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Syntheses and investigation of thermal properties of copper complexes with azo-containing Schiff-base dyes

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Abstract

In the present study a series of azo dyes: 5-((4-pentyloxyphenyl)azo)-salicylaldimine-*N*-R (R = phenyl, 4-methoxyphenyl, cyclohexyl) and related copper(II) bis chelates have been synthesized and characterized by IR, NMR, mass spectroscopies and elemental analyses. The thermal stability of free ligands and related copper(II) bis(chelate) was studied by using differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA). The differences in the thermal stability were related to the structure of free ligands and copper complexes and decomposition products were characterized according to their X-ray diffraction pattern.

Keywords: Schiff base; Azo dyes; Thermal stability; Recording materials

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1. Introduction

Azo compounds, with two phenyl rings separated by an azo (−N═N−) bond, are versatile molecules and have received much attention in research areas both fundamental and application. The strong electronic absorption maximum can be tailored by ring substitution to fall anywhere from the ultraviolet to red-visible regions, allowing chemical fine-tuning of color [1,2]. This, combined with the fact that these azo groups are relatively robust and chemically stable, has prompted extensive study of azobenzene-based structures as dyes and colorants. Furthermore, the light-induced interconversion allows systems incorporating azo group to be used as photoswitches, effecting rapid and reversible control over a variety of chemical, mechanical, electronic, and optical properties [3,4].

Because of the good thermal stability of azo compounds, one of the most important applications of azo compounds is in the optical data storage. In general, cyanine dyes, phthalocyanine dyes, and metal−azo complex dyes are used for DVD-R (digital versatile disc-recordable) as recording layer. As for cyanine dyes, they are unstable against light and not durable for repeated reading use. Phthalocyanine dyes also have demerits, such as a worse solubility and higher cost than cyanine dyes. On the other hand, organic azo compounds and metal−azo complexes are more stable than cyanine dyes against light, provide easier control of the wavelength according to the substituted groups, and have good thermal stability with a metal complex [5–7].

Based upon the consideration of the above requirements, the thermal properties of azo compounds play an important role in application of azo dyes and their metal−azo dyes. Because of the importance of azo-containing compounds and in continuance of our interest in syntheses of azo-based compounds [8–14], we report herein the syntheses and study of the thermal properties of new Schiff-base azo compounds and their copper complexes (see Scheme 1).

2. Experimental

2.1. Reagents

All reagents and solvents used were supplied by Merck chemical company and used without further purification.

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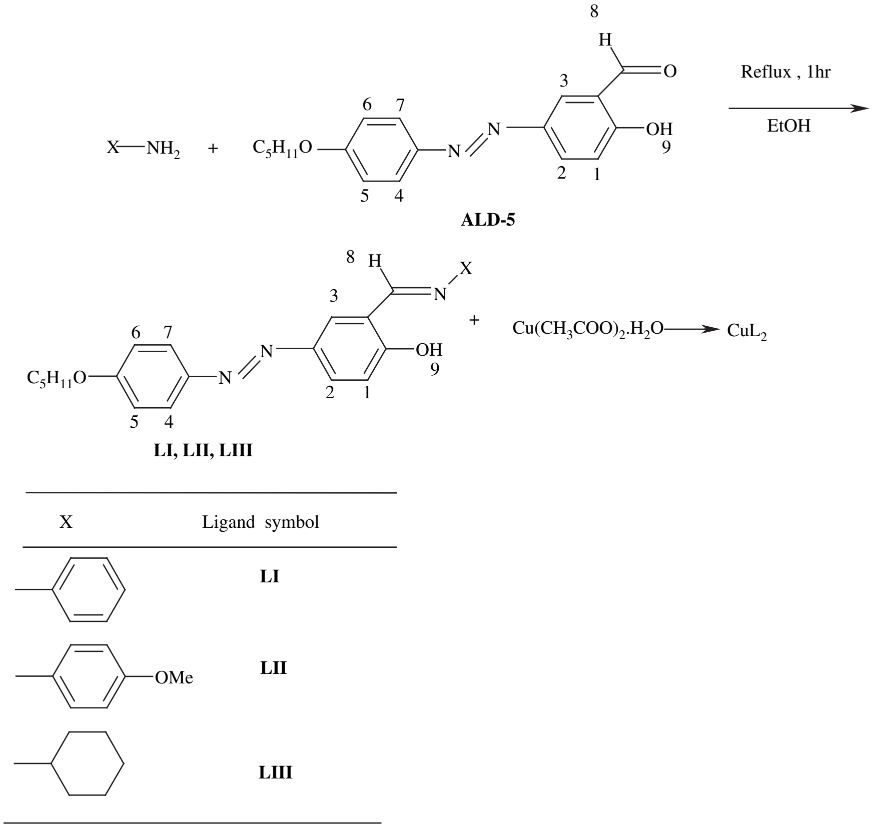

