Synthesis new legand{[5-(furan-2yl)-1,3,4-thiadiazole-2-yl]imino}ethanol with some transition metal complexes

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ABSTRACT —The solid complexes of Fe(II), Cr(III), Co(II), Ni(II), andCu(II)) with Synthesis of {[(5-(Furan-2-yl)-1,3,4-thiadiazol-2-yl)imino}ethanal]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 542–563 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: synthesis .characterization.complexes.thiadiazole

1.Introduction

1,3,4-Thiadiazole is a sulfur-containing aromatic heterocyclic with nitrogen atoms at the 3-and 4-positions and is numbered as shown in its structure 1.1,3,4-Thiadiazole exists in two partially reduced (dihydro-) forms,2 and 3 and named as 1,3,4-Thiadiazolines depending on the position of the double bond. the completely reduced (tetrahydro-)1,3,4-Thiadiazole is known as 1,3,4-Thiadiazolidine 4.

1,3,4-Thiadiazole exhibit varying biological activity and are ,therefore find their uses in the fields of pharmaceuticals (acerazolamide 5 as diuretic and 2-amino-1,3,4-Thiadiazole 6 antitumor agent in dogs) and agrochemicals (methidathion 7 as an insecticide and 8 as herbicidic).[1]

The therapeutic effects of compounds containing 1,3,4-thiadiazole and rings have been well studied for a number of pathological conditions including inflammation [2, 3], pain [4,5,6] or hypertension [7]. Moreover, synthesis of thiadiazoles has attracted widespread attention due to their diverse applications as antibacterial [8], antimycobacterial [9,10], antimycotic [11,12] ,antifungal [13,14] and antidepressant agents [15].

The coordination chemistry of transition metal complexes of heterocyclic compounds, involving thiadiazole 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) Mahasin Alias, Huda Kassum, Carolin Shakir They were concluded metal complexes of 1,3,4-oxadiazole Ligand exhibited more biologically active compared to those of the parent ligands against both microorganism species Pseudomonas aeruginosa (as gram negative strain bacteria) and Staphylococcus aureus (as gram positive strain bacteria) was examined using two different concentrations (10 and 5 M) in nutrient agar media and some complexes showed noticeable activity against the tested microorganisms comparaing them to ampicillin as the standard drug. [16] .

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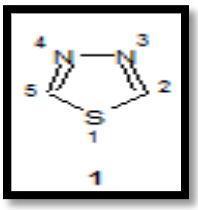

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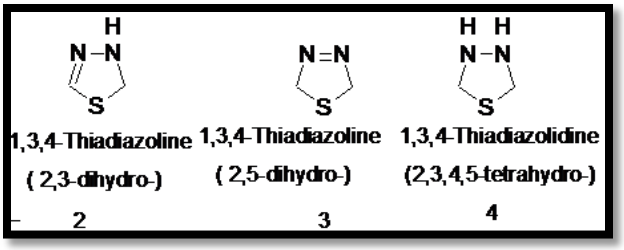
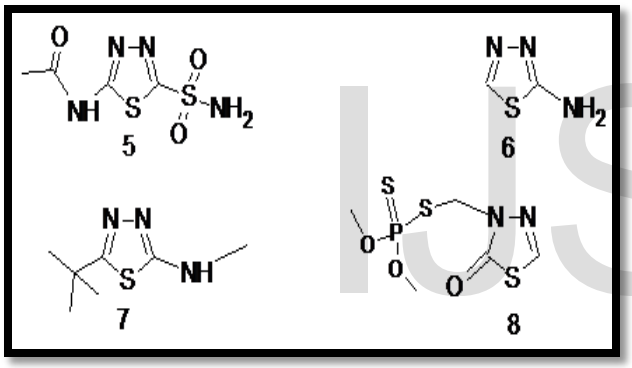




2. Expermental work:-

2.1 Preparation of Ligand :-

First step :-Synthesis of 5-(furan-2-yl)-1,3,4-thiadiazol-2-amine

A mixture of thiosemicarbazide (9.11 g, 0.1mol),benzoic acid (11.2g,0.1 mol), and conc.Sulphuric acid (5 ml) in 100 ml of ethanol was refluxed for 5 hour and poured onto crushed ice. The solid separated out was filtered, washed with cold water and recrystallized from ethanol to separate the first step product [A]. The purity of the compound was followed by TLC. Yield(87.2%) , m.p. 257 – 259 C .[17]

