SYNTHESES, CHARACTERIZATION AND LIQUID CRYSTALLINE PROPERTIES OF NEW BIS[5-((4-^{n}ALKOXYPHENYLAZO)-N-(^{n}ALKYL)-SALICYLALDIMINATO] COPPER(II) AND NICKEL(II) COMPLEX HOMOLOGUES

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Abstract

A series of bidentate Schiff base ligands, 5-((4- ^{n}alkoxyphenyl)azo)-N-(^{n}alkyl)-salicylal-dimine (^{n}alkoxy = octyloxy, dodecyloxy, ^{n}alkyl=Butyl, ^{n}hexyl) homologues, have been synthesized and characterized by IR, NMR, mass spectroscopy and elemental analyses. For all the ligands the nickel(II) and copper (II) complexes have been synthesized and characterized by elemental analyses and IR spectroscopy. The mesomorphic character of these compounds was studied by using differential scanning calorimetry (DSC) and polarizing microscope equipped with a heating and cooling stage. None of the Schiff-base ligands exhibit liquid crystalline properties but some of the copper complexes show a nematic mesophase.

Key words: Schiff bases, salicylaldimine, metallomesogen, nematic, copper complexes

Introduction

Syntheses and investigation of metallomesogens is one of the interesting fields for the liquid crystals community and also coordination chemistry and attracted considerable attention in the past two decades. The work in this area has been reviewed extensively.[1] The introduction of extra parameters such as color, magnetism, birefringence, dielectric anisotropy, coordination geometry and also reactivity by metal center into a liquid crystalline system attract great attention for synthesis and investigation of metallomesogens.[2] Metal complexes of Schiff bases derived from salicylaldimine are among best known complexes that display mesogenic properties in metallomesogenic system.[3] Moreover in recent years significant amount research has been done on photonic materials based on light-induced phase transitions because these

types of materials are very useful in new information processing technology.[4] 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.[5,6]

Recently, some metallomesogens containing isomerizable azo moieties have been reported.[6] Sudhadevi and co-workers[7] reported the syntheses and photophysical properties of the azopyridine containing silver mesogens. We also recently reported the synthesis and liquid crystalline character of Cu(II) bis(chelates) based on azo-linked bidentate salicylaldimine[8] and tetra dentate azo-linked N,N′ salicylideneiminato Ni(II), Cu(II) and VO(IV) complexes.[9] In this work we report the synthesis and investigation of liquid crystalline properties of new bis[5-((4-^{n}alkoxyphenyl)azo)-N-(^{n}alkyl)-salicylaldiminato] copper(II) and nickel(II) complex homologues (see scheme 1).

Results and discussion

Synthesis

Schiff base ligands, **2a-2d**, were synthesized in a four-step process, in which the hydroxy group in 4-nitrophenol is first replaced by an alkoxy chain followed by reduction of nitro group to amine. In the third step, salicylaldehyde coupled with the diazonium chloride obtained from the 4-alkoxyaniline and finally the Schiff base ligands were obtained by reaction of 5-(4-alkoxyphenylazo) salicylaldehyde homologues (**1a**, **b**) with an appropriate alkyl amine (scheme 1) by refluxing in absolute ethanol using a few drops of acetic acid as catalyst. The Schiff-bases, **2a-2d**, were purified by repeated crystallization in the ethanol/chloroform mixture. The 5-(4-^{n}alkoxyphenylazo) salicylaldehydes and ligand homologues were characterized by IR, ^{1}HNMR, mass spectroscopy and elemental analyses. Metal complexes were characterized by C, H, N elemental analysis and IR spectroscopy. Some physical and characterization data for ligands and complexes are given in the experimental section. Representative IR spectra are given in figure 1 and selected IR data are reported in Table 1. The IR spectra of metal complexes show that the stretching frequency of the C=N bond was shifted to lower wavenumbers (ca. 15 cm^{-1}) in comparison to free ligand after coordination. This

