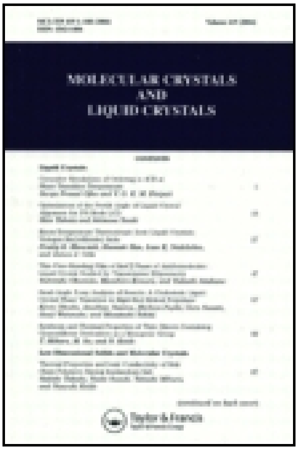

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Copper Atom Interaction with Mesogenic Cyanobiphenyls in Solid Co-Condensates

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Copper Atom Interaction with Mesogenic Cyanobiphenyls in Solid Co-Condensates

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New metal-mesogenic systems based on copper and mesogenic cyanobiphenyls 5CB and 8CB have been produced by low temperature co-condensation of their component vapors. The formation of low temperature complexes of copper atoms with the cyanobiphenyl π-system in the solid state at 80–150 K was shown by ESR- and UV-Vis spectroscopic data. The thermal stability of the complexes and their thermal behavior on warming of the co-condensate samples up to room temperature are discussed.

Keywords: copper; cryosynthesis; low temperature ESR-spectroscopy; metal-mesogens

INTRODUCTION

Metal-containing mesogenic compounds can be considered as a special type of nanostructured system [1]. The introduction of metals in the liquid crystalline system can lead to the appearance of new mesophases [2–3], growth of anisotropic nanoparticles and formation of highly ordered metal-mesogenic nanostructures [4], and the synthesis of new materials with special electric and magnetic properties [5]. In the present work, the specific interactions in low temperature copper – 4-pentyl-4′-cyanobiphenyl (5CB) solid co-condensate films were studied by ESR and UV-Vis-spectroscopy.

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EXPERIMENTAL SECTION

Preparation and study of the samples were performed in a special vacuum cryostat [4]. Copper-containing cyanobiphenyl film samples were obtained by co-condensation of the reagent vapors on the cooled surfaces of calcium fluoride and quartz under molecular beam conditions. Metal vapor was prepared by resistive heating of bulk copper over the temperature range 1300–1400 K, mesogenic cyanobiphenyl: 4-pentyl-4-cyanobiphenyl (5CB) and 4-octyl-4-cyanobiphenyl (8CB) were evaporated at 380–390 K under vacuum (10^{-4} Torr). The ESR spectra were registered on the X-band ESR spectrometer (model P-1307) with modified electronic scheme using a special cryostat for ESR spectroscopy supplied by moving vacuum connection [6]. All equipment was functioning under a computer programme suite in OS-2 Warp 4.0 operating system. The values of the microwave frequency and the magnetic field were measured by frequency divider and gaussmeter, respectively. The UV-VIS spectra were obtained on a "Specord M-40" spectrometer (Carl Zeiss Jena, Germany), using a special cryostat for optical spectroscopy [4].

The samples were prepared at 77 K. Then the temperature was raised up to 200 K in 10 K steps, and ESR and UV-VIS spectra were recorded at each annealing step. To compensate for the temperature dependent changes, ESR spectra were recorded at two temperatures: at annealing temperature and after re-cooling to 77 K. In both cases, high precision sample temperature control was used, which allowed us to support the temperature value in ±1 K intervals.

After ESR and UV-VIS investigation of the samples, they were removed from the cryostat and the concentration of the metal was determined by photometry chemical analysis; the accuracy of metal quantitative determination is in (±10%) interval.

RESULTS AND DISCUSSION

The ESR spectra of copper-cyanobiphenyl (Cu/5CB and Cu/8CB) co-condensate samples obtained at 77 K consist of at least two signals. One is the quartet signal (marked as A on Figure 1) due to copper-cyanobiphenyl π-complex structure formation. The other is a narrow, almost isotropic, signal at 3250 G (marked as B) with g-factor close to the value for a free electron $g_e = 2.0032$, which can be considered due to the conducting electron spin resonance of copper nanoclusters. Signal A has a strong anisotropy with perpendicular hyperfine splitting (HFI) constant of approximately 28 G. These relatively small HFI constant values and strong signal anisotropy pointed to a p-type

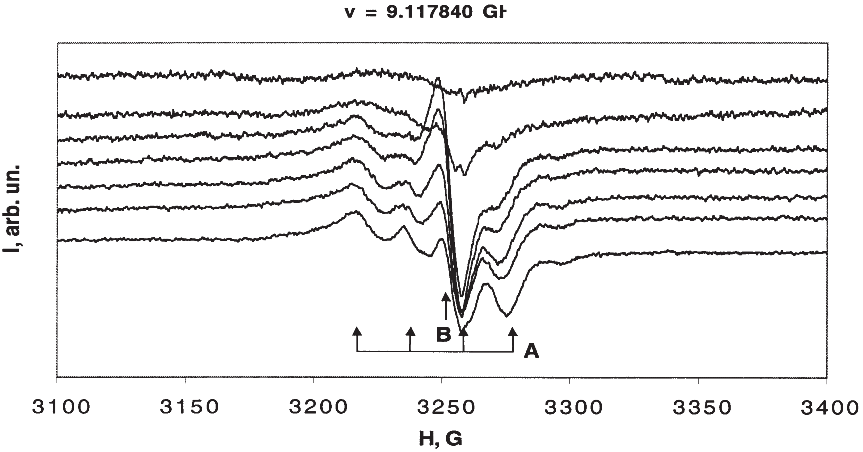

FIGURE 1 ESR spectra of copper-5CB co-condensate film at different temperatures, from bottom to top 77 K, 108 K, 120 K, 140 K, 150 K, 182 K, 200 K.

