Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

New metallomesogens with enaminoketonato ligands

Uladzimir M. Kauhanka[a]; Mikalai M. Kauhanka[a]
[a] Institute of Applied Physics Problems, 220064 Minsk, Belarus

To cite this Article Kauhanka, Uladzimir M. and Kauhanka, Mikalai M.(2006) 'New metallomesogens with enaminoketonato ligands', Liquid Crystals, 33: 2, 213 — 218
To link to this Article: DOI: 10.1080/02678290500429638
URL: http://dx.doi.org/10.1080/02678290500429638

Liquid Crystals, Vol. 33, No. 2, February 2006, 213–218

New metallomesogens with enaminoketonato ligands

ULADZIMIR M. KAUHANKA* and MIKALAI M. KAUHANKA
Institute of Applied Physics Problems, Kurchatov str. 7, 220064 Minsk, Belarus

(*Received 13 April 2005; in final form 27 July; accepted 27 August 2005*)

Several metallomesogens based on enaminoketonato ligands have been prepared. 1-Amino-1-(4′-butoxy-4-biphenyl)oct-1-en-3-one was synthesized by heterocycle hydrogenolysis in 3-(4′-butoxy-4-biphenyl)-5-amyl-isoxazole. Liquid crystalline complexes were obtained by reaction of this enaminoketone with nickel(II) or copper(II) acetates. Hydrogenolysis of the heterocycle in 3-(4-hydroxyphenyl)-5-amylisoxazole led to 1-amino-1-(4-hydroxyphenyl)oct-1-en-3-one. The corresponding copper(II) enaminoketonate was then obtained. The subsequent reaction of this compound with 4-alkoxy-benzoic acid chlorides gave liquid crystalline complexes with ester bridges in the core. A nematic phase was observed for all the synthesized metallomesogens. The bridging group influence on melting points, mesophase ranges and thermal stability of copper(II)complexes is discussed.

1. Introduction

Up to the present time a wide variety of metallomesogens has been synthesized [1–5]. Different 1,3-difunctional compounds are commonly used as chelating ligands for liquid crystalline complex formation. Substituted β-enaminoketones are also used in metallomesogen preparation [6–19]. Many metal cations form mesomorphic complexes with these types of ligands.

The most commonly used route to obtain enaminoketonato ligands involves Claisen condensation of substituted acetophenones with esters [6–16, 19]. Further reaction of the resulting β-dicarbonyl compounds with aromatic or aliphatic amines leads to the desired enaminoketones containing a secondary amino group [6, 16, 19]. Tetradentate enaminoketonato ligands may prepared when various diamines are used [9–13]. These substances contain two secondary amino groups.

It is well known that the cleavage of an isoxazole ring leads to β-enaminoketones having primary amino groups [20]. Recently we used this transformation of 3-aryl-5-alkylisoxazoles for the preparation of liquid crystalline 3-aryl-5-alkyl-1H-pyrazoles [21]. In the present work we used the cleavage of the 3-aryl-5-alkyl-isoxazole ring as the key stage for the preparation metallomesogens of based on novel enaminoketonato ligands containing primary amino groups.

*Corresponding author. Email: kauhanka@bsu.by

2. Results and discussion

2.1. *Synthesis*

We used for the synthesis of the required isoxazoles the oxidation of the corresponding 2-isoxazolines. This method provides the unsymmetrical 3,5-disubstituted isoxazoles in a regioselective manner [21].

The synthetic route to the new metallomesogens **4a, b** with a biphenyl fragment in the core is shown in scheme 1. The 2-isoxazoline **1** was chosen as the key intermediate. The preparation of this compound from 4′-butoxybiphenyl-4-carbaldehyde was reported in our previous communication [22]. The reaction of 2-isoxazoline **1** with *N*-bromosuccinimide (NBS) and subsequent dehydrobromination of intermediate 4- and 5-bromo-2-isoxazolines by the action of triethylamine gave isoxazole **2**. Further isoxazole ring hydrogenolysis over Raney nickel led to β-enaminoketone **3**, having primary amino group; we used this as ligand for the preparation of the target metallomesogens. Nickel(II) and copper(II) were chosen as the central metals. It is known that these cations form square planar complexes with enaminoketones [4, 7, 12, 19], ensuring the planarity of the central part of the core in metallomesogens [4, 19]. The enaminoketonates **4a, b** were obtained by refluxing the ethanol solution of enaminoketone **3** with nickel(II) or copper(II) acetates, respectively.