shift is due to the 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.[8-10] On the other hand, the disappearance of the OH band of free ligands in metal complexes indicates that the OH group has been deprotonated and coordinated to the metal ion as –O⁻. Based on these observations and elemental analyses we concluded that the Schiff-base ligands are coordinated to metal atoms as bidentate (N-O) ligands in 2:1 ratio.
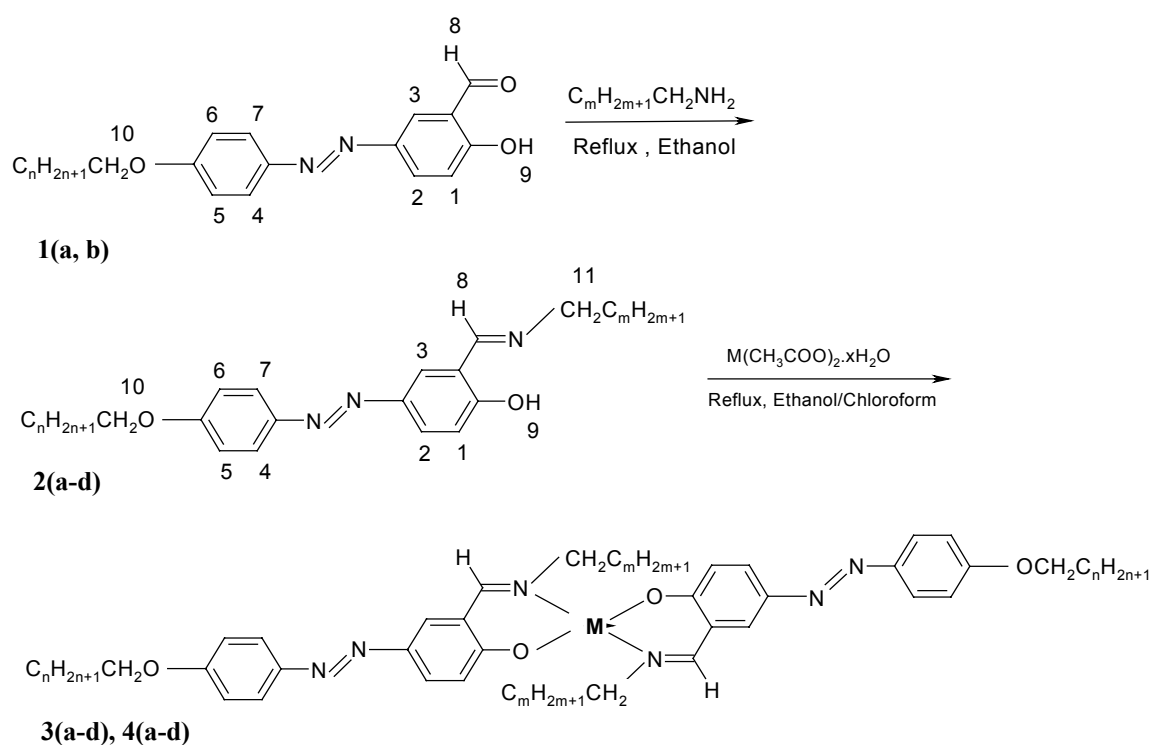
Compound No.	n	m	M
1a	7	-	-
1b	11	-	-
2a	7	3	-
2b	7	5	-
2c	11	3	-
2d	11	5	-
3a	7	3	Cu
3b	7	5	Cu
3c	11	3	Cu
3d	11	5	Cu
4a	7	3	Ni
4b	7	5	Ni
4c	11	3	Ni
4d	11	5	Ni

Scheme 1

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.[11]

We recently reported the crystal structure of bis[5-((4-^{n}propyloxyphenyl)azo)-*N*-(^{n}-pentyl-salicylaldiminato)]Ni(II) which has similar coordination environment to that of the title complex of this work. In this type of complexes the schiff bases ligands have an approximately trans-planar configuration around Ni central ion and the structure is square planar. However, it is suggested that the Ni(II) is square planar or nearly square planar coordination based on the similar coordination environment with the recently reported nickel(II) complex.[12]

Table 1. Selected IR data for Schiff base ligands and metal complexes.

