

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

Radi A. Huraiz

Department of chemistry, College of Science, Thi-Qar University, 6004, Iraq
radhi.awad@utq.edu.iq

Ibrahim. A. Flifel

Department of chemistry, College of Science, Thi-Qar University, 6004, Iraq
Ibrahimflifel2017@gmail.com

Abstract. The current research included synthesis new Ligand 5-(2-((7-methoxynaphthalen-2-yl)methylene) hydrazineyl)-1,3,4-thiadiazole-2-thio(L). the various metal ion complexes of Cr(III), Fe(II), Ni(II) and Co(II) were synthesized. Spectral methods were used to characterize the Ligand and its complexes spectra techniques including ¹H-NMR, ¹³C-NMR Mass spectra and molar conductivity. Cyclovoltammetry 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 atoms and one sulfur atom and always exists in only four isomeric forms[3]:



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 the technique, TLC($R_1=3$ ethylacetate 7 Hexane) and then reaction was stopped and placed in

An ice bath was placed at a temperature between 0-5 °C, 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 immersed in the lead acetate solution, the reaction was stopped ,filtered and water was added to the filtrate. 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 °C 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 asilver 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 °C

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, Thenreflused 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) CrCl₃.6H₂O , FeCl₂.6H₂O, NiCl₂.6H₂O and CoCl₂.6H₂O) 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)

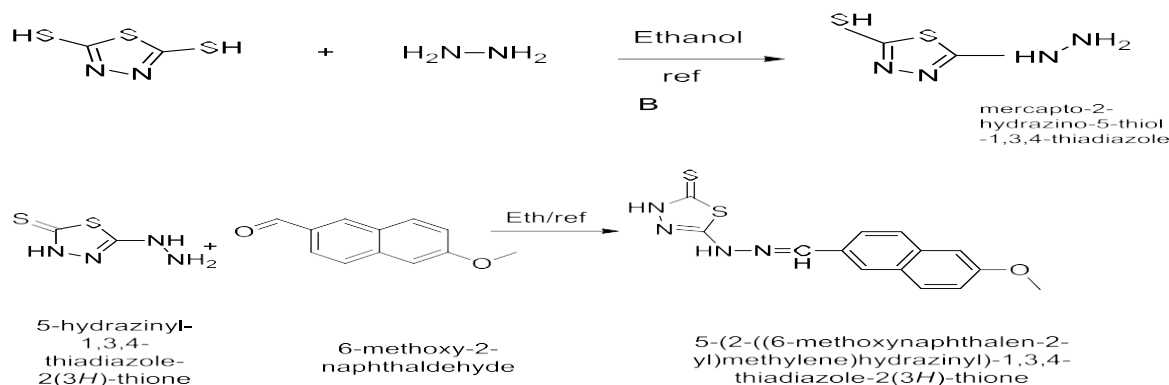


Figure 2

Table 1. physical properties ,molar conductivity and magnetic susceptibilities

No	Com.	Formula	M.W	Color	M.P°C	Yield%
1	L1	C ₁₄ H ₁₂ N ₄ OS ₂	316	Lemon yellow	120-122	82
2	[Cr(L ₁)Cl ₃]H ₂ O	C ₁₆ H ₂₂ Cl ₃ CrN ₄ O ₂ S ₂	525	yellow	118-120	84
3	[Fe(L ₁)Cl ₂]H ₂ O	C ₂₈ H ₂₄ Cl ₂ FeN ₈ O ₄ S ₄	817	Light Brown	293-295	75
4	[Co(L ₁)Cl ₂ H ₂ O]	C ₃₀ H ₃₄ Cl ₂ CoN ₈ O ₄ S ₄	829	Olive Green	286-288	79
5	[Ni (L ₁)Cl ₂]2H ₂ O	C ₁₄ H ₁₄ Cl ₂ N ₄ NiO ₂ S 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 (ν cm-1)

	NH	C-H Ar	C-H ALPH	C=C Ar	C=N HETRO	C-O-C ASY		M-N	M-Cl
L ₁	3336	3055	2856	1475	1624	1269	1172		
L ₁ Co	3545	3055	2848	1544	1604	1244	1139	551	478
L ₁ Cr	3572	3055	2920	1477	1622	1269	1678	515	476
L ₁ Fe	3508	3055	2865	1618	1680	1269	1618	675	476
L ₁ Ni	1616	3048	2876	1618	1678	1271	1479	781	613

3.3. ¹NMR 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 ¹³CNMR 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 [C₁₄H₁₂N₄O₅S₂] = 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)

