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Synthesis, Characterization, Thermal Studies, and Antioxidant Activities of Azo Dye[2-[(3-Hydroxyphenyl)diazinyl]-1,2-Benzothiazol-3(2H)-one-1,1-Dioxide]and Metal Ion Complexes

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Abstract

The new azo dye was synthesized *via* the reaction of the diazonium salt form of 3-aminophenol with 2-hydroxyquinoline. This dye was then used to access a series of complexes with the chlorides of manganese, iron, zinc, cadmium, and vanadium sulfate. The prepared ligand and its complexes were characterized by FT-IR spectroscopy, UV-visible spectroscopy, mass spectrometry, thermogravimetric analysis, differential scanning calorimeter, and microelemental analysis. Conductivity, magnetic susceptibility, metal content, and chlorine content of the complexes were also measured. The ligand and cadmium complex were identified using^{1}H NMR and ^{13}C NMR spectroscopy. The results showed that the shape of the ligand is a trigonal planner, and the complex shapes are tetrahedral, except for vanadium, which isa square-based pyramid. Additionally, the findings demonstrated that the complexes include water inside the coordination field and that each and every one of them is a non-electrolyte. The dye used the complexes prepared from it to determine their ability to inhibit free radicals by measuring their ability as antioxidants using DPPH as a free radical.D-ascorbic acid was employed as a standard substance in determining the value of IC_{50}, as it was found that the ligand had a high ability to inhibit free radicals. The ability to inhibit the complexes varied according to the value of IC_{50}, and the results are as follows: H_2L > D-ascorbic acid >Zn-complex >Fe-complex > V-complex >Cd-complex > Mn-complex.

Keywords:3-Aminophenol, Antioxidant,Azodye complexes, 2-Hydroxyquinoline ,Thermodynamic parameter.

تحضير، تشخيص، دراسة التحلل الحراري وانشطة مضادات الاكسدة لصبغة ازو (2-(3-هايدروكسي فنيل) دايازنيل)-1، 2-بنزوثايزول-3-اون 1، 1-ثنائي اوكسايد) مع معقدات ايونات الفلزات

فاطمة الزهراء شاكر حاتم و عباس علي صالح الحمداني
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الخلاصة

حضرت صبغة الازو الجديدة من تفاعل ملح الديازونيوم من 3-امينو فينول مع 2-هايدروكسي كوينولين استخدمة الصبغة لتحضير سلسلة من المعقدات مع كلوريدات كل من المنغنيز والحديد والخارصين والكادميوم وكبريتات الفناديوم، شخص الليكاند والمعقدات المحضرة بطيف الاشعة تحت الحمراء وطيف الاشعة فوق البنفسجة-المرئية وطيف الكتلة والتحاليل الحرارية الوزنية والمسعر التفاضلي والتحليل الدقيق للعناصر. وقياس

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التوصيلية والحساسية المغناطيسية ومحتوى الفلز ومحتوى الكلور للمعقدات. تم التحقق من الليكاند ومعقد الكادميوم بطيف الرنين النووي المغناطيسي للبروتون والكاربون. أظهرت النتائج ان الليكاند ثلاثي السن والمعقدات رباعية السطوح عدا الفناديوم كان هرم مربع القاعدة. فضلاً عن احتواء المعقدات على الماء داخل مجال التناسق وان جميعها غير الكتروليتية. استخدم الصبغة المعقدات المحضرة منها لتحدد قابليتها على كبح الجذور الحرة من خلال قياس قابليتها كمضادات اكسدة باستخدام مادة DPPH كجذر حر وحامض الاسكوربك كمادة قياسية وتحديد قيمة IC_{50} حيث وجد ان الليكاند يمتلك قابلية عالية على كبح الجذور الحرة والمعقدات تفاوتت قابليتها على الكبح حسب قيمة IC_{50} وكانت النتائج كما يلي:

(H_2L >Ascorbic acid >Zn−complex >Fe−complex > V−complex >Cd−complex > Mn−complex)

الكلمات المفتاحية:مضاداتالاكسدة, 3-امينو فينول , معقدات اصباغ الازو, الثوابت الثرموديناميكية و2-هيدروكسيكوينولين.

1.Introduction

Azo dyes are among the most widely used, useful, and important types of chemical compounds, with diverse applications in science and technology[1-2]. The presence of an azo moiety (-N=N-) coupled with two monocyclic or polycyclic moieties identifies azo compounds[3]. Aromatic or heterogeneous systems are either unique or homologous[4]. Because of their distinctive physical and chemical characteristics and biological activities, they have a broad variety of uses in the pharmaceutical, cosmetic, food, dyeing, and textile industries [5]. However, their coloring job remains their most popular and favorite tool. The medicinal significance of azo compounds is widely recognized for their antibacterial, antifungal, and anti-HIV properties [6]. The majority of azo dyes are used to color textiles, and it is estimated that 10% of the dyes used in these dyeing procedures are not. They stick to the fibers and end up in wastewater treatment[7]. Some azo dyes are carcinogenic,andthis is due to degradation products such as benzidine,which activate various tumors in humans and animals. Aromatic amines found in many azo dyes affect human health, cause allergic reactions, and cause other diseases.Different metal quinoline complexes have been shown to be more effective than the parent quinoline because of their interesting bioactivity.Many studies have been performed on heterocyclic azo dyes and their metal chelators. Dyed azo metal chelates are of interest for use in molecular memory storage, nonlinear visualizations, and printing systems[8-10].This research aims to prepare novel complexes of the metal ions (Cd^{+2}, Zn^{+2},Fe^{+3},Mn^{+2}, and V^{+4}) using the azo ligand H_2L. Thereafter, characterizationby spectroscopic analysis, thermal stability, and thermal decomposition will be studied using DSC and TGA curves, and the antioxidant activity of these compounds will be assessed against the DPPH radical and compared with D-ascorbic acidas a reference.

2.Experimental

2.1.Material and Methods

All the materials used in this work were provided by SigmaAldrich, Merck, and other companies.The Urovector model EA/3000 singleV3O analyzer was used to record elemental microanalyses for carbon, hydrogen, nitrogen, and sulfur (C.H.N.S.).Through a gravimetric approach, mineralions were identified as M-O. Using DMSO as a solvent, a conductometer W-T-W estimated molar conductivities (1×10^{-3} M) at 25 °C. Mass spectrometry data were recorded using a Q-P-50-A-D-I Analysis Shimadzu QP(E170Ev)-2010-Pluss spectrometer. The UV-1800 Shimadzu Spectrophotometer was used to record the UV-visible absorption.The^{1}H and ^{13}CNMR spectra were measured using aBruker (400MHz) spectrometer. The Fourier Transform Infrared (FT-IR) spectra were recorded using an IR Prestige-21, and the instruments employed were the Braker 4000-500 cm^{-1} and the Shimadzu 4000-200 cm^{-1}.Metals were identified using a Shimadzu (F.A.A.) 680 G atomic clock. Magnetic properties were used with the balancing susceptibility model MSR-MKI. All earlier types of thermal analysis employed Perkin-Elmer Pyris Diamond DSC/TGA.

2.2.Synthesis of azo dye ligand: [2-[(3-hydroxyphenyl)diazenyl]-1,2-benzothiazol-3(2H)-one 1,1-dioxide]

To a solution of 3-aminophenol(1g,0.008mmol) inHCl (2 mL, xx N),ethanol (15mL), and distilled water (10 mL)at 0 to 5 °C,a solution of $NaNO_2$(1 g, 14.49mmol) in H_2O (10 mL)was added gradually. The reaction mixture was stirred for 45 minutes before adding a solution of 2-hydroxyquinoline (1.16 g, 0.008 mmol) in ethanol (15 mL). A change to a dark-colored solution was observed after 30 minutes of stirring. The solid crude material formed wasfiltrated and dried to give a brown precipitate with an 87% yield that melts at 253-255 °C.

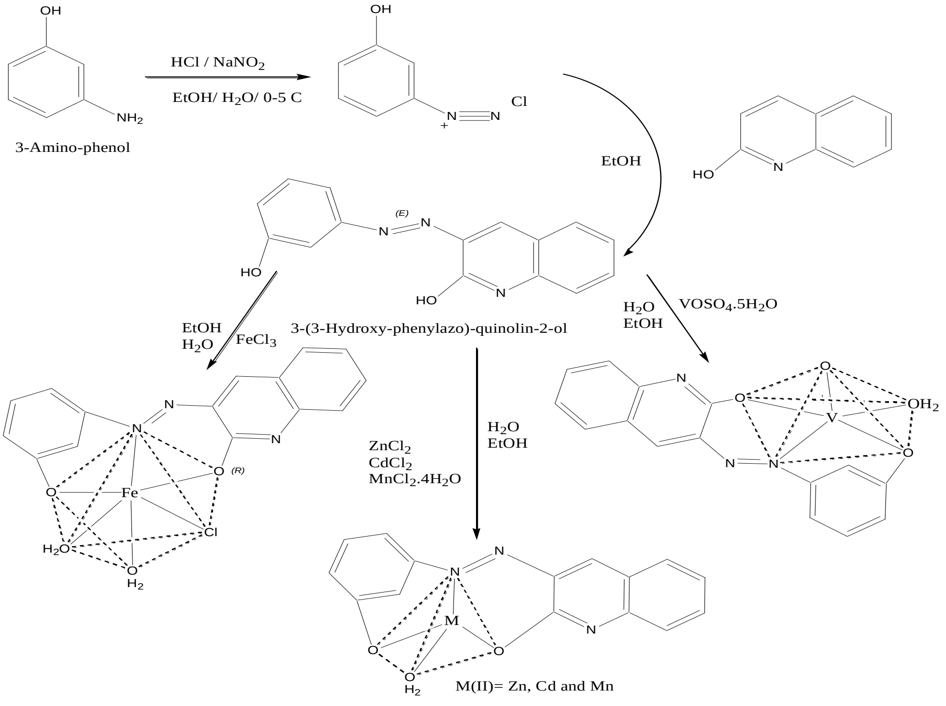
2.3.General approach for metal complexes synthesis

A solution of metal salt [$VOSO_4.5H_2O$ (0.1 g, 1 mmol), $FeCl_3$ (0.058g, 1 mmol), $MnCl_2.4H_2O$ (0.08g,1 mmol), $ZnCl_2$(0.05g, 1 mmol), or $CdCl_2$(0.07g, 1 mmol)] in water (10 mL). Azo ligand H_2L (0.1g, 1mmol) was added drop by drop to the solution before heating at 40 °C for 2 hours. By briefly submerging the solid complexes in hot ethanol, any unreached components were separated from them and eliminated. The complexes were gathered, dried, and weighed.

