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Synthesis, Characterization and Cyclic Vatammetry Study of 5-(2-((7-Methoxynaphthalen-2-yl)Methylene)Hydrazineyl)-1,3,4-Thiadiazole-2-Thiol and It's Metal Complexes

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Abstract. *The current research included synthesis new Ligand5-(2-((7-methoxynaphthalen-2-yl)methylene) hydrazineyl)-1,3,4-thiadiazole-2-thio(L).the various metal ion complexes ofCr(III), Fe(II),Ni(II)andCo(II) were synthesized. Spectral methods were used to characterize the Ligand and its complexes spectra techniques including , 1H-NMR ,13C-NMR Mass spectraand molar conductivity.Cyclovoltametry was used to study the oxidation-reduction processes (electrochemical properties) of both the Ligand and its complexes, providing further evidence for complex formation.The semi-empirical calculation using Hyperchem software to obtain the optimization molecular structure of the Ligand and its complexes, and to perform theoretical calculations to study the electrostatic potential. This provided information on suitable complexation sites and possible complex shapes by theoretically studying the energy of these complexes and using molar conductivity calculations., Based on the results obtained from spectral and theoretical methods, we propose octahedral geometrics for Cr (III), Fe (II) ,Ni (II) and Co(II).*

Keywords: *heterocyclic, thiadiazole, Ligand, complexes, characterization, Cyclic voltammetry.*

1. Introduction

It is an unverified cyclic aromatic compound belonging to the azole family. It was first discovered by Fischer in 1882[1], and its cyclic structure was confirmed by Freudo Kuhn in 1890. Thiadiazole has the chemical formula C2H2N2S[2]. It consists of a five-membered ring with two nitrogen atoms, two carbon atoms, and one sulfur atom. It is characterized by its ability to bind to any part of metals and is valued for its inherent properties, particularly in the context of intrinsic integration, as well as its biologically organic properties. It can also be used as an antioxidant and a reagent in metallurgical industries[3]. The thiadiazole nucleus includes two nitrogen atoms,two carbon atomand one sulfer atom and always exists in only four isomeric forms[3]:

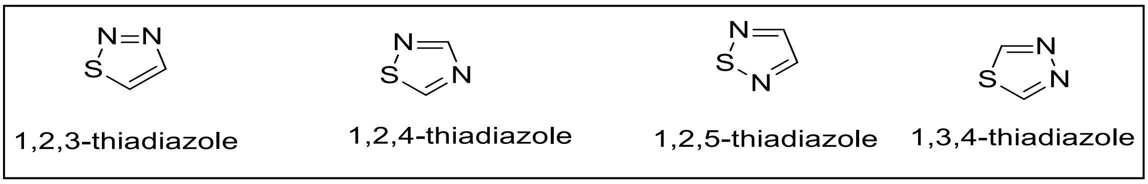

1,2,3-thiadiazole
1,2,4-thiadiazole
1,2,5-thiadiazole
1,3,4-thiadiazole

Figure 1

One of the most important thiadiazol ring isomers, compared to the other three, is 1,3,4-thiadiazol, due to its wide range of applications in various fields. It is also the most stable because, unlike the other isomers, it does not contain an S-N bond. This derivative is considered a weak base due to the inductive effect of the sulfur atom[4]. It is relatively inert towards electrophilic substitution but becomes more active upon nucleophilic attack due to the inductive attraction of the nitrogen atom. The presence of substituents at the 2,5 positions in this ring makes it more reactive. The formation of many derivatives has been used in numerous applications.In medicine[5], this isomer exhibits a number of biological properties due to the presence of the (N-C-S--) group in the thiadiazole ring, where it acts as a double electron donor system, enabling the formation of hydrogen bonds. Its derivatives have numerous applications in the fields of antimicrobials, anticancers, antipsychotics, antituberculosis, antihistamines, anticonvulsants, antiviral hepatitis, antileishmaniasis, antiparkinsonian agents, and antidiabetics. In industry, it has been used as a catalyst to accelerate vulcanization (the process of converting polymers into more durable materials by adding sulfur)[6], as a rust inhibitor and corrosion inhibitor, in the preparation of photoactive liquid crystals, and in polymer synthesis. In agriculture, it is used as an insecticide.

2.Experimental

All the chemicals and solvents were of chemically upgrade before using, All metal salts were utilized as chloride.

2.1. Physical Measurements

The melting point of the synthesized Ligand and their metal complexes were determined by capillary tube method in an electro thermal melting point apparatus. the FTIR spectra in the range (4000-200) cm^{-1} were recorded as CsI discs using a Shimadzu spectrophotometer,. Nuclear Magnetic Resonance Spectra were obtained using Bruker DXR System AL500 (500 MHz). Mass Spectra were obtained using (Network Mass Selective Detector 5973).

2.2. Preparation of the Ligand

Ligand5-(2-((6-methoxynaphthalen-2-yl)methylene)hydrazineyl)-1,3,4-thiadiazole-2-thio was prepared as follow:-

2.2.1. Synthesis of 1,3,4-thiadiazole-2,5-dithiol(A)

(22.5g)of(KOH) was dissolved with(150ml) of ethanol and the mixture was distilled retraceably for half an hour and (10ml) of hydrazine was added using an addition funnel and the retracement continued for two hour[7]. The reaction was monitored using thetechnique,TLC(R1=3ethylacetate7Hexane) and then reaction was stopped and placed in

An ice bath was placed at a temperature between 0-5 ℃,and(30)CS2 was add in batches,turning pink. The solution was then in adifide using asilver mirror-immersed paperindicating the continuation of the reaction.After the reaction was complex, when no color appeared and no silver mirror formed on the paper imm ersed in the lead acetate solution,the reaction was stopped ,filered and water was added to the filterate. The filtrate was then evaporated to half its volum . Acidization was carried out using 10% hydrochloric acid until the PH = 4. Awhite precipitate was observed, which (A) in the form of needle-like crystals with amelting point of 172 ℃ and a reaction yield of 75%

