



## Original Article

# Some Metal Ions Complexes With Azo [4-((8-hydroxyquinolin-7-yl)-N(4-methylisoxazol-3-yl)benzenesulfonamide] Synthesis, Characterization, Thermal Study and Antioxidant Activity

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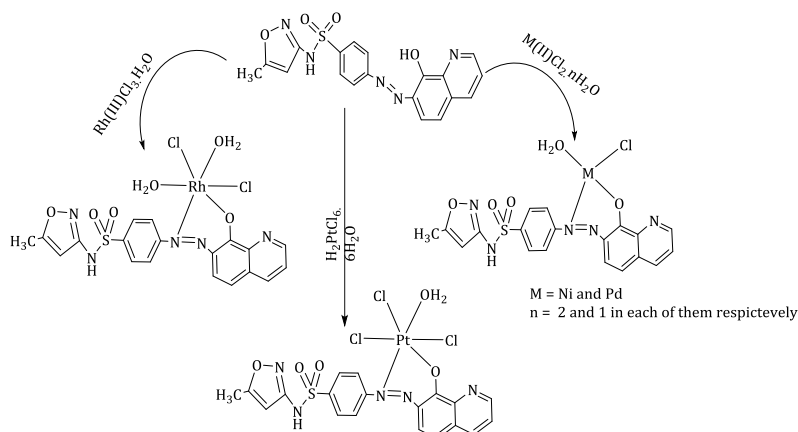
Azo dye

Thermal analysis

## ABSTRACT

A new azo (LH) ligand was prepared by coupling reaction between, diazonium salt of Sulfamethoxazole, and 8-hydroxyquinoline in a process called diazotization process resulting in azo-ligand [4-((8-hydroxyquinolin-7-yl)-N(4-methylisoxazol-3-yl) benzene sulfonamide]. The azo ligand was identified by using spectroscopic techniques to detect and characterize the formation of ligand and complexes of Ni<sup>2+</sup>, Pt<sup>4+</sup>, Pd<sup>2+</sup>, and Rh<sup>3+</sup> metal ions, and to determine the chelating behavior of ligand and also its bind position. All complexes have a [1:1] [M-ligand] ratio and all complexes are non-electrolytes and most of the complexes have octahedral geometry, while Pd<sup>2+</sup> complex gave square planer geometry and Ni<sup>2+</sup> complex indicate tetrahedral geometry. Thermal decomposition TGA and DSC results reveal the presence of coordinated water molecules in the complexes. Antioxidant activities of these compounds were evaluated against (DPPH) radical and were compared with the standard natural antioxidant, ascorbic acid. The findings show that these compounds exhibit excellent radical scavenging activities. The geometries were detected depending on Ultra Violet-visible (UV-Vis) technique and according to the Fourier Transform Infrared Spectroscopy (FT-IR) and Liquid Chromatography-mass (LC-Mass) studies; we can also detect the chelating behavior of ligand. While the conductivity properties can be detected by conductivity measurements. In addition, element micro analysis and atomic absorption gave compatible results with theoretically calculated results, and many other techniques support the formation of ligand and occurrence of coordination including (Proton and Carbon-nuclear magnetic resonance (<sup>1</sup>H & <sup>13</sup>C-NMR) and magnetic quantifications.

## GRAPHICAL ABSTRACT



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## Introduction

Azo dyes represent the largest production volume of dye chemistry today, and their relative importance may even increase in the future. They play a crucial role in the governance of the dye and printing market. These dyes are synthesized from a simple method of diazotization and coupling. Different routes and modifications are made to obtain the desired color properties, yield, and particle size of the dye for improved dispersibility [1]. Azo dyes are the most used dyes and account for more than 60 % of total dyes [2, 3]. Approximately, 70 % of all the dyes used in industry are azo dyes [4, 5]. These compounds are characterized by the functional group (-N=N-) uniting two symmetrical and/or asymmetrical identical or non-azo alkyl or aryl radicals [6]. Most azo dyes are synthesized by diazotization of an aromatic primary amine, followed by coupling with one or more electron-rich nucleophiles such as amino and hydroxy [7]. There are other methods of azo dyes synthesis among which [8, 9], the reduction of nitroaromatic derivatives in alkaline medium, the reduction of nitroso compounds by  $\text{AlLiH}_4$ , the oxidation of primary amines by permanganate potassium or lead tetraacetate, the condensation of hydrazines and quinones, the condensation of primary amines with nitroso derivatives, etc. are mentioned. The azo group may be bonded to benzene rings, naphthalenes, aromatic heterocycles, or to enolizable aliphatic groups [10]. These are essential to give the dye color, with their shades of different intensities. Azo compounds are commonly used in various industries, such as the textile industry and biomedical research [11]. They can also be utilized in food, pharmaceutical, and cosmetic products. One of the enzymes inhibiting the growth of bacteria in the human intestine is the azo reductase [12]. This enzyme is produced by various microorganisms in the intestine. Although sulfonamides were used before penicillin, they are still utilized today to prevent bacterial development [13, 14]. These drugs, known as sulfa drugs, are pharmacologically important compounds with numerous clinical applications and are successfully applied to treat both Gram-positive

and Gram-negative bacteria [15-17]. Sulfonamides have been utilized to treat cancer as a chemotherapeutic agent and a number of diseases greater than antifungals, non-peptide vasopressin receptor antagonists, antihypertensive agents, anti-inflammatory, antibacterial, translation initiation inhibitors, antineoplastic agents, diuretics, thyroid inhibitors, antitumor, carbonic anhydrase inhibitors, and glucocorticoid inhibitors are among the 30 sulfonamide derivatives in clinical use [18-21]. Blood, potassium channels, carboxypeptidase inhibitors, hepatitis viral (HCV) polymerase inhibitors, protease inhibitors, and the HIV-1 integrity [22-25]. In this work, we attempted to use a diazotization coupling reaction between sulfamethoxazole (a sulfur-containing organic compound) and (8-hydroxyquinoline) to form [4-((8-hydroxyquinolin-7-yl)-N(4-methylisoxazol-3-yl)benzene sulfonamide(HL)], which is classified as an azo-compound that coordinates with each of Ni(II), Pt(IV), Pd(II), and Rh(III). The usage of acidic media to prepare the intermediate compound is the basis for the preparation of important azo compounds with widespread applications in various fields in such reactions. The aim of this research is to synthesize a novel azo ligand from an aromatic amine by using spectroscopic analysis (NMR, Mass, IR, and UV-Vis) and to investigate thermal decomposition and thermal stability by using TGA and DSC its composition, as well as the synthesis of Ni (II), Pt (IV), Rh (III), Pd (II), and complexes by spectroscopic analysis, the assay of thermal decomposition, and thermal stability.

