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Synthesis, Characterization, and Thermal Analysis of a New Acidicazo Ligand's Metal Complexes

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Abstract:

The researchers wanted to make a new azo imidazole as a follow-up to their previous work. The ligand 4-[(2-Amino-4-phenylazo)-methyl]-cyclohexane carboxylic acid as a derivative of trans-4-(aminomethyl) cyclohexane carboxylic acid diazonium salt, and synthesis a series of its chelate complexes with metalions, characterized these compounds using a variety technique, including elemental analysis, FTIR, LC-Mass, ^{1}H-NMRand UV-Vis spectral process as well TGA, conductivity and magnetic quantifications. Analytical data showed that the Co (II) complex out to 1:1 metal-ligand ratio with square planner and tetrahedral geometry, respectively while 1:2 metal-ligand ratio in the Cu(II), Cr(III), Mn(II), Zn(II), Ru(III)and Rh(III)complexes with octahedral geometry except Mn complex has tetrahedral geometry. The Ligand functions as a neutral tridentate ligand in all complex investigations, coordinating Cr(III), Zn(II), Ru(III), and Rh(III) ions via the N atom of amine and azo groups, as well as the O phenolic OH group. When coordinated with the Cu(II), Co(II), and Mn(II) ions via the two N atoms of the amine and azo groups, this Ligand functions as a neutral bidentate.

Keywords: Acidicazo ligand, Mass spectroscopy, Metal complexes, Spectroscopic studies, Thermal analysis.

Introduction:

Azo dyes are one of the most diverse, useful, and important classes of organic compounds and a great importance in a different fields of chemical analysis due to their containment more than one effective group able to form coordination complexes with a various metal ions , which are characterized by their colors , In general, azo dyes have great coloring qualities and produce vibrant hues ranging from yellows through oranges, reds, and blues, as well as high molar absorption and stability, making them suitable for a variety of applications in science and technology. They also play a significant role in food and analytical chemistry.[1-3]Azo dyes are utilized in a variety of applications, including textile dyeing, biomedical research, and advanced chemical synthesis. Antibacterial, antifungal, antibiotic, antiviral, and cytotoxic properties are among the many biological actions of these colors.[4-7]Azo-dyes are chemical compounds comprising one or more aromatic or heterocyclic moieties with at least one conjugated chromophoricazobond (-N=N-). As a result, they constitute the most important group of disperse dyes, as they are characterized by the presence of an azo moiety (N=N) in their structure. [4]They've found a wide range of uses, primarily in the dyestuffs sector, but also in cosmetics, and medicines industries.[3-5]As reagents for extracting and determining the trace amount of metal ions in various materials, azo dyes have gotten a lot of interest. Azo dye complexes have received a lot of attention because of their intriguing features and potential applications as catalysts, antimicrobials, colorants, corrosion inhibitors, and anticancer agents.[8]The aim of this work is to synthesize a novel azo ligand from an aliphatic amine with spectroscopic analysis of its composition as well as to synthesize Cu(II), Cr(III), Mn(II), Zn(II), Ru(III), and Rh(III)complexes with spectroscopic analysis and studying of thermal decomposition and thermal stability by using TGA and DSC.

Materials and Methods:

Experimental:

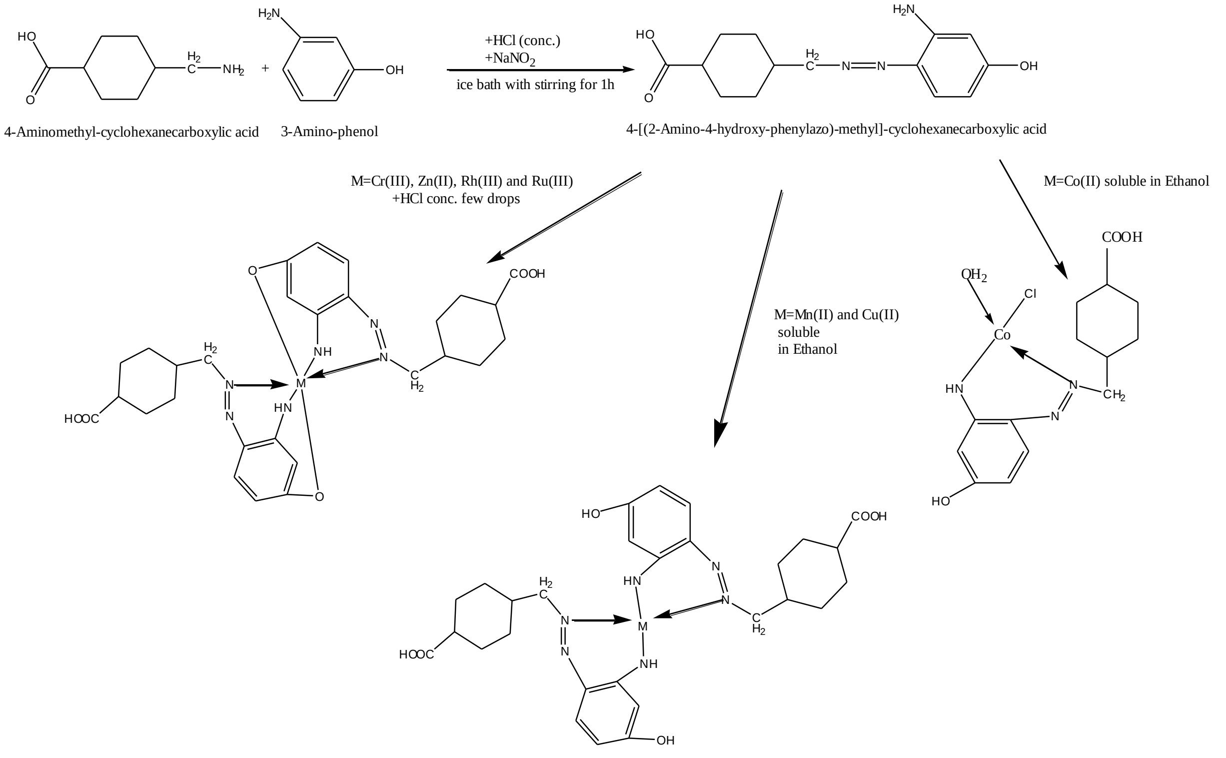
1. Materials and equipment: All chemicals and reagents were purchased commercially (Sigma-Aldrich, Merck, and others) and utilized without further purification. The Single-V Euro vector model EA/3000. 3.O-single, was used to conduct elemental analyses (C, H, and N Metal ions were estimated as metal oxides using a gravimetric method. The complexes' molar conductance was measured using a temperature of 25 °C and a concentration of 1103 M, the conductometer WTW was used. Dimethyl form amide was used to dissolve all of the complexes (DMF On a mass spectrometry (MS) QP50A: DI Analysis ShimadzuQP-2010-Plus (E170Ev) spectrometer, mass spectra for substances were recorded The UV–Vis spectrophotometer UV-1800 Shimadzu was used to study the spectra in the ultraviolet–visible (UV–Vis) range A Brucker300 MHz was used to record the proton nuclear magnetic resonance (^{1}H-NMR) spectrum for ligand in DMSO-d6. The IR Prestige-21 was used to study the Fourier transform infrared (FTIR) spectra, and the Perkin-Elmer Pyris Diamond TGA and DSC were used to conduct thermo gravimetric investigations.

