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# Synthesis, spectral and thermal studies of Co(II), Ni(II) and Cu(II) complexes 1-(4,6-dimethyl-pyrimidin-2-ylazo)-naphthalen-2-ol

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## Abstract

The electronic absorption spectra of 1-(4,6-dimethyl-pyrimidin-2-ylazo)-naphthalen-2-ol is studied in organic solvents of different polarity as well as in buffer solutions of varying pH values at different temperatures and different ratios of methanol. The probable structure of the azodye has been assigned on the basis of spectral studies (IR and <sup>1</sup>H NMR). The effect of Co(II), Ni(II) and Cu(II) ions on the emission spectrum of the free azodye is also assigned. The stoichiometry of the metal complexes is determined spectrophotometrically and conductometrically. Novel complexes of Co(II), Ni(II) and Cu(II) with the pyrimidine azodye have been synthesized and characterized on the basis of elemental analyses, molar conductance, magnetic susceptibility measurements, IR, electronic as well as ESR spectral studies The thermal decomposition of the metal complexes is studied by TGA and DTA techniques. The kinetic parameters like activation energy, pre-exponential factor and entropy of activation are estimated.

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Keywords: Azopyrimidine; Complexes; Spectral; Thermal studies

## 1. Introduction

Azodyes have the remarkable property of forming complexes and serve as the most important class of N-donor ligands. Azodyes and their metal complexes are becoming increasing important as analytical agents [1]. Heterocyclic azo compounds have been used to establish low oxidation state of different metals ions [2]. Recent years have a great deal of interest in the synthesis and characterization of azo compounds [3] as well as their metal complexes [4]. Several transition metal azodye complexes have been found to possess interesting biological properties [5]. In view of the biological significance and coordination behaviour of azo compounds, it was considered worthwhile to prepare and study azodye complexes of Co(II), Ni(II) and Cu(II) ions. In the present article we report the preparation and characterization of a hydroxy pyrimidine azodye

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as ligand, as well as its Co(II), Ni(II) and Cu(II) metal complexes.

The coordination behaviour of the azodye towards transition metal salts is investigated via the elemental analysis, IR, electronic, ESR, magnetic moments and molar conductance measurements. The thermal behaviour of the thermal decomposition was also studied and the thermodynamic parameters were reported.

# 2. Experimental

### 2.1. Synthesis of azodye ligand (L)

2-Amino-4,6-dimethyl pyrimidine (0.01 mol) was mixed with ~3 ml HCl (10 M) and diazotized below 5 °C with (0.01 mol) NaNO<sub>2</sub>. The resulting diazonium chloride was coupled with an alkaline solution of  $\beta$ -naphthol (0.01 mol) below 0 °C. The azodye product was filtered off, recrystallized from ethanol and dried over vacuum CaCl<sub>2</sub>. The purity of the azodye was firstly checked by the mp con-

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Table 1		
Analytical data of t	he isolated	complexes

Complex	Formula	% Elemental analysis <sup>a</sup>			$\Lambda_{\rm m}{}^{\rm b}$	$\mu_{\mathrm{eff}}$ (BM)	IR spectra (cm <sup>-1</sup> )		Electronic		
		C	Н	Ν	Metal			N=N	М—О	M—N	spectra (cm <sup>-1</sup> )
1	[CoL(AcO)(H <sub>2</sub> O) <sub>3</sub> ]H <sub>2</sub> O	46.4 (46.0)	5.1 (4.6)	12.0 (11.7)	12.4 (12.4)	0.05	4.82	1399	532	453	17857, 20000
2	$[CoL_2(H_2O)_2]$	59.2 (58.8)	4.6 (4.2)	17.3 (16. 9)	8.9 (8.9)	0.05	4.95	1396	484	455	17857, 19230
3	[NiL(AcO)(EtOH)3]H2O	52.4 (51.7)	6.5 (6.0)	10.2 (9.6)	10.5 (9.9)	0.05	2.74	1386	580	424	15625, 25923
4	[NiL <sub>2</sub> (EtOH) <sub>2</sub> ]H <sub>2</sub> O	59.8 (59.3)	5.5 (5.0)	11.1 (10.8)	8.0 (7.9)	0.06	2.85	1462	520	425	15625, 23809
5	[CuL(AcO)H <sub>2</sub> O]	51.7 (51.0)	4.3 (4.0)	13.4 (13.2)	15.2 (15)	0.05	1.20	1398	524	433	20000
6	[CuL <sub>2</sub> ]	62.2 (61.8)	4.2 (3.8)	18.1 (17.7)	10.4 (10.1)	0.04	1.69	1459	569	437	19608

AcO = acetate.

