

Spectrochemical and Thermal Studies for Bivalent Metal Complexes of Azodye Ligand Containing Pyrimidine Ring

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Abstract - A new series of divalent metal complexes of Co(II), Ni(II), Cu(II) and Cd(II) have been prepared with (H₄L) azo ligand derived from coupling of MDA with barbituric acid affording half unit (L:M), sandwich (2L:2M) and binuclear (1L:2M) complexes. The elemental analyses, spectral methods (IR, UV-visible, ¹H NMR and ESR), magnetic moments and thermal studies were used to support the mode of bonding and geometrical structure for the ligand and its metal complexes. The IR spectral data showed that H₄L ligand binds with some metal ions in keto-enol form. The ligand behaves as a neutral bidentate moiety in Co(II) and Cu(II) complexes, while, it acts as a neutral tetradentate fashion in Ni(II) and Cd(II) chelates. The spectra revealed that azo group participates in chelation in all complexes in addition to oxygen atom of enol form or carbonyl group. The absorption data established an octahedral structure for Co(II), Cd(II) complexes, whereas, square pyramidal and square planar geometries for Ni(II) and Cu(II) complexes, respectively. The molar conductance measurements proved non-electrolytic nature for all complexes. Thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses revealed the presence of lattice EtOH in outer sphere in all complexes. The thermal decomposition of complexes occurs in two-three stages ended with the formation of metal as a final residue. ESR spectrum of Cu(II) complex demonstrates that the free electron is cited in (d_{x²-y²}) orbital.

Keywords: Azodye ligand, bivalent metal complexes, infrared spectra, electronic absorption spectra, thermal studies.

I-INTRODUCTION

The importance of pyrimidine compounds in many biological systems exists in nucleic acids found in living systems, several vitamins, antibiotics and coenzymes. The pyrimidine compounds also have therapeutic importance and are used as hypnotic drugs producing depressive effect on the central nervous system [1,2]. The existence of various binding sites in the structure of pyrimidine compounds led to their use in coordination chemistry.

Barbiturates are one of most important pyrimidine derivatives. Barbituric acid (pyrimidine-2,4,6-(1H,3H,5H)-trione) is utilized in manufacturing of pigments, dyes, plastics, polymer and vitamin B₂ (riboflavin) synthesis. Barbiturates are a type of drugs that are used as anesthetics and sleeping agents and are utilized for the treatment of anxiety, epilepsy and possess effects on the motor and sensory functions [3]. The azo compounds are chemically rich accompanied with various important biological reactions like nitrogen fixation, azo reduction monoamine

oxidase inhibition mutagenic, protein synthesis, carcinogenesis, immunochemical affinity labeling and important medical uses [4]. Azo compounds are used industrially in synthesis organic dyes due to their versatile application in various fields, such as dyeing textile fiber, biomedical studies, and advanced application in organic synthesis and high technology areas such as laser, liquid crystalline displays, and electro optical devices [5]. Azo dye derivatives were considered important compounds due to their industrial, analytical, biological and medicinal applications. They displayed antimicrobial, antifungal, anti-HCV, antioxidant, antitumor activities, antiviral and cytotoxic activities [5]. In addition to these uses, azo dyes are also used as colorimetric sugar sensors, as ligands in coordination chemistry and even in high technology fields such as electronic devices, linear and nonlinear optics, reprography, and sensors [5]. Azo dyes compounds have been utilized to determine polar graphically some trace metals such as iron, gallium, aluminum, lanthanides and are also used as chromogenic reagents in spectrophotometric analysis to estimate the trace metals in food and drinking water [6,7].

II. EXPERIMENTAL

II.1. Materials and Methods

All the reagents and solvents were of analytical grade and given from Aldrich and Sigma without purification. Elemental analyses (C, H) were performed in the micro Analytical Unit of Cairo University. Cobalt(II), nickel(II), copper(II) and cadmium(II) ions were estimated by compleximetric titration against EDTA [8]. Infrared spectra of samples were recorded on a Nicolet FT-IR spectrophotometer in the range 4000-400 cm⁻¹. ¹H NMR spectrum of the ligand was measured in DMSO-d₆ on a Varian Gemini 200 NMR spectrophotometer at 300 MHz. The electron spin resonance (ESR) spectrum of copper(II) complex was recorded on a Varian E-109C model spectrometer equipped with a field modulation unit at frequency 100 kHz. Measurements were effected in the X-band on a microcrystalline powder at room temperature; the microwave power was around 10 mW. The absorption electronic spectra were measured in Nujol mulls using a Perkin Elmer Lambda 4B spectrophotometer. Molar conductivity of metal complexes was measured in DMSO solution (10⁻³ M) at room temperature using a type CD6N Tacussel conductimeter. The thermogravimetric analyses

(TG/DTG) were carried out with a heating rate of 10°C/min under N₂ atmosphere with a flowing rate of 20 mL/min using a Shimadzu DAT/TG-50 thermal analyzer. Magnetic susceptibility measurements were estimated at room temperature by Gouy method using a Johnson Matthey magnetic susceptibility balance.

Diamagnetic corrections were calculated using Pascal's constants [9]. The effective magnetic moments were calculated from the equation $\mu_{\text{eff}} = 2.84(X_M^{\text{corr}} T)^{1/2}$, where, X_M^{corr} is the molar magnetic susceptibility corrected for diamagnetism of all atoms in the compounds.

II.2. Preparation of Azo Ligand (H₄L)

A general procedure was applied. 4,4'-methylenedianiline (MDA) (0.1mol) was dissolved in (0.2 mol) of concentrated HCl soluble in 25 mL of distilled water, then, it was kept in ice bath below 5°C. After that, (0.2 mol) of sodium nitrite dissolved in 30mL of distilled water was added dropwise to the amine hydrochloride with continuous stirring to form diazonium salt. Then, it was coupled with alkaline solution containing (0.2 mol) of 2-barbituric dissolved in 20% of sodium hydroxide (50 mL) and the reaction mixture was allowed to stand in an ice bath below 5°C. The reaction mixture was diluted with hydrochloric acid till it became acidic. The product was filtered, washed several times with distilled water, then ethanol and dried in a vacuum dissector over anhydrous CaCl₂ for one day.