2. Synthesis of azo dye ligand: 4-[(2-Amino-4-phenylazo)-methyl]-cyclohexane carboxylic acid

Tranexamic acid (0.1577 g,1mmole) melted in a mixture (5ml ethanol, 3ml HCl conc.), and diazotized at 5°C with 10% solution of $NaNO_2$. For 3-aminophenol, a diazotized solution was added with stirring to a cooled ethanolic solution at (0.109g, 1mmole). Then after mixing directly, a dusky colored mix andazo ligand precipitation was seen. This deposit was filtered, washed a number of ounces for a (1:1) (C_2H_5OH: H_2O) mixture, and then dried. Scheme 1 depicts the reaction.

3. General method for the preparation of metallic ions complexes

An ethanolic solution of the ligand (0.280 g , 1mmole) H_2L was added gradually with stirring to(0.357g, 1mmol) Co(II)chloride salt of [1:1] metal:ligand (M:L) ratio and Cu(II) (0.364g, Cr(III) 0.158g, Zn(II)0.136g, Mn(II) 0.198g, Rh(III) 0.314g, and Ru(III) 0.311, 2 mmol chloride salts respectively, of Cr(III), Cu(II), Zn(II), Mn(II), Rh(III), and Ru(III)chloride salts respectively with an ethanolic solution of the ligand (0 .140g , 1mmole) of [1:2] M:L ratio dissolved in 5 mL pure ethanol from azo ligand dissolved in 10 mL pure. The mixture was heated to 65°C for 2 hours, then cooled in an ice bath till precipitation occurred, before being left overnight. The reactions are depicted in Scheme 1. The solid complexes were separated and rinsed with distilled water and a small amount of heated ethanol to eliminate any unreacted components. Finally, vacuum desiccators were used to dry the complexes. The analytical and physical properties of the ligand and its metal complexes are summarized in Table 1.



Scheme1. Synthesis of ligand and its complexes

Results and Discussion:

1. Physical and chemical properties of azo dye ligand

This amorphous appearance, which takes the shape of a fine brown powder, distinguishes the azo dye ligand (HL). This synthesisligand is water and DMSO soluble, however it is only sparsely soluble in ethanol. In the presence of air, the metallic ion and azoligand complexes remained stable.

Table 1. Physical and analytical properties of ligand and itscomplexes

Comp.	ChemicalFormula M.Wtg.mol^{-1}	Color	m.p °C	Elemental microanalysis%				
				C Found C Calc	H Found H Calc.	N Found N Calc.	O Found O Calc.	M Found M Calc.
H_2L	$C_{14}H_{19}N_3O_3$	Brown	280-281	62.11	5.02	17.05	16.03	-
	277			60.6	6.85	15.16	17.3	-
$[Cu(HL)_2]$	$C_{28}H_{36}N_6CuO_6$	Dark green	299-301	55.43	4.90	15.19	17.11	-
	615.5			54.59	5.85	13.65	15.60	-
$[Co(HL)(H_2O)Cl]$	$C_{14}H_{20}ClN_3CoO_4$	Deep Brown	300-302	42.44	3.54	13.11	17.94	14.85
	388.4			43.27	5.15	10.85	16.54	15.18
$K[CrL_2]$	$KC_{28}H_{34}N_6CrO_6$	Brown	261 d	54.01	4.11	15.41	13.13	9.16
	641			52.41	5.34	13.10	14.89	8.11
$[Mn(HL)_2]$	$C_{28}H_{36}N_6MnO_6$	Brown	289 d	55.00	3.97	15.51	12.92	9.00
	606.9			52.17	5.32	13.04	14.89	-
$K_2[ZnL_2]$	$K_2C_{28}H_{34}N_6ZnO_6$	Brown	244 d	47.12	4.98	13.87	14.67	-
	693.4			48.46	4.90	12.11	13.84	-
$K[RhL_2]$	$KC_{28}H_{34}N_6RhO_6$	Deep Brown	271 d	46.75	5.77	14.51	10.99	-
	692			51.455	5.2	12.86	14.7	-
$K[RuL_2]$	$KC_{28}H_{34}N_6RuO_6$	Deep Brown	289 d	49.94	3.41	14.16	15.11	-
	690.68			51.559	5.217	12.889	14.731	-

d= decompose

2. ^{1}H-NMR spectra

The ligand^{1}H-NMR spectra revealed a peak at δ (1.38) ppm, which was attributed to chemical shifts of N=N–CH_2. The chemical shift of (CH_2-CH_2) protons on the Tranexamic acid was assigned to the peaks at δ (1.9) ppm. The multiple signals noted at δ (2.69) ppm for ligand, these were referred to CH_2-COO proton in cyclohexane ring. The NH_2 group which appear as singlet at 4. 61ppm.The different peaks at (6.82–7.56) ppm are attributed to the aromatic protons of benzene groups. The proton (OH) of the carboxyl group COOH is responsible for the singlet signal at (11.49) ppm. [9,10]

3. Electronic spectra measurements

Table 2 and of the ligand H_2 L andits complexes. The n⟶π* transition of the (N=N) azo group in the free ligand produced a peak with a high intensity band with absorption maxima at (302 nm, 33112.5 cm^{-1}) and two peaks at 330 and 426 ascribed to the n⟶π* transition of the (N=N) azo group in the free ligand. [11] These peaks were shifted in all metal complex spectra, indicating that the azo group was involved in coordination. ^{4}Spin transitions at 360, 465, and 651 nm were seen in the electronic spectrum of Cr(III) complex due to $^4A_2g \rightarrow {}^4T_1g$ (P) (ν_3), $^4A_2g \rightarrow {}^4T_1g$ (F) (ν_2), and $^4A_2g \rightarrow {}^4T_2g$ (F) (ν_1), respectively, indicating an octahedral geometry of the complex.The magnetic moment of the complex was weighed at room temperature to be 3.61 B.M., which is close to the spin alone value, implying an octahedral geometry around the chromium ion.[12] The spectrum of $[Mn(L)_2]$ complex exhibited bands at;21505, 25000 and 34722cm^{-1} attribute to $^6A_1 \rightarrow {}^4T_{1(G)}$ and$^6A_1 \rightarrow {}^4T_{2(G)}$transitions beside ligand field band, respectively.[13,14] The spectrum of Co(II) complex contained four bands at 324, 480, 614, and 677nm attributed to L.F, C–T ,$^4A_{2(F)} \rightarrow {}^4T_{1(P)}$ and $^4A_{2(F)} \rightarrow {}^4T_{2(F)}$ transitions, respectively assigned to tetrahedral Co(II) ion, which is indicative of a tetrahedral geometry.The metal ion is in a tetrahedral environment, as evidenced by this. Due to Jahn-Teller distortion, square planar Cu(II) complexes have a strong absorption band between 600 and 700 nm. The Cu(II) complex's spectrum exhibits a maximum at 635 nm, showing this. [13] Because d-d transitions are not feasible, electronic spectra did not provide any useful information, and the magnetic susceptibility of the Zn(II) complex showed that it contains diamagnetic moments. In fact, this conclusion is in good agreement with prior work on octahedral geometry.[15, 16] Bands at 25575 cm^{-1} and 31056 cm^{-1} in the electronic spectrum of the Rh(III) complex have been assigned to $^1A_1g \rightarrow {}^1T_1g$ and $^1A_1g \rightarrow {}^1T_2g$ transitions, respectively, whilst the band at 34843 cm^{-1} is a charge transfer transition, the octahedral geometry of the Rh(III) complex can be ascribed.[17] Ruthenium(III) complex (displayed three bands at 331, 400 and 480 nm. The second band is due to LMCT transition and the third is assigned to $^2T_2g \rightarrow {}^2A_2g$ [18] transition. UV–vis analysis also indicated the development of metal (II)/(III) azo-dye complexes. In DMSO solution, electronic spectra of the produced azo-dye ligand and its metal complexes in the wavelength range 200–1100 nm (1 × 10−3 M).[10,19].