Second step:- Synthesis of {[5-(furan-2-yl)-1,3,4-thiadiazol-2-yl]imino} ethanal

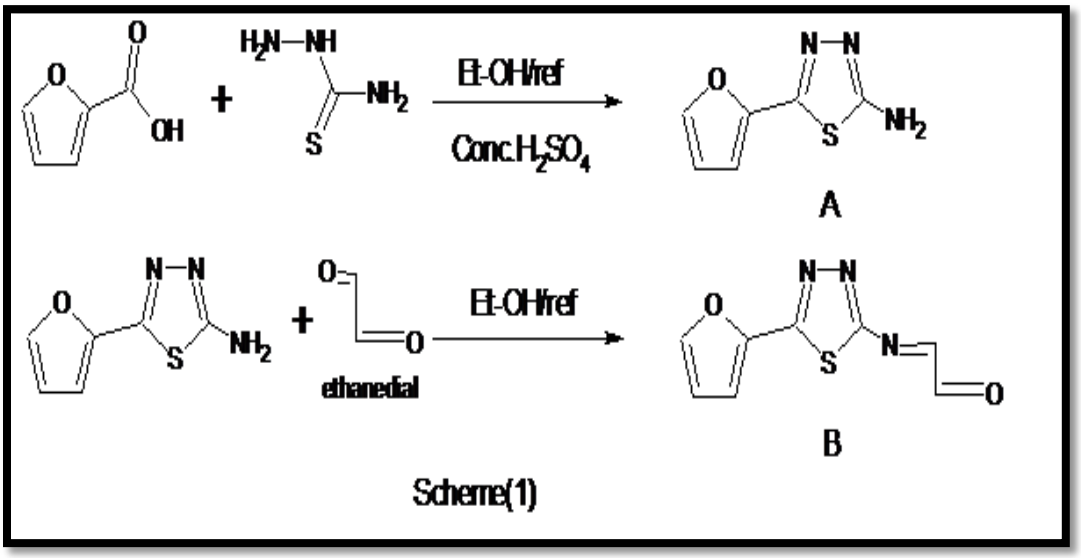
A mixture of [A] (1.92 g , 0.01 mol) and ethanedial (1.849 g,0.01mol)was refluxed in absolute ethanol (35 mL) for (7) hours The brown {[5-(furan-2-yl)-1,3,4-thiadiazol-2-yl]imino}ethanol [B]was filtered ,dried and recrystallized from ethanol .The purity of the compound was followed by TLC. Yield(1.64 g , 82.7. %) , m.p. 268 – 270 C .[18]

2.2 Preparation of complexes :

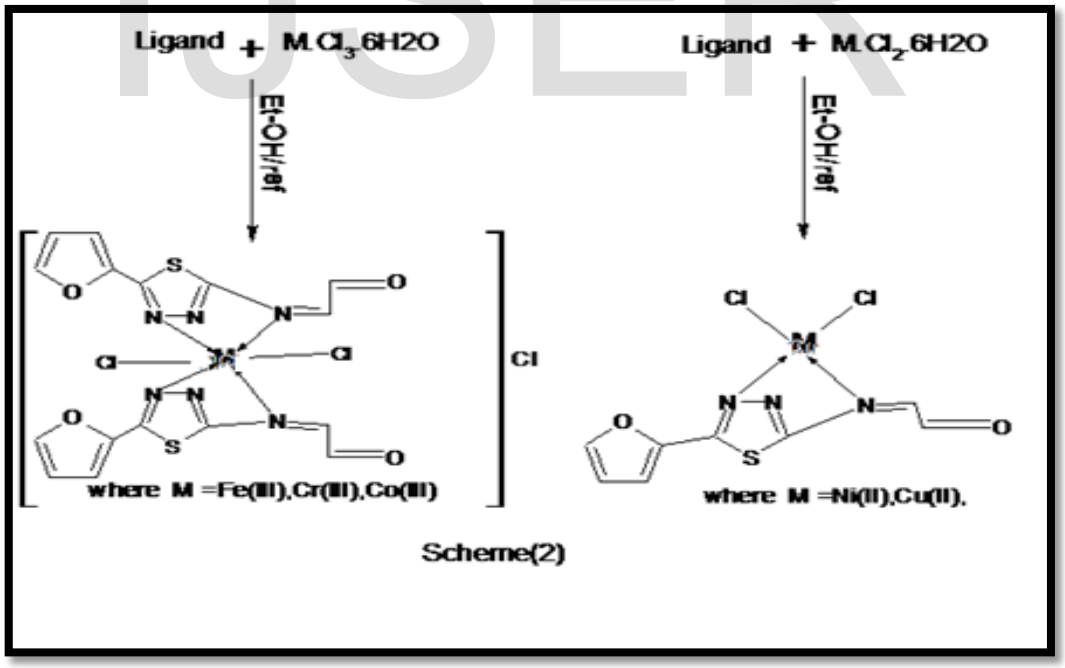
The hydrated metal chloride salts of The Fe(III), Cr(III), Co(III), Ni(II) and Cu(II) (0.01 mol) was added to solution of the ligand 2.21gm (0.01mol) in hot absolute ethanol (40 mL) and the mixture was refluxed on a water bath for 2 hours and the solvent was evaporated in vacuum to half of the original volume and then cooled . The isolated complexes were filtered off , washed several times with ethanol and finally dried in air. [19]

3. Present 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 Specrta Figure(1,2,3,4,5,6) Infra-Red Spectroscopy tabulated inTable(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 .