<sup>a</sup> Calc. (found).

<sup>b</sup>  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

stancy, elemental analyses and finally by spectral methods (mp 85 °C; analysis found: C, 68.8; H, 4.9; N, 19.7%, Cal. For  $C_{16}H_{14}N_4O$ , C, 69.0; H, 5.04; N, 20.1%



2.2. Synthesis of metal complexes

A solution of the appropriate metal acetate (0.01 mol) in EtOH (10 ml) was mixed with a solution of the azodye (0.01 or 0.02 mol) in the same solvent (30 ml) and the resulting mixture was stirred under reflux for ~12 h where upon the complexes precipitated after cooling. The solid complexes were then filtered off, washed several times with ethanol, dried and kept in a desiccator over dried silica gel. The analytical and spectral data are collected in Table 1.

#### 2.3. Measurements

The IR spectra were recorded as KBr discs on a Perkin Elmer 1430 spectrophotometer in the  $4000-200 \text{ cm}^{-1}$  range. The electronic spectra were recorded using a Shimadzu 240 UV-vis spectrometer. The <sup>1</sup>H NMR spectrum of the ligand was performed using a Varian EM 390-90 NMR spectrometer in d<sup>6</sup>-DMSO as solvent using tetramethylsilane (TMS) as an internal standard. The X-band ESR spectra of the complexes were recorded at room temperature on a JOEL-X-band spectrometer equipped with an E 101 microwave bridge. Diphenyl picryl hydrazide free radical (DPPH) was used as internal standard (g = 2.0036). The fluorescence measurements were recorded with the aid of Shimadzu RF-510 spectrofluorometer; excitation and emission bandwidth was 10 nm, scan rate 100 nm/min and excitation wavelength was 370 nm. Magnetic susceptibilities were measured by employing the Faraday balance technique. The equipment was calibrated with Hg[Co(CNS)<sub>4</sub>]. Diamagnetic corrections were calculated from Pascal constants. The thermal analysis (TGA and DTA) were carried out using computerized Shimadzu TG-50 thermal analyzer up to  $800 \,^{\circ}$ C at a heating rate  $10 \,^{\circ}$ C/min. in an atmosphere of N<sub>2</sub>. Microanalyses of C, H and N were made using Heraeus CHN elemental analyzer. The Co(II), Ni(II) and Cu(II) contents were estimated by complexometric EDTA titration (after complete decomposition of the complexes in aqua regia several times) using Xylenol Orange (pH 6), Eriochrome Black T (pH 10) and Fast Sulphon Black F (5 ml conc. NH<sub>3</sub>).

## 3. Results and discussion

#### 3.1. Characterization of the ligand

The electronic spectrum of the pyrimidine azodye (L) in methanol shows mainly three bands at 210 (medium energy  $\pi - \pi^*$  transition within the phenyl moiety  ${}^1L_a - {}^1A$ ), 260 nm (low energy  $\pi - \pi^*$  transition within the phenyl ring  ${}^1L_b - {}^1A$ ) and 375 nm (CT band within the whole molecule). The application of the dielectric relations given by Gati and Szalay [6], Suppan [7] or the molecular-microscopic solvent parameters  $\pi$  (dipolarity), Z [8] and  $E_T$  values [9] show non-linear relations indicating that the change in the position of the CT band is to be considered as being the resultant of the different factors governed by the various parameters. This may be additive, counter-acting or may even cancel each other.