3. Results and discussion

3.1.Physical and analytical data for the ligand(H_2L) and the complexes synthesized

The reaction of metal salts and ligandafforded the desired complexes as shown in Scheme 1. The findings of the elemental analysis show that all compounds have a 1:1 ratio of M:L.The results of the microelemental analysis were consistent with the theoretical calculations, as shown in Table 1.



Scheme1- Formation for ligand (H_2L) and their metal complexes

Table 1: Some elemental physical characteristics investigations of ligand and complexes

Compound no.	Formula Molecular weight	m.p.(°C)	Ratio	C (%)	H (%)	N (%)	M (%)	Cl (%)	Conductivity In DMSO cm^2 Ω^{-1}mol^{-1}
1	$C_{15}H_{11}N_3O_2$ 265.27	253-255	found	67.92	4.18	15.84		-	
			Calculated	67.09	3.72	16.81			
2	$C_{15}H_{11}N_3O_4V$ 348.21	289-291	found	51.74	3.18	12.07	14.63	-	12
			Calculated	50.62	3.83	12.28	14.88		
3	$C_{15}H_{11}N_3O_3Mn$ 336.20	276-278	found	53.59	3.35	12.50	16.34	-	16
			Calculated	52.69	3.09	13.16	13.02		
4	$C_{15}H_{13}N_3O_4ClFe$ 390.58	292-294	found	46.13	3.35	10.76	14.30	9.08	19
			Calculated	46.89	3.97	11.89	13.54	9.57	
5	$C_{15}H_{11}N_3O_3Zn$ 346.66	277-280	found	51.97	3.20	12.12	18.86	-	11
			Calculated	50.99	4.11	13.10	18.55		
6	$C_{15}H_{11}N_3O_3Cd$ 393.68	296-299	found	45.76	2.82	10.67	28.55	-	10
			Calculated	44.89	3.55	11.89	28.22		

3.2.^{1}H NMR and ^{13}C NMR data of theazo ligandand Cd complex

The ^{1}HNMR and ^{13}CNMR spectra of azo ligand are displayed in Figure 1. The ^{1}HNMR data in DMSO-d_6 (ppm) are 2.45 (2H, s,N-H),7.26(1H, s,Ar-H), 7.72-7.71(1H, d, Ar-H), 11.68-11.66(1H, s, 2OH)[11].^{13}CNMR data in DMSO-d_6 (ppm) are 127.5 (C1) 149.0 (C2),118.2 (C3) 145.0 (C4), 157.2 (C5), 169.8 (C6), 132.2 (C7) 165.3 (C8), 137.3 (C9), 166.9 (C10) I55.2 (C11), 122.2 (C12), 178.1 (C13), 182.0 (C14), 189.75 (C15)[12].

The ^{1}H NMR and ^{13}C NMR spectra of Cd-complex are displayed in Figure 2. The ^{1}H NMR data of Cd complex in DMSO-d_6 (ppm) are 3.34 (DHO impurities),8.46-7.36 (9H, m, Ar-H).^{13}C NMR data in DMSO-d_6 (ppm) are106.6 (C1), 189.8 (C2), 145.5 (C3) 181.7 (C4), 190.2 (C5), 118.6 (C6) 137.6 (C7), 127.8 (C8), 132.5 (C9),155.4 (C10), 172.6 (C11), 158.0 (C12),178.7 (C13), 165.8 (C14), 196.2 (C15)[11].

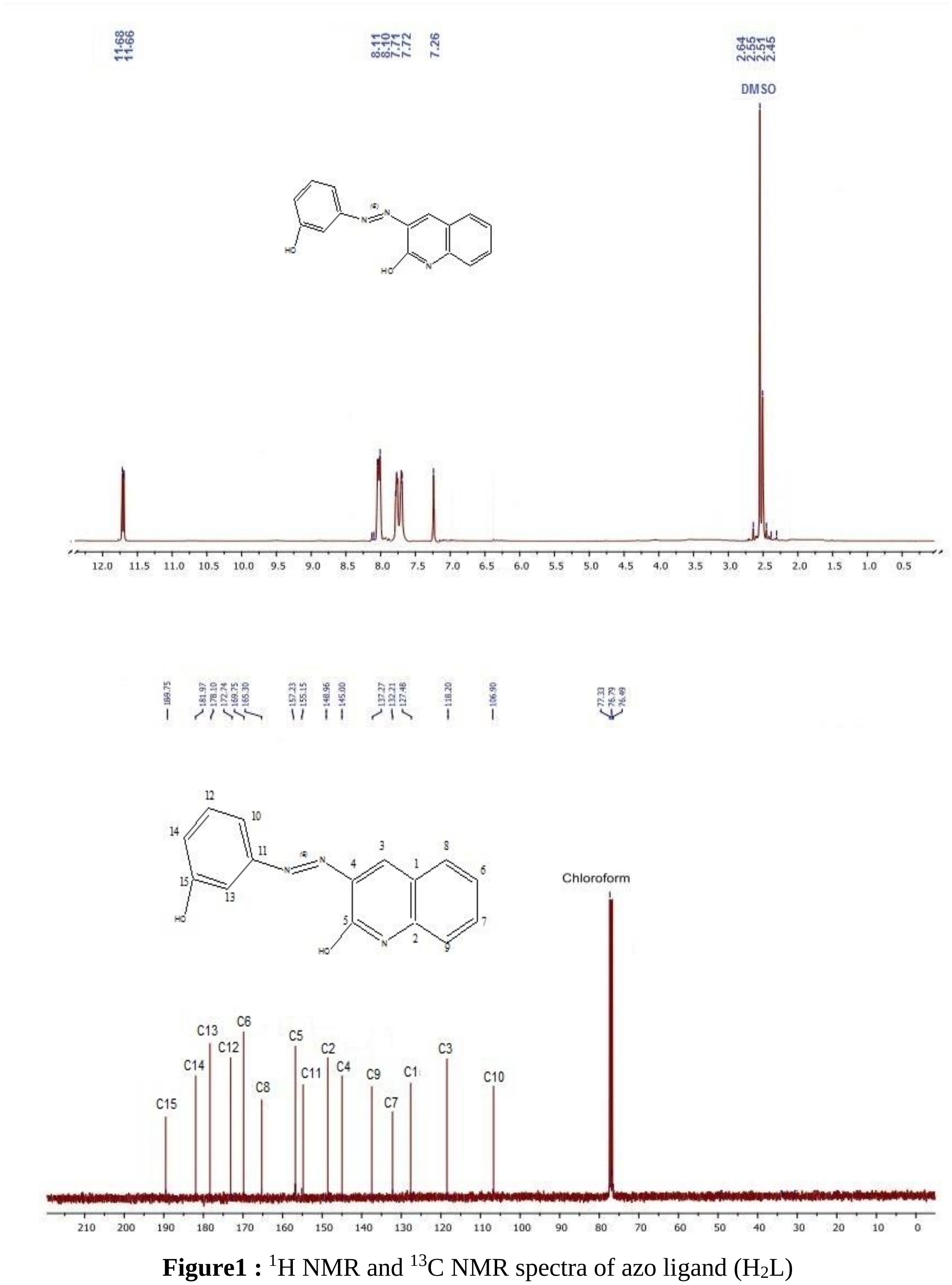


Figure1 : ^{1}H NMR and ^{13}C NMR spectra of azo ligand (H_2L)