## Experimental

All chemicals and reagents were acquired from the commercial sources (Sigma-Aldrich, Merck, and others). The eurovector model EA/3000, single-V.3.0, was used to conduct elemental analyses (C, H, N, S, and O). Metal ions were estimated as metal oxides by using a gravimetric method. The complexes molar conductance was measured via Conduct meter WTW at 25 °C and a concentration of  $1 \times 10^{-3}$  M. DMSO was used to dissolve all of the complexes. Mass spectra for substances were collected by a mass spectrometry (MS) QP50A :DI Analysis Shimadzu QP(E170Ev) -2010-Plus

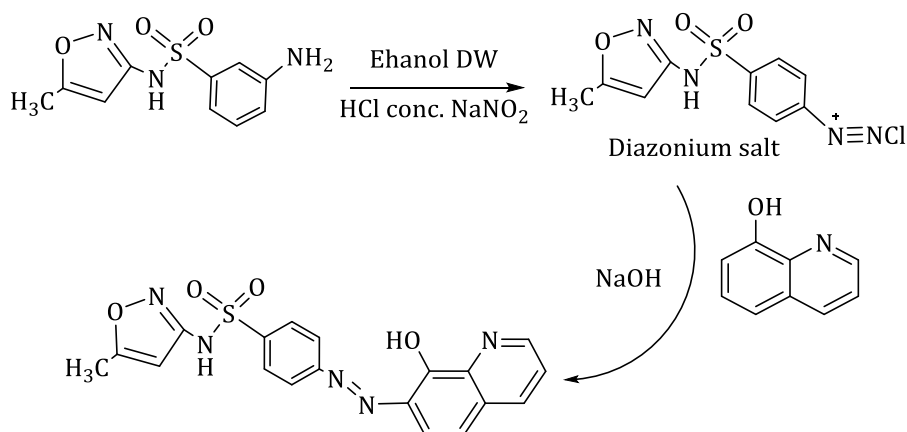


spectrometer. The spectra were analyzed by using a Shimadzu UV-1800 UV-visible spectrophotometer. The photonuclear magnetic resonance ( $^1\text{H}$  &  $^{13}\text{C}$ -NMR) spectra for ligand in  $\text{DMSO-d}_6$  were recorded by a Bruker 400 MHz. The IR Prestige-21 was used to investigate the Fourier transform infrared (FTIR) spectra.

*The preparation of 4-((8-hydroxyquinolin-7-yl)-N(4-methylisoxazol-3-yl) benzene sulfonamide*

The ligand Synthesis :Sulfamethoxazole (0.5 g, 0.0019 mol) was dissolved in a solution of 5% (25 mL) concentrated hydrochloric acid HCl, 15% (15 mL) ethanol and distilled water. The solution is cooled to  $0\text{ }^\circ\text{C}$  –  $5\text{ }^\circ\text{C}$  before adding (1 g, 5 mol equals to 10 %, ) of hydrated sodium nitrite  $\text{NaNO}_2$  into the solution with constant stirring to avoid

any increase in temperature any temperature increase above  $5\text{ }^\circ\text{C}$ . The salt solution was gradually added with continuous stirring onto (0.28 g, 0.0019 mol) of 8-hydroxyquinoline dissolved in 20 mL of ethanol after being left in the solution for about 45 minutes to perform the diazotization process, which produced diazonium salt. While stirring for about 30 minutes to complete the reaction, the color of the solution changed to dark. When the solution was stable, a few drops of NaOH solution were added to equivalence the middle of the reaction until it reached 6.8 pH at which point, the ligand precipitated perfectly. Finally, the solution of the ligand was filtered and recrystallized by methanol before drying, yielding 1.34g, 90.70%,  $133\text{--}135\text{ }^\circ\text{C}$  m. p orange precipitate (Scheme 1).



**Scheme 1: Synthesis of ligand**

*A general method for preparing metallic ion complexes*

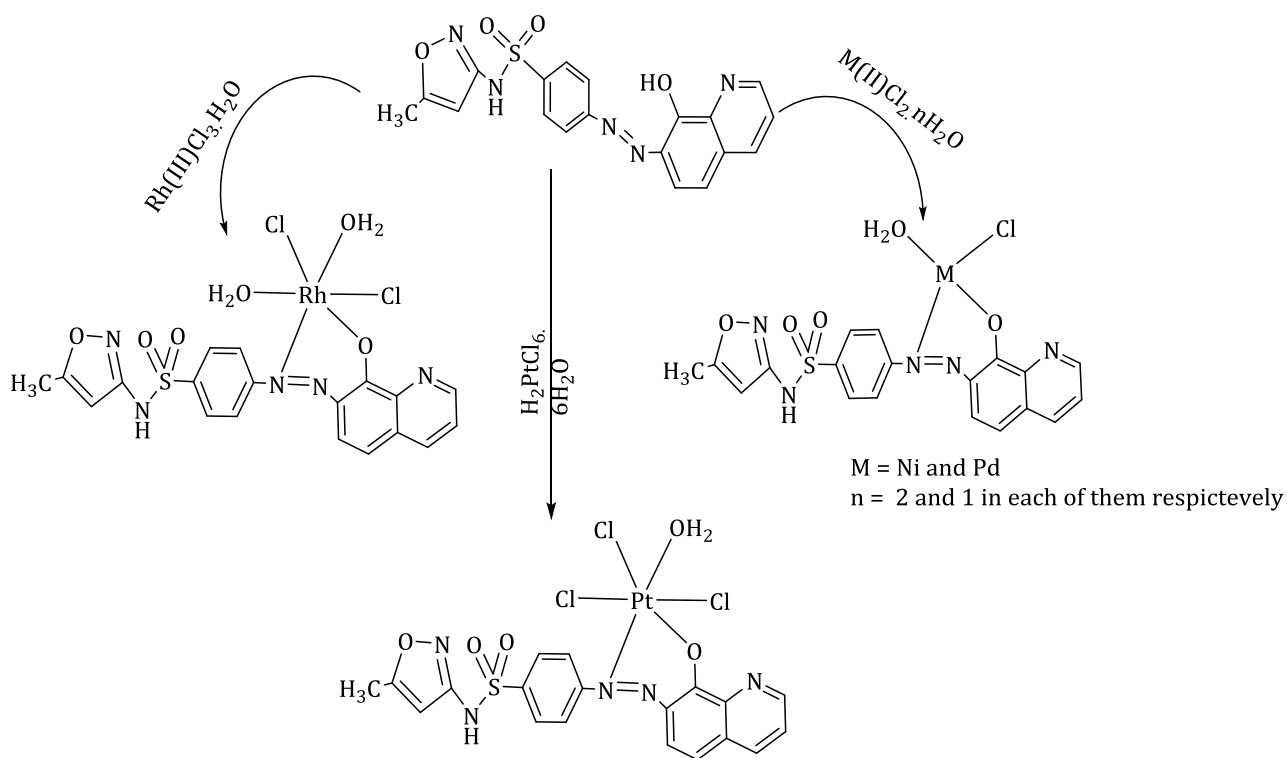
Metallic ions complexes for  $\text{Ni}^{2+}$ ,  $\text{Pt}^{4+}$ ,  $\text{Pd}^{2+}$ , and  $\text{Rh}^{3+}$  were created by using metal chlorides A (0.1 g (0.001 mol) amount of [1:1] M:L for  $\text{Ni}^{2+}$ ,  $\text{Pt}^{4+}$ ,  $\text{Pd}^{2+}$ , and  $\text{Rh}^{3+}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{PdCl}_2$ ,  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , and  $\text{RhCl}_3 \cdot \text{H}_2\text{O}$  was gradually added in dropwise with stirring to a (0.1 g, 0.001 mol) amount of ligand, dissolved in 10 mL absolute. The mixture was heated at  $(50\text{--}70)\text{ }^\circ\text{C}$  for two hours, and then it was put in an ice bath until precipitation occurred and left overnight. To remove any remaining contaminants, complex solution was filtered to separate the solid complexes and washed with distilled water and a small amount of

hot ethanol. Unreacted substances should be removed. Finally, the complexes were dried by using vacuum desiccators. Table 1 summarizes all compounds which were analyzed and their analytical properties were determined (Scheme 2).

