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Journal of Organometallic Chemistry 655 (2002) 105–110

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis and mesomorphic properties of new imines and copper(II) complexes

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Received 10 April 2001; received in revised form 6 February 2002; accepted 12 February 2002

Abstract

The synthesis and mesomorphic properties of a serie of 4-(alkyloxy)-*N*-(4-hexylphenyl)-2-hydroxybenzalimine (**2**) and their copper(II) complexes (**3**) are reported. The compounds were characterized by spectroscopic methods (IR, ^{1}H-, ^{13}C-NMR and MS). The calamitic liquid crystal series of imines (**2**) and copper(II) complexes (**3**) exhibited smectic mesophases, which were characterized by differential scanning calorimetry (DSC) analysis and optical polarizing microscopy. © 2002 Published by Elsevier Science B.V.

Keywords: Liquid crystals; Metallomesogens; Schiff bases; Copper(II) complexes

1. Introduction

Metal-containing liquid crystals have attracted increasing attention in recent years due to the different interesting properties they display [1,2]. In literature, complexes of various metals with salicylaldimines carrying different organic moieties are found [1,2]. The copper(II) unit is well known for its ability to coordinate four donor atoms, which makes it possible to obtain structures that favour calamitic and discotic mesomorphism [1–3]. Schiff base copper (II) complexes containing alkylanilines have also attracted considerable attention with regard to structure–property relationship. These complexes display smectic mesomorphism and the smectic A phases are especially common [1–8].

In this paper the synthesis, characterization and mesomorphic properties of a new serie of tetracoordinate copper(II) complexes (**3**) of Schiff bases (**2**) derived from aldehydes (**1**) (see Scheme 1) are presented.

2. Results and discussion

The synthesis of the ligands were carried out under a nitrogen atmosphere and in a two-step process. The starting alkyloxy aldehydes (**1**) were obtained in the usual way [9] by the reaction of 2,4-dihydroxybenzaldehyde with the appropriate *n*-alkylbromide, using DMF instead of acetone. The standard chemicals, 2,4-dihydroxybenzaldehyde, 1-bromoalkanes, and 4-hexylaniline, were used as supplied (Aldrich Chemical Co.).

The imines (**2**) were prepared in the usual way [10] by the *p*-toluensulfonic acid catalyzed condensation of the corresponding aldehydes (**1**) with 4-hexylaniline (see Section 4).

The copper complexes (**3**) were prepared by reacting the appropriate ligand with copper(II) acetate dihydrate in ethanol (see Section 4). The complexes were isolated in good yields and are soluble in chloroform, toluene, dioxane and insoluble in ethanol, methanol and hexane.

The new imine compounds **2a**–**d** presented here were characterized by various spectroscopic methods, e.g. ^{1}H-, ^{13}C-NMR (CDCl$_3$), UV–vis, IR and mass. The proposed structures are in full agreement with these spectroscopic data. The copper(II) complexes **3a**–**d** were characterized by UV–vis, IR and mass spectroscopy. The data are also consistent with the expected square planar structure for the complexes.

