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Synthesis of New Metallomesogens with Enaminoketone Chelating Ligands

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Abstract—New liquid crystalline copper(II) enaminoketonates containing bridging ester groups were synthesized by hydrogenation of the heteroring in 3-(4-hydroxyphenyl)-5-pentylisoxazole to 1-amino-1-(4-hydroxyphenyl)oct-1-en-3-one, treatment of the latter with copper(II) acetate, and benzoylation of the coordination compound thus formed with 4-alkoxybenzoyl chlorides.

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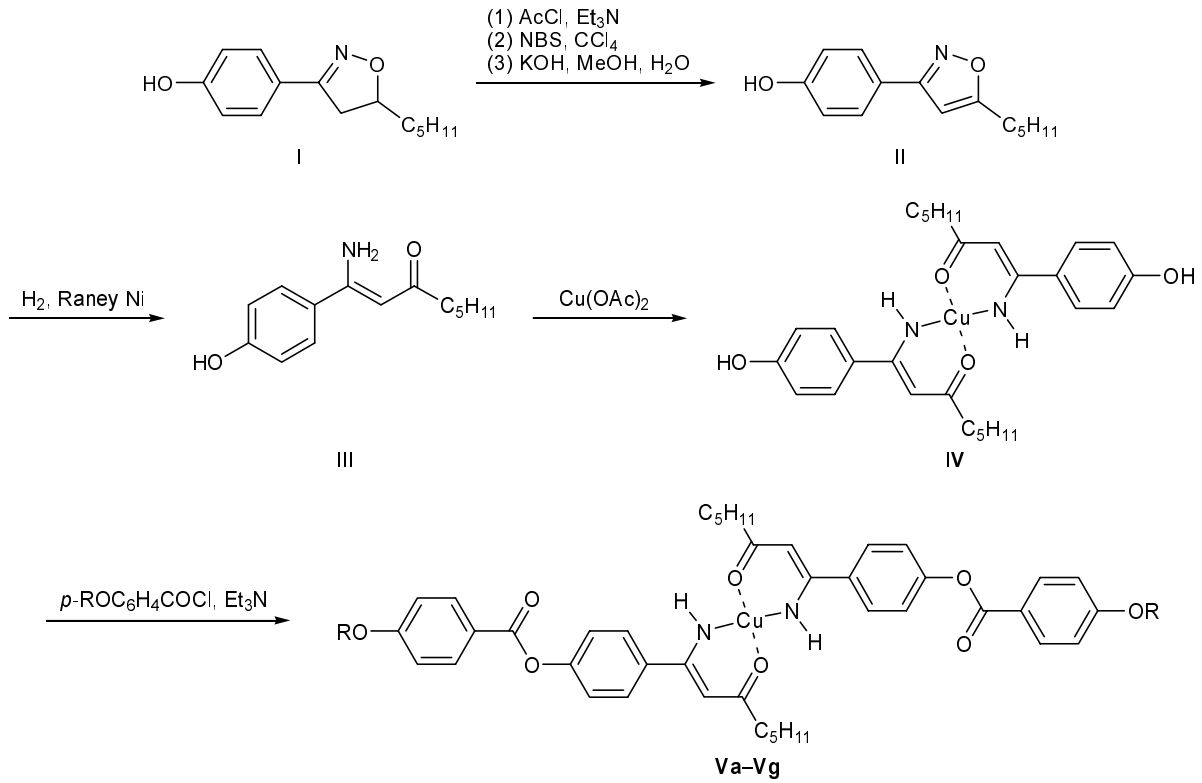
Metallomesogens are coordination compounds of metal cations with various organic chelating ligands, which possess properties of liquid crystals [1–4]. Different 1,3-difunctional compounds are used most frequently as ligands in such complexes [1–8]. Enaminoketones also belong to this class of ligands, and liquid crystals on their basis were recently synthesized [4, 9–12]. We previously reported on the synthesis of a new class of liquid crystalline copper and nickel enaminoketonates from the corresponding enaminoketones having biphenyl fragments [12]. As ligands we used enaminoketones containing a primary amino

Scheme 1.



R = C_3H_7 (**a**), C_4H_9 (**b**), C_5H_{11} (**c**), C_6H_{13} (**d**), C_7H_{15} (**e**), C_8H_{17} (**f**), C_9H_{19} (**g**).

group; these compounds are readily available via catalytic hydrogenation of appropriately disubstituted 3-aryl-5-alkylisoxazoles.