**Results and Discussion**

The azo dye ligand (LH) has an amorphous appearance that resembles a high-quality orange powder. This synthesized ligand is soluble in DMSO and DMF, but much more so in ethanol. In the presence of air, the produced metallic ion compounds were stable.





Scheme 2: Synthesis of complexes

Table 1: Physical properties and analytical data of ligand and their complexes.

Compound	Chemical Formula M.wt	Color	m.p °C	Elemental microanalysis%						
				C Fou.	H Fou.	N Fou.	O Fou.	S Fou.	M Fou.	Cl Fou.
				C Calc.	H Calc.	N Calc.	O Calc.	S Cal.	M Calc.	Cl Calc.
LH	C <sub>19</sub> H <sub>15</sub> N <sub>5</sub> O <sub>4</sub> S 409.42	Brown red	133-135	55.55	3.65	17.55	15.49	7.76	-	-
				54.45	3.20	18.65	15.20	8.50	-	-
[Ni(L)Cl(H <sub>2</sub> O)]	C <sub>19</sub> H <sub>16</sub> N <sub>5</sub> NiO <sub>5</sub> SCl 520.57	Brown orang	207d	43.88	2.88	12.73	14.98	7.77	12.21	5.55
				43.79	3.07	13.44	15.27	6.14	11.25	6.87
[Pd(L) (H <sub>2</sub> O)Cl]	C <sub>19</sub> H <sub>16</sub> N <sub>5</sub> PdO <sub>5</sub> SCl 568.30	Brown	222 d	39.99	2.74	13.74	13.56	5.94	18.84	5.19
				40.11	2.81	12.31	13.98	5.63	18.72	6.22
[Rh(L)Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	C <sub>19</sub> H <sub>18</sub> N <sub>5</sub> RhO <sub>6</sub> SCl <sub>2</sub> 618.25	Brown dark	230 d	37.73	3.33	12.11	16.61	4.00	16.11	10.11
				36.87	2.91	11.32	15.43	5.17	16.64	11.45
[Pt(L) (H <sub>2</sub> O)Cl <sub>3</sub> ]	C <sub>19</sub> H <sub>16</sub> N <sub>5</sub> PtO <sub>5</sub> SCl <sub>3</sub> 727.86	Brown dark	205d	31.35	2.22	9.62	10.99	4.41	26.80	14.61
				31.32	2.19	9.61	10.92	4.39	26.80	14.59

D = decompose

### Nuclear Magnetic Resonance Spectra

As displayed in Figure 1, the magnetic nuclear resonance spectrum of the new azo ligand was studied by using dimethyl sulfoxide DMSO-*d*<sub>6</sub> as a solvent and TMS as a standard reference. Figure 1 demonstrates the chemical shifts of these spectra. <sup>1</sup>H-NMR spectrum of the ligand indicates the following signals, as mentioned in Table 2: singlet signals (1H) at 10.25 ppm belongs to Ar-OH, 11.14 ppm belongs to N-H, 6.75 ppm belongs to C-H aromatic, and 3.34 ppm belongs to 3H of CH<sub>3</sub>.

Douplet signals 1H at 6.84-6.87 belongs to the C-H group of ortho – quinolone nearby to N, multiplet signal belongs to 8H of Ar- H at 7.78-7.87 ppm in addition to the signal of the solvent which in turn appears at 2.31-2.64 ppm. As depicted in Figure 1 <sup>13</sup>C-NMR spectrum 1 demonstrates the next signals : (100.622 MHz, DMSO-*d*<sub>6</sub>) : d 30.36 (C1), 102.11 (C13), 111.10 (C7), 114.90 (C18), 119.84 (C19), 133.31 (C15), 137.61 (C17), 140.59 (C9), 142.52 (C8), 146.52 (C16), 148.35 (C13), 155.61



(C11), 157.59 (C5), 159.52 (C12), 165.52 (C14), 175.52 (C4), 177.52 (C10), and 185.12 (C2) [26].

