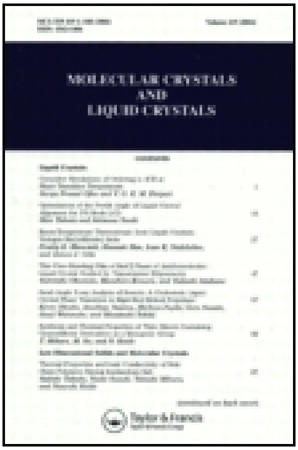

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# Investigation of Liquid Crystalline Behavior of Copper(II) Complexes Derived from Azo-Containing Salicylaldimine Ligands with Lateral Hydroxyl Group

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# Investigation of Liquid Crystalline Behavior of Copper(II) Complexes Derived from Azo-Containing Salicylaldimine Ligands with Lateral Hydroxyl Group

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*The one-step metal promoted reaction between 5-(4-alkoxyphenylazo) salicylaldehyde (alkoxy = decyloxy, dodecyloxy, tetradecyloxy) and 2-propanolamine in the presence of Cu* $(CH_3COO)\cdot 4H_2O$ *yields new azo-containing salicylaldimine based copper(II) bis(chelates) as a result of the [1 + 1] Schiff base condensation. The mesogenic properties of these complexes were studied by differential scanning calorimetry (DSC) and polarizing microscope equipped with a heating and cooling stage. Copper complexes containing dodecyloxy and tetradecyloxy chain gave liquid crystalline character, while decyloxy containing copper complex was non-mesomorphic.*

**Keywords:** azo; copper complexes; metallomesogen; salicylaldimine; schiff bases; smectic A

## INTRODUCTION

Azo-containing polymeric liquid crystal systems and 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 [1–5]. In addition, molecules with large conjugated π-systems including azo group are very promising active materials for investigation of nonlinear phenomena [6,7]. The mesogenic properties of dyes are

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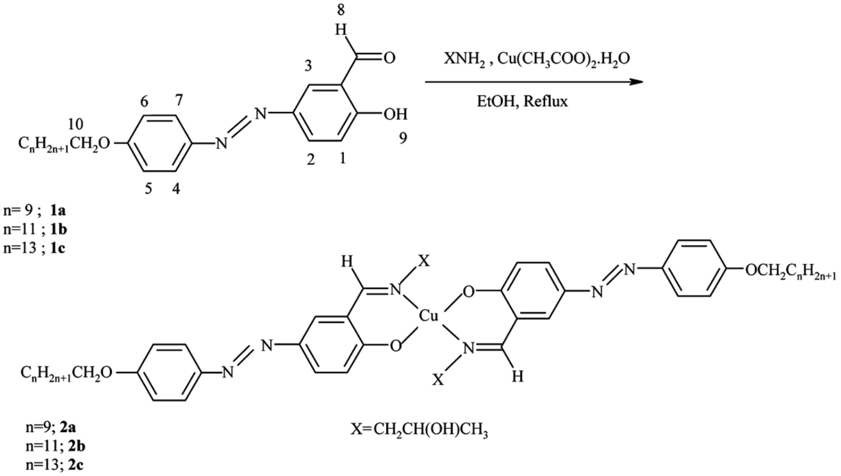
of great importance for nonlinear applications. Consequently, the kind of azo dye molecules that are used as side chain moieties in polymers are of great attraction, and hence are currently subject of intensive research [8–10].

We recently reported the synthesis and liquid crystalline character of Cu(II) bis(chelates) based on azo-linked bidentate salicylaldimine [11–13] and tetra dentate azo-linked N,N′ salicylideneiminato Ni(II), Cu(II), and VO(IV) complexes [14]. More metallomesogens containing uncomplexed azo moieties are also reported by other research groups [11–13,15–17]. Furthermore, the liquid crystalline character of copper complexes derived from 5-((4-alkoxyphenyl)azo)-N-(ethanol)-salicylaldimine homologues as the first example of azo-containing metallomesogens with a lateral OH group are also reported by our group [18]. These copper complexes can be attached as an azo-containing mesogenic side chain to non-liquid crystalline polymers (for example polyurethanes) through OH group to induce liquid crystalline character to these polymers [19].

The goal of this project was to develop new liquid crystalline copper complex dyes with lateral hydroxyl group capable of attaching as a side chain to polymers. In this work we report the synthesis and liquid crystalline properties of new copper complex homologues named bis [5-((4-nalkoxyphenyl) azo)-N-(2-propanol) salicylaldiminato] copper (II) complex (see Scheme 1).



