

# Preparation and Spectroscopic Studies of Some Metal complexes with Azo ligand derived from 2-aminobenzothiazole and 4-Hydroxycoumarin

Abbas Bayader F., Abdulla Zeyad S. and Abid Al-jibouri Mahmoud N.\*

Department of Chemistry, College of Science, Mustansiriyah University, Baghdad, IRAQ

\*mahmoud\_inor71@uomustansiriyah.edu.iq

## Abstract

The present study describes the synthesis and characterization of some transition metal complexes derived from azo ligand derived from condensation 4-hydroxycoumarin and 2-aminobenzothiazole. The azo ligand was characterized by C.H.N.S elemental analyses, GC-Mass spectroscopy, <sup>1</sup>H NMR and FT-IR spectra. The metal complexes with the new azo dye were isolated by the direct reactions of the metal chlorides of cadmium(II), zinc(II), cobalt(II), nickel(II) and copper(II) ions with the alkaline solution of free ligand to afford the following complex  $[ML(H_2O)_2Cl]$  where  $M=Co(II)$ ,  $Cd(II)$ ,  $Cu(II)$  and  $Zn(II)$ .

The results obtained from FAAS, elemental analyses, UV-visible spectra, LC-MS and magnetic susceptibility measurements confirmed the tetrahedral environment for  $[CdLCl]$  complex and octahedral environment around copper(II), cobalt(II) and nickel(II) complexes. The time and mole ratios factors were studied to recommend the optimized conditions of metal complexes formations and the observed data was investigated for the deprotonation of the azo-dye at pH 6-7.0 with 6.5 minutes as time of reaction to afford the crystalline complexes.

**Keywords:** Azo benzothiazole ligands, transition metal complexes, 2-aminobenzothiazole, azo ligands.

## Introduction

The azo dyes are considered to be one of the most common compounds used as ligands. These ligands have high tendency towards many metal ions, since stable chelated complexes of five- or six- membered rings were usually formed<sup>1,2</sup>. The coordination chemistry of cobalt(II), copper(II) and nickel(II) ions with azo ligands is of interest in the pharmaceutical and analytical fields<sup>3,4</sup>. The presence of azo group with a lone pair of electron on the nitrogen atoms provides a binding site for coordination with the metal ion.

Other coordination sites may also be provided represented by the presence of other donor atoms such as nitrogen, oxygen or sulfur on the aromatic rings on both sides of the azo group<sup>5,6</sup>. The poly dentate ligands of thiazole azo derivatives have focused on the coordination chemistry of catalysts and LED industry<sup>7,8</sup>. The five and six coordinate

numbers of 3d-complexes with azo ligands have interested many researchers to afford novel geometry and poly nuclear cluster complexes.<sup>9,10</sup>

## Material and Methods

**Apparatus:** The melting points of the ligand and metal complexes were determined by Stuart melting point apparatus. The molecular weights of the ligand and some selected metal complexes were measured by their mass spectra on the methods Shimadzu model GC MS QP 1000EX. The UV-Visible spectra of azo dye solution and its complexes in ethanol and DMSO solvents were measured on UV-1800 Shimadzu spectrometer apparatus in the range 200-1000 nm. The nuclear magnetic resonance spectroscopy was carried out in *d*<sub>6</sub>-DMSO solvent on Bruker-400 MHz NMR spectrometer at A-Bait University, Amman, Jordan.

The main features of vibration frequencies of azo dye ligand and its metal complexes were scanned on Shimadzu FT-IR spectroscopy in the range 4000-200 cm<sup>-1</sup>. The pH of the solutions was measured by 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. The magnetic susceptibility of the solid complexes was measured by Bruker Magnetic Balance at room temperature via Farady's method at Mustansiriyah University, College of Science, Chemistry Department. The starting 2-aminobenzothiazole and 4-hydroxycoumarin were supplied by Merck Company and the metal salts of CoCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O, ZnCl<sub>2</sub> and CdCl<sub>2</sub> were supplied by Sigma Aldrich Company, Amman, Jordan.

**Synthesis of Azo Ligand:** The azo dye was synthesized according to the modified classical procedure established in literature by dissolving 1.88 g, 0.01mmoles from 2-aminobenzothiazole in absolute ethanol (10 ml) followed by addition of 12% (v/v) HCl (5 ml). To this solution, a cooled aqueous solution of sodium nitrite (0.55, 6 m moles) was added by maintaining the temperature of the reaction at 0-2 °C. The formed diazonium salt was gradually added to an alkaline solution of 0.02 moles, 3.22 g of 4-hydroxycoumarin with stirring for 45 minutes. After that the resulting solution was neutralized to pH to about 6.5 by drop wise addition of 10% sodium hydroxide. The pale red precipitate filtered, washed several times with water and ethanol and then dried as in scheme 1. The re-crystallization from hot ethanol afforded dark orange crystals of azo dye ligand.

**Synthesis of metal complexes:** The metal complexes were prepared by dissolving  $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$  (10 m moles, 0.171 g) or  $\text{CdCl}_2$  (1 m mole, 1.118 g) in (15 mL) hot water and ethanolic solution of (20 m moles, 2.44 g) of azo dye. The mixture was stirred on water bath for 1 hour, then dark red and brown precipitates of zinc(II) and cadmium(II) complex were separated and filtered off. The complexes of cobalt (II) and nickel (II) were precipitated on refluxing equal moles quantities of their metal chlorides with azo dye solution in hot ethanol for about 30-50 minutes and then kept for several hours at room temperature to settle down the pure colored complexes and dried in oven at 120-150 °C. The brown crudes were isolated and then washed several times with hot ethanol and diethyl ether as in table 1.

