

Preparation and Spectroscopic Studies of Cadmium(II), Zinc(II), Mercury(II) and Vanadium(IV) Chelates Azo Ligand Derived from 4-Methyl-7-hydroxycoumarin

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Abstract: The present paper demonstrates the synthesis and characterization of some transition elements complexes derived from (E)-7-hydroxy-6-((4-methoxyphenyl)diazenyl)-4-methyl-2H-chromen-2-one. The ligand was prepared in the general route of azo dyes by coupling the diazonium salt of 4-methoxyaniline with 4-methyl-7-hydroxycoumarin in sodium hydroxide 10% (w/v) solution. The azo ligand was identified on the basis of elemental analyses, MS, H-NMR and FT-IR spectra. The products of complexes with the new azo dye were isolated by the direct reactions of the metal chlorides of cadmium(II), zinc(II), vanadium(IV) and mercury(II) ions with the alkaline solution of free ligand to afford the colored in the following formulas, complexes $[ML_2] \cdot 2H_2O$ formula, $M = Cd(II)$ and $Zn(II)$. However the vanadium(IV) complex was square pyramid in $[VOL_2]SO_4 \cdot 2H_2O$ chemical formula. As well as the tetrahedral environment was suggested for mercury(II) complex in formula $[HgL_2]$. The time and mole ratio factors were studied to obtain the optimized conditions of metal complexes formations and the observed data investigated the deprotonation of the azo-dye at pH to range (7-7.5) with 30 min as time of reaction to get pure metal chelates. The TG-DSC study confirmed the thermal stability of complexes at a wide range of average heating in inert gas of analysis and the results observed from loss weight percent investigated the proposed structures of the prepared metal complexes.

Keywords: azo ligands; metal complexes of coumarin; spectroscopic studies

■ INTRODUCTION

The major branch of coordination chemistry has been partially allocated with the azo dyes of 4-hydroxycoumarin and their derivatives [1-2]. The inorganic complexes of chromen-2-one rings mainly could possess applications in catalysis, manufacturing of dyes and pharmaceutical drugs [3-5]. The pentagonal and hexagonal coordination complexes of dyes involving imine and hydroxyl groups have shown a wide range of applications in the diodes and solar cells fields [6-7]. The common coordination compounds derived from azo dyes of chromen-2-one have interested in wide spectrum of applications in the emission studies like fluorescence and phosphorescence [8-10].

Recently the researchers have encouraged enhancing the electronic and geometrical features of complexes of azo dyes that they would have exhibited nonlinear optical elements and printing systems [11-14]. All the above mentioned about the development of coumarin azo dyes with their chelation ability afford us to prepare and characterize new azo dye complexes of Zn(II), Cd(II), V(IV) and Hg(II) derived from (E)-7-hydroxy-6-((4-methoxyphenyl)diazenyl)-4-methyl-2H-chromen-2-one.

■ EXPERIMENTAL SECTION

Materials

The starting 4-methoxyaniline and 4-methyl-7-hydroxycoumarin and 4-methoxyaniline were supplied

via Merck Company and the metal salts of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 , CdCl_2 and HgCl_2 were supplied from Quaternary Group Merck Chemicals Companies and used as supplied without purification.

