Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 75 (2007) 653−657
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

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

Kamellia Nejati [a,*], Zolfaghar Rezvani [b], Bakhshali Massoumi [a]

[a] *Department of Chemistry, Payam Noor University-Tabriz Center, Emamieh, Hakim Nezami Street, Tabriz, Iran*
[b] *Department of Chemistry, Faculty of Science, Azarbaijan University of Tarbiat Moallem, Tabriz, Iran*

Received 6 July 2006; received in revised form 19 July 2006; accepted 19 July 2006
Available online 11 September 2006

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

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

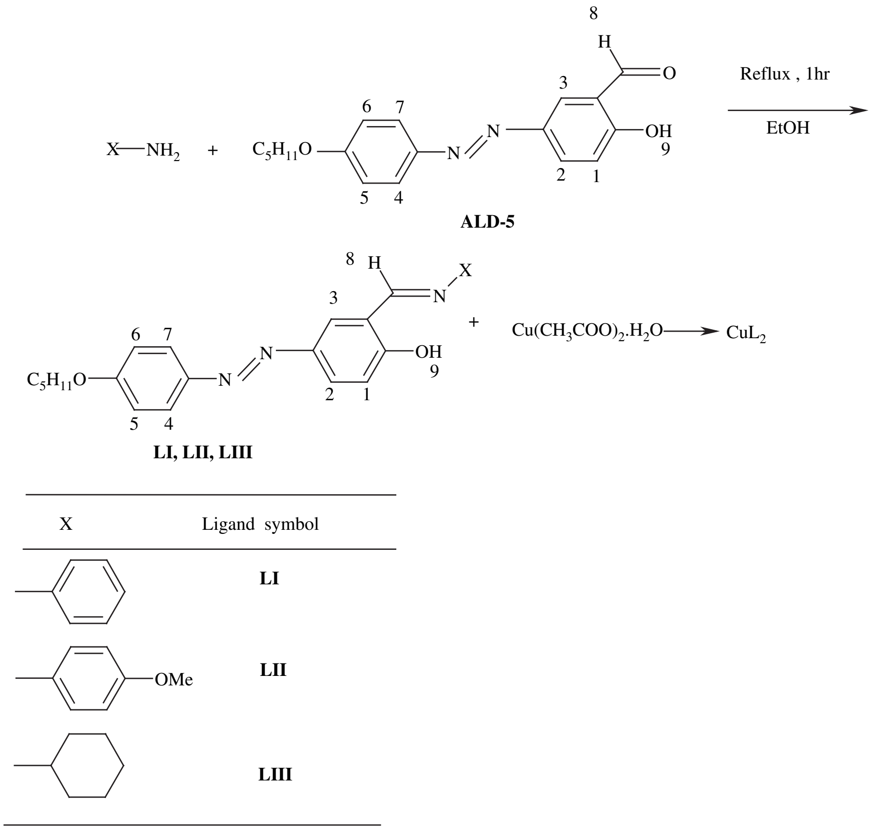
2.1. Reagents

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

---

* Corresponding author. Tel.: +98 411 5412117; fax: +98 411 5412108.
E-mail address: nejati_k@yahoo.com (K. Nejati).

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.07.019



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).