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Synthesis and Liquid-Crystalline Properties of *N,N′*-di-(5-(4-Alkoxyphenyl)azo)-Salicylidene-1,2-Phenylene Diiminato Nickel(II) Complexes

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The synthesis, characterization, and liquid-crystal properties of two new tetradentate N,N′-di-(5-(4-alkoxyphenyl)azo)-salicylidene-1,2 phenylene diimine ligands (alkoxy = octloxy, decyloxy) and their nickel(II) complexes are reported. The ligands were prepared by the condensation of the 5-((4-alkoxyphenyl)azo)salicylaldehydes homologous with 1,2 phenylene diamine. The ligands and their nickel complexes have been characterized by infrared (IR), ^{1}H nuclear magnetic resonance (NMR), mass spectroscopy, and elemental analyses. The liquid-crystalline properties of the ligands and the related nickel 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 exhibited liquid-crystalline behavior but the copper complexes demonstrated an enantiotropic smectic A mesophase.

Keywords Liquid crystal; nickel complexes; salicylaldimine; Schiff base; smectic A; tetradentate

Introduction

Metallomesogens occupy a specific place among a large number of presently known liquid-crystalline substances [1–3]. These liquid crystals are coordination compounds of metal cations with various organic chelating ligands. Their specific physical properties give rise to a variety of applications in modern electronics. The chemistry and physics of metallomesogens have recently been described in several review articles and books [4–7].

In recent times, azo-containing liquid crystals have been extensively studied for their various electro-optical characteristics, such as photochromism and photoisomerization [8–10]. On the other hand, metallomesogens containing uncomplexed azo moieties, and therefore keeping their potential for photoisomerization, have

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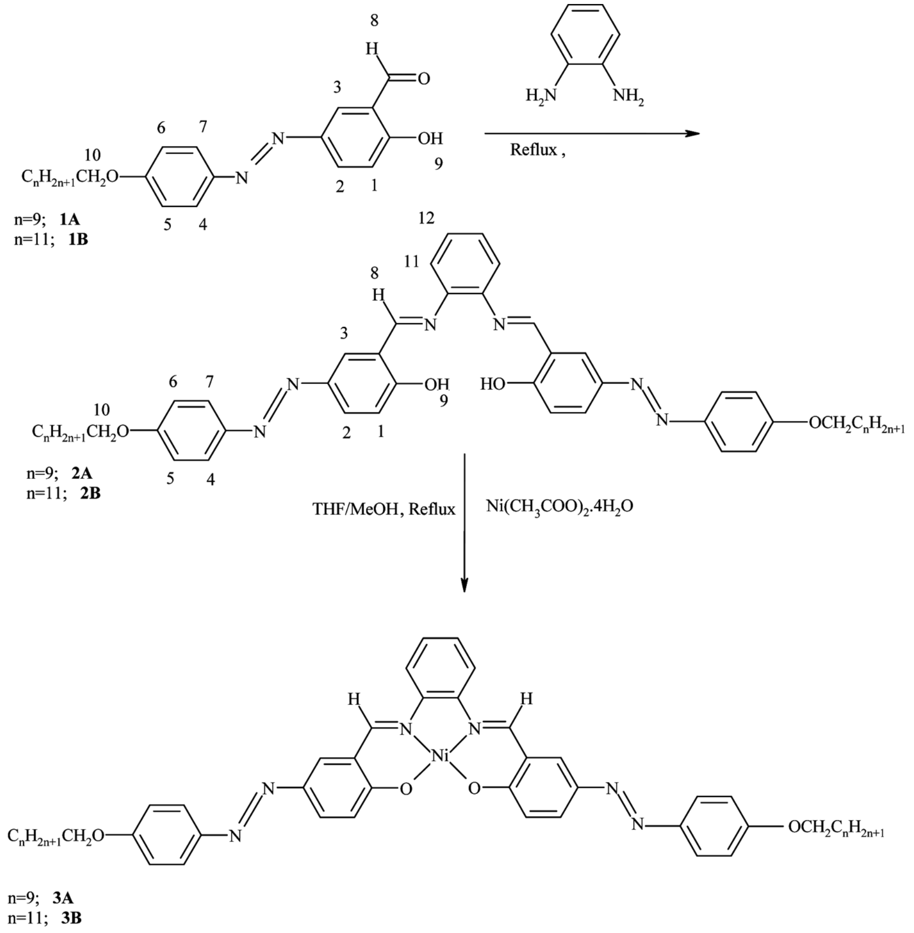


Scheme 1. Synthetic route to the nickel complexes.