Scheme 1.

4-Pentyloxynitrobenzene homologues were obtained by the reaction between 4-nitrophenol with 1-bromopentane in DMF as solvent and K_2CO_3 as base by refluxing for 3 h [15] and then crude 4-pentyloxynitrobenzene was purified by recrystallization from ethanol. 4-Pentyloxyaniline was prepared by reduction of the corresponding 4-pentyloxynitrobenzene as described in literature [16].

2.2. Physical measurements

Elemental (C, H and N) analyses were carried out on a Perkin–Elmer automatic equipment model 240B. Electron impact (70 eV) mass spectra were recorded on a Finnegan-Mat GC–MS–DS spectrometer model 8430. Infrared spectra were taken with a Bruker FT-IR spectrometer model vector 22, using KBr pellets in the 400–4000 cm^{-1} range. The DSC thermograms of the compounds were obtained on a Mettler–Toledo DSC 822e module, which was calibrated with indium metal ($T = 156.6 \pm 0.3$, $\Delta H = 28.45 \pm 0.6$ J g^{-1}). Samples of 2–5 mg in solid form were placed in aluminum pans (40 μl) with a pierced lid, and heated or cooled at a scan rate of 10 °C min^{-1} under a nitrogen flow. TGA were carried out on a Mettler–Toledo TGA 851e at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. X-ray powder diffraction patterns were recorded on a Bruker D8 powder diffractometer (Cu Kα: 1.541 Å). ^1H NMR spectra were obtained in deuterated chloroform as solvent on a Bruker FT-NMR AC-400 (400 MHz) spectrometer. All chemical shifts are reported in δ (ppm) relative to the tetramethylsilane as internal standard.

2.3. Materials

2.3.1. 5-(4-Pentyloxyphenylazo) salicylaldehyde (**ALD-5**)

This compound was prepared as described in literature [10] Yellow, yield 75%, mp 135 °C. MS *m/z* (relative intensity): 313.3 (M + 1, 15), 312.2 (M, 40). Anal. Calc. for $C_{18}H_{20}N_2O_3$: C 69.24, H 6.40, N 8.96. Found: C 69.11, H 6.18, N 8.78. ^1H NMR (400 MHz, $CDCl_3$): δ 11.25 (s, H-8), 10.01 (s, H-9), 8.18 (d, *J* 3.2 Hz, H-3), 8.15 (dd, *J* 3.1, 8.4 Hz, H-2), 7.91 (dd, *J* 3.11, 7.10 Hz, H-4, H-7), 7.11 (d, *J* 8.7 Hz, H-1), 7.01 (dd, *J* 3.6, 8.3 Hz, H-5, H-6), 4.05 (t, *J* 7.1 Hz, CH_2O), 1.82 (m, *J* 7.2 Hz, O–C–CH_2), 1.38–1.40 (m, O–C–C–CH_2CH_2–), 0.95 (t, *J* 7.1 Hz, –CH_3).

2.4. Syntheses of the ligands

The related amine (0.025 mol) and 0.025 mol of 5-(4-^{n}pentyloxyphenylazo) salicylaldehyde were dissolved in 100 ml absolute ethanol with a few drops of glacial acetic acid as a catalyst. The solution was refluxed for 1 h and then left at room temperature. After cooling, the ligands were obtained as yellow microcrystals. The microcrystals were filtered off, washed with 15 ml of cold absolute ethanol and then recrystallized for several times in ethanol–chloroform (1:3 v/v).

