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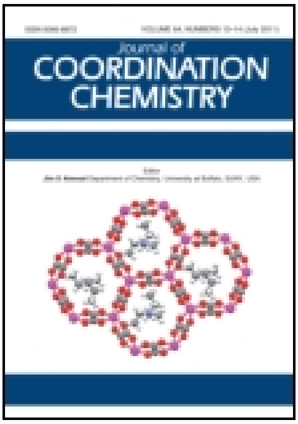

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis and mesomorphic properties of symmetric tetradentate Schiff bases based on azo-containing salicylaldimines and their copper(II) complexes

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Published online: 25 May 2011.

To cite this article: Kamellia Nejati , Zolfaghar Rezvani , Eslam Alizadeh & Razie Sammimi (2011) Synthesis and mesomorphic properties of symmetric tetradentate Schiff bases based on azo-containing salicylaldimines and their copper(II) complexes, Journal of Coordination Chemistry, 64:11, 1859-1870, DOI: 10.1080/00958972.2011.582644

To link to this article: http://dx.doi.org/10.1080/00958972.2011.582644

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Journal of Coordination Chemistry
Vol. 64, No. 11, 10 June 2011, 1859–1870

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Synthesis and mesomorphic properties of symmetric tetradentate Schiff bases based on azo-containing salicylaldimines and their copper(II) complexes

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(*Received 13 January 2011; in final form 24 March 2011*)

Two new tetradentate Schiff bases, in which two identical aromatic bent core mesogenic units containing phenylazo are connected *via* a 1,2-phenylene spacer, N,N′-di-(5-(4-alkoxyphenyl)azo)-salicylidene-1,2-phenylene diimine (alkoxy = decyloxy, dodecyloxy), and their copper(II) complexes were synthesized and studied for their mesomorphic character. The ligands were prepared by the condensation of 5-((4-alkoxyphenyl)azo)salicylaldehydes with 1,2-phenylene diamine. The ligands and their copper complexes have been characterized by IR, ^{1}H-NMR, electronic spectra, mass spectroscopy, and elemental analyses. The copper complexes were also studied by magnetic moment and electrical conductance measurements. The liquid crystalline properties of the ligands and the related copper complexes were investigated 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 the copper complexes display an enantiotropic smectic C mesophase.

Keywords: Schiff base; Salicylaldimine dimer; Copper complexes; Metallomesogen; Azo compounds; Smectic C

1. Introduction

Chemistry of metal-containing liquid crystals (metallomesogens) has been studied for 30 years due to the possibility of combining physico-chemical properties of the metal (color, magnetism, polarizability, redox behavior, etc.) with those of the organic framework [1–4]. Such compounds have properties that are typical for both liquid crystals and d-group transition metals or rare earth metals. In the mesophase, the molecules of metallomesogens are ordered like in classic organic liquid crystals, and

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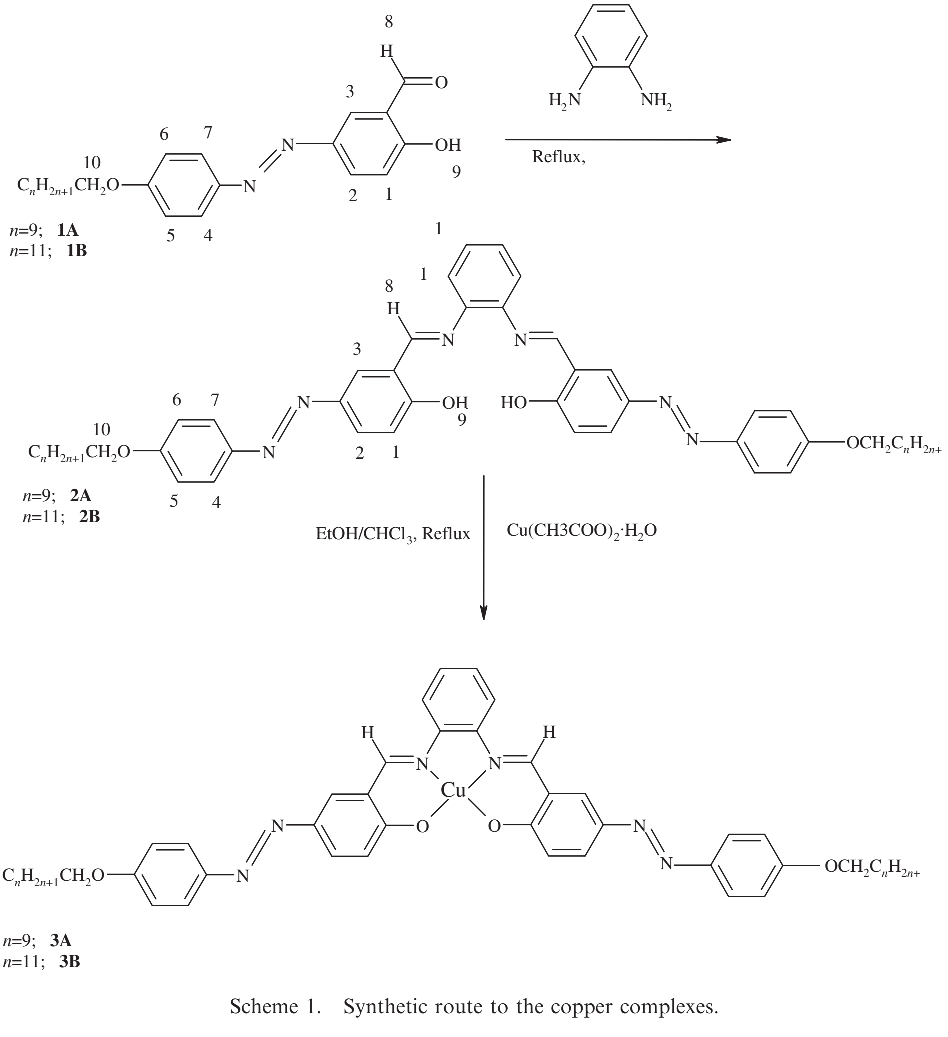
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2011.582644

