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Syntheses and mesomorphic properties of new oxygen-bridged dicopper complex homologous derived from azo-containing salicylaldimine Schiff base ligands

Zolfaghar Rezvani [a,*], Mohammad Ali Ghanea [a], Kamellia Nejati [b], Sara Abodollahzadeh Baghaei [a]

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

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ABSTRACT

The synthesis, characterization and liquid crystal properties of a homologous series of new tridentate 5-((4-^{n}alkoxyphenyl) azo)-N-(3-ydroxypropyl) salicylaldimine ligands (alkoxy = octloxy, decyloxy, dodecyloxy and tetradecyloxy) and their dicopper(II) complexes are reported. These ligands were prepared by the condensation of the 5-((4-^{n}alkoxyphenyl)azo)salicylaldehydes homologous with 3-amino-1-propanol. The ligands and their dicopper complexes have been characterized by IR, ^{1}H NMR, mass spectroscopy and elemental analyzes. The liquid crystalline properties of the ligands and the related dicopper complexes were studied by differential scanning calorimetry (DSC) and by using a polarizing microscope equipped with a heating and cooling stage. None of the free ligands exhibit liquid crystalline behavior but all of the dicopper complexes demonstrate a smectic A mesophase.

1. Introduction

The synthesis and characterization of metallomesogens has been a subject of extensive research over the past two decades [1–6]. In these compounds, the unique properties of the anisotropic fluids (anisotropy of physical properties and fast orientational response to external fields) are combined with the specific properties of the metals (large polarizability, rich coordination chemistry, magnetic and electronic properties). One of the several advantages of the metallomesogens is the potential magnetic properties of these materials. For example, metal-containing liquid crystals with unpaired electrons are paramagnetic liquid crystals, and the required magnetic field strength to align paramagnetic liquid crystals is much smaller than that required to align diamagnetic liquid crystals [7–10]. On the other hand, metallomesogens containing uncomplexed azo moieties have been attracting much attention recently due to their possible applications in the area of photon-mode high density data storage and photo-switching devices [11–15]. Due to the clean photochemistry of azobenzene, and substantial change in material properties during light irradiation, it has been investigated as an active component for a variety of applications, such as lithography, non-linear optical devices and optical switches. [16–18]. From a basic point of view, azo dyes belong to the simplest physical systems in which light illumination induces cis–trans isomerization and a local change in the structure of the liquid crystalline phases. These changes can be responsible for the variation of the different electro-optical applications. The function of liquid crystal devices is based on the controlled reorientation of the director in an electric field. Anisotropic effects in dyes are more pronounced when a dye exhibits mesogenic properties. In such cases a better orientation of dye molecules on the substrates and a strong orientational optical non-linearity can be expected [19–21].

Our research group has synthesised liquid crystalline mononuclear Cu(II) complexes based on salicylaldimine with uncomplexed azo moieties in the past decade [22–25]. Furthermore, we recently reported liquid crystalline mononuclear copper complexes derived from azo-linked salicylaldimine homologous as the first example of azo-containing metallomesogens with a lateral OH group [26,27].

In this work we present the synthesis and liquid crystalline properties of a homologous series of 5-((4-^{n}alkoxyphenyl)azo)-N-(3-hydroxypropyl)salicylaldimine ligands and their binuclear copper(I1) complexes (see Scheme 1).

2. Experimental

2.1. Reagents

All reagents and solvents were used as supplied by the Merck chemical company and were used without further purification. The 4-^{n}alkoxynitrobenzene homologous were obtained by the reaction between 4-nitrophenol with 1-bromoalkane in DMF as the solvent and K_2CO_3 as the base by refluxing for 3 h [28], and

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* Corresponding author. Tel./fax: +98 412 4327526.
E-mail address: z_rezvani@yahoo.com (Z. Rezvani).