The electron absorption spectrum of the azodye (L) in universal buffer solutions containing different percentage of methanol is recorded. The spectra are approximately the same within the pH range 2–5. In the pH range 6–7.5, only one band is observed with  $\lambda_{max}$  at 380 nm which splitted to two bands at pH  $\geq$  8, one at 380 and the other at 420 nm. The pK<sub>a</sub> value of the azodye is calculated using the recommended methods at two different wavelengths [10]. The pK<sub>a</sub> values decrease with increasing the percentage of methanol (Fig. 1). The ionization of the azodye occurs in two steps. The first step represents the ionization of the protonated form (pH 2–7) while the second step involves the ionization of the deprotonated form at pH = 7. The ionization of both forms increases



Fig. 1. Effect of vol.% of methanol on  $pK_a$  values on azodye (L).

with increasing the methanol ratio due to the solvation effect which stabilizes the ionized form.

The electronic spectra of the azodye in solutions of various pH values and containing 50% methanol are recorded at different temperatures (25–50 °C). The p $K_a$  values increase with rising the temperature (Fig. 2). The thermodynamic parameters  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  were calculated using the data estimated from (Fig. 3). The negative value of  $\Delta H$  (-80.6 kJ mol<sup>-1</sup>) reveals that the dissociation of the azodye (L) is exothermic in 50% methanolic solution and the value of  $\Delta S$  (-405.5 J mol<sup>-1</sup>) due to increasing order as result of solvation process. The positive value of  $\Delta G$  (45 kJ mol<sup>-1</sup>) indicates that the dissociation of the azodye (L) is not spontaneous.

The IR spectrum of the azodye exhibits a broad band at  $3405 \text{ cm}^{-1}$  corresponding to the stretching vibration of the



Fig. 2. Effect of temperature on the  $pK_a$  values of L in 50% methanol.

OH group. The stretching vibration of the C=N group of the pyrimidine ring appears at  $1534 \text{ cm}^{-1}$ . The stretching vibration of the azo group is observed at  $1422 \text{ cm}^{-1}$ .

A further support for the structure of the azodye is gained from the <sup>1</sup>H NMR spectrum. The spectrum exhibits signals at 2.2 and 9.15 ppm corresponding to the protons of CH<sub>3</sub> and OH groups, respectively. The multisignals within the range 7.4–8.15 ppm can be assigned to the aromatic protons.

### 3.2. Study of complexes in solution

Investigations were carried out to establish the most favorable conditions to give a highly color intensity and to achieve maximum color development in the quantitative determination of the metal ions. The influence of each of the following variables on the complexation reaction was tested.



Fig. 3.  $pK_a - 1000/T$  relationship for L in 50% (v/v) methanol-universal buffer media.

The optimum pH for the complex formation was detected by scanning the absorption spectra of the complexes using different types of buffer solutions (universal, borate, acetate and phosphate). The acetate buffer solutions of pH values 4.5, 5.5 and 6.3 are suitable for Co(II), Ni(II) and Cu(II) complexes, respectively. The complexes are formed instaneously and the color of the complexes is stable for 24 h. Temperature exhibits no apparent influence on the color development. The suitable wave length for the complex formation was also determined and found at 440, 450 and 480 nm for Co(II), Ni(II) and Cu(II) complexes, respectively. The results of three different sequences of additions to select the most suitable one for developing the color of the complexes show the sequences, metal-buffer-azo, azo-metal-buffer and azo-buffer-metal for Co(II), Ni(II) and Cu(II) complexes, respectively.

The composition of the complexes in solution was established at the optimum conditions described above using the molar ratio (MRM) and continuous variations (CVM) methods. The results indicate the presence of complexes in solution having the stoichiometric ratios 1:1 and 1:2 (M:L) complexes. The conditional formation constant calculated using Harvey and Manning equation applying the data obtained from the above two methods are listed in Table 2. The values obtained show that the species 1:2 (M:L) are nearly twice stable as 1:1 (M:L) species. The free energy  $(G^*)$  of formation of the metal complexes was also calculated. The stoichiometry of the complexes was also determined by conductometric titrations. The data obtained indicate the formation of 1:1 (M:L) complexes. The increase in conductance indicates that the reaction between the metal ions and azodye occurs via the formation of a covalent linkage with the oxygen atom of the OH group.