their optical, magnetic, electric, and mechanical properties are anisotropic [5]. Their specific physical properties give a variety of applications in modern electronics.

Azo-containing liquid crystals have attracted attention because of their potential applications in optoelectronics, holographic gratings, and optical storage. The azo dyes possess *trans–cis* isomerization under irradiation at an appropriate wavelength, leading to reorientation of the azo groups reducing optical anisotropy [6]. Metallomesogens containing uncomplexed azo moieties, and therefore keeping their potential for photoisomerization, have attracted attention due to their possible applications in photon-mode high density data storage and photo-switching devices [7, 8].

As a part of our systematic investigation [9–13] on structural, mesomorphic, and thermal studies of Cu^{+2}, Ni^{+2}, and VO^{+2} metal complexes with azo-linked salicylaldimine Schiff bases, we report here the synthesis and liquid crystalline character of tetradentate Schiff-base ligands, N,N′-di-(5-(4-alkoxyphenyl)azo)-salicylidene-1,2-phenylene diimine, and their corresponding copper(II) complexes (scheme 1).



Scheme 1. Synthetic route to the copper complexes.

2. Experimental

2.1. *Reagents*

All reagents and solvents were supplied by Merck chemical company and used without purification. 4-Alkoxynitrobenzene homologs were obtained by the reaction between 4-nitrophenol with 1-bromoalkane in DMF and K_2CO_3 as base by refluxing for 3 h [14] and then purified by recrystallization from ethanol. 4-Alkoxy aniline homologs were prepared by reducing the corresponding 4-alkoxynitrobenzene as described [15].

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 from 400 to 4000 cm^{-1}. Differential scanning calorimetry (DSC) thermograms of the compounds were obtained on a Mettler-Toledo DSC 822 e 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 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 nitrogen. Thermogravimetric analysis (TGA) thermograms were carried out on a Mettler–Toledo TGA 851e at a heating rate of 10°C min^{-1} under a nitrogen atmosphere. 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 in deuterated chloroform on a Bruker FT-NMR AC-400 (400 MHz) spectrometer. All chemical shifts are reported in δ(ppm) relative to the tetramethylsilane. X-ray powder diffraction patterns were recorded on a Bruker D8 powder diffractometer (Cu-Kα: 1.541 Å). Molar conductivities were measured using a Jenway 4010 conductivity meter. Absorption spectra were recorded from 300 to 800 nm on a Shimadzu model 1601 PC UV-Vis spectrophotometer. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature using $Hg[Co(SCN)_4]$ as calibrant.

2.3. *Materials*

All homolog materials were prepared similarly as described in the literature [16].

2.3.1. 5-(4-Decyloxyphenylazo) salicylaldehyde (1A). Yellow, yield 80%, m.p. 124°C. MS m/z (relative intensity): 383.4 (M + 1, 14), 382.3 (M, 38), 121 ($M-C_{10}H_{21}OC_6H_4N_2$, 100). Anal. Calcd 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. ^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 (19H, alkyl chain). IR(KBr): $\nu = 3186$(O–H), 3065(C–H, aromatic), 2923, 2957(C–H, aliphatic), 1661(C=O), 1599(C=C, aromatic) cm^{-1}, 1501(N=N), 1245(C–O, etherial), 1149(C–O, phenolic) cm^{-1}.