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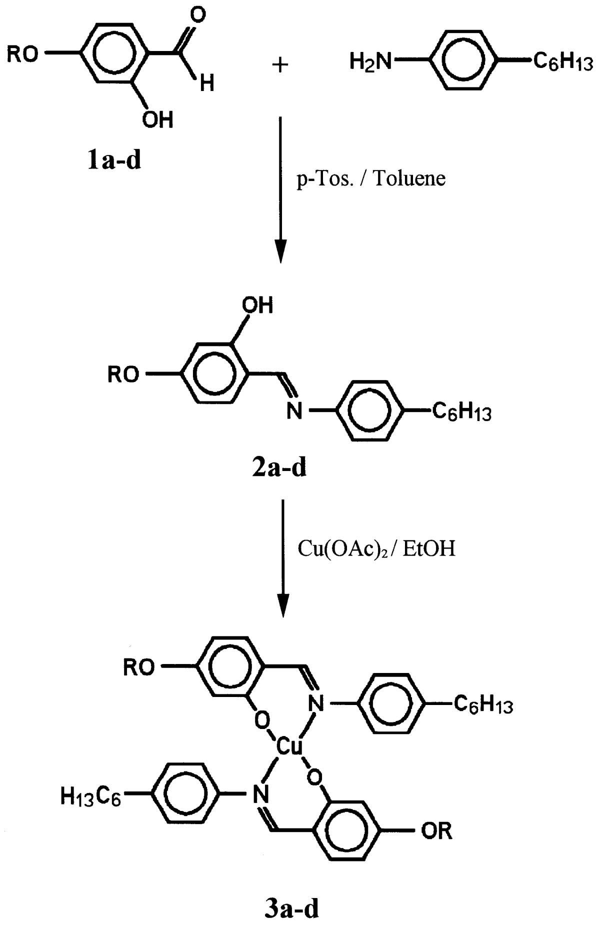
PII: S0022-328X(02)01425-0



Scheme 1. **a**: R = C_8H_{17}; **b**: R = $C_{10}H_{21}$; **c**: R = $C_{16}H_{33}$; **d**: R = $C_{18}H_{37}$.

The NMR data of the imine compounds **2a**–**d** give definite evidence for the molecular structure. The δ(HC=N) value of $\approx$8.50 ppm for the ligands (**2**) is well within the range expected for imine compounds [6,8,10].

The electronic spectra of the imines **2a**–**d** show the absorption band between 341 and 343 nm, whereas the absorption band of the complexes **3a**–**d** shift to 378–383 nm (see Fig. 1).

The IR spectra of both the ligands **2a**–**d** and the complexes **3a**–**d** show the C=N stretching at the expected values of 1624 and 1617 cm^{-1}, respectively. Similarly Marcos et al. [7,8] have described the infrared spectra of the metal complexes analogous for **3**, that show a stretch band around 1614 cm^{-1} (assigned to ν(C=N)) which has shifted to a lower frequency by ca. 5–9 cm^{-1} as compared to that of the free Schiff bases.

The mass spectra of the complexes **3a**–**d** are consistent with their proposed structures (see Section 4).

The new imines and their copper(II) complexes exhibit liquid crystalline properties and show thermotropic mesophases. The investigations by polarizing microscopy and differential scanning calorimetry (DSC) show that they exhibit smectic mesophases (for the phase transition data see Tables 1 and 2).

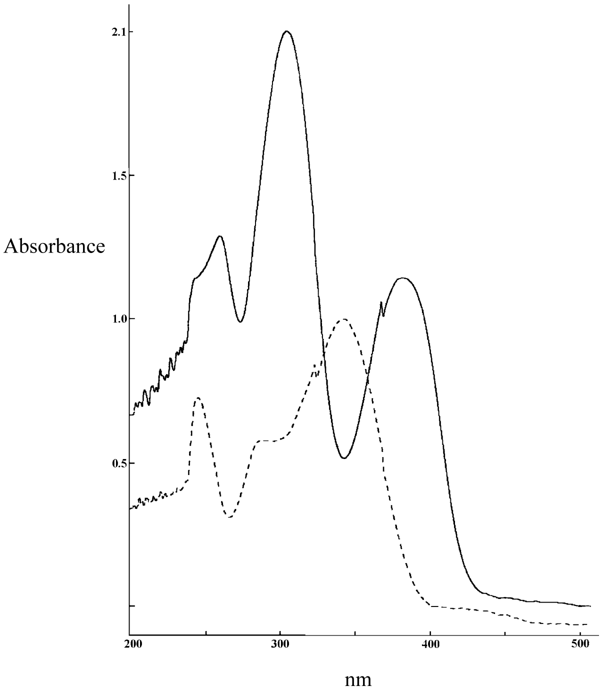


Fig. 1. Electronic spectra of the ligand **2a** (- - -), and the corresponding Cu(II) complex **3a** (—).