Table 2. Electronic spectral data and molar conductivity of metal complexes with H_2L ligand in DMSO (1×10^{-3} M)

Complexes Geometry	λ_{max} (nm)	υ cm^{-1}	ABS	ε_{max} L $mol^{-1}cm^{-1}$	Assignment	Λ_m cm^2 $\Omega^{-1}mol^{-1}$
H_2L	302	33113	0.248	248	$\pi \rightarrow \pi^*$	-
	330	30303	0.235	235	$n \rightarrow \pi^*$	
	426	23474	0.204	204	$n \rightarrow \pi^*$	
$K[CrL_2]$ Octahedral	282	35461	0.056	56	$\pi \rightarrow \pi^*$	33
	465	21505	0.172	172	C.T.	
	651	15361	0.021	21	$^2A_1g \longrightarrow {}^2T_1g$	
$[Mn(HL)_2]$ Tetrahedral	288	34722	0.127	127	$\pi \rightarrow \pi^*$	21
	400	25000	0.192	192	$^6A_1 \rightarrow {}^4T_{2(G)}{}^6A_1 \rightarrow {}^4T_{1(G)}$	
	465	21505	0.197	197		
$[Co(HL)(H_2O)Cl]$	324	30581	1.17	1170	$\pi \rightarrow \pi^*$	20
	(340-520)	27624-22472	0.477	477	C.T.	
Tetrahedral	614	14925	0.26	260	$^4A_{2(F)} \rightarrow {}^4T_{1(P)}$	
	677	10204	0.011	11	$^4A_{2(F)} \rightarrow {}^4T_{2(F)}$	
$[Cu(HL)_2]$ Square planner	292	34247	2.377	2377	$\pi \rightarrow \pi^*$	23
	923	10834	0.055	55	$^2Eg \rightarrow {}^2T_{2g}$	
$K_2[ZnL_2]$ Octahedral	287	38911	0.117	117	$\pi \rightarrow \pi^*$	77
	399	25063	0.194	194	C.T.	
	490	20408	0.208	208		
$K[RuL_2]$ Octahedral	331	30211	0.102	102	$\pi \rightarrow \pi^*$	42
	400	25000	0.111	111	C.T.	
	481	20833	0.112	112	$^2T_{2g} \rightarrow {}^2A_{2g}$	
$K[RhL_2]$ Octahedral	250	40000	0.310	310	$\pi \rightarrow \pi^*$	44
	287	34843	0.280	280	$n \rightarrow \pi^*$	
	322	31056	0.229	229	$^1A_1g \longrightarrow {}^1T_1g$	
	391	25575	0.191	191	$^1A_1g \longrightarrow {}^1T_2g$	

4. Liquid chromatography–mass spectrometry (LC–MS) measurements

The electron impact of fragmentation was used to obtain the mass spectra of the novel ligand and metal complexes. High-resolution MS was used to examine the free azo ligand and its complexes, as well as massive fragments associated with breakdown products. Fig.1 depicts the ligand H_2L electron impact mass spectrum. This ligand molecular weight has been determined to be 277g/mol. A peak at 276 m/z was attributed to [M]+ and related to a novel azo moiety $C_{14}H_{19}N_3O_3$ in the spectra. Different fragments could be responsible for the peaks at 137, 84, and 55 m/z. Their intensity shows the pieces' stability.[20] Fig.2 depicts the mass spectrum of the Cr(III) complex. A peak at 618 m/z was found in the spectra, which corresponded to the complexmoiety $[C_{28}H_{34}N_6O_6Cr]^-$. Other distinctive peaks at 276, 173 and 156 m/z could be attributed to different components. Fig.3 depicts the mass spectrum of the Mn(II) complex. The compound moiety $C_{28}H_{36}N_6MnO_6$ was identified by a peak at 605 m/z in the spectra. Other distinctive peaks at 260, 195, and 156 m/z could be attributed to different fragments. Fig.4 depicts the mass spectrum of the Rh(III) complex. The complexmoiety $[C_{28}H_{34}N_6RhO_6]^-$ had a peak at 653 m/z, which corresponded to this moiety. Other fragments could be responsible for the unusual peaks at 224, 154, 148, and 127 m/z. Schemes 2–5 discuss suggested fragmentation paths and fragment structural assignments.[10]