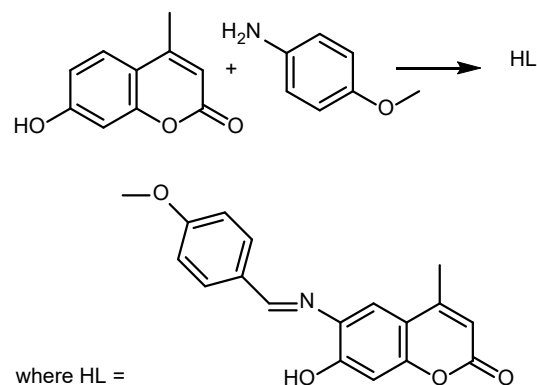
Instrumentation

The melting points temperature of the coumarin derivatives and metal complexes were determined on the Stuart melting point apparatus. The molecular weights of the ligand and some selected metal complexes were measured their mass spectra on a Shimadzu model GC MS QP 1000EX at college of science, Mustansiriyah University. The electronic spectra of ligand and its complexes in ethanol and DMSO solvents was determined with UV-1800 Shimadzu spectrometer apparatus. The nuclear magnetic resonance spectroscopy was carried out in d_6 -DMSO solvent on Bruker-500 MHz NMR spectrometer. The main features of vibration frequencies of azo dye ligand and its metal complexes were scanned on Shimadzu FT-IR spectroscopy in the range $(4000\text{--}200)\text{ cm}^{-1}$. The pH of the solutions was checked using a Jenway 3020 pH meter. Furthermore, the percentages of metal ions were determined with GBC 933 model FAAS at Ministry of Industry, Ibn-Cina company, Baghdad, Iraq.

Procedure

Synthesis of azo ligand

The azo dye was synthesized according to the modified classical procedure established in literature, by dissolving (1.83 g, 0.01 mmol) from 4-methoxyaniline in hot distilled water (10 mL) then followed by an addition of 36% (v/v) HCl (5 mL). To this solution, a cooled aqueous solution of sodium nitrite (0.45 g, 5 mmol) was added by maintaining the temperature of the reaction at $0\text{ }^\circ\text{C}$. The formed diazonium salt was gradually added to an alkaline solution of 4-methyl-7-hydroxycoumarin (0.02 mol, 3.90 g) with stirring for 30 min, after that the resulting solution was neutralized to pH of about 6.5 by addition drops of 10% NaOH. The dark orange crude was then filtered, washed several times with water and ethanol, then dried. The re-crystallization from hot ethanol afforded dark orange crystals of azo dye ligand, L, Scheme (1).



Scheme 1. Synthesis of azo dye, HL

Synthesis of metal complexes

The metal complexes were prepared by dissolving ZnCl_2 (10 mmol, 1.45 g) or $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ (1 mmol, 1.118 g) in (15 mL) hot water and ethanolic solution of (20 mmol, 1.44 g) of azo dye, L. The mixture was stirred on water bath for 1 h then red precipitates of ZnL and CdL complexes were separated and filtered off. The Hg(II) complex was prepared by mixing (10 mmol, 1.45 g) of azo dye in (15 mL) hot ethanol with (10 mmol, 0.272 g) in (10 mL) hot water with stirring on a water bath for 2 h, the white off separated precipitate was filtered of and dried in oven at $90\text{ }^\circ\text{C}$. However, the vanadium(IV) complex was isolated in its solid state from oxovanadium sulfate penta hydrate after adjusting the mole ratios 1:2 of (M:L) with respect to dissolving $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ in (15 mL) hot water with (20 mmol, 1.45 g) of azo dye then refluxed the mixture for 2 h. The brown precipitate was filtered, dried in air then washed several times with hot ethanol and diethyl ether, Table 1.

RESULTS AND DISCUSSION

Physical Properties and Elemental Analyses

Table 1 list the main physical properties of ligand and its complexes and show the thermal stability of almost complexes through the elevated their decomposition points. All the complexes are colored and sparingly soluble in most organic solvents except DMSO and DMF. The micro-analyses (C.H.N.) confirm the suggested chemical formula for all complexes beside the structure of azo dye. The calculation of mole ratios was in good agreement of their formation procedure and

Table 1. Some physical properties and elemental analyses of Azo dye and its complexes