The preparation of the new liquid crystalline complexes **9a–g** with ester bridges in the core between aromatic rings is shown in scheme 2. The 2-isoxazoline

Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2006 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290500429638

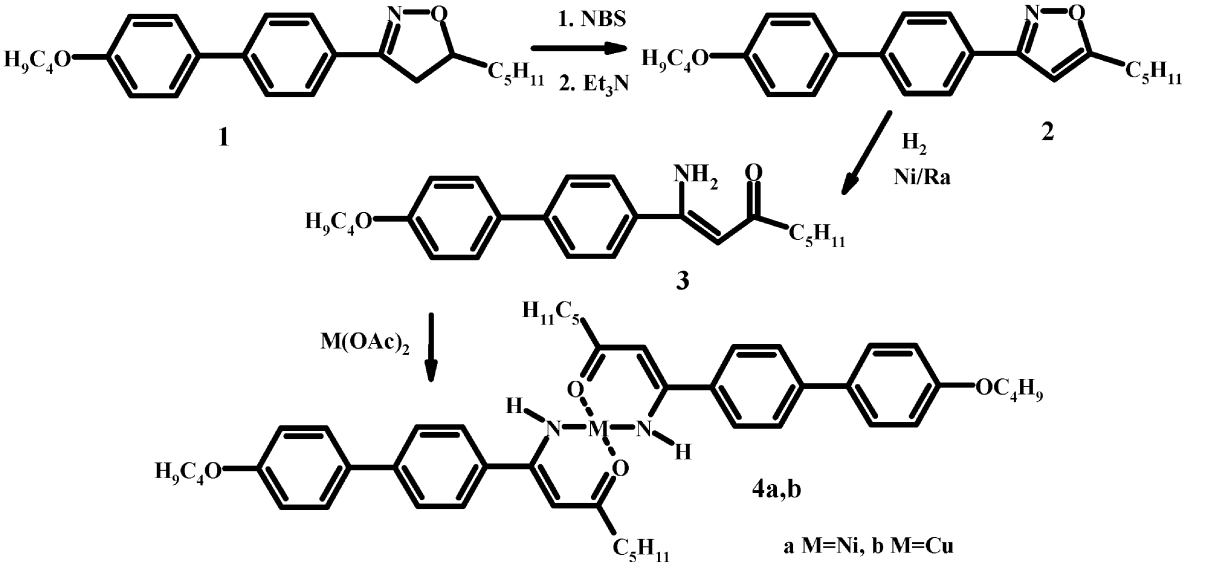
5 with a phenolic hydroxy group was chosen as the key intermediate. This compound was prepared from 4-hydroxybenzaldehyde [23]. The synthesis of isoxazole **6** from compound **5** was previously described in our investigation of liquid crystalline 3-aryl-5-alkylisoxazoles and pyrazoles [21]. Hydroxy group protection, bromination with NBS and subsequent dehydrobromination and OH group deprotection by the action of potassium hydroxide furnished the required isoxazole **6**. Enaminoketone **7** was obtained from isoxazole **6** by hydrogenolysis over Raney nickel catalyst. Reaction with copper(II) acetate in refluxing ethanol gave the complex **8** in 94% yield. Unfortunately these reaction conditions were unsuccessful for the synthesis of the corresponding nickel(II) enaminoketonate. This may be explained by the negative influence of the hydroxy group in the ligand on complex formation. The target copper(II) enaminoketonates **9a–g** with ester bridges were synthesized by esterification of phenol **8**. The reaction of compound **8** with 4-alkoxybenzoic acid chlorides in the presence of triethylamine led to complexes **9a–g** in 58–87% yields.