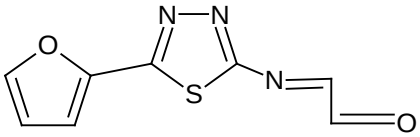
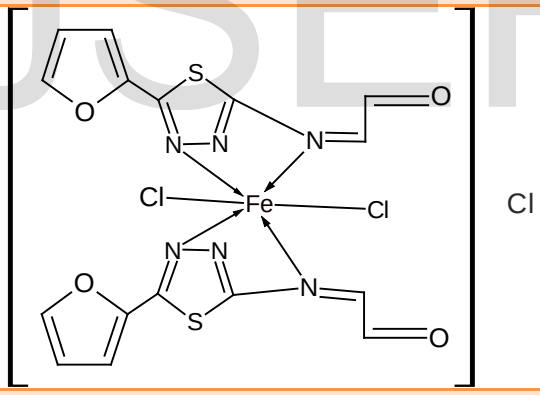
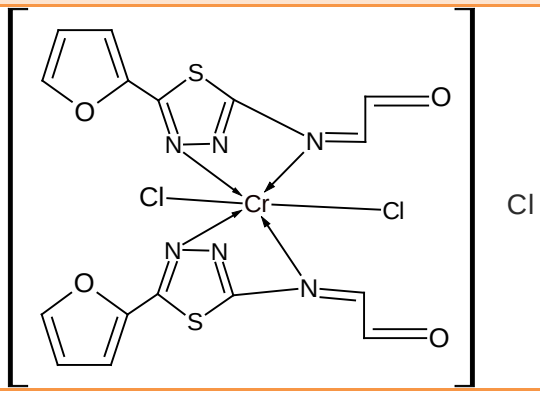
NO	Formula	M.Wt	Color	M.P C	Yield %
L	$C_{10}H_{11}N_3OS$	207	Brown	268-270	82.7
1	$[Fe(L)_2Cl_2]Cl$	576	Pale Brown	261-263	85.8
2	$[Cr(L)_2Cl_2]Cl$	572	Green	233-235	91.5
3	$[Co(L)_2Cl_2]Cl$	579	Deep brown	279-281	88.1
4	$[Cu(L)Cl_2]$	341	Pale yellow	254-256	85.4
5	$[Ni(L)Cl_2]$	336	Pale green	242-244	88.5

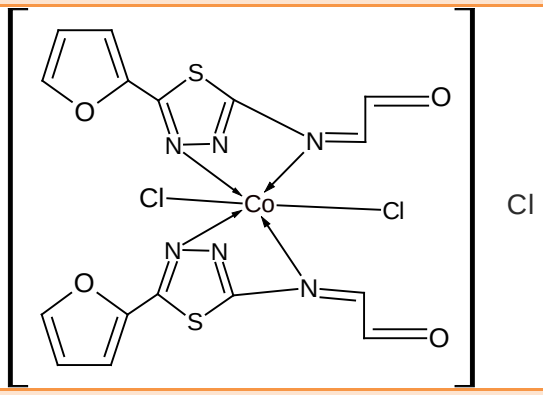
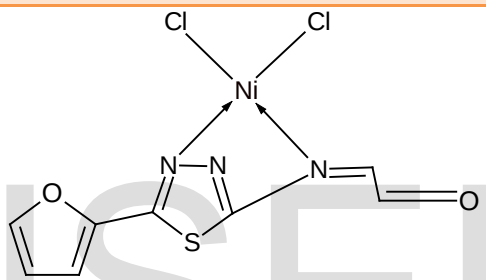
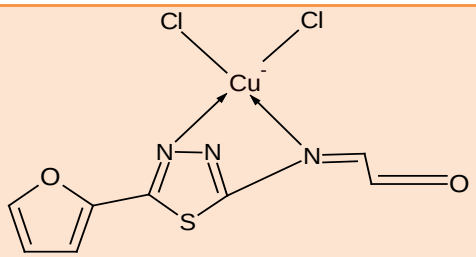
Table 2. molar conductance data of all complexes measurements were made in anhydrous DMSO at 25^oC ,Concentration 10^- at 298K .