2.2.2. Synthesis of mercapto-2- hydrazine- 5-1,3,4- thiadiazole(B)

(20g 0.1 mole) of compound (A) was mixed with (25ml) of ethanol and (10ml) of hydrazine . Reduce the mixture for 20 hours. the reaction was monitored using the TLC techniqueand detecting the emission of hydrogen sulfide gas using apaper immersed in lead acetate solution[[8], The paper will turn black and asilvery mirror will form. Continue monitoring until the reaction is complete. Filter the reaction product, forming awhite to grayish precipitate of compound(B) Yield 65% melting point 265 ℃

2.2.3. synthesis of Ligand(L)

Mix (0.5g,0.01mole) of compound (B) with (0.6324g,0.01mole) of 6-methoxy-2-naphthaldehyde dissolve 10 ml of ethanol, Thenrefluxed for 3 hours and monitored the reaction using TLC using ethyl acetate: -hexane (7:3 v/v) After the reaction was complete, a yellowish precipitate was filtrate. Theprecipitate was recrystallized with ethanol to form light yellow .melting point 255°C. yield is 70%.

2.2.4 Preparation of complexes

(0.001mole) $CrCl_3.6H_2O$, FeCl2.6H2O, $NiCl_2$.6H2O and $CoCl_2$.6H2O) were mixed separately with Ligand(0.001 mol) in ethanol , the mixture was heated under refluxed for 3 hrs .the resulting precipitated was filtered, washed with absolutes ethanol.

2.3 Electrochemistry

Cyclic voltammetry (CV) was performed using a PARSTAT4000 POTENTIOSTAT/GALVANOSTAT/EIS ANALYSER from AMETEK, France. Argon was used as the inert gas. Measurements were calculated in the Chemistry Department, University of Thi-Qar. The measurements were performed using a standard three-electrode, single-chamber electrochemical cell. Tetrabutylammonium perchlorate was used as the supporting electrolyte in an aqueous medium with a concentration of 0.1 M in dimethylformamide. The working electrode was a glassy carbon disc. A potential scanning rate of 100 mV/s was used in the CV experiments. Before the measurements began, the working electrode was polished with 0.05 µm alumina paste, washed with distilled water, and then rinsed with dimethylformamide before each recording. The auxiliary electrode was a platinum wire. The reference electrode was made of silver. The calibration method used in the calculations was a semi-reference silver electrode (for the official ferrosinium/ferrocene pair potential (Fc+/Fc) in dimethylformamide, which was estimated to be +0.07 V under our experimental conditions. Auto-compensation for ohmic drop was systematically performed when using cyclic voltammetry (18-23).

2.4. Electrostatic potential (MEP) Molecular

Electrostatic potential is very important in finding the active site in the molecule system with a positive point charge[9]. The species that have positive charge tend to attack a molecule where the electrostatic potential is strongly negative (electrophilic attack) as shown in figure (3). The semi-experimental method in Hyperchem software was used to plot the optimal molecular formula of the Ligand and its complexes.

3. Result and discussion

3.1 Synthesis of Ligand

The Ligand(L) was prepared many steps which has been observed in figure(2), First the main intermediate (B) was synthesized in three step(1-3) starting from methyl 2-hydroxybenzoate. The Compound(B)reactwith (6- methoxy-2- naphthaldehyde) afforded the desiredLigand(L)

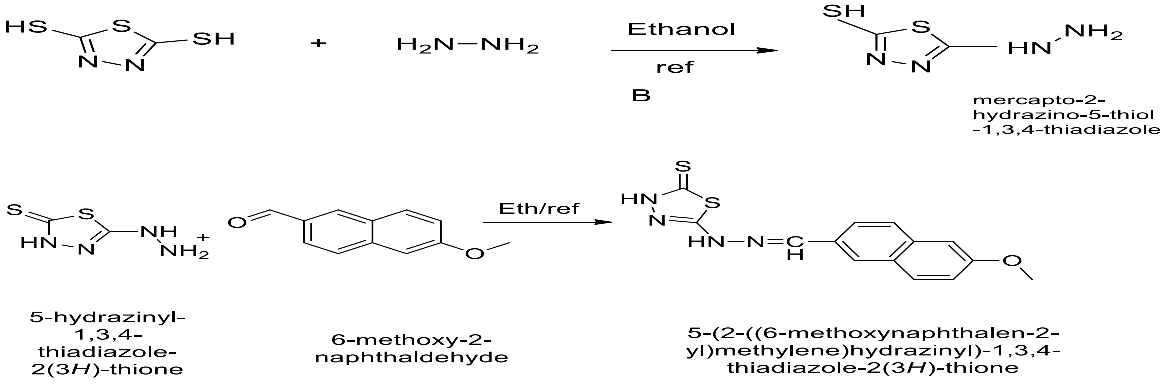


Figure 2

Table 1. physical properties ,molar conductivity and magnetic susceptibilities

No	Com.	Formula	M.W	Color	M.P℃	Yield%
1	L1	$C_{14}H_{12}N_4OS_2$	316	Lemon yellow	120-122	82
2	$[Cr(L_1)Cl_3]H_2O$	C16H22Cl3CrN4O2S2	525	yellow	118-120	84
3	$[Fe(L1)Cl2]H_2O$	C28H24Cl2FeN8O4S4	817	Light Brown	293-295	75
4	$[Co(L_1)Cl_2H_2O]$	C30H34Cl2CoN8O4S4	829	Olive Green	286-288	79
5	$[Ni (L_1)Cl_2]2H_2O$	$C_{14}H_{14}Cl_2N_4NiO2S_2$	468	Dark Brown	288-290	75

3.2. FT-IR spectral

The L1 aligand spectrum showed ceramic bands at cm^{-1} (3336, 3055, 1624) attributed to the NH, C-H, and C=N groups on the plate. Other ceramic bands appeared at cm^{-1}[10] (1475, 1269) attributed to the C=C and C-O-C groups on the silk spectrum, as well as at the (1172) cm^{-1} site, attributed to the movement of the thiadiazole ring. The complex spectrum showed a change in the positions and intensity of the absorption bands for N=CH and C=N, indicating that these groups share the working field with the central ion. Bands not present in the aligand spectrum were also observed at (781-551) attributed to (M-N) and (613-478) attributed to (M-Cl), as shown in Fig(9-13) an Table (2).