2.2. *Spectroscopic study*

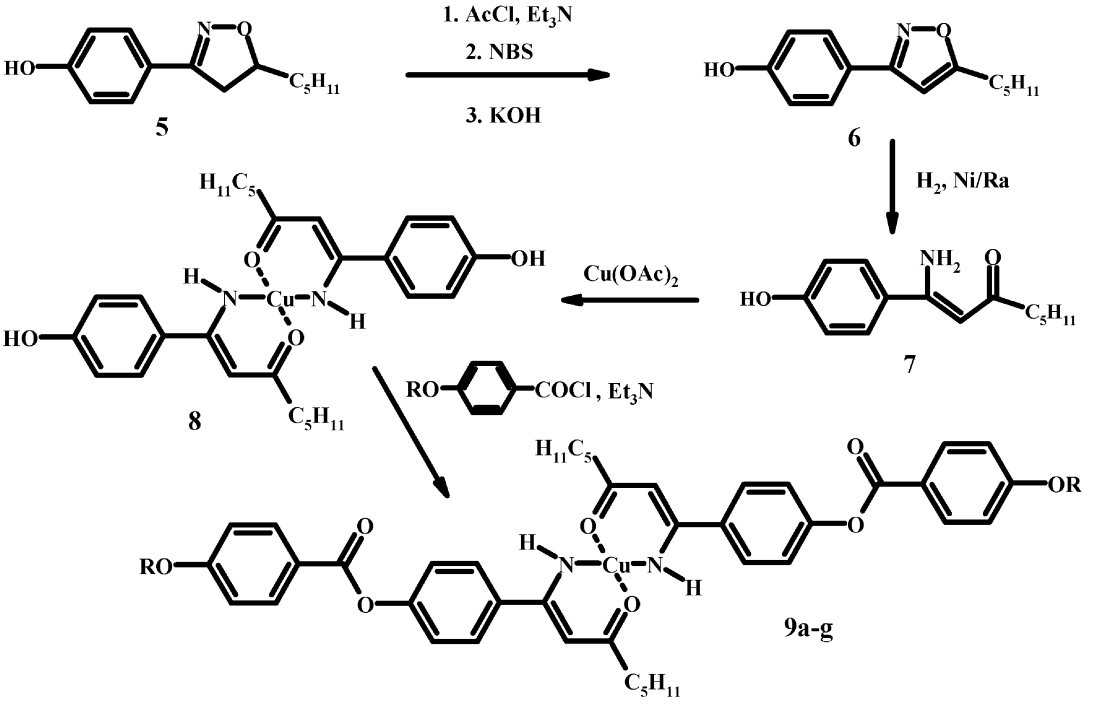
UV, IR and ^{1}H NMR spectra confirmed the presence of the enaminoketone function in compounds **3** and **7**. Absorption maxima in UV spectrum for substance **3** is at 334 nm. Enaminoketone **7** absorbed at 256 and 320 nm. The first maximum corresponds to aromatic ring absorption and the second to the absorption of the conjugated enaminoketonate function of compound **7**. Intense bands at 1480–1600 cm^{-1} in IR spectra of these enaminoketones correspond to vibrations of the conjugated double C=O and C=C bonds. The singlets associated with the vinyl 2-CH protons in ^{1}H NMR spectra of substances **3** and **7** appeared at δ 5.75 and 5.44 ppm respectively. The presence of the NH_2 group in enaminoketone **3** was confirmed by a band at 3475 cm^{-1} in the IR spectrum and two broad singlets at δ 8.31 and 10.74 ppm in ^{1}H NMR. For compound **7** these values are 3480 cm^{-1} in the IR and broad singlets at δ 5.25 and 10.04 ppm in ^{1}H NMR.

