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THE ESR STUDY OF COMPLEXATION AND NANOCLUSTERS GROWTH IN SILVER–LIQUID CRYSTAL SYSTEM

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The ESR spectrum of Ag-5CB (C_5H_{11}-C_6H_4-C_6H_4-CN) and Ag-5Py (C_5H_{11}-C_5H_3N-C_6H_4-CN) co-condensate film at 90 K showed two doublet lines due to silver atoms included in π-complexes with cyanobiphenyls and wide anisotropic singlet line with g-factor equal to 2.0030, that could be referred to small silver clusters. It was found the integral intensity of doublet lines decreased during the annealing of samples in temperature range 80–200 K due to thermal decomposition of Ag-5CB complex followed by the aggregation of silver atoms.

Keywords: metallomesogens; nanoclusters; cryosynthesis; ESR

INTRODUCTION

Metal atom chemistry, which studies the interactions between metal atoms and organic components, has developed rapidly in recent years [1,2]. Reactions of metal atoms and organic mesogen molecules are of particular interest due to the possibility of formation of anisotropic metal-mesogenic nanostructures [3] and synthesis of novel liquid crystalline materials [2]. The goal of this work is to obtain ESR-spectrum of new new metall-mesogen complexes: silver - 4-pentyl-4′-cyanobiphenyl(5CB) and silver-4-pentyl-4′-cyanophenylpyridine(5Py), to determine temperature interval of complex stability and to study the kinetics of thermal decomposition of these complexes.

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EXPERIMENT

Silver containing cyanobiphenyl and cyanophenylpyridine film samples ($1 = 20$–$50\,\mu m$) were obtained by reagent's vapors co-condensation on the cooled surfaces of quartz under molecular beam conditions. Metal vapor was prepared by resistive heating of the bulk metal over temperature range 1100–1200 K, organic components were evaporated under resistive heating at 380–390 K. During co-deposition, the temperature of quartz surface was held by liquid nitrogen at 80 K.

Metall/ligand ratio was estimated with the aid of chemical analysis with dithizon reagent [4], and varied from 1:10 to 1:100 (mol/mol).

The ESR spectroscopic studies of the samples were carried out in situ, in vacuum, using special vacuumed cryostat [5]. ESR-spectra were recorded on a "Rubin" ESR-spectrometer at 3 cm band with 100 kHz high frequency modulation.

Thermal behavior of samples obtained was studied in the temperature range 90–200 K, due sample temperature was maintained within ± 1K interval.

RESULTS AND DISCUSSION

The ESR-spectrum of silver-5CB co-condensate film at 80 K (Fig. 1) consists of two doublet lines (A and B parts on Fig. 1). The properties of this signal is: $g(Ag^{107}) = 2{,}001$; $a(Ag^{107}) = 485$ G; $a(Ag^{109}) = 2{,}003$;

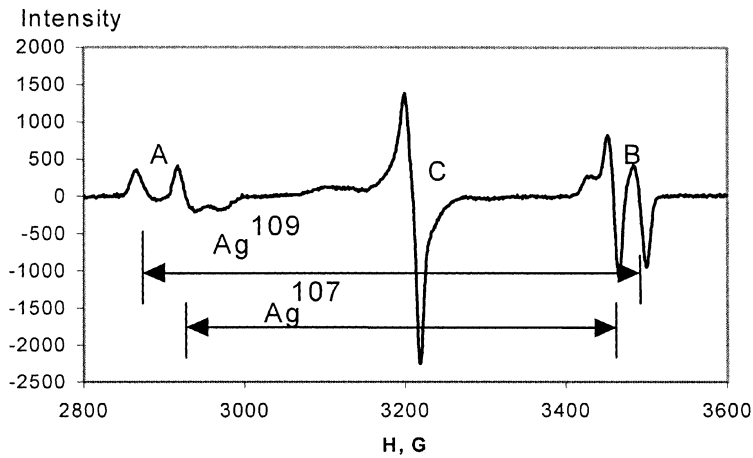

FIGURE 1 Typical ESR-spectrum of Ag-5CB co-condensate sample at 80 K.

$a(Ag^{109}) = 557{,}5$ G. The a(Ag)-values obtained in present work in comparison for silver atoms isolated in inert matrices [6] allowed us to estimate the s-electron spin density on silver in Ag-5CB complexes: $\rho_M = 0{,}77$. This value is characteristic for metal atom π-complexes and shows the electron density donation from silver atom to the π*-orbital of ligand molecule. There is also the central wide anisotropic singlet line in the spectrum (C part on Fig. 1). This line could be referred to non-valent silver atom aggregates or small clusters [6]. The aggregation of silver atoms and/or small clusters via complex decomposition and formation of silver nanosize metal particles could cause this line appear.