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].

As a part of our systematic investigation [16–21] on structural and thermal studies of Cu^{+2}, Ni^{+2}, and VO^{+2} metal complexes with azo-linked salicylaldimine Schiff-base derivatives, we report here the results of our investigation on the synthesis and liquid-crystalline character of tetradentate Schiff base *N*,*N*′-di-(5-(4-alkoxyphenyl)azo)-salicylidene-1,2 phenylene diimine and the corresponding nickel(II) complexes (see Scheme 1).

Experimental

Reagents

All reagents and solvents used were supplied by Merck Chemical Company (Germany) and were used without further purification. 4-Alkoxynitrobenzene homologues were obtained by reaction between 4-nitrophenol with 1-bromoalkane in dimethyl formamide (DMF) as solvent and K_2CO_3 as base by refluxing for

3 h [22] and then crude 4-alkoxy nitro benzene homologues were purified by recrystallization from ethanol. 4-Alkoxy aniline homologues were prepared by reducing of the corresponding 4-alkoxynitrobenzene as described in the literature [23].

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, vector 22 fourier transform infrared (FTIR) spectrometer using KBr pellets in the 400–4,000 cm^{-1} range. The differential scanning calorimetry (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. Thermogravimetric analysis (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 nuclear magnetic resonance (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 δ(ppm) relative to the tetramethylsilane as internal standard. X-ray powder diffraction patterns were recorded on a Bruker D8 powder diffractometer (Cu K_α : 1.541 Å).

Materials

All homologue materials were prepared as described in the literature [24].

5-(4-Decyloxyphenylazo)salicylaldehyde (1A). Yellow, yield 80%, mp 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. 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. ^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): $\nu = 3{,}186$ (O-H), 3,065 (C-H, aromatic), 2,923, 2,957 (C-H, aliphatic), 1,661 (C=O), 1,599 (C=C, aromatic), 1,501 (N=N), 1,245 (C-O, ethereal), 1,149 (C-O, phenolic) cm^{-1}.

5-(4-Dodecyloxyphenylazo)salicylaldehyde (1B). Yellow, yield 80%, mp 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. Calc. 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. ^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). IR (KBr): $\nu = 3{,}190$ (O-H), 3,065 (C-H, aromatic), 2,921, 2,851 (C-H, aliphatic), 1,661 (C=O), 1,600 (C=C, aromatic), 1,500 (N=N), 1,245 (C-O, ethereal), 1,148 (C-O, phenolic) cm^{-1}.

Syntheses of the Ligands

All homologue materials were prepared in a similar manner. Thus, 0.02 mol of the 1,2-phenylene diamine and 0.04 mol of related 5-(4-alkoxyphenylazo)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 several times in ethanol-chloroform (1:2, v/v).

N,N′-Di-(5-(4-decyloxyphenyl)azo)-salicylidene-1,2 phenylene diimine (2A). Red, yield 80%, mp 164.5°C. MS m/z (relative intensity): 857.7 (M + 1, 13), 856.7 (M, 42), 332.4 (M-2 × $C_{10}H_{21}OC_6H_5N_2$, 100). Anal. Calc. 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 (19H, alkyl chain). IR (KBr): $\nu = 3{,}416$ (O-H), 3017 (C-H, aromatic), 2,850–2,920 (C-H, aliphatic), 1,617 (C=N), 1,600 (C=C, aromatic), 1,502 (N=N), 1,252 (C-O, ethereal), 1,149 (C-O, phenolic) cm^{-1}.

N,N′-Di-(5-(4-dodecyloxyphenyl)azo)-salicylidene-1,2 phenylene diimine(2B). Red, yield 77%, mp 154.5°C. MS m/z (relative intensity): 913.7 (M + 1, 14), 912.7 (M, 40), 332.4 (M-2 × $C_{12}H_{25}OC_6H_5N_2$, 100). Anal. Calc. 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 (19H, alkyl chain). IR (KBr): $\nu = 3{,}418$ (O-H), 3,016 (C-H, aromatic), 2,852–2,922 (C-H, aliphatic), 1,619 (C=N), 1,600 (C=C, aromatic), 1,502 (N=N), 1,251 (C-O, ethereal), 1,148 (C-O, phenolic) cm^{-1}.