LI. Yellow, yield 80%. MS *m/z* (relative intensity): 388.24 (M + 1, 15), 387.24 (M, 65). Anal. Calc. for $C_{24}H_{25}N_3O_2$: C 74.43, H 6.45, N 10.84. Found: C 74.30, H 6.21, N 10.72. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.77 (s, H-9), 8.76 (s, H-8), 7.99–8.02 (H-4, H-7), 7.87–7.89 (H-2, H-3), 7.44–7.48 (2H, phenylimine), 7.26–7.34 (3H, phenylimine), 7.13 (d, *J* 3.1 Hz, H-1), 7.01 (dd, *J* 3.2, 8.7 Hz, H-5, H-6), 4.04 (t, *J* 6.6 Hz, O–CH_2), 1.82 (m, *J* 7.1 Hz, O–C–CH_2), 1.38–1.50 (m, O–C–C–CH_2CH_2–), 0.96 (t, *J* 7.0 Hz, –CH_3).

LII. Yellow, yield 87%. MS *m/z* (relative intensity): 418.25 (M + 1, 13), 417.25 (M, 60). Anal. Calc. for $C_{25}H_{27}N_3O_3$: C 71.95, H 6.47, N 10.06. Found: C 71.74, H 6.25, N 9.94. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.96 (s, H-9), 8.70 (s, H-8), 7.96–7.98 (H-4, H-7), 7.86–7.89 (H-2, H-3), 7.30 (d, *J* 3 Hz, H-5, H-6), 7.10 (d, *J* 3.0 Hz, H-1), 6.98 (dd, *J* 3.2, 8.8 Hz, phenylimine), 4.03 (t, *J* 6.5 Hz, OCH_2), 3.85 (s, OCH_3), 1.83 (m, *J* 7.0 Hz, O–C–CH_2), 1.36–1.60 (m, O–C–C–CH_2CH_2–), 0.95 (t, *J* 7.1 Hz, C–CH_3).

LIII. Yellow, yield 87%. MS *m/z* (relative intensity): 393.24 (M + 1, 12), 392.24 (M, 63). Anal. Calc. for $C_{24}H_{30}N_3O_2$: C 73.48, H 7.64, N 10.70. Found: C 73.25, H 7.51, N 10.63. ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.45 (s, H-9), 8.42 (s, H-8), 7.93 (dd, *J* 3, 6.8 Hz, H-2), 7.83–7.87 (H-3, H-4, H-7), 6.97–7.00 (H-1, H-5, H-7), 4.03 (t, *J* 6.4 Hz, OCH_2), 3.33 (m, CH–N, cyclohexyl), 1.24–1.89 (17H, alkyl chain and cyclohexyl), 0.95 (t, *J* 7.1 Hz, C–CH_3).

2.5. Syntheses of copper complexes

Copper complexes were prepared in a similar manner using the method described by Nejati and Rezvani elsewhere [10]. Thus, a solution of 4 mmol of $Cu(CH_3COO)_2 \cdot H_2O$ in 10 ml of ethanol was added to an ethanol–chloroform (1:1 v/v) solution containing 8 mmol of ligand and was refluxed for 2 h. The obtained solution was left at room temperature. Copper complexes were obtained as brown microcrystals, and nickel complexes were obtained as green microcrystals. The microcrystals were filtered off, washed with absolute ethanol and then recrystallized from ethanol–chloroform (1:3 v/v).

CuLI. Brown, yield 80%. Anal. Calc. for $C_{48}H_{48}N_6O_4Cu$: C 68.93, H 5.74, N 10.05. Found: C 68.77, H 5.51, N 9.94.

CuLII. Brown, yield 85%. Anal. Calc. for $C_{50}H_{52}N_6O_6Cu$: C 66.99, H 5.80, N 9.38. Found: C 66.84, H 5.64, N 9.23.

