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# Synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes involving hydroxy antipyrine azodyes

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#### Abstract

The complexes formed between some hydroxy antipyrine azodyes and Co(II), Ni(II) and Cu(II) ions were studied spectrophotometrically in solution. The stoichiometry and stability constants of the metal chelates were determined. The spectrophotometric determination of the titled metal ions and titration using EDTA were reported. The chelating behaviour of the azodyes was confirmed by preparing the solid chelates in which their structures are elucidated using molar conductance, elemental, thermogravimetric (TGA) analyses, IR, ESR and electronic spectra as well as the magnetic measurements. Kinetic parameters are computed from the thermal decomposition data. The electrical properties for the metal complexes are measured from which the activation energies are calculated. © 2007 Elsevier B.V. All rights reserved.

Keywords: Azoantipyrine; Complexes; Spectral and thermal studies

## 1. Introduction

A lot of work has been reported on the spectrophotometric studies of the heterocyclic azo compounds, their metal complexes and analytical applications [1–14]. A number of workers have used antipyrine and its derivatives as ligands in synthesizing complexes with transition metal ions [15]. Considerable studies have been devoted to azodyes derived from 4-aminoantipyrine and their metal complexes [16]. Thus, we have initiated a program of studying the metal complexes of some hydroxy azo compounds derived from 4-aminoantipyrine.

The aim of the present work is to study of the most favourable conditions for complex formation, stoichiometry and spectrophotometric determination of some metal ions using the titled azodyes. The formation of the metal complexes is confirmed by preparing the solid complexes and studying their spectral, conductance, magnetic and thermal properties.

# 2. Experimental

# 2.1. Synthesis of azo compounds $(L^1 - L^3)$

A solution of 4-aminoantipyrine (0.01 mol) was prepared in a least amount of HCl (~2 ml, 10 M). A cold solution (0.01 mol) of NaNO<sub>2</sub> below 5 °C was then added to the amine solution dropwise with continuous stirring. A solution (0.01 mol) of resorcinol (L<sup>1</sup>),  $\beta$ -naphthol (L<sup>2</sup>) or 2-hydroxy-3-naphthoic acid  $(L^3)$  was prepared by dissolving in NaOH solution (2-3 g of NaOH in 50 ml bidistilled water), then colded to 0 °C. The cold diazonium salt solution was added to the hydroxy solution dropwise with stirring. The azodye was separated by slight acidification, then filtered off, recrystallized from ethanol and dried in vacuo over anhydrous CaCl<sub>2</sub>. The purity of the azodyes was confirmed by elemental analysis, m.p. constancy as well as by IR spectral studies (L<sup>1</sup>: m.p. = 263 °C, analysis: found, C 62.8; H 4.8; N 17.4%, Calcd for C<sub>17</sub>H<sub>16</sub>N<sub>4</sub>O<sub>3</sub>, C 62.96; H 4.93: N 17.28%; L<sup>2</sup>: m.p. = 165 °C, analysis: found, C 69.9; H 4.8; N 15.3%, Calcd for C<sub>21</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>, C 70.39; H 5.03; N 15.64%; L<sup>3</sup>: m.p. = 158 °C, analysis: found, C 65.4; H 4.3; N 13.7%, Calcd for C<sub>22</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>, C 65.67; H

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4.48; N 13.93%. The azo compounds have the following structures:



### 2.2. Synthesis of complexes

The solid complexes were synthesized by the addition of the appropriate metal chloride, perchlorate or acetate solution (0.01 mol) in ethanol (10 ml) to the ethanolic solution (20 ml) of the respective azodye (0.01 mol). The resulting mixture was stirred under reflux for ~2 h where upon the complexes were precipitated. The solid chelates were filtered off, washed several times with ethanol, dried, kept in a desiccator over dried silica gel and then subjected to elemental analyses. The analytical data along with the conductance values of  $10^{-3}$  M metal chelates in DMF at 25 °C are given in Table 1.

