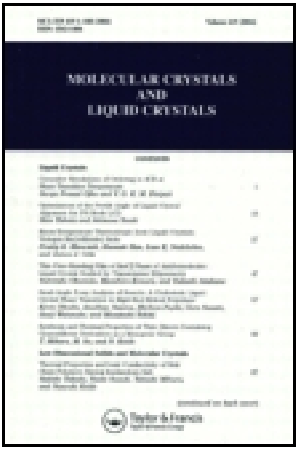

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Liquid Crystalline Complexes of Cu(II) and Pd(II) with Ferrocene-Containing Ligands

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Liquid Crystalline Complexes of Cu(II) and Pd(II) with Ferrocene-Containing Ligands

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The new liquid crystalline heteronuclear complexes Cu(II) **1a** and Pd(II) **1b** with a non-mesogenic ferrocene-containing β-enaminoketone $\mathbf{L_1}$ of the formula $C_5H_5FeC_5H_4$-C_6H_4-NH-C_2H_2-(CO)-$C_6H_4OC_{12}H_{25}$, showing monotropic nematic and smectic A phases, are studied. The *ortho*-palladated Cl-bridged dimeric complex **3** with a non-mesogenic ferrocene-containing Schiff's base $\mathbf{L_2}$ of the formula $C_5H_5FeC_5H_4$-C_6H_4-N=CH-$C_6H_4OC_{10}H_{21}$, forming a stable smectic A phase, has been synthesized. The novel mixed-ligand heteronuclear complexes **4–7** have been obtained by treatment of the *ortho*-palladated complex **3** with appropriate ligands. Some of the resulting products exhibit the rather low-melting (below 100 °C) smectic A phases. Structures of the compounds are studied by elemental analysis, ^1H and ^{13}C NMR, and ESR spectroscopies.

Keywords: metallomesogens; ferrocene derivatives; heteronuclear complexes; cyclopalladated complexes

INTRODUCTION

The interest in the synthesis and investigation of liquid crystal compounds containing transition metals has greatly increased during the last years[1-4].

This kind of mesogenic systems combines the optical and electrical behaviour of conventional liquid crystals with the magnetic and electronic properties of transition metal-containing complexes. Particularly the synthesis of mesogenic molecules which contain different kind of metal centers are attractive from this point of view. For instance, we have reported on the paramagnetic liquid crystalline heteronuclear complexes on the basis of ferrocene-containing ligand, and Cu(II), V(IV) and Fe(III) as second metal centers[5-7]. The strong antiferromagnetic interaction between metal centers have been observed in nematogenic μ-oxo-bridged Fe(III) complex with 6 iron atoms in a molecule[7].

Previously we have synthesized heteronuclear complexes which exhibited liquid crystallinity in a rather high-temperature range as well as relatively low-melting iron(III) complexes. Therefore the aim of this work was to synthesize new heteronuclear liquid crystalline compounds with improved temperature behaviour. In some cases the formation of coordination bonds leads to the increase of molecular anisometry and anisotropy of polarisability, and lead to mesogenic complexes from non-mesogenic ligands[8,9,12-14]. This factor was used in the present study for the design of low-melting heteronuclear mesogens.

In this contribution we report on the synthesis and thermal studies of the Cu(II) and Pd(II) complexes with ferrocene-containing enaminoketone and various cyclopalladated complexes on the basis of ferrocene-imine derivative.

EXPERIMENTAL

Synthesis

The 4-aminophenylferrocene was prepared according to a procedure described earlier[6] and used as starting material for a preparation of