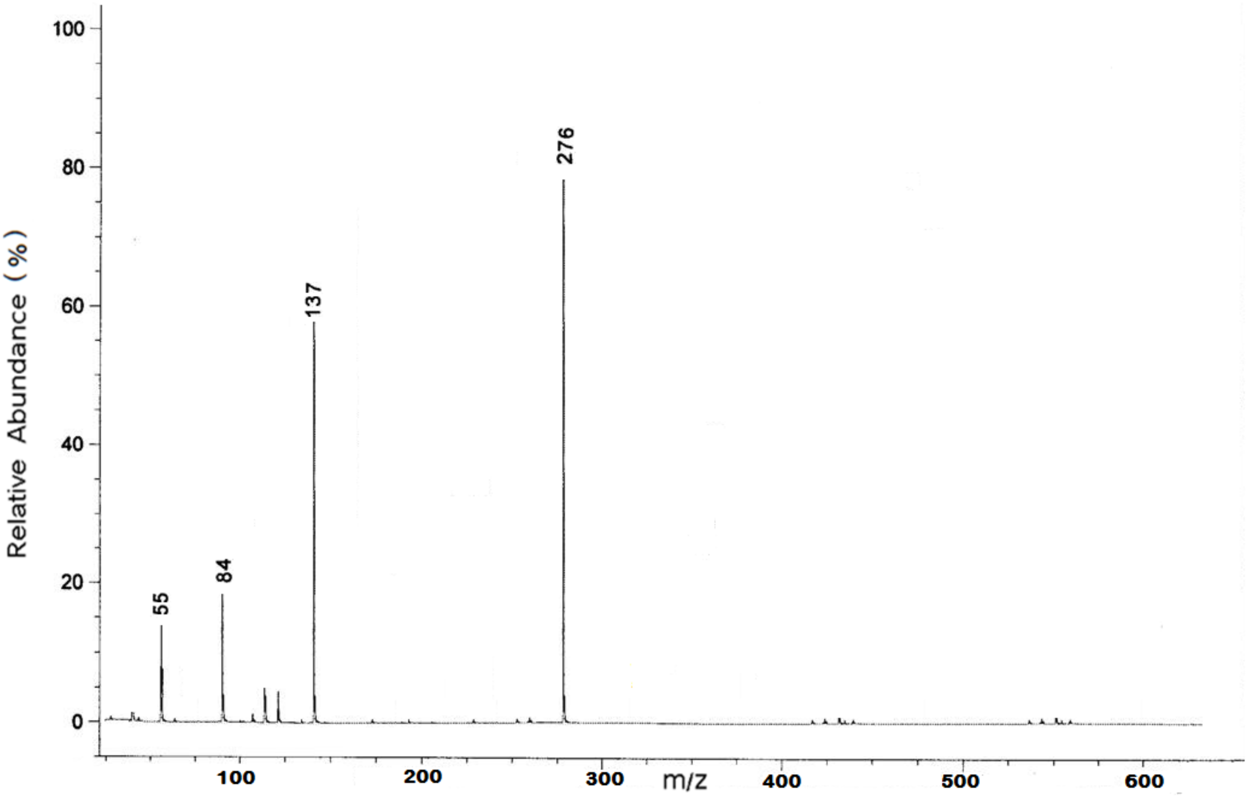


Figure 1. (LC–MS) spectrum of ligand

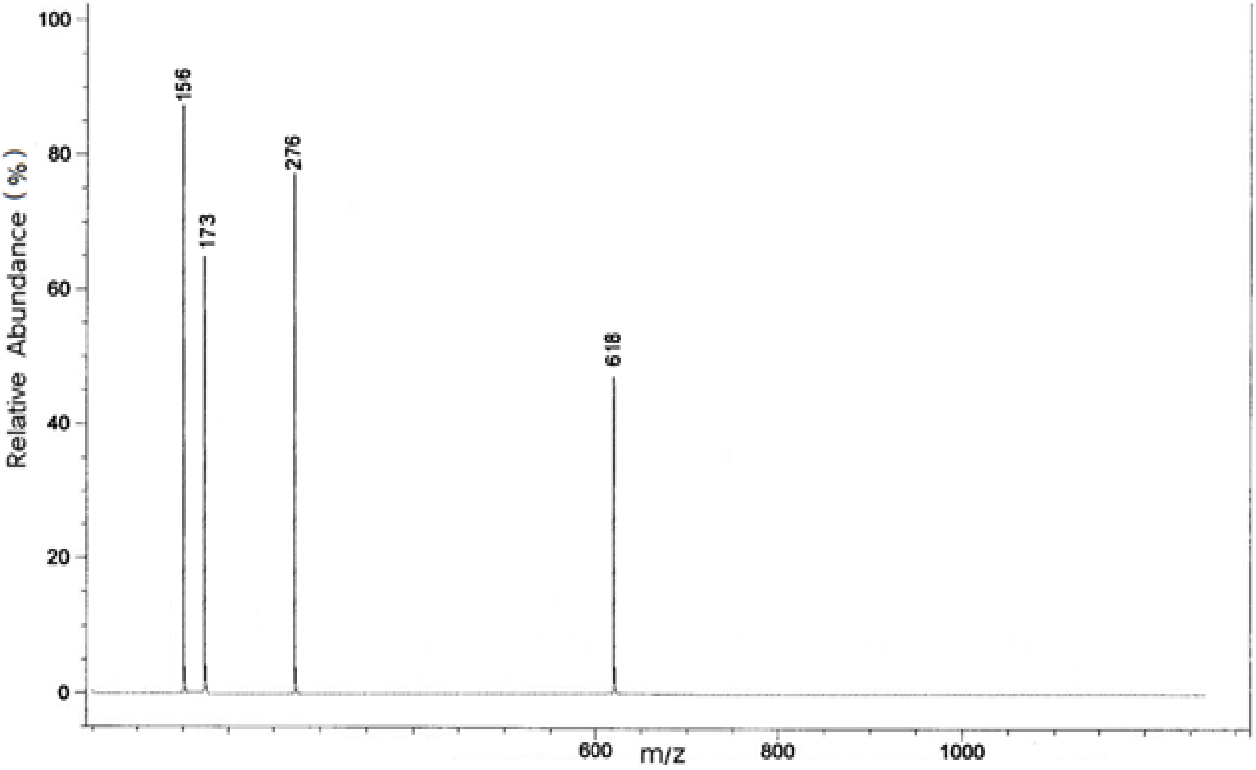


Figure 2. (LC–MS) spectrum of Cr-complex

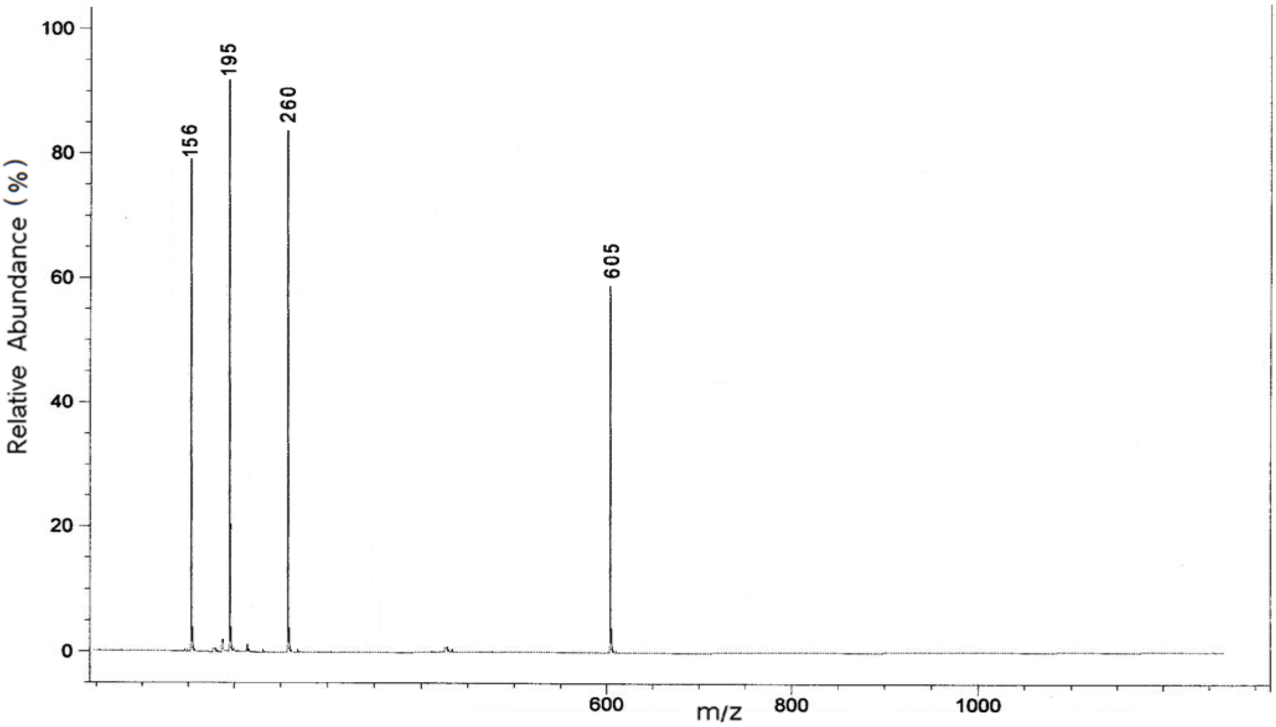