Compound	ν, cm^{-1}					
	O-H	C-H (aromatic)	C-H (aliphatic)	C=N	C-O (etheric)	C=O
1(a, b)	3185-90(br, m)	3069-71(m)	2950-2850(s)		1241-3(s)	1661-2(s)
2(a-d)	3450-68(br,m)	3050-60(m)	2955,2860(s)	1631-7(s)	1255-86(s)	–
3(a-d)	–	3045-60(m)	2920-2849(s)	1621-22(s)	1244-7(s)	–
4(a-d)	–	3040-60(m)	2920-2845(s)	1621-26(s)	1245-8(s)	–

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

Mesomorphism

The mesomorphic properties of 5-(4-^{n}alkoxyphenylazo) salicylaldehyde homologues (**1a**, **b**), the Schiff base ligands and related Cu(II) and Ni(II) complexes have been studied by polarizing optical microscopy observations using a heating-cooling stage and the phase transition temperature and enthalpy were obtained by differential scanning calorimetry (DSC). Phase transition temperatures along with the corresponding enthalpy values for copper and nickel complexes are summarized on table 2. Aldehyde homologues, Schiff-base ligands, nickel and copper complexes did not show any liquid crystalline character on heating. All metal complexes, except the **4a** exhibited solid polymorphism which was identified by DSC. These compounds clearly melted and transformed into isotropic liquids and no mesophase was observed on the heating cycle on optical observations. The melting points of the ligands decrease with increasing the N-alkyl chain length (m, see scheme1), but increase with increasing alkoxy chain (n). In case of metal complexes, the melting points increase with increasing the N-alkyl chain length, but decrease with increasing the alkoxy chain (n).
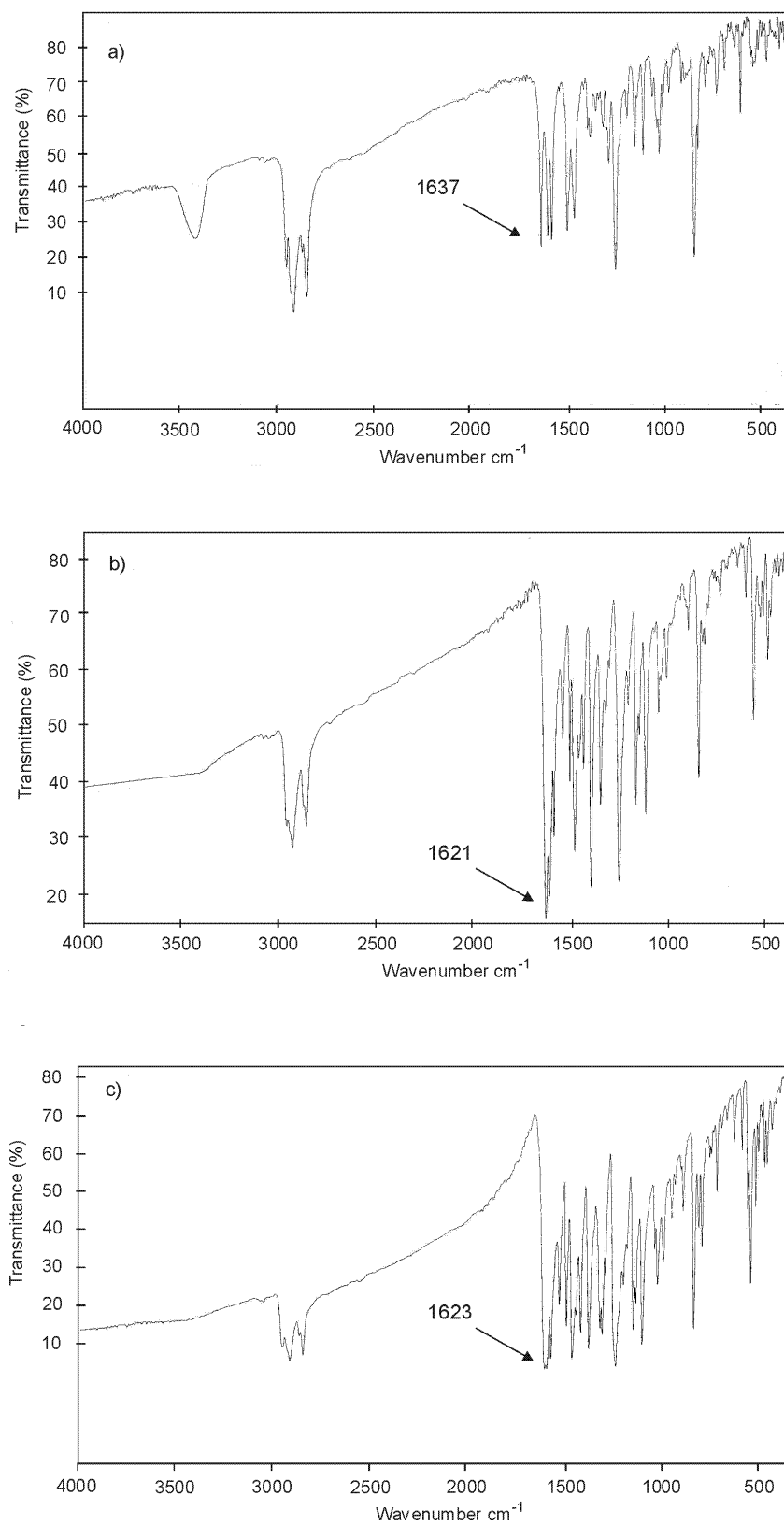
Figure 1. Representative IR spectra of a) Free ligand (2b), b) Copper complex (3b), and c) Nickel complex (4b).