NO	Formula	$\Lambda_M(S.cm^2.mol^{-1})$	Electrolyte Type
1	$[Fe(L)_2Cl_2]Cl$	31.4	1:1
2	$[Cr(L)_2Cl_2]Cl$	36.8	1:1
3	$[Co(L)_2Cl_2]Cl$	28.2	1:1
4	$[Cu(L)Cl_2]$	19.0	Non Electrolyte
5	$[Ni(L)Cl_2]$	22.7	Non Electrolyte

Table3. elemental analysis data for the ligand

Experimental			Theoretical		
C%	H%	N%	C%	H%	N%
46.91	2.66	19.85	46.37	2.43	20.28

Table 4. The mass spectrum of ligand and its complexes		
Ion	Structure	Molecular Ion
L		207
$[C_7H_4N_3OS]^{+\cdot}$		178
$[C_6H_3N_2OS\ ]^{+\cdot}$		151
$[C_4H_2N_3OS]^{+\cdot}$		140
$[C_3H_2N_2OS]^{+\cdot}$		114
$[C_5H_3OS]^{+\cdot}$		111
$[C_5H_3NO]^{+\cdot}$		93
$[C_4H_3O]^{+\cdot}$		67
$[CNS]^{+\cdot}$		58
$[C_2H_2NO]^{+\cdot}$		56
$[Fe(L)_2Cl_2]Cl$		576
$[Fe(L)_2Cl_2]^{+\cdot}$		541
$[Fe(L)_2Cl]^{+\cdot}$		505
$[Fe(L)_2]^{+\cdot}$		470
$[Cr(L)_2Cl_2]Cl$		572

$[Cr(L)_2Cl_2]^{+\cdot}$		537
$[Cr(L)_2Cl]^{+\cdot}$		501
$[Cr(L)_2]^{+\cdot}$		466
$[Co(L)_2Cl_2]Cl$		579
$[Co(L)_2Cl_2]^{+\cdot}$		544
$[Co(L)_2Cl]^{+\cdot}$		508
$[Co(L)_2]^{+\cdot}$		473
$[Ni(L)Cl_2]$		336
$[Ni(L)Cl]^{+\cdot}$		301
$[Ni(L)]^{+\cdot}$		265
$[Cu(L)Cl_2]$		341
$[Cu(L)Cl]^{+\cdot}$		306
$[Cu(L)]^{+\cdot}$		270