2.3.2. 5-(4-Dodecyloxyphenylazo) salicylaldehyde (1B). Yellow, yield 80%, m.p. 123°C. MS m/z (relative intensity): 411.6 ($M+1$, 13), 410.6 (M, 42), 121 ($M-C_{12}H_{25}OC_6H_4N_2$, 100). Anal. Calcd for $C_{25}H_{34}N_2O_3$: C, 73.06; H, 8.28; N, 6.82. 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 6.7 Hz, H-10), 1.84–0.87 (23 H, alkyl chain). IR(KBr): $\nu = 3190$(O–H), 3065(C–H, aromatic), 2921, 2851(C–H, aliphatic), 1661(C=O), 1600(C=C, aromatic) cm^{-1}, 1500(N=N), 1245(C–O, etherial), 1148(C–O, phenolic) cm^{-1}.

2.4. *Syntheses of the ligands*

The Schiff bases were prepared in similar manner. Thus, 2.16 g (0.02 mol) of the 1,2-phenylene diamine and 0.04 mol of related 5-(4-alkoxyphenylazo) salicylaldehyde were dissolved in 0.1 L 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 red microcrystals. The microcrystals were filtered off, washed with 15 mL of cold absolute ethanol, and then recrystallized several times in ethanol–chloroform (1 : 2, v/v).

2.4.1. N,N′-Di-(5-(4-decyloxyphenyl)azo)-salicylidene-1,2-phenylene diimine (2A). Red, yield 80%, m.p. 164.5°C. MS m/z (relative intensity): 857.7 ($M+1$, 13), 856.7 (M, 42), 332.4 ($M-2\times C_{10}H_{21}OC_6H_5N_2$, 100). Anal. Calcd for $C_{52}H_{64}N_6O_4$: C, 72.84; H, 7.47; N, 9.81. Found: C, 72.4; H, 7.0; N, 9.5. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 13.85 (s, H-9), 8.81 (s, H-8), 8.03–8.05 (H-2, H-3), 7.90-7.92 (dd, J 7.8, 2.4 Hz, H-4, H-7), 7.42–7.45 (H-11), 7.33–7.35 (H-12), 7.20(d, J 8.2 Hz, H-1), 7.03 (d, J 8.1 Hz, H-5, H-6), 4.07 (t, J 6.5 Hz, H-10), 0.90–1.88 (19 H, alkyl chain). IR(KBr): $\nu = 3416$(O–H), 3017(C–H, aromatic), 2850–2920(C–H, aliphatic), 1617(C=N), 1600(C=C, aromatic) cm^{-1}, 1502(N=N), 1252(C–O, etherial), 1149(C–O, phenolic) cm^{-1}.

2.4.2. N,N′-Di-(5-(4-dodecyloxyphenyl)azo)-salicylidene-1,2-phenylene diimine (2B). Red, yield 77%, m.p. 154.5°C. MS m/z (relative intensity): 913.7 ($M+1$, 14), 912.7 (M, 40), 332.4 ($M-2\times C_{12}H_{25}OC_6H_5N_2$, 100). Anal. Calcd for $C_{56}H_{72}N_6O_4$: C, 73.63; H, 7.89; N, 9.20. Found: C, 73.2; H, 7.5; N, 8.9. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 13.83 (s, H-9), 8.80 (s, H-8), 8.03–8.05 (H-2, H-3), 7.90–7.92 (dd, J 7.7, 2.4 Hz, H-4, H-7), 7.42–7.45 (H-11), 7.33–7.35 (H-12), 7.19(d, J 8.1 Hz, H-1), 7.03 (d, J 8.1 Hz, H-5, H-6), 4.07 (t, J 6.5 Hz, H-10), 0.89–1.88 (19 H, alkyl chain). IR(KBr): $\nu = 3418$ (O–H), 3016 (C–H, aromatic), 2852–2922 (C–H, aliphatic), 1619(C=N), 1600(C=C, aromatic) cm^{-1}, 1502(N=N), 1251(C–O, etherial), 1148(C–O, phenolic) cm^{-1}.

2.5. *Syntheses of the copper complexes*

Copper complexes were prepared similarly using the method described elsewhere [9]. Thus, a solution of 0.798 g (0.004 mol) of $Cu(OAc)_2 \cdot H_2O$ in 0.01 L of ethanol was added to an ethanol–chloroform (1 : 1 v/v) solution containing 0.004 mol of ligand and refluxed for 2 h. The obtained solution was kept at room temperature. 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).