Compound	Molecular Weight (g/mol) Formula	Color	M.P. (°C)	%C Found (Calc.)	%H Found (Calc.)	%N Found (Calc.)	%M Found (Calc.)
HL	310.09 C ₁₇ H ₁₄ N ₂ O ₄	Dark brown	178–180	65.00 (65.81)	4.22 (4.55)	8.88 (9.03)	--
ZnL	683.03 C ₃₄ H ₂₆ ZnN ₄ O ₈	Red	> 288	57.90 (58.232)	3.49 (3.89)	10.11 (9.36)	7.99 (9.22)
CdL	732.22 C ₃₄ H ₂₈ CdN ₄ O ₁₀	Orange	> 300	52.21 (53.33)	4.80 (3.90)	9.04 (10.01)	15.38 (16.22)
HgL	820.53 C ₃₄ H ₂₆ HgN ₄ O ₈	Brown	277–279	55.22 (56.11)	3.22 (3.99)	10.80 (9.82)	
VOL	746.79 C ₃₄ H ₃₀ N ₄ SO ₁₄ V	Dark brown	> 295	55.33 (56.73)	5.33 (5.90)	12.60 (11.99)	15.44 (16.30)

stoichiometric and it is based on flame atomic absorption data. The flame atomic absorption spectroscopy for metal contents (M%) in the solid complexes are experimentally determined through standard addition method and the observed analyses are in good agreement with the calculated data confirming the structures of all the prepared complexes. However the molar conductivity measurements reveals that all complexes do not show electrolytic nature [15], except vanadium(IV) complex solution in DMF that exhibits conductivity motion due to the presence of sulfate counter ion in the structure.

Mass Spectra

The mass spectrum of azo-dye ligand showed peak at molecular ion $m/e = 310$ which indicates the unstable molecular weight of the expected C₁₇H₁₄N₂O₄ formula due to losing methoxy and methyl groups in the gas-phase of GC conditions for the MS spectra then confirms formation of the azo dye [13]. The peaks observed at around $m/e = 116$ and 89 would be resulted from cleavage of chromen ring and points of -CH₃ and -OH respectively [12]. As well as the mass spectrum of vanadium (II) complex shows weak intensity peak at 747 that is allocated to the molecular ion of complex in the gas phase [14,17].

NMR Spectra

The H and ¹³C-NMR were displayed only for the azo dye with chemical shifts in (ppm) units and are relative to residual proton solvent signals. The spectrum of the ligand is in a good agreement with the number of protons

and their assignments of nuclear spins of Ar-H and methyl protons. The ¹H-NMR spectrum of the ligand, Fig. 1 shows a singlet signal at δ (7.9–8.99) ppm corresponding to the -C=C-H of chromen ring. The peak showed at around δ (14.50) ppm was also recorded in the ligand spectrum, due to the -OH proton that is directly attached to C7 of chromen ring. The doublet of doublet peaks at around δ (12.45) ppm reflects mainly the spin coupling of aromatic protons adjacent to each other in aromatic substituted [12-13]. Furthermore, the aliphatic protons of -CH₃ groups attached at C-4 were resonated at around 4.43.

The ¹³C-NMR spectrum of azo ligand showed multiple peaks at 75 ppm related to -CH₃ aliphatic carbon atom and 96 ppm related to -C=OH moiety [12-13]. The peaks at 125–135 ppm may be related to resonance of aromatic carbon atoms while the deshielded -C=N=N- and -C=C- of coumarin may be assigned to effect of withdrawing groups and showed at 145–165 ppm, respectively. As well as the H-NMR spectrum of CdL complex displayed remarkable changes in some resonated aromatic protons and disappearance of -OH moiety. These data of NMR confirmed the coordination of Cd(II) ion with the HL azo dye through -C=N- and OH with deprotonation in the chelation reaction. As well as the deshielded protons of -HC=CH- of chromene ring and hydrated water molecules was downfield shifted due to the electron donation of the active site toward the empty orbitals of Cd(II) ion [16-17].