Table 2. Transition temperatures and enthalpy changes of copper(II) and nickel(II) complexes.

Compound	Transition[a]	T[b]/ °C	ΔH^b/ KJ mol^{-1}
3a	K_1---K_2	105. 4	2.0
	K_2---K_3	112.0	15.5
	K_3---K_4	139.3	5.9
	K_4---I	143.8	41.3
3b	K_1---K_2	107.7	3.9
	K_2---I	151.4	44.5
3c	K_1---K_2	108.2	11.8
	K_2---I	123.5	44.2
	(I---N)[c]	116.2	2.0
3d	K_1---K_2	83.5	22.7
	K_2---I	133.5	42.2
	(I---N)[c]	122.3	1.8
4a	K---I	158.4	60.8
4b	K_1---K_2	128.2	13.6
	K_2---I	155.0	44.6
4c	K_1---K_2	90.0	1.6
	K_2---K_3	102.7	34.5
	K_3---I	130.7	39.3
4d	K_1---K_2	85.8	3.7
	K_2---K_3	96.1	14.7
	K_3--- I	137.8	63.6

[a] K: Crystal, N: Nematic, I: Isotropic liquid. [b] Data obtained from first DSC cycle. [c] Monotropic transition.

Copper complexes of Schiff base ligands containing dodecyloxy substitution (**3c** and **3d**) exhibit liquid crystalline behavior as revealed by DSC and polarizing optical microscopy. These complexes show monotropic nematic mesophase, which has been identified by the typical nematic droplets[13] on cooling from the isotropic liquid. A microscopic picture from nematic mesophase for complex **3c** is illustrated in Figure 2. In the first heating scan, **3c** showed two endothermal peaks at 108.2 °C and 123.5 °C. In the second heating scan, only one peak at 123 °C was observed (table 2). When the isotropic melt of **3c** was cooled at a cooling rate of 10 Kmin[-1], a mesophase with a low viscosity was formed at 116.2 °C. The texture was observed as two and four brushes under polarized light. The formation of mesophase was reproducible on frequent cooling cycles. By applying light mechanical pressure to the cover glass plate the anisitropic liquid between two glass plates became thinner. From these data, we propose that the observed mesophase is nematic. This nematic mesophase is stable until the compound