The formation of enaminoketonates **4a, b** led to the appearance of absorption maxima in UV spectra at 299 and 298 nm, respectively. Bands at 3335 and 3345 cm^{-1} associated with N-H bond vibrations are seen in the IR spectra of complexes **4a, b** respectively. A doublet at δ 5.30 ppm in the ^{1}H NMR spectrum of nickel(II) enaminoketonate **4a** corresponds to the vinyl 2-CH proton. A singlet of the amino group proton appeared at δ 5.50 ppm in the ^{1}H NMR spectrum of compound **4a**.

Complex **8** absorbed at 283 and 326 nm in the UV. The formation of esters **9a–g** led to a shift of the aromatic absorption maximum to 263 nm, while the maximum at 328 nm associated with the enaminoketone fragment remained similar to that in starting compound **8**. The intense bands at 1715–1725 cm^{-1} in the IR spectra of complexes **9a–g** correspond to C=O vibrations of the ester moieties. Bands at 3340–3355 cm^{-1} in the IR spectra of enaminoketonates **9a–g** correspond to N–H bonds. These spectral data



Scheme 1.



Scheme 2.

suggested the formation of benzoates, not benzamides, in the esterification stages.

It is well known that the presence of the paramagnetic copper(II) cation leads to the broadening or disappearance of multiplets in ^{1}H NMR spectra [24]. This was established for all the copper complexes **4b, 8** and **9a–g**. The multiplets of enaminoketone protons (2-CH and NH), neighbouring the copper atom, are absent in the spectra of compounds **4b** and **9a–g**. The broadening of signals of the amyl chain protons is observed in these substances. However the multiplets of benzoate substitutes in the ^{1}H NMR spectra of esters **9a–g** are only slightly deformed. This probably reflects that these signals are less influenced by the copper atom.

Additional confirmation of the structure of complexes **9** was obtained from the reaction of compound **9a** with dilute hydrochloric acid. The corresponding enaminoketone **10** (see § 3) was isolated in quantitative yield. UV, IR and ^{1}H NMR spectra suggested the presence of a primary amino group and a phenyl 4-propoxy-benzoate fragment. This confirmed chemioselective ester formation in the reaction of complex **8** with acid chlorides.

2.3. *Mesomorphic properties*

Nickel(II) complex **4a** was obtained as a dark yellow solid, while copper complexes **4b, 8, 9a–g** were obtained as dark green needles. The phase transition temperatures of the synthesized metallomesogens **4a, b** and **9a–g** are summarized in table 1. As can be seen, all of these compounds are mesomorphic and form an enantiotropic nematic phase.

Compounds **4a, b**, with biphenyl fragments in the core, have high melting points. The nematic phase thermal stability is higher for nickel(II) complex **4a** than for copper(II) complex **4b**. The temperature for the N–I transition for compound **4b** is approximate, as the material rapidly decomposed near the clearing point.

Complex **8**, with a phenolic hydroxy group, is not mesomorphic and melts with decomposition at about 220°C. Esterification elongates the molecular core and esters **9a–j** form nematic phases a range of 65–88°C. In general, the melting and clearing points of benzoates **9a–j** decrease with increasing alkoxy chain length; however, compounds **9c–e** have similar melting and clearing points. The 4-butyloxy benzoate **9b** has a higher clearing point and larger mesophase range.

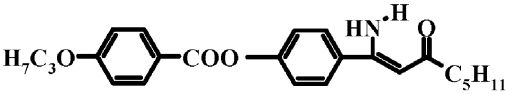
As can be seen from table 1, the introduction of an ester bridge leads to a decrease in melting point and increase in mesophase range in the case of copper(II) complexes **4b** and **9b**. The thermal stability of the materials also increases. Partial decomposition of esters **9** was found in some cases, only after several heating-cooling cycles.

Table 1. Transition temperatures (°C) of metallomesogens **4a, b** and **9a–g**.