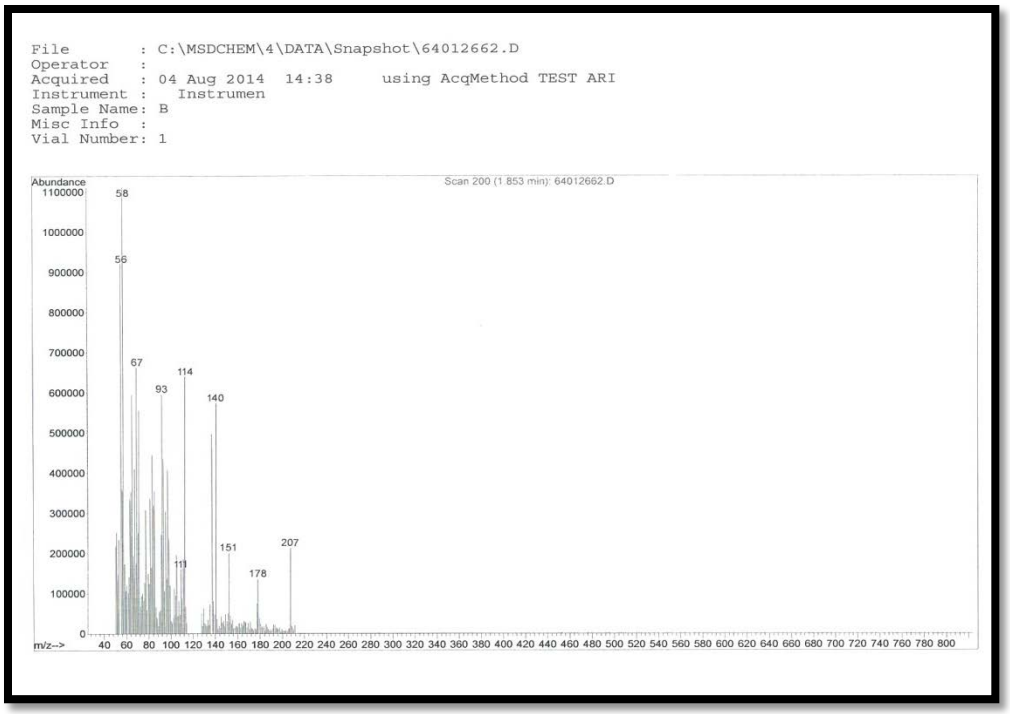


Figure (1) mass spectra of ligand

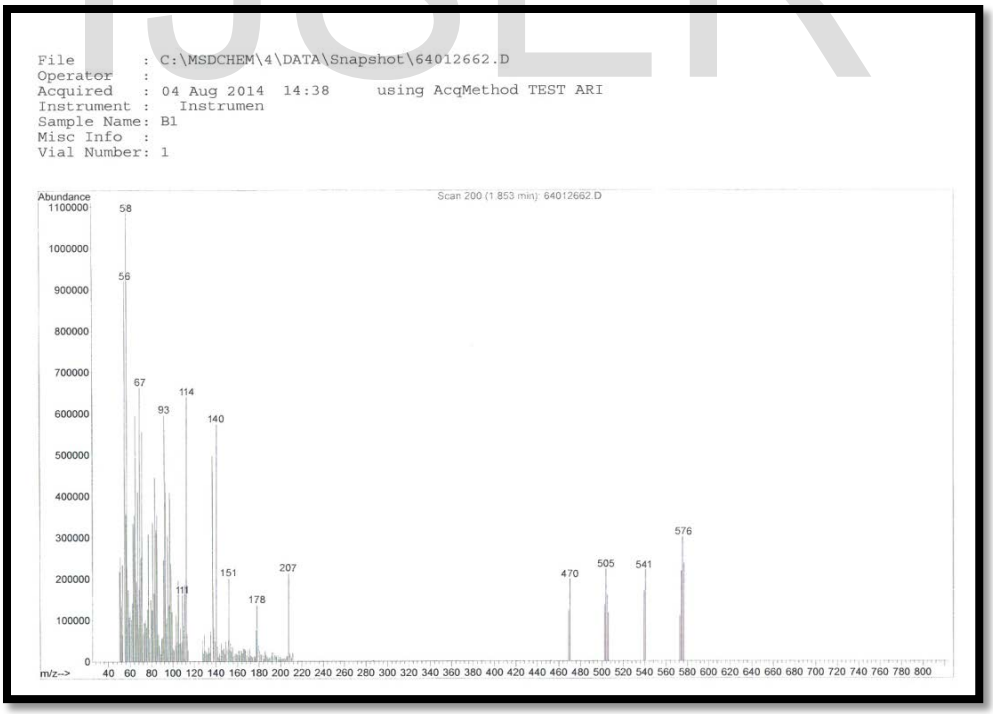


Figure (2) mass spectra of [Fe (L)2Cl2] Cl cm-1

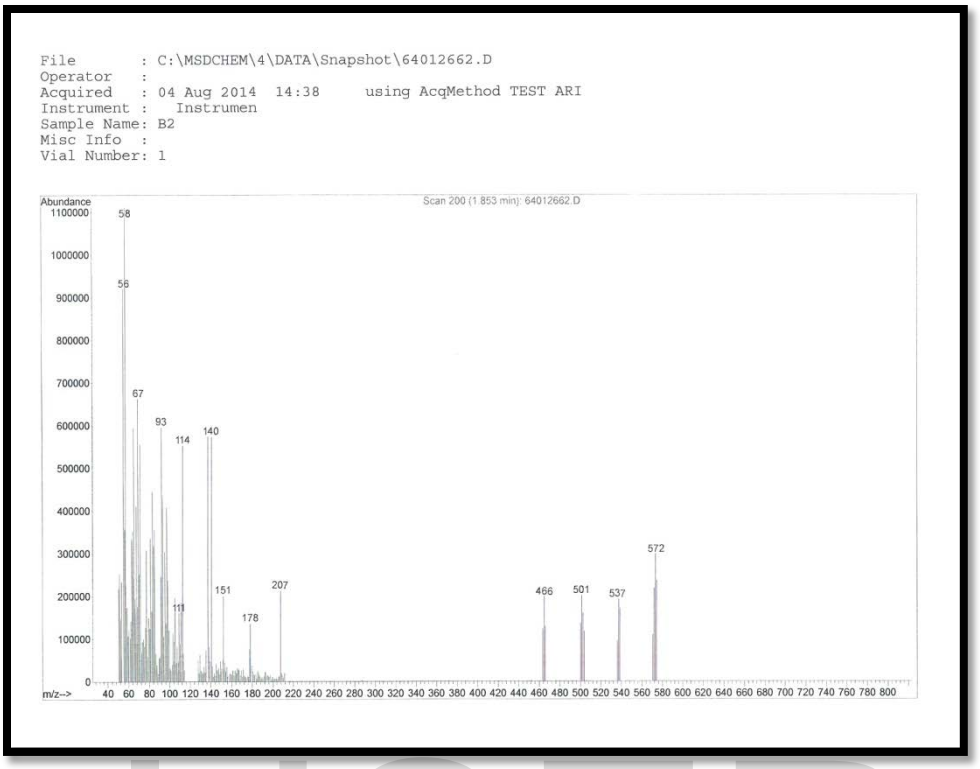


Figure (3) mass spectra of [Cr (L)2Cl2]Cl cm-1

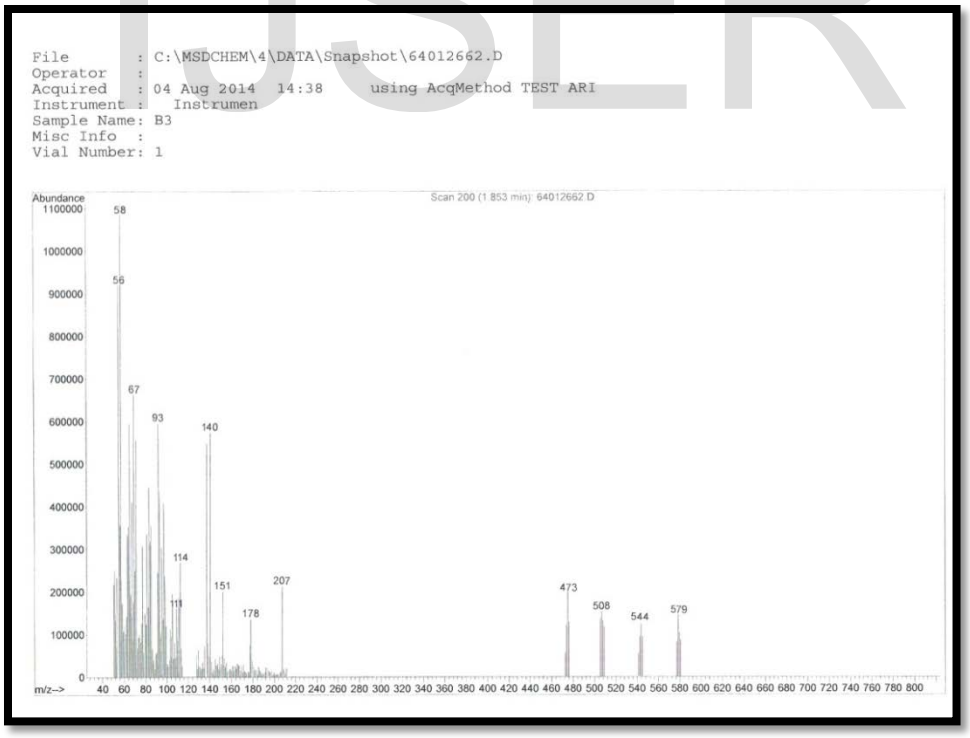


Figure (4) mass spectra of [Co(L)2Cl2]Cl cm-1

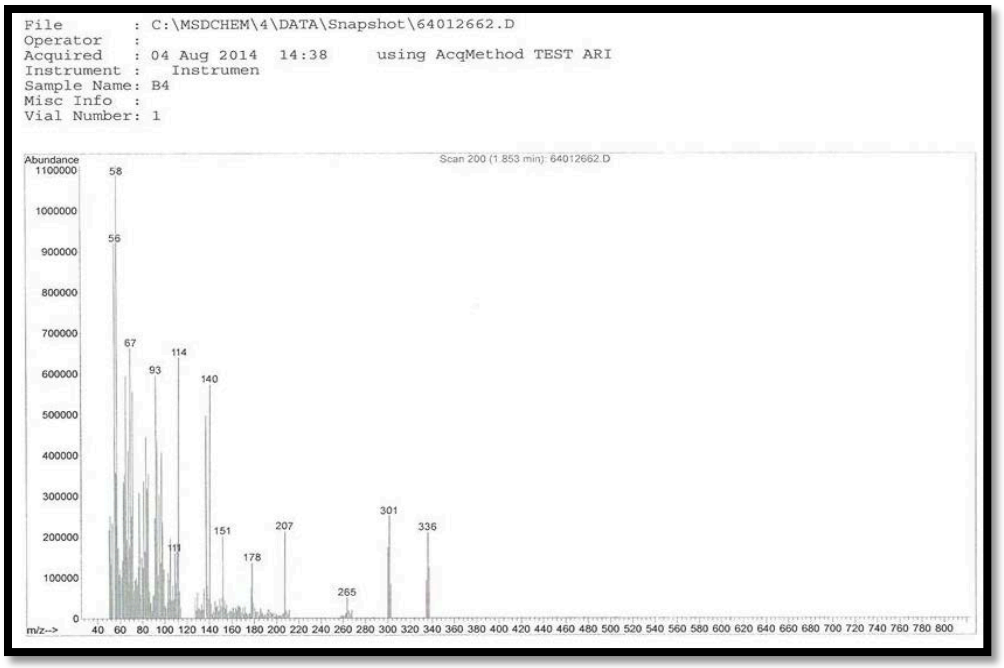


Figure (5) mass spectra of [Ni(L)2Cl2]Cl cm-1

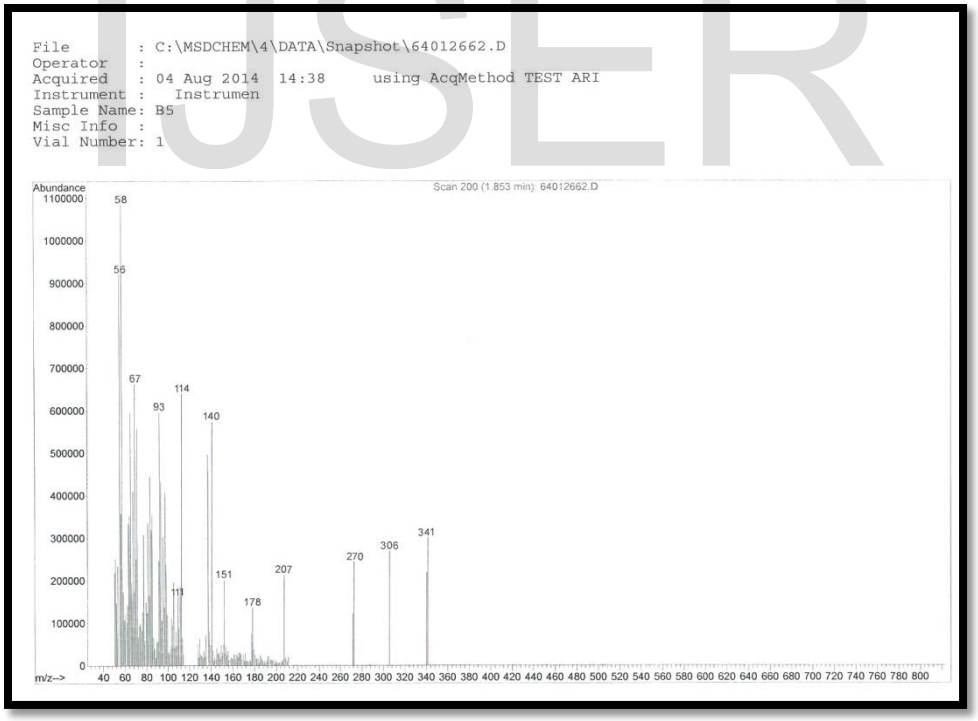