2.5.1. 3A. Brown, yield 80%. Anal. Calcd for $C_{52}H_{62}N_6O_4Cu \cdot 1.5C_2H_6O$: C, 68.29; H, 7.35; N, 8.69. Found: C, 67.8; H, 6.9; N, 8.2. IR (KBr): $\nu = 3420$(O–H, alcoholic), 3058(C–H, aromatic), 2850, 2922(C–H, aliphatic), 1607(C=N), 1590(C=C, aromatic), 1499(N=N), 1247(C–O, etherial), 1148(C–O, phenolic) cm^{-1}. $\Lambda_m = 1.6\,\Omega^{-1}\,cm^2\,mol^{-1}$ in DMF. $\mu_{eff} = 1.70$ BM.

2.5.2. 3B. Brown, yield 80%. Anal. Calcd for $C_{56}H_{70}N_6O_6Cu \cdot 1.5C_2H_6O$: C, 69.24; H, 7.73; N, 8.21. Found: C, 68.7; H, 7.3; N, 7.8. IR (KBr): $\nu = 3404$(O–H, alcoholic), 3069(C–H, aromatic), 2922, 2849(C–H, aliphatic), 1608(C=N), 1581(C=C, aromatic), 1499(N=N), 1247(C–O, etherial), 1147(C–O, phenolic) cm^{-1}. $\Lambda_m = 1.6\,\Omega^{-1}\,cm^2\,mol^{-1}$ in DMF. $\mu_{eff} = 1.72$ BM.

3. Results and discussion

3.1. *Synthesis*

The Schiff bases were synthesized in a four-step process, in which the hydroxyl in 4-nitrophenol is first replaced by an alkoxy chain followed by the reduction of nitro to an amine. In the third step, salicylaldehyde is coupled with the diazonium chloride obtained from the 4-alkoxyaniline. Subsequent reaction of 5-(4-alkoxyphenylazo) salicylaldehyde with 1,2-phenylene diamine (scheme 1) by refluxing in absolute ethanol using a few drops of acetic acid as catalyst afforded the Schiff bases, which were purified by repeated crystallization from ethanol/chloroform. Structures of pre-ligands (**1A** and **1B**) and ligands (**2A** and **2B**) were checked and confirmed by elemental analyses, IR, ^{1}H-NMR, and mass spectra. The copper complexes were characterized by C, H, and N elemental analysis, IR spectroscopy, conductivity measurements, and magnetic moments data. Some physical and characterization data for the pre-ligands, ligands, and complexes are given in the experimental section. Elemental analyses and spectroscopic data for the new compounds are in good agreement with the proposed formula. The ^{1}H-NMR proton numbering schemes of **1A**, **1B**, **2A,** and **2B** are represented in scheme 1. A strong band is observed in IR spectra of **1A** and **1B** at 1660–1666 cm^{-1}, which can be assigned to ν(C=O). The absence of ν(C=O) in IR spectra of **2A** and **2B** together with the presence of new ν(C=N) at 1617–19 cm^{-1} clearly indicated that a Schiff base had formed in each case. Comparison of the IR spectra of the metal complexes with those of the free ligands shows that the C=N stretch is shifted to lower wavenumbers (10–11 cm^{-1}) after coordination. This shift is due to the reduction of the double-bond character of the C=N bond as a result of coordination of nitrogen to metal, in agreement with the results obtained for similar complexes [17–19]. The broad band of medium intensity at 3404–3420 cm^{-1} is due to the O–H stretch of the lattice ethanol.

The magnetic moments of complexes (as BM) were measured at room temperature and diamagnetic corrections were calculated from Pascal's constants [20]. The magnetic

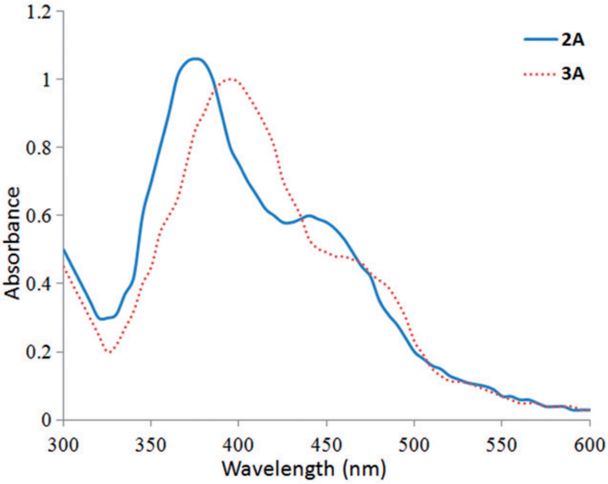


Figure 1. UV-Vis spectrum of **2A** and **3A**.

moment values of the copper complexes (1.70 and 1.72 BM) lie in the range observed for complexes with one unpaired spin (1.69–1.73 BM). In addition, the complexes in *ca* 10^{-3} mol L^{-1} solutions in DMF at 25°C have very low conductance, indicating that the complexes are neutral [21].