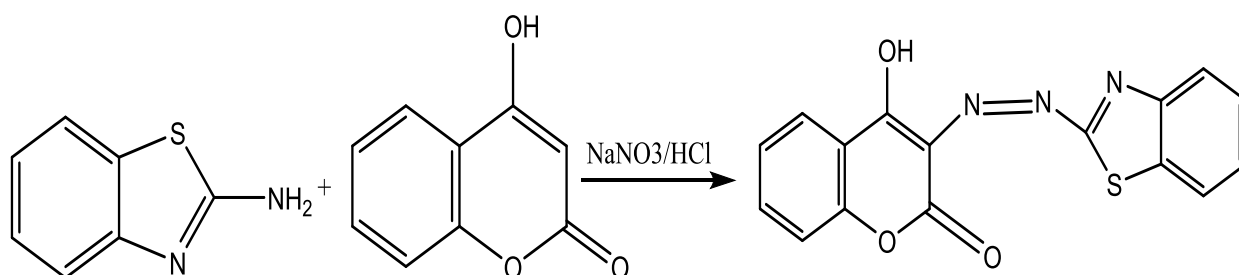
## Results and Discussion

**Physical Properties and elemental analyses:** Table 1 shows the physical properties of ligand and its complexes and shows the thermal stability of almost all the complexes through the elevated decomposition points. All the complexes are colored and sparingly soluble in most organic

solvents except DMSO and DMF. The micro-analyses (C.H.N.) revealed the suggested chemical formula for all complexes besides the structure of azo dye. However, the calculation of mole ratios was in good agreement with their formation procedure and stoichiometry and it is based on flame atomic absorption data.

The molar conductivity measurements reveal that all complexes do not show electrolytic nature<sup>13</sup> except cadmium(II) complex solution in DMF which exhibits conductivity motion due to the presence of sulfate counter ion in the structure<sup>13,14</sup>.

**Mass Spectra:** The mass spectrum of azo-dye ligand showed peak at molecular ion  $m/e=346$  which indicates the unstable molecular weight of the expected  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_4$  formula due to losing of OH moiety<sup>15</sup>. The association of methyl radical to the chemical structure of azo dye in the gas phase has resulted in increasing the molecular weight of the expected chemical formula. The low intensity peaks at  $m/e=289$  and 246 may be assigned to the fragmentation of  $-\text{OH}$  and  $-\text{CH}_3$  moieties respectively as in figure 1.



Scheme 1: Synthesis of azo dye, HL

Table 1  
Physical properties and analytical data of the azo dye and its metal complexes.

No	Compound	Color	M.wt	Yield %	M.p c°	Micro Elemental Analysis Found (calc.)				Metal content Found (calc.)
						C%	N%	H%	S%	
L	$\text{C}_{16}\text{H}_9\text{N}_3\text{O}_3\text{S}$	Pale red	322	80	188-190	(60.8) 59.05	(13.5) 12.58	(3.66) 2.56	(8.28) 7.49	-
C1	$\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2\text{Cl}$	Red	455.30	88	155 Dec.	(55.89) 54.98	(16.86) 17.78	(4.26) 4.34	(6.20) 6.98	(13.38) 12.61
C2	$\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2\text{Cl}$	Orange	488.30	95	295 Dec.	(56.50) 55.30	(13.76) 14.43	(4.22) 3.13	(6.14) 5.27	(11.20) 10.80
C3	$\text{Co}(\text{L})_2(\text{H}_2\text{O})_2\text{Cl}$	Brown	477.90	77	288 Dec.	(40.46) 40.78	(13.49) 12.99	(4.49) 4.55	(5.99) 5.37	(11.42) 10.22
C4	$\text{Zn}(\text{LCl})$	Brown	418.90	88	299 Dec.	(40.96) 40.54	(14.62) 15.78	(3.41) 3.36	(6.06) 5.43	(15.81) 14.72
C5	$\text{Cd}(\text{L})\text{Cl}$	Red	490.06	70	300 Dec.	(40.50) 40.32	(12.50) 13.22	(3.37) 3.21	(6.00) 5.49	(17.07) 16.86