The ESR-spectrum of silver-5Py co-condensate film at 80 K showed there is only wide anisotropic singlet in the center of spectrum. However, at the higher amplification, two doublet lines (arrows on Fig. 2) can be seen too.

The integral intensity of doublet lines irreversible decreased during the annealing of samples in temperature range 80–200 K. At higher temperatures doublet lines disappeared at all. The intensity and singlet line shape reversible changed by the annealing of samples and were completely repaired when temperature was rise down.

Typical kinetics curve of the thermal decomposition of Ag-5CB complex at temperature 100 K is presented at Figure 3. It was shown the kinetics during thermal decomposition of silver-cyanobiphenyl complex is anomalously retarded at temperatures below 110 K. At temperatures above 120 K the reaction rate obey common 1st order kinetic law.

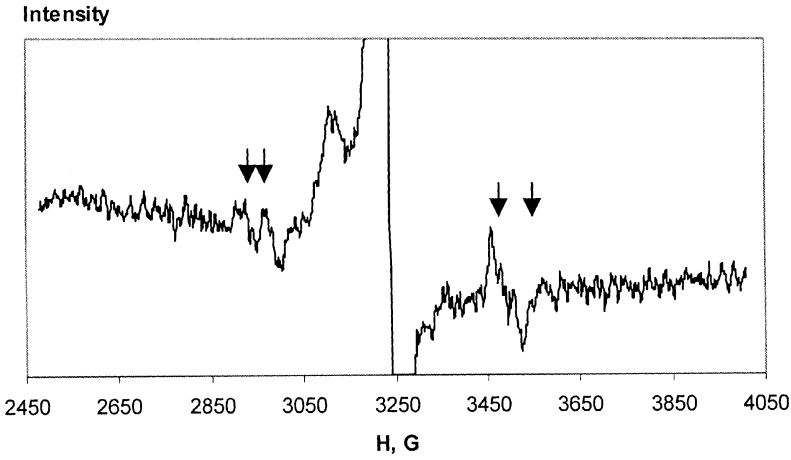

FIGURE 2. Typical ESR-spectrum of Ag-5PY co-condensate sample at 80 K and high amplification.

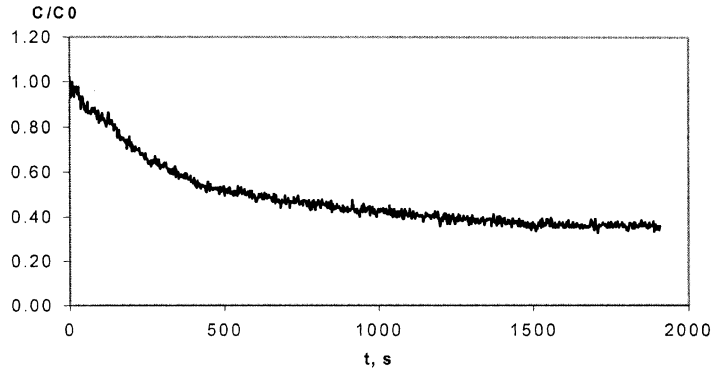

FIGURE 3 Kinetics of thermal decomposition of Ag-5CB complex at temperature 100 K.

TABLE 1 Reaction Rate Constants for Thermal Degradation of Ag-5CB Complex at Different Temperatures

T, K	k_{min}, c^{-1}	k_{max}, c^{-1}
100	$(5{,}0 \pm 0{,}1)\cdot10^{-5}$	$(3 \pm 1)\cdot10^{-3}$
105	$(9{,}6 \pm 0{,}1)\cdot10^{-5}$	$(2 \pm 1)\cdot10^{-3}$
110	$(2{,}80 \pm 0{,}08)\cdot10^{-4}$	$(4 \pm 1)\cdot10^{-4}$
115	$(5{,}94 \pm 0{,}06)\cdot10^{-4}$	
120	$(6{,}74 \pm 0{,}06)\cdot10^{-4}$	

Assuming reaction rate constant distribution is taking place [7] minimal and maximal values of rate constants have been calculated (Table 1).

CONCLUSIONS

Silver-containing cyanobiphenyl and cyanophenylpyridine mesogenic systems were obtained by low temperature co-condensation of metal and organic component vapors under molecular beam conditions. ESR-spectroscopic study of these films showed the formation of labile silver-CB π-complex with 0,23 electron donation from silver to p-system of ligand. It was shown the complex is stable only at temperature below 90 K. There At temperature range 90–110 K thermal decomposition of complexes is strongly retarded and above 120 K the reaction rate obey 1st order kinetic law.

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