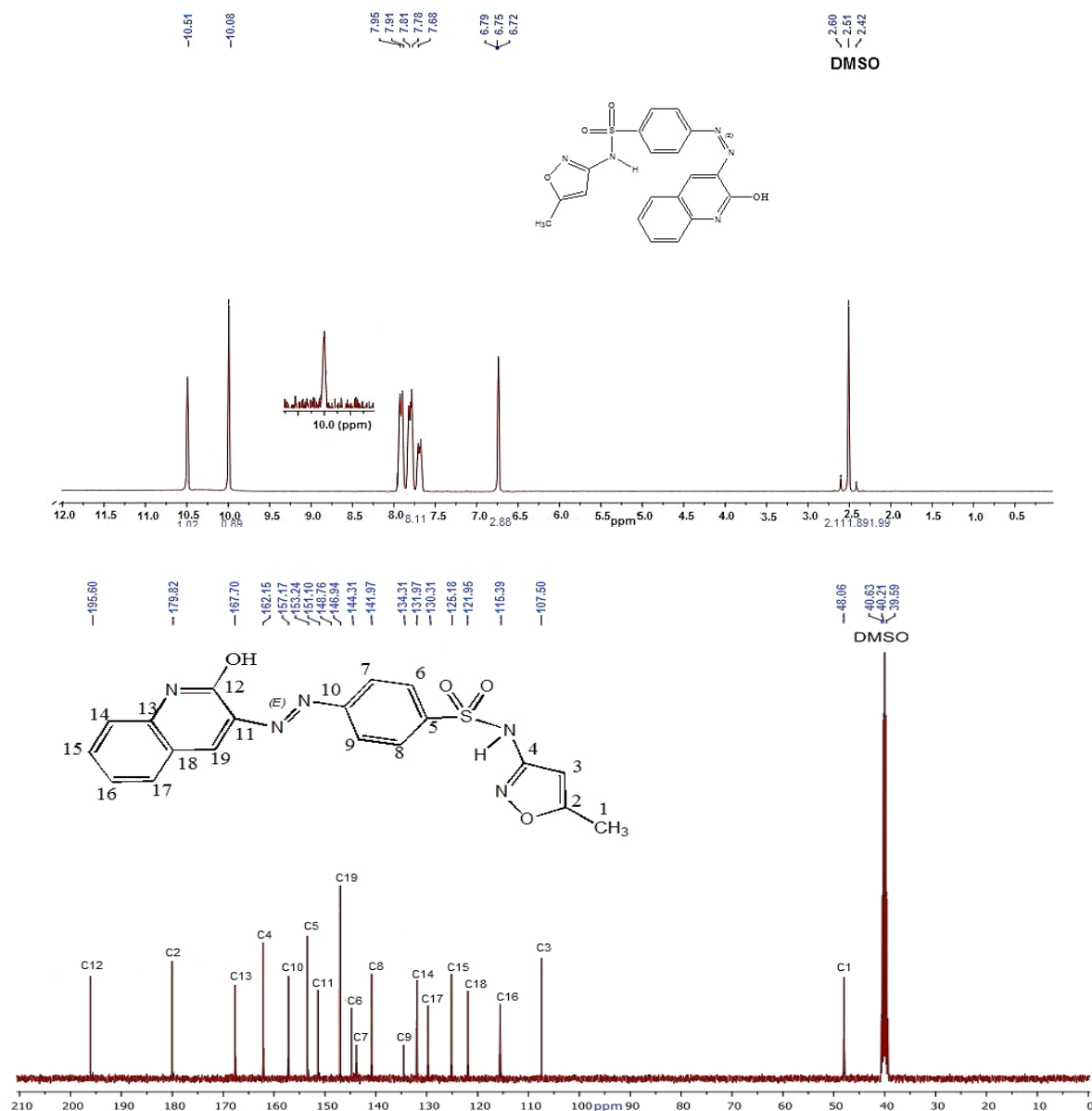


Figure 1:  $^1\text{H}$  &  $^{13}\text{C}$ -NMR spectra of ligand

### Measurements of electronic spectra

Table 2 presents the UV-Vis spectral data of the ligand and its complexes. With absorption maxima at (259 nm, 38610  $\text{cm}^{-1}$ ) ascribed to the transition  $\pi \rightarrow \pi^*$  and peak at (411 nm, 24330  $\text{cm}^{-1}$ ) attributed to the transition  $n \rightarrow \pi^*$  a peak with a high intensity band formed with absorption maxima. There were five absorption peaks in the electronic spectrum of the  $[\text{Ni}(\text{L})\text{Cl}(\text{H}_2\text{O})]$  complex, as displayed in Figure 2. The peaks at 298 nm is ascribed to the ligand, while the

( $\pi \rightarrow \pi^*$ ) complex, the peak at 429 nm is ascribed to the ligand, and the  $n \rightarrow \pi^*$  complex and three peaks in the (512, 676 and 778 nm) while the three peak at are attributed to the (d-d) electronic transitions types  $^3\text{T}_{1(\text{F})} \rightarrow ^3\text{T}_{1(\text{F})}$ ,  $^3\text{T}_{1(\text{F})} \rightarrow ^3\text{A}_2$ , and  $^3\text{T}_{1(\text{F})} \rightarrow ^3\text{T}_{1(\text{P})}$ , respectively. All the above-mentioned data correspond to a tetrahedral geometry of Ni-complex [27]. Pd (II) complex was ascribed to the peak at 306 nm is ascribed to the ligand, while the ( $\pi \rightarrow \pi^*$ ), the two peaks at 521 nm and 637 nm, was assigned to the  $^1\text{A}_{1\text{g}} \rightarrow ^1\text{B}_{1\text{g}}$ ,

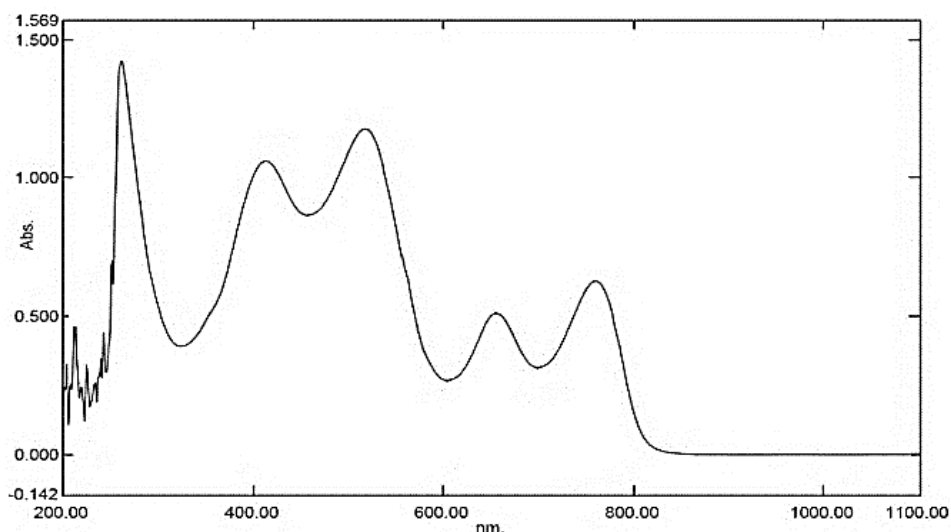


$^1A_{1g} \rightarrow ^1A_{2g}$ , transition indicating a square planer geometry. Besides, the electronic spectra of the  $Rh^{3+}$  complex revealed to the peak at 304 nm is ascribed to the ligand, while the  $(\pi \rightarrow \pi^*)$ , the peak at 364 nm is ascribed to  $(n \rightarrow \pi^*)$ , the peak at 420 nm is ascribed to the C.T (charge transfer transition) and two peaks in the (583 nm) and (793 nm) to  $^1A_{1g} \rightarrow ^1T_{2g}$ ,  $^1A_{1g} \rightarrow ^1T_{1g}$ , indicating an octahedral in Figure 3. The electronic spectrum of

the diamagnetic  $Pt^{4+}$  complex ascribed to the peak at 319 nm is ascribed to the ligand, while the  $(\pi \rightarrow \pi^*)$ , the peak at (376 nm) is ascribed to  $[n \rightarrow \pi^*]$ , the peak at (496 nm) is ascribed to C.T and three peaks at (580, 769, and 918 nm) was assigned to the  $^1A_{1g} \rightarrow ^1T_{2g}$ ,  $^1A_{1g} \rightarrow ^1T_{1g}$ , and  $^1A_{1g} \rightarrow ^3T_2$  transition, respectively, indicating an octahedral geometry diamagnetic [29, 28].