The ligands **2a**–**d** show similar mesomorphic properties with the previously synthesized analogs [4,6,11]. The transition temperatures and the thermodynamic data for the new Schiff base ligands (**2**) and the previously reported analogs [6,11] are given in Table 1.

As seen in Tables 1 and 2, the imine compounds generally have the S_1 mesophase and the complexes have the S_2 mesophase. From optical observations the S_1 mesophase shows textures similar to smectic C and the S_2 is similar to smectic A phase (see Fig. 2).

The melting points of the imine compounds (**2**) increase with increasing chain length of the alkyloxy group. The imine compounds (**2a**–**c**) show smectic phase (S_1), which exhibit Schlieren and broken fan textures. On cooling of the ligands from isotropic phase smectic mesophase (S_1) with broken fan-shaped texture can be observed. Increase of the chain length further (**2d**: R = $C_{18}H_{37}$) leads only to a monotropic smectic (S_1) phase with Schlieren texture. For the transition temperatures versus number of carbon atoms in the alkoxy chain of ligands **2** (see Fig. 3).

All the new copper(II) complexes **3a**,**c**,**d** show thermotropic mesophases like the previously reported complexes of similar structure [4–6,8]. The compounds **3a**–**d** (R = C_8H_{17}, $C_{10}H_{21}$[5], $C_{16}H_{33}$, $C_{18}H_{37}$, respectively) are microcrystalline solids at room temperature that upon heating and/or cooling from the isotropic liquid, display smectic mesophase (see Table 2). The mesophases shown

Table 1
Phase transition temperatures [a] (°C) and enthalpies [a] (kJ mol^{-1}) of imine compounds (**2**): Cr: crystalline, S: smectic, N: nematic and Iso: isotropic mesophase

Compound	R	Cr	S_1 [b]	S_A	N	Iso
[11]	C_6H_{13}	● 45	● 76.8	–	● 88.8	●
2a	C_8H_{17}	● 35.1 (30.0)	● 81.4 (2.1)	–	–	●
2b	$C_{10}H_{21}$	● 42.0 (24.3)	● 96.4 (5.7)	–	–	●
[6]	$C_{12}H_{25}$	● 51	● 90	● 95	–	●
2c	$C_{16}H_{33}$	● 60.6 (40.4)	● 85.0 (1.5)	–	–	●
2d	$C_{18}H_{37}$	● 67.8 (40.6)	{● 56} [c]	–	–	●

[a] Heating rates are 5 K min^{-1} for the melting and for the clearing processes; the enthalpies are in parentheses. The values of monotropic transitions are given in {...}.

[b] S_1 mesophase shows textures similar to S_C phase from optical observations.

[c] This monotropic phase transition could be detected by hot stage polarizing microscopy only (heating rate 10 K min^{-1}).

by the complexes were identified by polarizing microscopy as smectic A by their optical textures (see Fig. 2).

The effect of the alkylchain length on the melting points of the complexes (**3a**–**d**) show the opposite trend with respect to the ligands, i.e. a consistent decrease of melting points is observed. The complexes melt at higher temperatures than the ligands. On cooling of compounds **3a**, **3b** [5] and **3c** from isotropic phase a smectic mesophase (S_2) with fan-shaped texture can be observed. The compound **3d** presents a crystal-crystal transition and exhibits only monotropic S_2 phase. The transition temperatures vs. number of carbon atoms in the alkoxy chain in copper(II) complexes **3** are given in Fig. 4.

3. Conclusion

The comparison of the synthesized new imines and their copper(II) complexes with their previously reported analogs [4–6,8], show that they exhibit similar mesomorphic properties. The imine compounds and their copper(II) complexes described in this paper have presented enantiotropic smectic phases but the compound **3a** ($R = C_8H_{17}$) and the longest chained ligand **2d** ($R = C_{18}H_{37}$) and its copper(II) complex **3d** have only monotropic behaviour.

The formation of the complexes has also effected the mesophase properties. All the ligands (**2a**–**d**) exhibit smectic C phase (S_1) by their optical textures. After complexation, a S_2 mesophase is observed which is identified by polarizing microscope as smectic A by its optical texture.