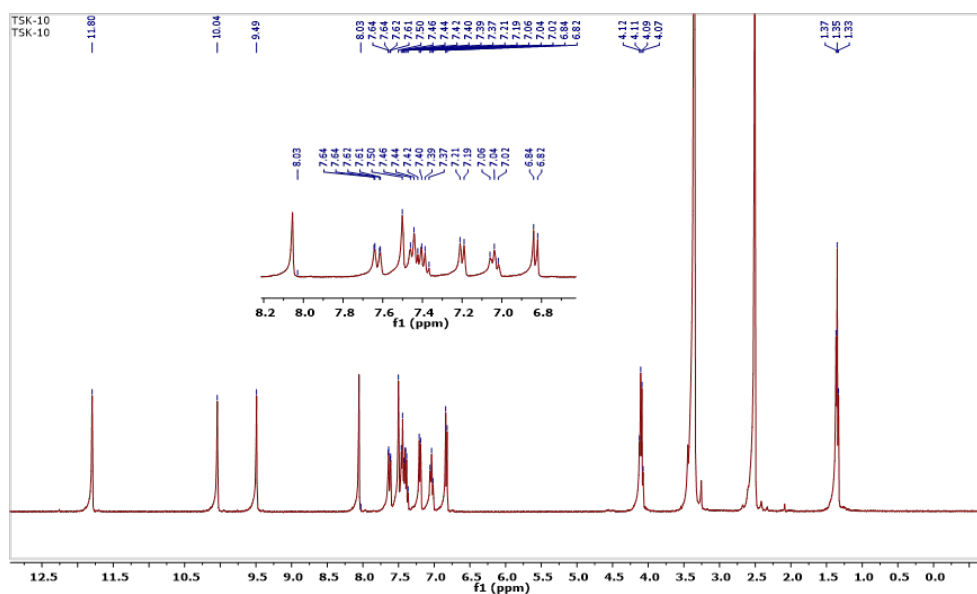


Fig 1. H NMR of azo ligand in DMSO- d_6 solvent

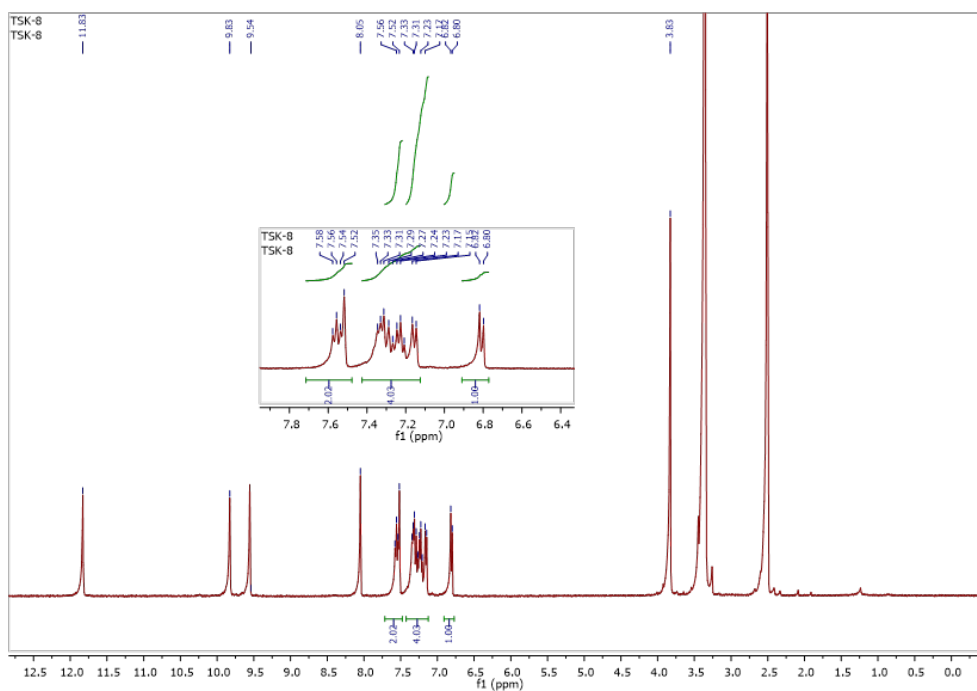


Fig 2. H-NMR of CdL complex in DMSO- d_6 solvent

IR Spectra of the Ligand and Complexes

The IR spectra of the synthesized complexes in CsI were compared with that of the azo dye. The spectra of the complexes showed the absorption bands characteristic of the ligand with some differences ascribed to the formation of respective ion associated, which showed the more characteristic infrared spectral bands of the free ligand