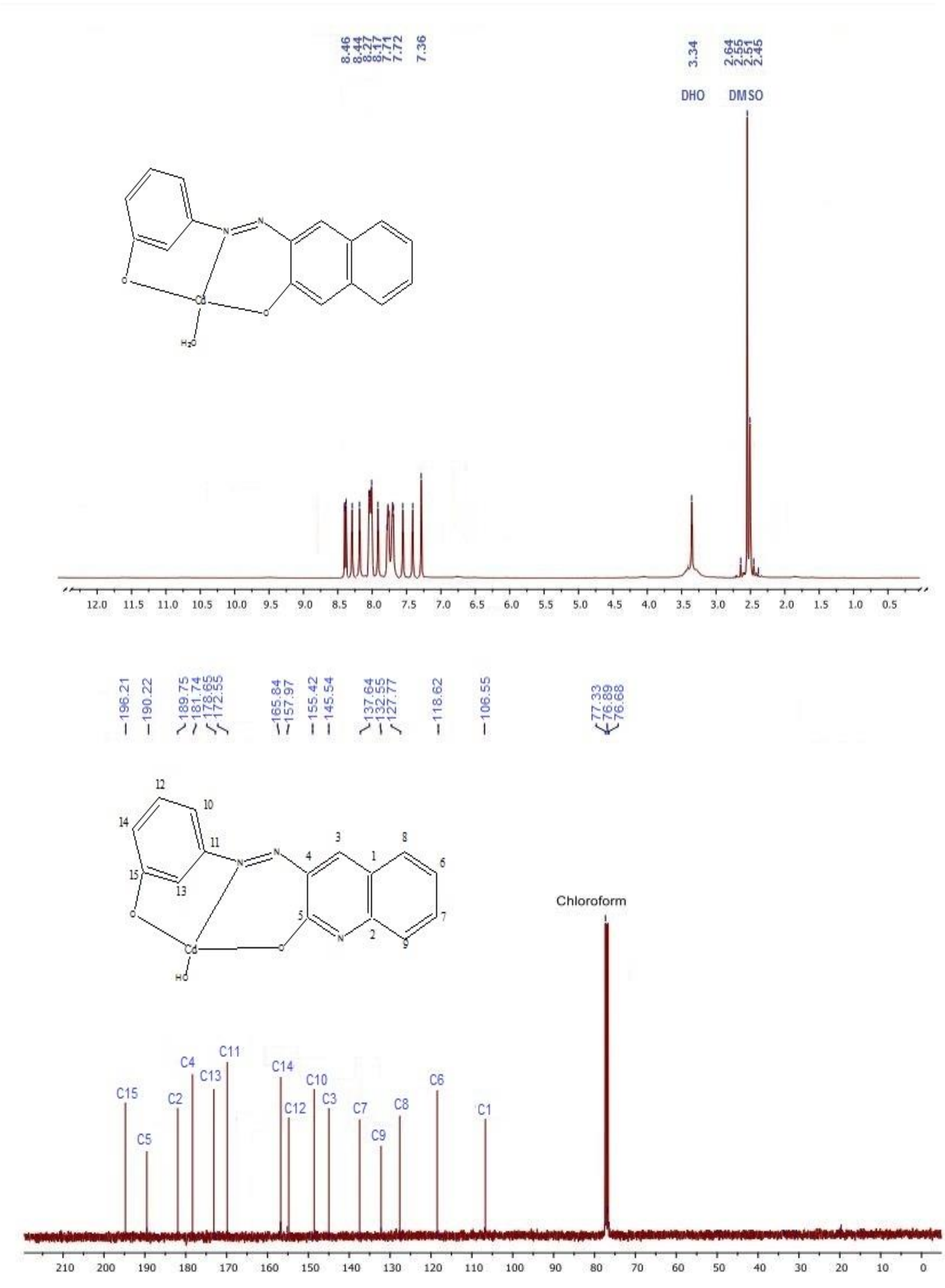


Figure 2: ^{1}H NMR and ^{13}C NMR spectra of the Cdcomplex

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3.3. LC-mass spectra for ligand and its complexes

One of the most crucial methods for characterizing the ligand (H_2L) and some products is LC-Mass spectrum testing. This method is supplementary to the other methods that estimate the molecular weight of the chemical using the relationship (m/z)[13].The fragmentation pattern and the extract mass for each pattern are shown in Scheme 2. The fragment's molecular ion peak [M]$^+$of $C_{15}H_{10}N_3O^+$ is easily visible,and its relative abundance is about 67% in Figure 3.Other peaks observed at 45, 32, and 88% belong to the $C_{15}H_{10}N_3^+$,$C_9H_6N^+$,and $C_6H_5N_2^+$ ions, respectively[8]. For the [Cd(L)H_2O] (Figure 4 and Scheme 2),we can observe the molecular ion peak (M$^+$) at 392.33m/z with a relative abundance of 10%, and the next patterns are $C_{15}H_7CdN_3O_2^{+\bullet}$,$C_{15}H_8CdN_3O^{+\bullet}$,$C_{15}H_8CdN_2O^{+\bullet}$, $C_9H_4CdN_2O^{\cdot+}$ and $C_6H_5^+$,which correspond to 374.58 m/z,358.78 m/z, 344.64 m/z,267.69m/z, and77.84m/z,respectively.Inthe [Mn(L)H_2O]complex (Scheme 2), the fragments (M$^+$) at336.42m/z with a relative abundance of 10%,and the next patterns are $C_{15}H_8N_3O_2Mn^+$,$C_9H_4N_3OMn^+$, $C_9H_4N_2OMn^+$,$C_9H_4NOMn^{+\bullet}$and$C_6H_4O^{\bullet+}$, whichcorresponded to 317.42m/z, 255.02 m/z, 211.35m/z, 197.42m/z, and 92.33m/z. For[Fe(L)$(H_2O)_2$Cl] complex(Scheme5), the fragments (M$^+$) at390.44m/z witha relative abundance of 15% and the next patternsare $C_{15}H_9ClFeN_3O_2^+$, $C_{15}H_9FeN_3O_2^+$,$C_{15}H_9FeN_3O^+$, $C_9H_5FeNO^+$, $C_6H_5N_2^+$,$C_7H_5N_2^{\bullet+}$ and C_2HFeO^+ corresponded to 354.64m/z,319.08 m/z, 303.32m/z, 198.14 m/z, 105.44 m/z,103.21m/z, and 96.89m/z. In the [VO(L)H_2O]complex (Scheme 2), the fragments(M$^+$) at 348.34m/z with relative abundance 20% and next pattern:$C_{15}H_8N_3O_3V^+$,$C_9H_4N_3O_2V^+$, $C_9H_4N_2O_2V^+$,$C_9H_4NO_2V^{+\bullet}$ and $C_6H_4O^{+\bullet}$,which corresponded to329.22m/z, 237.01m/z, 223.22 m/z,209.41m/z, and 92.36m/z.Forthe [Zn(L)H_2O] complex in Scheme 2, the next fragments (M+) are at345.86m/z with a relative abundance of 25%and the next patterns are$C_{15}H_8N_3O_2Zn^+$,$C_{15}H_8ZnN_3O^{\bullet+}$,$C_{15}H_8ZnN_2O^{\bullet+}$,$C_9H_3ZnN_2O^{\bullet+}$and $C_6H_5^+$which correspond to 327.63m/z, 311.65 m/z, 297.35m/z,and 220.54m/z,respectively[14].