4. Experimental

The characterizations of the compounds **2**, **3** presented here are based on various spectroscopic data, e.g. ^{1}H-, ^{13}C-NMR (Varian VXR-400, AM-270 spectrometer, respectively, $CDCl_3$ solutions), UV–vis (PU 8740, $CHCl_3$ solutions), FT-IR (Mattson 1000, $CHCl_3$ solutions), MS (Varian MAT 711 or Intectra GmbH, AMD 402) and EA (CHNS-932, Leco Co.). Only structurally relavent resonances are given, see below.

The mesophases were investigated by polarizing microscopy and by DSC. Microscopy was performed on an Leitz Laborlux 12 Pol polarizing microscope, equipped with a Linkam THMS 600 hot stage and a Linkam TMS93 temperature controller. DSC-thermograms were recorded on a Mettler TA 3000/DSC-30 S with TA 72.5 software or Perkin–Elmer DSC-7.

Table 2
Phase transition temperatures [a] (°C) and enthalpies[a] (kJ mol^{-1}) of copper(II) complexes (**3**): Cr: crystalline, S: smectic and Iso: isotropic mesophase

Compound	R	Cr_1	Cr	S_2 [b]	Iso
[5]	C_6H_{13}	–	● 153.9 (45.3)	{● 145.8}	●
3a	C_8H_{17}	–	● 139.5 (31.9)	{●133} [c]	●
3b	$C_{10}H_{21}$ [d]	–	● 131.7 (26.6)	● 144.3 (10.1)	●
[6]	$C_{12}H_{25}$	–	● 119	● 140	●
3c	$C_{16}H_{33}$	–	● 82.4 (19.8)	● 112.5 (6.6)	●
3d	$C_{18}H_{37}$	● 41.4 (17.6)	● 94.4 (40.5)	{● 85} [c]	●

[a] Heating rates are 5 K min^{-1} for the melting and for the clearing processes; the enthalpies are in parentheses. The values of monotropic transitions are given in {...}.

[b] S_2 mesophase shows textures similar to S_A phase from optical observations.

[c] This monotropic phase transition could be detected by hot stage polarizing microscopy only (heating rate 10 K min^{-1}).

[d] In Ref. [5] for compound **3b**: Cr 130.5 °C (31.3) → S_A 145.1 °C (10.1) → Iso.