Table 2. Infrared spectra of L and its metal complexes (υ cm-1)

	NH	C-H Ar	C-H ALPH	C=C Ar	C=N HETRO	C-O-C ASY	الحركة الهيكلية	M-N	M-Cl
L_1	3336	3055	2856	1475	1624	1269	1172		
L_1C0	3545	3055	2848	1544	1604	1244	1139	551	**478**
L_1Cr	3572	3055	2920	1477	1622	1269	1678	515	**476**
L_1Fe	3508	3055	2865	1618	1680	1269	1618	675	**476**
L_1Ni	1616	3048	2876	1618	1678	1271	1479	781	**613**

3.3. ^{1}NMR SPECTRA

The nuclear magnetic resonance spectrum of the first ligand showed a signal at [7.25-8.43 ppm (m,6H)] attributed to the protons of the two naphthalene rings, and a signal at [12.90 ppm (S,1H)] attributed to the proton of the thiol/amide group (N-H) in the thiadiazole ring or chain. The spectrum also showed a signal at [10.05 ppm(S,1H)] which can be attributed to the proton of the azomethine group CH=N and a signal at [3.99 ppm(S,1H)] attributed to the proton of the methoxy group (OCH3)Figure (1)

3.4 ^{13}CNMR spectra

The 13C-NMR spectrum of the first ligand (L1) showed a shift of (192.98ppm) due to C=N inside the thiadiazole ring, a shift of (160.30ppm) due to an aromatic carbon attached to a different atom, which is nitrogen, shifts of (120.21-138.30ppm) representing the nuclei of the naphthalene rings present in the structure, a shift of (106.88ppm) due to a carbon in the aromatic ring close to the donor group, and a shift of (55.94ppm) due to an aliphatic carbon of the methoxide group (-OCH3). The peaks (39.32-40.58ppm) are due to the solvent (DMSO-d6).figure (2).

3.5. Mass spectr

The first ligand spectrum was characterized by the appearance of the molecular ion band m/z [C14H12N4OS2] = 316, in addition to the basic band at m/z [C2H2N2S2O] = 185. The spectrum was also characterized by the appearance of several bands at (118, 146, 286) m/z as shown in figure(3).

The mass spectral of the Fe(II),This spectrum is characterized by the appearance of a band at 817 m/z, belonging to the molecular ion, in addition to the base band at 258 m/z. The band at 785 m/z indicates the loss of two water molecules, followed by a loss of [unclear]. The bands at 724 and 758 indicate the loss of two chlorine atoms, respectively.. The mass spectral of theCO(II) complexThis spectrum is characterized by the presence of the molecular ion band at (829) in addition to the ground band at (115) m/z. The spectrum also showed a water loss band at (811) m/z, while the bands at (757, 696) m/z confirmed the loss of two chlorine atoms one after the other. The band at (59) m/z is attributed to the cobalt ion.. The mass spectral of the Ni(II) complexThis spectrum is characterized by the appearance of the z/m(468) band belonging to the molecular ion, in addition to the base band z/m(186). The two bands at (429,375)m/z confirm the loss of two chlorine atoms respectively, and the presence of a band at (59)m/z confirms the presence of the nickel ion..The mass spectral of the Cr(III) complexThis spectrum is characterized by the appearance of a band at (525) m/z belonging to the molecular ion, in addition to the base band at (186) m/z. The bands (370, 406, 440) m/z indicate the loss of a water molecule and the loss of three chlorine atoms, respectively. respectively as shown in figures (3-8)