Figure 1 depicts electronic absorption spectra of free ligand (**2A**) and related copper complex (**3A**) in DMF from 300 to 800 nm. Electronic absorption spectra of free ligand (**2A**) display bands at 375 and 440 nm with high extinction coefficients and are attributed to π–π* transitions [22]. The λ_{max} of free ligand (**2A**) in copper complex (**3A**) is red-shifted to 395 and 460 nm, respectively. In view of the strong absorptions of the complexes in the near-ultraviolet region, these features cannot be ascribed to d–d electron transitions of Cu^{2+}, which are generally weak and may be easily obscured by the strong absorption band of the azo ligand. Therefore, the obvious bathochromic effect seen for the copper azo complex most probably arises from the energy change of the intense π–π* transition of the conjugated chromophore due to chelation by copper [23].

Tverdova *et al.* [24] recently reported planar structure of N,N′-phenylene bis(salicylideneamino)copper(II), which has a similar ONNO coordination environment to the complexes of this study. It is suggested that the Cu(II) coordination geometry is square planar on the basis of the similarity of its coordination environment, and we conclude that the Schiff bases are coordinated to metal as tetradentate (ONNO) ligands in a 1 : 1 ratio.

3.2. *Mesomorphism*

Thermal stability of these materials was checked by TGA. All other thermal characterizations were then carried out below the decomposition temperature. Supplementary material shows the TGA and DSC thermograms of **2A** at a heating rate of 10°C min^{-1}; **2B** has similar DSC and TGA. Decomposition starts at 220°C as

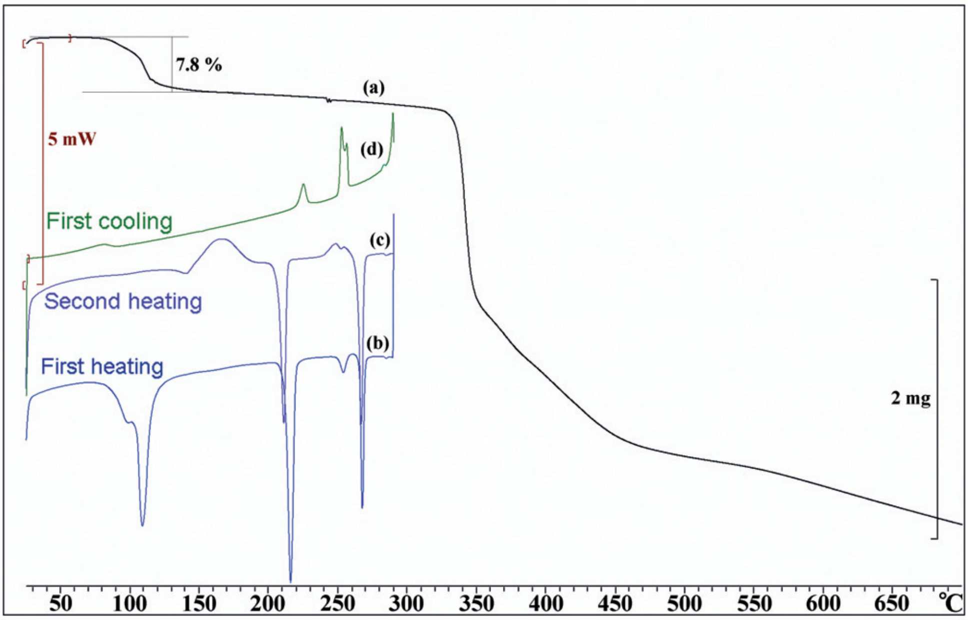


Figure 2. (a) TGA curve, (b) first heating cycle, (c) second heating cycle, and (d) first cooling cycle of DSC curve for **3A**.

confirmed by TGA and DSC thermograms. The mesomorphic properties of 5-(4-alkoxyphenylazo)salicylaldehyde homologs (**1A**, **1B**), the Schiff bases (**2A**, **2B**), and related Cu(II) complexes (**3A**, **3B**) have been studied by polarizing optical microscopy (POM) observations using a heating–cooling stage and the phase transition temperatures; enthalpies were obtained by DSC complexes. **1A**, **1B**, **2A**, and **2B** were not mesomorphic, clearly melting and transforming into isotropic liquids; no mesophase was observed during heating or cooling.