#### 2.3. Measurements

The C, H and N elemental analyses were performed using Heraeus CHN elemental analyzer. The metal contents were estimated by compleximetric EDTA titration (after complete decomposition of the complexes in aqua regia several times) and atomic absorption technique. Conductivity measurements were made using a Hanna 8733 conductometer. The thermogravimetric analysis (TGA) of the solid complexes was performed using Shimadzu TG-50 thermogravimetric analyzer in the temperature range 25-800 °C with 10 °C/min heating rate. IR spectra were recorded over the 4000–200 cm<sup>-1</sup> range on a Perkin-Elmer 1430 spectrophotometer using KBr discs. Electronic spectra in Nujol mull were determined using Shimadzu UV-Vis 240 spectrophotometer. The magnetic measurements were carried out at room temperature employing the Faraday balance technique. The equipment was calibrated with Hg[Co(CNS)<sub>4</sub>]. Diamagnetic corrections were made using Pascal's constants. The ESR spectra of powder samples were recorded by means of a Jeol model JES-FE 2XG (Japan) spectrometer equipped with an E101 microwave bridge. Diphenyl picrylhydrazide free radical (DPPH) was used as a reference material (g = 2.0023). The electrical conductivity measurements were made on a Super Megohmmeter (Model RM 170) electrometer. The samples were pressed into discs of 13 mm diameter and 1.5-1.6 mm thickness at a pressure  $\sim$ 700 kg cm<sup>-2</sup>. The surfaces of the discs were painted carefully with a silver paste. The temperature was measured in air using a Cu/CuNi Comark thermometer placed closed to the sample.

## 3. Results and discussion

## 3.1. Study of complexes in solution

The evaluation of the optimum conditions for complexation of Co(II), Ni(II) and Cu(II) ions with antipyrine azodyes includes a careful investigation of all factors involved in the procedure such as pH, time, sequence of addition. Selection of suitable wavelength is also included. The results are listed in Table 2. The results indicate that the optimum pH values recommended for the subsequent studies of properties of the Cu–L<sup>1</sup> complexes are 9, 10 and 11 for chloro, acetato and perchlorato complexes, respectively. For Cu(II) complexes of L<sup>2</sup> and L<sup>3</sup>, the optimum pH values are 4 and 8, respectively. Solutions of pH 8–11 are the most suitable for the formation of Co(II) and Ni(II) complexes with L<sup>1</sup>–L<sup>3</sup>. At the suitable

Table 1

Elemental analyses data, molar conductivities and magnetic values of the metal complexes

No.	Complex (colour)	Elemental anal	Elemental analysis (a)				
		%M	%C	%H	%N		
1	$[CoL^{1}(AcO)(H_{2}O)_{2}]2H_{2}O$ (faint brown)	11.3 (11.5)	44.4 (44.5)	3.4 (3.5)	10.7 (10.9)	12.9	4.7
2	$[NiL^{1}(AcO)(H_{2}O)_{2}]^{2}H_{2}O$ (faint brown)	11.2 (11.4)	44.2 (44.5)	3.4 (3.5)	10.6 (10.9)	10.8	2.9
3	$[CuL^{1}(AcO)(H_{2}O)_{2}]2H_{2}O$ (reddish brown)	12.0 (12.3)	43.7 (44.1)	3.3 (3.0)	10.5 (10.8)	10.8	1.8
4	$[CuL^{1}Cl(H_{2}O)_{2}]$ (reddish brown)	13.7 (13.9)	44.3 (44.5)	3.4 (3.3)	11.9 (12.2)	19.9	1.82
5	$[CuL^{1}(ClO_{4})(EtOH)_{2}]$ (reddish brown)	10.8 (10.99)	43.8 (43.6)	4.6 (4.7)	9.9 (9.7)	20.3	1.8
6	$[CoL^{2}(AcO)(H_{2}O)_{2}]H_{2}O$ (brown)	10.9 (11.1)	51.9 (52.2)	3.6 (3.8)	10.2 (10.6)	13.3	4.9
7	$[NiL^{2}(AcO)(H_{2}O)_{2}]H_{2}O$ (faint brown)	10.8 (11.1)	51.8 (52.2)	3.5 (3.8)	10.3 (10.6)	11.4	2.95
8	$[NiL^2Cl(H_2O)_2]2H_2O$ (faint brown)	10.9 (11.2)	47.8 (48.2)	3.0 (4.2)	10.8 (10.7)	19.3	2.85
9	$[CuL^{2}(AcO)(H_{2}O)_{2}]H_{2}O$ (brown)	11.8 (11.4)	51.3 (51.7)	3.5 (3.7)	10.4 (10.5)	11.3	1.79
10	$[CoL^{3}(AcO)]4H_{2}O$ (brown)	10.0 (9.8)	48.7 (48.4)	3.4 (4.3)	9.5 (9.2)	12.9	4.7
11	[NiL <sup>3</sup> (AcO)]3H <sub>2</sub> O (orange brown)	10.2 (10.0)	50.2 (49.4)	3.5 (3.2)	9.8 (9.4)	12.2	_
12	$[CuL^{3}(AcO)]2H_{2}O$ (reddish brown)	11.3 (11.0)	51.5 (51.3)	3.6 (3.4)	10.0 (9.8)	11.9	1.8