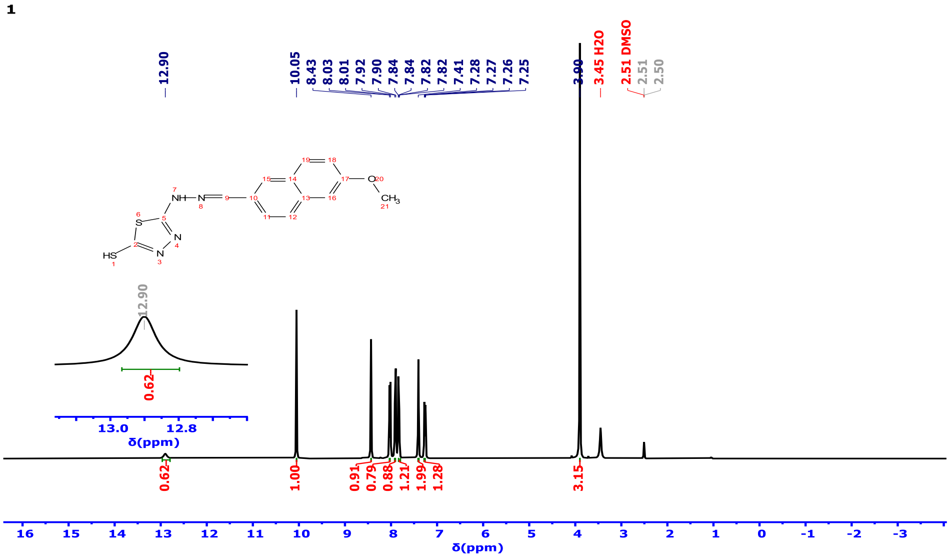


Figure 3. NMR Spectra of Ligand

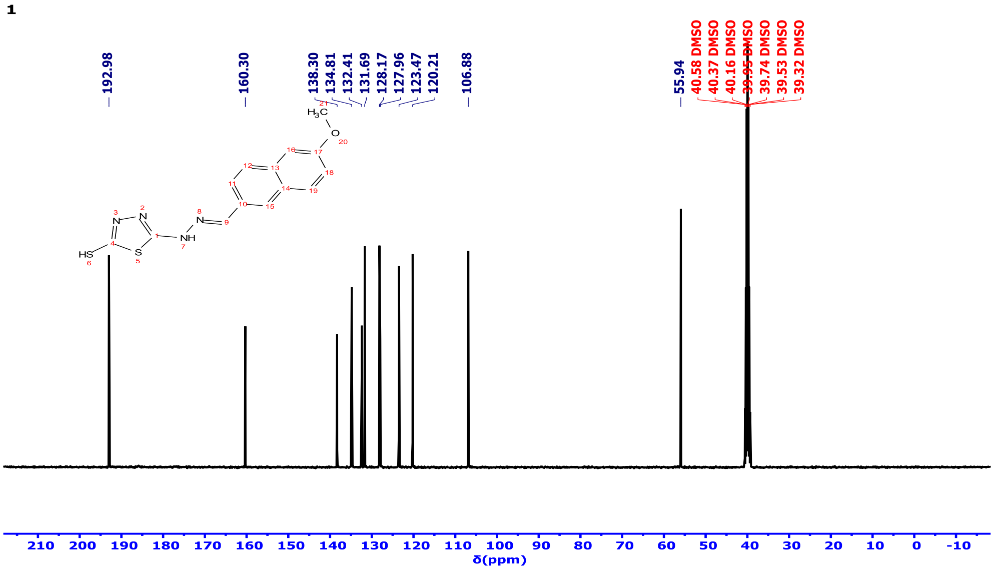
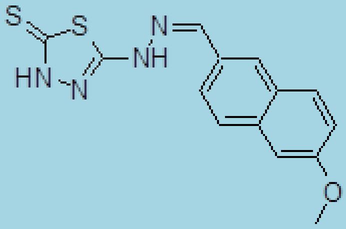
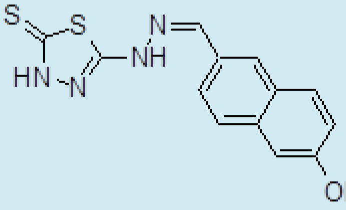
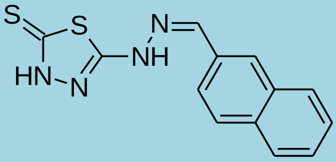
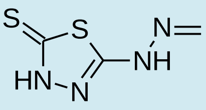
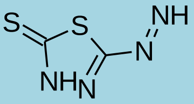


Figure 4.13C- NMR Spectra of Ligand

Fregment	Formula	M/e	No
	C14H14N4OS2	316	**1**
	C13H10N4OS2	302	**2**
	C13H10N4S2	286	**3**
	C3H4N4S2	159	**4**
	C2H2N4S2	146	**5**

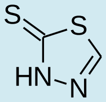
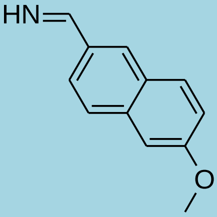
	C2H2N2S2	118	**6**
	C12H11NO	185	**7**