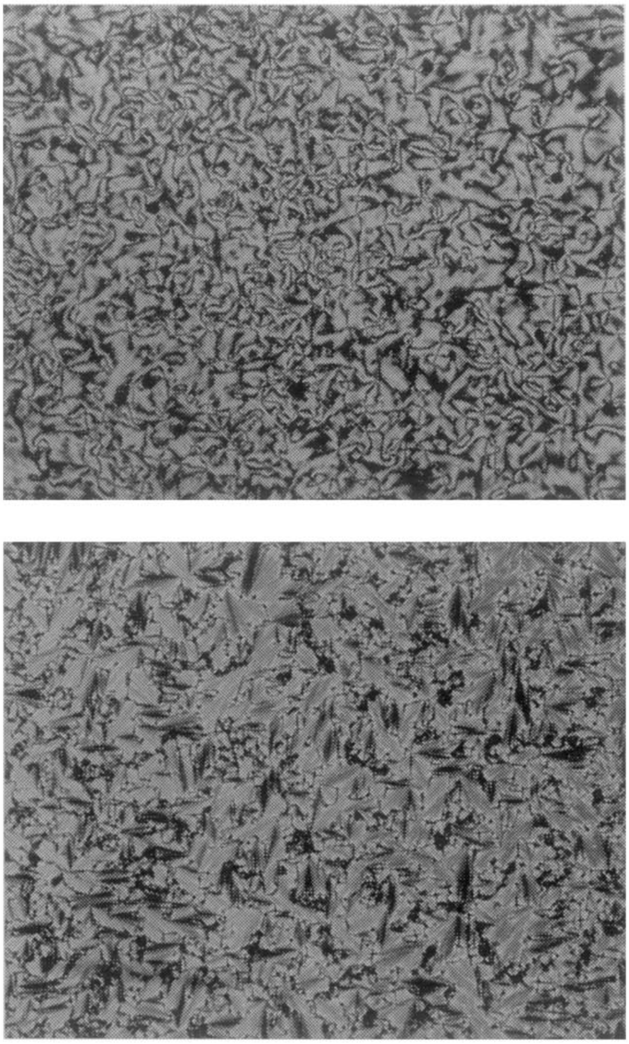


Fig. 2. Optical texture (200 ×) observed on cooling from the isotropic phase for imine ligand **2c**: S_1 (S_C) phase at 70.2 °C (top) and copper(II) complex **3c**: S_2 (S_A) phase at 106.4 °C (bottom).

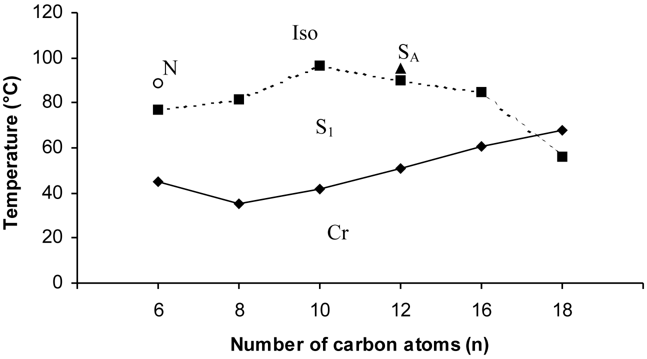


Fig. 3. Plot of transition temperatures versus number of carbon atoms (n) in the terminal chain (R) for the imine compounds (**2**). (◆) Cr–S_1 or Iso; (■) S_1–Iso, N, S_A or Cr; (▲) S_A–Iso; (○) N–Iso.

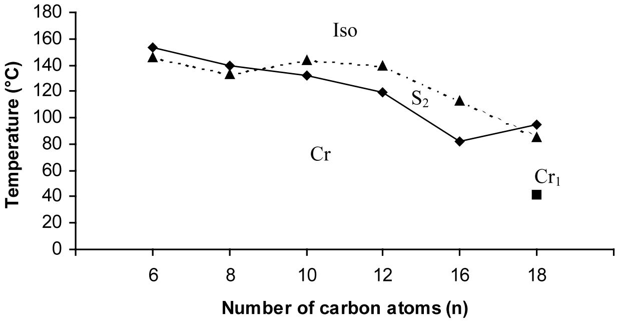


Fig. 4. Plot of transition temperatures versus the number of carbon atoms (n) in the terminal chain (R) for the copper(II) compounds (**3**). (◆) Cr–S_2 or Iso; (■) Cr_1–Cr; (▲) S_2–Iso or Cr.

4.1. Synthesis of the imine compounds **2**

The imines **2a**–**d** were prepared in the usual way [10] by a *p*-toluensulfonic acid (40 mg) catalyzed condensation of 4-alkyloxy-2-hydroxybenzaldehyde (5 mmol) with 4-hexylaniline (6 mmol) in toluene (25 ml) and purified by crystallization from acetone/ethanol.

The melting points of the imines are given in Table 1.

4.1.1. 4-(Octyloxy)-N-(4-hexylphenyl)-2-hydroxybenzalimine (**2a**)