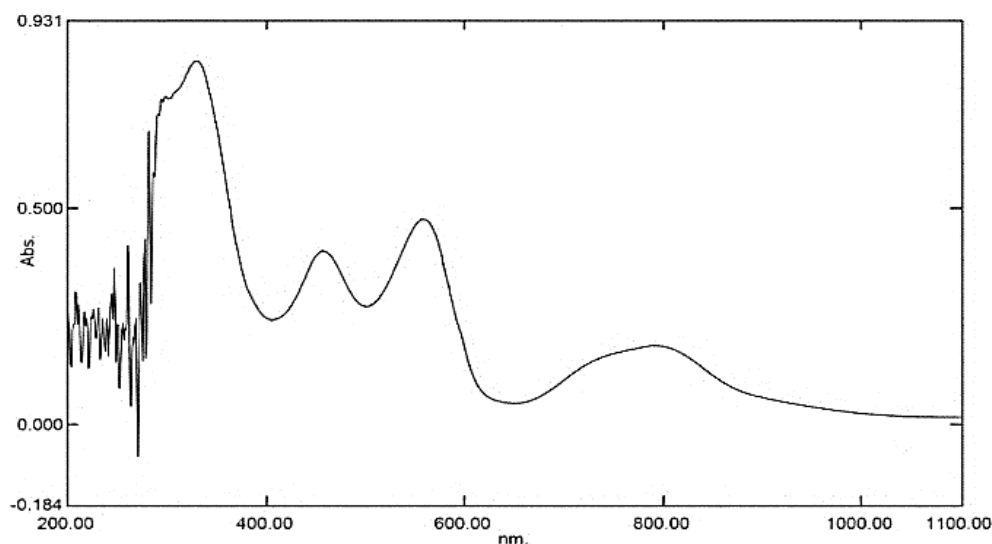
**Table 2:** Metal complexes with ligand (LH) electronic spectral data and conductivity

Compounds Geometry	Wave length nm	Wave number $cm^{-1}$	Absorptio n	$\epsilon_{max} L$ $mol^{-1}cm^{-1}$	Assignment	$\Delta_m cm^2 \Omega^{-1} mol^{-1}$
LH	259 411	3861 2433	1.182 2.571	1123 993	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^* + C.T(L \rightarrow L)$	-
[Ni(L)Cl(H <sub>2</sub> O)] (Tetrahedral)	298 429 512 676 778	33557 23310 19531 14792 12853	1.423 1.093 1.203 0.505 0.614	1400 1050 1150 500 600	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $^3T_{1(F)} \rightarrow ^3T_{1(F)}$ $^3T_{1(F)} \rightarrow ^3A_2$ $^3T_{1(F)} \rightarrow ^3T_{1(P)}$	11
[Pd(L) (H <sub>2</sub> O)Cl] (Square planer)	306.7 521.9 637.6	32605 91608 15683	0.536 0.176 0.113	530 120 100	$\pi \rightarrow \pi^*$ $^1A_{1g} \rightarrow ^1B_{1g}$ $^1A_{1g} \rightarrow ^1A_{2g}$	10
[Rh(L)Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] (Octahedral)	304.6 364.2 420.6 583.4 793.5	12602 17140 23775 27457 32829	0.432 0.493 0.404 0.813 0.702	200 450 400 700 650	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ C.T M $\rightarrow$ L $^1A_{1g} \rightarrow ^1T_{2g}$ $^1A_{1g} \rightarrow ^1T_{1g}$	8
[Pt(L) (H <sub>2</sub> O)Cl] (Octahedral)	319.6 376.2 496.5 580.9 769.4 918.9	31289 26581 20141 17241 13003 108826	1.963 2.199 1.064 1.211 0.398 0.266	1900 2050 1050 1300 350 200	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ C.T M $\rightarrow$ L $^1A_{1g} \rightarrow ^1T_{2g}$ $^1A_{1g} \rightarrow ^1T_{1g}$ $^1A_{1g} \rightarrow ^3T_2$	15