a, Calcd (found). b,  $\Lambda_{\rm m}$  (ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>).

 Table 2

 Analytical data of the metal complexes of antipyrine azodyes

Lig.	$M^{2+}$	$\lambda$ (nm)	pН	Log $\beta$ (	(MRM)	Log $\beta$ (	CVM)	3	Beer's law up to M	SD	CC
				1:1	1:2	1:1	1:2				
$L^1$	Со	500	9.0	4.33	10.41	4.19	10.87	12,171	$8 \times 10^{-5}$	0.0003	0.999
	Ni	490	9.0	4.29	9.56	3.82	8.63	17,054	$6 \times 10^{-5}$	0.006	0.988
	Cu	505	10.0	4.64	_	5.02	9.32	40,301	$3.5 \times 10^{-5}$	0.006	0.994
	Cu	505	_	4.10	9.05	5.18	7.67	18,977	$10 \times 10^{-5}$	0.022	0.994
$L^2$	Со	510	9.0	4.86	9.87	5.23	_	_	_	_	_
	Ni	495	8.0	4.79	10.21	8.89	_	_	_	_	_
	Cu	500	4.0	4.74	10.31	5.29	_	22,040	$3 \times 10^{-5}$	0.0008	0.996
	Cu	505	_	_	_	4.41	_	19,210	$4 \times 10^{-5}$	0.0007	0.996
$L^3$	Со	520	10.0	3.9	8.20	_	_	_	_	_	_
	Ni	500	11.0	3.9	8.25	_	_	_	_	_	_
	Cu	510	8.0	3.82	8.21	4.77	9.07	_	_	_	_
	Co	475	_	_	_	3.77	8.43	_	_	_	_
	Ni	480	_	_	_	3.68	7.8	_	_	_	_
	Cu	490	_	-	-	3.67	8.46	23,422	$4 \times 10^{-5}$	0.0014	0.997

ε, molar absorptivity (L mol<sup>-1</sup> cm<sup>-1</sup>); SD, standard deviation; CC, correlation coefficient.

wavelength the sequence of addition buffer— $L^1$ -metal and  $L^2$  or  $L^3$ -metal buffer are the most suitable.

Also, it was found that the complexes are completely developed spontaneously and remain stable for more than 24 h. The stoichiometry of the metal complexes was investigated with the aid of the standard spectrophotometric methods namely, mole ratio, MRM [17] and continuous variation, CVM [18] methods. The results of the first method indicate the formation of 1:1 and 1:2 (M:L) complexes, except for Cu-L<sup>1</sup> complex at pH 10 which forms 1:1 complex only. The second method showed the formation of 1:1 and 1:2 (M:L) complexes, except for complexes Cu-L<sup>1</sup> at pH 10, Cu-L<sup>2</sup>, Cu-L<sup>3</sup> at pH 8, Co-L<sup>2</sup> and  $Ni-L^2$  at pH 8 where only 1:1 complexes were formed. The logarithmic stability constants of the formed complexes were calculated from the data of the mole ratio and continuous variation methods applying the Harvey and Manning equation [19]. The results listed in Table 2 show that 1:2 (M:L) complexes are more or less twice as stable as 1:1 (M:L) complexes.