Yield: 1.65 g (80%) of yellow crystals. ^{1}H-NMR: $\delta =$ 13.74 (s; OH), 8.49 (s; HC=N), 7.24, 7.20, 7.17 (3d, $J \approx$ 8.5 Hz each; 1, 2 and 2 arom. Hs, respectively), 6.55–6.44 (m; 2 arom. Hs), 3.99 (t, $J \approx 6.5$ Hz; $\mathrm{OCH_2}$ group), 2.61 (t, $J \approx 6.5$ Hz; α-$\mathrm{CH_2}$ group). ^{13}C-NMR: $\delta =$ 164.09, 163.56, 145.66, 141.40, 112.90 (5s; 5 arom. Cs), 160.46 (d; HC=N), 133.32, 129.27, 120.69, 107.57, 101.61 (5d; 1,2,2,1 and 1 arom. CH, respectively), 68.27 (t; $\mathrm{OCH_2}$ group), 35.52 (t; α-$\mathrm{CH_2}$ group). UV–vis: λ (nm) = 341.9. IR: $\gamma = 1624$ cm^{-1} (C=N). $\mathrm{C_{27}H_{39}NO_2}$ (409.61); MS (HR): m/z (%) = 409.2988 $[\mathrm{M}]^+$, Calc. 409.2981.

4.1.2. 4-(Decyloxy)-N-(4-hexylphenyl)-2-hydroxybenzalimine (**2b**)

Yield: 1.56 g (71%) of yellow crystals. ^{1}H-NMR: $\delta =$ 13.88 (s; OH), 8.51 (s; HC=N), 7.24, 7.21, 7.17 (3d, $J \approx$ 8.5 Hz each; 1, 2 and 2 arom. Hs, respectively), 6.49–6.45 (m; 2 arom. Hs), 3.99 (t, $J \approx 6.5$ Hz; $\mathrm{OCH_2}$ group), 2.62 (t, $J \approx 6.5$ Hz; α-$\mathrm{CH_2}$ group). ^{13}C-NMR: $\delta =$ 164.13, 163.48, 145.92, 141.33, 113.04 (5s; 5 arom. Cs), 160.58 (d; HC=N), 133.32, 129.25, 120.73, 107.49, 101.67 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 68.22 (t; $\mathrm{OCH_2}$ group), 35.47 (t; α-$\mathrm{CH_2}$ group). UV–vis: λ (nm) = 343.2. IR: $\gamma = 1624$ cm^{-1} (C=N). $\mathrm{C_{29}H_{43}NO_2}$ (437.66); MS (EI): m/z (%) = 437 (100) $[\mathrm{M}]^+$, 297 (95) $[437 - \mathrm{C_{10}H_{20}}]$; Anal. Calc.: C, 79.59; H, 9.90; N, 3.20. Found: C, 79.44; H, 9.83; N, 3.34%.

4.1.3. 4-(Hexadecyloxy)-N-(4-hexylphenyl)-2-hydroxybenzalimine (**2c**)

Yield: 1.98 g (76%) of yellow crystals. ^{1}H-NMR: $\delta =$ 13.86 (s; OH), 8.50 (s; HC=N), 7.22, 7.19, 7.16 (3d, $J \approx$ 8.5 Hz each; 1, 2 and 2 arom. Hs, respectively), 6.47–

6.43 (m; 2 arom. Hs), 3.98 (t, $J \approx 6.5$ Hz; OCH_2 group), 2.60 (t, $J \approx 6.5$ Hz; α-CH_2 group). ^{13}C-NMR: $\delta =$ 164.16, 163.51, 145.77, 141.38, 112.95 (5s; 5 arom. Cs), 160.52 (d; HC=N), 133.31, 129.29, 120.73, 107.51, 101.57 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 68.22 (t; OCH_2 group), 35.49 (t; α-CH_2 group). UV–vis: λ (nm) = 343.0. IR: $\gamma = 1624$ cm^{-1} (C=N). $C_{35}H_{55}NO_2$ (521.83); MS (HR): m/z (%) = 521.4231 $[M]^+$, Calc. 521.4233.