The goal of the present work was to synthesize new liquid crystals on the basis of enaminoketonates in which the aromatic rings in the ligands are linked through an ester moiety rather than directly. It is known [1–4, 8] that the presence of an ester bridging group increases flexibility and mobility of particular parts of a liquid crystal molecule and hence affects the type of mesophase and its temperature range. On the other hand, introduction of an ester bridging group between aromatic rings does not break conjugation of the latter with the enaminoketonate fragment, which is an important factor responsible for good liquid crystal parameters of metallomesogens.

As initial chelating ligand we selected enaminoketone **III**. The procedure for the preparation of this compound was developed by us previously while studying liquid crystals on the basis of 3-aryl-5-alkyl-1*H*-pyrazoles [13]. The synthetic scheme includes oxidation of the 4,5-dihydroisoxazole ring in compound **I** [14, 15] to isoxazole **II**, followed by hydrogenation of the heteroring in **II** and complex formation of enaminoketone **III** having a primary amino group (Scheme 1). The presence of a phenolic hydroxy group in molecule **III** makes it possible to introduce various mesogenic substituents to obtain the target metallomesogens with a bridging group in the aryl fragment of the enaminoketonate ligand.

As in the synthesis of liquid crystalline enaminoketonates described in [12], we planned to use copper(II) and nickel(II) as complexing metals. Our choice was based on the fact that these cations with bidentate 1,3-difunctional compounds form planar complexes [1–4]. Planar structure of the central part of a metallomesogen molecule is a necessary condition responsible for good liquid crystal parameters [7–12].

By reaction of enaminoketone **III** with copper(II) acetate we obtained 94% of coordination compound **IV**. Its structure was confirmed by spectral data. The UV spectrum of **IV** contained an absorption mximum at λ 283 nm due to the aromatic fragment and a maximum at λ 326 nm due to conjugated enaminoketonate chromophore; the corresponding maxima in the UV spectrum of initial enaminoketone **III** were located at λ 256 and 320 nm [13]. Compound **IV** showed in the IR spectrum absorption bands in the region 1495–1605 cm^{-1}, which belong to stretching vibrations of the C=O and C=C bonds. Signals in the ^1H NMR spectrum of **IV** were strongly broadened due to the presence of paramagnetic copper(II) ion [6]. The observed distortion of the ^1H NMR spectral pattern may be regarded as an additional qualitative support to the formation of a coordination compound.

We previously synthesized both copper(II) and nickel(II) enaminoketone complexes [12]. However, we failed to isolate the corresponding nickel(II) complex in the reaction of enaminoketone **III** with nickel(II) acetate. Presumably, nickel(II) is less prone to complex formation, as compared to copper(II). Furthermore, the presence in molecule **III** of a free phenolic hydroxy group which possesses acidic properties hampers chelation with nickel(II) ion.

In the next stage, we tried to obtain the target metallomesogens by esterification of the phenolic hydroxy groups in **IV** with mesogenic acids. Analogous esters were synthesized by us previously [14, 15] by direct reaction of the corresponding phenols with *para*-substituted benzoic acids in the presence of *N*,*N*′-dicyclohexylcarbodiimide and *N*,*N*-dimethylaminopyridine. However, application of this procedure to esterification of compound **IV** gave no desired results. We succeeded in synthesizing metallomesogens **Va**–**Vg** in 58–87% yield by benzoylation of **IV** with 4-alkoxybenzoyl chlorides in tetrahydrofuran in the presence of triethylamine. The structure of compounds **Va**–**Vg** was proved by the UV, IR, and ^1H NMR spectra. In the UV spectra of **Va**–**Vg** we observed absorption maxima at λ 263 and 328 nm, i.e., the maximum corresponding to the aromatic fragment was displaced to shorter wavelengths, as compared to initial phenol **IV**, while that belonging to the enaminoketonate fragment almost did not change its position. These data indicate that the esterification of **IV** gave just benzoates **Va**–**Vg** rather than benzamides. Another support for the presence of ester group in the product was obtained by the IR spectra which contained absorption bands typical of ester carbonyl at 1715–1725 cm^{-1} and N–H bond at 3340–3355 cm^{-1}. Strong bands in the region 1485–1600 cm^{-1} were assigned to stretching vibrations of the conjugated C=C–C=O bond sequence. Enaminoketonates **Va**–**Vg** showed in the ^1H NMR spectra broadened multiplets which were analogous to those present in the spectrum of initial complex **IV**. In addition, we observed almost undistorted multiplets from protons in the benzoyl fragments which are remote from the central part containing paramagnetic copper(II) ion. In particular, the spectra of all compounds **Va**–**Vg** contained triplets at δ 3.98–4.02 ppm from the OCH_2

protons and multiplets at δ 6.88–6.98 and 8.00–8.10 ppm from the aromatic protons.

