$	372
23	[Cu(L)2] $^{+\cdot}$	337
24	[Ni(L)2Cl2] $^{+\cdot}$	403
25	[Ni(L)2Cl] $^{+\cdot}$	367
26	[Ni(L)2] $^{+\cdot}$	332

7.1 Infra-Red Spectroscopy

The FTIR spectrum for synthesized Ligand *N*-(5-sulfanyl-1,3,4-thiadiazol-2-yl)benzene sulfonamide shows A characteristic stretching absorption bands at 3300 cm-, 3027cm-1,2760 cm-1,1635 cm-1 and 1480 cm-1, which were assigned to υ N-H ,υC-H Aro, υS-H, υC=N of ring and υS=O consequently. 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 complexion had happened [13]. The IR data of the Ligand and complexes are shown in Table (5) and figure(5,6). The Characteristics groups exhibited by the ligands and complexes.[13]

Table5. Infra-Red Spectroscopy absorption bands of ligand and its complexes.

No	Compound	υN-H	υC-H	υS-H	υ C=N
1	Ligand	3380	3055	2811	1605
2	[Fe(L)2Cl2]Cl	3390	3070	2825	1612
3	[Co(L)2Cl2]Cl	3390	3070	2825	1612
4	[Cr(L)2Cl2]Cl	3390	3070	2825	1612
5	[Ni(L)Cl2]	3390	3070	2825	1612
6	[Cu(L)Cl2]	3390	3070	2825	1612
		υS=O	**υM-N**	**υM-O**	**υM-Cl**
1	Ligand	1445	------	------	------
2	[Fe(L)2Cl2]Cl	1460	600	485	305
3	[Co(L)2Cl2]Cl	1460	603	488	307
4	[Cr(L)2Cl2]Cl	1460	604	486	306
5	[Ni(L)Cl2]	1460	608	487	309
6	[Cu(L)Cl2]	1460	602	485	302

Conclusion

In the present work, a series of Co(III), Fe(III), Cr(III), Ni(II), Cu(II) complexes with new ligand (L),have been prepared and characterized on the basis of IR,1HNMR, Mass spectroscopic as well as by elemental analyses C,H,N and Molar conductance. According to all and the physiochemical measurements as the prepared complexes, we can suggested the chemical configuration for the complexes. The ligand Synthesis of *N*-(5-sulfanyl-1,3,4-thiadiazol-2-yl) benzenesulfonamide was successfully synthesized. The ligand was treated to different transition metal salt to form the corresponding complexes as shown in the scheme (3). It may be concluded that the ligand coordinate through sulfonamide oxygen and thiadiazole nitrogen atoms.This view is further supported by the appearance of a band corresponding to the metal– nitrogen , metal – oxygene stretching Vibration at 542–563 and 500-600 cm–1 respectively in the complexes . (Cr(III),Fe(III)and Co(III) leading to the formation Octahedral geometry complexes .while the Cu(II) and Ni(II) atoms leading to the formation tetrahedral geometry complexes.