**SCHEME 1** Synthetic route to the copper complexes.

# EXPERIMENTAL

## Reagents

All reagents and solvents were used as supplied by Merck chemical company and used without further purification. 4-Alkoxynitrobenzene homologues were obtained by reaction between 4-nitrophenol with 1-bromooctan,1-bromododecane or 1-bromotetradecane in n,n-dimethylformamide as solvent and $K_2CO_3$ as base by refluxing for three hrs [20], and then crude 4-alkoxy nitro benzene homologues were purified by recrystallization from ethanol. 4-Alkoxy aniline homologues prepared by reducing of the corresponding 4-alkoxynitrobenzene as described in the literature [21].

## 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 an 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 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. Thermal Gravimetric Analyses (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 Linkam THMS 93 programmable temperature-controller. $^1H$ NMR spectra were obtained in deutrated chloroform as solvent on a Bruker FT-NMR AC-400 (400 MHz) spectrometer. All chemical shifts are reported in $\delta$(ppm) relative to the tetramethylsilane as internal standard.

## Materials

All homologue materials were prepared similarly.

**5-(4-Decyloxyphenylazo) Salicylaldehyde (1a)**. This compound was prepared as described in the literature [22]. Yellow, yield 80%, mp 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.

$^1$HNMR (400 MHz, $CDCl_3$) $\delta$ 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).

**5-(4-Dodecyloxyphenylazo) Salicylaldehyde (1b).** Yellow, yield 80%, mp 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. $^1$HNMR (400 MHz, $CDCl_3$) $\delta$ 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 (23 H, alkyl chain).

**5-(4-Tetradecyloxyphenylazo) Salicylaldehyde (1c).** Yellow, yield 80%, mp 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. $^1$HNMR (400 MHz, $CDCl_3$) $\delta$ 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 (23 H, alkyl chain).

**Syntheses of the Copper Complexes.** Copper complexes were prepared in similar manner using the method described elsewhere [23]. Thus, an alcoholic solution containing 10 mmol of 2-propanol amine was added to a solution of 5-alkoxyphenylazo salicylaldehyde (10 mmol) in 50 ml of boiling absolute ethanol. Then 10 mmol sodium acetate in 10 ml water was added to the above reaction system. Finally, 50 ml boiling ethanol solution containing 10 mmol $Cu(CH_3COO)_2 \cdot H_2O$ was added. The reaction mixture was kept boiling for 30 min. The crystals precipitated from the solution, and recrystallization was performed from the ethano/chloroform (1:1 v/v) solution. Copper complexes were obtained as brown microcrystals. The microcrystals were filtered off, washed with absolute ethanol, and then recrystallized from ethanol-chloroform (1:3 v/v).

**2a:** Brown, yield 85%. Anal. Calc. for $C_{52}H_{72}N_6O_6Cu$: C 66.42, H 7.66, N 8.94. Found: C 66.05, H 7.26, N, 8.52.

**2b:** Brown, yield 80%. Anal. Calc. for $C_{56}H_{80}N_6O_6Cu$: C 67.51, H 8.04, N 8.44. Found: C 67.14, H 7.75, N, 8.14.

**2c:** Brown, yield 75%. Anal. Calc. for $C_{60}H_{88}N_6O_6Cu$: C 68.39, H 8.45, N 7.97. Found: C 68.42, H 8.11, N 7.80.

# RESULTS AND DISCUSSION

## Synthesis

5-(4-alkoxyphenylazo) salicylaldehyde homologues (**1a–c**; see Scheme 1) were synthesized in a three-step process as described elsewhere [14], in which the hydroxy group in 4-nitrophenol is first replaced by an alkoxy chain followed by reductions of nitro group to amine. In the third step, salicylaldehyde coupled with the diazonium chloride obtained from the 4-alkoxyaniline. **1a–c** were purified by repeated crystallization from ethanol to give a single spot on thin layer chromatography and characterized by IR,$^1$HNMR, mass spectroscopy, and elemental analyses. Copper complexes were obtained in good yield and purity, and characterized by C, H, N elemental analysis and IR spectroscopy. These copper compounds are all paramagnetic, and their $^1$HNMR spectra display only broad alkoxy signals. All other proton signals close to the paramagnetic copper centers are unobserved. The elemental analysis and spectroscopic data for new compounds gave satisfactory results. Some physical and characterization data for 5-(4-alkoxyphenylazo) salicylaldehyde homologues, and copper complexes are given in the experimental section and selected IR data are tabulated in Table 1.