II.3. Preparation of Azo Metal Complexes

All the complexes were prepared in a similar way. An ethanolic solution (30mL) containing (0.2 mol) of the

appropriate metal salt was added to (0.1 mol) of azo barbituric ligand dissolved in (50 mL) ethanol. The reaction mixture was refluxed for six hours. The formed complex was filtered off, washed several times with ethanol and dried in vacuum dissector over CaCl₂ for one day.

III. RESULTS and DISCUSSION

III.1. Analytical Data

The ligand and its bivalent metal complexes were isolated in pure nature having various colors. All metal complexes did not melt up to 360°C. The elemental analyses, infrared, electronic absorption spectral data and thermal results were collected in Tables (1), (2 and 3), (4) and (5), respectively. The metal complexes are agree well with 1:1, 1:2 and 2:2 (L:M) molar ratios having different formulae. The formed complexes are air stable at room temperature and insoluble in water and common organic solvents but soluble in soluble in dimethylsulfoxide. The molar conductance values for complexes in (10⁻³ M) DMSO solution were found within range 13.8-30.6 Ω⁻¹cm² mol⁻¹ indicating non-electrolytic nature for all complexes [10].

III.2. ¹H NMR Spectrum of H₄L ligand

The ¹H NMR spectrum of ligand, displays two slightly overlapped signals at 11.8 and 12.2 ppm with a broad nature corresponded to protons of amidic groups (4NH) in hydrogen bonding [1,11]. The two singlet signals at 3.96 and 3.31 ppm assigned to group protons of CH₂ group and C₅-H of barbituric acid, respectively [1,9,10]. In addition, the multiple signals in range 7.48-7.23 due to aromatic protons [10,12].

Table 1: Physical and Analytical Data for H₄L Ligand and its Metal Complexes
All metal complexes did not melt up to 360°C, ^a: Ω⁻¹cm²mol⁻¹

No.	Compound	color	Empirical Formula Formula Weight	Yield%	Elemental Analysis Found (Calcd.)%				^a Λ _M
					C	H	X	M	
	H ₄ L.3EtOH	Dark brown	C ₂₇ H ₃₄ N ₈ O ₉ (614.63)	16	53.01 (52.76)	5.7 (5.49)	-	-	-
1	[Co(H ₄ L)Cl ₂ (H ₂ O) ₂].2.75EtOH	Brown	C _{26.5} H _{36.5} N ₈ O _{10.75} Cl ₂ Co (769.04)	48	41.70 (41.39)	4.60 (4.78)	9.40 (9.23)	7.24 (7.66)	28.6
2	[Ni ₂ (H ₄ L)Cl ₂ (OH) ₂ (H ₂ O) ₂].3EtOH	Brown	C ₂₇ H ₄₀ N ₈ O ₁₃ Cl ₂ Ni ₂ (873.07)	50	37.10 (37.14)	4.10 (4.62)	8.60 (8.13)	13.53 (13.45)	30.6
3	[Cu(H ₄ L)Br ₂].5EtOH	Dark green	C ₃₁ H ₄₆ N ₈ O ₁₁ Br ₂ Cu (930.27)	54	40.10 (40.03)	4.70 (4.98)	17.50 (17.20)	6.60 (6.83)	14.0
4	[Cd ₂ (H ₄ L) ₂ Cl ₄].0.5H ₂ O.8.5EtOH	Orange	C ₅₉ H ₈₄ N ₁₆ O ₂₁ Cl ₄ Cd ₂ (1720.23)	47	41.20 (41.19)	5.10 (4.92)	8.50 (8.25)	13.08 (13.07)	13.8

III.3. Infrared Studies

The infrared spectrum of H₄L ligand and its assignment is observed in Table (2) and demonstrated in Figure (1). The stretching vibration bands cited at 1741, 1708, 1666 cm⁻¹ assigned to three carbonyl groups, ν(C₂=O), ν(C₄=O) and ν(C₆=O), respectively [1] which are appeared as symmetrically splitted having strong features. The observed bands at 3226, 3088, 1445 and 707 cm⁻¹ were attributed to ν, δ and γ of NH amide groups, respectively. The IR spectrum of the ligand displayed bands at 3447, 1195 and 1570 cm⁻¹ attributed to ν(OH) (enolic OH of barbituric acid and solvent), δ(OH) and ν(C=N) of barbituric acid rings, respectively [13,14,15,16]. The above mentioned assignments indicate that one ring of barbituric acid has keto-enol structure, whereas, the second one exists in keto form. Also, the spectrum exhibits additional spectral

bands at 3015, 824; 2924,1355 and 2841, 878 cm⁻¹ corresponding to ν(CH), CH bending of p-disubstituted phenyl rings; stretching, wagging of CH₂ group and ν(CH), δ(CH) of C₅-H of barbituric acid moieties [10,15], respectively. The strong band located at 1260 cm⁻¹ is due to ν(N-ph) overlapped with ν(C-O) group. The observed band at 1500 cm⁻¹ due to ν(N=N) emphasize the azo coupling was achieved. The appearance of ν(C₅-H) of barbituric rings as well as ν(N=N) confirming azo not hydrazo structure for the ligand.

The infrared spectral bands and their assignments of ligand and its metal complexes are listed in Table (3) and represented in Figure (2). The spectra of all complexes showed that ν(N=N) undergoes shift to higher value via