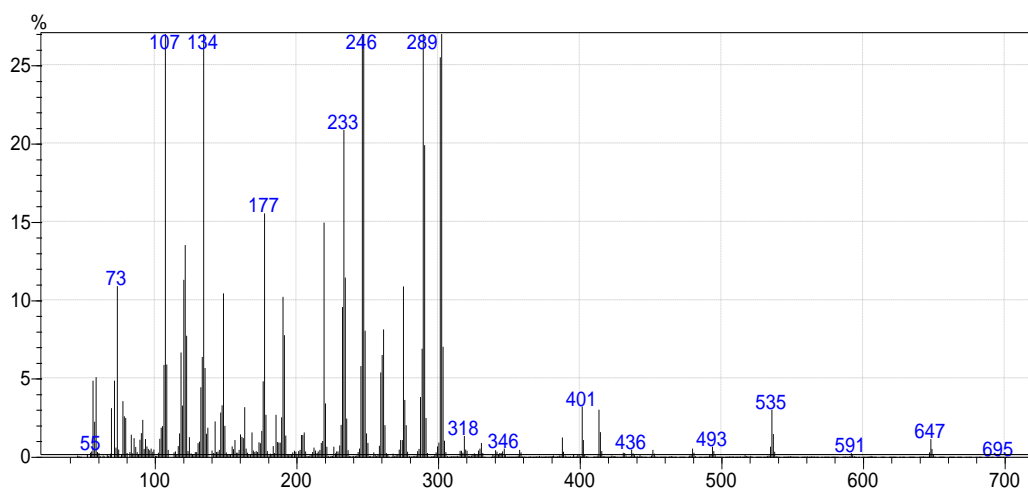


Figure 1: MS spectrum of azo dye

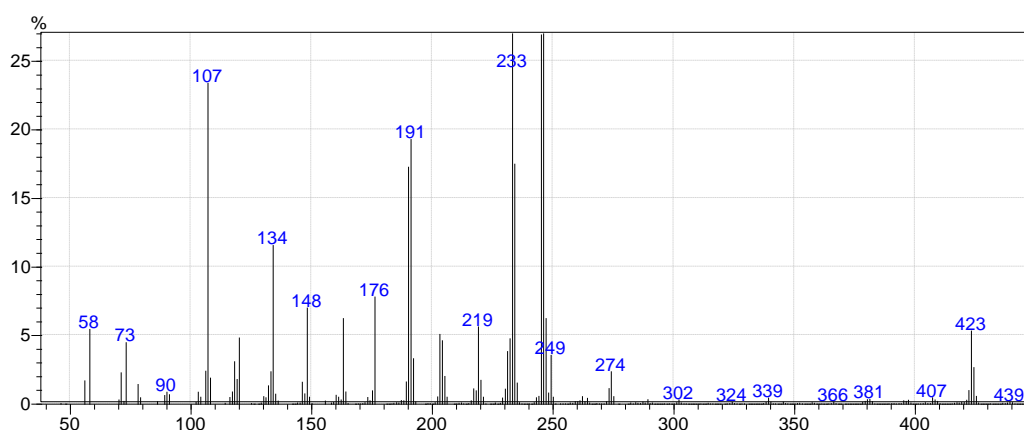


Figure 2: MS spectrum of [CdLCl] complex

The MS spectrum of cadmium(II) complex showed molecular ion at  $m/e=423$  with low relative intensity ( $I=10\%$ ) due to the unstable phase of  $[\text{CoLCl}_2]^+$  ion and the variable peaks at 274, 191 and 233 confirmed the cleavage of water molecules and Cl ion respectively<sup>16</sup>.

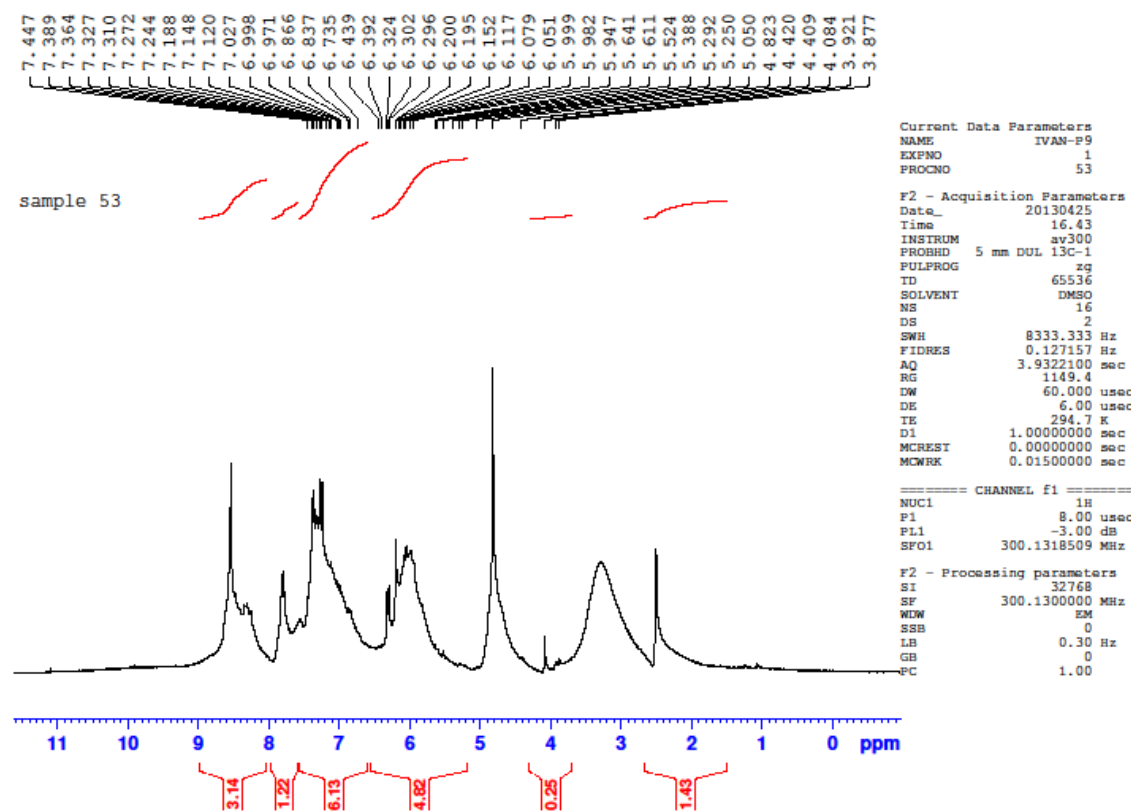
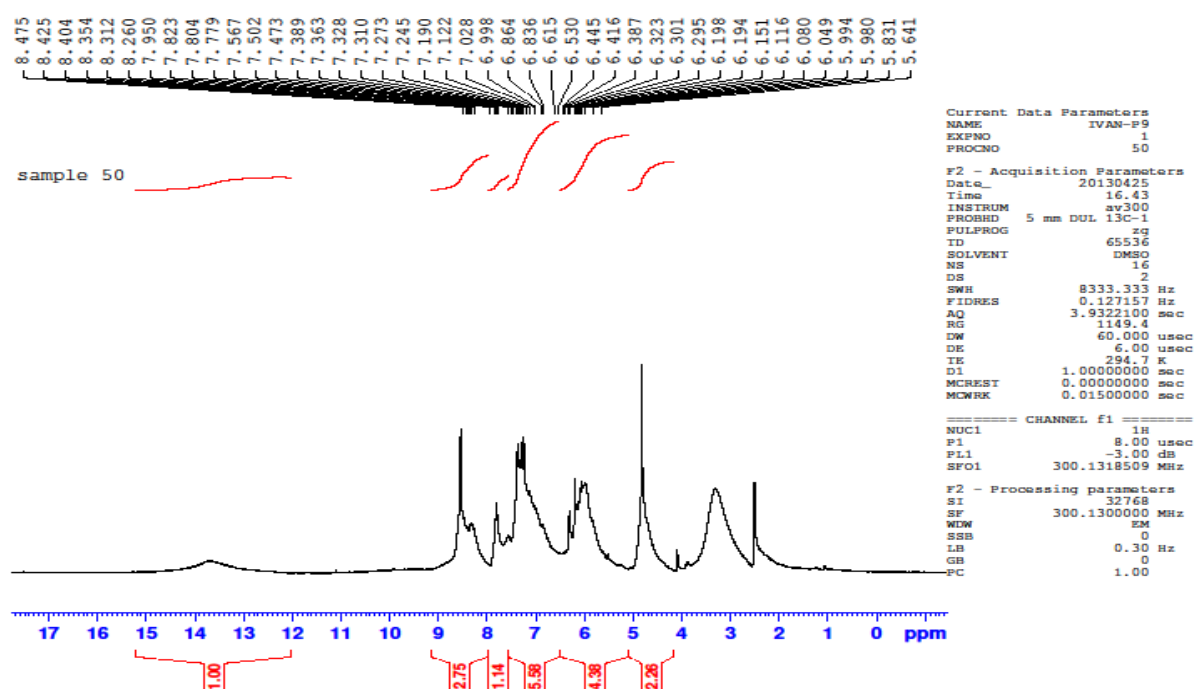
The appearance of molecular ions in the free ligand and its metal complexes supports mainly the proposed structures of the azo ligand and the isolated complexes as in figure 2.