**Figure 2:** Electronic spectra of Ni-complex



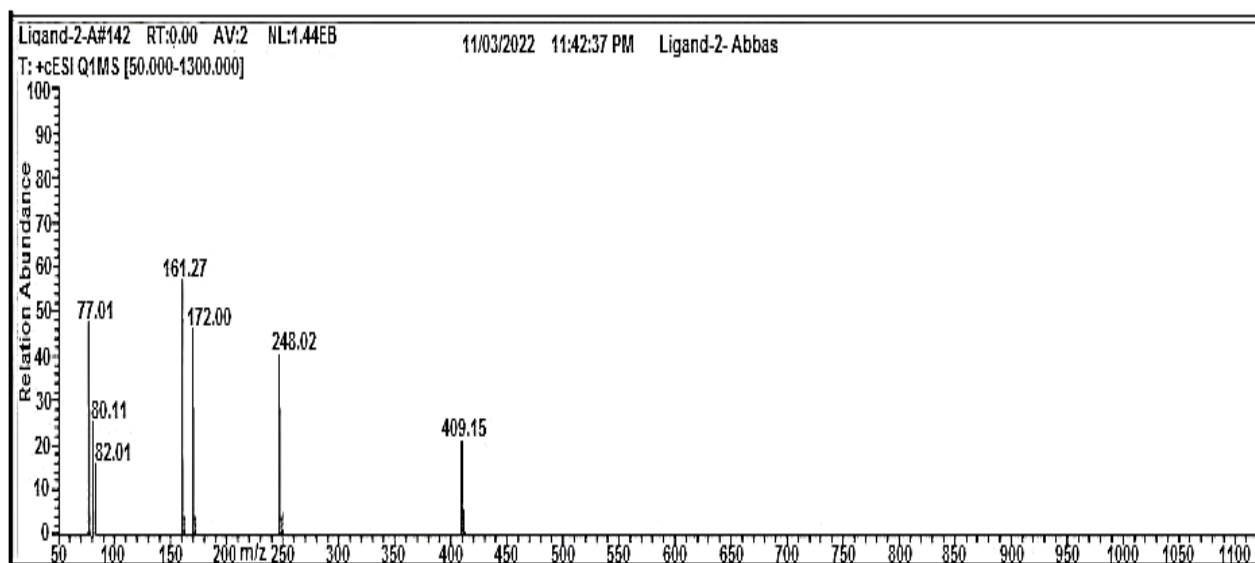


**Figure 3:** Electronic spectra of Rh(III) complex

#### LC-Mass liquid chromatography-mass spectrometry

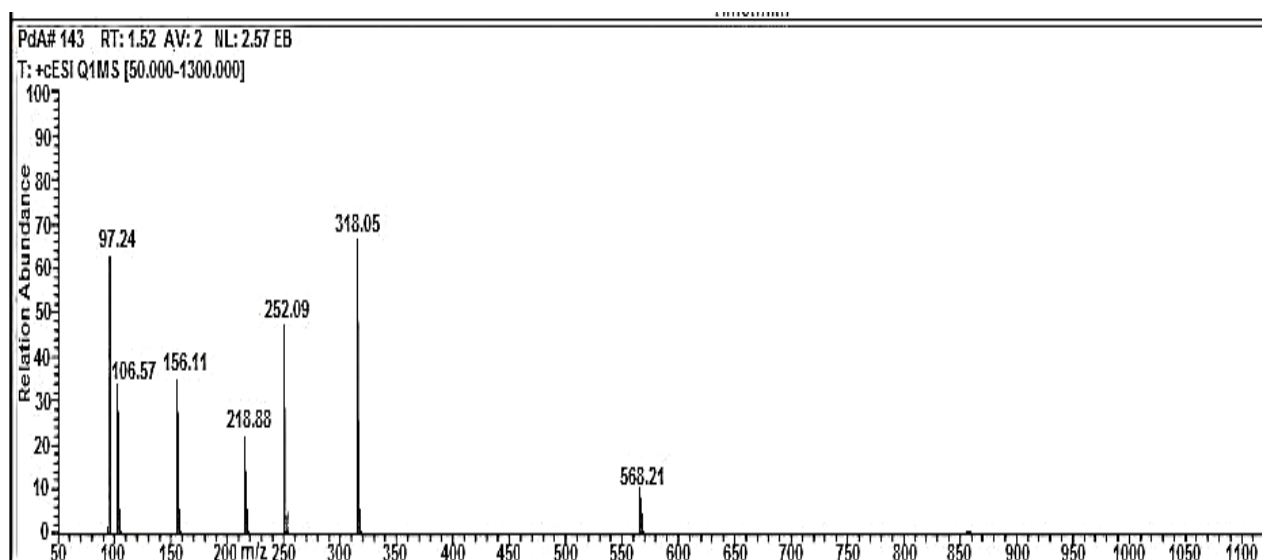
Fragmentation's electron impact is used to generate new compounds. High-resolution mass spectrometry revealed the free ligand and its complexes, as well as the significant fractions associated with cracking products. The electron hit mass spectrometry of the ligand is displayed in Figure 4. The molecular weight of this ligand is calculated to be 409.42g/mol. A peak at 409 m/z in the spectrum was attributed to  $[M]^+$  and correlated with a new azo moiety  $C_{19}H_{15}N_5O_4S$ . Other pieces could be responsible for the peaks at 248, 172, 161, 82, and 77 m/z. Their brightness indicates the stability of the pieces. The mass

spectrum of the  $Ni^{2+}$  complex, the complex moiety  $C_{19}H_{16}SClN_5NiO_5$  in the spectrum had a peak at 520.57 m/z, which was equivalent to the complex moiety  $C_{19}H_{16}SClN_5NiO_5$ . Other pieces could be responsible for the peaks at 520, 467, 371, 213, 159, and 97 m/z. The mass spectrum of the  $Rh^{3+}$  complex, the compound moiety  $C_{19}H_{18}N_5O_6RhCl_2S$  was identified in the spectra by a peak at 618.25 m/z. Other pieces could be responsible for the peaks at 618, 318, 218, 156, and 97 m/z. The electron effect mass spectrometry of the  $Pd^{2+}$  complex is depicted in Figure 5. The complex moiety  $C_{19}H_{16}N_5O_5PdClS$  was identified in the spectra by a peak at 568.30 m/z. Other pieces may have contributed peaks at 568, 318, 252, 218, 156, 106, and 97 m/z [29].



**Figure 4:** LC-Mass spectrum of ligand





**Figure 5:** LC-Mass spectrum of Pd-complex

#### *Infrared spectroscopic measurements*

The azo-ligand spectra and metal chelates complexes with compiled complexes are listed in Table 3. The infrared spectra of the ligand and its complexes were measured on KBr pellets in the region 4000-400  $\text{cm}^{-1}$ . The ligand infrared spectrum showed bands due to (OH phenol) at

(3378)  $\text{cm}^{-1}$ , (N-H amines) absorbed at (3291)  $\text{cm}^{-1}$ , (3085)  $\text{cm}^{-1}$  due to (C-H) stretching vibration of aromatic ring, (2980)  $\text{cm}^{-1}$  due to (C-H) stretching vibration of aliphatic, (1163, 1086, and 1030)  $\text{cm}^{-1}$  due to  $\text{SO}_2$ . When the infrared spectra of the complexes are compared with the spectrum of the ligand, the phenol band disappears and the azo bands wind which denotes the bonding [30, 31].

**Table 3.** The IR spectra bands ( $\text{cm}^{-1}$ ) of the free ligand and its complexes

Compounds	$\nu(\text{H}_2\text{O})$ aqua	$\nu(\text{NH})$	$\nu(\text{C-H})$ aromatic	$\nu(\text{C-H})$ aliphatic	$\nu(\text{N=N})$	$\nu(\text{SO}_2)$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
LH	-	3291	3085	2980	1461 1394	1163 1086 1030	-	-
[Ni(L)(H <sub>2</sub> O)Cl]	3435 1636	3282	3074	2982	1414 1357	1089 1057	444	577
[Pd(L)(H <sub>2</sub> O)Cl]	3509 1602	3298	3096	2978	1487 1407	1163 1083	421	547
[Rh(L)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]	3738 1643	3293	3049	2977	1447 1343	1164 1084	435	485
[Pt(L)(H <sub>2</sub> O)Cl <sub>3</sub> ]	3740	3298	3018	2984	1458 1407 1346	1165 1084	409	488

#### *Study of Thermogravimetric Analysis for Compounds*

The thermal and weight stability of the prepared compounds were determined by using DSC and

TGA techniques, as well as the determination of the exothermic and endothermic given in Table 4 and Figures 6-7. The elemental analysis results confirm the proposed formula, based on Table 4 and Scheme 7. The bonding showed little thermal



stability at 41 °C, and complexes with low thermal stability in the range 64.786 °C for Rh and 72.829 °C for Pd, which indicates the presence of water

molecules in Pd complex and Rh complex whether water aqua or hydrate [32-34].

