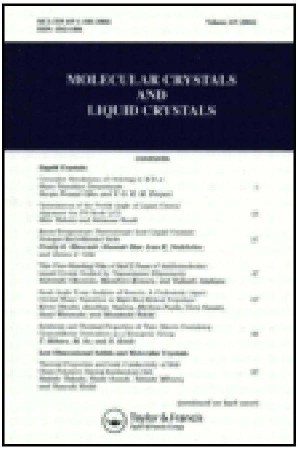

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Spectroscopic Study of Silver-Containing Mesogenic Cyanobiphenyls in Solid Phase

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Silver-containing mesogenic alkylcyanobiphenils (CB): C_nH_{2n+1}-C_6H_5-C_6H_5-CN, where n=5 (5 CB), 7 (7 CB), and 8 (8 CB) systems were obtained by low temperature co-condensation of metal and organic component vapours. The formation of low *temperature* Ag-CB complexes was shown by IR-, UV-visible and ESR techniques. Thermal degradation of the complexes led to the formation of nanosize (15–30) silver particles and their further aggregation in anisotropic matrices.

Keywords: metallomesogens; nanostructures; cryosynthesis

INTRODUCTION

Metal atom chemistry, which studies the interactions between vaporised metal atoms and organic component at low temperatures, has developed rapidly in recent years [1,2]. Reactions of transition metal atoms and organic mesogen molecules are of particular interest because of formation anisotropic metal-mesogenic nanostructures and synthesis of novel liquid crystalline materials. These materials have been shown to exhibit technically interesting properties such as nonlinear optical and special electrophysical properties [3]. Here the search of new metal-mesogenic systems via low

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temperature co-deposition of metal and mesogenic cyanobiphenyls vapours is presented.

EXPERIMENTAL

Silver containing cyanobiphenyl film samples (l=20-50 μm) were obtained by reagent vapour co-condensation on the cooled surfaces of special spectral cryostats under molecular beam conditions [4]. We used the quartz, KBr or CaF_2 spectral windows for transmission UV-vis and IR-spectroscopy and polish copper cube for reflection IR- spectroscopy studies. Metal vapour was prepared by resistive heating of the bulk metal over temperature range 1100-1200 K, cyanobiphenyl components were evaporated under resistive heating at 380-390 K.

Metal/ligand ratio was estimated with the aid of special calibration procedure of the evaporation cells and varied from 1:1 to 1:100. Triple silver-cyanobiphenyl-decane systems were obtained by reagent vapours co-deposition with decane added in 10-100 molar excess .The IR , UV-vis and ESR spectroscopic studies of the samples were realized in situ , in vacuo, using special spectral cryostats [4,5]. The IR spectra were recorded on a Specord 75 IR spectrometer in reflection mode and on a Specord M80 spectrometer in transmission mode over the range 4000-400 cm^{-1}. The UV-vis. spectra were recorded in transmission mode with a Specord M40 instrument in the region 200-900 nm (50000-11000cm^{-1}). ESR-spectra were recorded on a Rubin ESR-spectrometer at 3 cm band with 100 kHz high frequency modulation.

RESULTS AND DISCUSSION

At the first stage we have made the IR-spectroscopic study of silver/cyanobiphenyl co-condensates of different metal-to-ligand ratio (from 1:1 to 1:100) in temperature range 80-300 K.. The IR-study of Ag-/5 CB and Ag/5CB/decane (iso-octane) systems of different components ratio varied from 1:1 to 1:50 and from 1:1:10 upto 1:1:100 at low temperatures shows the existence of Ag-5 CB complexes due to Ag interaction with π-electronic system of CB molecules [6]. It was indicated by the appearance of two new bands in the region of CN-stretching vibrations at 2030 and 2080 (2130) cm^{-1} . The shift of about 100 cm^{-1} to lower frequencies is similar to π-complexes of zero-valent transition metal complexes with π-molecules [7,8]. We also recorded the appearance of a new band at 650-660 cm^{-1} and considered it as metal-ligand vibrations [9]. Similar results were obtained for higher CB homologies. It was shown that Ag-CB complexes are stable only at low temperatures and degrade upon heating upto 200 K.