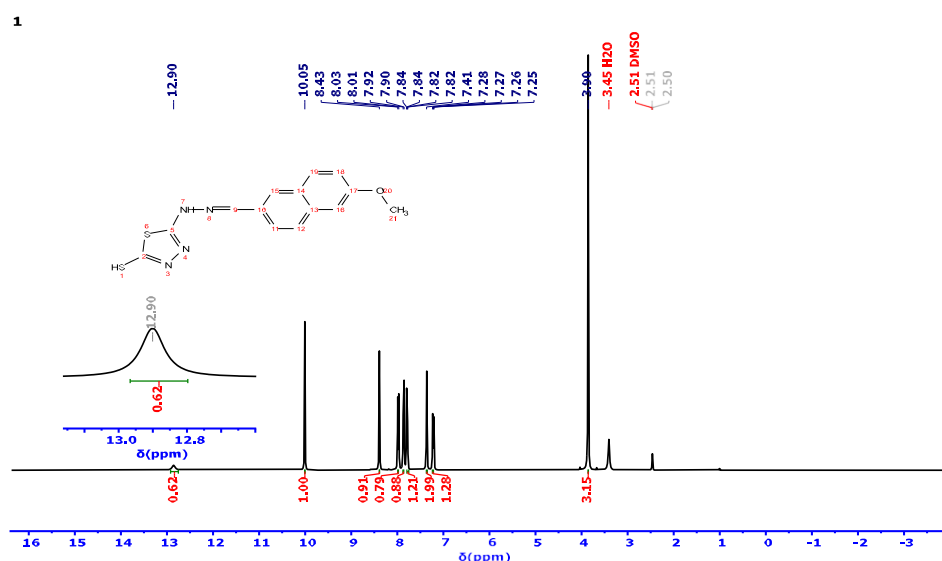


Figure 3. NMR Spectra of Ligand

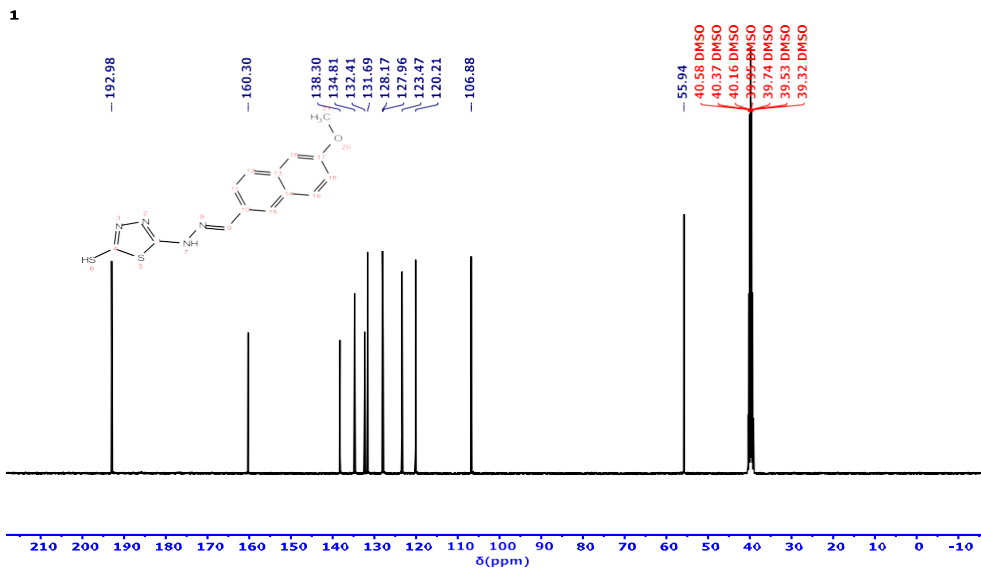


Figure 4.13C- NMR Spectra of Ligand

Fregment	Formula	M/e	No
	C ₁₄ H ₁₄ N ₄ O ₂ S ₂	316	1
	C ₁₃ H ₁₀ N ₄ O ₂ S ₂	302	2
	C ₁₃ H ₁₀ N ₄ S ₂	286	3
	C ₃ H ₄ N ₄ S ₂	159	4
	C ₂ H ₂ N ₄ S ₂	146	5

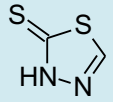
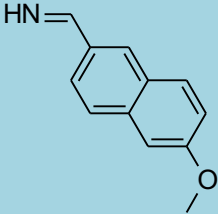
	C ₂ H ₂ N ₂ S ₂	118	6
	C ₁₂ H ₁₁ NO	185	7