The structure of metallomesogens **Va**–**Vg** was additionally confirmed by treatment of compound **Va** with dilute hydrochloric acid; as a result, the corresponding enaminoketone **VI** was obtained in quantitative yield. The UV, IR, and ^{1}H NMR spectra of compound **VI** indicated the presence in its molecule of a primary amino group and a 4-propoxybenzoate fragment, i.e., chemoselective formation of esters in the reactions of **IV** with 4-alkoxybenzoyl chlorides.

Compounds **Va**–**Vg** were found to exhibit pronounced liquid crystalline properties: they formed nematic phase in a broad temperature range (see table). Comparison of these data with the corresponding parameters of previously synthesized copper(II) enaminodiketonate having a biphenyl fragment shows that introduction of an ester bridge into the aromatic part of the ligand considerably improves liquid crystal parameters: the resulting metallomesogens are characterized by appreciably reduced temperature of formation and extended temperature range of nematic phase. Moreover, metallomesogens **Va**–**Vg** are more thermally stable that their biphenyl analog.

Phase transition temperatures of compounds **Va**–**Vg**

Compound no.	mp, °C	Nematic phase	Clarification temperature, °C
Va	148	●	213
Vb	139	●	227
Vc	128	●	209
Vd	127.5	●	205
Ve	131	●	205
Vf	121	●	187
Vg	109	●	179

EXPERIMENTAL

The IR spectra were measured in the range from 4000 to 400 cm^{-1} on a Specord 75IR spectrometer from solutions in chloroform (unless otherwise stated) using KBr cells. The electronic absorption spectra were recorded in the range from 220 to 900 nm on a Specord M40 spectrophotometer from solutions in tetrahydrofuran (unless otherwise stated). The ^{1}H NMR spectra were obtained on a Bruker Avance 400 spectrometer (400 MHz) from solutions in chloroform-*d* using HMDS as internal reference. The progress of reactions and the purity of products were monitored by TLC on Kieselgel 60 F_{254} plates (Merck). The melting points and phase transition temperatures were determined using a heating block coupled with a polarizing microscope. The phase transition temperatures of compounds **Va**–**Vg** are given in table.

Bis[1-amino-1-(4-hydroxyphenyl)oct-1-en-3-onato]copper(II) (IV). A hot solution of 0.365 g (1.83 mmol) of copper(II) acetate monohydrate in a mixture of 15 ml of water and 7 ml of ethanol was added to a boiling solution of 0.850 g (3.65 mmol) of 1-amino-1-(4-hydroxyphenyl)oct-1-en-3-one (**III**) (which was synthesized according to the procedure described in [13]) in 10 ml of ethanol. The mixture was heated for 1 min under reflux, cooled, and diluted with 15 ml of water. The dark green precipitate of complex **IV** was filtered off, washed on a filter in succession with 30 ml of water and 3 ml of a cold 1:2 ethanol–water mixture, dried, and recrystallized from propan-2-ol–toluene. Yield 0.903 g (94%), dark green needles, mp 220–221°C (decomp., from propan-2-ol–toluene). UV spectrum, λ_{max}, nm: in MeOH: 279.5, 330; in dioxane: 283, 326. IR spectrum, ν, cm^{-1}: 3600–3040 (OH, NH); 1605, 1585, 1555, 1495 (C=O, C=C, C=C_{arom}); 1340. ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 0.91 br.s (CH_3), 1.06–1.24 m (CH_2), 8.60–8.74 m (H_{arom}).

Bis{1-amino-1-[4-(4-propoxybenzoyloxy)phenyl]-oct-1-en-3-onato}copper(II) (Va). One drop of dimethylformamide and 0.3 ml (4.17 mmol) of thionyl chloride were added to a solution of 0.075 g (0.417 mmol) of 4-propoxybenzoic acid in 5 ml of methylene chloride. The mixture was heated for 1 h under reflux, and the solvent and excess thionyl chloride were distilled off under atmospheric pressure. For more complete removal of thionyl chloride and gaseous products, the residue was dissolved in 5 ml of methylene chloride, and the solvent was distilled off under reduced pressure. The residue, 4-propoxybenzoyl chloride, was dissolved in 5 ml of tetrahydrofuran, 0.4 ml (2.88 mmol) of triethylamine and 0.100 g (0.189 mmol) of enaminoketonate **IV** were added, the mixture was stirred for 2.5 h at 20°C, and 15 ml of chloroform and 15 ml of water were added. The organic phase was separated, and the aqueous phase was extracted with 10 ml of chloroform. The extract was combined with the organic phase, washed with 15 ml of water, and dried over sodium sulfate, the solvent was distilled off under reduced pressure, and the residue was recrystallized from chloroform–propan-2-