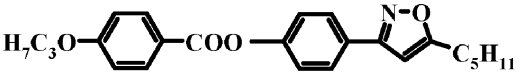
Compound	Cr		*N*		I
4a	•	194	•	270	•
4b	•	207	•	234[a]	•
9a	•	148	•	213	•
9b	•	139	•	227	•
9c	•	128	•	209	•
9d	•	127.5	•	205	•
9e	•	131	•	205	•
9f	•	121	•	187	•
9g	•	109	•	179	•

[a] With decomposition.

Table 2. Transition temperatures (°C) of enaminoketone **10** and isoxazole **11**.

10 

Cr 110 (*SmA* 80) *I*

11 

Cr 118.5 *N* 149 *I*, ref [21]

Liquid crystalline properties have been observed in compounds with an enaminoketone function [16, 19, 25, 26]. An intramolecular hydrogen bond leads to 1,4-disubstituted six-member quasi-ring formation and mesophase stabilization. In substances **3** and **10**, this intramolecular interaction leads to 1,3-disubstituted six-member quasi-ring formation. Enaminoketone **3** melts at 117–118°C without mesophase formation. Benzoate **10** shows a monotropic smectic phase A (see table 2). It should be noted that the nematic phase was observed for the corresponding isoxazole **11** [21]; thus the cleavage of the heterocycle changes the mesomorphism considerably.

The structures of metallomesogens **4** and **9** are similar to the complexes derived from substituted aryl–alkyl-propanediones (see figure 1) [2, 4, 27]. The chelating moiety in these compounds contains NH and oxygen (**4, 9**) or two oxygen atoms. The liquid crystalline properties of the described β-diketonates are determined by the central metal type, aryl core type and alkyl chain length. Calamitic and columnar mesophases have been found in such β-diketonates [2, 4, 27]. However it is well known that a mixture of *cis*- and *trans*-1,3-diketonates can be obtained from unsymmetrical β-diketones [24, 27]. This is explained by the formation of two non-equivalent enol forms during the complexation. Only one enaminoketone form could be prepared by the reduction of 3,5-disubstituted isoxazoles. As a result, enaminoketonates **4** and **9** were obtained as the single *trans*-isomers.

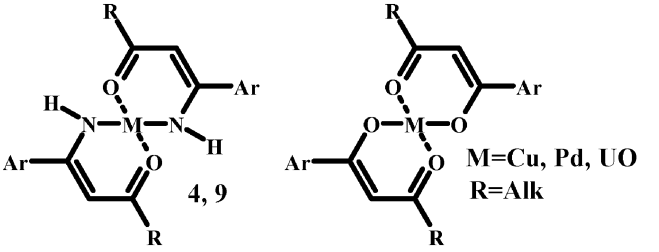


Figure 1.

3. Experimental

Experimental details have been described in previous publications [22, 28]. UV spectra were recodered with a Specord M40; IR spectra were obtained using a Specord 75IR instrument. ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer with hexamethyldisiloxane (δ 0.055 ppm) as internal standard. The reaction progress and product purity were checked using TLC on Kieselgel 60 F_{254} (Merck). Phase transition temperatures were measured using a heating stage in conjugation with a polarizing microscope.

3.1. *Bis[1-(4′-Butoxy-4-biphenyl)-3-amyl-1-aminoprop-1-en-3-onato]nickel(II) (4a)*