**NMR Spectra:** The  $^1\text{H}$  NMR was displayed only for the azo dye with chemical shifts in ppm units 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  $^1\text{H}$  NMR spectrum of the ligand as in figure 3 shows a singlet signal at  $\delta$  (8.22) ppm corresponding to the  $-\text{C}=\text{C}-\text{H}$  of coumarin ring. The residual solvent  $d_6$ -DMSO peak has been observed at 2.5 and 3.40 ppm. The characteristic sharp peaks of aromatic protons of benzothiazole ring were absorbed at 6.8-7.90 ppm. The peak at around  $\delta$  11.50 ppm was also recorded in the ligand spectrum due to the  $-\text{OH}$  proton that is directly attached to C4 of coumarin ring. The doublet of doublet peaks at around  $\delta$  (8.90) ppm reflects mainly the spin coupling of aromatic protons adjacent to

each other in aromatic substituted chromene-2-one moiety ring<sup>14,15</sup>.

The  $^1\text{H}$  NMR spectrum of CdL complex in  $d_6$ -DMSO showed remarkable changes in the chemical shifts of active sites like disappearance of  $-\text{OH}$  due to coordination of  $\text{Cd}^{2+}$  ion with the lone pairs of OH and  $-\text{N}=\text{N}-$  groups. However, the shift in the chemical shifts of Ar-H and benzothiazole protons to region (6.33-8.30) ppm supports the formation of complex CdLCl as in figure 4.

**IR Spectra of the Ligand and Complexes:** The FT-IR spectrum characterized a new ligand L and its complexes showed new bands at 3300, 2712, 1590-1480 and 1290  $\text{cm}^{-1}$  indicating the vibration modes  $\nu(\text{OH coumarin})$ ,  $\nu(\text{C}-\text{H})$ ,  $\nu(\text{N}=\text{N})$  and  $\nu(\text{C}-\text{O})$  respectively. The comparison of ligand spectrum with FT-IR spectra of all prepared metal complexes showed the shift of  $\nu(\text{N}=\text{N}-)$  and  $\nu(\text{C}=\text{C}-)$  imine in their positions and changed the shape or intensity of band compared with the ligand (L) attributable to the coordination of this ligand with the metal ions and gave an indication that the complexes were formed. These remarkable changes would have given strong evidences for the active sites of azo  $-\text{N}=\text{N}-$  moiety and oxygen  $-\text{C}-\text{O}$  leading to stable six-member ring up on chelation.

Figure 3:  $^1\text{H}$  NMR of azo ligand in  $\text{DMSO}-d_6$  solventFigure 4:  $^1\text{H}$  NMR of CdL complex in  $\text{DMSO}-d_6$  solvent

The observed absorptions at around 1619-1614  $\text{cm}^{-1}$  and 1211-1235  $\text{cm}^{-1}$  and a singlet at 3160  $\text{cm}^{-1}$  confirming the presence of coordinated water molecules in the inner sphere of cobalt(II), nickel(II) and copper(II) complexes<sup>18,19</sup>. The results of IR spectra concluded that the azo ligand, (L) behaves as mono basic bi dentate ligand through nitrogen of azo group ( $-\text{N}=\text{N}$ ) and (OH phenolic). However, the new weak bands at 550-200  $\text{cm}^{-1}$  are associated with (M-N), (M-O) and (M-Cl) coordination bonds<sup>20,21</sup>.