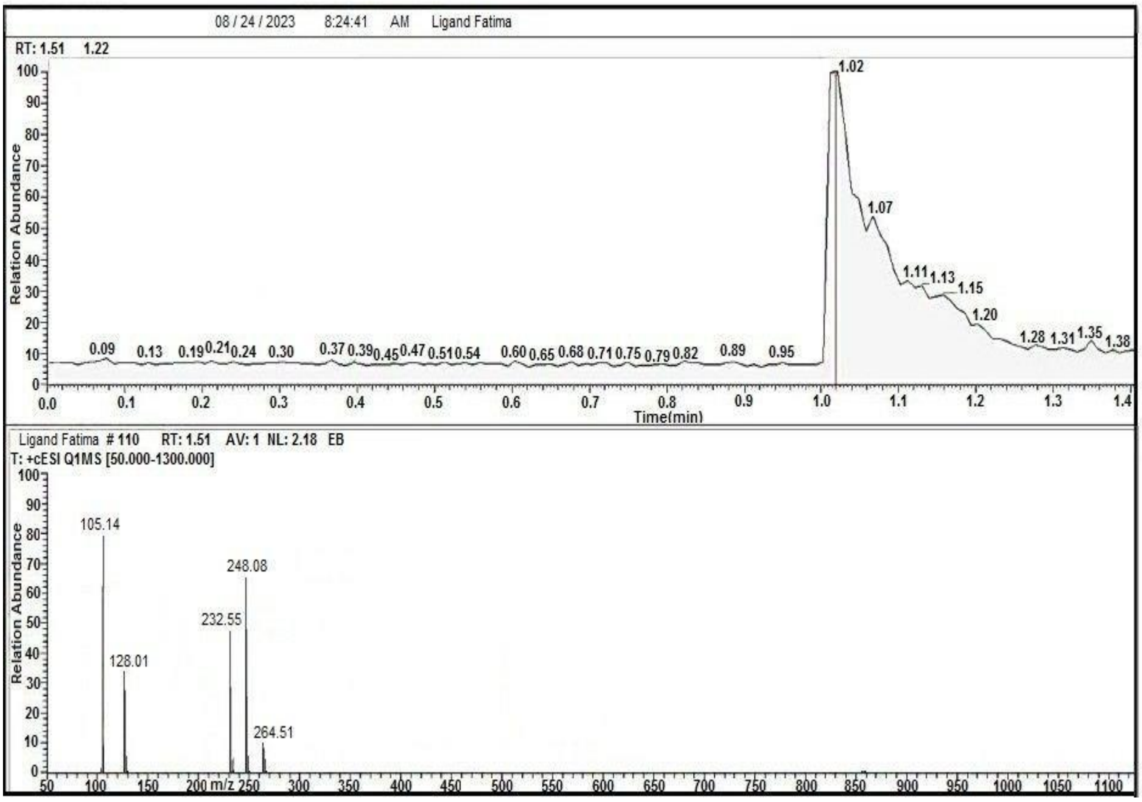


Figure 3: Mass spectrum of ligand H_2L

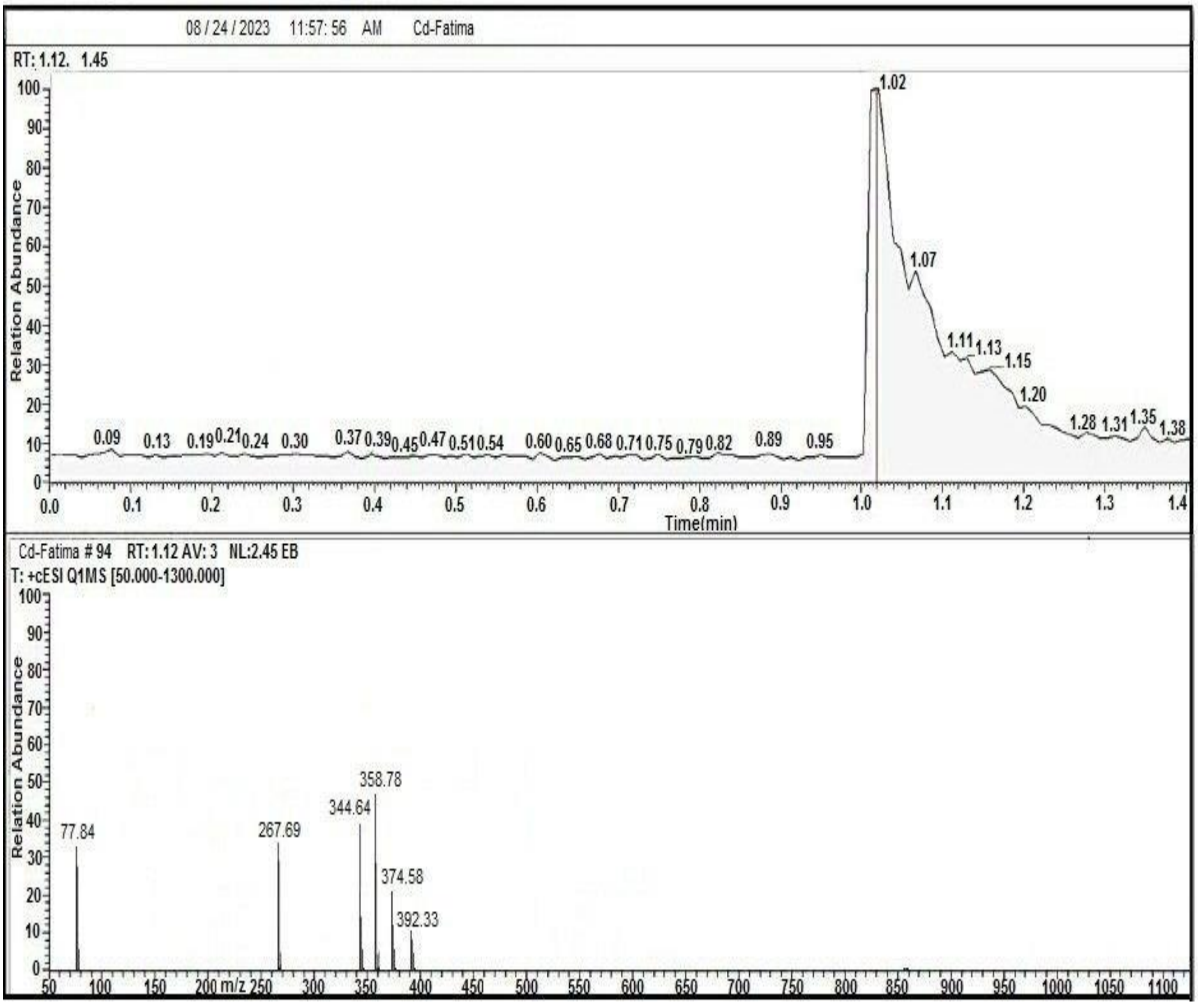
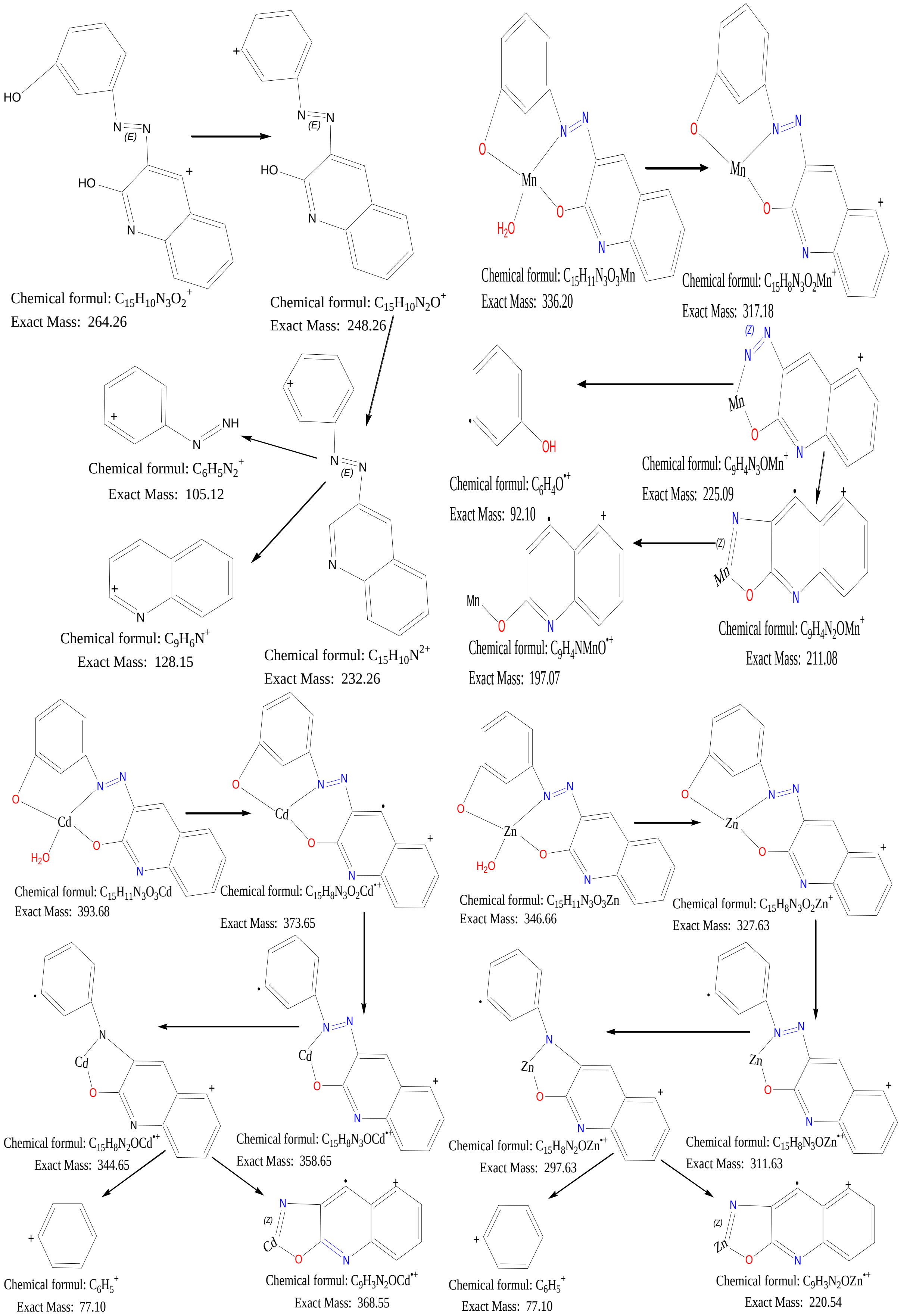
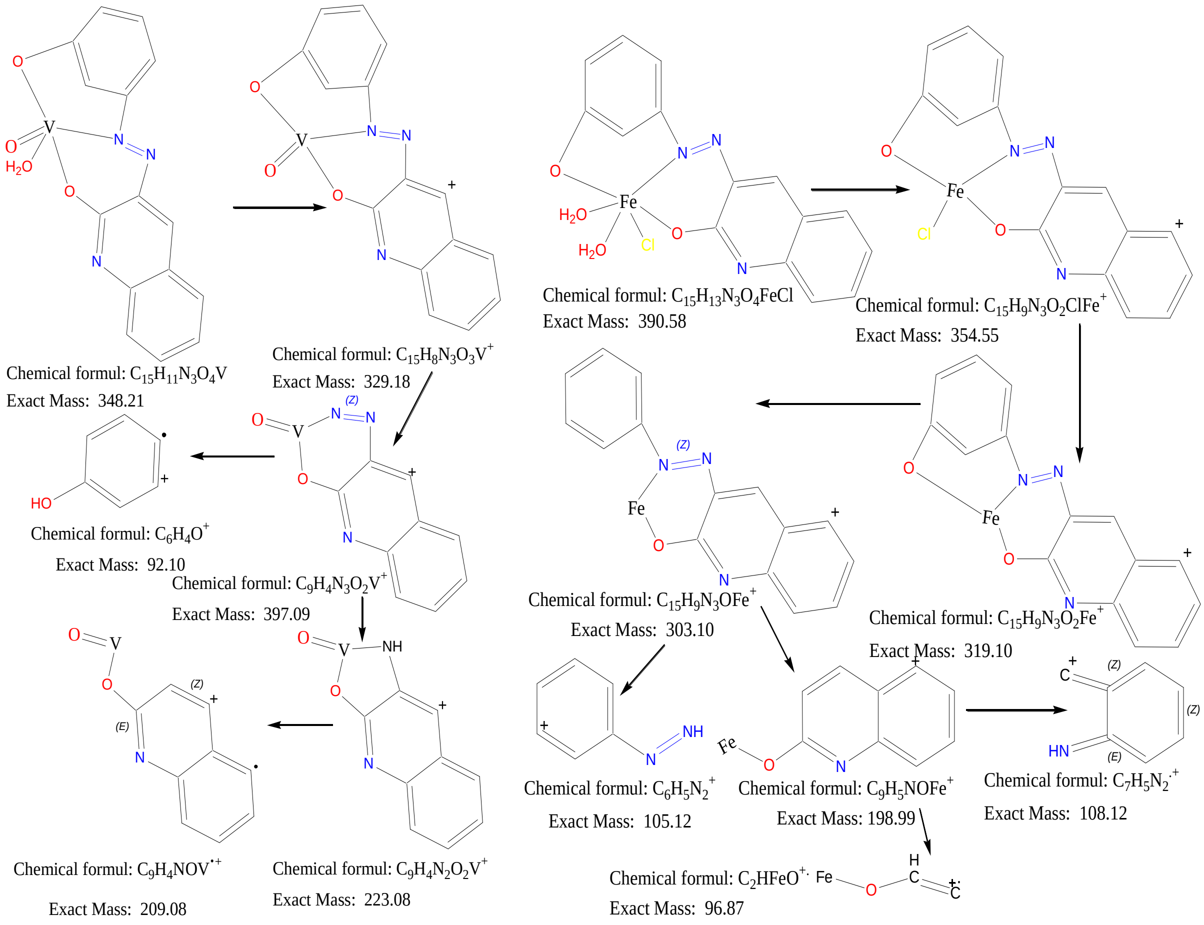