start to crystallize at 101 °C. For compound **3d**, nematic mesophase formed at 122.3 °C upon cooling from isotropic liquid and transformed to crystal at 99 °C.
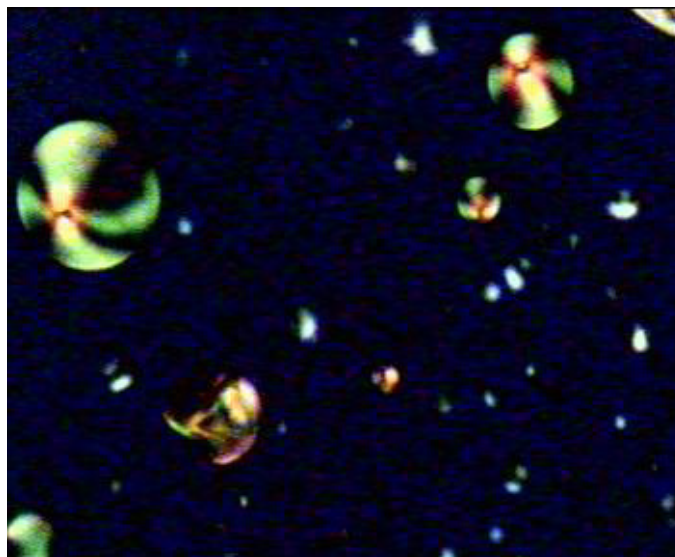

Figure 2. Optical texture observed for 3c through crossed polarizers upon cooling from the isotropic liquid to 116 °C.

Similar mesomorphic properties were previously reported for copper complexes based on salicylaldimine Schiff bases ligands.[14] Some non-mesogenic Schiff bases, which also give mesogenic compounds upon complexing with copper, have been reported.[7,8,15] These complexes represent a further example of a mesomorphic complex derived from a non-mesogenic ligand.

The absence of liquid crystalline behavior in the free ligands can be attributed to the strong intermolecular dipolar repulsion brought about by the presence of the lateral hydroxide group.[18]

The induction and the formation of mesophases are mainly controlled and/or determined by attractive interactions between neighboring molecules. These weak interactions are of various types, for example dipole-dipole, dispersion, hydrogen bonding, charge transfer and dative coordination.[1a] Transition metal ions can induce mesomorphism in non-mesogenic ligands. The coordination geometry of the metal center in this type of material greatly influences the molecular packing in the formation of mesophase. While in classic organic structures, the intention is, frequently, to incre-

ase intermolecular contacts to induce mesomorphism, in coordination compounds the objective is to avoid intermolecular contacts and strong dipolar interaction that are sufficiently strong to cause three-dimentional order.[19] The coordination geometry of copper complexes is different from nickel complexes therefore the magnitude of intermolecular interaction in copper complexes is also different from nickel analogous. Hence, it is fundamentally important to achieve a delicate balance in the magnitude of molecular interactions by tuning the molecular geometries in order to optimize the liquid crystalline behavior. The addition of a long aliphatic chain to the rigid nucleus furnishes both the anisotropy and irregular packing needed to promote mesomorphism.

Due to coordination geometry difference between nickel and copper complexes, the intermolecular interactions are slightly different,[20] therefore, it causes that mesomorphism (nematic monotropic) settle in copper complexes but not in nickel complexes.

Conclusion

In this work we have prepared two series of copper and nickel complexes derived from 5-((4-*n*alkoxyphenyl)azo)-N-(*n*alkyl)-salicylaldimine homologues. Mesomorphic behavior was found to be controlled by side chain length (n) and nature of central metal ion. Copper complexes containing dodecyloxy chain give liquid crystalline character while all nickel complexes and copper complexes containing low alkyl chain length are non-mesomorphic.

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-bromoctan or 1-bromododecane in DMF as solvent and K_2CO_3 as base by refluxing for three hrs[16] and then crude 4-alkoxynitrobenze homologues were purified by recrystallization from ethanol. 4-alkoxyaniline homologues prepared by reducing of the corresponding 4-alkoxynitrobenzne as described in the literature.[17]

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 Finnigan-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±0.3, ΔH= 28.45 ±0.6 Jg^{-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.

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 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.

Materials

All homologue materials were prepared similarly.