However, the appearance of strong absorption at around 3400  $\text{cm}^{-1}$  in the IR spectra of Cd(II) and Zn(II) complexes indicates the participation of  $-\text{C}=\text{O}$  in coordination to the metal ions with neutral behavior. The lowering in the wavenumbers of  $-\text{C}=\text{O}$  of chromene ring to 1680-1675  $\text{cm}^{-1}$  regions investigates the linkage of such moiety to Zn(II) and Cd(II) ion resulting in stable five-member ring<sup>18,21</sup>.

### Electronic Spectra and Magnetic Susceptibility Measurements:

The electronic spectrum of the azo dye ligand in DMSO within the range (200-1000) nm display mainly two peaks. The first at (288 nm) was assigned to the moderate energy  $\pi \rightarrow \pi^*$  transition of the aromatic rings. The broad ( $\lambda_{\text{max}}$ ) peak at (390 nm) was related to the  $\pi \rightarrow \pi^*$  transition of intermolecular charge-transfer taken place through the azo group ( $-\text{N}=\text{N}-$ ).

On comparing 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 nm are consistent with the chelation of empty orbitals of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions<sup>21</sup> with the lone pairs of the donating atoms in the active sites of azo dye. The intra-ligand charge transfer of  $-\text{N}=\text{N}-$  moiety was shifted to longer or shorter wavelengths due to the linkage of lone pair to the empty orbitals of metal ions in the region (380-500) nm as in table 2.

The diamagnetic properties of zinc (II) and cadmium (II) complexes with the association of elemental analyses confirm the tetrahedral environment. The red solution of nickel (II) complex displayed two spin-allowed peaks at 622 and 480 nm that are attributed to  $^3\text{A}_{2g} \rightarrow ^3\text{T}_{2g}$  and  $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}$  transitions respectively<sup>11,20</sup>. The value of magnetic moment of solid complex of nickel(II) at 27 °C to 2.80 BM revealed the presence of two unpaired electron in its outer level 3d<sup>8</sup> and forms the possibility of six-coordinate complex with a bi dentate azo-dye ligand through two active site –  $\text{N}=\text{N}$  and  $-\text{OH}$  groups<sup>19,20</sup>.

The cobalt complex showed two-spin allowed transitions at around 575 and 388 nm assigning to  $^4\text{T}_{1g} \rightarrow ^4\text{T}_{2g}$  and  $^4\text{T}_{1g} \rightarrow ^4\text{T}_{1g}(\text{P})$  transitions respectively. The experimental value of magnetic moment of cobalt(II) complex was at 4.90 BM confirming the presence of orbital contribution of octahedral geometry of this complex as in table 2. The distorted octahedral complex of CuL was concluded from the appearance of broad absorption at 800 nm beside the CT band at 355 nm (Cl-Cu) charge transfer<sup>20</sup>.

### Thermal Analysis of Cobalt(II) and Nickel(II) complexes:

The TG analyses of cobalt (II) and nickel (II) complexes were screened at inert nitrogen gas and average heating (10 °C per minute) with DTA curves that confirmed the thermal stability of the prepared complexes as in figure 5. The TG curves at around (120-180) °C and (188-279) °C for CoL and NiL complexes are attributed for fragmentation of coordinated water molecules in the inner-sphere of their structures with % weight loss 4.43 and 12.06 respectively<sup>22,23</sup>. The agreement of weight losing in the TG curves afforded the suggested structures as in figure 6. However, the cleavage of chlor ions in the step-wise TG curves with exothermic processes indicate the strong point of Co-Cl and Ni-Cl bonding comparing with metal-OH moiety as in table 3.

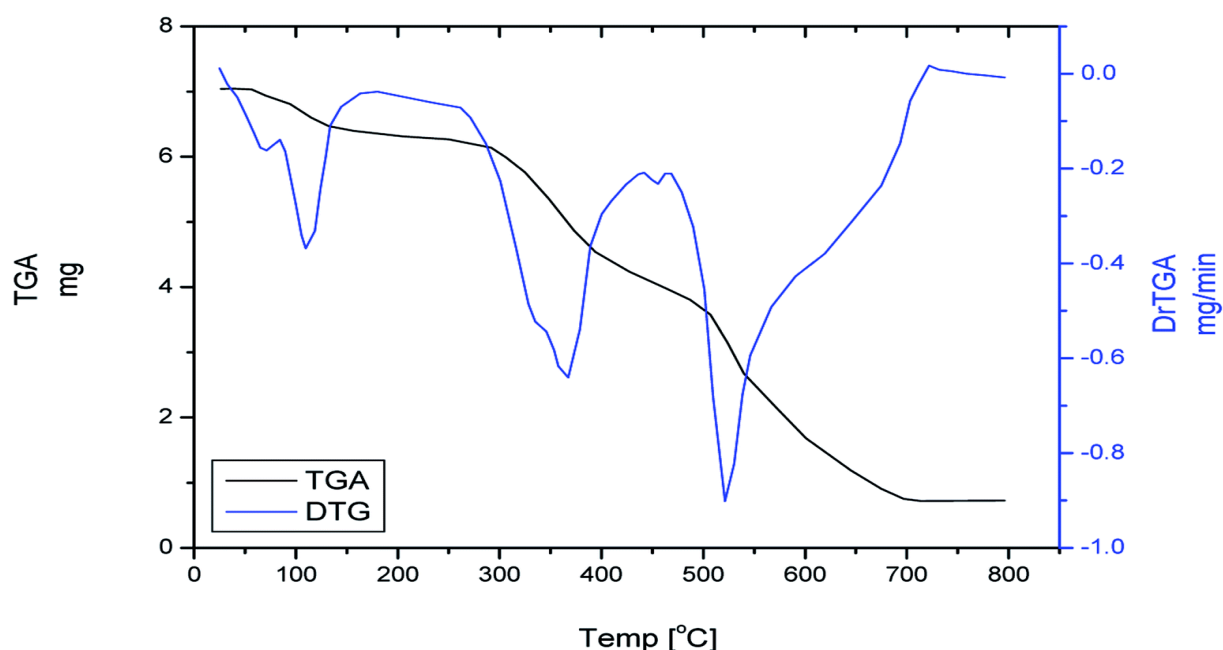
Table 2  
Electronic spectra and molar extinction coefficient ( $\text{\AA}$ ) for complexes