The TGA and complete set of DSC thermograms for **3A** are shown in figure 2. The thermal behavior of both copper complexes was similar. Two major mass loss steps are observed for each complex. The first has a decomposition temperature range of 75–135°C, with a mass loss of 7.8% for **3A** and 6.53% for **3B**, corresponding to a loss of 1.5 molecules of lattice ethanol (Calcd 7.14% for **3A** and 6.75% for **3B**). The second mass loss at 320–450°C is attributed to decomposition.

Complexes **3A** and **3B** display liquid crystalline character, as revealed by POM and DSC thermograms.

The thermal behaviors of **3A** and **3B** are similar as apparent from the DSC heating scan curves, therefore we describe the behavior of **3A** as the representative. Complex **3A** shows five endothermal peaks at 103.8, 211.7, 250.1, 265.4, and 289.3°C (figure 2b–d) in the first heating scan. The first peak at 103.8°C (overlapped with a previous transition) associated with the TG mass loss from 75°C to 135°C is attributed to the removal of lattice ethanol. Peaks at 211.7°C and 250.1°C with ΔH values of 33.9 and 2.0 $\mathrm{kJmol^{-1}}$ are solid–solid transitions. The two endothermal peaks at 265.4°C and 289.3°C are attributed to the crystal-to-mesophase and mesophase-to-isotropic liquid transitions, respectively. The texture of mesophase was investigated by POM. For **3A** and **3B**,

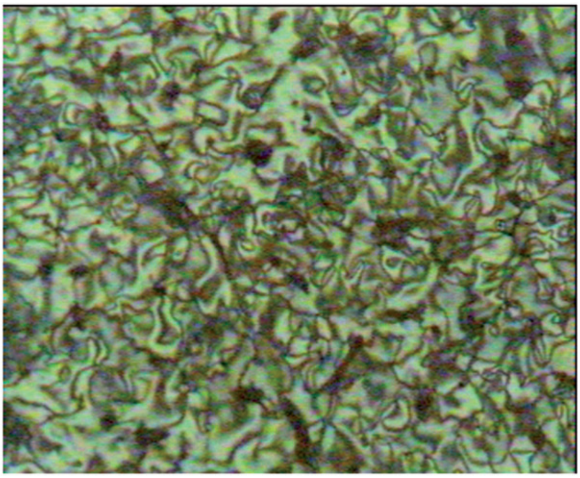


Figure 3. Optical texture observed for **3A** through crossed polarizers at 275°C.

highly viscous mesophases with a typical Schlieren texture [25] were observed under POM after melting or cooling from the isotropic liquid, indicating the formation of enantiotropic Smectic C(S_mC) mesophase. Continued heating of **3A** or **3B** mesophases causes decomposition at 320°C, which has been detected by exothermic peaks in the DSC trace, TGA thermograms, and optical observations. In the first cooling scan, **3A** showed two exothermal peaks at 256.5°C and 228.2°C (figure 2d) corresponding to the isotropic liquid-to-Smectic C mesophase and Smectic C mesophase-to-crystalline phase transitions, respectively. In the second heating scan, an exothermal peak at 145.2°C with enthalpy of $-25.9\,\mathrm{kJ\,mol^{-1}}$ is ascribed to crystallization. Four endothermal peaks at 207.8°C, 249.2°C, 265.4°C, and 288.8°C are attributed to solid–solid transitions, crystal-to-mesophase and mesophase-to-isotropic liquid transitions, respectively. A microscopic picture from the S_mC mesophase for **3A** is illustrated in figure 3 as a representative example.

The structural changes during desolvation and solid–solid transitions have been confirmed using powder X-ray diffraction (XRD). The powder XRD patterns of virgin copper complexes recorded at room temperature prior to heating indicated a typical crystalline phase (figure 4a and b). The virgin crystals of **3A** and **3B** annealed at 140°C for 15 min are determined according to the DSC thermograms and then, XRD pattern was recorded at ambient temperature (figure 5a and b). The virgin crystals of **3A** and **3B** are not isostructural with the annealed samples, which indicates that the annealing of virgin crystals of **3A** and **3B** causes crystal structural change during mass loss at 75°C–135°C due to the removal of lattice solvent.

These complexes represent a further example of a mesomorphic complex derived from a non-mesogenic ligand. Copper complexes based on tetradentate salicylidenic ligands containing uncomplexed azo moiety with 1,2-phenylene diamine bridge have not been reported as liquid crystalline materials and the copper complexes reported in this study are the first example of metallomesogens based on azo-linked salicylidenic Schiff base with a 1,2-phenylene diamine bridge. This complex represents a further example of a mesomorphic complex derived from a non-mesogenic ligand.