ol. Yield 0.112 g (69%), dark green needles. UV spectrum, λ_{max}, nm: 263, 328. IR spectrum, ν, cm^{-1}: in $CHCl_3$: 3355 (NH); 2955, 2930, 2870, 2855 (C–H_{aliph}); 1725 (C=O, ester); 1600, 1555, 1525, 1500, 1490 (C=O, C=C, C=C_{arom}); 1250, 1200, 1165, 1065 (C–O); in THF: 1735 (C=O, ester); 1635, 1600, 1555, 1520, 1490 (C=O, C=C, C=C_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.91 m (CH_3), 1.04 t (3H, CH_3, J = 7 Hz), 1.08–1.36 m, 1.83 sext (2H, CH_2, J = 7 Hz), 3.98 t (2H, OCH_2, J = 7 Hz), 6.88–6.98 m (2H, H_{arom}), 8.00–8.10 m (2H, H_{arom}).

Compounds **Vb**–**Vg** were synthesized following a similar procedure.

Bis{1-amino-1-[4-(4-butoxybenzoyloxy)phenyl]-oct-1-en-3-onato}copper(II) (Vb). Yield 87%. UV spectrum (dioxane), λ_{max}, nm: 263, 328. IR spectrum, ν, cm^{-1}: in $CHCl_3$: 3350 (NH); 3000 (C–H_{arom}); 2955, 2925, 2870 (C–H_{aliph}); 1725 (C=O, ester); 1595, 1550, 1500, 1490 (C=O, C=C, C=C_{arom}); in THF: 1730 (C=O, ester); 1595, 1550, 1490 (C=O, C=C, C=C_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.84–0.96 m (CH_3), 0.97 t (3H, CH_3, J = 7 Hz), 1.06–1.24 m, 1.44–1.56 m (2H, CH_2), 1.79 quint (2H, CH_2, J = 7 Hz), 4.02 t (2H, OCH_2, J = 7 Hz), 6.92 br.d (2H, H_{arom}, J = 7 Hz), 8.00–8.10 m (2H, H_{arom}).

Bis{1-amino-1-[4-(4-pentyloxybenzoyloxy)phenyl]oct-1-en-3-onato}copper(II) (Vc). Yield 73%. UV spectrum, λ_{max}, nm: 262, 330. IR spectrum, ν, cm^{-1}: 3345 (NH); 2945, 2920, 2855 (C–H_{aliph}); 1715 (C=O, ester); 1590, 1550, 1520, 1495, 1485 (C=O, C=C, C=C_{arom}); 1240, 1200, 1155, 1055 (C–O). ^{1}H NMR spectrum, δ, ppm: 0.93 t (3H, CH_3, J = 6.5 Hz); 0.84–1.00 m (3H, CH_3); 1.04–1.28 m, 1.32–1.48 m, and 1.80 quint (2H, CH_2, J = 6.5 Hz), 4.01 t (2H, OCH_2, J = 6.5 Hz), 6.88–6.98 m (2H, H_{arom}), 8.00–8.10 m (2H, H_{arom}).

Bis{1-amino-1-[4-(4-hexyloxybenzoyloxy)phenyl]oct-1-en-3-onato}copper(II) (Vd). Yield 73%. UV spectrum, λ_{max}, nm: 268, 330. IR spectrum, ν, cm^{-1}: 3345 (NH); 2940, 2915, 2850 (C–H_{aliph}); 1720 (C=O, ester); 1590, 1550, 1520, 1500, 1490 (C=O, C=C, C=C_{arom}); 1240, 1200, 1155, 1055 (C–O). ^{1}H NMR spectrum, δ, ppm: 0.84–1.00 m (6H, CH_3); 1.04–1.24 m, 1.28–1.40 m, and 1.46 m (2H, CH_2); 1.80 m (2H, CH_2); 4.01 t (2H, OCH_2, J = 6 Hz), 6.88–6.98 m (2H, H_{arom}), 8.00–8.10 m (2H, H_{arom}).