At suitable pH characteristic for each system, the linearity of the absorbance-concentration relation was satisfied up to  $8 \times 10^{-5}$ ,  $6 \times 10^{-5}$ ,  $3.5 \times 10^{-5}$ ,  $3 \times 10^{-5}$  and  $4 \times 10^{-5}$  M for Co-L<sup>1</sup>, Ni-L<sup>1</sup>, Cu-L<sup>1</sup>, Cu-L<sup>2</sup> and Cu-L<sup>3</sup>, respectively. Without using buffer solutions the relation was satisfied up to  $10 \times 10^{-5}$  and  $4 \times 10^{-5}$  M for Cu-L<sup>1</sup> and Cu-L<sup>2</sup> complexes, respectively.

The standard deviation values are very low indicating the high reproducibility coefficient of the results with high correlation coefficient. The high molar absorptivity values indicate the sensitivity of the present method for the spectrophotometric determination of the metal ion. Cu–L<sup>1</sup> complex has higher  $\varepsilon$  value indicating high sensitivity more than the Cu–L<sup>2</sup> and Cu–L<sup>3</sup> complexes. For one and the same azodye, Cu–L<sup>1</sup> complex has higher molar absorptivity value than Co–L<sup>1</sup> and Ni–L<sup>1</sup> complexes. The application of azodyes  $(L^1-L^3)$  as indicators for spectrophotometric titration of Co(II), Ni(II) and Cu(II) ions with EDTA has been ascertained. Cu(II) ion exhibits a good response up to 23.2, 24.8 and 21.3 µg/ml for azodyes L<sup>1</sup>, L<sup>2</sup> and L<sup>3</sup>, respectively. Co-L<sup>1</sup> and Ni-L<sup>1</sup> complexes show good response up to 16.5 and 15.6 µg/ml, respectively.

## 3.2. Characterization of the solid complexes

The solid complexes of azodyes  $(L^1-L^3)$  with Co(II), Ni(II) and Cu(II) ions were prepared and investigated by elemental analysis, thermal analysis (TGA), IR, ESR, electronic spectra, magnetic measurements as well as conductance measurements. The complexes are air stable and soluble in DMF or DMSO. The higher melting points of the complexes than those of the ligands can be taken as an evidence for the bonding to the metal ion with chelate ring formation. The values of molar conductance in  $10^{-3}$  M DMF (Table 1) indicate that the complexes are non-electrolyte [20], i.e., the chloride, perchlorate and acetate ions are involved inside the coordination sphere. The presence of chloride ion inside the coordination sphere was also confirmed by the chemical reaction with AgNO<sub>3</sub> where precipitation of chloride ion was not observed. Addition of the FeCl<sub>3</sub> solution to the solution of the acetato complexes dose not give red brown, confirming coordination of the acetate ion on complex formation. These results are further confirmed from IR spectra.

The mode of bonding of the azodyes complexes was elucidated by investigating the IR spectra of the metal complexes as compared with those of the free azodyes. The N=N bands at 1488, 1499 and 1496 cm<sup>-1</sup> of the free dyes  $L^1$ ,  $L^2$  and  $L^3$ , respectively, exhibit a shift to higher wave number on complexation which may taken as evidence for the participation of the N=N group in coordination.