Figure 3. (LC–MS) spectrum of Mn-complex

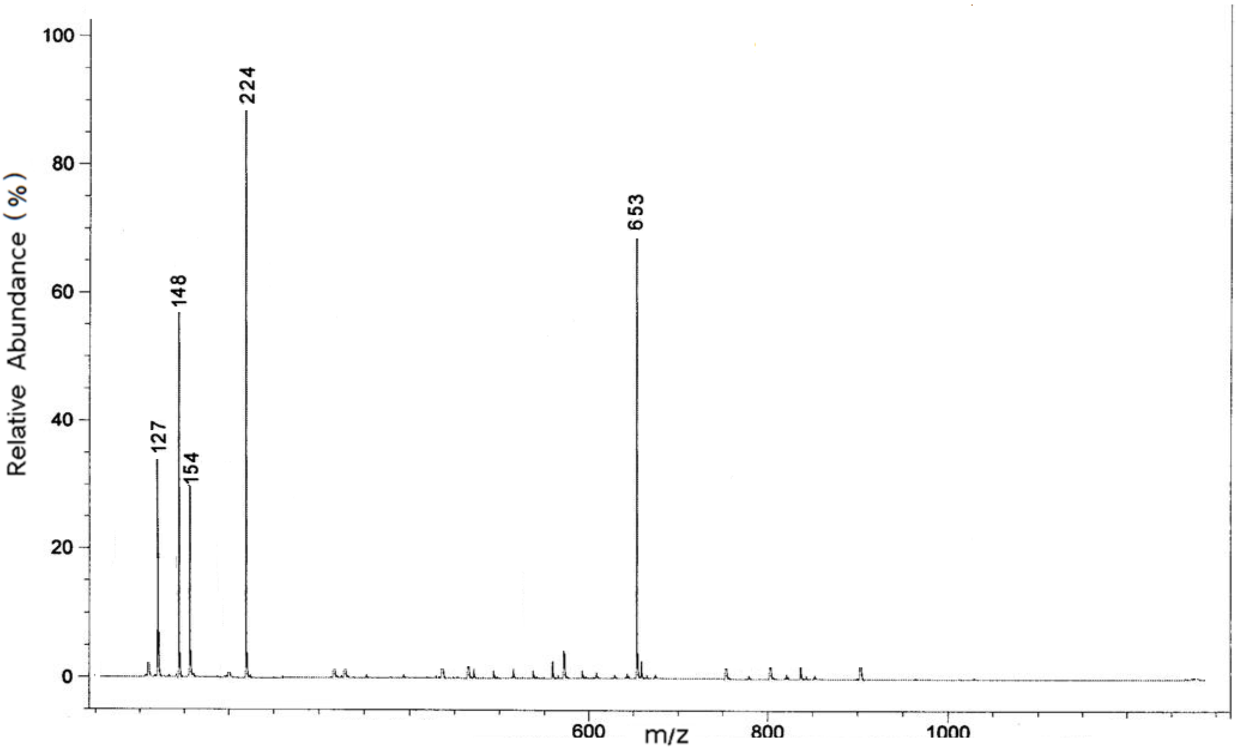
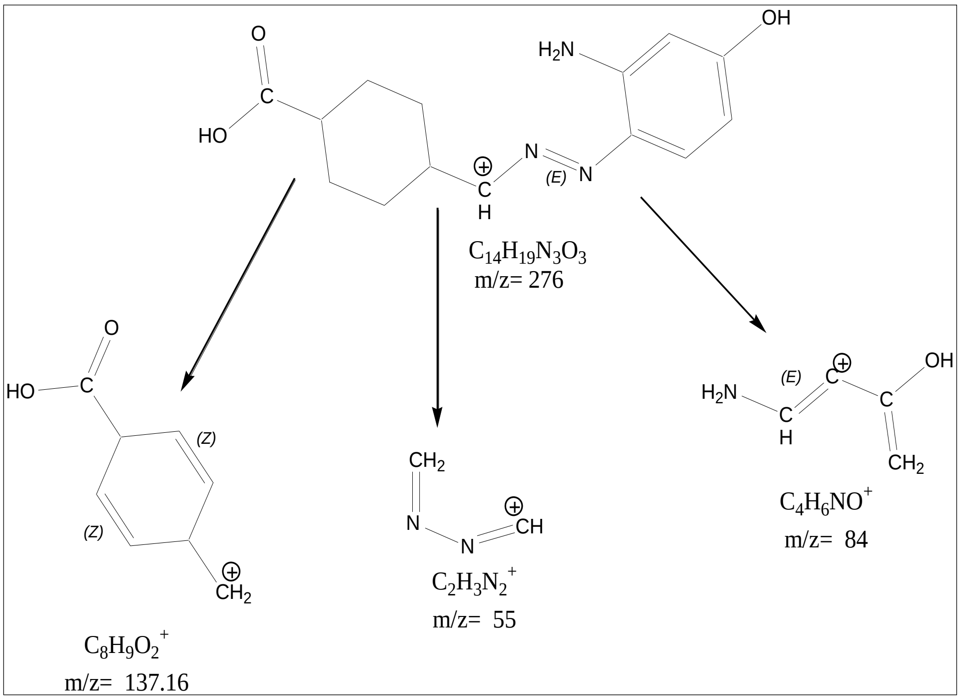
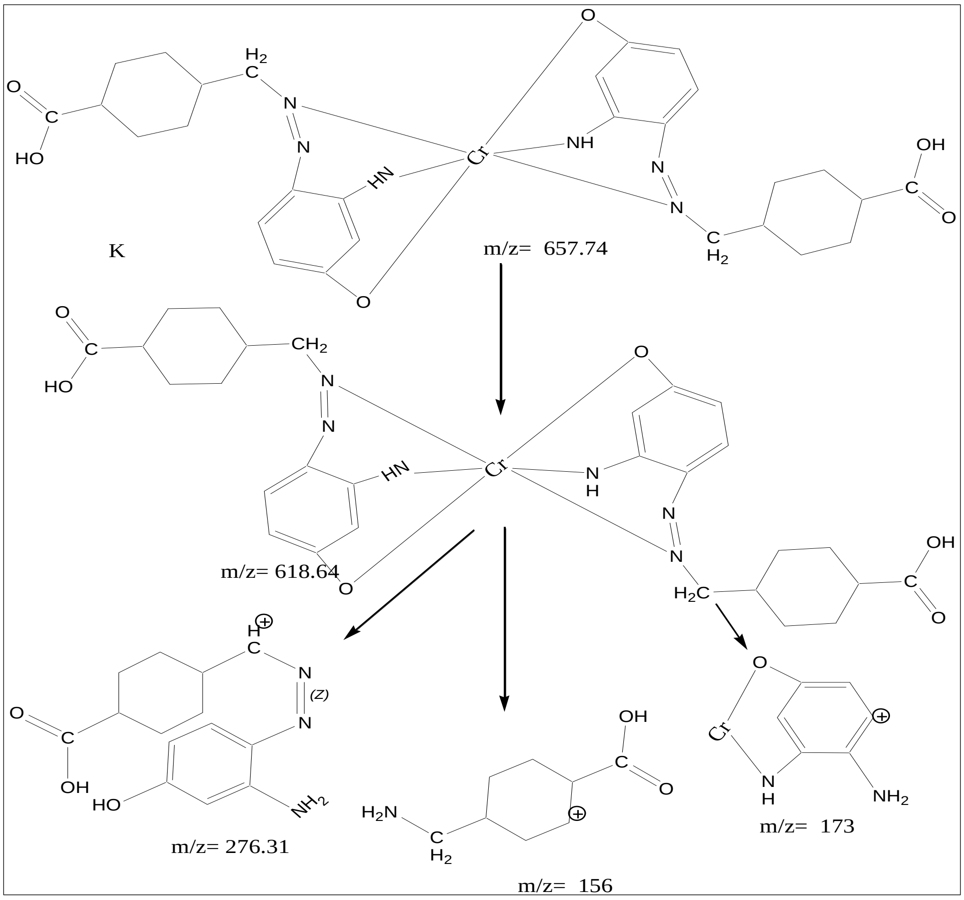


