Organometallic Chemistry

Liquid-crystalline Cu^{II} and Pd^{II} complexes with nonmesogenic ferrocene-containing β-aminovinyl ketone

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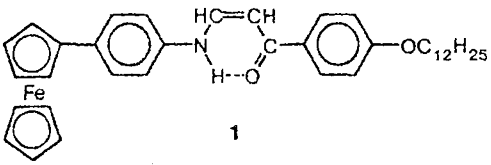
New liquid-crystalline heteropolynuclear complexes L_2M ($M = Cu^{2+}$ (**2a**), Pd^{2+} (**2b**)) were synthesized by the reactions of $C_5H_5FeC_5H_4-C_6H_4NH-C_2H_2-(CO)-C_6H_4OC_{12}H_{25}$ (**1**, LH) with copper(II) and palladium(II) acetates. Compound **2b** was found to possess monotropic nematic and smectic phases; **2a** exhibits the monotropic nematic phase and a phenomenon of "double melting." The compositions and structures of compounds **1** and **2a,b** were established by elemental analysis, ^1H and ^{13}C NMR, ESR, and IR spectroscopy.

Key words: ferrocene, coordination compounds, liquid crystals, metallomesogens.

An interest in metal-containing liquid crystals is continuously increasing due to their unique physical properties.[1-4] The magnetic, electric, and optical properties of metallomesogens are due precisely to metal atoms in their molecules. Liquid-crystalline systems with several different metal atoms in the molecule are of doubtless interest.

We have observed previously heteropolynuclear liquid-crystalline complexes of transition metals with ferrocene-containing Schiff bases.[5,6] In this work, we present the result of the synthesis and study of complexes based on the ferrocene-containing ligand **1**, in which the β-aminovinyl ketone fragment is the chelate-forming center.



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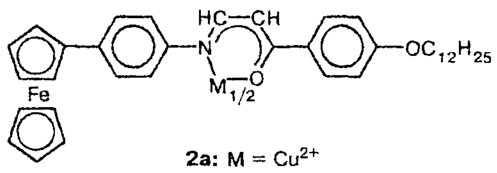

2a: $M = Cu^{2+}$
2b: $M = Pd^{2+}$

Ligand **1** was obtained by the reaction of the sodium salt of the enolic form of 4-dodecyloxybenzoylacetalde-

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hyde with 4-aminophenylferrocene in the presence of HCl. Complexes **2a** and **2b** were synthesized from ligand **1** and Cu^{II} and Pd^{II} acetates, respectively. The composition and structure of the compounds obtained were established from the data of elemental analysis, ESR, ^{1}H NMR, and IR spectroscopy.

The shapes of ^{1}H and IR spectra of ligand **1** correspond to the enaminoketone form; these data for the structure of analogous compounds have previously been discussed.[7] The IR spectrum of compound **1** contains frequencies of stretching vibrations of the N—H bond at 3315 and 3440 cm^{-1}, and the chemical shift of the signal of the proton of this group (~12 ppm) and its splitting on the proton of the adjacent vinyl fragment (~12 Hz) in the ^{1}H NMR spectrum are typical of the enaminoketone tautomer with the intramolecular hydrogen bond.

Complex **2a** has the ESR parameters characteristic of *trans*-planar-square Cu^{II} complexes (A_0 = 68 Oe, g_0 = 2.113; $A_{\parallel}$ = 161 Oe, $g_{\parallel}$ = 2.215).[6,7] During the complex formation, the frequencies of stretching vibrations of C=O (1655 cm^{-1}) and C=C of the vinyl fragment (1602 cm^{-1}) are shifted by 30—40 cm^{-1} to a long-wave region. Comparison of the ^{1}H NMR spectra of the ligand and complex **2b** shows that the signal of NH is absent in the spectrum of the complex, and the chemical shifts of protons of the benzene rings and the vinyl fragment are shifted downfield. The latter is explained by the disappearance of the descreening effect of the carbonyl group on these protons in the complex and by the presence of the donor metal atom localized closely. Complex formation affects the chemical shifts of signals in the ^{13}C NMR spectrum (Table 1) only for the carbonyl C atom, whose signal is shifted from 190.5 ppm in the ligand to 182.7 ppm in complex **2b**.