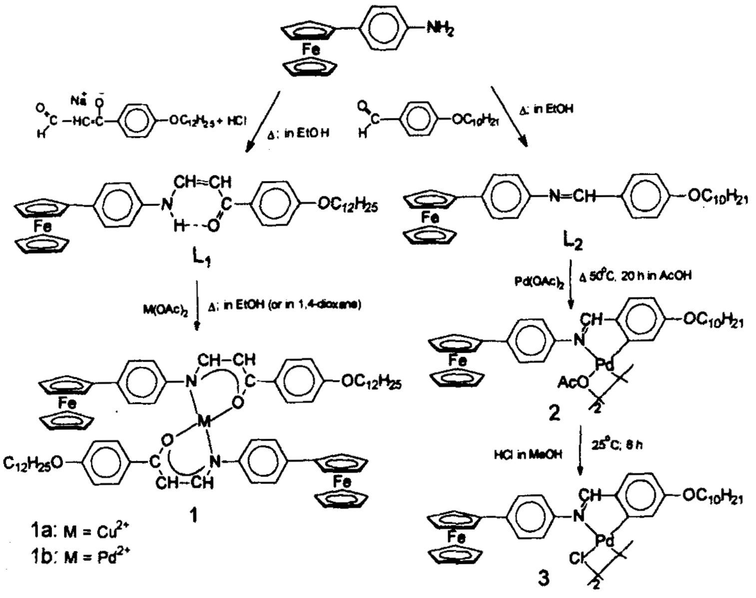

FIGURE 1 Scheme of the synthetic processes.

the ferrocene-containing ligands L_1 and L_2 (see Figure 1). Condensation of the 4-aminophenylferrocene in boiling EtOH during 15-20 minute with a commercially available 4-decyloxybenzaldehyde gave rise to the ferrocene-containing Schiff's base L_2. The ferrocene-containing β-enaminoketone L_1 was synthesized by treatment of the 4-aminophenylferrocene with a sodium salt of 2-(4'-dodecyloxybenzoil)acetaldehyde, the synthesis of which described elsewhere[8,10,11], in the presence of HCl in equimolar quantity. The syntheses of the 1-(4'-dodecyloxyphenyl)-3-(N-octadecylamino)-2-propenone -1 L_3 (see Figure 2) and N-octadecyl-4-dodecyloxysalicylidene-imine L_4 have been published[8,9]. The 4-dodecyloxysalicylidene-4'-imino-2',2',6',6'-tetramethylpiperidinyloxy L_5 was obtained by condensation of 4-

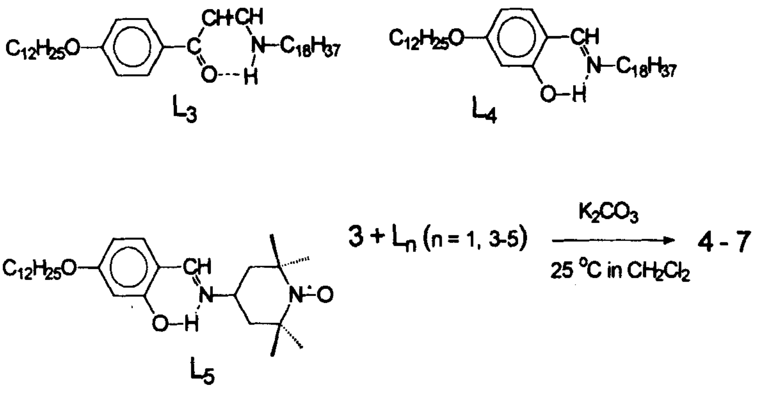

FIGURE 2 The chemical structures of the ligands **L_3**, **L_4** and **L_5**, and the common scheme of the syntheses of the mixed-ligand heteronuclear complexes **4-7**.

dodecyloxysalicylaldehyde with 4-amino-TEMPO in ethanol and filtering of precipitate.

The copper(II) complex **1a** (see Figure 1) was easily obtained by refluxing copper(II) acetate with the ligand **L_1** in ethanol during 15 minutes. The product was obtained as a light orange powder after filtering and drying. To prepare the palladium(II) complex **1b**, the ligand **L_1** in 1,4-dioxane was stirred for 20 minutes with a palladium(II) acetate. The product was precipitated by dilution with ethanol and then filtered. A light brown powder was gained after drying.

Cyclopalladation of the ligand **L_2** was carried out by stirring of palladium(II) acetate and the ligand **L_2** in a glacial acetic acid at 50 °C during 20 hours, similar to a procedure described elsewhere[12-15]. This led to the acetato-bridged dimer **2** which was isolated and dried as a brown powder. The chloro-bridged complex **3** was formed by treatment of the crude complex