Figure 5. proposed fragmentation pathway of the Ligand

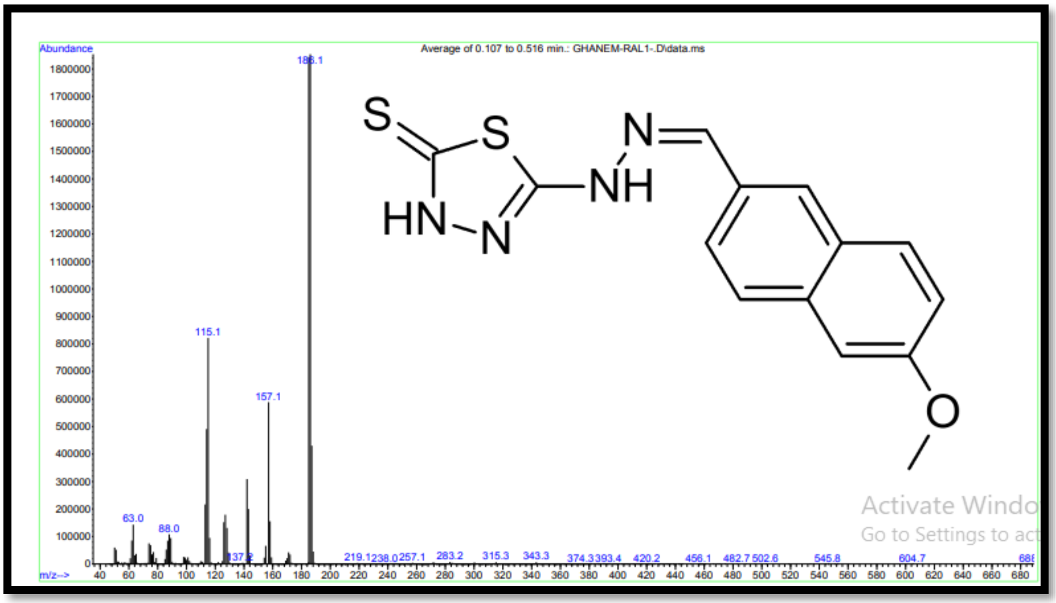


Figure 6. mass spectra of Ligand

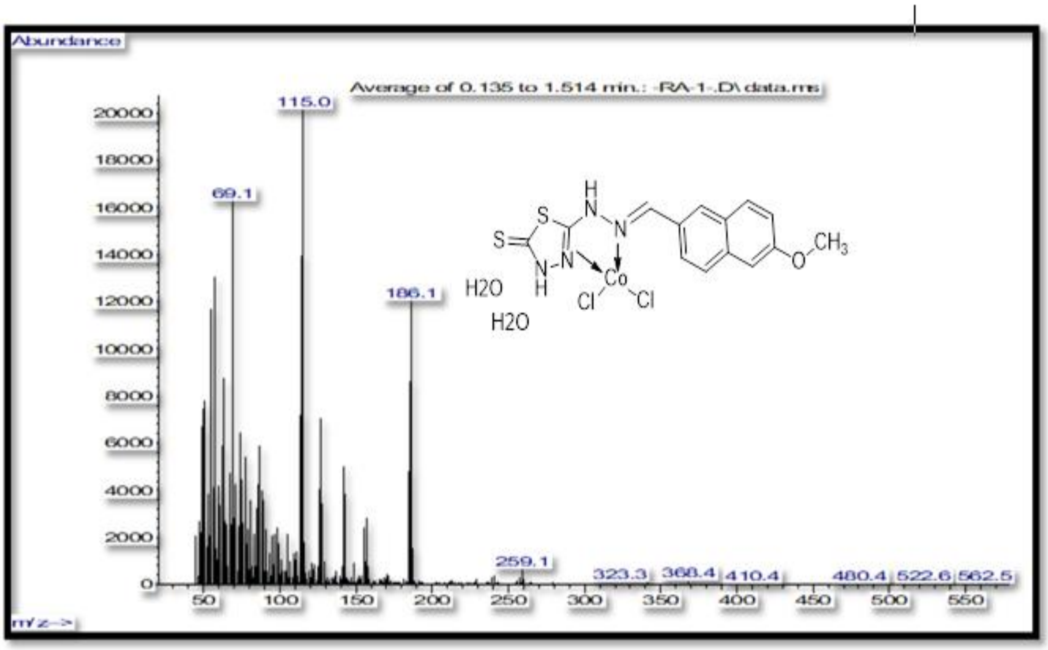


Figure 7. mass spectra of [Co(L)$_2$Cl

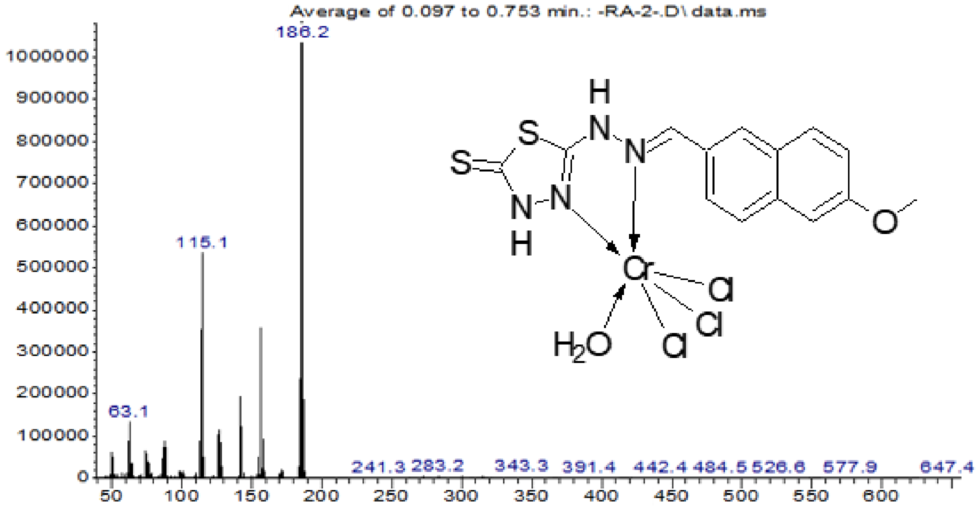


Figure 8. mass spectra of [Cr(L)Cl3]