Compounds	Molar Conc.	nm $\lambda$	$\text{\AA}\cdot\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$	Assignment	$\mu$ (BM)
C1	$1 \times 10^{-3}$	622 480 365	8000 27000 13000	$^3\text{A}_{2g} \rightarrow ^3\text{T}_{2g}(\text{F})$ $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{F})$ LMCT	2.80
C2	$1 \times 10^{-4}$	575 388 289	110 90 2900	$^4\text{T}_{1g} \rightarrow ^4\text{T}_{2g}(\text{F})$ $^4\text{T}_{1g} \rightarrow ^1\text{T}_{1g}(\text{P})$ LMCT	4.90
C3	$1 \times 10^{-5}$	800 355 250	20000 12700 3000	$^2\text{E}_g \rightarrow ^2\text{T}_{2g}(\text{D})$ MLCT $\pi \rightarrow \pi^*$	1.80
C5	$1 \times 10^{-5}$	455 300 260	30100 12700 19020	MLCT INCT $\pi \rightarrow \pi^*$	Dia
C5	$1 \times 10^{-5}$	455 300	11700 10000	MLCT INCT	Dia

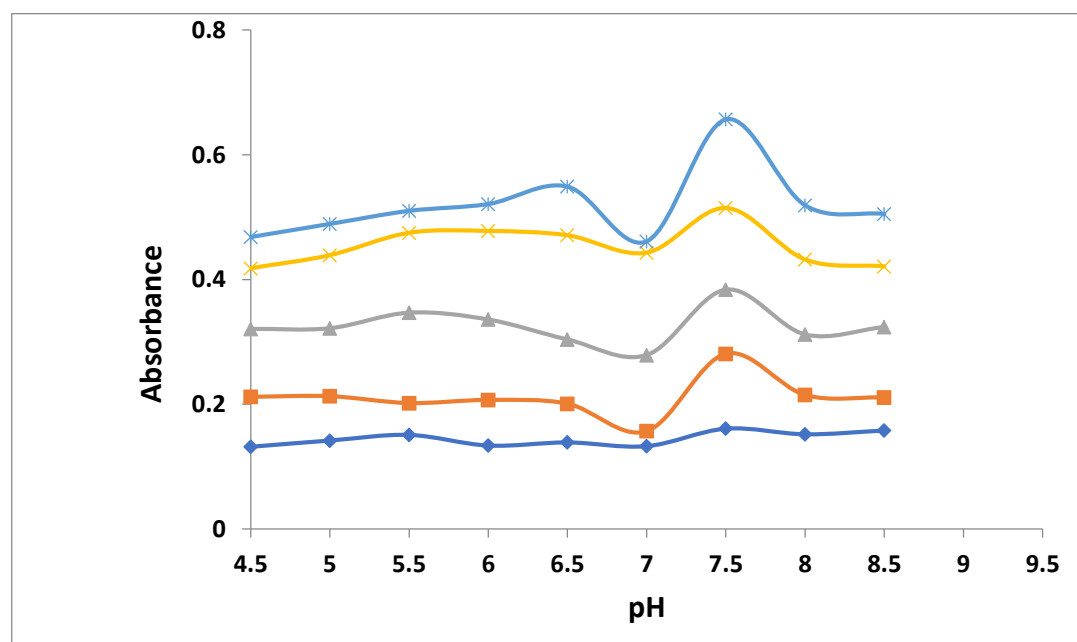
Dia=Diamagnetic, LMCT and MLCT are charge transfer from ligand to metal or vice-versa