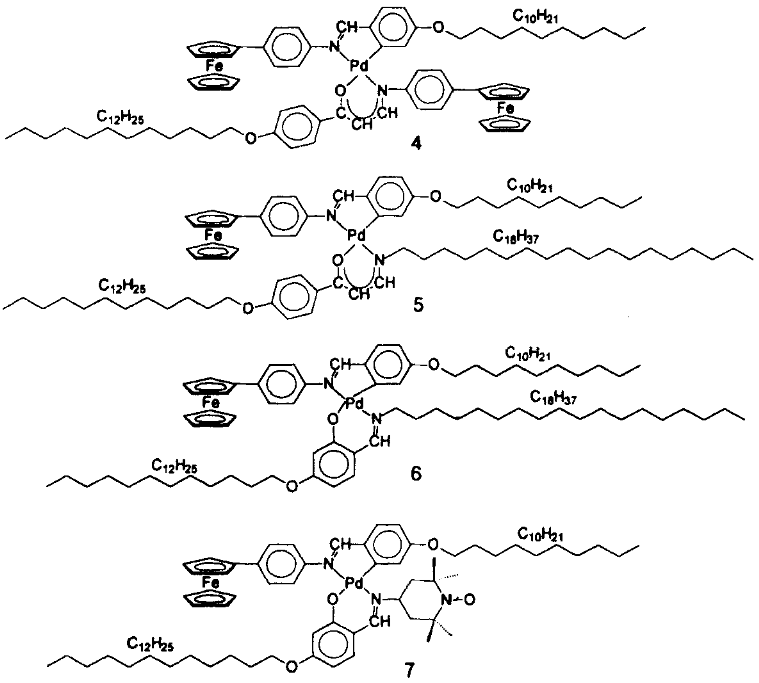

FIGURE 3 The chemical structures of the mixed-ligand heteronuclear complexes **4-7**.

2 in dichloromethane with equimolar quantity of HCl in methanol overnight at room temperature. The solvent was evaporated and residue was purified by column chromatography. An orange powder of the complex **3** was precipitated from a dichloromethane solution by dilution with ethanol.

The treatment of the complex **3** with appropriate ligands $\mathbf{L_n}$ (n=1, 3-5) in dichloromethane in the presence of anhydrous potassium carbonate (see Figure 2) gave rise to the complexes **4-7** of the structures illustrated in Figure 3. Potassium carbonate was removed by filtration, and the products were precipitated from a filtrate by ethanol. All of the products were obtained after filtering and drying as orange powders.

The elemental analysis data, ^{1}H and ^{13}C NMR, and ESR spectra of the synthesized compounds are in a full agreement with the proposed structures. ^{1}H and ^{13}C NMR spectra were recorded on «Varian UNITY-300» and ESR spectra were obtained on «Brucker ER-200 E-SRC» device.

Liquid crystalline behaviour

The liquid crystalline properties were investigated by thermal polarizing microscopy and differential scanning calorimetry.

RESULTS AND DISCUSSION

Chemical structure studies

The ^{1}H NMR spectra of the ligand $\mathbf{L_1}$ in $CDCl_3$ correspondent to an β-enaminoketone tautomer with an intramolecular hydrogen bond. The splitting of the N-H proton signal at 12.13 ppm into doublet by C-H proton of the ethene group is observed. This signal disappears in the palladium(II) complex **1b**, and protons of the ethene group afford two doublets at 5.63 ppm and 7.13 ppm, instead of a doublet at 5.99 ppm and doublet of doublets at 7.48 ppm in the spectrum of the ligand $\mathbf{L_1}$. There are few alterations in the ^{13}C NMR spectrum of the complex **1b** in comparison with that of the ligand $\mathbf{L_1}$, except the signal of C=O at 190.55 ppm in the ligand is shifted to 182.71 ppm in the complex.

The presence of copper(II) in the complex **1a** confers paramagnetic properties to it. ESR parameters of the complex **1a** (A_0=68 Oe, g_0=2.113; $A_{\|}$=161 Oe, $g_{\|}$=2.215) are close to the ESR parameters of other liquid crystalline copper(II) complexes with a square planar coordination site[5-7].

There are no essential differences in aspects of the ^1H NMR spectra of the cyclopalladated complexes **2** and **3**, in comparison with the well studied cyclopalladated imino-derivatives[12-15]. The acetato-bridged complex **2** was found as a mixture of the *trans* (94%) and inseparable *cis* isomer (6%). A ratio of the isomers was calculated from the relative intensities of the iminic proton signals in the ^1H NMR spectrum. Due to the «open book» structure of the compound **2**, diastereomeric OCH_2 protons of the alkoxy-chains give rise to two quartets at 3.52 and 3.74 ppm in the *trans* isomer. The Cl-bridged dimer **3** of a pure *trans* configuration has a planar structure according to its ^1H NMR spectrum.