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Appendices

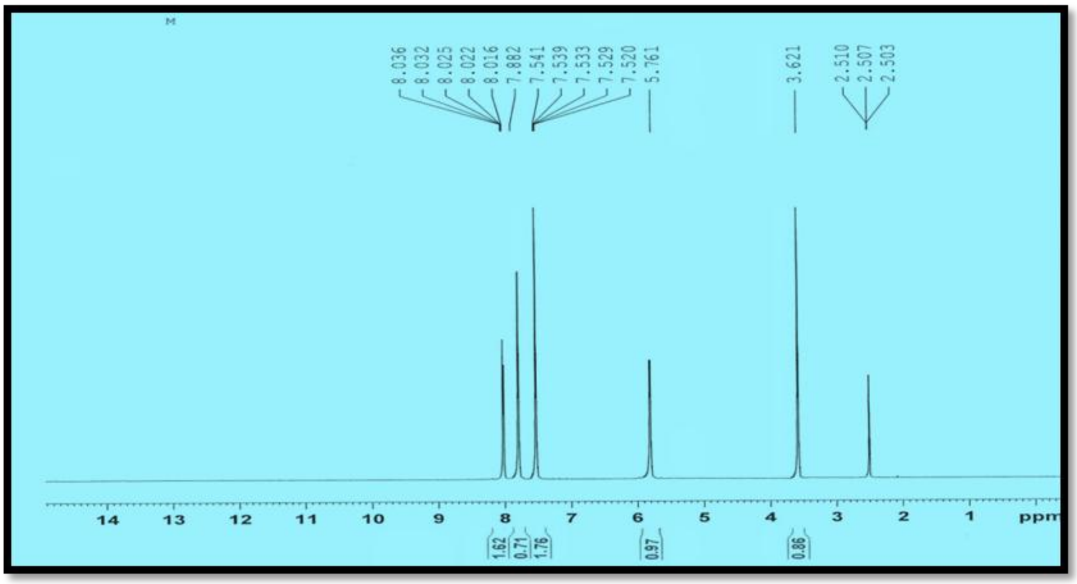

Figure (1) NMR spectra of the ligand

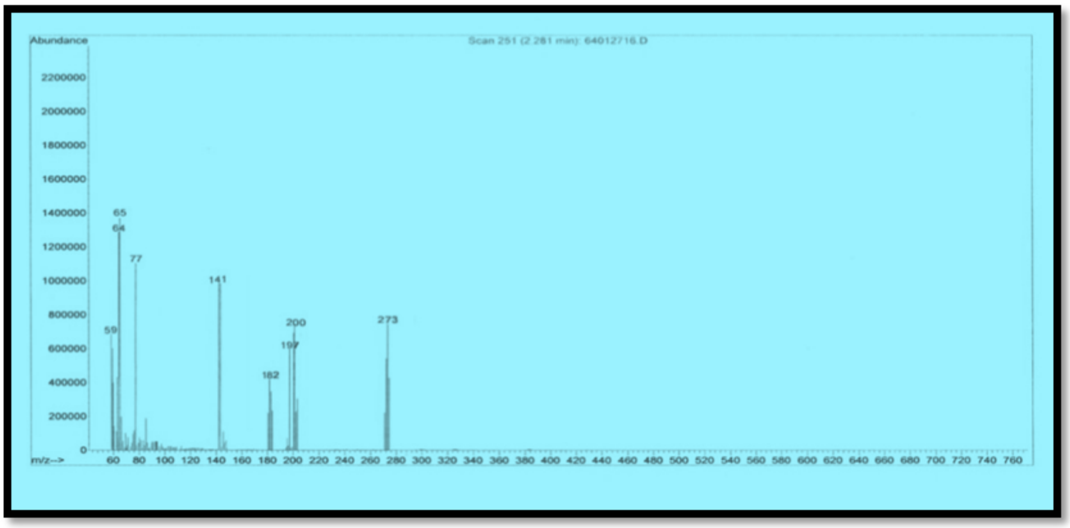

Figure (2) mass spectra of Ligand

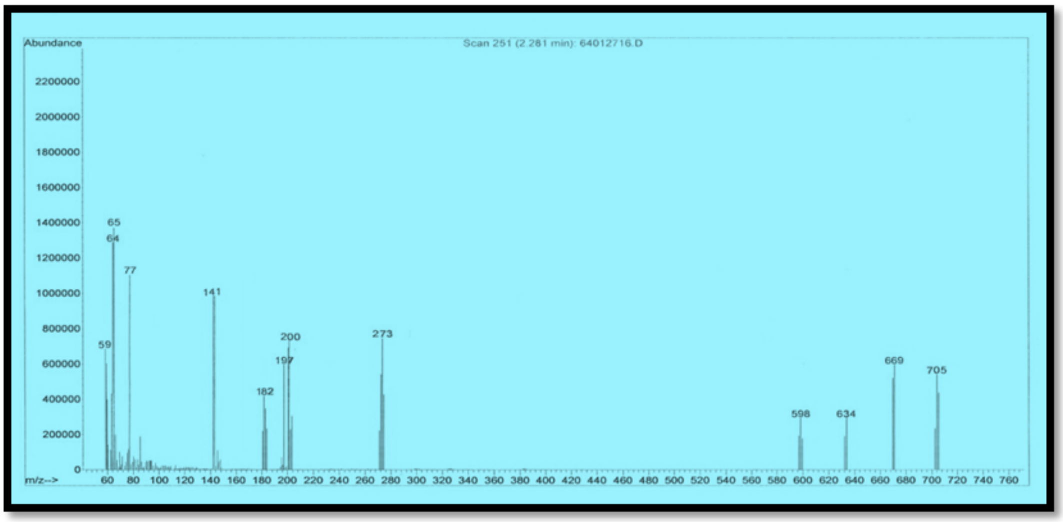