The IR spectral frequencies of synthesized compounds were carried out using KBr pellets as described in the experimental section. In the compounds **1a–c**, the hydroxyl group was observed at 3190 cm$^{-1}$ because the intramolecular hydrogen bonding between OH and formyl group in compound **1** leads to decreasing the stretching frequency of OH, and the carbonyl group was observed at 1666 cm$^{-1}$ [13]. In the IR spectra of copper complexes(**2a–c**), the phenolic OH group disappeared, and free lateral OH group was observed as a broad peak centered at 3240–60 cm$^{-1}$ [23]. In addition, the C=N group was observed at 1623 cm$^{-1}$. It is well characterized that the C=N stretching

**TABLE 1** Selected IR Data for Schiff-Base Ligands and Metal Complexes

| | $\nu$/cm$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| Compound | O-H | C-H (aromatic) | C-H (aliphatic) | C=N | C-O (etheric) | C=O |
| **1(a–c)** | 3185–90(br,s) | 3069–71(m) | 2850–2950(s) | – | 1241 | 1665-6(s) |
| **2(a–c)** | 3240–3260(br,s) | 3040–50(m) | 2920,2851(s) | 1620–3(s) | 1244–75(s) | – |

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

frequency in bidentate salicylidenic schiff base ligands with N-alkyl structure appears at 1635–1640 $\mathrm{cm}^{-1}$ region [11–14,24], so the appearance of C=N at 1623 $\mathrm{cm}^{-1}$ (in the lower wave numbers than free schiff base ligands) in copper complexes demonstrates that the C=N has been formed by $[1+1]$ condensation reaction and coordinated to the copper center. On the other hand, the lack of phenolic OH group in copper complexes indicates that the OH group has been deprotonated and coordinated to the metal ion as $-\mathrm{O}^{-}$. Reduction of the double bond character of the C=N bond, which caused by the coordination of nitrogen into the metal center and is in agreement with the results obtained from the other similar complexes described previously [11–14,24]. Based on these observations and elemental analysis results, we concluded that the Schiff-base ligands are coordinated to metal atoms as bidentate (N-O) ligands in 2:1 ratio.

On the basis of literature data for copper complexes with similar coordination environment, the OH group is free of coordination [23] and has not been bonded to the metal center. This fact may be related to the strong John–Teller effect in $d^9$ $\mathrm{Cu}^{+2}$, which avoid the coordination of OH to the metal center. Therefore, it is suggested that the Cu(II) have square planar or nearly square planar coordination according to the common stereochemistry of this kind of compounds [25].

## Mesomorphism

The thermal stability of these complexes was checked by thermogravimetric analysis (TGA) at first. All other thermal characterizations were then carried out below the decomposition temperature. Figure 1 shows the TGA and DSC thermograms of 2a as a representative example. All the copper complexes have similar TGA thermograms at a heating rate of 10°C/min and illustrates that decomposition starts at 250°C.

The liquid crystalline character of 5-(4-$^{n}$alkoxyphenylazo) salicylaldehyde homologues (**1a–c**) and Cu(II) complexes were investigated by polarizing optical microscopy (POM) observations using a heating–cooling stage. The phase transition temperatures and enthalpies were measured by carrying out DSC thermal analysis. Phase transition temperatures along with the corresponding enthalpy values for copper complexes are summarized in Table 2 Aldehyde homologues (**1a–c**) did not show any liquid crystalline character. These compounds clearly melted and transformed into isotropic liquids and no mesophase was observed on the heating or cooling cycle on optical observations.

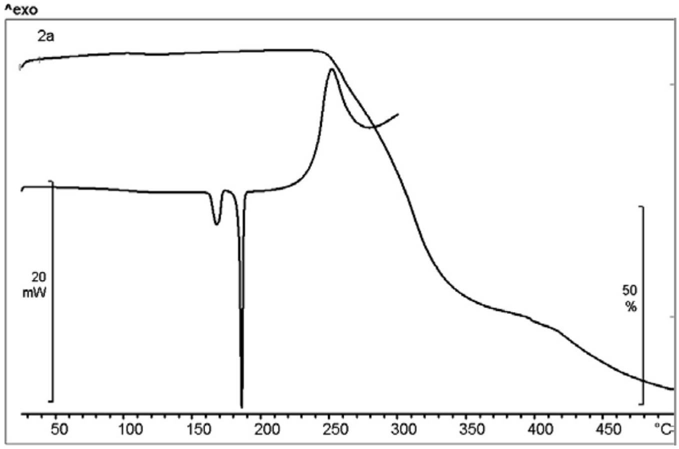


**FIGURE 1** TGA and DSC thermograms of 2a.

Figure 2 illustrates the DSC curves of copper complexes for the period of the first heating cycle. Two endothermal peaks were observed for 2a at 162.8°C and 184.2°C. The peak at 162.8°C ($\Delta H = 20.95\,kJ\,mol^{-1}$) corresponds to a solid–solid transition, and the one at 184.2°C is assigned to a crystal-isotropic liquid transition. The compounds 2b and 2c exhibit one endothermic peak at 165.0°C and 157.9°C, respectively. These peaks refer to a crystal-isotropic liquid transition. These compounds clearly melted and transformed