Figure 4: Mass spectrum of Cdcomplex


Chemical formula: $C_{15}H_{10}N_3O_2^+$ Exact Mass: 264.26
Chemical formula: $C_{15}H_{10}N_2O^+$ Exact Mass: 248.26
Chemical formula: $C_{15}H_{11}N_3O_3Mn$ Exact Mass: 336.20
Chemical formula: $C_{15}H_8N_3O_2Mn^+$ Exact Mass: 317.18
Chemical formula: $C_6H_5N_2^+$ Exact Mass: 105.12
Chemical formula: $C_6H_4O^{\bullet+}$ Exact Mass: 92.10
Chemical formula: $C_9H_4N_3OMn^+$ Exact Mass: 225.09
Chemical formula: $C_9H_6N^+$ Exact Mass: 128.15
Chemical formula: $C_{15}H_{10}N^{2+}$ Exact Mass: 232.26
Chemical formula: $C_9H_4NMnO^{\bullet+}$ Exact Mass: 197.07
Chemical formula: $C_9H_4N_2OMn^+$ Exact Mass: 211.08
Chemical formula: $C_{15}H_{11}N_3O_3Cd$ Exact Mass: 393.68
Chemical formula: $C_{15}H_8N_3O_2Cd^{\bullet+}$ Exact Mass: 373.65
Chemical formula: $C_{15}H_{11}N_3O_3Zn$ Exact Mass: 346.66
Chemical formula: $C_{15}H_8N_3O_2Zn^+$ Exact Mass: 327.63
Chemical formula: $C_{15}H_8N_2OCd^{\bullet+}$ Exact Mass: 344.65
Chemical formula: $C_{15}H_8N_3OCd^{\bullet+}$ Exact Mass: 358.65
Chemical formula: $C_{15}H_8N_2OZn^{\bullet+}$ Exact Mass: 297.63
Chemical formula: $C_{15}H_8N_3OZn^{\bullet+}$ Exact Mass: 311.63
Chemical formula: $C_6H_5^+$ Exact Mass: 77.10
Chemical formula: $C_9H_3N_2OCd^{\bullet+}$ Exact Mass: 368.55
Chemical formula: $C_6H_5^+$ Exact Mass: 77.10
Chemical formula: $C_9H_3N_2OZn^{\bullet+}$ Exact Mass: 220.54



Scheme 2: Pattern of fragmentation of ligand and their complexes

3.4.The ligand (H_2L) and its complexes are studied by UV-Vis

The electronic spectrum for ligand (H_2L) in Figure 5 exhibits strong absorptions at275nm and 36363.64cm^{-1} ascribed to the π⟶π* transition and a peak at350nm and 28571.43cm^{-1}attributed to the n⟶π* transition, a peak with a high intensity band formed withabsorption maxima[15]. The electronic transition of the V^{+4}complex depicts peaks of 280,345,390,620, and780 nm assigned toπ→ π*, n→ π*, $^{2}B_{2}g\rightarrow{}^{2}Eg$, and $^{2}B_{2}g\rightarrow{}^{2}B_{1}g$, respectively, which is indicative of a square pyramidal geometry.The electronic spectrum of the divalent zinc compound was studied, and it was found that it does not give d-d transitions because it contains (d^{10}) in the valence shell.However, it gave two peaks, each belonging to the ligand spectrum: peaksat 290nm and 470 nm assigned to π→π* and n→π*, respectively, which is indicative of a tetrahedral.The electronic spectrum of the Cd^{+2} compound was studied, and it was found that it does not give d-d transitions because it contains (d^{10}) in the valence shell, but it gave three peaks, each belonging to the ligand spectrum, peaks in 255, 340, and 390 nm assigned to π→π*,n→π*,and C.T. M→L, respectively, which is indicative of a tetrahedral.The electronic absorption of Mn^{2+}complex exhibited peaks of 235, 295, 325, 595, and 785 nm ascribed to the π→π*, n→π*,C.TML,$^{6}A_{1}g\rightarrow{}^{4}Eg_{(G)}$, $^{6}A1g\rightarrow{}^{4}T_{2}g_{(G)}$,$^{6}A_{1}g\rightarrow{}^{4}T_{1}g_{(G)}$,and $^{6}A_{1}g\rightarrow{}^{4}T_{2}g_{(D)}$, respectively, which is indicative of a tetrahedral.The electronic transition of Fe^{+3}complex show in Figure 6 exhibited peaks of 270,310,545, and 720 nm assigned toπ→π*, n→π*, C.T M→L, $^{6}A_{1}g\rightarrow{}^{4}T_{2}g_{(G)}$,$^{6}A1g\rightarrow{}^{4}T_{1}g_{(G)}$, and $^{6}A_{1}g\rightarrow{}^{4}Eg_{(D)}$, respectively,which is indicative of anoctahedral geometry.Table2 displays the electronic assignment of metal complexes[16,17].All complexes are non-electrolytes.

Table 2: The ligand (H_2L) and its complexes are studied by UV-Vis

Compound	λ nm	ύcm^{-1}	Abs	Ɛ$_{max}$ Lmol^{-1} cm^{-1}	Assignment	μ$_{eff}$ (B.M) found (calculate)	Hybridization	Distribution
Ligand H_2L	275 350	36363.64 28571.43	1.89 2.13	1890 2130	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$			
$[VO(L)H_2O]$ Square pyramidal	280 345 390 620 780	35714.29 28985.51 25641.03 16129.03 12820.51	1.200 1.120 0.400 0.260 0.250	1200 1120 400 260 250	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ C.T $^2B_2g \rightarrow ^2Eg$ $^2B_2g \rightarrow ^2B_1g$	1.81 (1.73)	dsp^3	$t_2g^1eg^0$
$[Mn(L)H_2O]$ Tetrahedral	235 295 325 595 785	42553.19 33898.31 30769.23 16806.72 12738.85	2.125 1.895 0.890 0.625 0.595	2125 1895 890 625 595	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ C.TM→L $^6A_1g \rightarrow ^4Eg(G)$ $^6A_1g \rightarrow ^4T_2g(G)$	5.44 (5.91)	SP^3	$e^2t_2^3$
$[Fe(L)H_2OCl]$Octahedral	270 310 545 720	37037.04 32258.06 18348.62 13888.89	2.115 1.998 0.250 0.125	2115 1998 250 125	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $^6A_1g \rightarrow ^4Eg(G)$ $^6A1g \rightarrow ^4T_2g(G)$	5.17 (5.91)	SP^{3}d^2	$T_2g^3eg^2$
$[Zn(L)H_2O]$ Tetrahedral	290 470	34482.76 2127.66	2.315 0.525	2315 525	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	Diamagnetic (0)	SP^3	$e^4\ t_2^6$
$[Cd(L)H_2O]$ Tetrahedral	255 340 390	39215.69 29411.76 25641.03	2.120 1.980 0.890	2120 1980 890	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ C.T M→L	Diamagnetic (0)	SP^3	$e^4\ t^6_2$

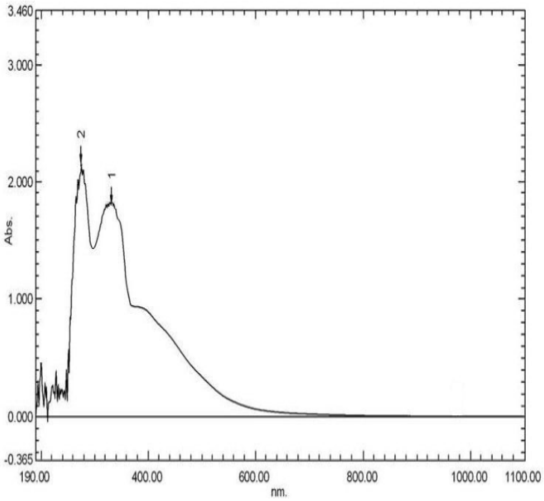


Figure 5 UV-Vis spectrum of ligand (H_2L)