Syntheses of the Nickel Complexes

Nickel complexes were prepared in a similar manner using the method described elsewhere [17]. Thus, a solution of 0.004 mol of $Ni(OAc)_2 \cdot 4H_2O$ in 10 mL 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 left at room temperature. Nickel complexes were obtained as red microcrystals. The microcrystals were filtered off, washed with absolute ethanol, and then recrystallized from ethanol-chloroform (1:3 v/v).

3A. Red, yield 77%. Anal. Calc. for $C_{52}H_{62}N_6O_4Ni.1.5C_2H_6O$ (981.7): C, 67.23; H, 7.23; N, 8.56; Found: C, 66.8; H, 6.8; N, 8.2. IR (KBr): $\nu = 3{,}417$ (O-H, alcoholic), 3,223 (OH, phenolic), 3,069 (C-H, aromatic), 2,955, 2,918, 2,849 (C-H, aliphatic), 1,638 (C=N), 1,604 (C=C, aromatic), 1,503 (N=N), 1,251 (C-O, ethereal), 1,152 (C-O, phenolic) cm^{-1}.

3B. Brown, yield 80%. Anal. Calc. for $C_{56}H_{70}N_6O_6Ni.1.5C_2H_6O$: C, 68.23; H, 7.61; N, 8.09; Found: C, 67.8; H, 7.2; N, 7.7. IR (KBr): $\nu = 3{,}417$ (O-H, alcoholic), 3,223 (OH, phenolic), 3,069 (C-H, aromatic), 2,955, 2,918, 2,849 (C-H, aliphatic), 1,638

(C=N), 1,604 (C=C, aromatic), 1,503 (N=N), 1,251 (C-O, ethereal), 1,152 (C-O, phenolic) cm^{-1}.