**TABLE 2** Transition Temperatures and Enthalpy Changes of Copper(II) Complexes

| Compound | Transition[a] | $T^b$/°C | $\Delta H^b$/KJ $mol^{-1}$ |
|---|---|---|---|
| **2a** | Cr1---Cr2 | 162.8 | 20.95 |
|  | Cr2---I | 184.2 | 59.78 |
|  | (I---Cr)[c] | (157.7) | 48.65 |
| **2b** | Cr---I | 165.0 | 86.35 |
|  | (I---SmA) | (152.1) | 4.36 |
|  | (SmA---Cr) | (146.1) | 36.91 |
| **2c** | Cr---I | 157.9 | 64.36 |
|  | (I---SmA) | (145.5) | 2.17 |
|  | (SmA---Cr) | (132.2) | 42.00 |

[a] Cr: Crystal, SmA: Smectic A, I: Isotropic liquid.
[b] Data obtained from first heating DSC cycle.
[c] Data in parenthesis obtained from first cooling DSC cycle.

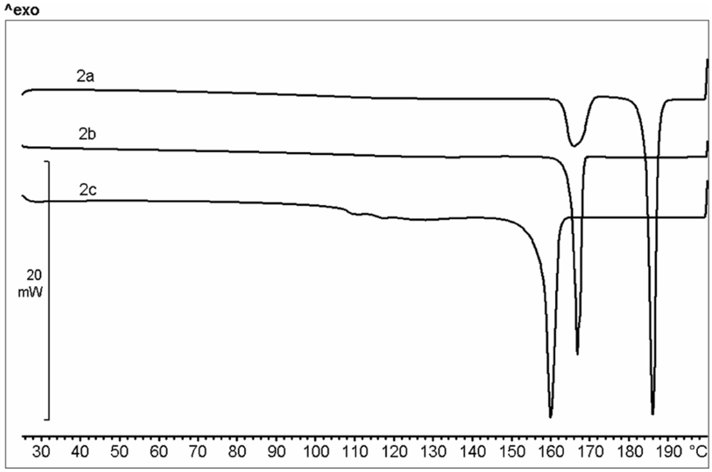


**FIGURE 2** DSC therograms of copper complexes for the period of the first heating cycle. Heating and cooling rate: 10 K $min^{-1}$.

into isotropic liquids, and no mesophase was observed on the heating cycle, neither on optical observations nor in DSC measurements. The melting points of the complexes decrease with increasing the alkyl chain length (n, see Scheme 1).

Figure 3 shows the DSC curves of copper complexes in the first cooling cycle. Only one exothermal peak was observed for 2a at 157.7°C ($\Delta H = 48.65$ kJ $mol^{-1}$) which corresponds to an isotropic liquid–solid transition. Compound 2b exhibits two exothermal peaks at 152.1°C, 146.1°C and compound 2c at 145.5°C, 132.2°C. The peaks at 152.1 ($\Delta H = 4.36$ kJ $mol^{-1}$) and 145.5 ($\Delta H = 2.17$ kJ $mol^{-1}$) are corresponding to isotropic liquid–mesophase transitions for 2b and 2c, but the peaks at 146.1 ($\Delta H = 36.91$ kJ $mol^{-1}$) and 132.2°C ($\Delta H = 42.00$ kJ $mol^{-1}$) are corresponding to mesophase–solid transitions for 2b and 2c, respectively. The mesophase was also studied by hot-stage polarized optical microscopy (POM). As an example, the texture under crossed polarizers for 2c is shown in Figure 4. As it is apparent from Figure 4, a typical batonnet texture was observed on cooling from the isotropic liquid. Based on the optical observations and DSC measurements, the mesophase structure assigned to a monotropic smectic A phase [26].