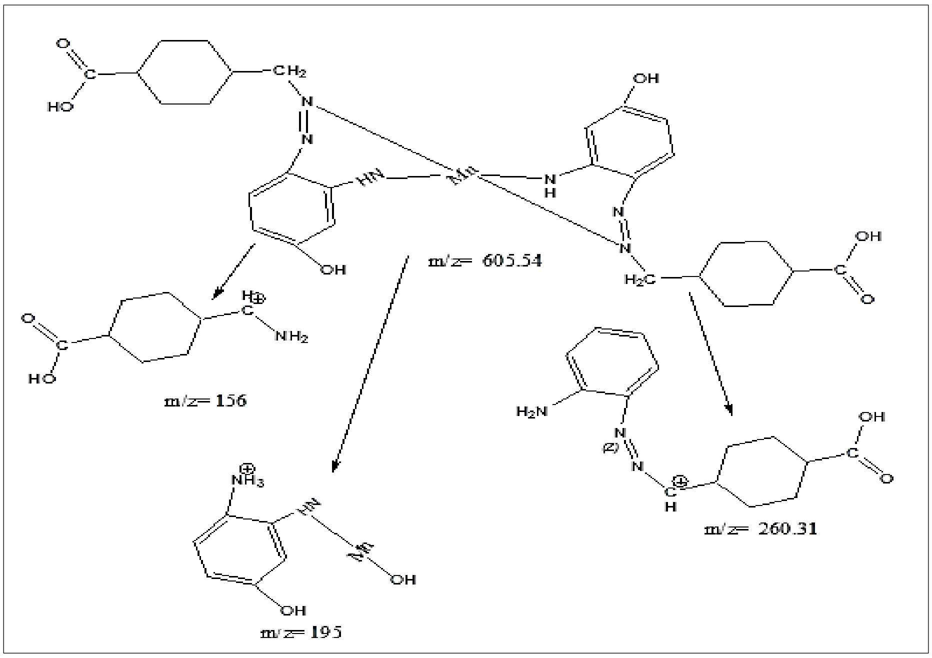
Figure 4. (LC–MS) spectrum of Rh-complex



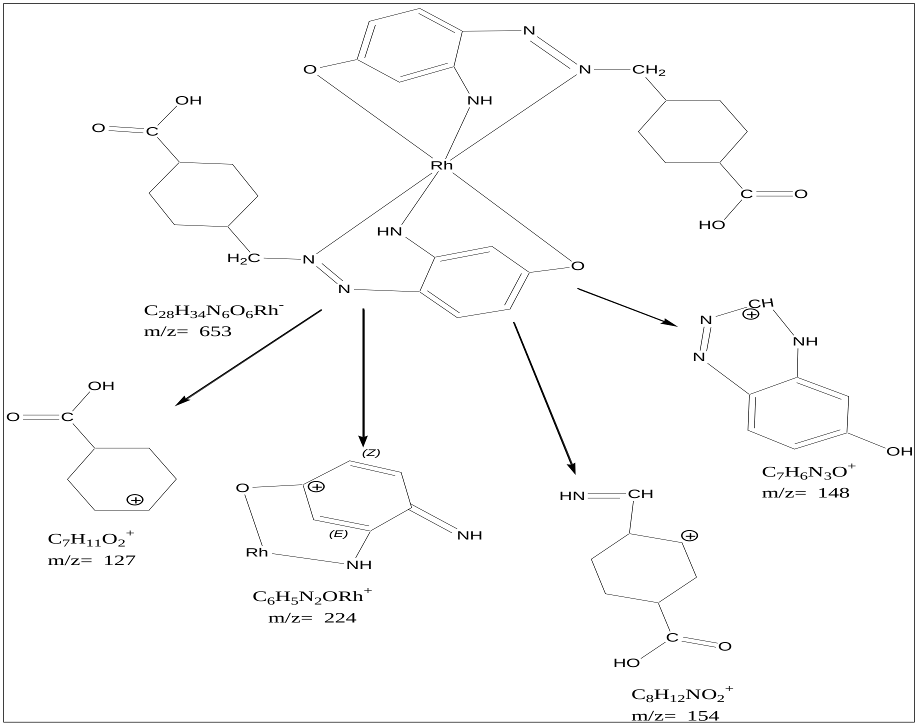
Scheme 2 Fragmentation pattern of ligand



Scheme 3 Fragmentation pattern of Cr-complex



Scheme 4. Fragmentation pattern of Mn-complex



Scheme 5: Fragmentation pattern of Rh-complex

5. Infrared spectra measurements

FTIR data was used to determine the functional groups in molecules (especially organics), and it can provide indications for the creation of complexes in some cases, where coordination occurs through the changing of functional group frequencies (that have the donating atom The spectra of azo ligand and their metal chelates complexes with Cr(III), Co(II), Mn(II), Zn(II), Ru(III), and Rh(III) were gathered and organized in Table 3.Spectrum of the ligand exhibited bands at 3429 and 3275 cm^{-1} which were assigned to stretching vibration of υ(NH_2), at the spectra of allproduced compounds these bands have been removed to lower frequency implying the coordination with metal ion.[10,20] The (N=N)stretching vibration was given to the band found at 1454 cm^{-1} [21-23] in the unbound azo ligand (H_2L). This band was discovered in the compounds' spectra around 1454-1456 cm^{-1}. The azo group of the azo ligand shifting confirmed that the azo group was involved in chelation. [22-24]In addition, earlier study has shown that in the presence of transition metals, the azo-dye nitrogen is always more likely to favor complexation. [25,26] It was difficult to confirm that the Co(II)complex was engaged in chelate formation due to the presence of coordinated water molecules. The existence of OH bands in the IR spectra of Co(II) complex in the 3423 cm1 region was attributed to the presence of coordinated water molecules in the coordination sphere. Stretching vibrations in the range (869, 696 cm^{-1}) were also discovered to match to υ(M-OH_2). This is a strong evidence that water molecules are involved in the coordination for the unbound ligand, the IR spectra revealed a large stretching vibration band at 3462 cm^{-1}, which could correlate to the phenolic group's OH.[27]. This band suffers little displacement because of the coordinate with the Cr(III), Zn(II), Ru(III) and Rh(III) complexes and the band appearing at 1284 cm^{-1} was attributed tothe ν(C-O) stretching vibration of the phenolic group ofthe free azo-dye ligand. This band was shifted in Cr(III), Zn(II), Ru(III) and Rh(III) complexes, indicating coordination through the deprotonated phenolic OH group[28]. When comparing the spectra of all complexes to the freeligand, new bands showed solely in the produced complexes, indicating that they had been synthesized successfully. The Co(II) complex has three bands: ν(M–N), (M–O), and (M–Cl), whereas the Cr(III), Zn(II), Ru(III), and Rh(III) complexes have two bands each: (M–N) and (M–O). [23, 29, 30] Finally, the azo-dye ligand connected to the metal ions through three sites: the nitrogen site of the azo group, the main amine, and the oxygen site by deprotonation of the amine and phenolic groups, as determined by the IR spectra of all produced compounds.[23, 30, 31]Therefore, the ligand behaved as a N,N,O tridentate ligand in the Cr(III), Zn(II), Ru(III) and Rh(III) complexes and N,N bidentate ligand in the Cu(II), Co(II) and Mn(II) complexes.The spectrum of the ligand shows sharp absorption band at 1639 cm^{-1} due to ν(C=O) of carboxylic group. In the produced complexes spectra, it is noticed with a slight modification in form and moved to higher frequencies 1676-1670 cm^{-1}.[32,33] These variances point to hydrogen bonding between the carboxylic group's C=O and the orthogonal OH group. The azo group was shifted toward lower frequencies in their complexes spectra, and the primary amine group appeared within the (3436-3325) cm^{-1} region, as well as the disappearance of the resorcinol hydroxyl group. These findings can be explained by the participation of NH_2&azo- nitrogen in coordination with metallic ions, as seen in complexes spectra.[34-36]