Results and Discussion

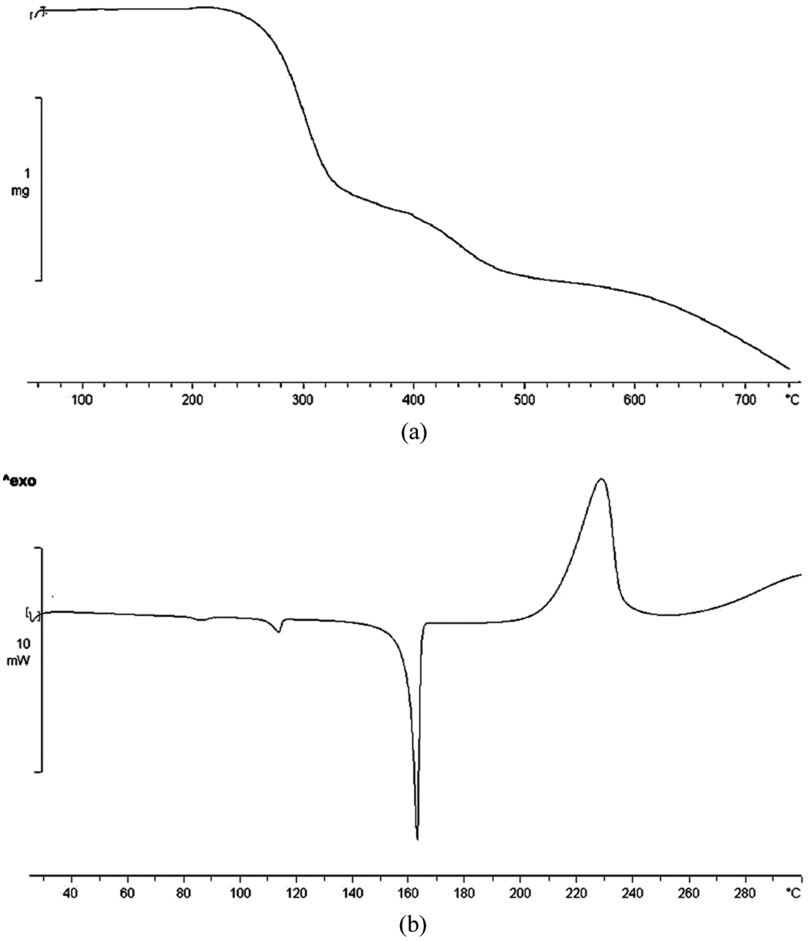
Synthesis

The Schiff-base ligands were synthesized in a four-step process, in which the hydroxyl group in 4-nitrophenol is first replaced by an alkoxy chain followed by reduction of the nitro group to an amine. In the third step, salicylaldehyde is coupled with the diazonium chloride obtained from the 4-alkoxyaniline. Subsequent reaction of the thus-formed 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-base ligands, which were purified by repeated crystallization from an ethanol/chloroform mixture. 5-(4-decyloxyphenylazo) salicylaldehyde (**1A**), 5-(4-Dodecyloxyphenylazo)salicylaldehyde (**1B**), and the Schiff-base ligands (**2A** and **2B**) were characterized by IR and ^1H NMR spectroscopy, mass spectrometry, and elemental analyses. The ^1H NMR proton numbering scheme of **1A, 1B, 2A**, and **2B** is represented in Scheme 1. The nickel complexes were characterized by C, H, N elemental analysis and IR spectroscopy. Some physical and characterization data for the ligands and complexes are given in the Experimental section. The elemental analyses and spectroscopic data for the new compounds are in good agreement with the proposed formula.

In the compounds **1A** and **1B**, the hydroxyl group was observed at 3,186–90 cm^{-1} because the intramolecular hydrogen bonding between OH and the formyl group in compound **1** leads to decreasing the stretching frequency of OH, and the carbonyl group was observed in the region 1,660–1,666 cm^{-1} [21]. The total absence of ν(C=O) absorption in the IR spectra of **2A** and **2B** together with the presence of new ν(C=N) absorption at 1,617–19 cm^{-1} clearly indicated that a new Schiff-base ligand had formed in each case. Comparison of the IR spectra of the metal complexes with those of the free ligands shows that the stretching frequency of the C=N bond is shifted to lower wavenumbers (11–12 cm^{-1}) after coordination. This shift is due to reduction of the double-bond character of the C=N bond as a result of coordination of the nitrogen to the metal center and is in agreement with the results obtained for other similar complexes described previously [25–27]. The broad band of medium intensity in the 3,404–3,450 cm^{-1} region is due to the O-H stretching vibration of the lattice ethanol. Based on these observations and the results of elemental analyses, we conclude that the Schiff-base ligands are coordinated to metal atoms as tetradentate (ONNO) ligands in a 1:1 ratio.

Mesomorphism

The thermal stability of these materials was checked by TGA. All other thermal characterizations were then carried out below the decomposition temperature. Figures 1a and 1b show the TGA and DSC thermograms of compound **2A** at a heating rate of 10°C/min. Compound **2B** has similar DSC and TGA thermograms. For Schiff-base ligands (**2A, 2B**) the decomposition process starts at 220°C as confirmed by TGA and DSC thermograms. The mesomorphic properties of 5-(4-alkoxyphenylazo) salicylaldehyde homologues (**1A, 1B**), the Schiff ligands (**2A, 2B**), and related Ni(II)



(a)