Figure 5. proposed fragmentation pathway of the Ligand

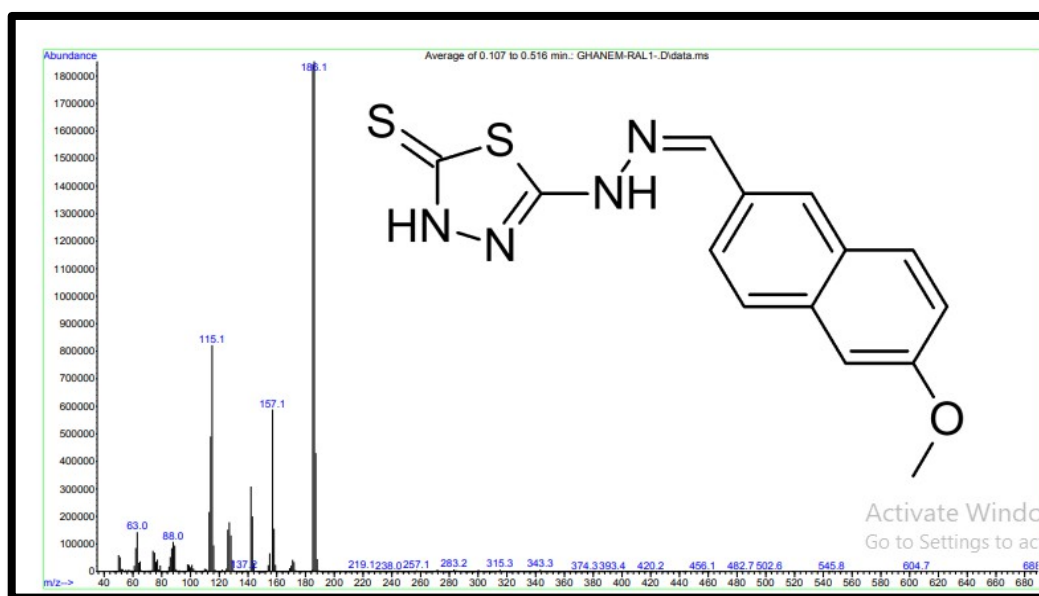


Figure 6. mass spectra of Ligand

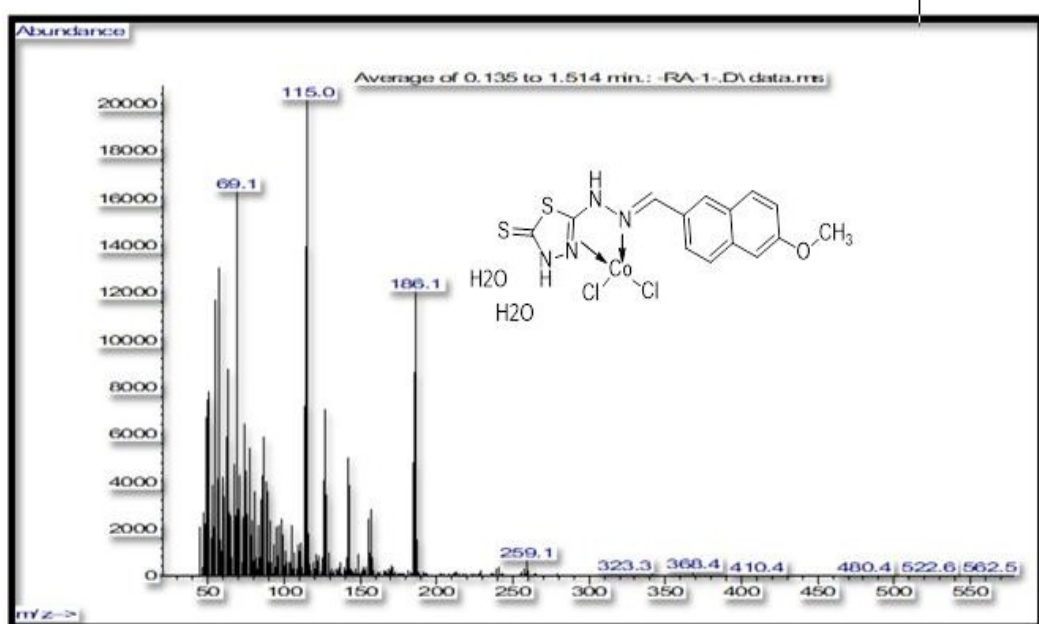


Figure 7. mass spectra of [Co(L)₂Cl]