4.1.4. *4-(Octadecyloxy)-N-(4-hexylphenyl)-2-hydroxybenzalimine (**2d**)*

Yield: 2.22 g (81%) of yellow crystals. ^{1}H-NMR: $\delta =$ 13.87 (s; OH), 8.51 (s; HC=N), 7.24, 7.21, 7.18 (3d, $J \approx$ 8.5 Hz each; 1, 2 and 2 arom. Hs, respectively), 6.50–6.44 (m; 2 arom. Hs), 3.99 (t, $J \approx 6.5$ Hz; OCH_2 group), 2.62 (t, $J \approx 6.5$ Hz; α-CH_2 group). ^{13}C-NMR: $\delta =$ 163.48, 158.54, 145.84, 141.37, 126.60 (5s; 5 arom. Cs), 160.54 (d; HC=N), 133.31, 129.29, 120.81, 107.50, 101.61 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 68.22 (t; OCH_2 group), 35.49 (t; α-CH_2 group). UV–vis: λ (nm) = 342.8. IR: $\gamma = 1624$ cm^{-1} (C=N). $C_{37}H_{59}NO_2$ (549.88); MS (HR): m/z (%) = 549.4549 $[M]^+$, Calc. 549.4546.

4.2. *Synthesis of the copper(II) complexes **3***

To a suspension of corresponding imine (0.5 mmol) in abs. ethanol (5 ml) stirred at room temperature (r.t.) were added potassium hydroxyde (0.5 mmol) in abs. ethanol (10 ml) and copper(II) acetate dihydrate (0.25 mmol). The mixture was stirred at room temperature for 4 h; the greenish or greenish brown solid formed was filtered and recrystallized from chloroform/ethanol.

The melting points of the copper(II) compounds are given in Table 2.

4.2.1. *bis[(N-4′-Hexylphenyl)-4-n-octyloxysalicylaldiminato]copper(II) (**3a**)*

Yield: 160 mg (73%) of greenish crystals. UV–vis: λ (nm) = 383.2. IR: $\gamma = 1617$ cm^{-1} (C=N). $C_{54}H_{76}N_2O_4Cu$ (880.76); MS (HR): m/z (%) = 879.5107 $[M]^+$, Calc. 879.5101. MS (EI): m/z (%) = 879 (44) $[M]^+$, 409 (100) $[C_{27}H_{39}NO_2]$, 297 (23) $[409-C_8H_{16}]$.

4.2.2. *bis[(N-4′-Hexylphenyl)-4-n-decyloxysalicylaldiminato]copper(II) (**3b**) [5]*

Yield: 154 mg (66%) of greenish crystals. UV–vis: λ (nm) = 380.8. IR: $\gamma = 1617$ cm^{-1} (C=N). $C_{58}H_{84}N_2O_4Cu$ (936.86); MS (EI): m/z (%) = 935 (15) $[M]^+$, 437 (100) $[C_{29}H_{43}NO_2]$, 297 (85) $[437-C_{10}H_{20}]$; Anal. Calc.: C, 74.36; H, 9.04; N, 2.99. Found: C, 74.35; H, 8.90; N, 2.89%.

4.2.3. *bis[(N-4′-Hexylphenyl)-4-n-hexadecyloxysalicylaldiminato]copper(II) (**3c**)*

Yield: 175 mg (63%) of greenish brown crystals. UV–vis: λ (nm) = 378.5. IR: $\gamma = 1617$ cm^{-1} (C=N). $C_{70}H_{108}N_2O_4Cu$ (1105.19); MS (EI): m/z (%) = 1105 (4) $[M]^+$, 522 (100) $[C_{35}H_{55}NO_2]$, 297 (75) $[522-C_{16}H_{33}]$.

4.2.4. *bis[(N-4′-Hexylphenyl)-4-n-octadecyloxysalicylaldiminato]copper(II) (**3d**)*

Yield: 210 mg (72%) of greenish brown crystals. UV–vis: λ (nm) = 378.4. IR: $\gamma = 1617$ cm^{-1} (C=N). $C_{74}H_{116}N_2O_4Cu$ (1161.30); MS (EI): m/z (%) = 1162 (2) $[M]^+$, 550 (100) $[C_{37}H_{59}NO_2]$, 297 (77) $[550-C_{18}H_{37}]$.