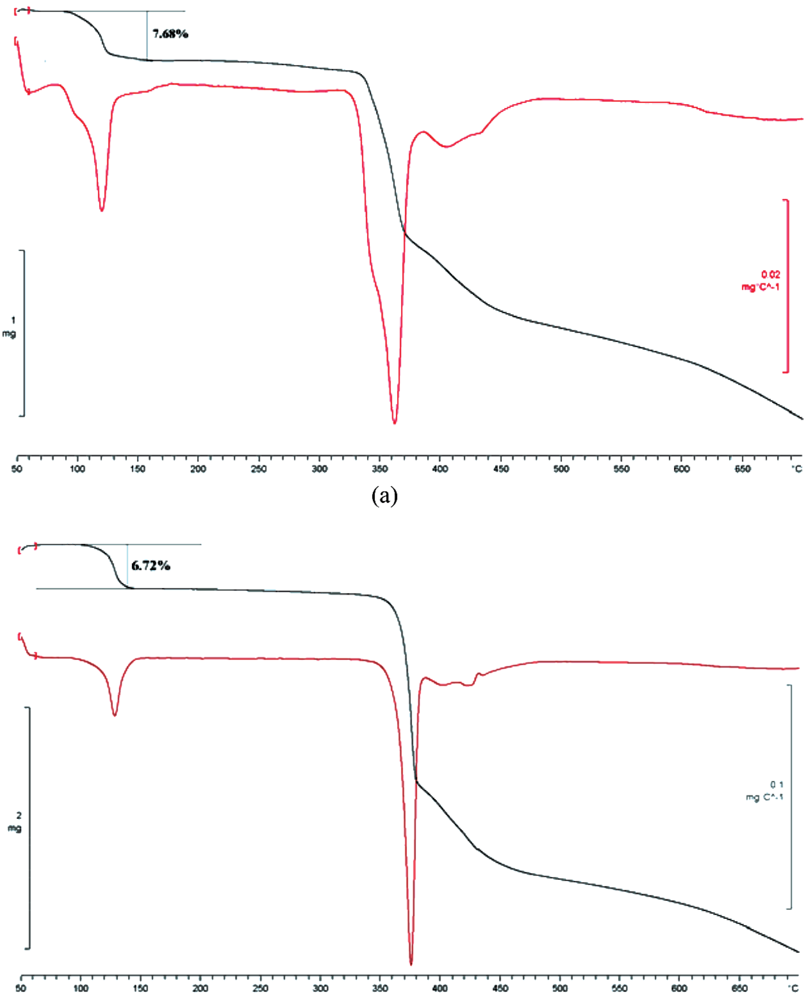
(b)

Figure 1. (a) TG curve of **2A** and (b) DSC curve of **2A**.

complexes (**3A, 3B**) have been studied by polarizing optical microscopy observations using a heating–cooling stage and the phase transition temperatures and enthalpies were obtained by DSC. Compounds **1A**, **1B**, **2A**, and **2B** were not mesomorphic. These compounds clearly melted and transformed into isotropic liquids and no mesophase was observed in the heating or cooling cycle on optical observations.

The thermal gravimetry (TG) and differential thermal gravimetry (DTG) curves for the nickel complexes (**3A** and **3B**) are shown in Figs. 2a and 2b. The thermal behavior of two nickel complexes is similar. Two major mass loss steps are observed for each complex. The first mass loss stage has a decomposition temperature range of 90–130°C, with a mass loss of 7.68% for **3A** and 6.72% for **3B**, which corresponds to the loss of 1.5 molecules of lattice ethanol (calcd. 7.03% for **3A** and 6.65% for **3B**). The percentages of calculated mass losses are in a good agreement with experimental values. The second mass loss step within the temperature range of 335°C–440°C is attributed to decomposition of the complex.

The nickel complexes (**3A, 3B**) display liquid-crystalline character as revealed by polarizing optical microscopy and DSC thermograms. Phase transition temperatures



(a)

(b)

Figure 2. TG and DTG thermogram of (a) **3A** and (b) **3B**.

along with the corresponding enthalpy values for the Schiff-base ligands (**2A, 2B**) and the nickel complexes (**3A, 3B**) are summarized in Table 1. Figure 3 shows a complete set of DSC curves for the nickel complexes.

The thermal behaviors of the complexes are similar as is apparent from the DSC heating scan curves. Here we describe the behavior of compound **3A** as a representative. Compound **3A** showed four endothermal peaks at 110.4°C, 182.8°C, 315.9°C, and 325.9°C (Fig. 3a) in the first heating scan.

The first peak at 110.4°C associated with the TG mass loss within the temperature range 90°C–130°C is attributed to the removal of lattice ethanol molecule. The peak at 182.8°C with ΔH values of 25.4 kJ mol^{-1} is related to solid–solid transition. The two endothermal peaks at 315.9°C and 325.9°C are attributed to the crystal-to-mesophase and mesophase-to-isotropic liquid transitions, respectively. The texture of the mesophase was investigated by polarizing optical microscopy (POM). For

Table 1. Thermal transitions and thermodynamic data of ligands and Ni complexes, heating and cooling rate: 10°C min^{-1}