Table 3. The free ligand and its complexes IR spectrum bands (cm^{-1})

Compounds	υOH phenolic	υOH carboxylic	υ(NH_2)	υ(NH)	υCO carboxylic	υ(N=N)	υ(H_2O) Coord.	υ M-N	υ M-O	υ M-Cl
H_2L	3462	3252	3429 3275	-	1639	1454	-	-	-	-
$[Cu(HL)_2]$	3461	3120	-	3419	1627	1415	-	(590,536)	-	-
$[Co(HL)(H_2O)Cl]$	3461	3200	-	3404	1616	1498	3423 869 696	(568,518	(480)	(376)
$[Mn(HL)_2]$	3643	3218	-	3377	1625	1461	-	(570,491)	-	-
$K[CrL_2]$	3396	3240	-	3325	1314	1456	-	(511,440)	(426)	-
$K_2[ZnL_2]$	3452	3259	-	3423	1625	1438	-	(524,480)	(424)	-
$K[RhL_2]$	3473	3242	-	3436	1618	1450	-	(522,472)	(420)	-
$K[RuL_2]$	3448	3255	-	3411	1614	1452	-	(514,453)	(443)	-

6. Thermal measurements

The TG and DSC results of heat breakdown of the ligand and related metal complexes are shown in Figs (5 and 6), Table 4 contains information on the thermal degradation process. The prepared compounds showed a decomposition in the thermogravimetric decomposition curve, where the ligand thermal stability was poor at 50°C, similar to the low stability complexes in the range of (40, 38, 65, 65, and 200 °C) for Co(II), Cr(III), Mn(II), Rh(III), and Ru(III), respectively, indicating the presence of water molecules only in the Co(II) complex, whether water hydrate or aqua,[37,38] Table 4 shows the findings of the study.Co(II), Cr(III), and Ru(III) decompose in two stages with an unbroken residue, while the ligand decomposes in three stages with an unbroken residue. [39,40] The Mn(II) and Rh(III) complexes disintegrate in one stage with an unbroken residue. This is in line with the calculated values and the formula recommended. [41-43]

Table 4. Thermal decomposition of Ligand and its complexes

Compound	Thermogravimetric range °C	DSC max °C	% Estimated (calculated) Mass loss	Total mass loss	Assignment
H_2L	50-170	83.3(Endo)	7.3(6.5)	92.53	$-H_2O$
	170-241	262.2(Exo)	7.33(5.8)	(93.52)	$-NH_2$
	241-389	299.5(Exo)	43.6(45.8)		$-C_7H_{11}O_2$
	389-600	390(Endo)	9.5(9.7)		-CHN
		500(Exo)	32.13 (32.22)		
$[Co(HL)(H_2O)Cl]$	40-330	104.5(Endo)	62.89(64.18)	88.43	$-H_2O+ CO_2+C_{12}H_{15}N_2$
	330-595	254.5(Endo)	25.54(26.28)	(90.46)	$-CH_3NCl+0.5CoO$
		284.9(Endo)	11.57(9.66)		-0.5CoO
		430(Exo)			
$K[CrL_2]$	38-310	115(Endo)	27.77(28.55)	95.42	$-H_2O+CO_2+KC_6H_{10}$
	310-595	246.9(Endo)	67.64(66.14)	(94.69)	$-C_{21}H_{22}N_6O_2+0.5CrO$
		346.7(Endo)	4.58(5.30)		-0.5CrO
		530(Exo)			
$[Mn(HL)_2]$	65-595	198.9(Endo)	79.47(78.68)	79.47	$-H_2O+CO_2+C_{26}H_{30}N_4O$
		309.5(Endo)	20.53(21.33)	(78.68)	$-CH_2N_2O+MnO$
		470(Exo)			
$K[RhL_2]$	65-595	-	37.74(38.87)	86.64(85.11)	$-H_2O+CO_2+KC_{11}H_{20}O$
			48.898(46.24)		$-C_{16}H_{12}N_6O_2$
			13.37(14.88)		-Rh
$K[RuL_2]$	200-325		26.38(26.5)	100.88	$-H_2O+CO_2+KC_6H_{10}$
	325-595	-	74.498(73.42)	(99.92)	$-C_{21}H_{22}N_6O_3Ru$