Nickel(II) acetate tetrahydrate (0.044 g, 0.177 mmol) was added to a solution of enaminoketone **3** (0.120 g, 0.329 mmol) in ethanol (10 ml). The resulting reaction mixture was heated under reflux for 1 min; it was allowed to cool and then diluted with water. The solid was filtered off and washed with water and cold ethanol. After drying *in vacuo*, a yield of 0.113 g (87%) of compound **4a** was obtained. An analytical sample (as a dark yellow powder) was obtained by recrystallization from ethanol/chloroform mixture. UV (λ_{max}, nm): 299 (dioxane). IR ($CHCl_3$, cm^{-1}): 3335 (N–H), 2990 (C–$H_{arom.}$), 2950, 2920, 2865 (C–H_{alkyl}), 1600, 1565, 1540, 1485 (C=O, C=C, C=$C_{arom.}$). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.88 (3H, t, J=7 Hz, CH_3), 0.98 (3H, t, J=7.5 Hz, CH_3), 1.20–1.35 (4H, m), 1.42–1.56 (4H, m), 1.79 (2H, quintet, J=7 Hz), 2.07 (2H, t, J=7 Hz) {CH_2–alkyl}, 4.00 (2H, t, J=7 Hz, OCH_2), 5.30 (1H, d, J=3 Hz, 2-CH), 5.50 (1H, br. s, NH), 6.97 (2H, d, J=9 Hz), 7.48–7.54 (4H, m), 7.56 (2H, d, J=8.5 Hz) (arom. protons).

Compounds **4b** and **8** were prepared by a similar procedure.

3.2. *Bis[1-(4-Hydroxyphenyl)-3-amyl-1-aminoprop-1-en-3-onato]copper(II) (8)*

Yield 94% (dark green needles), m.p. 220–221°C (2-propanol/toluene) (dec.). UV (λ_{max}, nm): 279.5, 330 (CH_3OH); 283, 326 (dioxane). IR (THF, cm^{-1}): 3600–3040 (OH, NH), 1605, 1585, 1555, 1495 (C=O, C=C, C=$C_{arom.}$), 1340. ^1H NMR ($(CD_3)_2CO$, δ, ppm): 0.91 (br. s, CH_3), 1.06–1.24 (m, CH_2-alkyl.), 8.60–8.74 (m, arom. protons).

3.3. *Bis{1-[4-(4-Propyloxybenzoyloxy)phenyl]-3-amyl-1-aminoprop-1-en-3-onato}copper(II) (9a)*

Triethylamine (0.4 ml, 2.88 mmol) and phenol **8** (0.100 g, 0.189 mmol) were added to a stirred solution of 4-propoxybenzoic acid chloride [obtained by the action of excess thionyl chloride on 4-propoxybenzoic acid (0.075 g, 0.417 mmol)] in THF (5 ml). The mixture was stirred for a further 2.5 h and then water was added. The product was extracted into chloroform (twice) and the combined extracts were washed with water and dried (Na_2SO_4). The solvent was removed *in vacuo* and the residue recrystallized (2-propanol/chloroform) to give dark green needles: yield 0.112 g (69%). UV ($\lambda_{max.}$, nm): 263, 328 (THF). IR ($CHCl_3$, cm^{-1}): 3355 (NH), 2955, 2930, 2870, 2855 (C–$H_{alkyl.}$), 1725 (C=$O_{ester.}$), 1600, 1555, 1525, 1500, 1490 (C=O, C=C, C=$C_{arom.}$), 1250, 1200, 1165, 1065 (C–O). IR (THF, cm^{-1}): 1735 (C=O_{ester}), 1635, 1600, 1555, 1520, 1490 (C=O, C=C, C=$C_{arom.}$). ^1H NMR ($CDCl_3$, δ, ppm): 0.91 (m, CH_3), 1.04 (3H, t, J=7 Hz, CH_3), 1.08–1.36 (m), 1.83 (2H, sextet, J=7 Hz, CH_2), 3.98 (2H, t, J=7 Hz, OCH_2), 6.88–6.98 (2H, m), 8.00–8.10 (2H, m) (arom. protons).

Compounds **9b–g** were prepared by a similar procedure to that described for the preparation of compound **9a** and those representative data are provided for just one additional homologue. The analytical samples were obtained by double recrystallization of the prepared materials from 2-propanol/chloroform mixture.