and its complexes. The broad absorption at 3500 cm^{-1} is assigned to $-\text{OH}$ of coumarin azo ligand. The strong band at 1651 is associated to $-\text{C}=\text{O}$ of chromene ring while the strong band at 1623 cm^{-1} is associated with $-\text{CH}=\text{CH}-$ of aromatic and $-\text{rings}$ respectively [12,15] as given in Fig. 3. The appearance of new band at 1477 cm^{-1} confirms the formation of azo $-\text{N}=\text{N}-$ moiety. The remarkable changes

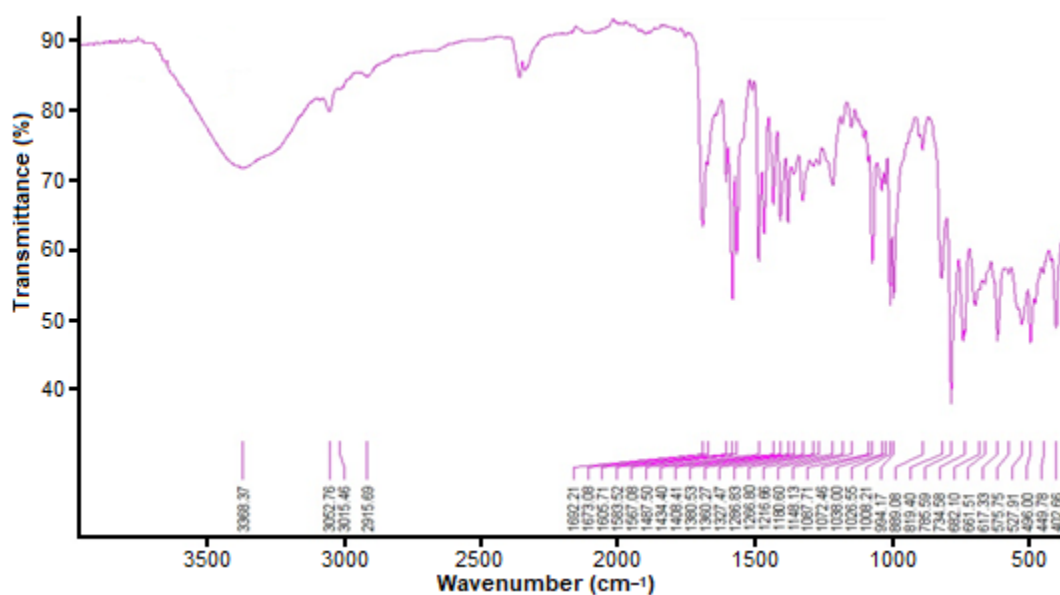


Fig 3. FT-IR spectrum of azo dye, HL in KBr disc

on $-N=N-$ to lower frequencies at $1450-1433\text{ cm}^{-1}$ confirm the coordination of ligand via nitrogen atom with $M-N$ formation beside the $-C=O$ shift and supports the bi dentate neutral ligand behavior as shown in Fig. 3. The vanadyl complex in Fig. 4 exhibits new band at 950.633 and 590 cm^{-1} confirming $V=O$ and $V-N$ bands [14-17].