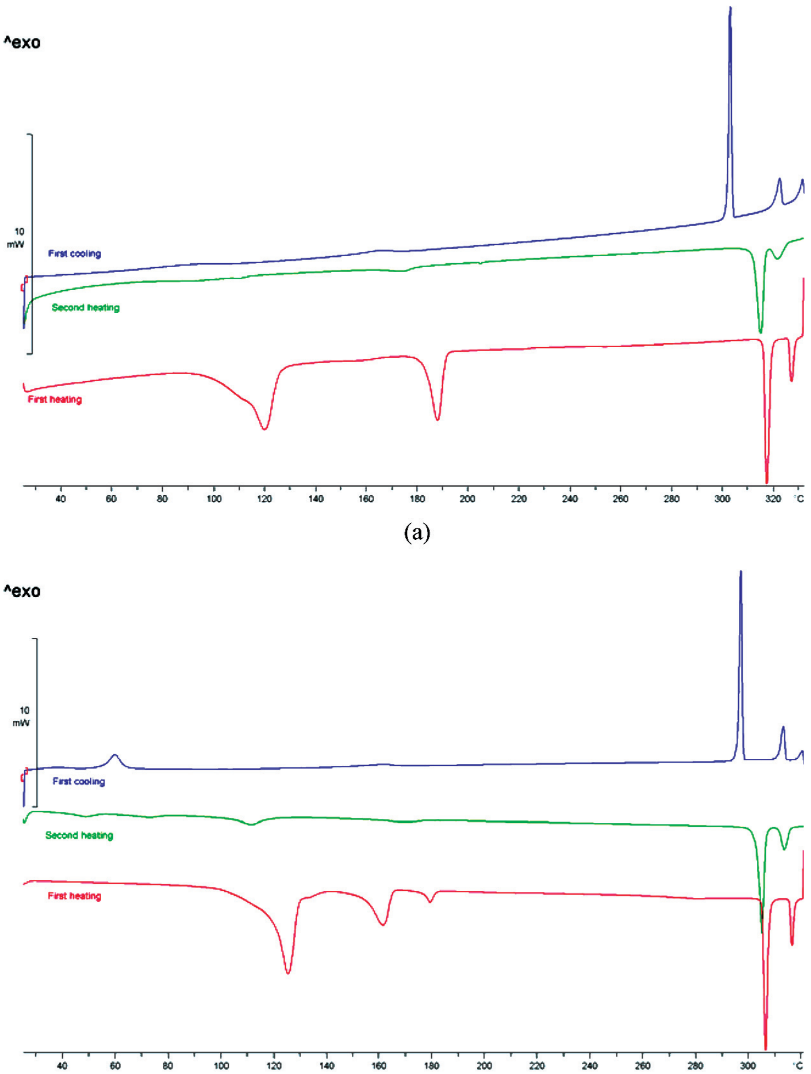
	Phase transitions (°C) and corresponding enthalpies (kJ mol^{-1}, in parentheses)[a]		
Compound	First heating scan	First cooling scan	Second heating scan
2A	Cr_1 112(3.2) Cr_2 164.5(51)I		
2B	Cr_1 109(3.1) Cr_2 154.5(47)I		
3A	Cr_1 100.2, 110.4[b] (54.8) Cr_2 182.8(25.4) Cr_3 315.9(20.3) S_mA 325.9(5.2)I	I, 323.9(4.6) S_mA 304.2(4.7) Cr_3	Cr_3 314.9(17.6) S_mA 323.2(3)I
3B	Cr_1 118.3(60) Cr_2 154.2(17.8) $Cr_3$176.6(2.6) Cr_4 304.9(19.5) S_mA 315.2(4.85)I	I, 314.3(5) S_mA 304.2(20) Cr_5 63.5(4.7) Cr_6	Cr_6 106.4(1.98) Cr_6 303.4(19.33) S_mA 312.2(4.5)I

[a] Cr = crystal; I = isotropic.
[b] Overlapped with a previous transition.

two nickel complexes, a viscous mesophase appears as a focal conic texture after melting process or cooling from the isotropic liquid, which indicates the formation of an enantiotropic smectic A(S_mA) mesophase. Continued heating of complexes **3A** or **3B** causes a considerable amount of decomposition at around 335°C, which was detected by exothermic peaks in the DSC trace, TGA thermograms, and optical observations. In the first cooling scan, Compound **3A** showed two exothermal peaks at 323.9°C and 304.2°C (Fig. 3a), corresponding to the isotropic liquid to the smectic A mesophase and the smectic A mesophase to the crystalline phase, respectively. In the second heating scan, two endothermal peaks at 314.9°C and 323.2°C with enthalpy values of 17.6 and 3 kJ mol^{-1} are ascribed to the crystal-to-mesophase and mesophase-to-isotropic liquid transition. The structural changes during desolvation and solid–solid transitions have been confirmed by using powder X-ray diffraction. A microscopic picture from the S_mA mesophase for complex **3A** is illustrated in Fig. 4 as a representative example.