This is supported by the appearance of a new band in the region 423–467 cm<sup>-1</sup> due to  $v_{(M-N)}$  [21]. The  $v_{(C=O)}$  bands at 1668, 1634 and 1630 cm<sup>-1</sup> for azo compounds  $L^1$ ,  $L^2$ and  $L^3$ , respectively, exhibit a shift to lower value on complex formation [22]. The appearance of new bands in the region 503–523 cm<sup>-1</sup> due to  $v_{(M-Q)}$  supports the coordination of the C=O group to the metal ions [23]. Further more, broad bands for all chelates, except complex 5, were observed within the wave number range 3380-2474 cm<sup>-1</sup> attributed to the stretching frequency of water molecules. The IR spectrum of complex 5 exhibits a strong splitted bands at 1189, 1110 and  $1042 \text{ cm}^{-1}$  assignable to coordinated nature of the perchlorate anion [24]. The acetate group in the acetato complexes act as monodentate ligand [25] and this is evidenced by the difference  $(140-145 \text{ cm}^{-1})$ between the  $v_{as}$  (1560–1585 cm<sup>-1</sup>) and  $v_s$  (1420–1440 cm<sup>-1</sup>) vibrations. The presence of the coordination water is supported by the presence of bands within the ranges 3420-3380, 1610–1600 and 970–950  $\text{cm}^{-1}$  due to OH stretching. HOH deformation and HOH rocking [25]. The presence of the bands within the range 1697–1728 cm<sup>-1</sup> indicates that the COOH group of  $L^{3}$  does not contribute to the complex formation.

The Co(II) complexes exhibited electronic spectral bands at 15,625 and  $18,182 \text{ cm}^{-1}$  for complex (1) and 15,748 and 18,519  $\text{cm}^{-1}$  for complex (6). These bands are  ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)(v_2)$  and  ${}^{4}T_{1o}(F) \rightarrow$ assigned to  ${}^{4}T_{1g}(P)(v_{3})$  transitions, respectively, characteristic of octahedral geometry [26]. The room temperature magnetic moment values for Co(II) complexes 1 and 6 are 4.79 and 4.98 BM, respectively, which are higher than the spin only value due to orbital angular momentum contribution in d<sup>7</sup> system and closer to the value required for an octahedral structure [27]. The relative strength of the ligand and geometry of the complexes can be illustrated by calculating the parameters of the ligand field splitting (10Dq) and of interelectronic repulse (B). The values of 10Dq ( $v_1$ ) and B are 8326 and 794 for complex 1 and 7350 and 815 for complex 6. The ratio  $(v_2/v_1)$  is found to be ~2.14 for complexes 1 and 6, as required for the octahedral Co(II) complexes [28]. The values of the Nephelauxetic parameter  $\beta$  are 0.71 and 0.73 for complexes 1 and 6, respectively. These values indicate the appreciable covalent character of the metal ligand bond.

The Co(II) complex (10) is paramagnetic with room temperature effective magnetic moment (4.1 BM) value which lies in the range expected for tetrahedral Co(II) complexes of a high spin type, i.e., this value is in agreement with the spin value for three unpaired electrons (3.89 BM) [29]. The bands at 15,385 and 19,230 cm<sup>-1</sup> may be assigned to the  ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(F)$  ( $v_{2}$ ) and  ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(P)$  ( $v_{3}$ ) transitions, respectively, supporting the tetrahedral geometry [30].

For the Ni(II) complexes (2, 7 and 8), the spectra display two bands within the ranges 15,152–15,625 and 19,230– 20,000 cm<sup>-1</sup> assignable to  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$  ( $v_{2}$ ) and  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$  ( $v_{3}$ ) transitions, respectively. These values are expected for the octahedral Ni(II) complexes [31]. The observed magnetic moments of the Ni(II) complexes in the range 2.81–2.94 BM confirm the octahedral structure of these complexes [32].

The Ni(II) complex (11) exhibited a band at 19,608 cm<sup>-1</sup> corresponding to square planar geometry. This band may be assigned to  ${}^{1}A_{1g}(D) \rightarrow {}^{1}B_{2g}(G)$  transition. This complex shows the diamagnetic behaviour indicating the square planar environment around the Ni(II) ion.

The solid state spectra of the Cu(II) complexes (3–5 and 9) showed two bands at 19,417–18,939 and 17,544–16,949 cm<sup>-1</sup>, assigned to  ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$  and  ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$  transitions, respectively [30], which are consistent with distorted octahedral geometry. The electronic spectrum of Cu(II) complex (12) exhibits a band at 16,950 cm<sup>-1</sup> which is agreement with those observed for square planar complex. The Cu(II) complexes have normal magnetic moments values (1.85–1.8 BM) corresponding to the mono-nuclear Cu(II) complexes [33].