Although ligand **1** possesses no mesogenic properties, the monotropic nematic phase was observed by the study of complex **2a** on a polarization microscope. We observed an interesting phenomenon of "double melting," which has previously been described for other liquid-crystalline systems,[8] including liquid-crystalline ferrocene derivatives.[9,10] During first melting at 144 °C, the substance is transformed into an isotropic melt without formation of intermediate phases. After cooling to 122 °C, the transition to the nematic state was observed, which can easily be identified by the characteristic "schlieren"-texture. Upon further cooling, the substance is vitrified with no change in the texture. During the second heating to 122 °C, the sample again undergoes the transition to the isotropic liquid, and further heating of the sample with a rate of 0.1 °C min^{-1} results again in the formation of crystals. The crystallization is finished at 130—135 °C; then at 144 °C the substance is melted again as during the first heating. The behavior of the substance remains the same when the heating—cooling cycles are repeated.

The palladium(II) complex **2b** exhibits the monotropic nematic and smectic C phases. Melting to the isotropic melt is observed at 205 °C. When the melt is cooled, the nematic phase at 198 °C and the smectic C phase at 195 °C are successively formed. As in the case of the complexes with ferrocene-containing Schiff bases,[6] the Pd^{II} complex **2b** has higher temperatures of the phases transitions as compared to the Cu^{II} complex **2a**.

Experimental

The temperatures and types of phase transitions were determined on a polarization microscope with a heating table with automated temperature control. IR spectra were recorded in Nujol on a Specord IR-75 spectrometer. ^{1}H and ^{13}C NMR spectra in CDCl$_3$ were obtained on a Varian Unity-300 spectrometer. The ESR spectrum of the copper complex in polycrystalline samples was obtained on an RE-1306 spectrometer.

1-(4′-Ferrocenylphenylamino)-2-(4″-dodecyloxybenzoyl)ethene (1). The sodium salt of the enolic form of dodecyloxybenzoylacetaldehyde (0.28 g, 0.8 mmol) was dissolved in ethanol (3 mL) with heating and addition of one—two droplets of water. A hot solution of aminophenylferrocene (0.22 g, 0.8 mmol) and an equivalent amount of concentrated HCl were added to the solution obtained. The reaction mixture was refluxed for 15 min and cooled. An orange precipitate that formed was filtered off. The product was recrystallized from a CHCl$_3$—EtOH (1 : 1) mixture. The yield was 0.31 g (65%), m.p. 166 °C. Found (%): C, 74.98; H, 7.63; N, 2.31.

Table 1. ^{13}C NMR spectra (CDCl$_3$) of ligand **1** and its complex with Pd^{II} (**2b**)

Compound	δ ^{13}C				
	Alkyl chains	Ferrocenyl group	Aromatic carbon atoms	Vinyl fragment	C=O
1	14.72, 23.37, 26.68, 29.60, 30.03, 30.28, 32.58, 68.82	66.83, 69.54, 70.25, 85.73	114.80, 116.85, 127.90, 129.94, 132.43, 135.20, 139.00, 162.76	94.03, 144.68	190.5, 5.0
2b	14.82, 23.38, 26.70, 29.86, 30.05, 30.33, 32.60, 68.85	66.86, 69.58, 70.29, 85.79	114.82, 116.86, 127.94, 129.96, 132.44, 135.21, 139.01, 162.76	94.01, 144.69	182.7, 1.0