3.4. *Bis-{1-[4-(4-Heptyloxybenzoyloxy)phenyl]-3-amyl-1-aminoprop-1-en-3-onato}copper(II) (9e)*

Yield 80%. UV ($\lambda_{max.}$, nm): 262, 330 (THF). IR ($CHCl_3$, cm^{-1}): 3345 (NH), 2940, 2920, 2850 (C–$H_{alkyl.}$), 1720 (C=$O_{ester.}$), 1590, 1550, 1525, 1495, 1490 (C=O, C=C, C=$C_{arom.}$), 1245, 1200, 1160, 1055 (C–O). ^1H NMR ($CDCl_3$, δ, ppm): 0.88 (3H, t, CH_3, J=7 Hz), 0.80–1.00 (CH_3, m), 1.08–1.40 m, 1.45 (2H, m, CH_2), 1.80 (2H, quintet, J=6 Hz, CH_2), 4.01 t (2H, Ar–OCH_2, J=6 Hz), 6.87–6.98 (2H, m), 7.97–8.16 (2H, m) (arom. protons).

3.5. *1-Amino-1-[4-(4-propyloxybenzoyloxy)phenyl]-oct-1-en-3-one (10)*

Diluted hydrochloric acid (5% solution, 0.5 ml) was added to a solution of compound **9a** (0.04 g, 0.047 mmol) in THF (5 ml). After 1 min the reaction mixture was diluted with water, and sodium bicarbonate solution was added. The product was extracted into chloroform (twice) and the combined extracts were washed with water and dried (Na_2SO_4). The solvent was removed *in vacuo* and the residue purified by the column chromatography (silica gel, ethyl acetate/petroleum ether 1/4); yield 0.036 g (97%). UV ($\lambda_{max.}$, nm): 263, 326 (CH_3OH); 255, 318 (THF). IR ($CHCl_3$, cm^{-1}): 3485, 3350–3100 (N–H), 3000 (C–$H_{arom.}$), 2955, 2930, 2875, 2860 (C–$H_{alkyl.}$), 1725 (C=$O_{ester.}$), 1600, 1575, 1525, 1505, 1485 (C=O, C=C, C=$C_{arom.}$), 1250, 1205, 1165, 1065 (C–O). ^1H NMR ($CDCl_3$, δ, ppm): 0.90 (3H, t, J=7 Hz, CH_3), 1.06 (3H, t, J=7 Hz, CH_3), 1.27–1.40 (4H, m), 1.65 (2H, quintet, J=7.5 Hz), 1.85 (2H, sextet, J=7 Hz), 2.39 (2H, J=7.5 Hz) (CH_2–alkyl), 4.01 (2H, t, J=7 Hz, OCH_2), 5.44 (1H, s, 2-CH), 6.97 (2H, d, J=9 Hz), 7.27 (2H, d, J=9 Hz), 7.61 (2H, d, J=9 Hz), 8.13 (2H, d, J=9 Hz) (arom. protons), 5.18 (1H, br. s), 9.94 (1H, br. s) (NH_2).

4. Conclusion

Metallomesogens based on novel enaminoketonato ligands have been prepared. The key step in the synthesis of these materials is the reductive cleavage of the heterocycle in 3-aryl-5-amylisoxazoles. Enaminoketones with a primary amino group were obtained in this manner. The target liquid crystals were prepared by complexation of these ligands with nickel(II) or copper(II) cations. Metallomesogens with an ester bridging group were synthesized by esterification of the corresponding OH-containing copper(II) enaminoketonate with 4-alkoxybenzoic acid chlorides.

An enantiotropic nematic phase was observed for all the prepared materials. A nickel(II) complex with a biphenyl fragment in the core forms a larger mesophase range and is more thermally stable than the corresponding copper(II) complex. Copper(II) enaminoketonates with ester bridges in the aryl part of the core are thermally more stable than the biphenyl analogues. Introduction of an ester linkage leads to decreasing melting point and increasing mesophase range.

References

[1] J.L. Serrano (Ed.). *Metallomesogens. Synthesis, properties and applications*. VCH, Weinheim (1996).