The ESR spectra of the Cu(II) complexes (3, 4, 5, 9 and 12) have been recorded as polycrystalline samples at room temperature (25 °C). The observed data show that for complexes 3–5 and 9,  $g_{\parallel} = 2.229 - 2.266$  and  $g_{\perp} = 2.055 - 2.065$ , Table 3. The calculated  $g_{av}$  values =  $(g_{\parallel} + 2g_{\perp})/3$  are in the range 2.112-2.132. The lowest g value was more than 2 consequently, to assign the tetragonal distorted symmetry associated with  $d_{\chi^2 - \gamma^2}$  ground state rather than  $d_7^2$  [34]. The value of the exchange interaction (G) between the Cu centers in a polycrystalline solid has been calculated using the relation  $G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$  [35]. If G > 4, the exchange interaction is negligible, while G < 4 indicates considerable exchange interaction in the solid complexes. The results listed in Table 3 indicate that there is no exchange interaction between Cu(II) ions. Kivelson and Neiman [36] noted that for an ionic environment  $g_{\parallel} > 2.3$ and for a covalent environment  $g_{\parallel} < 2.3$ . All complexes

Table 3 Electronic and ESR spectral parameters for Cu(II) complexes

No.	d-d Transition (cm <sup>-1</sup> )		$g_{\parallel}$	$g_{\perp}$	$g_{\mathrm{av}}$	G	$k_{\parallel}^2$	$k_{\perp}^2$	$k^2$
	$\varDelta_1$	$\varDelta_2$							
3	19,230	17,391	2.229	2.054	2.112	4.24	0.595	0.60	0.599
4	19,417	17,543	2.229	2.058	2.115	4.00	0.60	0.653	0.635
5	19,305	17,391	2.229	2.055	2.113	4.20	0.595	0.614	0.608
9	18,939	16,949	2.266	2.065	2.132	4.10	0.675	0.717	0.703
12	19,800	17,400	2.260	2.060	2.127	4.33	0.677	0.689	0.686

Table 4			
Thermal analysis data	of the complexes	of antipyrine az	o compounds

No.	Hydrated water		Coordinated wate	r	Decomposition	
	Temp. (°C)	% Found (calcd)	Temp. (°C)	% Found (calcd)	Temp. (°C)	% Found (calcd)
1	105	6.9 (7.1)	200-250	7.5 (7.6)	250-556	11.3 (11.5)
2	124	6.7 (7.0)	325-400	7.3 (7.6)	400-600	11.8 (11.4)
3	105	7.1 (7.0)	200-230	6.97 (7.0)	230-650	12.2 (12.3)
4	_	-	Up to 320 <sup>a</sup>	16.0 (15.8)	320-750	13.5 (13.9)
5	_	_	280–300 <sup>b</sup>	15.0 (14.9)	325-700	10.5 (10.2)
6	105	3.5 (3.4)	175–250, 300 <sup>°</sup>	6.8 (7.0), 12.5 (12.4)	300-600	10.9 (11.1)
9	125	3.5 (3.4)	125–314 <sup>°</sup>	17.3 (17.9)	314-800	11.86 (11.9)
10	100	11.9 (12.3)	_	_	200-500	9.9 (10.0)
11	95	9.5 (9.43)	_	_	150-500	9.99 (10.2)
12	100	6.24 (6.43)	_	_	200-500	11.1 (11.3)

<sup>a</sup> Loss of H<sub>2</sub>O and Cl content.

<sup>b</sup> Loss of ethanol.