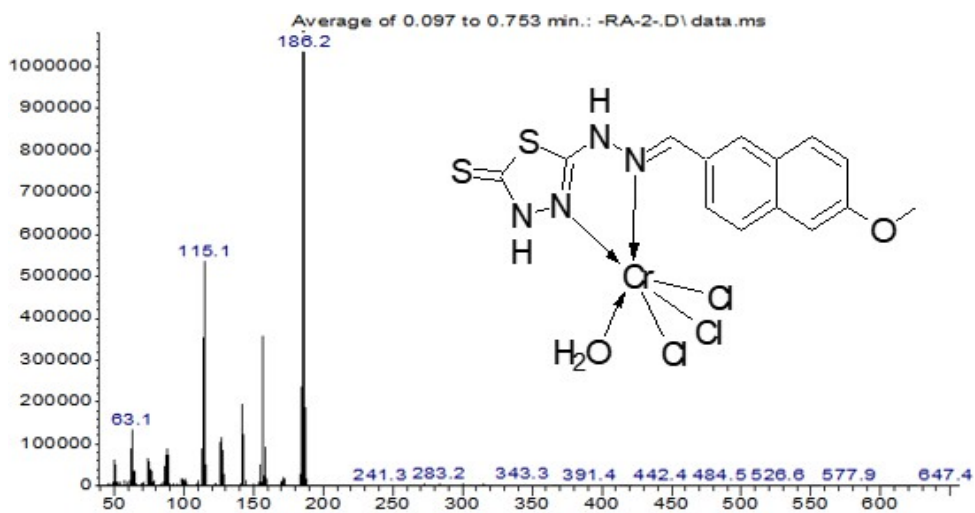


Figure 8. mass spectra of [Cr(L)Cl₃]