Table 2 lists the limits of obedience to Beer's law, molar extinction coefficient, specific absorptivity [11], Sandell sensitivity [12], standard deviation and correlation coefficient. These values confirm the possible application

Table 2			
Analytical	parameters for azodye (L)	com	olexes

of the method for the determination of the metal ions. It
is clear that the molar absorptivity values follow the order
Co-L>Ni-L>Cu-L complexes. Ringbom [13] concentra-
tion range was also determined and the results are listed in
Table 2

The spectrophotometric titration of Co(II), Ni(II) and Cu(II) ions with EDTA using azodye L as an indicator was carried out in the presence of suitable buffer of the recommended pH values. For this purpose, a series of methanolic solutions containing 1.0 ml of  $10^{-3} \text{ M}$  of azodye, 0.25 ml of  $10^{-4}$  M metal ion, 2.5 ml of the buffer of the recommended pH value (taken the sequence of addition in consideration) are prepared and successive amounts of 10<sup>-3</sup> M aqueous solution of EDTA were added, then completed with MeOH up to 5 ml. The absorbance at the optimum wavelength was measured for each complex using the same volume of azodye and buffer as a blank. The results indicated that the metal ions under investigation are successfully determined up to the range listed in Table 2 as well as the applied reagent can be used as an indicator for the spectrophotometric titrations of Co(II), Ni(II) and Cu(II) ions.

The effect of metal ions on the fluorescence spectrum of the azodye was also considered. The fluorescence spectrum of the azodye shows two bands and shoulder at 430, 460 and 490 nm respectively. In the presence of Co(II), Ni(II) and Cu(II) ions, the fluorescence of the azodye was quenched.

The quenching behaviour generally adhered to the Stern–Volmer equation [14]. At relatively high quencher concentrations Stern–Volmer plot (Fig. 4) shows positive deviation. The Stern–Volmer second order rate constants of the fluorescence quenching decrease with increasing ionic radius of the metal ions (Table 2).

# 3.3. Characterization of the solid complexes

Structure elucidation of Co(II), Ni(II) and Cu(II) complexes was accomplished on the basis of elemental analyses,

Parameter	Co	Ni	Cu			
Wavelength (nm)	440	450	480			
Buffer	Acetate	Acetate	Acetate			
рН	4.5	5.5	6.3			
$\log \beta_n$	4.52 (8.77) <sup>a</sup>	4.23 (8.5) <sup>a</sup>	4.34 (8.28) <sup>a</sup>			
$\Delta \overline{G}^*$	6.16 (11.96) <sup>a</sup>	5.77 (11.59) <sup>a</sup>	5.92 (11.3) <sup>a</sup>			
Molar absorptivity, $\varepsilon$ (×10 <sup>-3</sup> )	25.94	14.70	13.75			
Specific absorptivity, $a(\times 10^{-2})$	40.76	23.09	21.61			
Sandell sensitivity, S	2.454	0.43	4.63			
Standard deviation	$10^{-4}$	$8 \times 10^{-6}$	$8.3  imes 10^{-4}$			
Correlation coefficient	0.9975	0.9989	0.9995			
Beer's limit (ppm)	1.08	0.83	7.62			
Ringbom range (ppm)	0.4–1.05	0.24–0.63	0.63-5.1			
$A (\times 10^{-5} \text{ mol } 1^{-1})$	5	5	5			
$B(\times 10^{-5} \text{ mol } l^{-1})$	5	5.2	5.1			
$K_{\rm sy}$ (×10 <sup>-3</sup> 1 mol <sup>-1</sup> )	39.17	37.5	20.0			

A (concentration of prepared sample), B (concentration of sample determined experimentally).

<sup>a</sup> 1:2 (M:L) complexes  $\varepsilon$  (L mol<sup>-1</sup> cm<sup>-1</sup>), *a* (cm<sup>2</sup> g<sup>-1</sup>), *S* (µg cm<sup>2</sup>).



Fig. 4. Fluorescence quenching of L  $(5 \times 10^{-5})$  with metal ions: (a) Co<sup>2+</sup>, (b) Ni<sup>2+</sup> and (c) Cu<sup>2+</sup> acetate.