<sup>c</sup> Loss of H<sub>2</sub>O and/or acetate.

exhibit  $g_{\parallel} < 2.3$  suggesting covalent character of the Culigand bonding in the present complexes. The *g* values of copper(II) complexes with a <sup>2</sup>B<sub>1g</sub> ground state ( $g_{\parallel} > g_{\perp}$ ) may be expressed [37] by

$$k_{\parallel}^2 = (g_{\parallel} - 2.0023) \Delta_2/8\lambda, \quad k_{\perp}^2 = (g_{\perp} - 2.0023)\Delta_1/2\lambda, \ k^2 = [k_{\parallel}^2 + 2k_{\perp}^2]/3,$$

where  $k_{\parallel}^2$  and  $k_{\perp}^2$  are the parallel and perpendicular components, respectively, of the orbital reduction factor k,  $\lambda$  is the spin–orbit coupling constant (-828 cm<sup>-1</sup>) for free copper,  $\Delta_1$  and  $\Delta_2$  are the electronic transition  ${}^2B_{1g} \rightarrow {}^2E_g$  and  ${}^2B_{1g} \rightarrow {}^2B_{2g}$ , respectively. The values listed in Table 3 showed that  $k_{\parallel}^2 < k_{\perp}^2$  which is a good evidence for the assumed  ${}^2B_{1g}$  ground state. The lower values of  $k^2$  than the unity are indicative of their covalent nature which in agreement with the conclusion obtained from the values of  $g_{\parallel}$ .

The results of TGA are collected in Table 4. The metal chelates degrade mainly in two or three stages from which the percentage of water and the metal content were calculated. The first step corresponds to the loss of lattice water. The second step represents the removal of coordinated water and/or chloride (complex 4), ethanol (complex 5), acetate (complexes 6 and 9). The third weight loss step corresponds to the decomposition of the complexes with the formation of the metal oxide as a final product from which the percentage of the metal content was calculated and compared with those obtained from EDTA and atomic absorption spectra.

The thermal decomposition processes underlying the TGA of complexes 1–3, as example, can be schematically represented as:

$$\begin{bmatrix} ML(AcO)(H_2O)_2 \end{bmatrix} 2H_2O \stackrel{105-124}{\rightarrow} \stackrel{^{\circ}C}{\rightarrow} \begin{bmatrix} ML(AcO)(H_2O)_2 \end{bmatrix}$$

$$\stackrel{200-400}{\rightarrow} \stackrel{^{\circ}C}{\leftarrow} \begin{bmatrix} ML(AcO) \end{bmatrix} \stackrel{230-650}{\rightarrow} \stackrel{^{\circ}C}{\rightarrow} MO$$

The final stage of decomposition of selected complexes was studied in more details. The kinetic parameters such as, activation energy (*E*), enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ) and free energy of the decomposition ( $\Delta G$ ) as well as the order of the reaction (*n*) and the pre-exponential factor (*A*) are eval-

uated graphically by using Coats-Redfern [38] method using the relation:

$$\ln\{[1 - (1 - \alpha)^{1-n} / [T^2(1 - n)]\} = [M/T] + B \text{ for } n \neq 1$$
  
$$\ln\{[-\ln(1 - \alpha) / T^2\} = [M/T] + B \text{ for } n = 1,$$



Fig. 1.  $\ln[-\ln(1-\alpha)/T^2$  vs. (1000/*T*) plot for the final stage of decomposition of complexes 1–3, 6, 8 and 9.

 Table 5

 The kinetic and thermodynamic data of the thermal decomposition of azodye complexes

No.	п	$E (\mathrm{kJ}\mathrm{mol}^{-1})$	$A (s^{-1})$	$-\Delta S (\text{J mol}^{-1} \text{ K}^{-1})$	$\Delta H (\mathrm{kJ} \mathrm{mol}^{-1})$	$\Delta G (\mathrm{kJ}\mathrm{mol}^{-1})$
1	1	19.62	$1.25 \times 10^{9}$	77.5	14.0	66.1
2	1	24.64	$2.20 \times 10^{8}$	92.8	18.4	87.9
3	1	15.40	$7.00 \times 10^{8}$	81.6	10.3	60.3
4	0.66	18.13	$1.00 \times 10^{9}$	80.4	10.4	86.7
6	1	11.64	$7.30 \times 10^{8}$	82.7	5.6	65.4
8	1	28.80	$1.80 \times 10^{8}$	95.2	22.0	99.5
9	1	35.92	$1.94 \times 10^{8}$	96.1	27.8	121.3