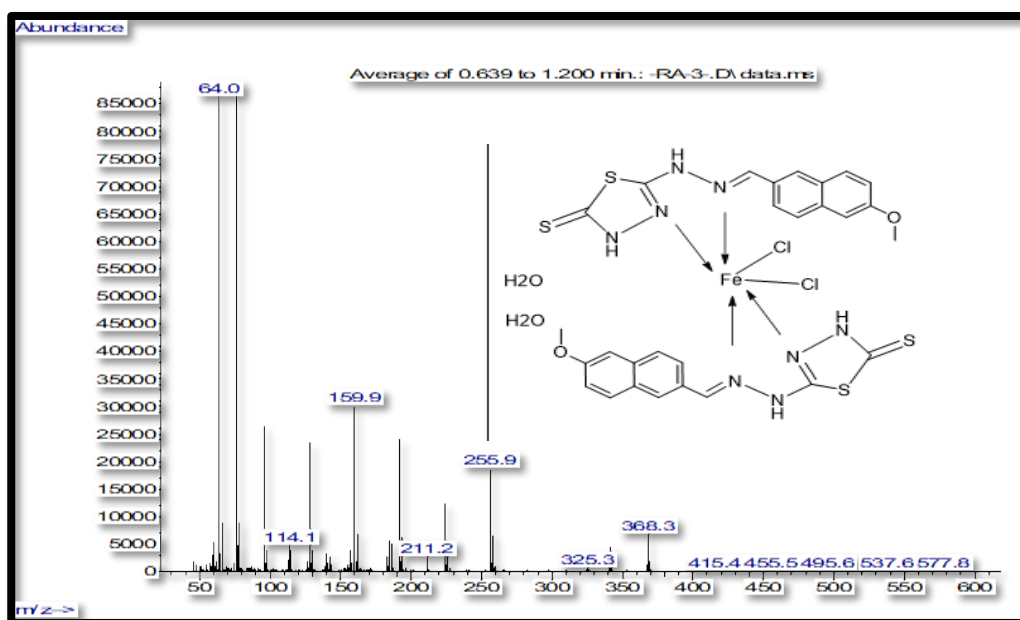


Figure 9. mass spectra of [Fe(L)₂Cl₂] 2H₂O

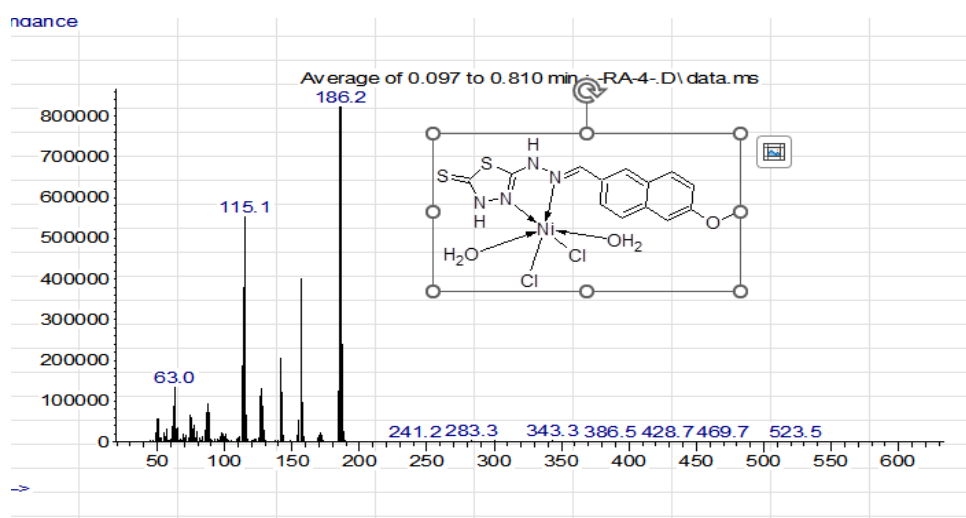


Figure 10. mass spectra of [Ni(L)₂Cl₂] H₂O

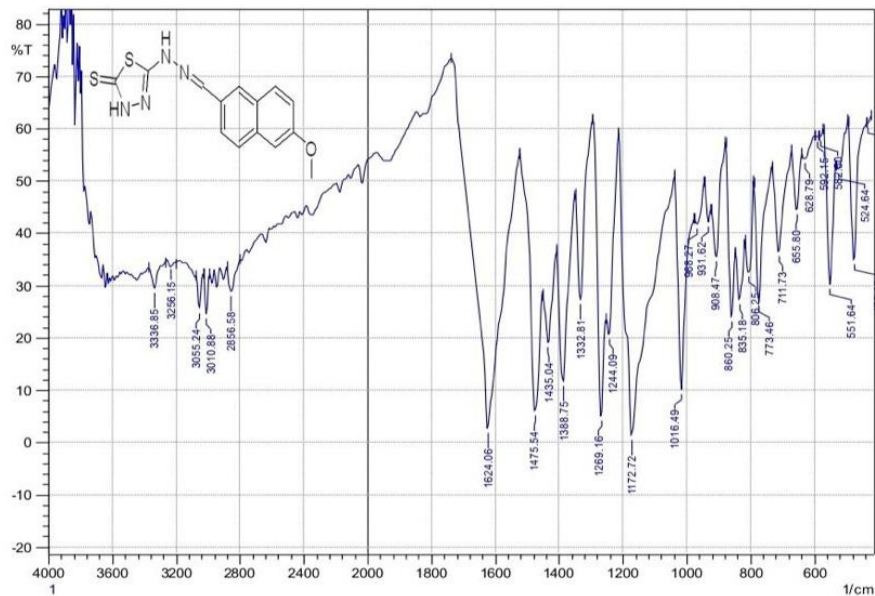


Figure 11. IR of Ligand(L)

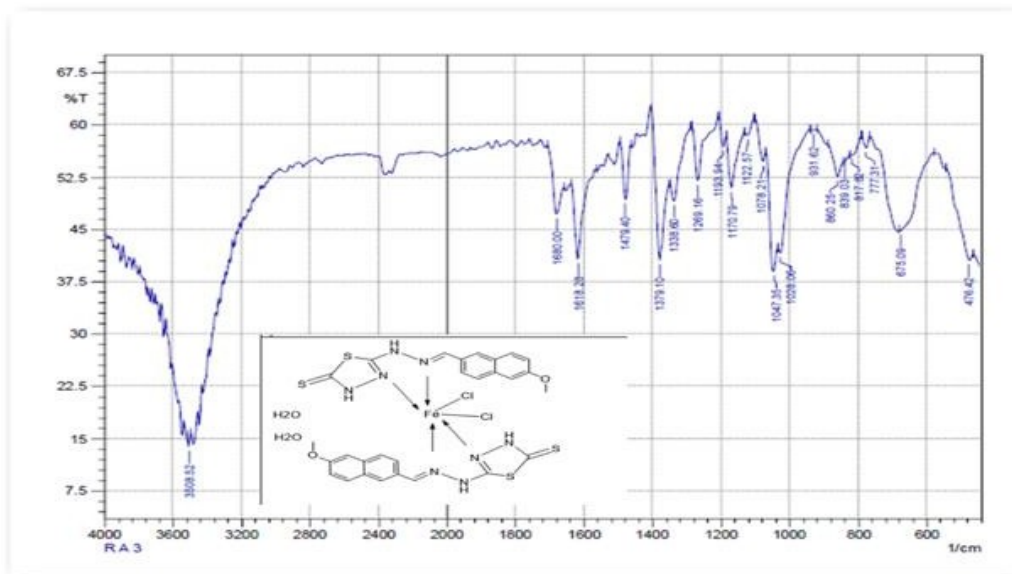


Figure 12. IR of complex [Fe(L)₂ Cl₂]