13-17 cm^{-1} relative to the free ligand, indicating participation of azo nitrogen atom in chelation. The appearance of different kinds of vibrations characterized to $(\text{C}_5\text{-H})$ shifted to higher value by 4-22 cm^{-1} in complexation, indicating that the ligand reacts with metal atoms through azo group. The far infrared spectra of complexes gave new bands in range 425-522 cm^{-1} due to $\nu(\text{M-N})$ [1]. The $\nu(\text{C=O})$ ligand bands not be affected in all complexes, except Ni(II) and Cd(II) complexes, while, the $\nu(\text{C=O})$ ligand band (1708 cm^{-1}) exhibits blue shift by 13 cm^{-1} in Ni(II) complex. This finding indicating the involvement of oxygen atom of C=O in binding only with Ni(II) ion. On the other hand, the $\delta(\text{OH})$ ligand band (1195 cm^{-1}) exerted shift at 5-18 cm^{-1} assignable to involvement the enolic oxygen atom of barbituric acid in chelation. The

above assignments refer to that the ligand reacts with metals as azo keto-enol neutral form. This is associated with the appearance of new band at 530-580 cm^{-1} assigned to $\nu(\text{M-O})$ [17]. According to IR data, the **H₄L** ligand behaves as neutral bidentate and reacts by its half unit in Co(II), Cu(II) complexes, while, the ligand behaves as neutral tetradentate and chelates by enolic oxygen and azo nitrogen atoms of one side, as well as, azo nitrogen and carbonyl oxygen atoms of other side are involved also in chelation to construct the sandwich Cd(II) and binuclear Ni(II) complexes. The ligand and its metal complexes display bands within range 1026-1078 cm^{-1} due to $\nu(\text{CH}_2\text{-OH})$ of ethanol. The $\nu(\text{OH})$ of ligand overlapped with $\nu(\text{OH})$ of solvents [18]. (H_2O /ethanol) to shift from its position or broadens.

Table 2 : Infrared Spectral Bands (cm^{-1}) of Azo Ligand H₄L

Band	Assignment
3447 (br)	$\nu(\text{O-H})$ of solvent and enolic OH
3226 (m.br)	$\nu(\text{N-H})$
3088	
3015	$\nu(\text{C-H})_{\text{Ar}}$
2924	$\nu(\text{CH}_2)$ of methylene
2841	$\nu(\text{C}_5\text{-H})_{\text{BA}}$
1741,1708,1666 (splitted peaks)	$\nu(\text{C}_2=\text{O}), \nu(\text{C}_4=\text{O}), \nu(\text{C}_6=\text{O})$
1570	$\nu(\text{C=N})$
1500	$\nu(\text{N=N})$
1445	$\delta(\text{N-H})$
1355	$\delta_w(\text{C-H}) + \nu(\text{C-N})_{\text{BA}}$
1260	$\nu(\text{N-Ph}) + \nu(\text{C-O})$
1195	$\delta(\text{O-H})$
878	$\delta(\text{C}_5\text{-H})_{\text{BA}}$
824	p-disubstituted benzene +CH out of plane
707	$\gamma(\text{N-H})$
603	$\gamma(\text{C=O})$

sh: shoulder, sp: splitted, vw: very weak, w: weak, m: medium, s:strong, b: broad

Table 3: Infrared Spectral Bands (cm^{-1}) for H₄L Ligand and its Metal Complexes

No.	Compound	$\nu(\text{O-H}), \delta(\text{O-H})/\text{solvent or BA}$	$\nu(\text{N-H})$	$\nu(\text{C}_5\text{-H})$ of BA acid	$\nu(\text{C}_2=\text{O}), \nu(\text{C}_4=\text{O}), \nu(\text{C}_6=\text{O})$	$\delta(\text{N-H}), \nu(\text{CH}_2\text{-OH})$	$\nu(\text{N=N})$	$\nu(\text{N-Ph}), \nu(\text{C-O})$	p-disubs tit. Ph. Ring, $\delta(\text{C}_5\text{-H})_{\text{BA}}$	$\gamma(\text{C=O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	Other bands
	H ₄ L.3EtOH	3447 m.br 1195	3226 m.br, 3088w	2841	1741 s, 1708 s, 1666 s	1445 1046	1500	1260	824 878	603	-	-	-
1	[Co(H ₄ L)Cl ₂ (H ₂ O) ₂].2.75 EtOH	3441w 1207	3248w 3093w	2859	1745 1708 1664	1448 1032	1515	1266	814 870	594	555	520 484	-
2	[Ni ₂ (H ₄ L)Cl ₂ (OH) ₂ (H ₂ O) ₂].3EtOH	3403w 1204	3240w 3178w 3088w	2844	1743 1695 1666	1445 1052	1514	1263	817 885	605	521	486	-
3	[Cu(H ₄ L)Br ₂].5EtOH	3452w 1203	3235w 3086w	2848	1743 1704 1666	1445 1032	1510	1265	811 884	603	557	522 486	-
4	[Cd ₂ (H ₄ L) ₂ Cl ₄].0.5H ₂ O.8 .5EtOH	3429w 1209	3254w 3089w	2863	1744 1705 1026 1658	1436 1060	1515	1265	- 894	606, 665	555 523	485	-

sh: shoulder, sp: splitted, vw: very weak, w: weak, m: medium, s:strong, b: broad