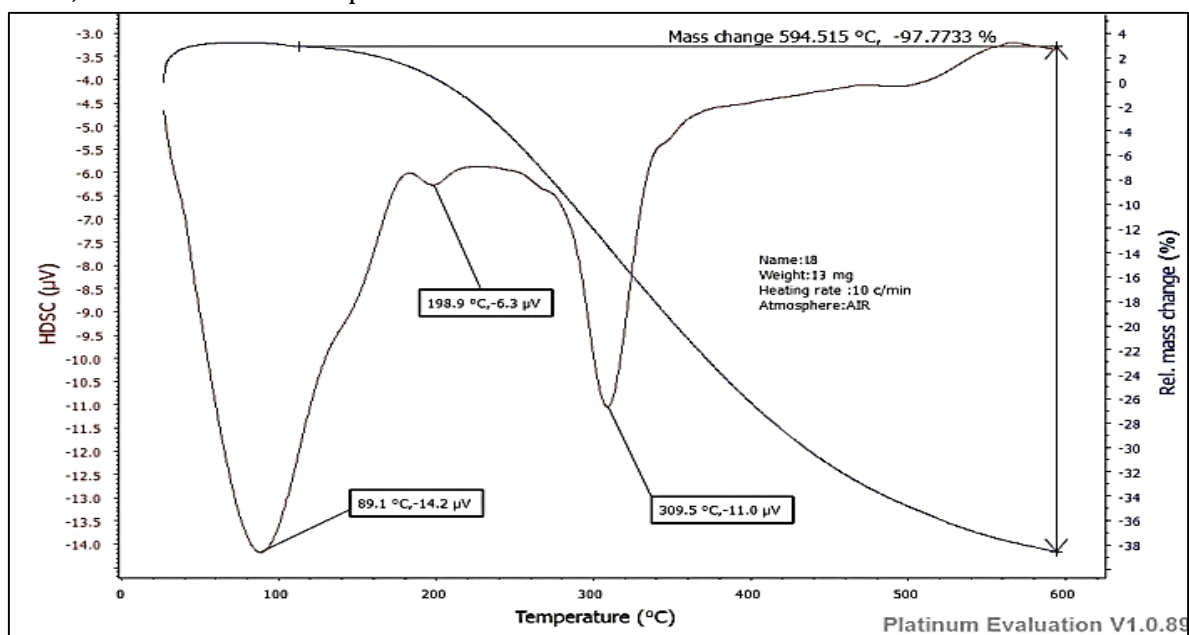


Figure 6: DSC and TGA curves of ligand

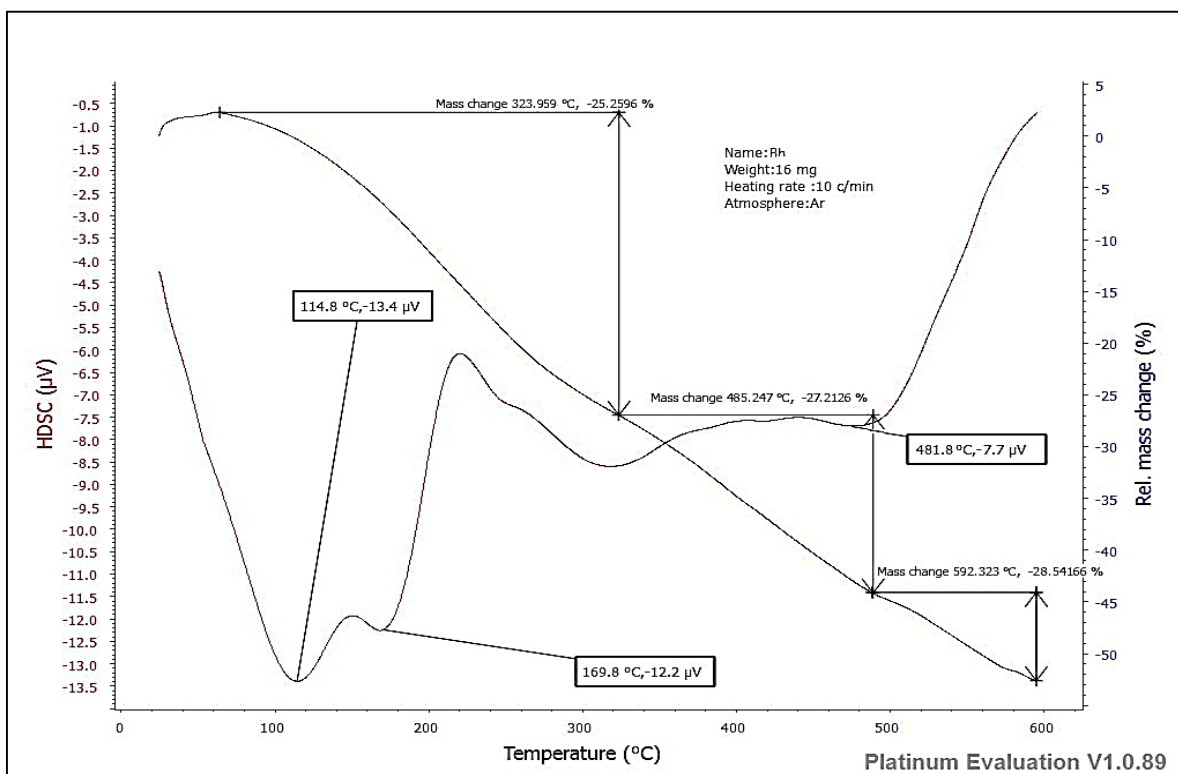
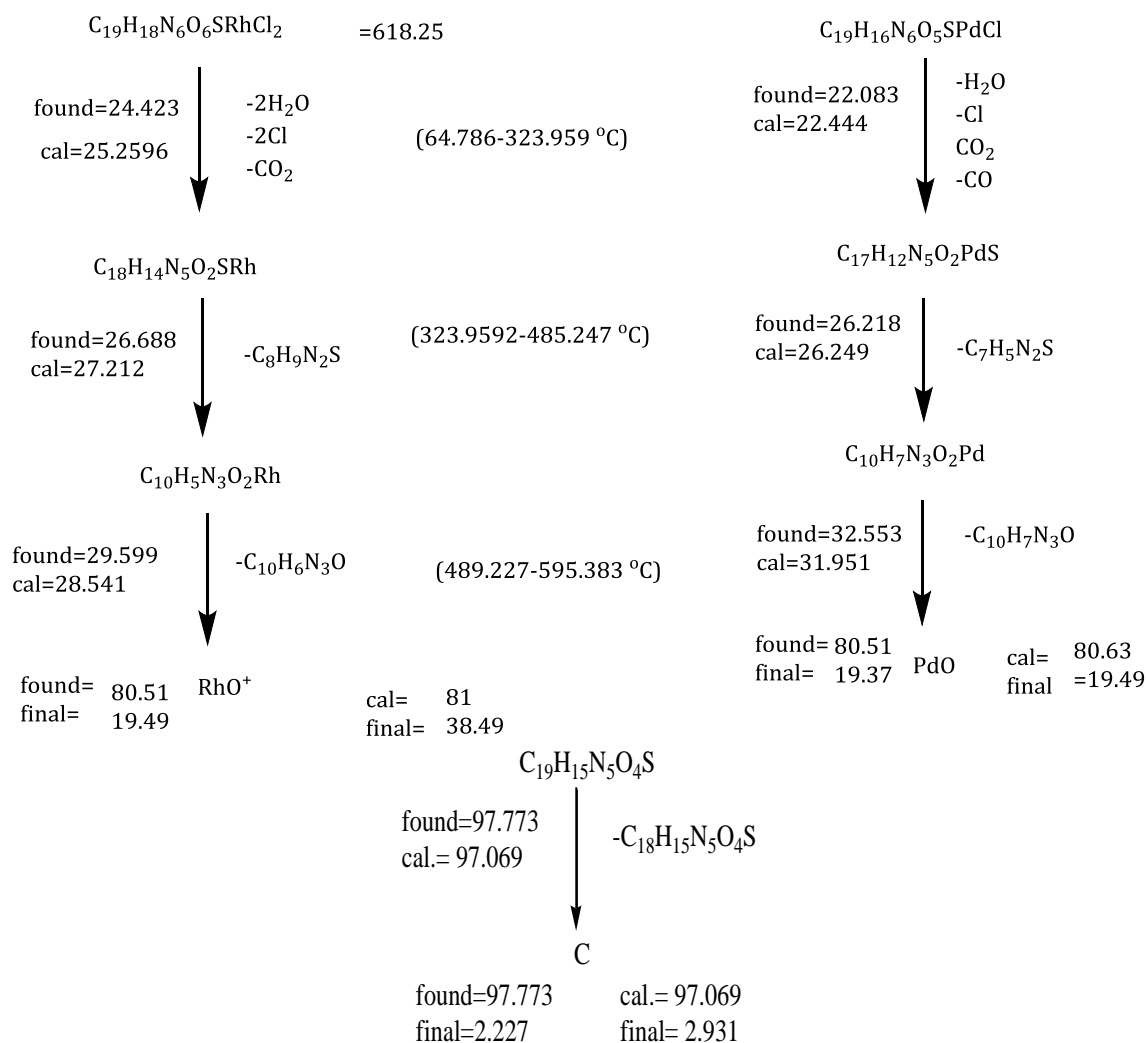