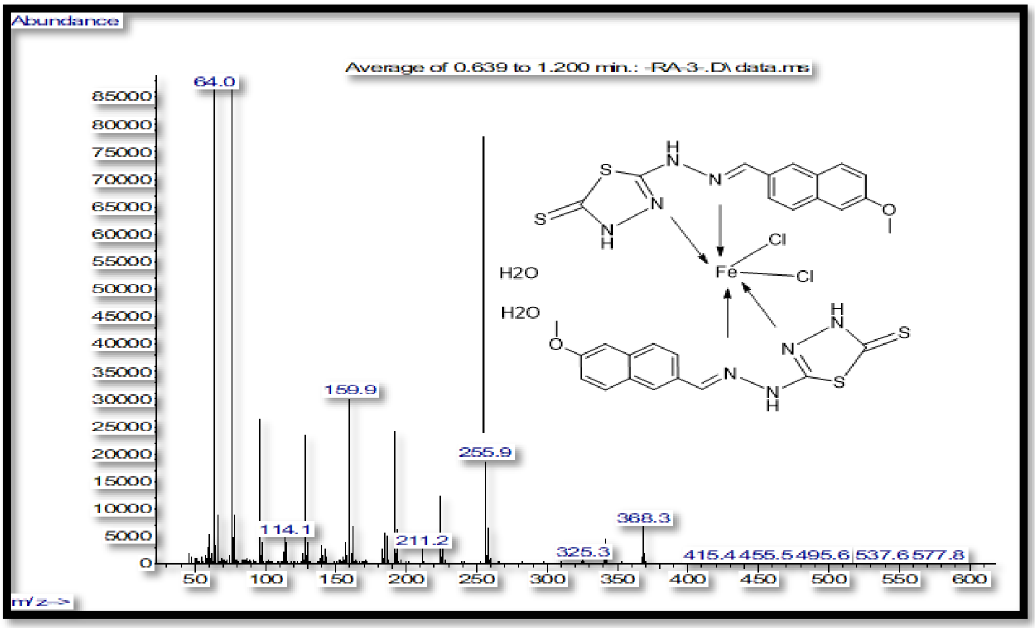


Figure 9. mass spectra of [Fe(L)₂Cl2] 2H2O

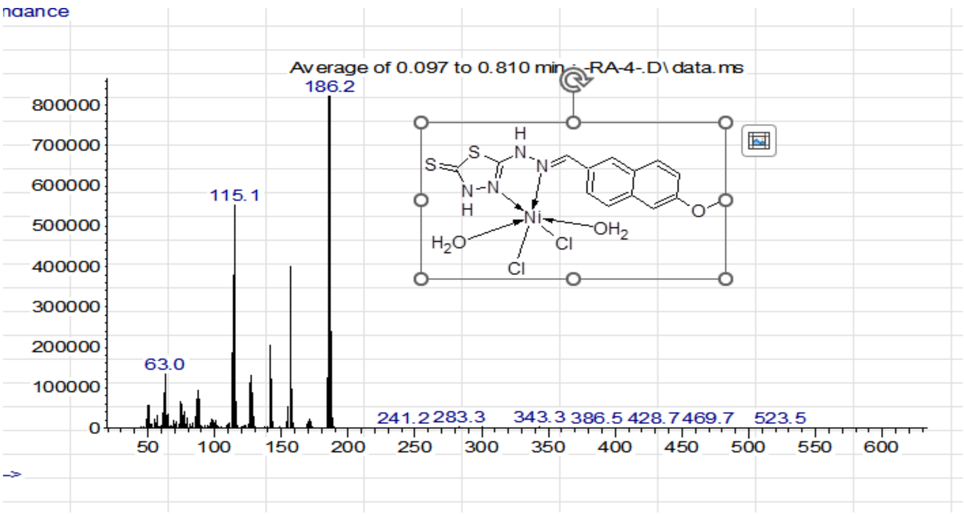


Figure 10. mass spectra of [Ni(L)2Cl2] H2O

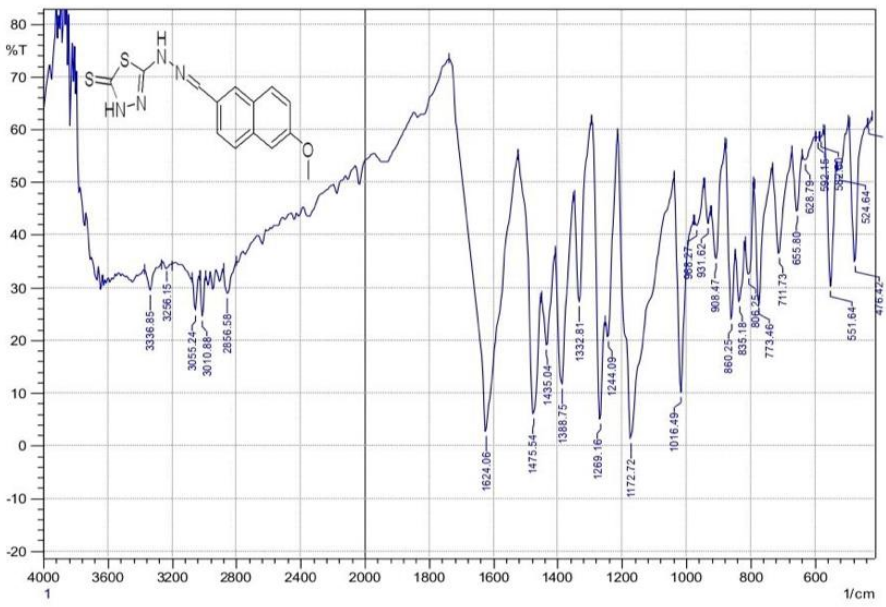


Figure 11. IR of Ligand(L)

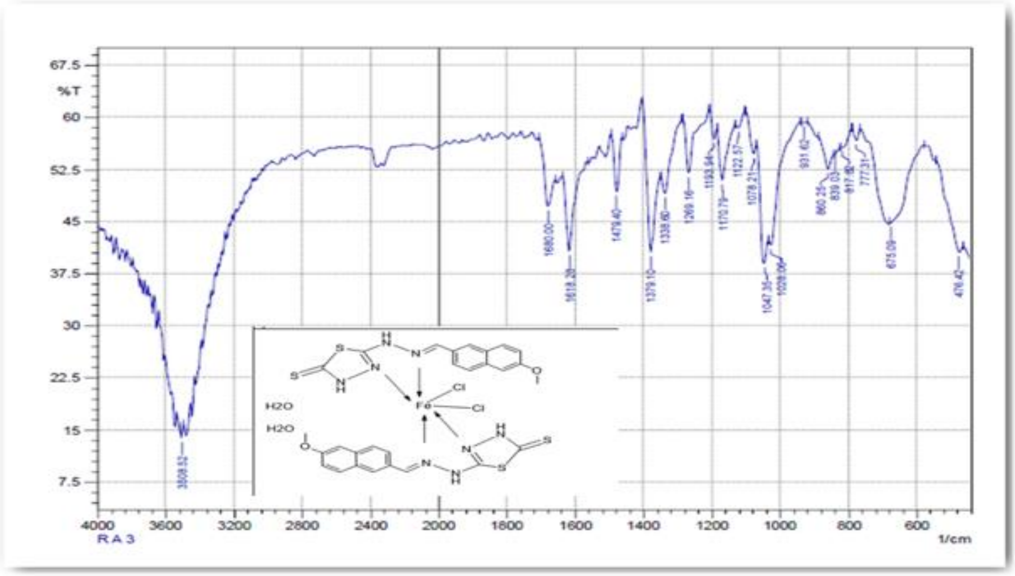


Figure 12. IR of complex $[Fe(L)_2 Cl_2$

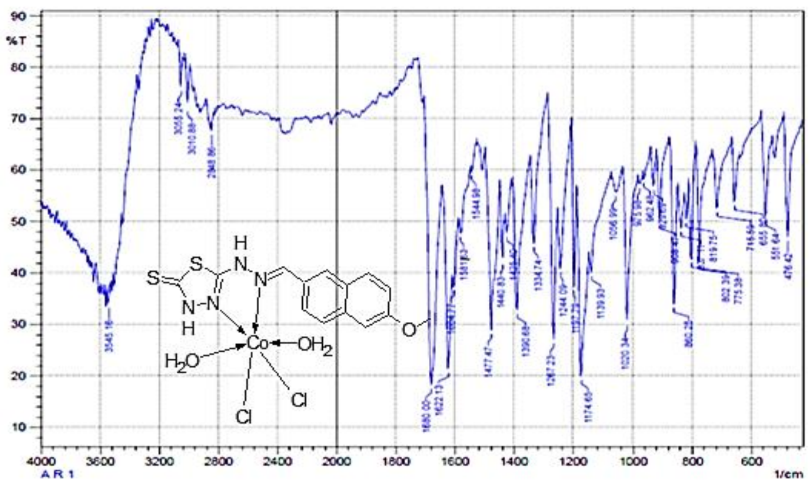


Figure 13. IR of complex [Co(L) Cl2]