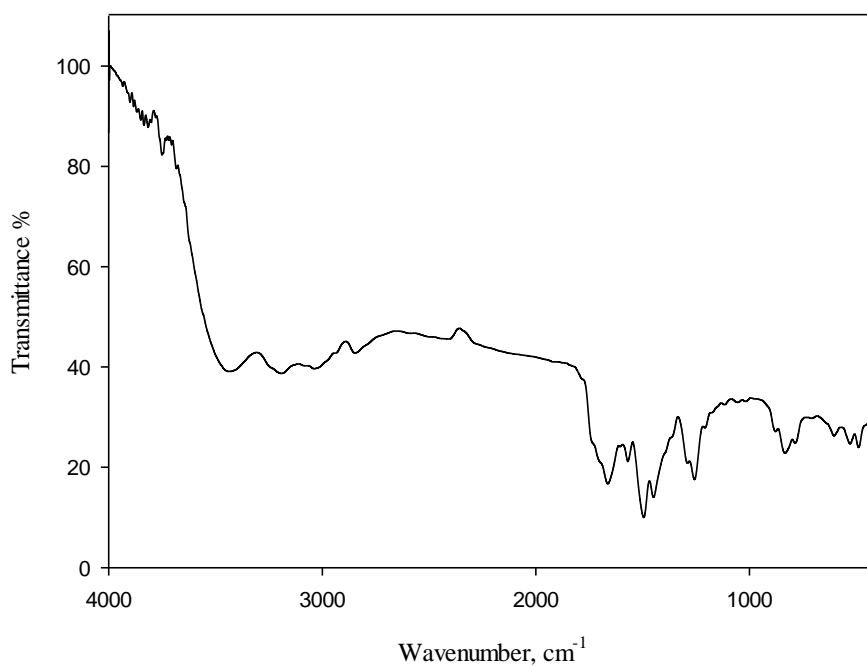


Figure 1: IR Spectrum of H₄L ligand

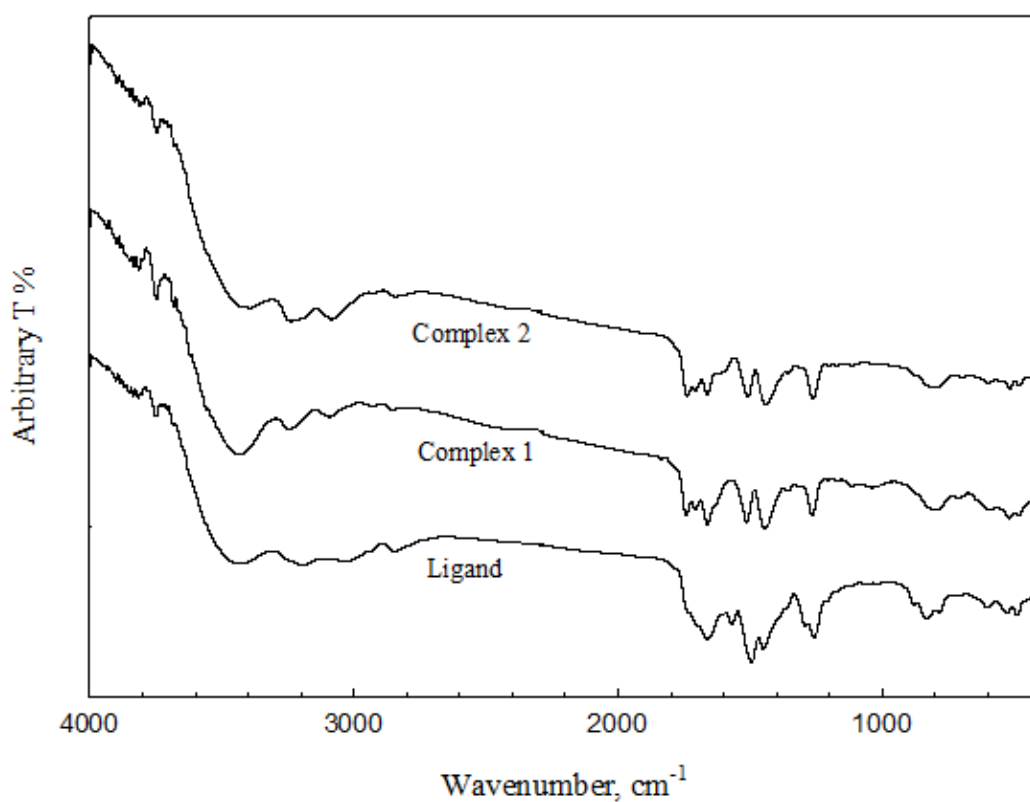


Figure 2: IR spectra of the ligand and [Co(H₄L)Cl₂(H₂O)₂].2.75EtOH complex (1), [Ni₂(H₄L)Cl₂(OH)₂(H₂O)₂].3EtOH complex (2) and [Cu(H₄L)Br₂].5EtOH complex (3)

III.4. Electronic Absorption Spectral Data

The electronic absorption spectra of ligand and its metal complexes were recorded in Nujol mull and their assignments were represented in Table (4).

The electronic spectrum of ligand displays bands at 247 and 288 nm due to $\pi-\pi^*$ of aromatic and heterocyclic rings, whereas, the splitted strong spectral bands at 472 and 511 nm assigned to $\pi-\pi^*$ and $n-\pi^*$ of carbonyl, azo groups which are overlapped with charge transfer bands. The strong absorption bands which are characterized for the complexes and appeared within range 470-518 nm can be assigned to ligand to metal charge transfer (LMCT) [10].

The electronic spectra of complexes showed that the $n-\pi^*$ ligand bands are shifted to higher/lower wavelength indicating that the central metals have effect on the absorption peaks of complexes where, the nitrogen atom of azo and oxygen atom of carbonyl groups involved in chelation.

The Nujol mull spectrum of Co(II) complex displayed two spectral bands near 704 and 554 nm owing to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_2) and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions

of an octahedral structure around Co(II) ion. This geometrical structure is also supported by its magnetic moment value (4.7 B.M) indicating a high-spin octahedral cobalt(II) complex [10.19]. In Ni(II) complex, two d-d transition bands were denoted at 768 and 580 nm corresponding to ${}^3B_{1g}(F) \rightarrow {}^3A_{1g}(F)$ (ν_2) and ${}^3A_{2g} \rightarrow {}^3E_g$ (ν_3), respectively, arises from square pyramidal geometry, which is confirmed by its magnetic moment value (3.1 B.M) [20]. The electronic absorption spectrum of Cu(II) complex demonstrated d-d transition bands at 726, 552 and 516 nm attributed to ${}^2B_{1g} \rightarrow {}^2B_{2g}$, ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$ consistent with distorted square planar geometry around Cu(II) ion [21]. The magnetic moment value of copper(II) complex lies at (2.1 B.M) which is compatible with the known values for copper(II) complexes [22]. The diamagnetic Cd(II) complex exhibits bands in regions 440-248 and 509-472 nm due to intraligand transition and ligand metal charge transfer. The octahedral geometry was proposed as the most stable one for diamagnetic complex based on the empirical formula.