Figure (3) mass spectra of [Cr(L)2Cl2]Cl

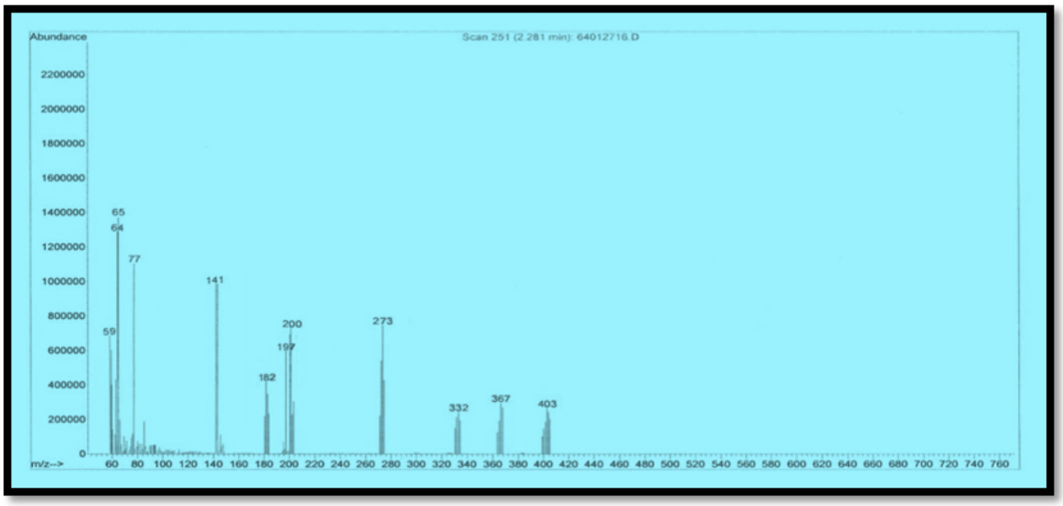

Figure (4) Mass spectra of the [Ni(L)2Cl2]

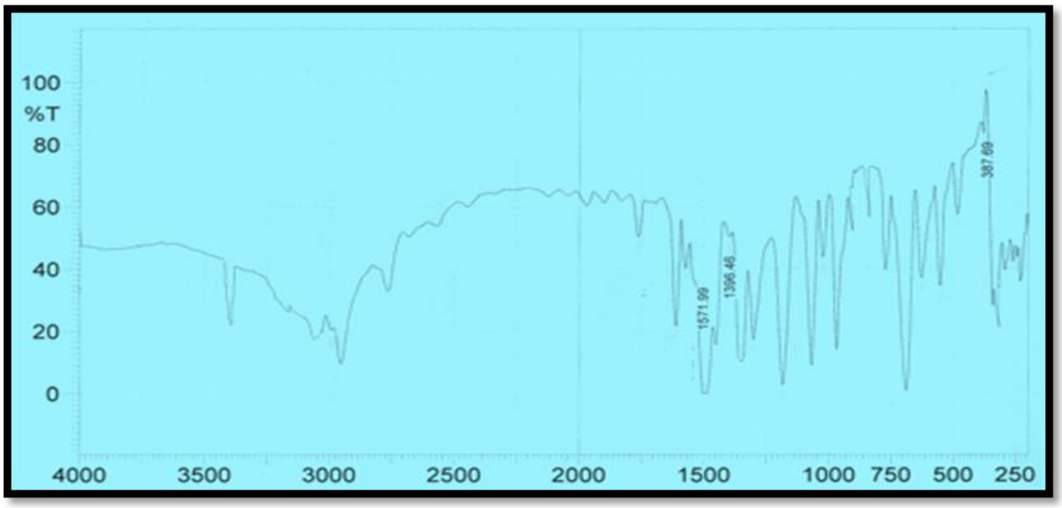

Figure (5) IR spectrum of the ligand

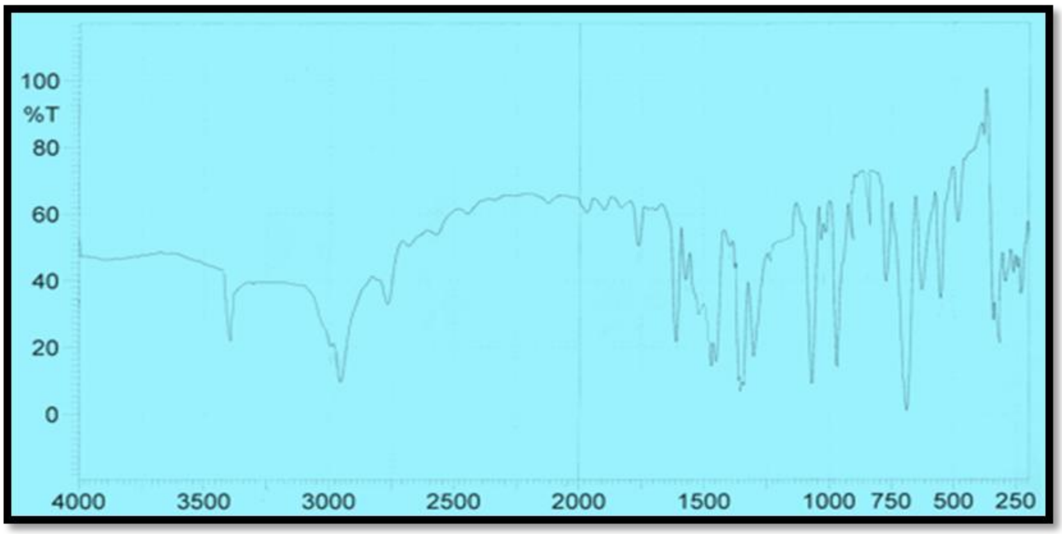

Figure (6) IR spectrum of the [Fe(L)2Cl2]C1