Figure (6) mass spectra of [Cu(L)2Cl2] cm-1

4.1 Infra-Red Spectroscopy :

The FTIR spectrum for L shows a characteristic stretching absorptionbands . 3051 cm-1589 cm-1, 1373,1431 cm-1,1624 cm-1 and 1570 cm-1, , assigned to ,υ C-H of furan, C=N of the thiadiazole ring, asymmetrical C-S-C, symmetrical C-S-C stretching ,C=N and C=O respectively. The C=N stretching vibrations areimportant 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 [20]. The IR data of the complexes are shown in Table (5) and figure(7,8). The Table lists the stretching frequency (υ) 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	υ C-H	υC=N of ring	υ C=N out ring	υ C-S-C Sy , Asy	υ C=O	υ M-N	υM-Cl
1	$C_8H_5N_3O_2S$	3051	1589	1624	1373 Sy 1431Asy	1570	----	----
2	$[Fe(L)_2Cl_2]Cl$	3022	1593	1630	1319 1365	1505	544	362
3	$[Cr(L)_2Cl_2]Cl$	3031	1594	1626	1322 1369	1519	542	368
4	$[Co(L)_2Cl_2]Cl$	3040	1580	1628	1345 1407	1533	549	372
5	$[Cu(L)Cl_2]$	3047	1586	1618	1366 1401	1538	563	374
6	$[Ni(L)Cl_2]$	3050	1588	1622	1370 1425	1562	551	377