Table 4: Electronic Spectral and Magnetic Moments of H₄L Ligand Metal Complexes

No	Compound	Electronic spectral bands (nm)	Assignment	μ_{eff} (B.M.) ^a
	H ₄ L.3 EtOH	247,288	$\pi-\pi^*$	–
		472	$\pi-\pi^*$	
		511	$n-\pi^* + \text{CT}$	
1	[Co(H ₄ L)Cl ₂ (H ₂ O) ₂].2.75EtOH	248,290	$\pi-\pi^*$	4.7
		439	$\pi-\pi^*$	
		480,511	$n-\pi^* + \text{LMCT}$	
		554	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3)	
		704	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_2)	
2	[Ni ₂ (H ₄ L)Cl ₂ (OH) ₂ (H ₂ O) ₂].3EtOH	248,280	$\pi-\pi^*$	3.1
		420	$\pi-\pi^*$	
		472,516	$n-\pi^* + \text{LMCT}$	
		580	${}^3A_{2g} \rightarrow {}^3E_g$ (ν_3)	
		768	${}^3B_{1g}(F) \rightarrow {}^3A_{1g}(F)$ (ν_2)	
3	[Cu(H ₄ L)Br ₂].5EtOH	248,288	$\pi-\pi^*$	2.1
		420	$\pi-\pi^*$	
		480	$n-\pi^* + \text{LM}-\text{CT}$	
		516	${}^2B_{1g} \rightarrow {}^2A_{1g}$	
		552	${}^2B_{1g} \rightarrow {}^2E_g$	
		726	${}^2B_{1g} \rightarrow {}^2B_{2g}$	
4	[Cd ₂ (H ₄ L) ₂ Cl ₄].0.5H ₂ O.8.5EtOH	248,288, 440,472, 509	Intraligand transition	Diamagnetic

III.5. Thermal Studies

TG and DTG curves of H₄L ligand show that it decomposed mainly in two stages in the temperature ranges 24-243 and 243-515°C. The first stag is represented by TG weight loss 8.05% due to removal one mol of ethanol (partially desolvation). This stage is associated by two weak DTG peaks with ($T_{\text{max}} = 81$ and 197°C). After that, the organic compound starts its decomposition at 243°C . The second decomposition stage is subdivided into two steps within temperature ranges 243-392 and 392-515°C and

associated with DTG peaks at ($T_{\text{max}} = 355$ and 413°C) in strong and medium nature, respectively. The first step exhibits 61.44% weight loss assigned to elimination of ($\text{N}_2 + 2\text{BA} + 0.5\text{C}$) as well as the rest two mol of lattice ethanol solvents. However, the second organic degradation step exhibits 22.8% weight loss corresponds to release one mol of N₂ gas and C_{8.5}H₁₀ which arise from the decomposition of diphenyl methane. The TG curve showed weight loss 2.85% up to 868°C due to release of 1.5 mol of carbon leaving 2.5 mol of carbon as a final residue.

The thermal decomposition behavior of metal complexes was investigated by thermogravimetric technique. The thermograms (TG and DTG) and the estimated thermoanalytical data are collected in Figure (3) and Table (5). Generally, the complexes display two or three successive steps for decomposition. The first step results from removal of some portion of solvent. The low onset and the broad range of temperature 25-342°C indicating that some solvents are in lattice voids not contributed in lattice forces. However, the rest solvent molecules associated with decomposition of chelates confirming the rest solvents are contributed in lattice forces. However, the deligation, removal of anions as well as the rest solvents take place in one step as in Co(II), Ni(II), and Cu(II) complexes. However, this process was completed through two continuous stages for the rest complexes end with formation of metal residue as a final product [23,24,25,26].

The thermal decomposition process of copper(II) complex, $[\text{Cu}(\text{H}_4\text{L})\text{Br}_2] \cdot 5\text{EtOH}$, occurs in two stages within temperature ranges 26-292 and 292-700°C corresponding to desolvation and removal of lattice solvent, one mol of halogen gathered with ligand pyrolysis. This process is accompanied with DTG peaks at ($T_{\text{max}}=48, 104; 360, 439, 548$ °C) with weight losses 7.39 and 85.90 %, respectively. The decomposition process ended with the formation of copper metal as final residue [23].

The thermal decomposition of Cd(II) complex occurs in three stages, 60-309, 309-399, 399-612°C. After partially desolvation, the first divided step takes place in temperature ranges 309-399 °C with weight losses 27.01 % which is equivalent to dehalogenation with removal of rest solvents and removal of one mol of BA moiety. The second divided process is characterized with weight losses 54.08 % up to 612 °C due to complete ligand pyrolysis associated with rest lattice ethanol. The decomposition processes afforded the corresponding Cd as an end product [24].