[2] S.A. Hudson, P.M. Maitlis. *Chem. Rev.*, **93**, 861 (1993).
[3] R. Giménez, D.P. Lydon, J.L. Serrano. *Curr. Opin. solid state mater. Sci.*, **6**, 527 (2002).
[4] B. Donnio, D.W. Bruce. *Struct. Bonding*, **95**, 193 (1999).
[5] K. Binnemans, C. Görller-Walrand. *Chem. Rev.*, **102**, 2303 (2002).
[6] Y.G. Galyametdinov, G.I. Ivanova, I.K. Ovchinnikov. *Zh. Obshch. Khim.*, **61**, 234 (1991).
[7] A. Krówczyński, D. Pociecha, J. Szydłowska, J. Przedmojski, E. Górecka. *Chem. Commun.*, 2731 (1996).
[8] A. Krówczyński, J. Szydłowska, D. Pociecha, J. Przedmojski, E. Górecka. *Liq. Cryst.*, **25**, 117 (1998).
[9] J. Szydłowska, A. Krówczyński, E. Górecka, D. Pociecha. *Inorg. Chem.*, **39**, 4879 (2000).
[10] U. Pietrasik, J. Szydłowska, A. Krówczyński, D. Pociecha, E. Górecka, D. Guillon. *J. Am. chem. Soc.*, **124**, 8884 (2002).
[11] J. Szydłowska, A. Krówczyński, U. Pietrasik, A. Rogowska. *Liq. Cryst.*, **32**, 651 (2005).
[12] C.K. Lai, Y.-S. Pang, C.-H. Tsai. *J. mater. Chem.*, **8**, 2605 (1998).
[13] C.-D. Yang, Y.-S. Pang, C.K. Lai. *Liq. Cryst.*, **28**, 191 (2001).
[14] C.K. Lai, R. Lin, M.-Y. Lu, K.-C. Kao. *J. chem. Soc. Dalton Trans.*, 1857 (1998).
[15] I. Bikchantaev, Y.G. Galyametdinov, O. Kharitonova, I.K. Ovchinnikov, D.W. Bruce, D.A. Dunmur, D. Guillon, B. Heinrich. *Liq. Cryst.*, **20**, 489 (1996).
[16] O.A. Turanova, Y.G. Galyametdinov, I.K. Ovchinnikov. *Russ. Chem. Bull.*, **50**, 805 (2001).
[17] A.G. Serrette, C.K. Lai, T.M. Swager. *Chem. Mater.*, **6**, 2252 (1994).
[18] H. Zheng, C.K. Lai, T.M. Swager. *Chem. Mater.*, **6**, 101 (1994).
[19] C.P. Roll, A.G. Martin, H. Görls, G. Leibeling, D. Guillon, B. Donnio, W. Weigand. *J. mater. Chem.*, **14**, 1722 (2004).
[20] P.G. Baraldi, A. Barco, S. Benetti, G.P. Pollini, D. Simoni. *Synthesis.*, 857 (1987).
[21] U.M. Kauhanka, M.M. Kauhanka. *Liq. Cryst.* (in the press).
[22] U.M. Kauhanka, M.M. Kauhanka. *Russ. J. org. Chem.* (in the press).
[23] U.M. Kauhanka, M.M. Kauhanka. *Liq. Cryst.*, **31**, 1547 (2004).
[24] J.L. Serrano, T. Sierra. *Chem. Eur. J.*, **6**, 759 (2000).
[25] D. Pociecha, A. Krówczyński, J. Szydłowska, E. Górecka, M. Glogarova, J. Przedmojski. *J. mater. Chem.*, **7**, 1709 (1997).
[26] O. Akopova, A. Alexandrov, T. Pashkova, L. Kotovicz, A. Kurnosov A Krowczynski. *Proc. SPIE*, **3319**, 63 (1998).
[27] S. Clark, J.M. Elliott, J.R. Chipperfield, P. Styring, E. Sinn. *Inorg. Chem. Commun.*, **5**, 249 (2002).
[28] U.M. Kauhanka, M.M. Kauhanka. *Russ. J. org. Chem.* (in press).