CuLIII. Brown, yield 80%. Anal. Calc. for $C_{48}H_{58}N_6O_4Cu$: C 68.12, H 6.86, N 9.93. Found: C 68.05, H 6.55, N 9.77.

3. Results and discussion

3.1. Synthesis

Schiff-base ligands, **LI–LIII**, were synthesized in a four-step process, in which the hydroxy group in 4-nitrophenol is first replaced by an alkoxy chain followed by reduction of nitro group to amine. In the third step, salicylaldehyde coupled with the diazonium chloride obtained from 4-pentyloxyaniline and finally the Schiff-base ligands were obtained by reaction of 5-(4-pentyloxyphenylazo) salicylaldehyde with an appropriate amine (Scheme 1) by refluxing in absolute ethanol using a few drops of acetic acid as catalyst. The Schiff-base ligands were purified by repeated crystallization in the ethanol–chloroform mixture. The 5-(4-^{n}pentyloxyphenylazo) salicylaldehydes and Schiff-base ligands were characterized by IR, ^{1}H NMR, mass spectroscopies and elemental analyses. Copper complexes were characterized by C, H, N elemental analyses and IR spectroscopy. Some physical and characterization data for ligands and complexes are given in the Section 2 and selected IR data are reported in Table 1.The IR spectra of metal complexes show that the stretching frequency of the C=N bond was shifted to lower wavenumbers (ca. 15 cm^{-1}) in comparison to free ligand after coordination. This shift is due to the reduction of the double bond characteristic of the C=N bond, which is caused by the coordination of nitrogen into the metal center and is in agreement with the results obtained for other similar complexes described previously [8,10,17]. On the other hand, the disappearance of the OH band of free ligands in metal complexes indicates that the OH group has been deprotonated and coordinated to the metal ion as $-O^-$. Based on these observations and elemental analyses, we concluded that the Schiff-base ligands are coordinated to metal atoms as bidentate (N–O) ligands in 2:1 ratio.

It is suggested that the Cu(II) complexes have square planar or nearly square planar coordination according to the common stereochemistry of this kind of compounds [18].

3.2. Thermal properties

The thermogravimetric (TGA) and differential scanning calorimetric (DSC) curves of the ligands are presented in Fig. 1(a–c). DSC curves presented a melting process at 109.6, 148.6 and 98.6 °C for **LI**, **LII** and **LIII**, respectively, followed by decomposition represented by exothermic processes. The melting point of ligands depends upon the attached

Table 1
Selected IR data for Schiff-base ligands and metal complexes

Compound	ν (cm^{-1})					
	O–H	C–H (aromatic)	C–H (aliphatic)	C=N	C–O (etheric)	C=O
ALD-5	3185–3190 (br, m)	3069–3071 (m)	2850–2950 (s)	–	1241–1243 (s)	1661–1662 (s)
L (**I**, **II**, **III**)	3420–3460 (br, m)	3041–3058 (m)	2850–2960 (s)	1632–1638 (s)	1248–1255 (s)	–
CuL	–	3040–3060 (m)	2850–2960 (s)	1614–1617 (s)	1243–1245 (s)	–

s: Strong, m: medium, br: broad.

group to the nitrogen atom of C═N. Ligand **LIII** with a bulky cylohexyl group has low melting point than **LI** and **LII** due to the influence of bulky group on molecular packing. The TGA curves indicate that ligands **LI**, **LII** and **LIII** start decomposition at 298, 305 and 266 °C, respectively. Comparison of T_d (decomposition temperature) of ligands shows that **LI** and **LII** decompose later than **LIII**. This is related to the structure of these ligands. In **LI** and **LII**, the group that is attached to the nitrogen atom of C═N is aromatic (phenyl and 4-methoxyphenyl, respectively) but in **LIII** is nonaromatic (cyclohexyl).The aromaticity of this group is a structural factor that causes **LI** and **LII** to be more stable than **LIII** and hence they decompose later.

