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Polyhedron 25 (2006) 1915–1920

POLYHEDRON

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Liquid crystalline properties of copper(II) complexes derived from azo-containing salicylaldimine ligands

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Received 11 November 2005; accepted 6 December 2005

Abstract

The one-step metal promoted reaction between 5-((4-alkoxyphenyl)azo) salicylaldehyde (alkoxy = decyloxy, dodecyloxy, tetradecyloxy) and ethanolamine in the presence of $Cu(CH_3COO) \cdot 4H_2O$ yields new salicylaldimine based copper(II) bis(chelates) as a result of the [1 + 1] Schiff base condensation. The liquid crystalline character of these complexes was examined using differential scanning calorimetry (DSC) and a polarizing microscope equipped with a heating and cooling stage. All copper complexes form the enantiotropic Smectic C mesophase.

Keywords: Schiff bases; Salicylaldimine; Azo; Metallomesogen; Smectic C; Copper complexes

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1. Introduction

In recent years metallomesogens have seen systematic research and development [1–5]. Considerable amounts of metallomesogens are based on transition metal coordination compounds with salicylaldimine-based ligands [6–8]. Moreover much attention has been paid to photonic materials based on light-induced phase transitions because these types of materials are very useful in new information processing technology. Azo-containing polymeric liquid crystal systems and metallomesogens containing uncomplexed azo moieties are suitable for this research field because these materials are able to change molecular shape via reversible *cis–trans* isomerization upon photoirradiation. These compounds have potential applications in optical switching, high-density optical data storage and optical computing [9,10].

Recently, some metallomesogens containing isomerizable azo moieties have been reported [11–13]. We also recently reported the synthesis and liquid crystalline character of Cu(II) bis(chelates) based on azo-linked bidentate salicylaldimine [14–16] and tetradentate azo-linked *N*,*N*′ salicylideneiminato Ni(II), Cu(II) and VO(IV) complexes [17]. In this work we report the synthesis and liquid crystalline properties of new bis[5-((4-^{n}alkoxyphenyl)azo)-*N*-ethanol salicylaldiminato]copper(II) complex homologues (see Scheme 1).

2. Experimental

2.1. Reagents

All reagents and solvents were used as supplied by Merck chemical company and were used without further purification. 4-Alkoxynitrobenzene homologues were obtained by reaction between 4-nitrophenol with 1-bromooctan, 1-bromododecane or 1-bromotetradecane in DMF as the solvent and K_2CO_3 as the base by refluxing for 3 h [18] and then the crude 4-alkoxynitrobenze homologues were purified by recrystallization from ethanol. 4-Alkoxyaniline homologues were prepared by reducing the corresponding 4-alkoxynitrobenzene homologue as described in the literature [19].

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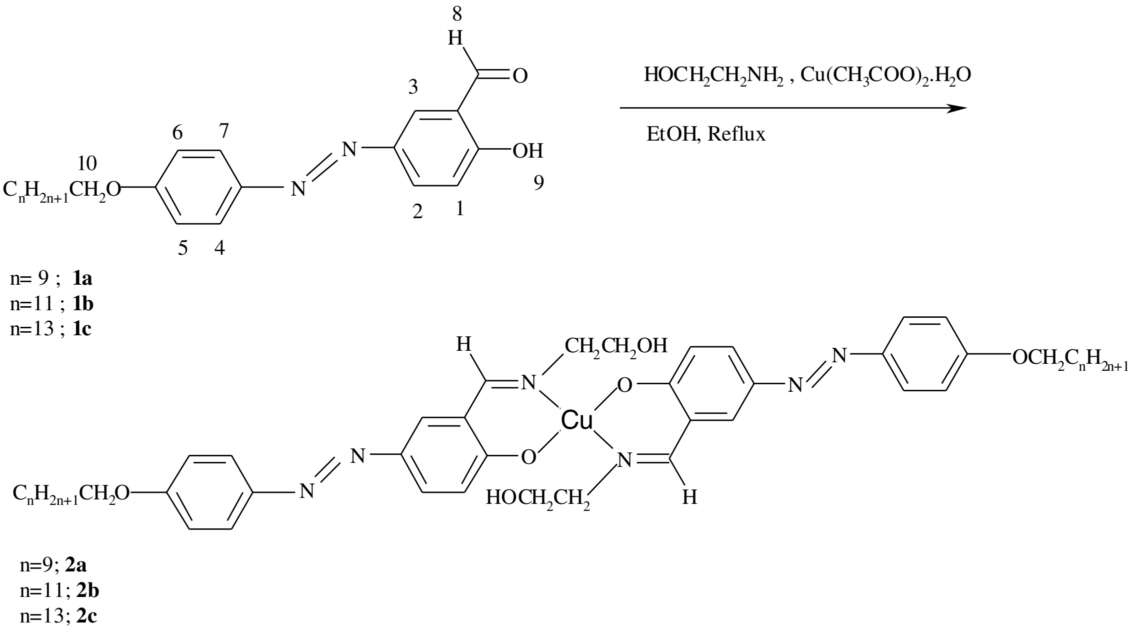
doi:10.1016/j.poly.2005.12.016



Scheme 1. Synthetic route to the copper complexes.