IR, UV–vis, ESR spectra, conductance and magnetic measurements as well as the thermal analysis (TGA and DTA). The analytical data of the isolated solid complexes are given in Table 1 which is in good agreement with the proposed structure. The solid complexes are stable in air and insoluble in common organic solvents but soluble in DMF and DMSO. The low molar conductance values of the isolated complexes measured in DMF solution  $(10^{-3} \text{ M})$  at room temperature suggest their non-electrolytic nature [15] indicating that the acetate anion is absent or situated inside the metal coordination sphere. The addition of FeCl<sub>3</sub> solution to 1:1 (M:L) complexes did not give the red brown coloration confirming coordination of the acetate ion.

A comparison of the IR spectrum of the free azodye ligand (L) with those of the metal complexes has been carried out to investigate the mode of bonding of the azodye ligand. In the IR spectrum of the free ligand, the band at  $1422 \,\mathrm{cm}^{-1}$ characteristic for N=N bond is shifted to lower frequency by  $35-23 \text{ cm}^{-1}$  upon coordination to the metal ions with the appearance of another mode of vibration at  $424-455 \text{ cm}^{-1}$ corresponding to M-N bond [16]. This confirms the involvement of azo nitrogen in complex formation. The IR spectra of the complexes show a new band at  $520-584 \text{ cm}^{-1}$  due to M–O bond [17] resulting from the interaction between phenolic oxygen atom and the metal ions. A broad band at  $3419-3473 \text{ cm}^{-1}$  is present in the spectra of the metal complexes. The presence of this band is associated with coordinated and/or hydrated water molecule [18]. The other stretching vibration of the free azodye is less affected by complex formation indicating that the azodye ligand behaves as monobasic bidentate ligand via the azo nitrogen and phenolic oxygen atoms. In the IR spectra of the acetate complexes, bands due to  $v_{as}$  and  $v_{s}$  of the acetate group are displayed within the ranges 1610-1625 and  $1380-1390 \text{ cm}^{-1}$ , respectively. This frequency separation is characteristic of monodentate acetate groups for 1:1 (M:L) complexes [19].

The electronic spectra of the complexes were measured as Nujoll mull. In the spectra of the Co(II) complexes 1 and 2, the two bands at 17,857 and  $23,809 \text{ cm}^{-1}$  are assigned to  ${}^{4}T_{1g} \rightarrow {}^{4}A_{2g}$  and  ${}^{4}T_{1g} \rightarrow {}^{4}T_{1g}(p)$  transitions [20], respectively. Also, the values of the magnetic moments (4.82 BM for complex 1 and 4.94 BM for complex 2) are in good agreement with those reported for an octahedral structure [21]. The electronic spectra of the Ni(II) complexes 3 and 4 exhibit two bands at  $(15,625, 24,390 \text{ cm}^{-1})$  and  $(15,625, 24,390 \text{ cm}^{-1})$  $25,000 \,\mathrm{cm}^{-1}$ ), respectively. These bands correspond to the  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F)$  ( $v_2$ ) and  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$  ( $v_3$ ) transitions, respectively indicating octahedral geometry [22]. The magnetic moment values are 2.74 and 2.85 BM for complexes 3 and 4, respectively compared with the spin only value of 2.83 BM expected for a  $d^8$  system in  $O_h$  symmetry [23]. The electronic spectra of Cu(II) complexes 5 and 6 show band at 20,000 and 19,608 cm<sup>-1</sup>, respectively. This band is assigned to  ${}^{2}E_{g} \rightarrow {}^{2}B_{1g}$  transition assuming square planar geometry around Cu atom [24]. The magnetic moment values are 1.2 and 1.69 BM for complexes 5 and 6, respectively, which are less than the spin only value (1.73 BM). This may be due to an antiferromagnetic effect. The X-band ESR spectrum of Cu(II) complex 5, in the solid state, was measured at room temperature. The spectrum shows an isotropic signal at g = 2.0061which agrees with recently studied complexes of Cu(II) with square planar configuration [25].

The thermal behaviour of the prepared complexes can be summarized in Table 3. The Co(II) complexes 1 and 2 decomposed in three steps. The initial weight loss occurring within the range 90–195 °C is attributed to the removal of hydrated and/or coordinated water molecules. This process is accompanied by two endothermic peaks at 90 and 187 °C for complexes 1 and 2, respectively. In the temperature range 265–390 °C, the mass loss is in a good agreement with the loss of one molecule of the ligand. The DTA curves show exothermic peaks at 330 and 260 °C for complexes 1 and 2, respectively. The final step of the thermal decomposition in the temperature range 330–500 °C is associated with exothermic peaks at 390 and 445 °C for complexes 1 and 2, respectively. It is due to the complete decomposition leading to CoO as a final product from which the metal content was calculated.