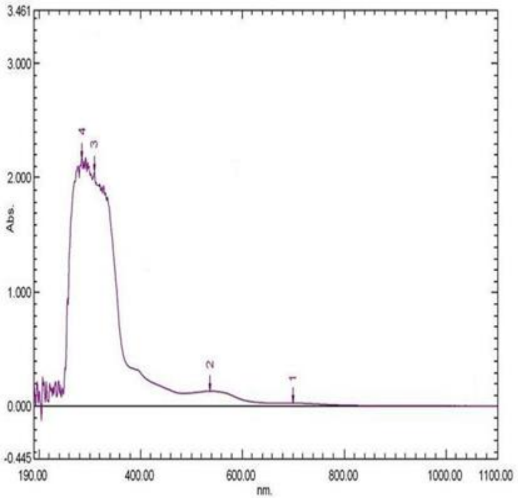


Figure6- UV-Vis spectrum of Fe-complex

3.5.Thermal analysis

The results of the thermal analysis can be seen in Tables 4 and 5 and in Figures 7 and 8 for the ligand (H2L) and the complexes that were made [18]. Scheme 8 outlines the potential breakdown response of metal complexes. Based on the thermograms, computations of the decomposition phases, temperature ranges, decomposition products, and weight loss complex percentages indicated consistency. That verifies the elemental analysis findings and recommended equations between their thermal decomposition results and computed values[10].In this work, it was noted that in the ligand and metal complexes of V^{+4},Fe^{+3},Zn^{+2},Cd^{+2}, and Mn^{+2}, the remaining ligand was carbon and the remaining metal oxide. Based on the results of the thermogravimetric studies, it can be shown that the complexes and the ligand form one to three distinct phases.Using the DCS curve, the thermodynamic parameters enthalpy ΔH, entropy ΔS and Gibbs free energy (ΔG)were calculated[19].

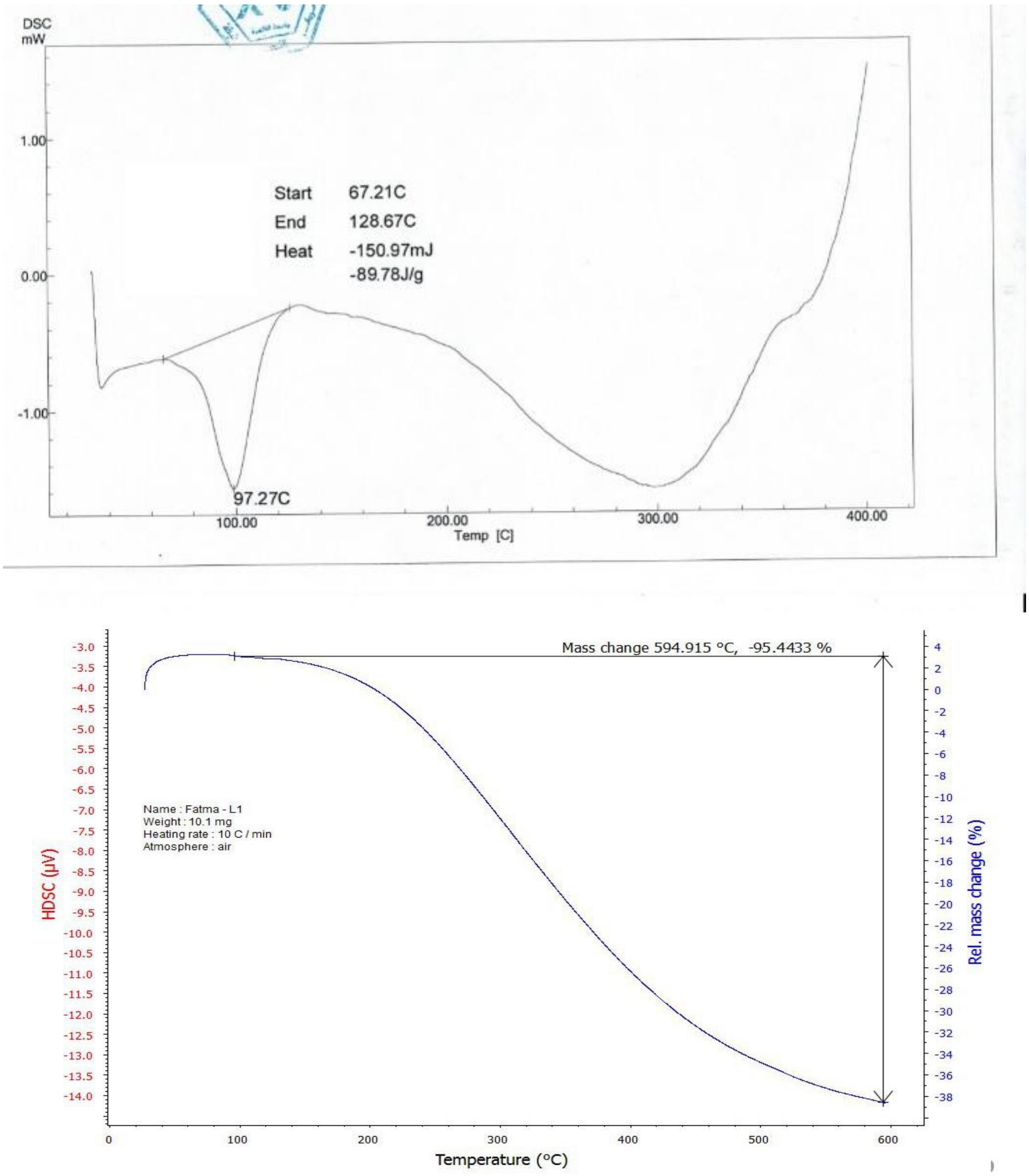


Figure 7: TGA&DSC curve of Ligand (H_2L)