of semi-occupied orbital localized on the copper atom. In this suggestion the value of anisotropic HFI interaction constant was $B = 51$ MHz. Comparing this value with $B_0 = 386$ MHz for the electron occupied p-orbital of the copper atom [7], the unpaired electron density on the $4p_z$ copper orbital can be estimated as 0.13. The process of electron promotion from the "s" to "p" copper orbital is known for bi-ligand π-complexes of zero-valence copper [7].

The relative intensity of signals A and B depends on the reagent condensation rate and on the copper/cyanobiphenyl (M/CB) ratio (Fig. 2). The more copper that is contained in the sample, the stronger feature B is. In the samples with low copper concentration, the feature A became dominant in the spectrum.

During annealing of the samples in the temperature range of 100–140 K the intensity of multiplet signal A decreased and the intensity of the narrow singlet B increased simultaneously, due to copper/5CB complex decomposition and copper atom aggregation with metal nanocluster formation. At temperatures higher than 170 K the intensity of the central signal irreversibly decreased due to the copper nanoclusters further aggregation in the cyanobiphenyl matrix.

In UV-VIS spectra of co-condensates of copper and 5CB (Fig. 3) there were two absorbance bands at 430 and 620 nm. These bands disappeared and a new absorption band at 490–520 nm appeared when the temperature became higher than 160 K. This region is also characteristic for absorption of the copper nanocluster [7].

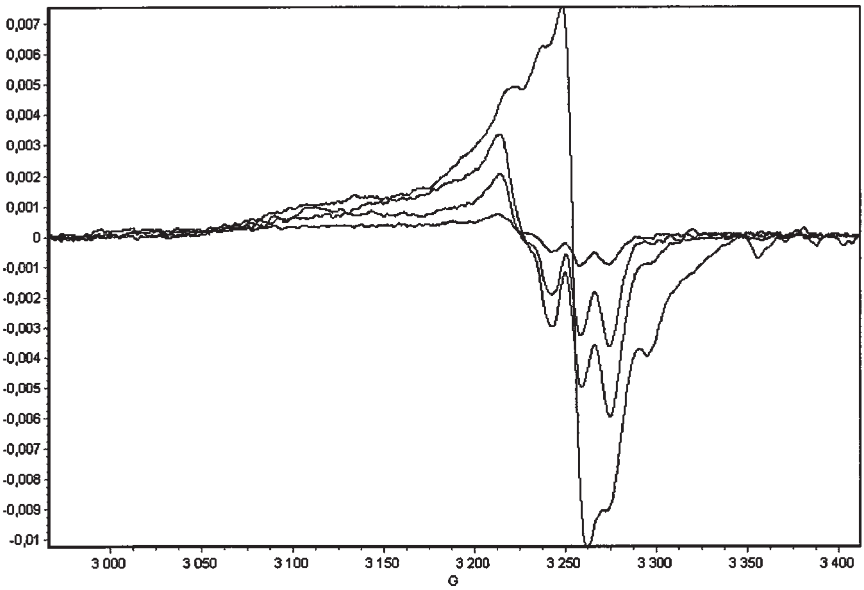

FIGURE 2 ESR spectra of the samples with different metal to ligand ratios (M/L) from bottom to top for the left part of spectra: M/CB = 0.001, 0.01, 0.03 and 0.1.

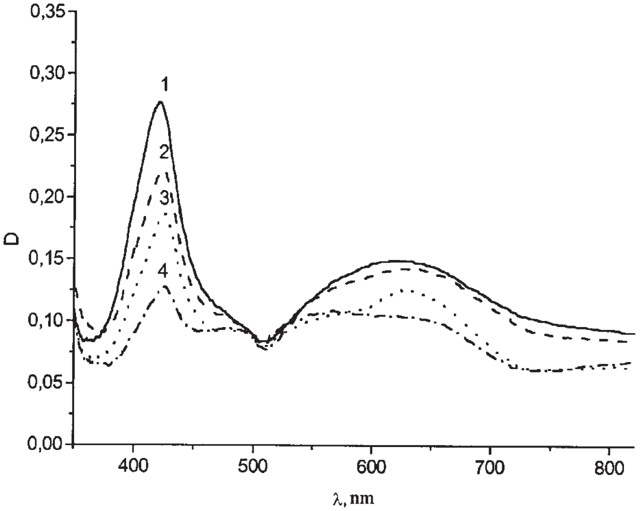

FIGURE 3 UV-VIS spectra of Cu/5CB co-condensates during annealing in temperature range 80–180 K: 1–80 K, 2–120 K, 3–180 K, 4–200 K. (The base spectrum of the neat cyanobiphenyl film is subtracted from the original co-condensate spectra.)

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