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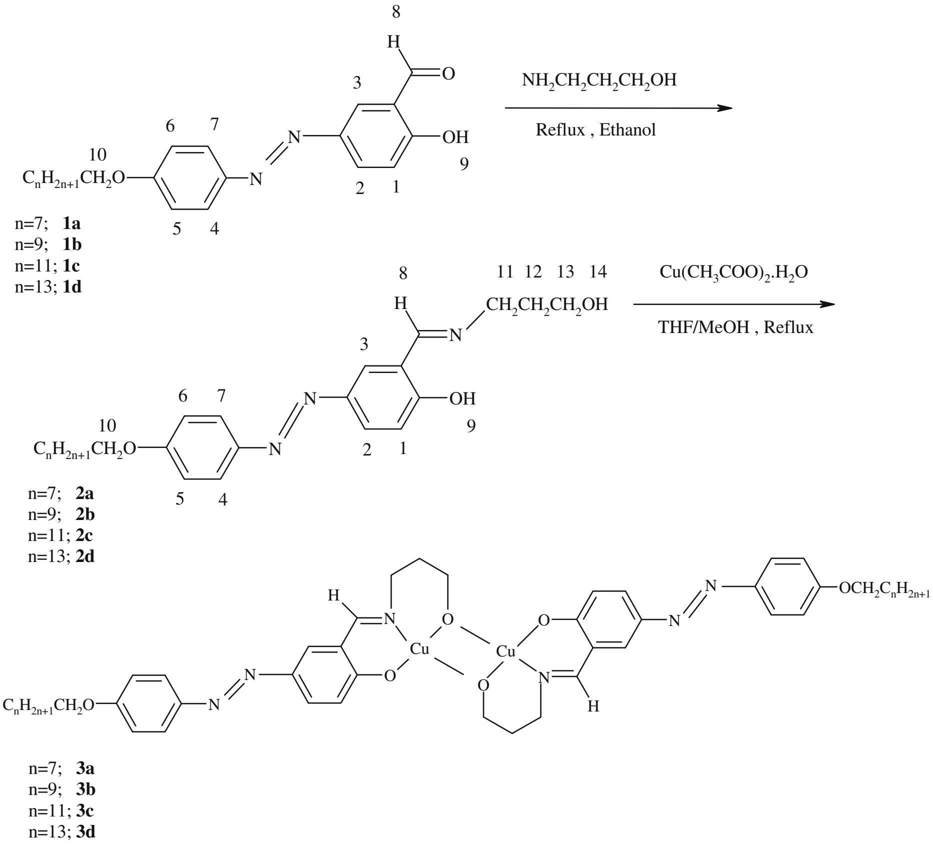

Scheme 1. Synthetic route to the dicopper complexes.

then the crude 4-^{n}alkoxynitrobenzene homologous were purified by recrystallization from ethanol. The 4-^{n}alkoxyaniline homologous prepared by reducing the corresponding 4-^{n}alkoxynitrobenzenes as described in the literature [29].

2.2. Physical measurements

Elemental (C, H and N) analyzes 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 thermograms were 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 Linkam THMS 93 programmable temperature-controller. ^{1}H NMR spectra were obtained in deuterated chloroform as the solvent on a Bruker FT-NMR AC-400 (400 MHz) spectrometer. All chemical shifts are reported in δ(ppm) relative to tetramethylsilane as an internal standard.

2.3. Materials

All homologous materials were prepared similarly as described in the literature [30].

2.3.1. 5-(4-Octyloxyphenylazo)salicylaldehyde (1a)

Yellow, yield 80%, mp 126 °C. MS m/z (relative intensity): 355.4 (M+1, 15), 354.3 (M, 40). *Anal.* Calc. for $C_{21}H_{26}N_2O_3$: C, 71.16; H, 7.39; N, 7.90. Found: C, 70.8; H, 7.1; N, 7.5%. ^{1}H 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 Hz, 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). IR (KBr, cm^{-1}) ν: 3416 (O–H), 3069 (C–H, aromatic), 2921, 2959 (C–H, aliphatic), 1661 (C=O), 1600 (C=C, aromatic), 1500 (N=N), 1245 (C–O, ether), 1150 (C–O, phenolic).

2.3.2. 5-(4-Decyloxyphenylazo)salicylaldehyde (1b)

Yellow, yield 80%, mp 124 °C. MS m/z (relative intensity): 383.4 (M+1, 15), 382.3 (M, 40). *Anal.* Calc. for $C_{23}H_{30}N_2O_3$: C, 72.19; H, 7.84; N, 7.32. Found: C, 71.8; H, 7.5; N, 7.0%. ^{1}H 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 Hz, 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 (19H, alkyl chain). IR (KBr, cm^{-1}) ν: 3417 (O–H), 3065 (C–H, aromatic), 2923, 2957 (C–H, aliphatic), 1661 (C=O), 1599 (C=C, aromatic), 1501 (N=N), 1245 (C–O, ether), 1149 (C–O, phenolic).

2.3.3. 5-(4-Dodecyloxyphenylazo)salicylaldehyde (1c)

Yellow, yield 80%, mp 123 °C. MS m/z (relative intensity): 411.6 (M+1,14), 410.6 (M, 45). *Anal.* Calc. for $C_{25}H_{34}N_2O_3$: C, 73.15; H, 8.35; N, 6.83. Found: C, 72.8; H, 8.2; N, 6.5%. ^{1}H 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