The copper complexes reported in this work are the further examples of metallomesogens with two ring salicylidenic Schiff-base ligand system with an azo moiety and a polar OH on the ligands ($N\text{-}CH_2\ CH(OH)CH_3$ ). Some other mesogenic copper complexes with similar structure to that of the title complexes of this work have been

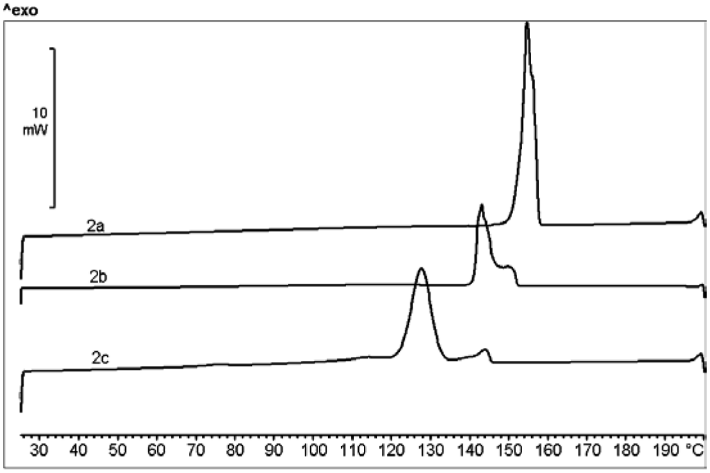


**FIGURE 3** DSC therograms of copper complexes for the period of the first cooling cycle. Heating and cooling rate: 10 K $min^{-1}$.

reported. We have reported the liquid crystalline properties of bis[5-((4-alkoxyphenyl) azo)-N- (ethanol)-salicylaldiminato]copper(II) complex homologues. These complexes exhibit enantiotropic smectic C (thermodynamically stable) liquid crystalline character [14]. We also

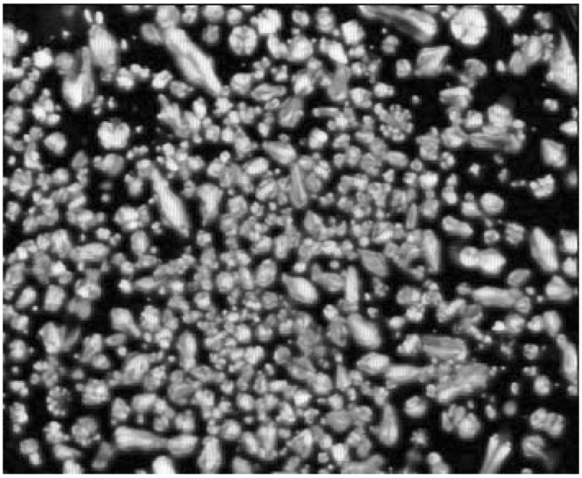


**FIGURE 4** Optical texture observed for compound 2c through crossed polarizers at 140°C.

have reported the liquid crystalline character of bis[5-((4-alkoxyphenyl)azo)-N- (alkyl)-salicylaldiminato] copper(II) complex homologues [12]; metallomesogens which are based on two ring salicylidenic Schiff-base ligand with an azo moiety and an alkyl group on the ligands (N-alkyl). These complexes exhibit monotropic nematic (thermodynamically unstable) liquid crystalline character. Furthermore, Hoshino [27], Cruso [28–30], Marcos [31,32], and Barbera [33] have reported the nematic liquid crystalline properties of bis [4-((4-alkoxy) benzoyloxy)-salicylaldimine-N-alkyl] copper(II) complexes. In comparison with similar complexes with no lateral hydroxyl group, the complexes with an OH lateral group reported in this study exhibit a high order mesophase (SmA). The comparison of the mesomorphic behavior of N-$CH_2CH(OH)CH_3$ complexes with N-alkyl analogous reveals the importance of the lateral OH group on the mesomorphic character. Due to this, we can conclude that in this type of metallomesogenic systems, the presence of the OH group on the ligand considerably improves the liquid crystalline behavior from monotropic nematic to monotropic smectic A phase. This fact may be related to the attractive intermolecular interactions between HO---Cu and/or HO---HO. Meanwhile, the comparison of liquid crystalline character of N-$CH_2$ $CH(OH)CH_3$ with N-$CH_2CH_2OH$ complexes shows that due to branching of lateral group, the order and thermodynamic stability of mesophase have been reduced from enantiotropic smectic C to monotropic smectic A.

## CONCLUSION

In this work we synthesized bis[5-((4-alkoxyphenyl)azo)-N-(2-propanol) salicylaldiminato] copper(II) complex homologues. Their mesomorphic properties were examined and compared with copper complexes reported previously. Decyloxy containing copper complexes do not show mesomorphic properties but other compounds exhibit monotropic smectic A mesophase. Mesomorphic temperature range was found to be controlled by side chain length (n) and increases with increasing of n. The lateral hydroxyl group had an important role in thermodynamic stability and order of mesophase.

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