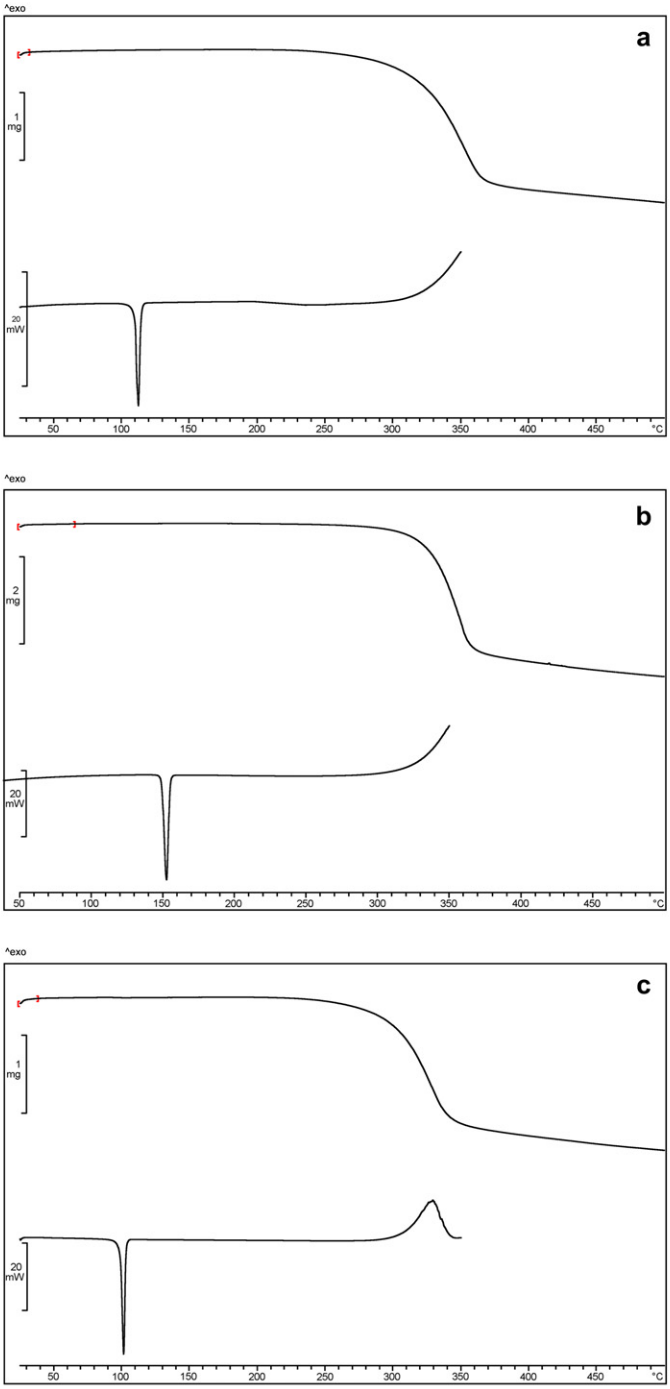

Fig. 1. TGA (above) and DSC (below) curves of ligands: (a) **LI**, (b) **LII**, and (c) **LIII**.

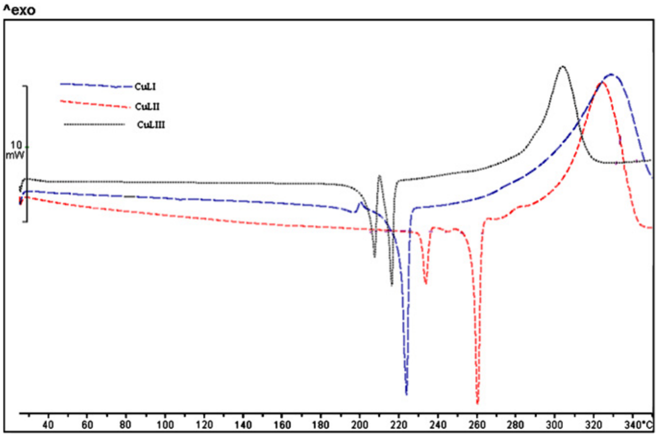

Fig. 2. DSC thermograms of copper complexes.