The Ni(II) complexes **3** and **4** are thermally decomposed in three decomposition steps. The first stage of decomposition within the temperature range 50-90 °C (associated with an endothermic peak at ~90 °C for the two complexes) may be attributed to the loss of one hydrated water molecule. The second step of decomposition occurs within the temperature ranges 290–310 and 295–305 °C associated with exothermic peaks at 300 and 299 °C corresponding to the liberation of acetate and ethanol molecule for complex **3** and one ligand molecule for complex **4**, respectively. The remaining step of decomposition occurs within the temperature ranges 310–486 and 305–460 °C, associated with exothermic peaks at 402 and 403 °C for complexes **3** and **4**, respectively cor-

Table 3 Thermal decomposition data of Co(II), Ni(II) and Cu(II) azodye complexes

Complex	Temperature (°C)	Peak temperature DTA (°C)	Mass loss (%); estim. (calc.)	Assignment
1	90–190	90(-)	15.9 (16.0)	Loss of 1H <sub>2</sub> O
	310-390	330(+)	60.0 (59.9)	Loss of 3H <sub>2</sub> O
	390-420	390(+)	9.8 (10.4)	Loss of ligand
2	120-195	187(-)	6.10 (5.5)	Loss of 2H <sub>2</sub> O
	265-330	260(+)	42.3 (43.0)	Loss of first L
	330-500	445(+)	42.2 (43.0)	Loss of second L
3	50-90	89(-)	3.3 (3.2)	Loss of H <sub>2</sub> O
	290-310	300(+)	35.0 (35.8)	Loss of EtOH, AcO
	310-486	402(+)	51.3 (50.7)	Loss of ligand
4	50-90	90(-)	2.5 (2.5)	Loss of H <sub>2</sub> O
	295-305	299(+)	42.5 (45.0)	Loss of first L
	305-460	403 (+)	45.0 (45.0)	Loss of L, ethanol
5	90-130	120(-)	5.5 (4.3)	Loss of H <sub>2</sub> O
	180-230	260(+)	63.2 (64.5)	Loss of L
	250-450	410(+)	15.2 (14.1)	Loss of Cu(AcO) <sub>2</sub>
6	220-250	225(+)	45.0 (44.8)	Loss of first L
	250-470	400 (+)	43.0 (44.8)	Loss of second L

L = azodye ligand, AcO = acetate, (-) endothermic, (+) exothermic.

responding to the complete decomposition of the complexes leading to NiO.

Cu(II) complex **5** exhibits the first mass loss in the temperature range 90–130 °C, with an endothermic peak at 120 °C in the DTA curve. It may be attributed to the liberation of the hydrated water molecule. The second mass loss at 180–230 °C, with an exothermic peak at 200 °C is due to the liberation of the organic ligand. Copper acetate was found as the solid product of the second thermal decomposition process which is transformed to the oxide at 250–450 °C with an exothermic peak at 410 °C.

For Cu(II) complex **6**, there is no mass loss up to  $220 \degree$ C indicating that either water or solvent molecules are absent in

the complex. It undergoes two stage of decomposition process. The first step within the temperature range 220–250 °C, with an exothermic peak at 225 °C is attributed to the decomposition of one ligand molecule. The second stage of decomposition starts at 250 °C and ends at 470 °C, with an exothermic peak at 400 °C leaving CuO residue from which the Cu content was calculated.

The kinetic parameters of decomposition process of the complexes namely, activation energy  $(E^*)$ , enthalpy  $(\Delta H^*)$ , entropy  $(\Delta S^*)$  and free energy of the decomposition  $(\Delta G^*)$  as well as the order (n) and pre-exponential factor (A), are evaluated graphically by using Coats–Redfern [26] method as shown in (Fig. 5).