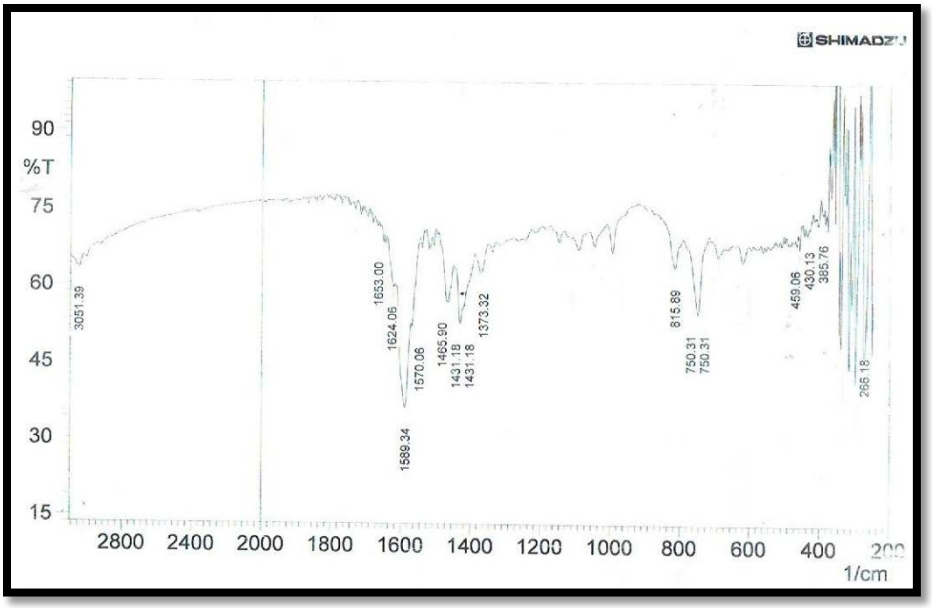


Figure (7) IR spectrum of the ligand cm-1

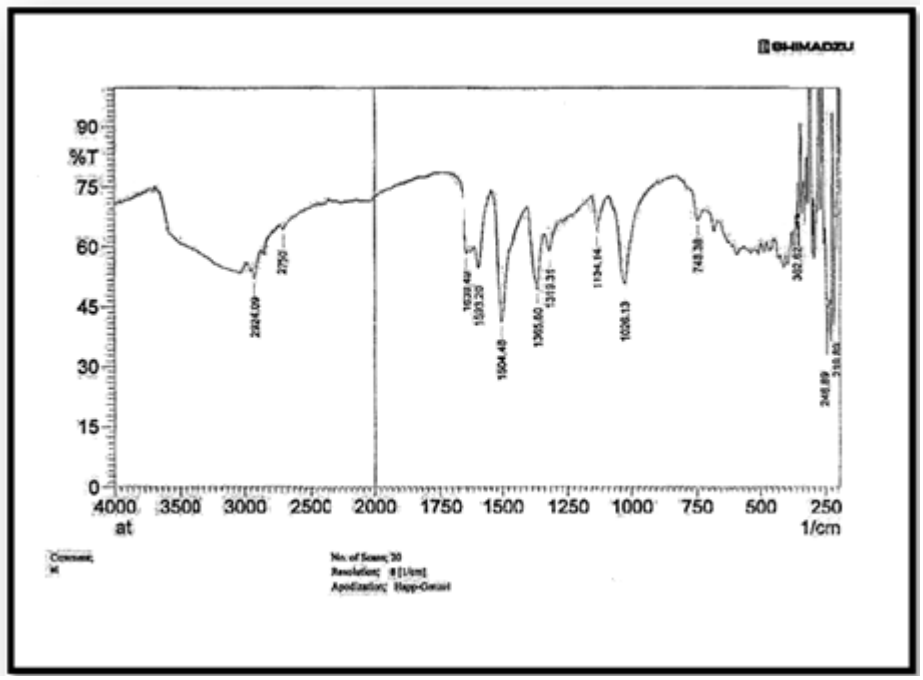


Figure (8) IR spectrum of the $[Fe(L)_2Cl_2]Cl$ cm-1

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 Furtural Protons, Isomethen proton and Aldehyde Protones signals, are shown in the regions of 6.5-7.0 , 8.7 and 9.2 respectively, The number of protons calculated from integration curves and the recorded chemical shifts in figure (9)[21] .

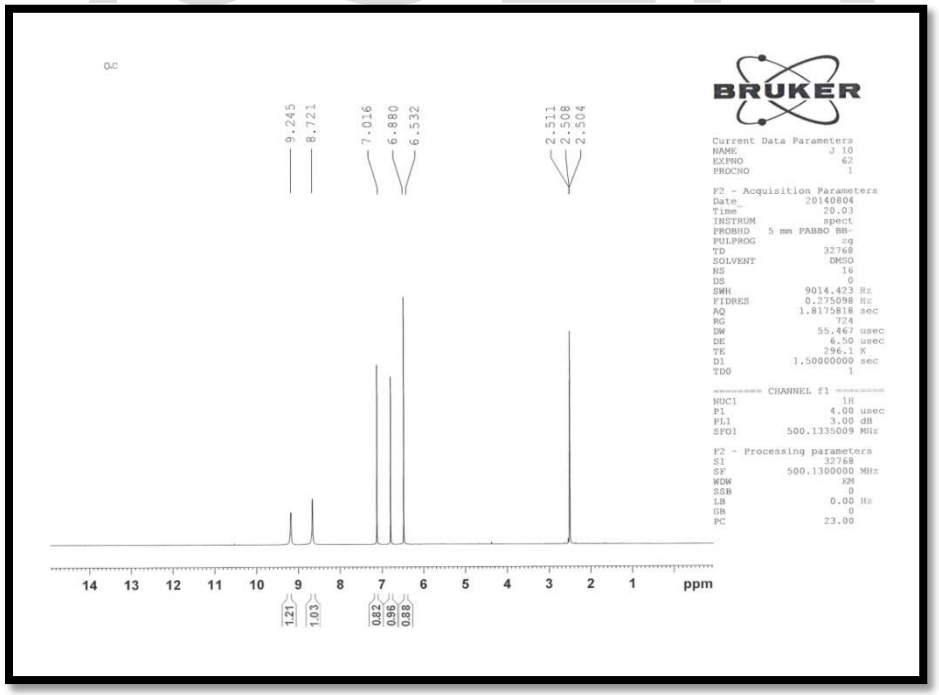


Figure (9) NMR spectra of the ligand

5.Conclusion

In the present work, a series ofof 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,1HNMR, 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 ({[5-(furan-2-yl)-1,3,4-thiadiazol-2-yl]imino}ethanal) was successfully synthesized. The ligand was treated to different transition metal salt to form the corresponding complexesas shown in the scheme (2). It may be concluded that the ligand coordinate through Nitrogen and atoms .This view is further supported by the appearance of a band corresponding to the metal–nitrogen stretching Vibration at 542–563 cm–1 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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