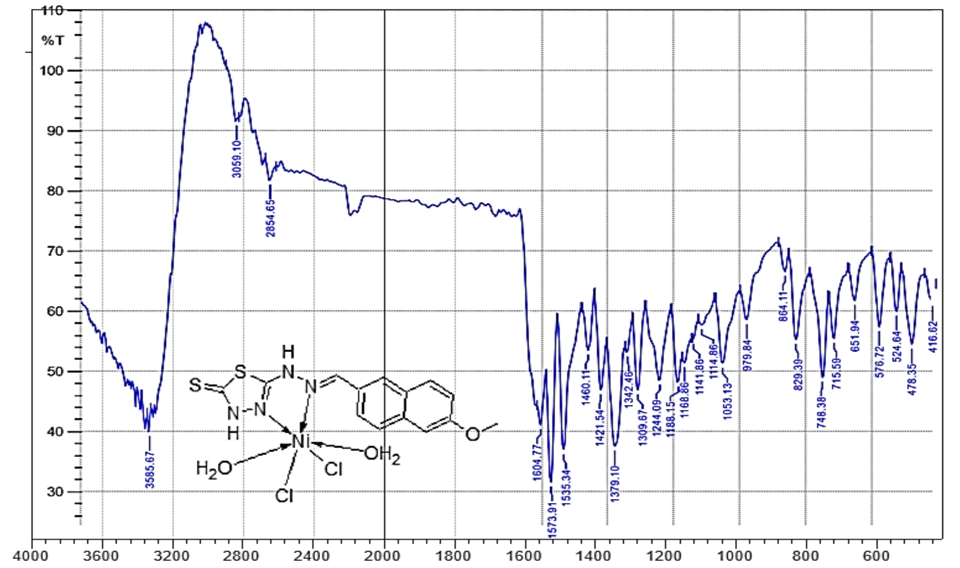


Figure 14. IR of complex [Ni(L) Cl_2]

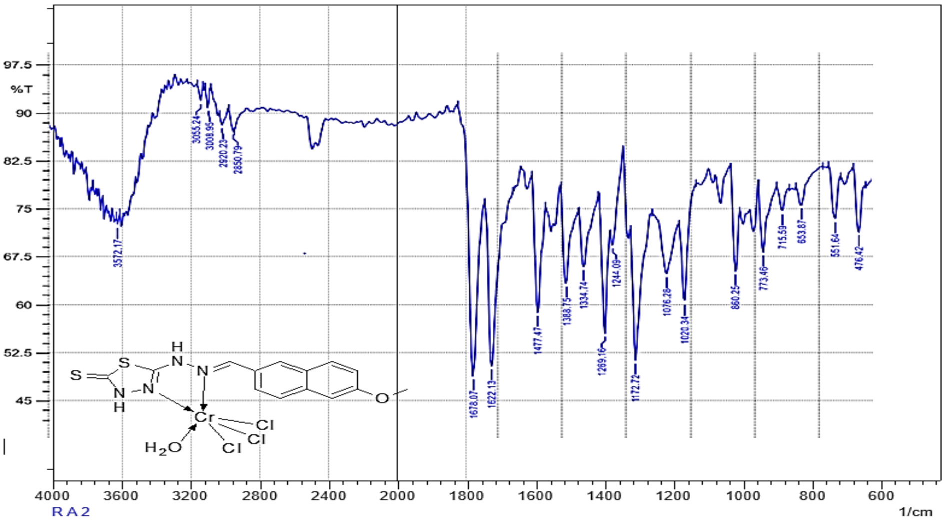


Figure 15. IR of complex [Cr(L) Cl3

3.6 electrochemical study:

The electrochemical properties of the Ligand ,its Cr^{+3}, Fe^{+2}, Co^{+2}, Ni^{+2} complexes and those of metal salts ($CrCl_3$,$FeCl_2$, $CoCl_2$ and $NiCl_2$) have been investigated in the (DMF+0.1 M TBAP) using voltammetry (CV)[11]. All the potential in the text are given against Ag-quasi reference electrode .in order to avoid a chemical oxidation of the electron generated compound under air[11], all the electrochemical experiment have been carried out at lab temperature under an Argon atmosphere using conventional three electrochemical cell[12] .A vitreous carbon disk electrode was used as working electrode and a platinum wire as auxiliary electrode. figures 15-22 depicted the CV_S and Data are summarized in the table 3

Table 3. Experimental voltammetric potentials for **L**,its complexes and metal complexes at 0.1 mV/s. Working electrode: 3mm Vitreous Carbon. Reference electrode: 0.1 M TBAP/DMF.