**Table 3**  
**Thermo gravimetric analysis (TGA) of the metal complexes**

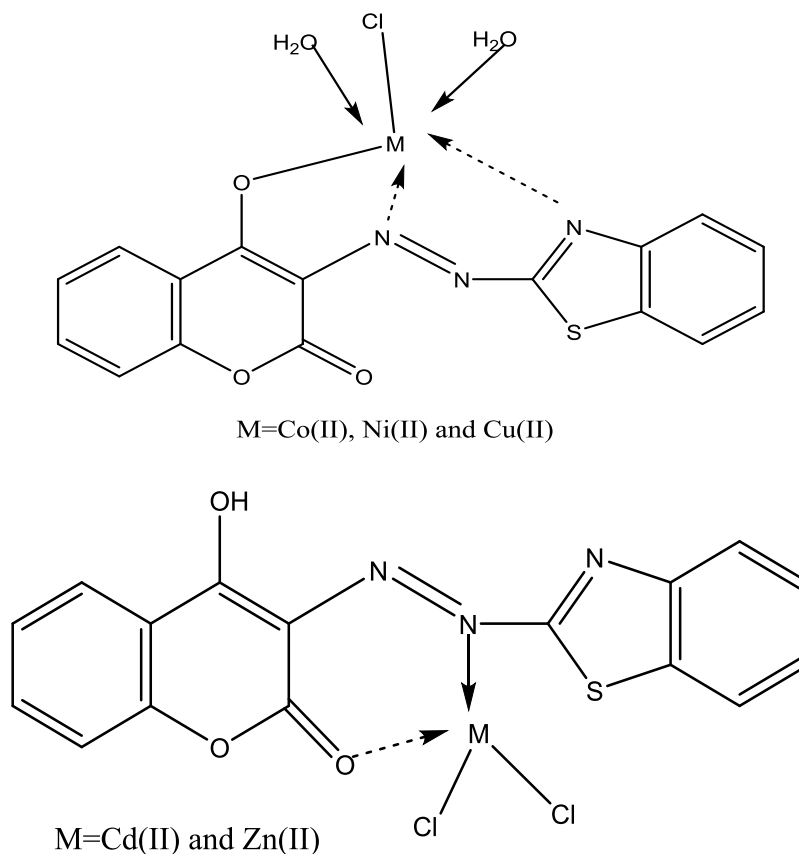
S.N.	Molecular formula	Temp. range (°C)	Mass loss%		Assignment
			Found	Calc.	
C1	[NiL]	120-180	4.43	5.66	Loss of H <sub>2</sub> O
		210-370	40.84	38.60	Further dissociation of the organic ligand and -Cl
		380-500	19.01	18.08	with formation of NiO + Ni <sub>3</sub> N <sub>2</sub> as final product
C2	[CoL]	188-279	12.06	13.14	Loss of 2 hydrated H <sub>2</sub> O molecules, -Cl
		300-420	41.13	40.26	Loss of phenyl, 2Cl anion and decomposition of the organic (2C <sub>6</sub> H <sub>3</sub> N <sub>2</sub> O)
		441-541	15.16	14.25	Loss of (C <sub>6</sub> H <sub>5</sub> O)
		541-930	5.16	4.43	Further dissociation of the organic ligand with formation of CoO as final product



**Figure 5: TG-DTA analysis of [CoLCl(H<sub>2</sub>O)<sub>2</sub>] complex at N<sub>2</sub> gas**



**Figure 6: Effect of pH on absorbance at  $\lambda_{\max}$  for Cu(II)-Ligand mixed solutions in different molar concentrations**



Scheme 2: Geometry of the prepared complexes

**Dependence of stability complexes on pH of solution:** The optimum concentration was chosen for complex solutions giving rise to a constant ( $\lambda_{\max}$ ) at different pH for composition of the copper(II)-azo dye complex. The absorbance and  $\lambda_{\max}$  of the complex solution were determined at different pH and concentrations. It is obvious that the concentration of  $1 \times 10^{-3} \text{M}$  is the optimum concentration. The influence of the pH was also studied at pH range 5.0-8.0. The absorbance pH curve as in figure 6 was carried out at certain ( $\lambda_{\max}$ ) and several concentrations. The curve exhibits a broad plateau at pH range (6-8.5) representing the presence of one species in the solution at this pH range. The descending part of the curves may represent the dissociation of the complex formed at basic medium. However, the results suggest pH 7.5 as an optimum pH for the formed complex in solution<sup>21,22</sup>.

## 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 octahedral geometry was approved for cobalt(II), nickel(II) and copper(II) whereas the cadmium(II) and zinc(II) complexes were having tetrahedral geometry with chelation of the ligand azo through oxygen of carbonyl and nitrogen of  $-\text{N}=\text{N}-$ . The TG-DTA analysis confirms the stability of metal complexes and it was proposed that the ligand behaves as mono basis tri dentate Lewis base through  $-\text{N}-\text{N}$  and  $-\text{O}-$  and  $-\text{C}=\text{N}-$  of benzothiazole ring moiety.

The IR spectra results approved the neutral behavior of azo dye up on linkage with both zinc(II) and cadmium(II) ions while the behavior of azo dye with cobalt(II), nickel(II) and copper(II) ions was monobasic through deprotonation of the hydroxyl moiety and donation of lone pairs of  $-\text{N}=\text{N}-$  group as in scheme 2.

## Acknowledgement

Authors appreciate all support and efforts provided by chemistry department, College of Science, Mustansiriyah University for measurements of mass spectroscopy and magnetic susceptibility. Authors are also grateful to the members of Al-Bait University, Amman for NMR measurements.

## References

1. Abdou M.M., 3-Acetyl-4-hydroxycoumarin: Synthesis, reactions and applications, *Arab. J. Chem.*, **10**, S3664-S3675 (2017)
2. Abdel-Aziz H.A., Elsaman T., Attia M.I. and Alanazi A.M., The reaction of ethyl 2-oxo-2 H-chromene-3-carboxylate with hydrazine hydrate, *Molecules*, **18**(2), 2084-2095 (2013)
3. Alghool S., Metal complexes of azo coumarin derivative: synthesis, spectroscopic, thermal and antimicrobial studies, *J. Coord. Chem.*, **63**(18), 3322-3333 (2010)
4. Al-Jibouri M.N., Synthesis and characterization of transition metal complexes with azo ligand derived from 4-hydroxy-6-methyl-2-pyranone, *Eur. Chem. Bull.*, **3**(5), 447-451 (2014)