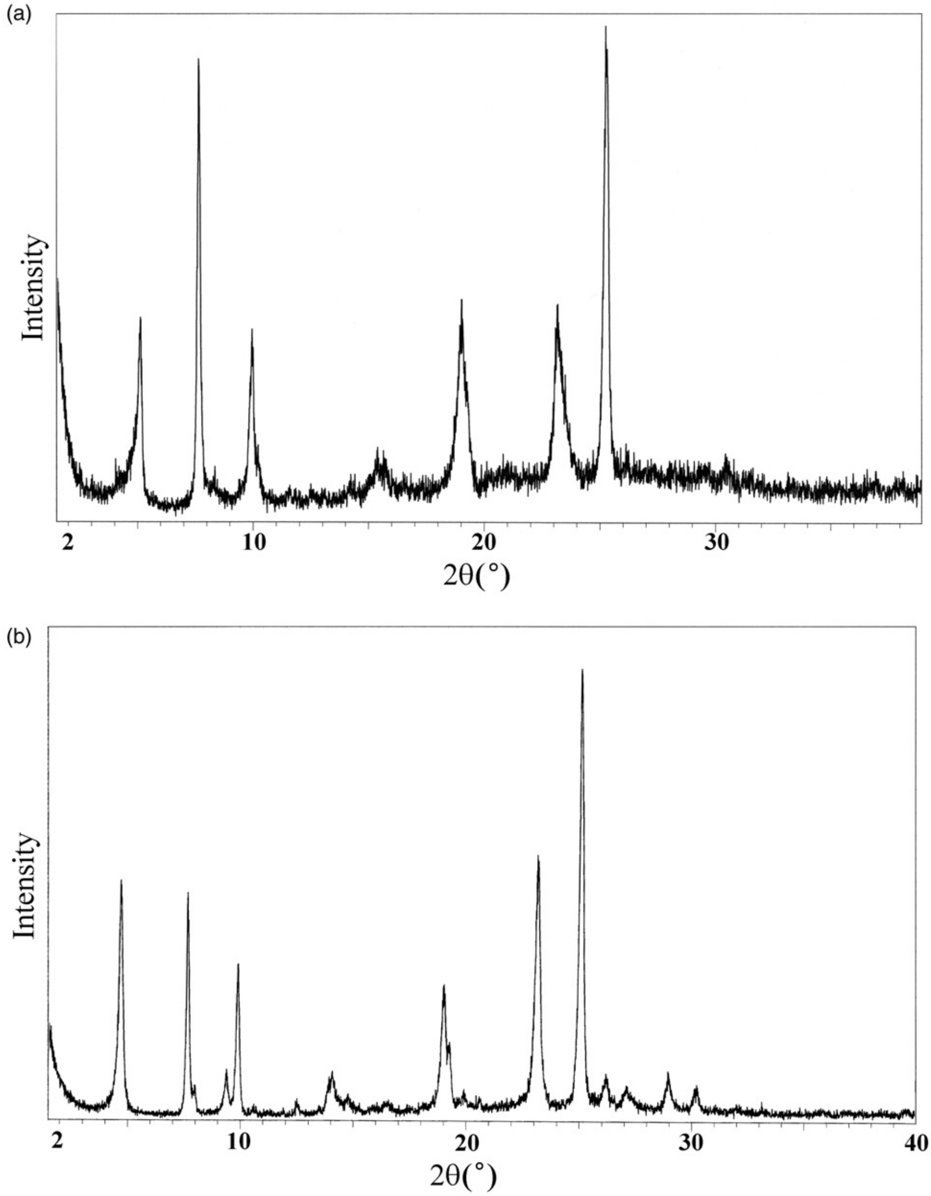


Figure 4. XRD patterns of virgin copper complexes crystallized from ethanol/chloroform, (a) **3A** and (b) **3B**.

Recently, some mesogenic complexes which have a similar structure to that of **3A** and **3B** were reported. We reported the liquid crystalline properties of bis(alkoxyphenylazo)-substituted N,N′-salicylidene diiminato Ni(II), Cu(II), and VO(IV) complexes based on 1,2-diaminoethane and 1,3-diaminopropane bridges [9]. These complexes exhibited smectic A liquid crystalline character and undergo considerable decomposition near the transition to the isotropic liquid. Similar mesomorphic properties were previously