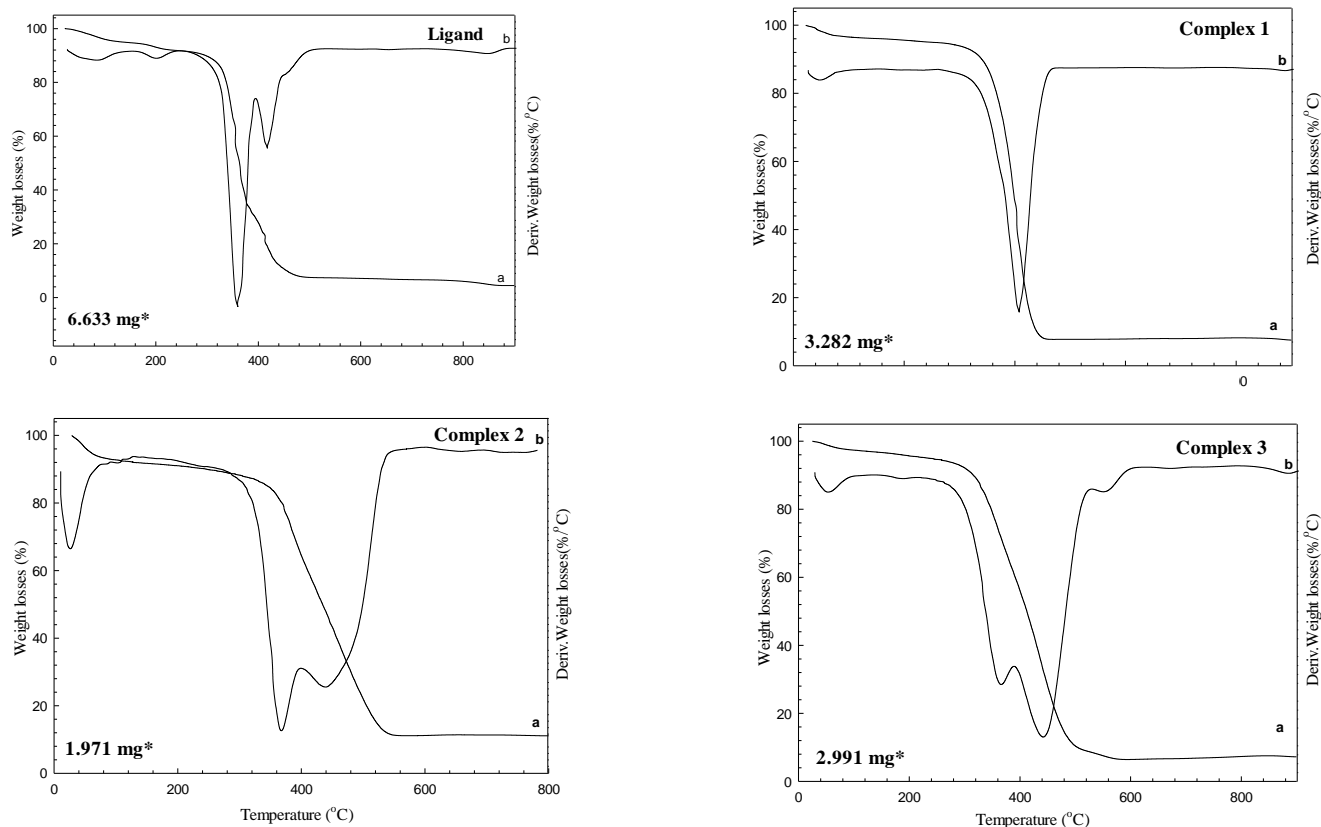


Figure 3: TGA/DTG curves for the ligand and its metal complexes

Table 5: Thermal Analytical Data for H₄L Ligand and its Metal Complexes

No.	Compound	TG range (°C)	DTG Peak (°C)	Mass Loss%		Assignment	T _s (°C)
				Found	Calcd.		
	H ₄ L.3EtOH	24-243 243-392 392-515 515-868 At 868	81w,197w 355 s 413m	8.05 61.44 22.80 2.85 4.88	7.49 61.88 22.81 2.93 4.89	-(One mol of EtOH) ^b -(2 Mol of lattice EtOH, one mol of N ₂ gas, 2 mol of BA and 0.5 mol C) ^d -(One mol of N ₂ gas, C ₈ H ₁₀ and 0.5 mol C) ^d -(1.5C) ^d (2.5C) ^f	243
1	[Co(H ₄ L)Cl ₂ (H ₂ O) ₂].2.75EtOH	26-317 317-472 At 472	42sh 404s	6.80 85.39 7.81	6.74 85.60 7.66	-(1.125 Mol of EtOH) ^b -(1.625 Mol of lattice EtOH, 2 mol of coordinated H ₂ O, one mol of Cl ₂ gas and one mol of H ₄ L) ^d (Co) ^f	317
2	[Ni ₂ (H ₄ L)Cl ₂ (OH) ₂ (H ₂ O) ₂].3EtOH	29-342 342-545 At 545	43w 383s 459w	14.00 72.47 13.53	14.51 72.04 13.45	-(2.75 mol of EtOH) ^b -(0.25 Mol of lattice EtOH, 2 mol of coordinated H ₂ O, 2 mol of coordinated OH, one mol of Cl ₂ gas and one mol of H ₄ L) ^d (2Ni) ^f	342
3	[Cu(H ₄ L)Br ₂].5EtOH	26-292 292-700 At 700	48sh 104w 360sh 439br, 548w	7.39 85.90 6.71	7.43 85.74 6.83	-(1.5 Mol of EtOH) ^b -(3.5 Mol of lattice EtOH, one mol of Br ₂ gas and one mol of H ₄ L) ^d (Cu) ^f	292
4	[Cd ₂ (H ₄ L) ₂ Cl ₄].0.5H ₂ O.8.5EtOH	27-60 60-309 309-399 399-612 At 612	149w, 231w 433s	2.04 5.83 27.01 54.08 13.08	Moisture 5.87 27.00 54.05 13.08	Moisture -(2.5 Mol of EtOH and 0.5 mol of H ₂ O) ^{a+b} -(4.25 Mol of lattice EtOH, 2 mol of Cl ₂ gas and one mol of BA) ^d -(2.25 Mol of lattice EtOH and complete ligand pyrolysis) ^d 2Cd) ^f	309

a:dehydration, b:desolvation, d:decomposition, f:final residue, r: remain, w: weak, m: medium, br: broad, s: strong, vw: very weak, and vs: very strong; sh:shoulder

III.6. Electronic Spin Resonance (ESR) Studies

The ESR spectrum of copper(II) complex is represented graphically in Figure (4).

The spectrum of the powdered complex is measured at room temperature implying that $g_{//}=2.141$ and $g_{\perp}=2.023$ producing axial symmetry with $g_{//} > g_{\perp} > 2.0023$. Also, the observed data pointed to the fact that the unpaired electron lies predominantly in the

$d_{x^2-y^2}$ orbital affording a $^2B_{1g}$ ground state [10,23,27,28]. In this complex the $g_{//} > 2.03$ where all the principal axes

aligned parallel indicating the tetragonal distorted structure for Cu(II) complex [23]. In addition, the $g_{//}$ values < 2.3 revealing a considerable covalence character in copper-ligand bonding. The geometric parameter (G) is calculated to measure the exchange interaction between Cu(II) ions using this relation $G = g_{//} - 2.0023 / g_{\perp} - 2.0023$. In this case the parameter G was found 6.7 indicating to the absence of the exchange interaction between Cu(II) ions.