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 FT-IR Bruker, vector 22 spectrometer 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 the 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 was carried out on a Mettler–Toledo TGA 851e at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. The optical observations were made with a Zeiss polarizing microscope equipped with a Linkam THMSG 600 heating and cooling stage and a Linkam THMS 93 programmable temperature-controller. ^1H NMR spectra were obtained on a Bruker FT-NMR AC-400 (400 MHz) spectrometer with deutrated chloroform as the solvent. All chemical shifts are reported in δ(ppm) relative to tetramethylsilane as an internal standard.

2.3. Materials

All homologue materials were prepared similarly.

2.3.1. 5-(4-Decyloxyphenylazo) salicylaldehyde (*1a*)

This compound was prepared as described in the literature [20]. Yellow, yield 80%, m.p. 126 °C. MS *m*/*z* (relative intensity): 355.4 (M+1, 15), 354.3 (M, 40), 241.2 ($M-C_{10}H_{21}$, 25), 121.0 ($M-C_{10}H_{21}OC_6H_4N_2$, 100). *Anal.* Calc. for $C_{23}H_{30}N_2O_3$: C, 71.16; H, 7.39; N, 7.90. Found: C, 70.71; H, 7.12; N, 7.54%. ^1H NMR (400 MHz, $CDCl_3$) δ 11.27 (s, H-8), 10.02 (s, H-9), 8.18 (d, *J* 3.2 Hz, H-3), 8.14 (dd, *J* 3.1, 8.4 Hz, H-2), 7.91 (dd, *J* 3.1, 8.2 Hz, H-4, H-7), 7.10 (d, *J* 8.7, H-1), 7.01 (dd, *J* 3.6, 8.3 Hz, H-5,H-6), 4.05 (t, *J* 7.1 Hz, H-10), 1.81–1.00 (15H, alkyl chain).

2.3.2. 5-(4-Dodecyloxyphenylazo) salicylaldehyde (*1b*)

Yellow, yield 80%, m.p. 123 °C. MS *m*/*z* (relative intensity): 411.6 (M+1, 15), 410.6 (M, 45), 242.5 ($M-C_{12}H_{25}$, 25), 121.6 ($M-C_{12}H_{25}OC_6H_4N_2$, 100). *Anal.* Calc. for $C_{25}H_{34}N_2O_3$: C, 73.15; H, 8.35; N, 6.83. Found: C, 72.73; H, 8.14; N, 6.47%. ^1H NMR (400 MHz, $CDCl_3$) δ 11.26 (s, H-9), 10.02 (s, H-8), 8.15 (d, *J* 2.8 Hz, H-3), 8.13 (dd, *J* 2.9, 8.2 Hz, H-2), 7.89 (dd, *J* 3.0, 7.9 Hz, H-4, H-7), 7.11 (d, *J* 8.1 Hz, H-1), 7.01 (dd, *J* 3.2, 7.9 Hz, H-5, H-6), 4.04 (t, *J* 6.7 Hz, H-10), 1.84–0.87 (23H, alkyl chain).

2.3.3. 5-(4-Tetradecyloxyphenylazo) salicylaldehyde (*1c*)

Yellow, yield 80%, m.p. 123 °C. MS *m*/*z* (relative intensity): 411.6 (M+1, 15), 410.6 (M, 45), 242.5 ($M-C_{14}H_{29}$, 25), 121.6 ($M-C_{12}H_{25}OC_6H_4N_2$, 100). *Anal.* Calc. for $C_{27}H_{38}N_2O_3$: C, 73.15; H, 8.35; N, 6.83. Found: C, 72.73; H, 8.14; N, 6.47. ^1H NMR (400 MHz, $CDCl_3$) δ 11.26 (s, H-9), 10.02 (s, H-8), 8.15 (d, *J* 2.8 Hz, H-3), 8.13 (dd, *J* 2.9, 8.2 Hz, H-2), 7.89 (dd, *J* 3.0, 7.9 Hz, H-4, H-7), 7.11 (d, *J* 8.1 Hz, H-1), 7.01 (dd, *J* 3.2, 7.9 Hz, H-5, H-6), 4.04 (t, *J* 6.7 Hz, H-10), 1.84–0.87 (23H, alkyl chain).

2.3.4. Syntheses of the copper complexes

The copper complexes were prepared in similar manners using a method described elsewhere [21]. Thus, an alcoholic solution containing 10 mmol of ethanolamine was added to a solution of 5-alkoxyphenylazo salicylaldehyde (10 mmol)