DSC and TGA thermograms of copper complexes are presented in Figs. 2 and 3, respectively. DSC curves show that copper complexes **CuLI**, **CuLII** and **CuLIII** have one solid–solid transition at 187.5, 230.7 and 203.6 °C and melting process at 219.9, 257.3 and 213.1 °C, respectively, followed by decomposition represented by exothermic processes. The TGA curves indicate that the copper complexes **CuLI**, **CuLII** and **CuLIII** start decomposition at 318, 322 and 294 °C, respectively. Thermal stability of copper complexes exhibits the similar trend in ligands. The comparison of ligands and copper complexes shows that the copper complexes were more thermally stable at about 18–27 °C higher than that of the azo dyes. The final decomposition product was CuO according to the X-ray diffraction pattern. Transition temperatures, enthalpy changes and decomposition temperatures of azo-dye ligands and related copper(II) complexes are tabulated in Table 2.

4. Conclusion

In this work, we have prepared a series of Schiff-base azo dyes derived from 5-((4-pentyloxyphenyl)azo)-salicylaldimine-*N*-R

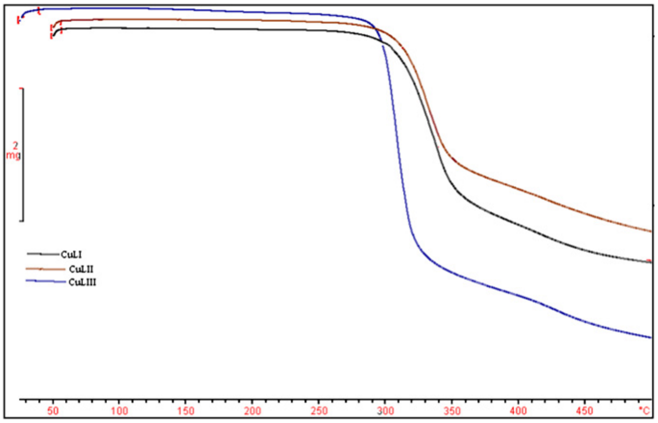

Fig. 3. TGA thermograms of copper complexes.

Table 2
Transition temperatures, enthalpy changes and decomposition temperatures of ligands and related copper(II) complexes

Compound	Transition[a]	T^{b}/°C	ΔH^{b}/k J mol^{-1}	T_{d}^{c}/°C
LI	$\mathrm{Cr}\cdots\mathrm{I}$	109.6	−87.63	298
LII	$\mathrm{Cr}\cdots\mathrm{I}$	148.9	−97.49	305
LIII	$\mathrm{Cr}\cdots\mathrm{I}$	98.6	−105.71	266
CuLI	$\mathrm{Cr_1}\cdots\mathrm{Cr_2}$	187.5	−3.42	318
	$\mathrm{Cr_2}\cdots\mathrm{I}$	219.9	−81.89	
CuLII	$\mathrm{Cr_1}\cdots\mathrm{Cr_2}$	230.7	−15.09	322
	$\mathrm{Cr_2}\cdots\mathrm{I}$	257.3	−46.93	
CuLIII	$\mathrm{Cr_1}\cdots\mathrm{Cr_2}$	203.6	−34.25	294
	$\mathrm{Cr_2}\cdots\mathrm{I}$	213.1	−38.30	

[a] Cr: crystal, I: isotropic liquid.

[b] Data obtained from first DSC cycle.

[c] Data obtained from TGA; 10 °C min^{-1} under N_2 gas.

(R = phenyl, 4-methoxyphenyl and cyclohexyl) and related copper complexes. The order of thermal stability found is **CuLII** > **CuLI** > **CuLIII** > **LII** > **LI** > **LIII**. This fact should be related with the structure of the ligands and copper complexes and suggests the cyclohexl containing compounds are unstable. On the basis of literature data, thermally stable compounds up to 250 °C are suitable for use as recording dyes [19], so according to the thermal stability of the above-mentioned azo dyes and related copper complexes we can conclude that these compounds are suitable for use as recording dyes.

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