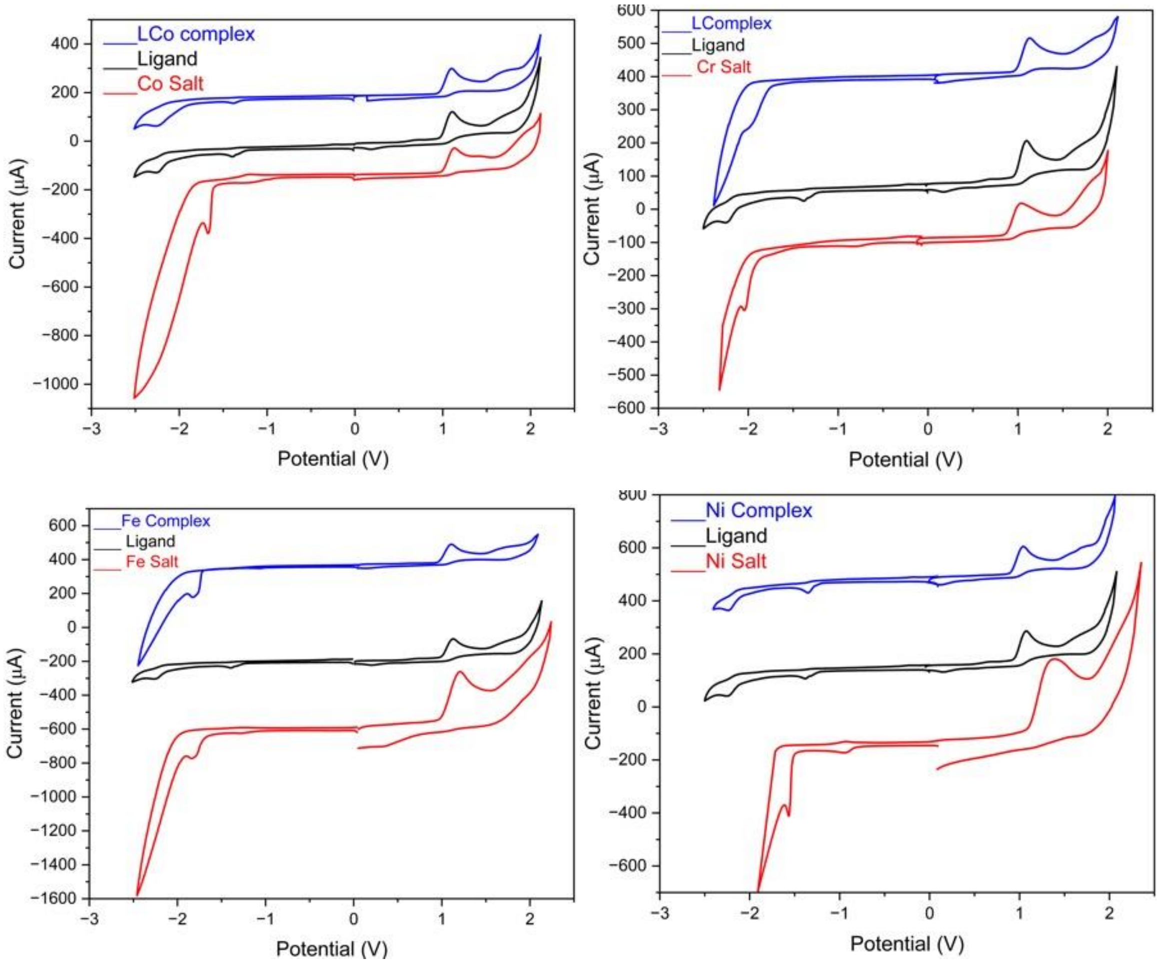
Compound	(V/s)	Conc. mM)(	E_{pc} (mV)	i_{pc} (µA)	E_{pa} (mV)	i_{pa} (µA)
L1	0.1	1	-1390 -2268	-28.253 -57.415	≈>-2118 -228.802 1108	-28.546 4.023 111.937
CrL	0.1	1	≈-2082	-143..185	- - 1040	- - 449.671
$CrCl_3$	0.1	1	-1988	-135.721	1184 >1968	81.56 128.586
FeL	0.1	1	-1893	-161.818	- 1045 1500>	- 109.57 52.216
$FeCl_2$	0.1	1	-1888 -1343	-135.541 -8.311	1145	291.14
CoL	0.1	<1	-1385 ≈-2275	-13.774 -91.084	1103 ≈-1709	6.548
$CoCl_2$	0.1	1	-1670	-194.191	≈2000	129.936
NiL	0.1	1	-1466 -2351	-38.326 -73.011	≈-2186 ≈>-1397 -299.345 1040 >1500	-28.60 -11.45 4.095 104.707 113.82
$NiCl_2$	0.1	1	-1673	-237.429	1290	273.75

The Ligand L1 shows an irreversible reduction process at -1390 mV which is easier happened upon the complexation with Co^{+2} ion (-1385 mV for CoL1). While the oxidation of the Ligand was noted at 1108 mV which was also Cathodically shifted to 1103 mV in CoL1 as evidence to the increase of electron density on Ligand upon complexation possibly due to back donation process . the oxidation of the free Co^{+2} ion(Co^{+2} → Co^{+3} +1e) happened at ≈ 2000 mV was noted less than 2000 mV in CoL1 due to the increase of electron density of the metal ion upon complexation [13]. the oxidation process noted foe Ligand L1 at -228.802 mV was disappears in the CV of its complexes CoL1 .

Both reduction of free Cr^{+3} and free Ligand happened at -1988 mV and -1390 mV respectively were absent in the complex CrL1[14] . the second reduction of the free Ligand noted at -2268 mV was anodically shifted to ≈ -2082 mV in complexed Ligand (in CrL1) due to density property of the L1 to the metal ion Cr^{+3} in the complex . the first oxidation of the free Cr^{+3} happened in the 1184 was easily noted in the CrL1 due to increase electron density that was transfer from Ligand[15].

Both the first reduction of free Ligand -1390 and free ion -1343 mV are absent in the CV of the of the FeL1 . the reduction of the complex FeL1 noted at -1893 mV is either easily or hardly compared with those of Ligand -2268 mV and free metal – 1888 mV respectively .two oxidation process are noted for FeL1 AT 1045 mV and >1500 mV respectively [16].

The two reduction of the complexed Ligand in NiL1 are noted at -1466 mV and -2351 mV .These two reduction are hardly occurred compared with those of the free Ligand L1 -1390 mV and -2268 mV respectively .these hard reduction could be assigned to the strong back donating especially if the outer orbital have been utilized[17]. The easier oxidation in the in the complexes NiL1 noted at the 1040 mV is consistent with either outer orbital's –complex metal or the complexed Ligand experienced to back donation , also new dramatic oxidation process was noted at >1500 mV .



Conclusions

This study report the preparation of the 1,3,4-thiadiazole as a noval ligand derivative and its complexes with transition metal ions (chromium(III), cobalt(II), iron(II), and nickel(II). The prepared ligand and its complexes were characterized using spectroscopic, analytical, and electrochemical methods, in addition to the molecular modeling studies using Hyperchem software. Based on the results obtained, we suggest octahedral shapes for all the prepared complexes.

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