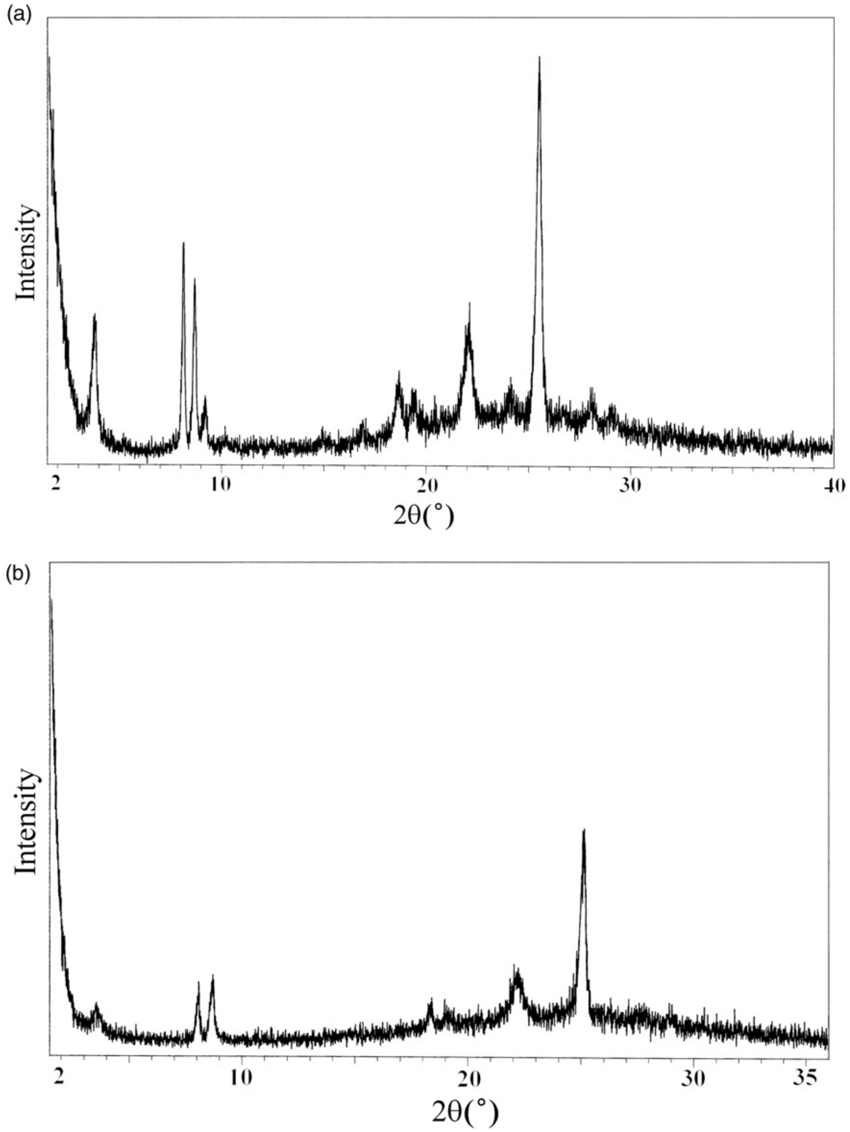


Figure 5. XRD patterns of copper complexes annealed at 140°C, (a) **3A** and (b) **3B**.

reported by Ghedini *et al.* [26] for copper complexes with a similar coordination environment based on tetradentate salicylaldimine Schiff bases, but with a 4-alkylphenylazo linkage. Nickel complexes [26] undergo considerable decomposition near the transition to isotropic. In addition, Rao *et al.* [27] reported the nematic liquid crystalline properties of nickel complex with N,N′-di-4-(4′-entyloxybenzoate)salicylidene diaminoethane. This complex exhibited low transition temperature in comparison with **3A** and **3B**, but undergo decomposition near the transition to the isotropic liquid. Finally, Aiello *et al.* reported a new type of zinc(II) complex derived from tetradentate salen-like Schiff bases containing uncomplexed alkylphenylazo with 1,3-diaminopropane and

1,3-diamino-2,2-dimethylpropane bridges. These complexes show nematic and smectic C(S_mC) mesophases [28]. However, the complexes described in this study are more thermally stable than ethylene and tri methylene bridged complexes, perhaps related to the presence of the phenylene bridge in **3A** and **3B**.

4. Conclusion

In this study, we prepared two copper homologs derived from tetradentate N,N′-di-(5-(4-alkoxyphenyl)azo)-salicylidene-1,2-phenylene diamine ligands. While the Schiff bases do not show liquid crystalline character, the complexes have mesomorphic properties and form a smectic C mesophase. For the copper complexes, the mesophase decomposed several degrees after clearing point. The mesophases have a narrow temperature range. The copper complexes undergo solid–solid transitions before transforming to liquid crystalline phase as confirmed by powder XRD patterns.

Acknowledgments

The authors sincerely appreciate the financial support from the ResearchVice Chancellor of Azarbaijan University of Tarbiat Moallem and the faculty of basic science.

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