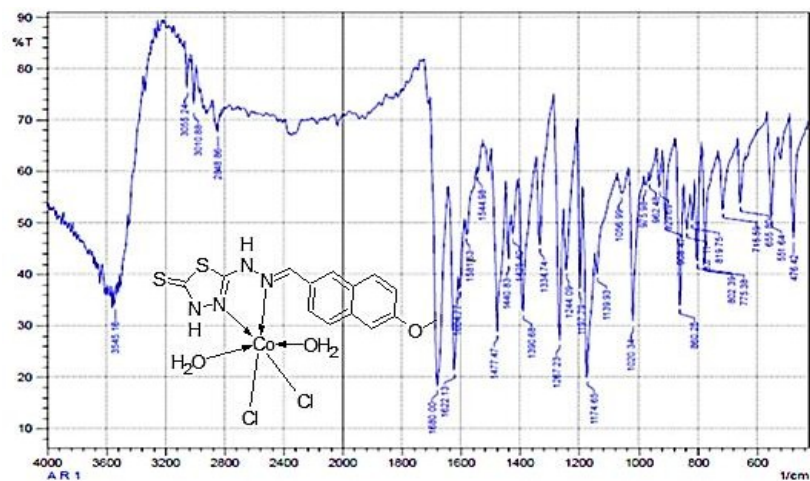


Figure 13. IR of complex [Co(L) Cl₂]

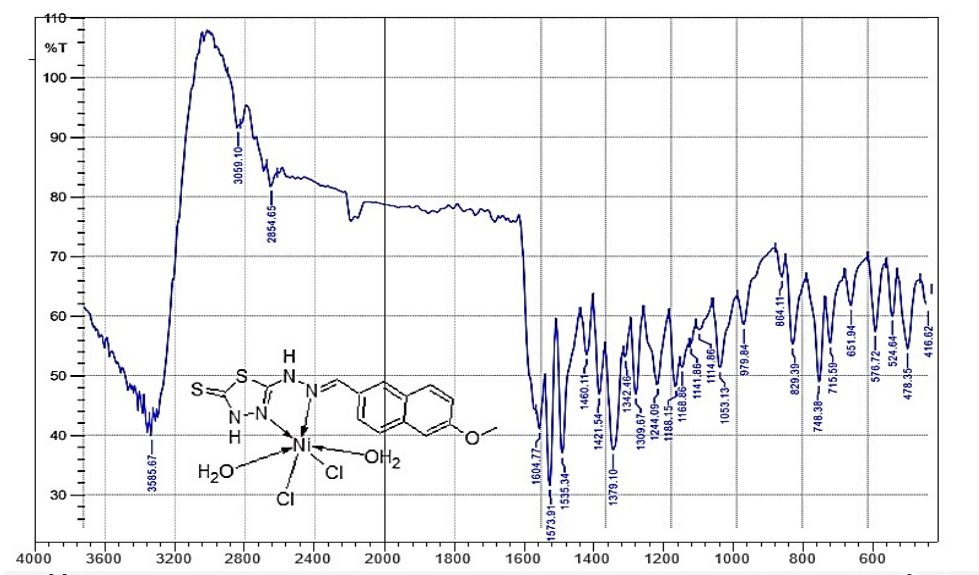


Figure 14. IR of complex [Ni(L)Cl₂]

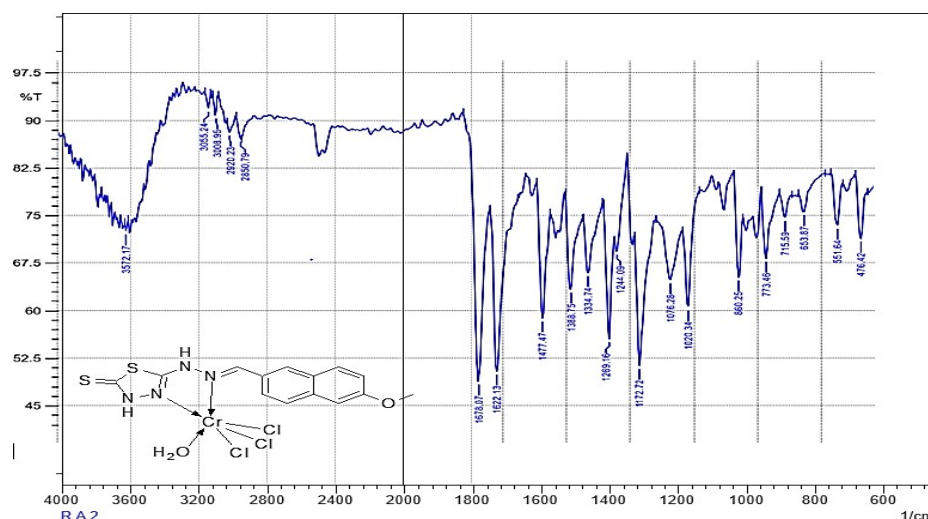


Figure 15. IR of complex [Cr(L)Cl₃]