Table 6 Electrical conductivity data of azodye  $[L^1]$  and its metal complexes

Comp.	Metallic		Semi.		Non temp. (°C)	Phase transfer (°C)	
	Temp. (°C)	Ea (eV)	Temp. (°C)	Ea (eV)			
$L^1$	40-103	0.11	103-130	0.36	_	130	
	158-227	0.10	130-158	0.08	_		
2	30-50	0.28	50-91	0.17	132-227	91	
			91-132	0.46	_		
3	37-89	0.18	89–135	0.35	135–253	_	
					_	_	
4	37-50	0.03	50-70	0.07	109–170	70	
			70-109	0.02	_		
5	182-253	0.01	60-100	0.01	34–60	_	
					100-189	_	
6	186-222	0.05	40-92	0.02	140–186	92	
			92–140	0.03	_		

Semi., semiconducting. Non, nonconducting.

where  $\alpha$  is the fraction of the material decomposed at a given temperature, M = -E/R and  $B = \ln[AR/QE]$ , R is the gas constant and Q is the heating rate.

A plot of the left-hand side of these equations against 1/T for different values of n, have been tested; Fig. 1. The correct value of (n) for the thermal reaction is the one which gives the best straight line. From the slope and intercept, the values of E and A were determined, respectively. The other kinetic parameters were determined using the standard equations [39]. According to the data listed in Table 5 the complexes have -ve entropy which indicates that the activated complexes have more ordered systems than reactants and that the reactions are slower than normal [40].

For complexes 6, 8 and 9, the lower thermal stability of the Co(II) complex 6 than the other two complexes may be due to the higher repulsion between the multiple bonding electron pairs (six bonds)] in the valence shell of cobalt as well as to higher repulsion obtained by non-bonded pairs of electrons on the axial donating oxygen of  $H_2O$  molecule and the bonded electrons [41].

The results of the electrical conductivity of azodye,  $L^1$ , and its Co(II), Ni(II) and Cu(II) complexes are listed in Table 6. The discontinuity in the semiconducting region can be ascribed to a molecular rearrangement or to crystallographic transitions. The metallic behaviour observed in the low temperature range may be attributed to the creation of some crystal voids and defects that function as traps



$$\begin{split} &X=H_2O\;,\quad Y=AcO\;,\qquad n=2\; \text{for complexes 1,2,3}\\ &X=H_2O\;,\quad Y=Cl\;,\qquad n=0\; \text{for complex 4} \end{split}$$

X = EtOH,  $Y = ClO_4$ , n = 0 for complex 5



Z = H or COOH

$\mathbf{X} = \mathbf{H}_2 \mathbf{O} , \ \mathbf{Y} = \mathbf{A} \mathbf{c} \mathbf{O} ,$	n = 1 for complexes 6,7,9				
$\mathbf{X} = \mathbf{H}_2 \mathbf{O} , \ \mathbf{Y} = \mathbf{C} \mathbf{I} ,$	n = 2 for complex 8				
$\mathbf{X} = 0 , \qquad \mathbf{Y} = \mathbf{A}\mathbf{c}\mathbf{O} ,$	n = 4 ,3 , 2 for complexes 10, 11, 12				
Fig. 2. The structures of the metal complexes.					

for the current carriers [42]. The temperature range in which the conductivity values remain constant indicates that the energy is consumed in the phase transition rather than in the thermal agitation of electrons [42].

## 4. Conclusion

The design and synthesis of a new hydroxy azodyes from 4-aminoantipyrine have been demonstrated. The IR spectra of the complexes indicate that the azo-compounds coordinate to the divalent metal ions (Co, Ni and Cu) through ONO as tridentate ligands. From the electronic, ESR spectra, conductance, magnetic moments and thermal analyses measurements, the structures of the complexes are given in Fig. 2. The reaction between the azodyes and Co(II), Ni(II) and Cu(II) ions are also studied spectrophotometry in solution. The optimum conditions for complex formation, stoichiometry and stability constants are determined. The results indicate that the investigated azodye can be used as an indicator for spectrophotometric determination of Co(II), Ni(II) and Cu(II) ions.

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