Acknowledgements

Financial support of our liquid crystal studies was provided by the Yıldız Teknik Üniversitesi Research Fond and Devlet Planlama Teskilati (DPT) (State Planning Organization Turkey). We are grateful to Professor C. Tschierske, Martin-Luther Universität Halle-Wittenberg, Germany, as well as to Dr. M. Horn, University of California, USA, for valuable information, DSC measurements and fruitful discussions.

References

[1] (a) J.L. Serrano (Ed.), Metallomesogens, Synthesis, Properties and Applications, VCH, Weinheim, 1996;
(b) A.M. Giroud-Godquin, in: D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds.), Handbook of Liquid Crystals, vol. IIB, Wiley–VCH, Weinheim, 1998, p. 901.

[2] (a) A.-M. Giroud-Godquin, P.M. Maitlis, Angew. Chem. Int. Ed. Engl. 30 (1991) 375;
(b) P. Espinet, M.A. Esteruelas, L.A. Oro, J.L. Serrano, E. Sola, Coord. Chem. Rev. 117 (1992) 215;
(c) D.W. Bruce, in: D.W. Bruce, D. O'Hare (Eds.), Inorganic Materials, Ch. 8, Wiley, Chichester, 1992;
(d) D.W. Bruce, J. Chem. Soc. Dalton Trans. (1993) 2983;
(e) A.P. Polishchuk, T.V. Timofeeva, Russ. Chem. Rev. 62 (1993) 291;
(f) S.A. Hudson, P.M. Maitlis, Chem. Rev. 93 (1993) 861;
(g) L. Oriol, J.L. Serrano, Adv. Mater. 7 (1995) 348.

[3] (a) K.P. Reddy, T.L. Brown, J. Mater. Chem. 1 (1991) 757;
(b) R. Iglesias, M. Marcos, J.L. Serrano, T. Sierra, M.A. Perez-Jubindo, Chem. Mater. 8 (1996) 2611;
(c) C.K. Lai, C.-H. Chang, C.-H. Tsai, J. Mater. Chem. 8 (1998) 599.

[4] (a) M. Ghedini, S. Armentano, R. Bartolino, N. Kirov, M. Petrov, S. Nenova, J. Mol. Liq. 38 (1988) 207;
(b) M. Ghedini, S. Armentano, R. Bartolino, F. Rustichelli, G. Torquati, N. Kirov, M. Petrov, Mol. Cryst. Liq. Cryst. 151 (1987) 75.

[5] M. Marcos, P. Romero, J.L. Serrano, C. Bueno, J.A. Cabeza, L.A. Oro, Mol. Cryst. Liq. Cryst. 167 (1989) 123.

[6] M. Ghedini, S. Morrone, D. Gatteschi, C. Zanchini, Chem. Mater. 3 (1991) 752.

[7] (a) M. Marcos, P. Romero, J.L. Serrano, Chem. Mater. 2 (1990) 495;
(b) M. Marcos, P. Romero, J.L. Serrano, J. Barbera, A.M. Levelut, Liq. Cryst. 7 (1990) 251.

[8] F.R. Diaz, N. Valdebenito, J.L. Serrano, M. Marcos, J.I. Martinez, P.J. Alonso, Liq. Cryst. 25 (1998) 217.

[9] K. Binnemanns, Y.G. Galyametdinov, S.R. Collinson, D.W. Bruce, J. Mater. Chem. 8 (1998) 1551.

[10] (a) K. Praefcke, D. Singer, B. Gundogan, Mol. Cryst. Liq. Cryst. 223 (1992) 181;
(b) K. Praefcke, B. Bilgin, J. Pickardt, M. Borowski, J. Organomet. Chem. 592 (1999) 155;
(c) B. Bilgin-Eran, D. Singer, K. Praefcke, Eur. J. Inorg. Chem. (2001) 111.

[11] G.S. Chilaya, Z.M. Elashvili, M.A. Gogadze, S.P. Tavzarashvili, K.D. Vinokur, S.A. Pikin, Liq. Cryst. 5 (1989) 1195.