Whereas the mixed-ligand complexes **4**, **5** according to their ^1H NMR spectra are pure N,N-*trans* isomers, the compounds **6** is a mixture of the N,N-*trans* and N,N-*cis* isomers in equal ratio. The comparable proton signals of the two isomers of the complex **6** have just equal integral intensities. The paramagnetic widening of signals are observed in the ^1H NMR spectrum of the complex **7**, and definite calculations of the isomers ratio is complicated. An approximate evaluation give about 30% of the *cis* isomer in the complex **7**.

The ligand $\mathbf{L_5}$ and heteronuclear complex **7** with nitroxyl radical were studied in a dichloromethane solution and in a solid by using ESR. Both of the compounds in a solid state have the ESR spectra with wide singlet (g_0=2.0057) due to the spin-spin interactions between molecules containing radicals. A triplet was observed in ESR spectra of the compounds in CH_2Cl_2 solution with the same g-factor for each of them. The complexation influences to the constants of hyperfine interaction only. The value of A is 14.9 Oe for the ligand $\mathbf{L_5}$ and 15.8 Oe for the complex **7**. Thus a free organic radical can be successfully introduced into a coordination compound.

Liquid crystalline properties

The phase transition temperatures of the synthesized compounds are summarized in Table 1.

It is worthy to note that none of the ligands L_n, used for the synthesis of the mesogenic heteronuclear complexes, exhibit mesogenic properties. The copper(II) complex **1a** with ferrocene containing β-enaminoketone L_1 show monotropic nematic behaviour. The nematic order appears after rapid cooling and persists in a glass state even at room temperature. A crystallization of the product occurs only either at very slow cooling from the isotropic liquid, or after second heating from the nematic state up to the transition N/I at 121 °C and keeping of the sample at near 130 °C during for some time. Thus the thermal behaviour of the complex **1a** is alike to multiple melting of the monotropic bis-(n-alkylxanthato)nickel(II) liquid crystals described by K.Ohta at al[16]. The analogous palladium(II) complex **1b** forms usual monotropic nematic and smectic A phases in a relatively high temperature range. Generally the phase transition temperatures of mesogenic palladium(II) complexes are higher in comparison with analogous copper (II) compounds[7].

The acetato-bridged cyclopalladated complex **2** with the ferrocene-containing Schiff's base L_2 is non-mesogenic, whereas the analogous Cl-bridged dimer **3** exhibits enantiotropic smectic A mesomorphism. Apparently the planar structure of the last compound is more preferable for the forming of liquid crystalline order. The DSC termogram of the complex **3** has a complicated aspect, but a more detailed study of the phase transitions on several heating-cooling cycles is hindered by decomposition of the compound after isotropization.

TABLE 1 **Transition temperatures (°C) of the ligands L_n (n=1-5) and heteronuclear complexes 1a, 1b and 2-7**

Compound	Phase behaviour
L_1	C 166 I
L_2	C 129 I
L_3	C 75 I
L_4	C 63 I
L_5	C 62 I
1a	C [121] N 144 I
1b	C [198] N [196] S_A 208 I
2	C 128 C_1 213 I
3	C 220 C_1 238 S_A 248 I
4	C 144 C_1 [138] S_A 174 I
5	C 48 S_A 115 I
6	C 39 S_A 75 I
7	G

The mixed-ligand complex **4** with two ferrocene moieties show monotropic smectic A phase. An inclusion of long n-octadecyl chain into molecules of the compounds **5** and **6** essentially lowers its transition temperatures. These mixed-ligand heteronuclear complexes exhibit enantiotropic smectic A mesomorphism in very close to room temperature range. The complex **7** with nitroxyl radical exists at room temperature as a non-textured glass, which softens at the higher temperature range. Though the complex **7** with organic radical is non-mesogenic, the synthesis and investigation of similar structures with potential mesogenic properties is of great interest. Both of NMR and ESR methods is available to investigate these compounds.

CONCLUSION

New series of low temperature heterometallic metallomesogens have been synthesized.

Acknowledgments

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