5. Abd El-Wahab Z. and Mohamed G.G., Salisaldehyde-2-aminobenzimidazole Schiff base complexes of Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), *J. Therm. Anal. Cal.*, **73**(2), 347-359 (2003)
6. Artym J., Jeleń M., Kocięba M., Morak B., Pluta B. and Zimecki K.M., Synthesis and selected immunological properties of 10-substituted 1, 8-diazaphenothiazines, *Med. Chem. Res.*, **24**(4), 1408-1418 (2015)
7. Bensalah D., Mnasri A., Chakchouk-Mtibaa A., Mansour L., Mellouli L. and Hamdi N., Synthesis and antioxidant properties of some new thiazolyl coumarin derivatives, *Green Chem. Lett. Rev.*, **13**(2), 155-163 (2020)
8. Bochmann M., Cotton F.A., Murillo C.A. and Wilkinson G., *Advanced Inorganic Chemistry*, John Wiley and Sons, Inc. (1999)
9. Bondle G.M., Chate A.V., Redlawar A.A., Lokwani D.K., Sarkate A.P. and Tiwari S.V., A new efficient domino approach for the synthesis of coumarin-pyrazolines as antimicrobial agents targeting bacterial D-alanine-D-alanine ligase, *New J. Chem.*, **43**(23), 9002-9011 (2019)
10. Jadhav Bhaskar L., Kasare Mangesh S., Dhavan Pratik P. and Suresh D.P., In-vitro antibacterial activity of Ni(II), Cu(II) and Zn(II) complexes incorporating new azo-azomethine ligand possessing excellent antioxidant, anti-inflammatory activity and protease, "In-vitro antibacterial activity of Ni (II), Cu (II) and Zn (II) complexes incorporating new azo-azomethine ligand possessing excellent antioxidant, anti-inflammatory activity and protective effect of free radicals against plasmid DNA, *Synth. Commun.*, **49**(23), 3311-3323 (2019)
11. Burkhardt A., Buchholz A., Görls H. and Plass W., Synthesis, structure and Magnetic Properties of a Tetranuclear Copper (II) Complex on the Basis of a 2-Substituted Glucopyranoside Schiff Base Ligand, Wiley Online Library (2006)
12. Carceller E., Novel azo derivatives as prodrugs of 5-aminosalicylic acid and amino derivatives with potent platelet activating factor antagonist activity, *J. Med. Chem.*, **44**(18), 3001-3013 (2001)
13. Chavan S.S., Sawant V.A., Sawant S.K. and Yamgar B.A., Copper (II) complexes of thiazolylazo dye with triphenylphosphine and or NCS- as coligands: synthesis, spectral characterization, electrochemistry and luminescence properties, *J. Coord. Chem.*, **62**(14), 2367-2374 (2009)
14. Cui R.R., Lv Y.C., Zhao Y.S., Zhao N. and Li N., Solid-state fluorescent materials based on coumarin derivatives: polymorphism, stimuli-responsive emission, self-assembly and optical waveguides, *Mater. Chem. Front.*, **2**(5), 910-916 (2018)
15. Gandioso A., Redesigning the coumarin scaffold into small bright fluorophores with far-red to near-infrared emission and large Stokes shifts useful for cell imaging, *J. Org. Chem.*, **83**(3), 1185-1195 (2018)
16. Govindarajan S., Ilanchelian M., Nithya P., Rajamanikandan R. and Simpson J., Solvent assisted synthesis, structural characterization and biological evaluation of cobalt (II) and nickel (II) complexes of Schiff bases generated from benzyl carbazate and cyclic ketones, *Polyhedron*, **145**, 200-217 (2018)
17. Gasser G., Metal complexes and medicine: A successful combination, *Chimia*, **69**(7-8), 442 (2015)
18. Jyothi S., Reddy E.R., Raju D.N., Swamy S.J. and Reddy E.R., Synthesis and spectral investigations of manganese (II), cobalt (II), nickel (II), copper (II) and zinc (II) complexes of new polydentate ligands containing a 1, 8-naphthyridine moiety, *Molecules*, **11**(12), 1000-1008 (2006)
19. Khan S.A. and Singh K.K., Synthesis and Characterization of Cobalt(II) Complexes with bidentate Schiff base ligand, *Res. J. Chem. Environ.*, **25**(10), 76-79 (2021)
20. Manzoor T., Niaz S. and Pandith A.H., Exploring the effect of different coumarin donors on the optical and photovoltaic properties of azo-bridged push-pull systems: A theoretical approach, *Int. J. Quantum Chem.*, **119**(18), e25979 (2019)
21. Nakamoto K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds (Part A: Theory and Applications in Inorganic Chemistry)(Volume 1A)(Part B: Applications in Coordination, Organometallic and Bioinorganic Chemistry)(Volume 1B)*, NY, John Wiley & Sons, Incorporated (1997)
22. Paidesetty S.K. and Sahoo J., Antimicrobial activity of novel synthesized coumarin based transitional metal complexes, *J. Taibah Univ. Med. Sci.*, **12**(2), 115-124 (2017)
23. Thoraya A.F. and Abdallah A.Z., Synthesis, azo-hydrazone tautomerism and antitumor screening of N-(3-ethoxycarbonyl-4,5,6,7-tetrahydro-benzothien-2-yl)-2-arylhydrazono-3-oxobutanamide derivatives, *ARKIVOC*, DOI:10.3998/ark.5550190.0009.h28, 295-305 (2008)
24. Tonelli M., Vazzana I., Tasso B., Boido V., Sparatore F., Fermeglia M., Paneni M.S., Posocco P., Priol S., La Colla P., Ibba C., Secci B., Collu G. and Loddo R. Antiviral and cytotoxic activities of aminoarylazo compounds and aryltriazene derivatives, *Bioorg Med Chem.*, **17**, 4425-4440 (2009).

(Received 20<sup>th</sup> September 2021, accepted 28<sup>th</sup> November 2021)