Electronic Spectra and Magnetic Susceptibility

The azo ligand showed one strong absorption around 379 nm which was assigned to intra-ligand charge transfer of $-N=N-$ moiety, then confirms the formation

of azo dye due to the high intensity band located near the visible region. On comparison the UV-Visible spectra of all complexes with the spectrum of the free ligand in DMSO solvent, it is noted that the new weak bands observed at around $(490-380)\text{ nm}$ are consistent with the chelation of empty orbitals of $Hg(II)$, $Zn(II)$, $Cd(II)$ and $V(IV)$ ions [18-19] with the lone pairs of the donating atoms in the active sites of azo dye. The intra-ligand charge transfer of $-N=N-$ moiety was shifted to longer or shorter wavelengths due to the linkage of lone

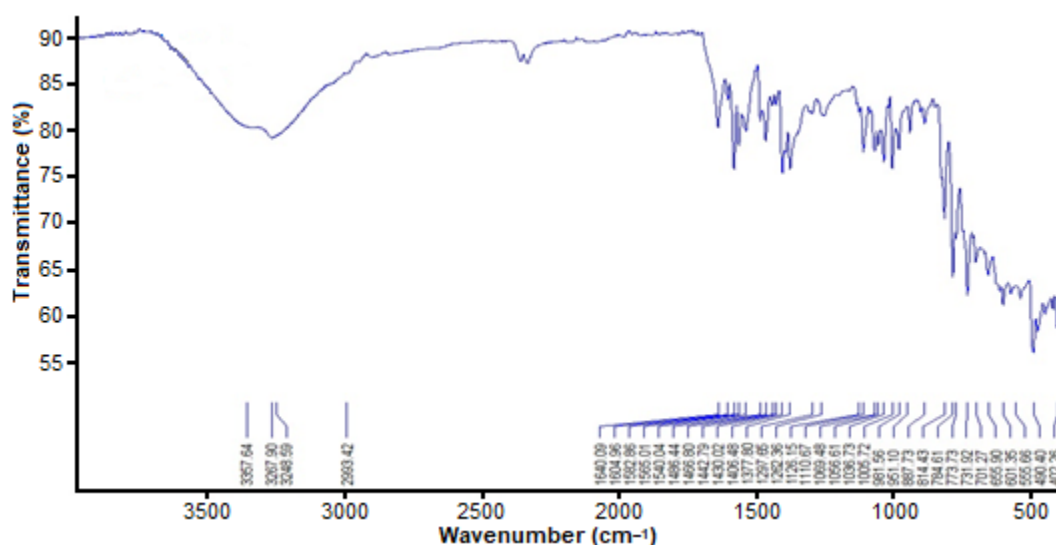


Fig 4. FT-IR spectrum of VOL complex in CsI disc

pair to the empty orbitals of metal ions in the region (380–500) nm, Table 2. The diamagnetic properties of zinc (II), cadmium (II) and mercury(II) complexes with the association of elemental analyses confirm the tetrahedral environment. The red solution of vanadium (IV) complex displayed two spin-allowed peaks at 650 and 490 nm that are attributed to ${}^2A_{1g} \rightarrow {}^2B_{1g}$ and ${}^2A_{1g} \rightarrow {}^2B_{2g}$ transitions respectively [20]. The value of magnetic moment of solid complex of vanadium(II) at 27 °C to 1.80 BM revealed the presence of unpaired electron in its outer level $3d^1$ and make it forms the possibility of five-coordinate complex with a bi dentate azo-dye ligand through two active site – N=N and –OH groups [18-19].

Thermal Analysis of C1 and C2 Complexes

The thermal stability of zinc(II) and cadmium(II) complexes was screened with TG-DTA analyses in the nitrogen atmosphere and presented in Table 3. The losing of weak points like M–Cl and methyl groups were shown in the first stages of analyses at range (190–270) °C temperature while the final stage of analysis for C1 complex was accomplished at (300–450) °C to give the stable phase of zinc(II) oxide [20]. As well as the hydrated cadmium(II) complex showed three stages of thermal analysis with losing of crystalline water at around (160–280) °C. The data observed from weight loss (%w) would be in agreement with the theoretical data