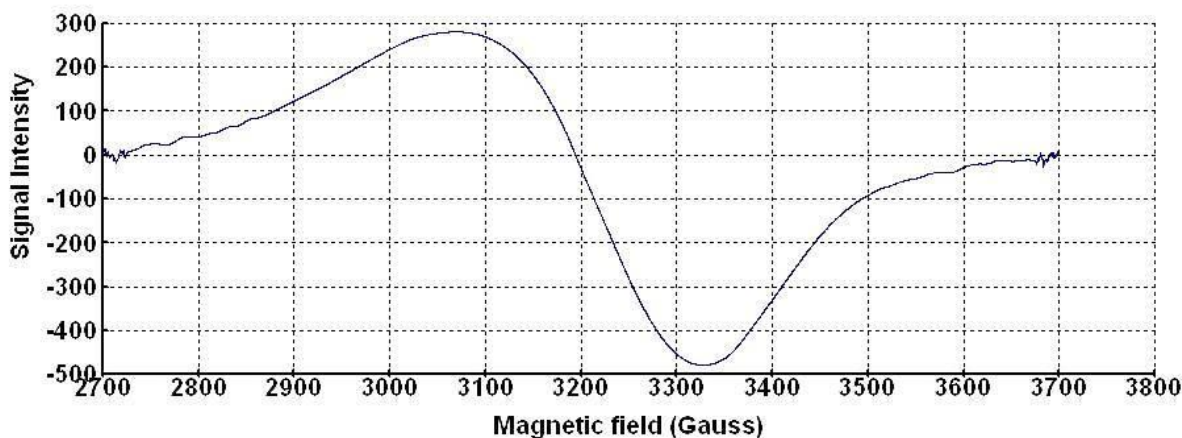


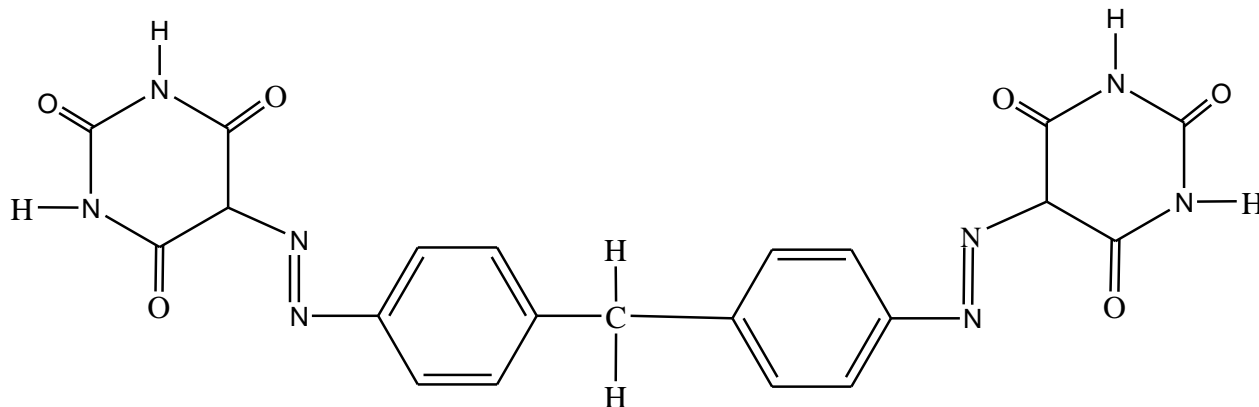
Figure 4: ESR Spectrum of Cu(II) complex, (3)

IV. CONCLUSION

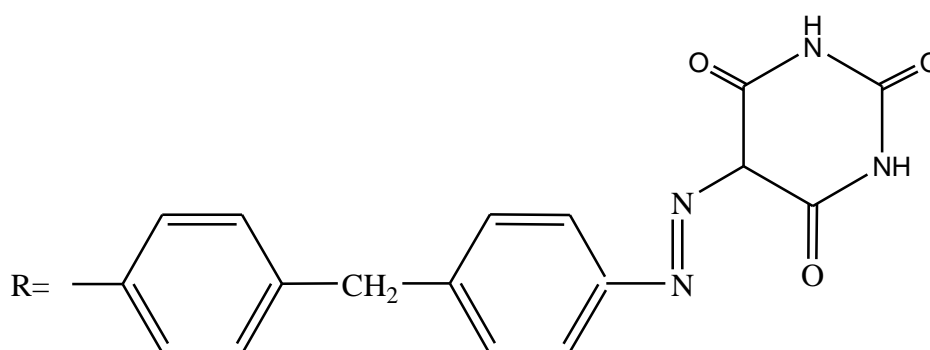
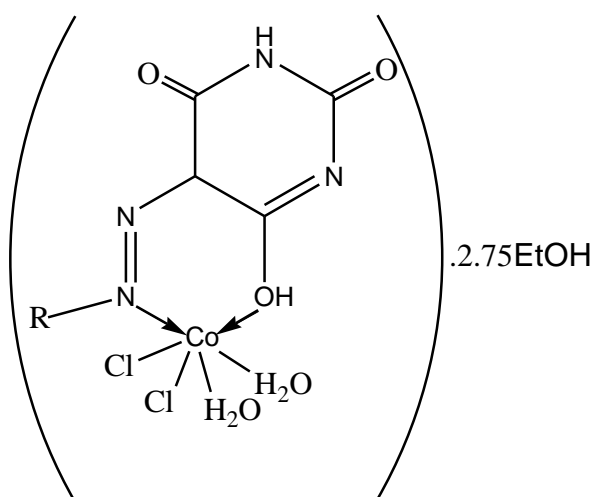
Four different divalent metal complexes with azo ligand **H₄L** have been prepared and structurally characterized using elemental analyses, spectral techniques and thermal studies. The present studies revealed octahedral geometries for the Co(II), Cd(II) complexes; square pyramidal and square planar structure for Ni(II) and Cu(II) complexes, respectively. The ligand acts in a neutral bidentate manner coordinating through nitrogen atom of azo group and

oxygen atom of enol form in cobalt(II) and copper(II) complexes. Also, **H₄L** azo ligand behaves as a neutral tetradentate fashion in Ni(II) and Cd(II) and binds by enolic oxygen and azo nitrogen atoms of one side, as well as, azo nitrogen and carbonyl oxygen atoms of other side are involved also in chelation.