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 (CrCl₃ ,FeCl₂ , CoCl₂ and NiCl₂) 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
CrCl₃	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
FeCl₂	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
CoCl₂	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
NiCl₂	0.1	1	-1673	-237.429	1290	273.75

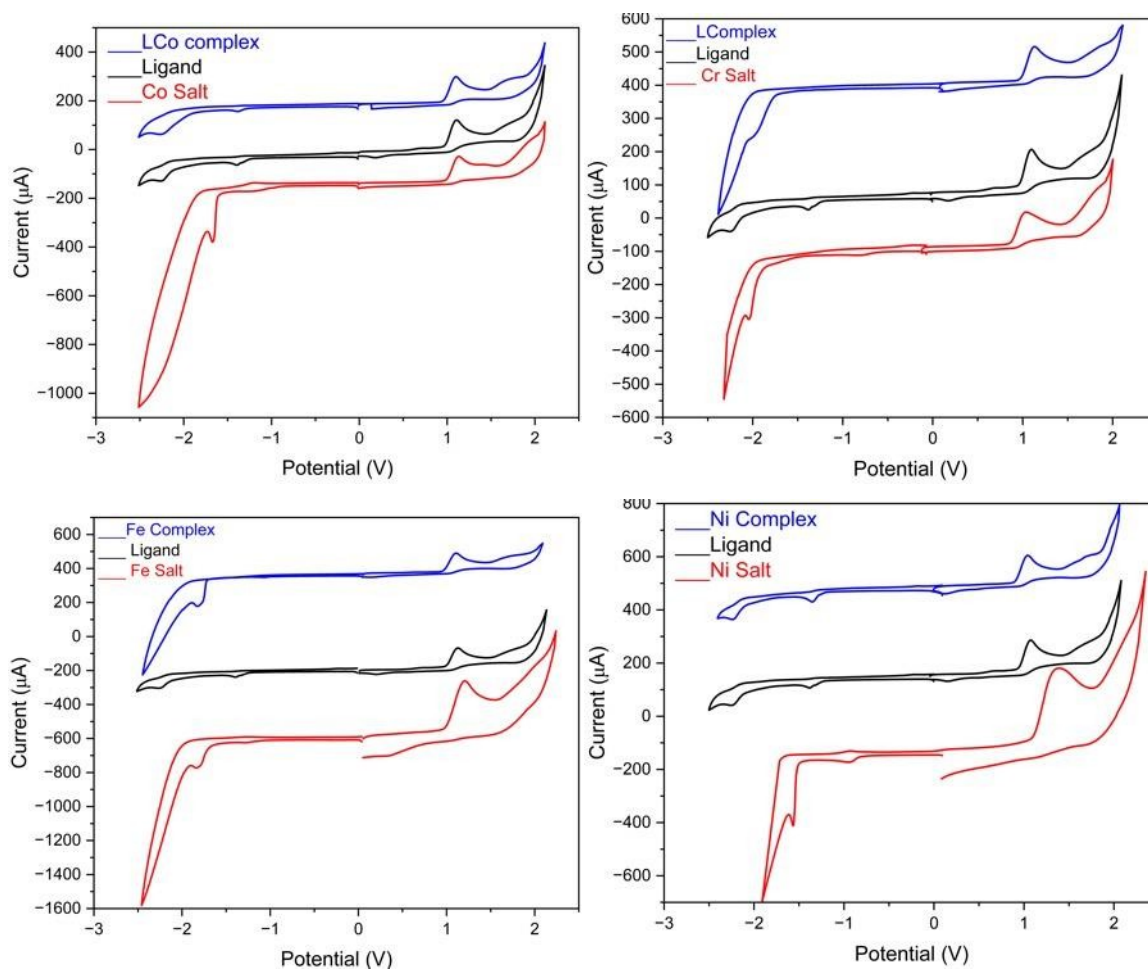
The Ligand L1 shows an irreversible reduction process at -1390 mV which is easier happened upon the complexation with Co⁺² ion (-1385 mV for CoL1). While the oxidation of the Ligand was noted at 1108 mV which was also Cathodically shifted to 1103 mV in CoL1 as evidence to the increase of electron density 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 for Ligand L1 at -228.802 mV 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.