These complexes represent a further example of a mesomorphic complex derived from a nonmesogenic ligand. Based on our knowledge, nickel complexes based on tetradentate salicylidenic ligands containing an uncomplexed azo moiety with a 1,2-phenylene diamine bridge have not been reported as liquid crystalline materials up to the present. However, the nickel complexes reported in this work are the first example of metallomesogens based on an azo-linked salicylidenic Schiff-base ligand system with a 1,2-phenylene diamine bridge. This complex represents a further example of a mesomorphic complex derived from a nonmesogenic ligand.

Recently, some mesogenic nickel complexes of a similar structure to the title complexes of this work have been reported. We have recently reported the investigation of 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 [17]. These complexes exhibitd smectic A liquid-crystalline character and undergo a considerable amount of decomposition near the transition to the isotropic liquid. Similar mesomorphic properties were previously reported by



(a)

(b)

Figure 3. DSC thermograms of (a) **3A** and (b) **3B**.

Aiello *et al.* [28] for nickel complexes with a similar coordination environment based on tetradentate salicylaldimine Schiff-base ligands but with a 4-alkyphenylazo linkage. In the case of the nickel complexes reported in Aiello *et al.* [28], the complexes undergo a considerable amount of decomposition near the transition to the isotropic. In addition, Singh *et al.* [29] have reported the nematic liquid-crystalline properties of nickel complex with a *N*,*N*′-di-4-(4′-entyloxybenzoate)salicylidene diaminoethane Schiff-base ligand. This complex exhibits low transition temperatures in comparison with the title complexes of this work and undergo decomposition near the transition to the isotropic liquid. Finally, Aiello *et al.* [30] reported a new type of zinc(II) complexes derived from tetradentate salen-like Schiff-base ligands containing

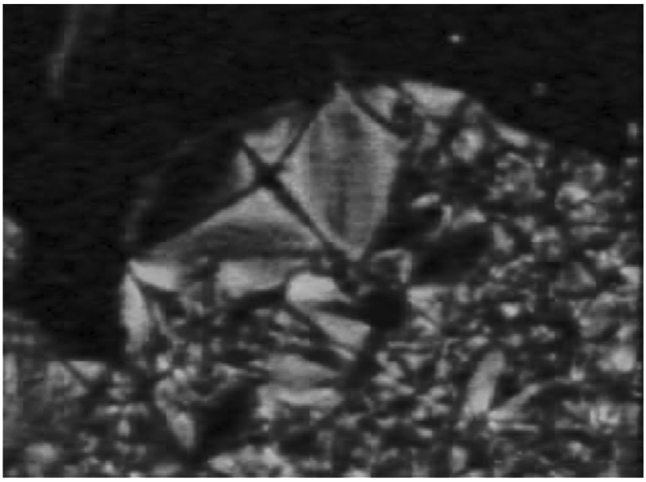


Figure 4. Optical texture observed for the copper complex **3a** through crossed polarizers at 320°C.

uncomplexed alkylphenylazo moiety with 1,3-diaminopropane and 1,3-diamino-2,2-dimethylpropane bridges. These complexes show nematic and smectic C(S_mC) mesophases [30]. However, the complexes described in this work are more thermally stable than those based on ethylene and trimethylene bridges. This fact may be related to the presence of the phenylene bridge in the structure of complexes.

Conclusion

In this work we have prepared two nickel complex homologues derived from tetradentate *N*,*N*′-di-(5-(4-alkoxyphenyl)azo)-salicylidene-1,2 phenylene diamine ligands. Though the Schiff-base ligands do not show any liquid-crystalline character, the nickel complexes have mesomorphic properties and form a smectic A mesophase as confirmed by the microscopic textures. For two nickel complexes decomposition occured several degrees after the clearing point. The mesophases have a narrow temperature range. The nickel complexes undergo a solid–solid transition before melting to the liquid-crystalline phase as confirmed by powder X-ray diffraction patterns.

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