5-(4-Octyloxyphenylazo) salicylaldehyde (1a). This compound was prepared as described in the literature.[12] Yellow, yield 80%, mp 126 °C. MS m/z (relative intensity): 355.4 (M+1, 15), 354.3 (M, 40), 241.2 (M-C_8H_{17}, 25), 121.0 (M-$C_8H_{17}OC_6H_4N_2$, 100). Anal. Calc. for $C_{21}H_{26}N_2O_3$: C 71.16, H 7.39, N 7.90. Found: C 70.71, H 7.12 N 7.54. ^{1}HNMR (400 MHz, CDCl$_3$) 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).

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$_3$) 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).

Syntheses of the ligands. 0.026 mol of the related amine (^{n}butyl amine or ^{n}hexyl amine) and 0.026 mol of 5-(4-^{n}alkoxyphenylazo) salicylaldehyde were dissolved in 100 mL absolute ethanol with a few drops of glacial acetic acid as a catalyst. The solution was then refluxed for 1 h. The solution was left at room temperature and after cooling, the ligands were obtained as yellow micro crystals. The micro crystals were filtered off, washed with 15 ml of cold absolute ethanol and then recrystallized for several times from ethanol-chloroform(1:3, v/v).

2a. Yellow, yield 85%, mp 72 °C. MS m/z (relative intensity): 410.5(M+1,12), 409.5 (M, 60), 296.3 (M-C_8H_{17}, 25), 176.1 (M-$C_8H_{17}OC_6H_4N_2$, 100). Anal. Calcd for $C_{25}H_{35}N_3O_2$: C 70.38, H 8.61, N 10.26. Found: C 70.02, H 8.33, N 9.94. ^{1}HNMR (400 MHz, CDCl$_3$) δ 14.04 (s, H-9), 8.41 (s, H-8), 7.96 (dd, J 2.8, 8.5 Hz, H-2), 7.93-7.83 (H-3, H-4, H-7), 7.13 (d, J 7.9 Hz, H-1), 6.98 (d, J 8.1 Hz, H-5, H-6), 4.04 (t, J 7.1 Hz, H-10), 3.69 (t, J 6.8 Hz, H-11), 1.85-0.88 (22H, alkyl chain).

2b. Yellow, yield 75%, mp 68 °C. MS m/z (relative intensity): 438.6 (M+1, 13), 437.4 (M, 100), 325.2 (M-C_8H_{17}, 25), 205.2 (M-$C_8H_{17}OC_6H_4N_2$, 80). Anal. Calcd for $C_{27}H_{39}N_3O_2$: C 74.10, H 8.98, N 9.60. Found: C 73.78, H 8.73, N 9.43. ^{1}HNMR (400 MHz, CDCl$_3$) δ 14.20 (s, H-9), 8.40 (s, H-8), 7.95 (dd, J 3.1, 8.0 Hz, H-2), 7.86-7.82 (H-3, H-4, H-7), 7.05 (d, J 7.8 Hz, H-1), 6.98 (d, J 7.8 Hz, H-5, H-6), 4.03 (t, J 7.1 Hz, H-10), 3.64 (t, J 6.8 Hz, H-11), 1.85-0.87 (26H, alkyl chain).

2c. Yellow, yield 65%, mp 77 °C. MS m/z (relative intensity): 466.6 (M+1, 12), 465.6 (M, 100), 296.3 (M-$C_{12}H_{25}$, 30),176.2 (M-$C_{12}H_{25}OC_6H_4N_2$, 65).Anal. Calcd for $C_{29}H_{43}N_3O_2$: C 74.79, H 9.31, N 9.02. Found: C 74.44, H 9.04, N 8.69. ^{1}HNMR (400 MHz, CDCl$_3$) δ 14.06 (s, H-9), 8.41 (s, H-8), 7.96 (dd, J 3.1, 8.1 Hz, H-2), 7.86-7.83 (H-3, H-4, H-7), 7.04 (d, 8.0 Hz, H-1), 6.99 (d, J 7.8 Hz, H-5, H-6), 4.03 (t, J 6.8 Hz, H-10), 3.68 (t, J 7.1 Hz, H-11), 1.85-0.86 (30H, alkyl chain).