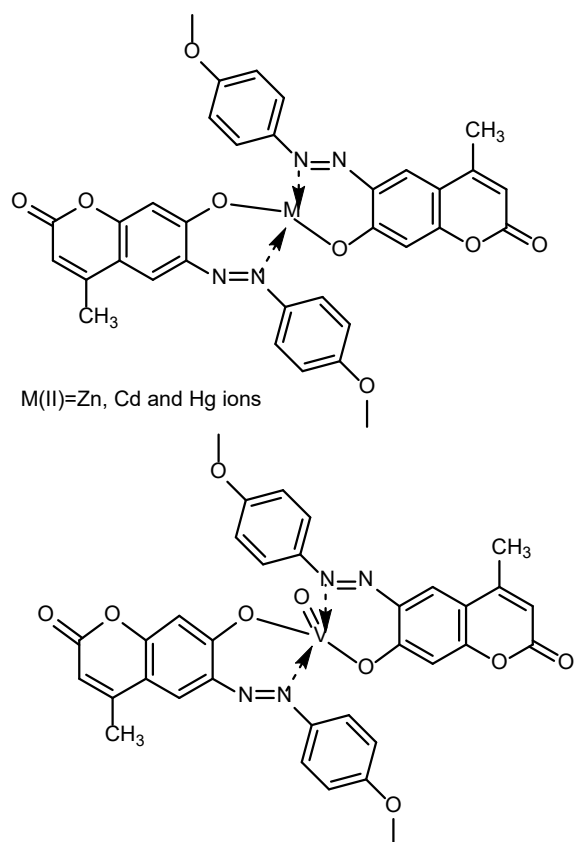
Table 2. Electronic spectra and molar extinction coefficients for complexes

Compounds	Molar Conc.	nmλ	$\Sigma \epsilon \text{L.mol}^{-1} \text{cm}^{-1}$	Assignment	μ (BM)
VOL	1×10^{-3}	655	110	${}^2A_{1g} \rightarrow {}^2B_{1g}$	1.80
		490	90	${}^2A_{1g} \rightarrow {}^2B_{2g}$	
		380	2900	LMCT	
ZnL	1×10^{-4}	455	8000	MLCT	Dia
		390	27000	INCT	
		280	13000	$\pi \rightarrow \pi^*$	
CdL	1×10^{-5}	500	20000	INCT	Dia
		470	12700	MLCT	
		250	3000	$\pi \rightarrow \pi^*$	
HgL	1×10^{-5}	455	11700	MLCT	Dia
		300	10000	INCT	

Dia = Diamagnetic, LMCT and MLCT are charge transfer from ligand to metal or vice-versa, and INCT = Intra-ligand charge transfer bands

Table3. Thermo gravimetric analysis (TGA) of the metal complexes

No.	Molecular formula	Temp. range (°C)	Mass loss%		Assignment
			Found	Calc.	
C1	[ZnL ₂]	190–270	6.43	8.66	Loss of Cl and –OH, –2OCH ₃
		300–450	33.84	3160	Further dissociation of the organic ligand (C ₈ H ₆ N ₂) with formation of ZnO + Zn ₃ N ₂ as final product
		160–280	16.01	17.08	
C2	[CdL ₂].2H ₂ O	290–390	10.06	9.14	Loss of 2 hydrated H ₂ O molecules, –OCH ₃
		400–560	52.13	52.26	Loss of phenyl, 2Cl anion and decomposition of the organic (2C ₆ H ₇ N ₂ O)
		441–541	15.16	14.25	Loss of (C ₆ H ₅ CH ₃)
		541–930	6.16	5.43	Further dissociation of the organic ligand (2C) with formation of CdO as final product



Scheme 2. Structures of metal complexes

and supports their structures [21-22].

■ CONCLUSION

According to the results obtained from elemental analyses, FT-IR, NMR and EI-MS spectra and electronic spectra in ethanol and DMSO solvents, the tetrahedral geometry was identified for zinc(II), cadmium(II) and mercury(II) complexes, while the vanadium(IV) complex was square-pyramid of five coordination number via optimization the mole ratios 2:1 of ligand azo to the metal ion. The thermal analyses and molar conductivity measurements confirmed the square-pyramid around vanadium(IV) ion and tetrahedral environment around zinc(II), cadmium(II) and mercury(II) ions, Scheme 2.

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