$C_{37}H_{45}FeNO_2$. Calculated (%): C, 75.11; H, 7.67; N, 2.37. IR (CCl_4), ν/cm^{-1}: 3440, 3315 (N—H), 1659 (C=O), 490, 479 ($C_5H_5FeC_5H_4$). ^1H NMR ($CDCl_3$), δ: 0.88 (t, 3 H, CH_3, J = 6.10 Hz); 1.20—1.50 (m, 18 H, CH_2); 1.80 (m, 2 H, $C\underline{H}_2CH_2O$); 4.01 (t, 2 H, CH_2O, J = 6.10 Hz); 4.05 (s, 5 H, C_5H_5Fe); 4.31 (br.s, 2 H, C_5H_4Fe); 4.61 (br.s, 2 H, C_5H_4Fe); 5.99 (d, 1 H, C=CH—CO, J = 7.93 Hz); 6.93 (d, 2 H, C_6H_4N, J = 8.54 Hz); 7.02 (d, 2 H, C_6H_4CO, J = 7.93 Hz); 7.43 (d, 2 H, C_6H_4N, J = 8.54 Hz); 7.48 (dd, 1 H, C=CH—N, J_1 = 7.93 Hz, J_2 = 12.21 Hz); 7.93 (d, 2 H, C_6H_4N, J = 8.54 Hz); 12.13 (d, 1 H, NH, J = 12.21 Hz).

Copper(II) bis[1-(4′-dodecyloxyphenyl)-3-(4″-ferrocenylphenylimino)-propen-1-olate-1] (2a). A mixture of ligand **1** (0.12 g, 0.2 mmol) and copper(II) acetate (0.02 g, 0.1 mmol) was boiled in ethanol for 10 min. An orange precipitate that formed was filtered off, washed with ethanol, and dried *in vacuo* to obtain the substance in 88% yield (0.11 g). Found (%): C, 71.65; H, 7.06; N, 2.17. $C_{74}H_{88}CuFe_2N_2O_4$. Calculated (%): C, 71.40; H, 7.12; N, 2.25. IR (CCl_4), ν/cm^{-1}: 1604 (C=O), 537, 517, 446 (Cu—O, Cu—N), 492, 477 ($C_5H_5FeC_5H_4$).

Palladium(II) bis[1-(4′-dodecyloxyphenyl)-3-(4″-ferrocenylphenylimino)-propen-1-olate-1] (2b). Ligand **1** (0.12 g, 0.2 mmol) and palladium(II) acetate (0.02 g, 0.1 mmol) in 1,4-dioxane (5 mL) were stirred at 80—85 °C for 30 min. A light-brown precipitate that formed was filtered off, washed with ethanol, and dried *in vacuo* to obtain the substance in 63% yield (0.08 g). Found (%): C, 68.89; H, 6.97; N, 2.23. $C_{74}H_{88}Fe_2N_2O_4Pd$. Calculated (%): C, 69.03; H, 6.89; N, 2.17. IR (CCl_4), ν/cm^{-1}: 1608 (C=O), 611, 549, 441 (Pd—O, Pd—N), 488, 479 ($C_5H_5FeC_5H_4$). ^1H NMR ($CDCl_3$), δ: 0.89 (t, 3 H, CH_3, J = 6.10 Hz); 1.20—1.50 (m, 18 H, CH_2); 1.60—1.70 (m, 2 H, $C\underline{H}_2CH_2O$); 4.08 (t, 2 H, CH_2O, J = 6.10 Hz); 4.08 (s, 5 H, C_5H_5Fe); 4.32 (t, 2 H, C_5H_4Fe, J = 1.83 Hz); 4.64 (t, 2 H, C_5H_4Fe, J = 1.83 Hz); 5.63 (d, 1 H, C=CH—CO, J = 6.71 Hz); 6.47 (d, 2 H, C_6H_4CO, J = 8.92 Hz); 6.79 (d, 2 H, C_6H_4CO, J = 8.92 Hz); 7.13 (d, 1 H, C=CH—N, J = 6.71 Hz); 7.25 (d, 2 H, C_6H_4N, J = 8.31 Hz); 7.45 (d, 2 H, C_6H_4N, J = 8.31 Hz).

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