Table 4

Thermodynamic data of the thermal decomposition of Co(II), Ni(II) and Cu(II) azodye complexes

Complex	Step	n	<i>T</i> (K)	$E^*$ (kJ mol <sup>-1</sup> )	$\Delta H^*  (\text{kJ mol}^{-1})$	$A(S^{-1})$	$-\Delta S^* (\mathrm{J}\mathrm{k}^{-1}\mathrm{mol}^{-1})$	$\Delta G^* (\mathrm{kJ}\mathrm{mol}^{-1})$
1	First	1	318.64	65.12	62.46	$7.6 \times 10^8$	75.46	86.55
	Second	1	559.65	41.08	36.42	$2.94 \times 10^{2}$	202.9	149.98
	Third	1	655.52	174.1	168.65	224	225.9	165.96
2	First	0	343.40	48.08	45.22	$3.4 \times 10^6$	121	120.8
	Second	0.66	550.90	83.81	79.23	79	232.8	145.9
	Third	1	675.00	67.58	61.96	62	236.5	221.5
3	First	1	332.02	41.33	38.57	39	215.3	110.1
	Second	0	550.18	136.83	132.26	132	209.4	247.5
	Third	1	658.85	86.1	80.62	8	234	234.8
4	First	1	318.98	32.32	29.66	29.7	217	98.9
	Second	1	553.63	202.72	198.12	198	206	312.2
	Third	1	640.56	108.49	103.16	103	213	239.6
5	First	1	421.03	102.46	98.96	99	209.5	187.2
	Second	0	468.30	117.27	113.38	113	209.4	211.4
	Third	0	589.54	63.95	59.05	59	216.7	186.8
6	First	0.33	502.93	413.46	408.55	$4.1 \times 10^2$	199.2	508.7
	Second	0	677.73	60.35	54.71	55	218.4	202.7



Fig. 5. Coats–Redfern plots for the decomposition steps of (A) complex **1**, (B) complex **2**, (C) complex **3**, (D) complex **4**, (E) complex **5** and (F) complex **6**: (a) first step, (b) second step and (c) third step;  $Y = \begin{cases} \ln\{[1 - (1 - \alpha)^{1-n}]/[T^2(1 - n)]\} & \text{for } n \neq 1 \\ \ln\{[-\ln(1 - \alpha)]/T^2\} & \text{for } n = 1 \end{cases}$ 

The calculated values of *n*, *E*, *A*,  $\Delta S$ ,  $\Delta H$  and  $\Delta G$  for the decomposition steps are given in Table 4.

From the activation energy values, one can concluded that the water molecules are easy to be eliminated from the complexes according to the following order Ni > Co > Cu. Also, the energy of activation for the second stage of decomposition for all complexes, except complexes 1 and 6, is higher than that of the first stage due to the less steric strain in the intermediate compounds obtained after the first stage of decomposition. On comparing the activation energy of the first stage of decomposition of Cu(II) complex with the second stage of Co(II) and Ni(II) complexes, Cu(II) complex shows remarkably higher value. This may be due to the stereo structure of the complexes and the electronic configuration of the metal ion.

The  $\Delta S^*$  values for all complexes were found to be negative. This indicates that the activated complex is more ordered than the reactants [27].

#### 4. Conclusion

The electronic spectrum of the pyrimidine azodye (L) was recorded in different solvents and in universal buffer solutions containing different percentages of methanol. The  $pK_a$ of the azodye was determined at different temperatures. The  $pK_a$  values increase with the rise of the temperature and decrease of the percentage of methanol. The various optimum conditions for complex formation were detected. The spectrophotometric titration of Co(II), Ni(II) and Cu(II) with EDTA in presence of the pyrimidine azodye indicated that the azodye can be used as an indicator. The fluorescence of the azodye was quenched in presence of Co(II), Ni(II) and Cu(II) ions. The calculated Stern–Volmer second order rate constant decreases with increasing the ionic radius of the metal ion. The solid complexes were prepared and characterized on the basis of elemental analysis, molar conductance, magnetic moments, spectral and thermal studies. The proposed chemical structures of the metal chelates suggest the octahedral geometry for Co(II) and Ni(II) chelates and square planar for Cu(II) chelate. From all of the above observations, the structure of the complexes is given as follows:



 $M=Co,\ Y=H_2O,\ n=0 \quad M=Ni,\ Y=EtOH,\ n=1 \quad M=Cu,\ Y=0,\ n=0$ 



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