References

1. Pirrello, C., *Exploring the role of downy mildew susceptibility genes in Vitis by studying the genetic variation and the in vivo function*. 2021.
2. RU, C.Y., *SYNTHESIS AND CHARACTERIZATION OF 1, 2, 4-TRIAZOLO-1, 3, 4-THIADIAZOLE DERIVATIVES*. 2022, Universiti Tunku Abdul Rahman.
3. Parcheta, M., et al., *Recent developments in effective antioxidants: The structure and antioxidant properties*. 2021. 14(8): p. 1984.
4. GEETALA, P.K., *Synthesis and characterizations of N-heterocyclic compounds via transition metal free CH functionalization for CC bond formation and CS bond formation using elemental sulphur*. 2024, RMIT University.
5. Žigrajová, D., V. Mikušová, and P.J.G. Mikuš, *Advances in chitosan derivatives: preparation, properties and applications in pharmacy and medicine*. 2024. 10(11): p. 701.
6. Zhang, Q., et al., *Polymers in lithium–sulfur batteries*. 2022. 9(2): p. 2103798.
7. Kharsyntiew, M.I. and M.T. Syiemlieh, *Year of support: 2012-13 No. of departments benefitted by the scheme: 4 (Botany, Chemistry, Physics & Zoology) List of courses run by different departments: Undergraduate*.
8. Sreelaya, V., V. Drisya, and L.J.J.o.H.M. Chakkumkumarath, *A pyrene-based fluorescent sensor for the discrimination and estimation of hydrazine and hydrogen sulfide and its application in assessing food spoilage*. 2025. 487: p. 137151.
9. Mohanty, M. and P.S.J.M.f.C.-C.M. Mohanty, *Molecular docking in organic, inorganic, and hybrid systems: a tutorial review*. 2023. 154(7): p. 683-707.
10. Boschetto, F., et al., *In vitro antibacterial activity of oxide and non-oxide bioceramics for arthroplastic devices: II. Fourier transform infrared spectroscopy*. 2018. 143(9): p. 2128-2140.
11. Alsanafi, A.M. and N.H.J.T.i.S. Al-Saadawy, *Synthesis, Characterization, Cyclic Voltammetry (CV), Theoretical Molecular Docking against Breast Cancer and Computational Study to Determine the Energy Gap of a Newly Series of Organotellurium Compounds Based on N-(4-Benzoylphenyl)-2-Tellurocyanoacetamide*. 2025. 22(9): p. 10416-10416.
12. Gatea A. H., Abdul-Hassan W. S. Ali S. A., Mahdi Z. M., Ligand adduct Ligand Adducts of Bis(acetylacetonato) Copper(II), Bis (3-chloroacetylacetonato) Copper(II) with 4,4'-bipyridine, and Propylene Spaced Bis-viologen. *Journal of Medicinal and Chemistry Sciences* 2023,6 (2), 280-303. DOI:10.26655/JMCHEMSCI.2023.2.10
13. Gatea A. H., Ali S. A., Abdul-Hassan W. S. Comparison study of cloud point and solvent extraction of copper by 3-chloro-2,4-pentanedione as complexing reagent. *Journal of Medicinal and Chemistry Sciences* 2022, 5 (5), 743-752. ID: JMCS-2201-1395
14. Musa A. M., Abdul-Hassan W. S. Iron (II), Cobalt (II) and Nickel (II) complexes of bis- (3-chloroacetylacetonate) ethylenediimine and bis-(acetylacetonate) ethylenediimine and their viologen molecular switches. *Eurasian Chemical Communications* 2023, 5 (6), 492-521. DOI: 10.22034/ecc.2023.370745.1556
15. Jassem I. A., Abdul-Hassan W. S., Flafel I. A., Ali S. A., Mahdi Z. M., Cloud point and solvent extraction of copper (II) by bis(3-chloroacetylacetonate) Ethylenediimine. *Journal of Medicinal and Chemistry Sciences* 2022, 5 (6), 988-1000. 10.26655/JMCHEMSCI.2022.6.12
16. Jassem I. A., Abdul-Hassan W. S., Flafel I. A., Jghebil H. O., Axial ligation for copper (II) complexes of bis (acetylacetonato) ethylenediimine and bis (3-chloroacetylacetonato) ethylenediimine. extraction of copper by 3-chloro-2,4-pentanedione as complexing reagent. *Eurasian Chemical Communications* 2023, 5 (2), 173-203. DOI: 10.22034/ecc.2023.363684.1533

17. Azouz J. A. and Abdul-Hassan W. S. Synthesis, characterization and redox-responsive novel molecular switching behavior of copper (II)-viologen adduct complexes. *Applied Chemical Engineering*, 2025, 8 (3), 1. DOI:10.59429/ace.v8i3.5751
18. Abdul-Hassan W. S., Saint-Aman É., Royal G., Kahlfuss C. Molécules et Matériaux Moléculaires Rédox- et Photo-Stimulables. *L'ACTUALITÉ CHIMIQUE* 2018, N° 430-431 79-84.