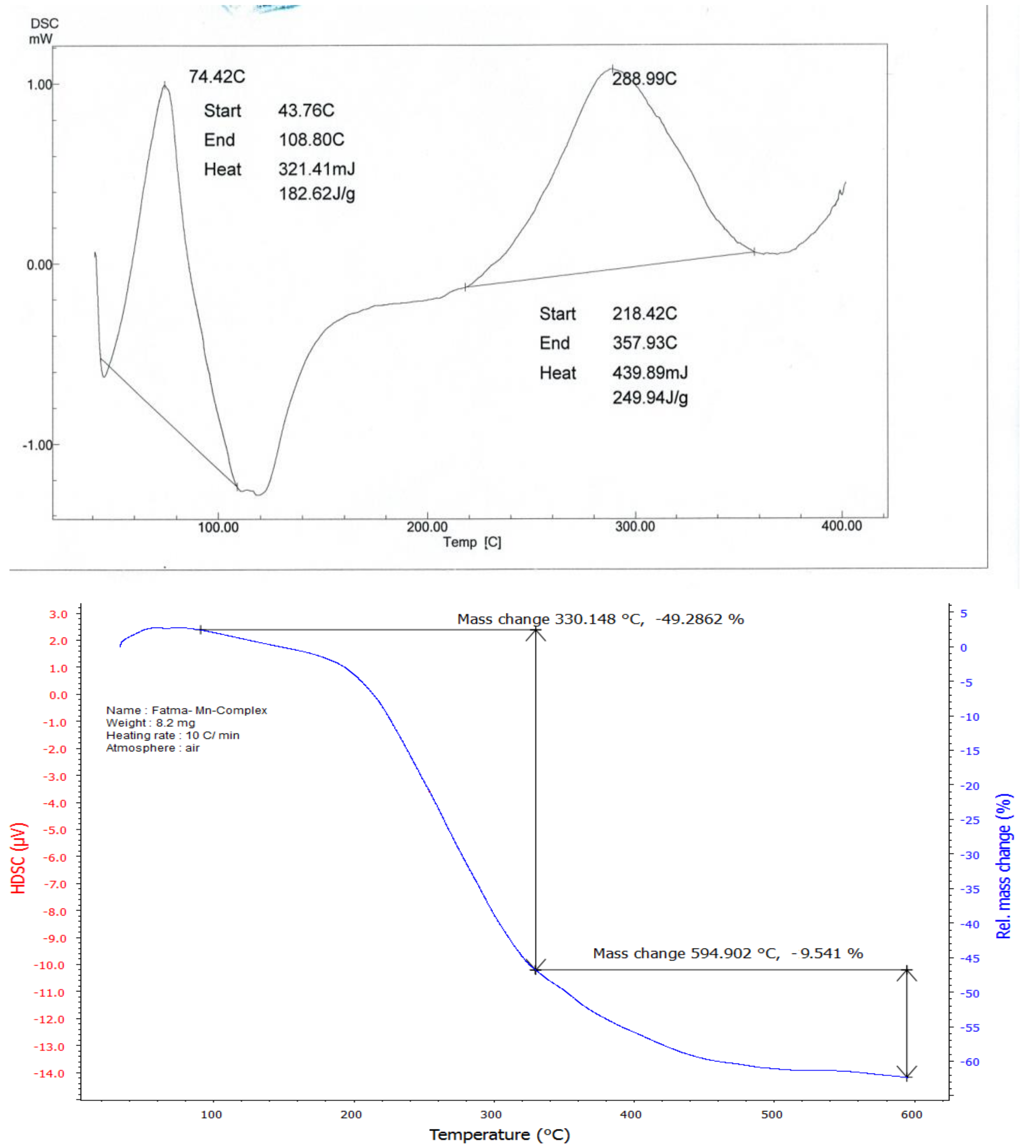
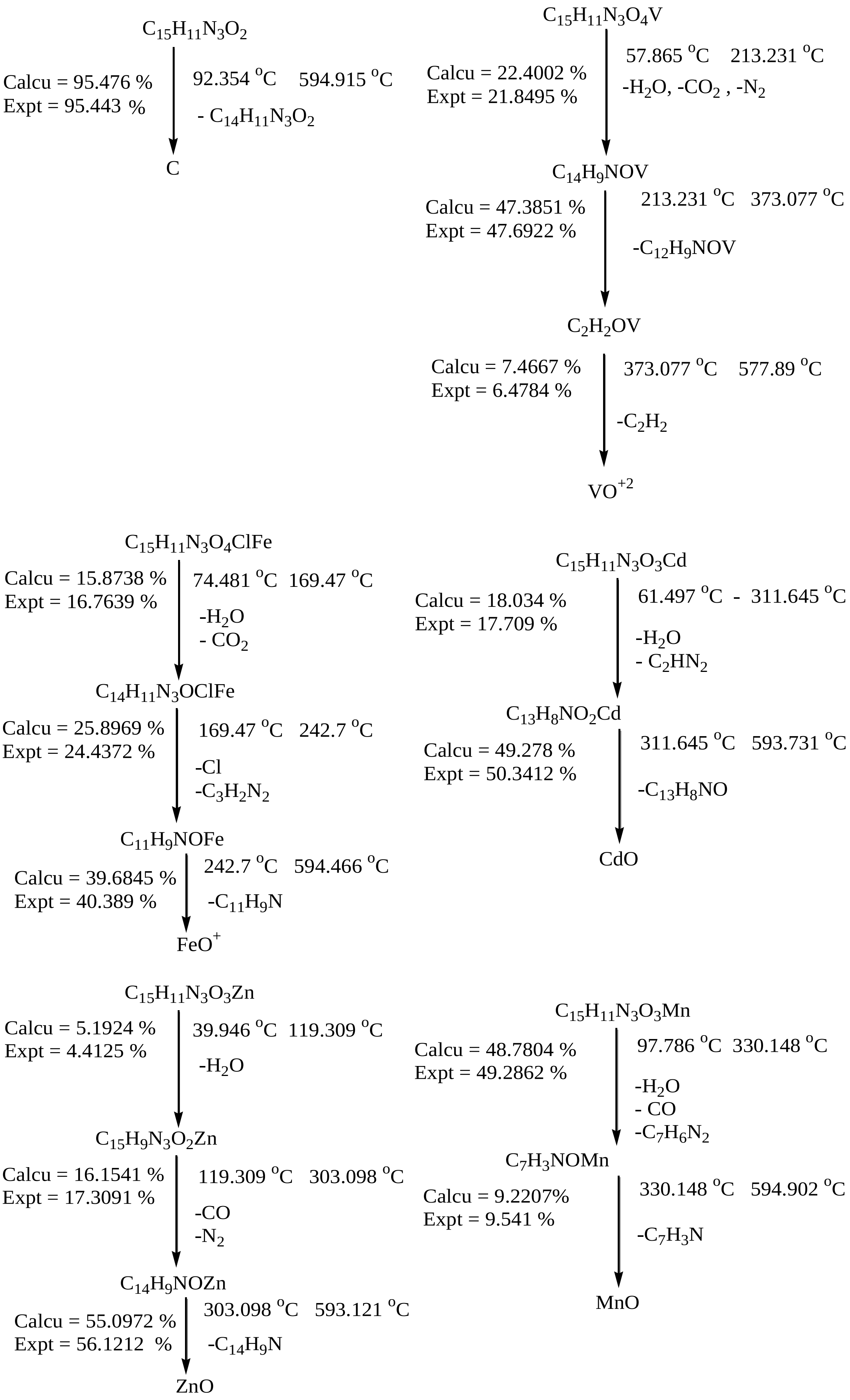


Figure 8: TGA&DSC curve of MnComplex



Scheme 8: Tentative decomposition reaction of ligand and metal complexes

Table3: Thermal decomposition DSC of Ligand and some complexes

Compound	$T_{i\ /°C}$	$T_{f/°C}$	Maximum temperature point (°C)	ΔH (J/g)	ΔS (J)	ΔG (J)	Type
H_2L	67.21	128.67	97.27	-89.78	-1.4608	52.31	endothermic
$[Fe(L)(H_2O)Cl]$	105.94 156.16 314.05	112.21 159.31 319.44	316.57	-1.19 -0.79 -2.78	-0.178 -0.251 -0.515	55.159 78.669 160.256	endothermic endothermic endothermic
$[Zn(L)H_2O]$	263.32 278.01	276.00 287.47	257.72 270.71 281.09	-36.90 -11.55	-2.910 -1.220	713.065 331.379	endothermic endothermic
$[Mn(L)H_2O]$	43.76 218.42	108.80 357.93	74.42 288.99	182.62 249.94	2.807 1.791	49.512 -267.641	endothermic exothermic
$[Cd(L)H_2O]$	387.65	395.13	392.40	-3.03	-0.405	155.892	endothermic
$[VO(L)H_2O]$	46.17 60.34 172.41 324.45	63.49 98.63 257.74 334.99	56.51 76.54 223.54 332.57	-1.63 -24.35 54.84 -1.75	-0.094 -0.635 0.642 -0.166	5.2179 24.252 -88.673 53.456	endothermic endothermic exothermic endothermic

Table 4: TGA data of the ligand H_2Landsome complexes

Compound	Step	$T_{i/°C}$	$T_{f/°C}$	Weight mass loss%		Reaction
				Calc	Found	
Ligand	1	92.354°C	594.915°C	95.476%	95.443%	$-C_{14}H_{11}N_3O_2$
						C
Calculated: 95.476% , Final= 4.524%, Estimated95.443%Final=4.557%						
Cd-complex	1	61.497°C	311.645°C	18.034%	17.709%	$-H_2O-C_2HN_2$
	2	311.645°C	593.731°C	49.278%	50.3412%	$-C_{13}H_8NO$
						CdO
Calculated: 67.312% Final= 32.688% Estimated 68.0502% Final 31.9498%						
Mn-complex	1	97.786°C	330.148°C	48.7804%	49.2862%	$-H_2O$, -CO $-C_7H_6N_2$
	2	330.148°C	594.902°C	9.2207%	9.541%	$-C_7H_3N$
						MnO
Calculated:58.0011% Final 41.9989% Estimated 58.8272% Final=41.1728%						
V-complex	1	57.865°C	213.231°C	22.4002%	21.8495%	$-H_2O-CO_2$ $-N_2$
	2	213.231°C	373.077°C	47.3851%	47.6922%	$-C_{12}H_9NO$
	3	373.077°C	577.89°C	7.4667%	6.4784%	$-C_2H_2$
						VO^{+2}
Calculated: 77.252% Final= 22.748% Estimated 71.8796% Final=28.1204% 28.1204%						
Fe-complex	1	74.481°C	169.47°C	15.8738%	16.7639%	$-H_2O-CO_2$
	2	16.47°C	242.7°C	25.8969%	24.4372%	-Cl, $-C_3H_2N_2$
	3	242.7°C	594.466°C	39.6845%	40.389%	$-C_{11}H_9N$
						FeO^+
Calculated: 81.4552% Final= 18.5448% Estimated 81.5901% Final=18.4099%						
Zn-complex	1	39.946°C	119.309°C	5.1924%	4.4125%	$-H_2O$
	2	119.309°C	303.098°C	16.1541%	17.3091%	-CO $-N_2$
	3	303.098°C	593.121°C	55.0972%	56.1212%	$-C_{14}H_9N$
						ZnO
Calculated: 76.4437% Final=23.5563% Estimated 77.8428% Final=22.1572%						

3.6.Infrared spectra

The infrared spectra of ligand H_2L and its metal complexes were recorded with Cd^{+2},Zn^{+2},Fe^{+3},Mn^{+2}, and V^{+4}, and the data has been organized in Table 5.The ligand showed bands at 3477, 3167,1546-1600, and 1257cm^{-1} that were ascribed to the stretching vibrations of O-H, C-H aromatic,C=C aromatic,and C-O [20].The infrared spectrum of the ligand showed a medium-intensity stretch band at frequency 1352cm^{-1}, which was attributed to the vibration frequencies of the doublebond N=N (Figure 9). The FT-IR spectra of all the prepared compounds showed that the azo-dye ligand was coupled to metal ions through two sites: the oxygen site *via* deprotonation of the phenolic group and the nitrogen site of the azo group[21]. New bands belonging to M-Nappeared at 611,617, 621, 615, and 619 cm^{-1} for the V^{4+},Mn^{2+}, Cd^{+2},Zn^{+2}, and Fe^{+3}complexes, respectively.M-O at 457, 462, 460, and 450 cm^{-1} for the complexes V^{4+},Mn^{2+}, Cd^{+2},Zn^{+2}, and Fe^{+3}, respectively. M-Cl at 385 cm^{-1} for the Fe^{+3}complex [22].