2d. Yellow, yield 91%, mp 71°C. MS m/z (relative intensity): 494.6 (M+1, 15), 493.6 (M, 100), 325.4 (M-$C_{12}H_{25}$, 25), 205.3 (M-$C_{12}H_{25}OC_6H_4N_2$, 80). Anal. Calcd for $C_{31}H_{47}N_3O_2$: C 75.41, H 9.60, N 8.51. Found: C 75.04, H 9.31, N 8.14. ^{1}HNMR (400 MHz, CDCl$_3$) δ 14.28 (s, H-9), 8.40 (s, H-8), 7.94 (dd, 2.9, 8.2 Hz, H-2), 7.91-7.81 (H-3, H-4, H-7), 7.06 (d, 8.2 Hz, H-1), 6.98 (d, J 8.2 Hz, H-5, H-6), 4.03 (t, J 6.7 Hz, H-10), 3.63 (t, J 6.5 Hz, H-11), 1.85-0.86 (34H, alkyl chain).

Syntheses of the copper and nickel complexes. Copper and nickel complexes were prepared in similar manners using the method described by Nejati et al. elsewhere.[9] Thus, a solution of 4 mmol of $Ni(CH_3COO)_2.4H_2O$ or $Cu(CH_3COO)_2.H_2O$ in 10 mL of ethanol was added to an ethanol-chloroform (1:1 v/v) solution containing 8 mmol of ligand and was refluxed for 2 hrs. The obtained solution was left at room temperature. Copper complexes were obtained as brown micro crystals, and nickel complexes were obtained as green micro crystals. The micro crystals were filtered off, washed with absolute ethanol and then recrystallized from ethanol-chloroform (1:3 v/v).

3a. Brown, yield 80%. Anal. Calcd for $C_{50}H_{68}N_6O_4Cu$: C 68.22, H 7.73, N 9.55. Found: C 68.12, H 7.63, N 9.39.

3b. Brown, yield 85%. Anal. Calcd for $C_{54}H_{76}N_6O_4Cu$: C 69.26, H 8.12, N 8.98. Found: C 69.00, H 7.92, N 8.69.

3c. Brown, yield 75%. Anal. Calc. for $C_{58}H_{84}N_6O_4Cu$: C 70.19, H 8.47, N 8.47. Found: C 69.91, H 8.24, N 8.14.

3d. Brown, yield 86%. Anal. Calcd for $C_{62}H_{90}N_6O_4Cu$: C 71.02, H 8.59, N 8.02. Found: C 70.81, H 8.32, N 8.03.

4a. Green, yield 74%. Anal. Calcd for $C_{50}H_{68}N_6O_4Ni$: C 68.59, H 8.02, N 9.60. Found: C 68.28, H 7.81, N 9.22.

4b. Green, yield 75%. Anal. Calcd for $C_{54}H_{76}N_6O_4Ni$: C 69.63, H 8.17, N 9.03. Found: C 69.24, H 7.89, N 8.84.

4c. Green, yield 80%. Anal. Calcd for $C_{58}H_{84}N_6O_4Ni$: C 70.54, H 8.51, N 8.51. Found: C 70.13, H 8.24, N 8.20.

4d. Green, yield 78%. Anal. Calcd for $C_{62}H_{90}N_6O_4Ni$: C 71.35, H 8.63, N 8.06. Found: C 71.00, H 8.43, N 7.81.

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Povzetek

Pripravili smo serijo bidendatnih ligandov, 5-((4-^{n}alkoksifenil)azo)-N-(^{n}alkil)-salicilaldimin (^{n}alkoksi = oktiloil, dodeciloil, ^{n}alkyl = butil, ^{n}heksil). in jih karakterizirali z IR, NMR, MS in elementno analizo. Z vsemi ligandi smo pripravili nikljeve(II) in bakrove(II) komplekse in jih karakterizirali z elementno analizo in IR spektroskopijo. Mezomorfizem teh spojin smo študirali z diferenčno dinamično kalorimetrijo (DSC) in s polarizacijkim mikroskopom, opremljenim z ogrevalno-hladilno ploščo. Ligandi nimajo lastnosti tekočih kristalov, pri nekaterih bakrovih kompleksih pa smo opazili nematično mezofazo.