Bis{1-amino-1-[4-(4-heptyloxybenzoyloxy)phenyl]oct-1-en-3-onato}copper(II) (Ve). Yield 80%. UV spectrum, λ_{max}, nm: 262, 330. IR spectrum, ν, cm^{-1}: 3345 (NH); 2940, 2920, 2850 (C–H_{aliph}); 1720 (C=O, ester); 1590, 1550, 1525, 1495, 1490 (C=O, C=C, C=C_{arom}); 1245, 1200, 1160, 1055 (C–O). ^{1}H NMR spectrum, δ, ppm: 0.88 t (3H, CH_3, J = 7 Hz), 0.80–1.00 m (CH_3), 1.08–1.40 m and 1.45 m (2H, CH_2), 1.80 quint (2H, CH_2, J = 6 Hz), 4.01 t (2H, OCH_2, J = 6 Hz), 6.87–6.98 m (2H, H_{arom}), 7.97–8.16 m (2H, H_{arom}).

Bis{1-amino-1-[4-(4-octyloxybenzoyloxy)phenyl]oct-1-en-3-onato}copper(II) (Vf). Yield 58%. UF spectrum, λ_{max}, nm: 262, 329. IR spectrum, cm^{-1}: 3340 (NH); 2915, 2850 (C–H_{aliph}); 1720 (C=O, ester); 1590, 1545, 1495, 1490 (C=O, C=C, C=C_{arom}); 1240, 1200, 1155, 1055 (C–O). ^{1}H NMR spectrum, δ, ppm: 0.88 t (3H, CH_3, J = 6.5 Hz), 0.84–0.98 m (3H, CH_3), 1.04–1.40 m and 1.45 m (2H, CH_2), 1.79 quint (2H, CH_2, J = 6.5 Hz), 4.01 t (2H, OCH_2, J = 6.5 Hz), 6.88–6.98 m (2H, H_{arom}), 8.00–8.10 m (2H, H_{arom}).

Bis{1-amino-1-[4-(4-nonyloxybenzoyloxy)phenyl]oct-1-en-3-onato}copper(II) (Vg). Yield 72%. UV spectrum, λ_{max}, nm: 262, 329. IR spectrum, ν, cm^{-1}: 3350 (NH); 2925, 2850 (C–H_{aliph}); 1725 (C=O, ester); 1600, 1550, 1525, 1500, 1490 (C=O, C=C, C=C_{arom}); 1260, 1200, 1160, 1060 (C–O). ^{1}H NMR spectrum, δ, ppm: 0.87 t (3H, CH_3, J = 6 Hz), 0.91 m (CH_3), 1.04–1.40 m and 1.45 m (2H, CH_2), 1.79 m (2H, CH_2), 4.01 m (2H, OCH_2), 6.88–6.98 m (2H, H_{arom}), 8.00–8.10 m (2H, H_{arom}).

1-Amino-1-[4-(4-propoxybenzoyloxy)phenyl]-oct-1-en-3-one (VI). Compound **Va**, 0.040 g (0.047 mmol), was dissolved in 5 ml of tetrahydrofuran, 0.5 ml of 5% hydrochloric acid was added, and the mixture was kept for 1 min and diluted with 30 ml of water. Chloroform, 20 ml, and a saturated aqueous solution of sodium hydrogen carbonate, 5 ml, were added, the organic phase was separated, and the aqueous phase was extracted with chloroform (2×10 ml). The extracts were combined with the organic phase and dried over sodium sulfate, the solvent was distilled off under reduced pressure, and the residue was applied to a column charged with silica gel. The column was eluted with ethyl–acetate–petroleum ether (1:4), and the eluate was evaporated under reduced pressure to isolate 0.036 g (97%) of enaminoketone **VI**. Phase transition temperatures, °C: heating: Cr 110 I; cooling: I 80 Sm*A* 61 Cr. UV spectrum, λ_{max}, nm: in MeOH: 263, 326; in THF: 255, 318. IR spectrum, ν, cm^{-1}: 3485, 3350–3100 (NH); 3000 (C–H_{arom}); 2955, 2930, 2875, 2860 (C–H_{aliph}); 1725 (C=O, ester); 1600, 1575, 1525, 1505, 1485 (C=O, C=C, C=C_{arom}); 1250, 1205, 1165, 1065 (C–O). ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, CH_3, J = 7 Hz), 1.06 t (3H, CH_3, J = 7 Hz), 1.27–

1.40 m (4H), 1.65 quint (2H, J = 7.5 Hz), 1.85 sext (2H, J = 7 Hz), 2.39 t (2H, J = 7.5 Hz) (CH_2), 4.01 t (2H, OCH_2, J = 7 Hz), 5.44 s (1H, 2-H), 6.97 d (2H, H_{arom}, J = 9 Hz), 7.27 d (2H, H_{arom}, J = 9 Hz), 7.61 d (2H, H_{arom}, J = 9 Hz), 8.13 d (2H, H_{arom}, J = 9 Hz), 5.18 br.s (1H), 9.94 br.s (1H) (NH_2).

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