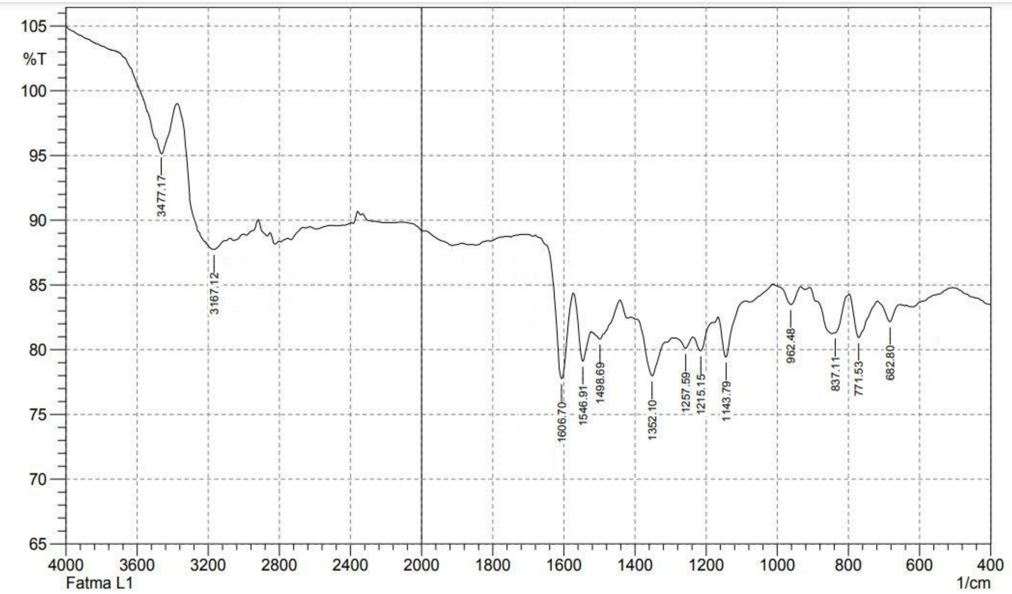


Figure 9: FT-IR spectrum of ligand (H_2L)

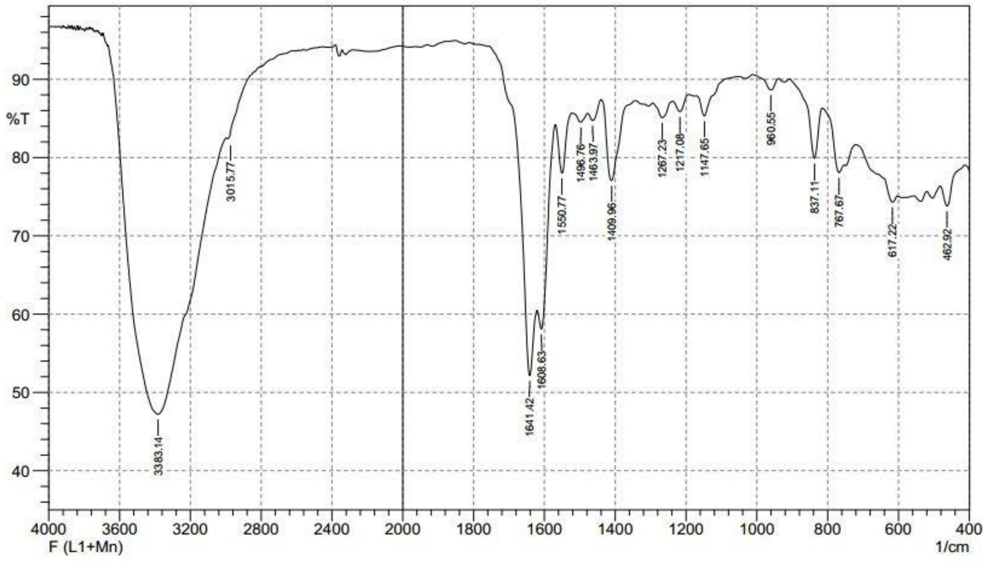


Figure 10 FT-IR spectrum of Mn complex

Table 5: The FT-IR spectra bands (cm^{-1}) of the ligand and its complexes

Compound	ν(H_2O) aqua	ν(C-H) aromatic	ν(C-O)	ν(N=N)	Other bands
H_2L	-	3167	1257	1352	
[VO(L)H_2O]	3410 1643 835	3169	1213	1419	611(V-N) 457(V-O) 979(V=O)
[Mn(L)H_2O]	3383 1641 837	3015	1217	1409	462(Mn-O) 617(Mn-N)
[Zn(L)H_2O]	3400 1640 834	3100	1220	1400	615(Zn-N) 460(Zn-O)
[Fe(L)(H_2O)Cl]	3385 1645 830	3050	1215	1415	619(Fe-N) 450(Fe-O) 385(Fe-CI)
[Cd(L)H_2O]	3388 1642 828	3160	1218	1412	621(Cd-N) 458(Cd-O)

3.7.Investigation of antioxidant activity

The antioxidant activity of H_2L and its mineral complexes was measured by ascorbic acid, and the DPPH assay was used to scavenge free radicals.Initially, each sample was diluted with the same volume of methyl alcohol, and then it was mixed with the same volume of a concentrated 0.135 mM DPPH solution. After adding the DPPH solution[23], the samples were kept at room temperature in the dark for 30 minutes.The absorbance of each sample was then determined to be 517 nm.The lower the IC_{50} value of the complexes compared to ascorbic acid, the greater their ability to suppress free radicals.As the ligand was the most effective free radical inhibitor, followed by zinc, which has the same value as ascorbic acid, followed by iron, vanadium, cadmium, and manganese[24,25], the values of $IC_{50}$are as follows: H_2L > D-ascorbic acid >Zn-complex >Fe-complex > V-complex >Cd-complex > Mn-complex (Figure 11).

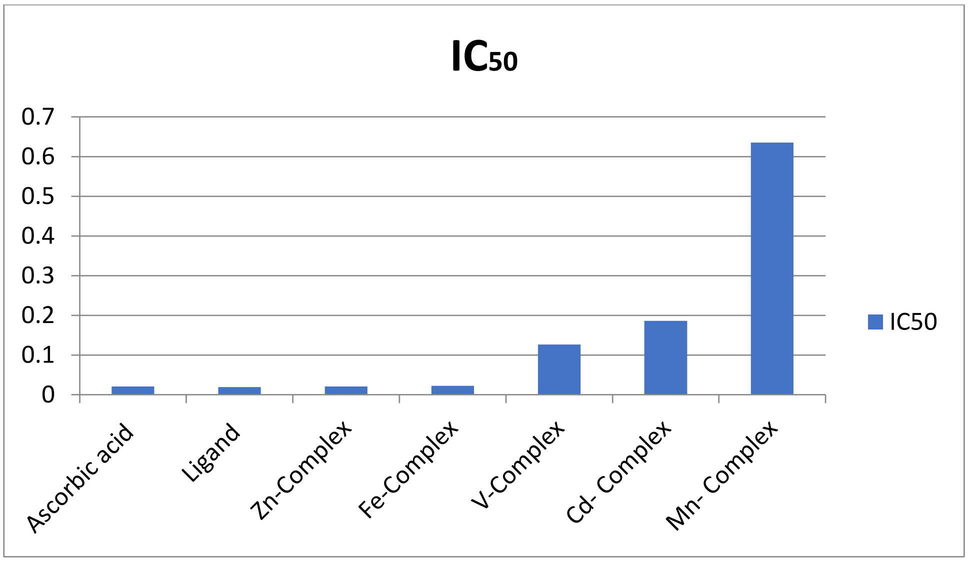


Figure 11: Variations of IC_{50} values for H_2L ligand and its complexes

Table 6: The antioxidant results (P1%, RSA% and IC_{50}) of H_2L and their metal complexes

Compound	Concentration (mg/mL)	PI (%)	RSA (%)	IC_{50} (mg/mL)
Ascorbic acid	0.374 0.186 0.03	12.29 36.75 58.74	87.80 63.25 41.26	0.021
LigandH_2L	0.375 0.186 0.093 0.046	18.37 42.18 64.17 77.91	81.63 57.82 35.83 22.09	0.019
Zn- complex	0.113 0.057 0.028 0.014	20.14 43.95 65.94 79.68	79.86 56.05 34.06 20.32	0.021
Fe-complex	0.374 0.186 0.093 0.046	15.27 39.08 61.07 74.81	85.19 62.07 40.74 27.41	0.022
V-complex	0.374 0.186 0.093 0.046	42.86 46.72 60.48 69.36	57.14 53.28 39.52 30.64	0.126
Cd- complex	0.113 0.057 0.028 0.014	67.48 82.38 97.28 99.14	32.52 17.62 2.72 0.86	0.186
Mn-Complex	2.326 1.285 0.764 0.503	68.49 87.54 91.98 96.14	31.51 12.46 8.02 3.86	0.635

4. Conclusion

A novel azo ligand was prepared *via* the reaction ofthe diazonium salt of 3-aminophenol with 2-hydroxyquinoline. This ligand was then employed to access new complexes with different metals.These complexes were identified using a number of analytical techniques, such as elemental microanalysis, metal chloride-containing, electrical conductivity measurement, magnetic susceptibility, ^1H and ^{13}C-NMR, FT-IR, and UV-Vis spectroscopy. Calculations of the thermodynamic parameters ΔH, ΔS, and ΔG were made using the DCS curve, and the atomic N,O, and O tridentate coordination sites in the ligand were identified by comparing their FT-IR spectra to those of the metal complexes. The M:L ratio in every compound was 1:1. The dye used the complexes prepared from it to determine their ability to inhibit free radicals by measuring their ability as antioxidants using DPPH as a free radical and D-ascorbic acid as a standard substance and determining the value of IC_{50}.The ligand exhibited a significant capacity to suppress free radicals, and its ability to inhibit the complexes varied depending on the IC_{50} value. The results are as follows: H_2L > D-ascorbic acid >Zn-complex >Fe-complex > V-complex >Cd-complex > Mn-complex.

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