Figure 7: DSC and TGA curves of Rh-complex



**Scheme 7:** Tentative decomposition reaction of compounds**The DPPH method for antioxidant activity investigation**

To investigate the antioxidant activity of the ligands and their metal complexes, Gallic acid was used as a phenolic reference. To provide a series of standards, five normal solutions of different concentrations (0.2, 0.4, 0.6, 0.8, and 1 mmol.l<sup>-1</sup>) of 10 mmol were prepared. By using a one-liter solution of Gallic acid and ethanol as a diluent, 6 mL of 45 g of DPPH solution was added to 100  $\mu$ L of each normal Gallic acid solution. After 30 minutes of incubation at room temperature in the dark, the absorbance of the reaction mixture was measured by using a UV-vis spectrophotometer at 517 nm. The following equation was used to calculate percentage of root scavenger DPPH. Because of its simplicity and reliability, the DPPH test is used by the majority of studies to evaluate the antioxidant activity of their targets. Table 5 presents the results of the radical scavenging activity of DPPH compounds. A lower IC<sub>50</sub> value

indicates a greater DPPH radical scavenging activity and depending on the IC<sub>50</sub> values, the order of oxidation activity are followed as (GA> HL> [Pt(L)(H<sub>2</sub>O)Cl]> [Ni(L)Cl (H<sub>2</sub>O)]> [Pd(L)(H<sub>2</sub>O) Cl]> [Rh(L)(H<sub>2</sub>O)<sub>2</sub>Cl<sub>2</sub>]). The table showed that almost all of the compounds had radical scavenging activities in the DPPH assay. It was important to observe that azo complex showed better antioxidant activity than azo, as indicated in Table 5. The presence of azo and -OH group has also an effect on the radical scavenging activity of DPPH, and the ethylene separator has no effect on the antioxidant property. Therefore, when the tested sample was added onto solution, it neutralizes the free radical by either donating hydrogen or an electron which neutralizes of the free radical. Less free radical will be present when the free radicals were neutralized by a test sample. The specific antioxidant activity of the compounds gave the activity of the compounds, in general,



compared with Gallic acid [32-35], as listed in Table 5.

**Table 4:** DSC and TGA data records for the compounds

TGA records							DSC data	
Compound	T <sub>i</sub> , °C	T <sub>f</sub> , °C	T <sub>DTG</sub> max	% Estimated (calculated)		Assignment	ΔH J/g	Maximum temperature point °C and Type
				Mass loss	Total mass loss			
Ligand	113.867	594.515	389.763	97.773 (97.069)	97.773 (97.06)	-C <sub>19</sub> H <sub>15</sub> N <sub>5</sub> O <sub>4</sub> S -C	-14.2 -6.3 -11.0	89.1 - endothermic 198.9 - endothermic 309.5 - endothermic
Calculated:97.069%, Final =2.931%; Estimated 97.773%, Final =2.227%								
[Pd(L) (H <sub>2</sub> O) Cl]	72.829	326.996	188.45	22.083 (22.444)	80.51 (80.63)	-H <sub>2</sub> O, -Cl -CO <sub>2</sub> , -CO	-12.2 8.6	169.8- endothermic 318.8- endothermic
	326.996	489.227	401.81	26.218 (26.249)		-C <sub>7</sub> H <sub>5</sub> N <sub>2</sub> S		
	489.227	595.383	527.67	32.553 (31.951)		-C <sub>10</sub> H <sub>7</sub> N <sub>3</sub> O		
						PdO		
	Calculated :80.63% final =19.49%;Estimated 80.51% final =19.37%							
[Rh(L) (H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]	64.786	323.959	183.72	24.423 (25.259)	80.69 (81.00)	-2H <sub>2</sub> O, 2Cl- CO <sub>2</sub>	-13.4 -12.2 7.7	114.8- endothermic 169.8- endothermic 481.8- endothermic
	323.959	485.247	409.72	26.688 (27.212)		-C <sub>8</sub> H <sub>9</sub> N <sub>2</sub> S		
	485.247	592.323	529.43	29.599 (28.541)		-C <sub>10</sub> H <sub>6</sub> N <sub>3</sub> O		
						RhO		
	Calculated :81%, Final =38.49%;Estimated80.51 %, Final =19.49%							

**Table 5:** Antioxidant activity of Azo dye and its complexes

Compounds	Mean	Standard deviation	Coefficient of variation %	Correlation coefficient	IC <sub>50</sub> (M) DPPH
Gallic acid	93.5600	2.0846	2.2281	0.9966	-6.0304
HL	55.0525	2.0632	3.7477	0.9962	-0.2722
[Pd(L)(H <sub>2</sub> O) Cl]	44.2200	11.5169	26.0445	0.9891	0.6310
[Rh(L)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]	32.1200	4.7841	14.8947	0.8807	1.5950
[Pt(L)(H <sub>2</sub> O)Cl]	55.5481	4.1687	7.5048	0.9937	0.1764
[Ni(L)Cl (H <sub>2</sub> O)]	51.2000	11.9054	23.2529	0.9965	0.5680

Note: IC<sub>50</sub>: the half-maximal inhibitory concentration

## Conclusion

Diazotization reaction in acidic media was carried out successfully in preparing a totally new azo-

ligand 4-((8-hydroxyquinolin-7-yl)-N(4-methylisoxazol-3-yl) benzene sulfonamide by using Sulfamethoxazole and 8-hydroxyquinoline



which in turn reacts with each of the next metal salts ; Ni(II), Pt(IV), Pd(II), and Rh(III) in [1M:1L] molar ratio. The ligand and its complexes were identified by using ( $^1\text{H}$  and  $^{13}\text{C}$ )-NMR, FT-IR, Uv-Vis, TGA, DSC, and mass spectroscopic techniques, these techniques proved the suggested geometries of complexes, bidentate behavior of ligand, and its bind positions depending on the modifications occurred in absorption bands (in FT-IR spectra) of the complexes compared with those that found in free ligand in addition to the spectral information obtained from other employed techniques, as detailed in the manuscript. The estimated values and the elemental microanalysis results were found to be in a good agreement with the theoretically calculated values. According to multinuclear NMR data, complexation occurs via the -NO moiety.

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All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

### Conflict of Interest

There are no conflicts of interest in this study.

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