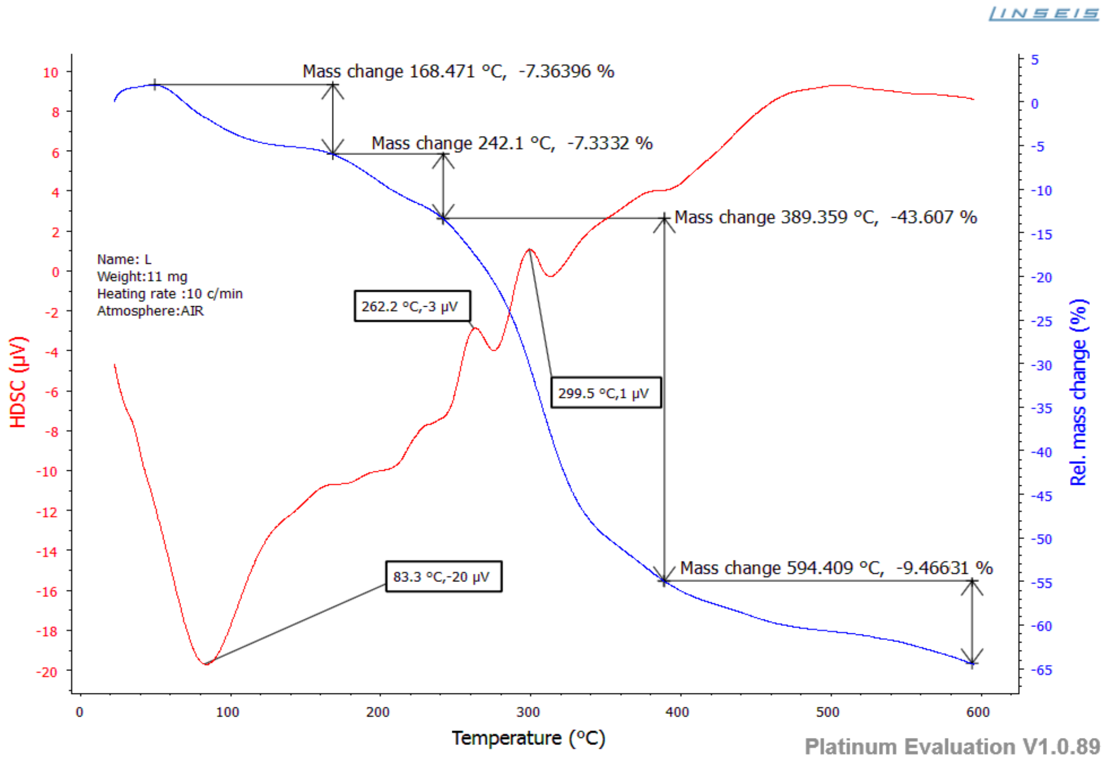


Figure 5. Thermo gravimetric of Ligand

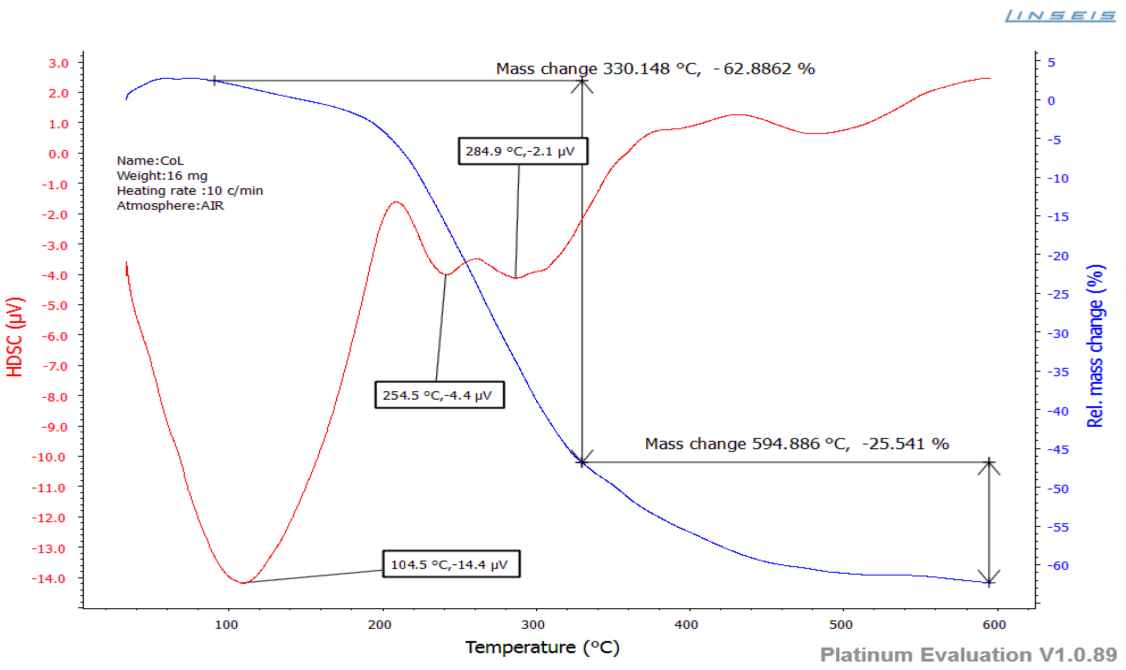


Figure 6. Thermo gravimetric of Co complex

Conclusion:

Many researchers have been interested in preparing these types of compounds and studying their properties and effectiveness, especially the difference between the aromatic rings attached to the nitrogen atoms of azo group ,that may be acidic group or basic or both ,and the distribution of the compensated groups at different sites in the aromatic ring relative to the group of azo, for example, hydroxyl group if attached at the ortho site that make up more importance due to share coordinated with metal ions to form Five chelating-ring called This type ofcompounds are ortho-hydroxyl azo. In this study we are synthesis of new azo ligand, this type of reagent was selected to contain multiple consistency sites and seven new chelates complexes with some metallic ions, and to characterization the ligand and Its complexes by using different techniques**.** All of the synthesized azo compounds were validated by fourier transform infrared (FT-IR), ^{1}H-NMR spectrum characterisation, and C.H.N. elemental analysis in this research, which concentrated on the creation of new azo.

Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscri Fig.5 depicts the mass spectrum of the Rh(III) complex. The complexmoiety $[C_{28}H_{34}N_6RuO_6]^-$ had a peak at 652 m/z, which corresponded to this moiety. Other fragments could be responsible for the unusual peaks at 222, 154, 148, and 127 m/z. .
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

Authors' contributions statement:

The authors R. K. H. A. and A. A. S. A. conceived, planned and carried out the experiments and the simulations. The authors contributed to sample preparation and contributed to the interpretation of the results and took the lead in writing the manuscript. The authors provided critical feedback and helped shape the research, analysis and manuscript.

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تحضير، تشخيص وتحليل حراري لبعض معقدات العناصر مع ليكاند آزو حامضية جديدة

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الخلاصة:

حضرت معقدات جديدة للكروم الثلاثي والنحاس الثنائي والكوبلت الثنائي والمنغنيز الثنائي والخارصين الثنائي والروثينيوم الثنائي والروديوم الثلاثي باستخدام ليكاندالآزو الجديد 4 -((2-امينو-4-فنيل ازو)-مثيل)-سايكلوهكسان حامض كاربوكسيلي تم تشخيص المركبات المحضرة باطياف (الاشعة تحت الحمراء الاشعة فوق البنفسجية – المرئية والكتلة والرنين النووي المغناطيسي البروتوني) اضافة الى التحليل الدقيق للعناصر ومنحنى التحلل الحراري الوزني مع قياس التوصيلية المولارية وتحديد نسبة الفلز ، اعطت نتائج التحليل ان الليكاند يسلك ثنائي السن مع الكوبلت والنحاس والمنغنيز بينما ثلاثي السن مع بقية العناصر المذكورة سابقا وقد اعطى الكوبلت والمنغنيز معقد رباعي السطوح بينما معقد النحاس مربع مستوي ومعقدات الكروم والروثينيوم والروديوم والخارصين ثماني السطوح وبينت دراسة التحلل الحراري استقرارية المركبات حراريا ووجود جزيئات ماء داخل مجال التناسق. يسلك الليكاند سلوك ثلاثية السن متعادل الشحنة في تناسقه مع ايونات الكروم الثلاثي والخارصين الثنائي والروثيميوم الثلاثي والروديوم الثلاثي من خلال ذرة النيتروجين لمجموعتي الامينية والازو وكذلك الاوكسجين لمجموعة الفينولية. بينما تناسق الليكاند مع النحاس الثنائي والكوبلت الثنائي والمنغنيز الثنائي يكون عن طريق النيتروجين لمجموعتي الامين والازو وبالتالي يسلك الليكاند ثنائية السن متعادل الشحنة.

الكلمات المفتاحية: المعقدات الفلزية، التحليل الوزني الحراري، دراسات طيفية، ليكاند الازو الحامضية، مطيافية الكتلة.