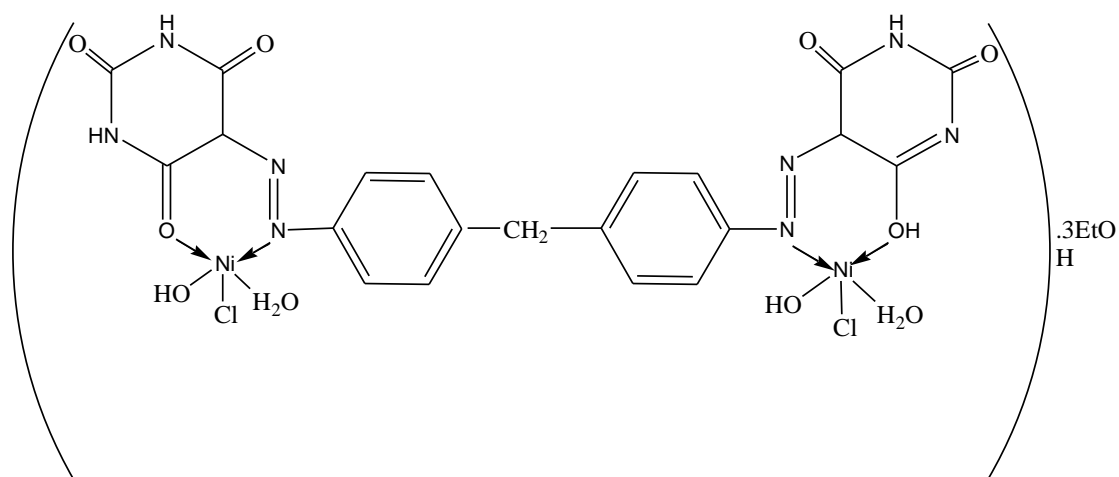
On the basis of elemental analyses, magnetic moment, molar conductance, IR, U.V.-Vis, ESR spectra, thermal analysis the structures are proposed (Figure 5).



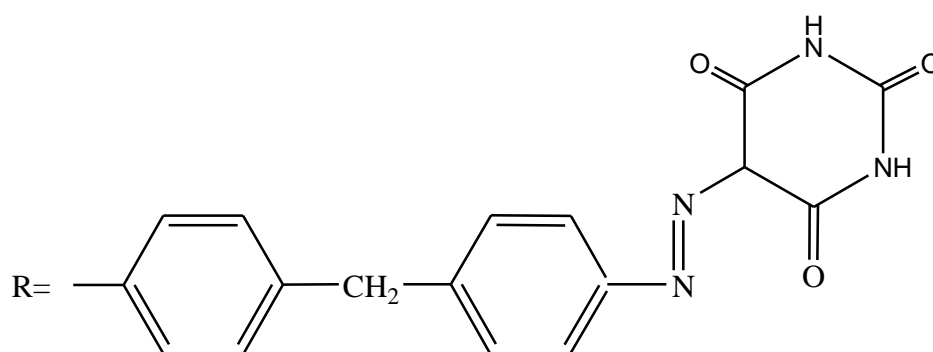
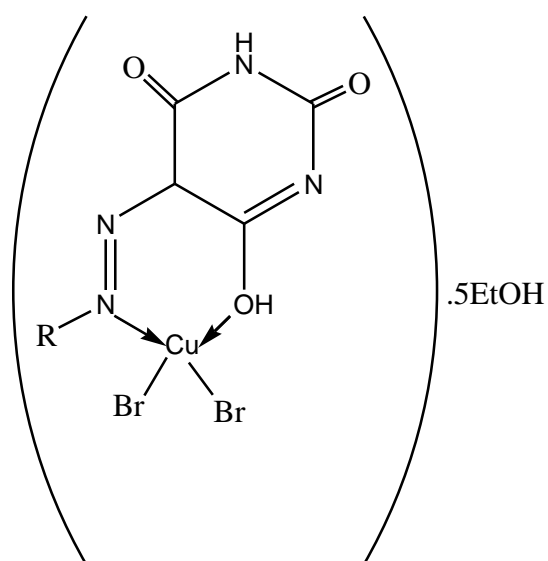
Structure of **H₄L** Ligand



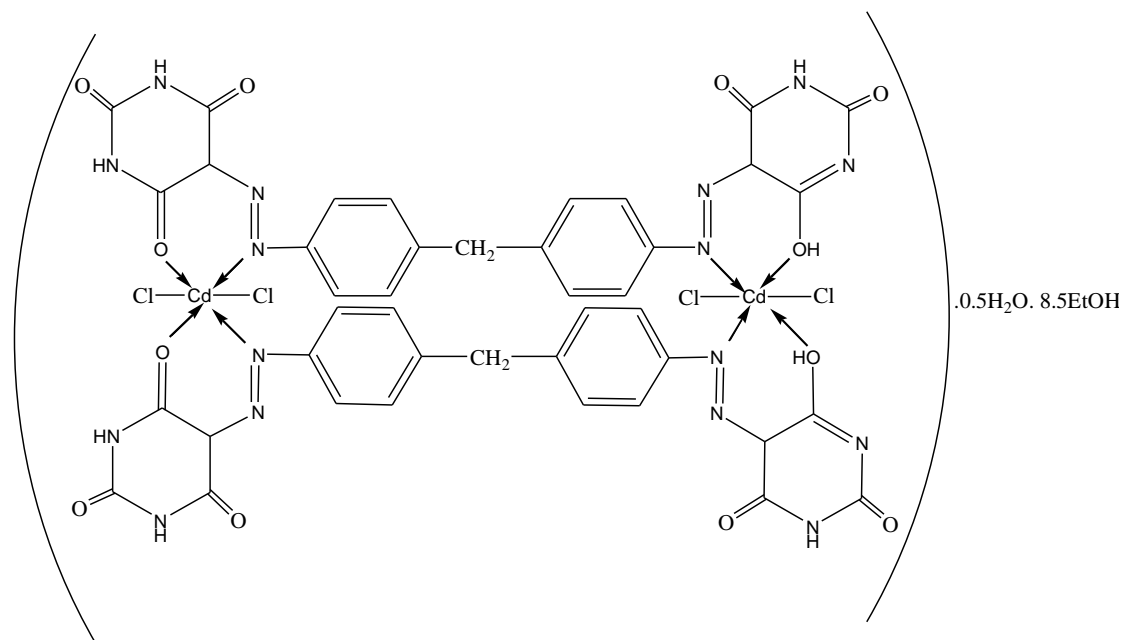
Complex (1), $[\text{Co}(\text{H}_4\text{L})\text{Cl}_2(\text{H}_2\text{O})_2] \cdot 2.75\text{EtOH}$



Complex (2), [Ni₂(H₄L)Cl₂(OH)₂(H₂O)₂].3EtOH



Complex (3), [Cu(H₄L)Br₂].5EtOH



Complex (4), $[Cd_2(H_4L)_2Cl_4].0.5H_2O.8.5EtOH$

Figure 5: Suggested structures for H_4L and its metal complexes

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