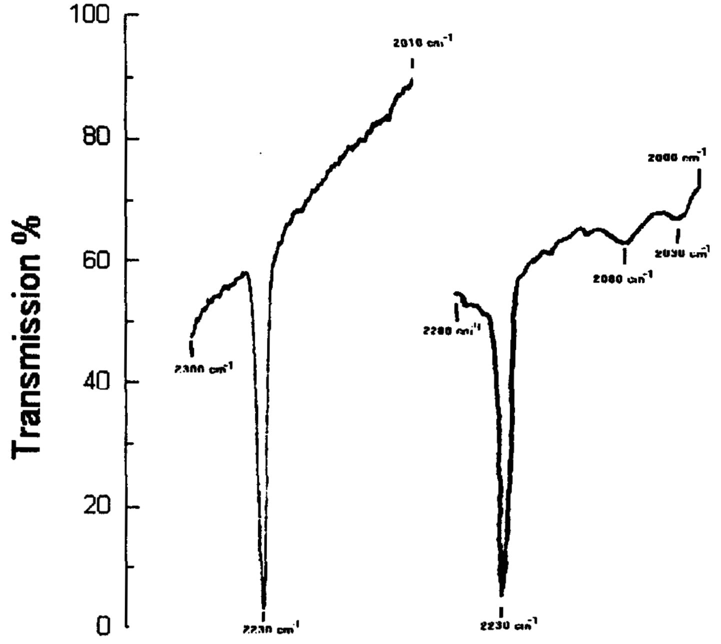

FIGURE 1. IR-spectrum of Ag-5CB co-condensate(right) and of neat 5CB film (left) in CN-stretching region, l=20 μm, T=90 K,

The complete ab initio geometry optimization and vibrational analysis on the base of quantum chemistry calculations was performed for the 5CB molecule and for its most important fragment, cyanobenzene PhCN.[10] The structure is very close to that predicted by the density functional calculations.[11,12]. Then a series of calculations has been carried out for the sandwich-like complex $Ag(PhCN)_2$ at majority of geometry parameters fixed and the analysis of electron density distributions as well as the curvatures of the potential energy surfaces along the C-N coordinates.[10] The GAMESS quantum chemistry package and the conventional Stevens-Bash-Krauss (SBK) pseudopotentials on all heavy atoms with the corresponding basis sets have been employed [10]. Then the structure presented in Figure 2 have been considered as a model for the silver-cyanobenzene π-complex ,that is according to the x-ray investigations[13-14] of the cyanobiphenyl molecules arranged in the films in pairs by the "head-to-tail" principle.

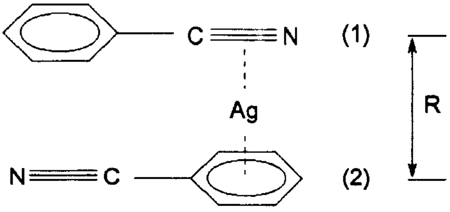

FIGURE 2. Model for the silver-cyanobenzene complex.

The system possesses the planar symmetry with the silver atom placed at equal distances from the ligands, namely, from the center of CN fragment of ligand (1) and from the center of the ring of ligand (2). In calculations, almost all the geometry parameters have been fixed at the values of the free PhCN molecule, the distance R between the planar ligands (1) and (2) has been varied. Pilot calculations showed that two Hartree-Fock solutions could compete for the ground state, one corresponded to the $(PhCN)_2Ag$ and another to the charge-transfer $(PhCN)_2^-Ag^+$ configurations. At large R (R > 4.7 A), the neutral silver atom is embedded into the cavity between the ligands, the charge-transfer $(PhCN)_2^-Ag^+$ configuration dominates at R < 4.7 A. This observation is confirmed by the direct calculations of the natural electronic charges on the fragments of the complex: Ag, PhCN (1) and PhCN (2). In the case of charge-transfer complex (R=4.4 A) the simulated red shifts in the CN vibrations (-150 and -175 cm^{-1}) correlate well with the observed experimentally for the Ag/5CB films (-150 and -200 cm^{-1}).

The ESR-spectrum of silver-5CB co-condensate film at 80 K showed two dublet lines: $g(Ag^{107})$=2.001 , $a(Ag^{107})$= 48.5 mT and $a(Ag^{109})$=2.003, $a(Ag^{109})$=72.75 mT. The a(Ag)-values obtained for co-condensate spectra in comparison with the a(Ag)-values for silver atoms isolated in inert matrices [15,16] allowed us to estimate the s-electrons spin density on silver in Ag-CB complexes: ρ_M=0.77. This value is characteristic for metal atom π-complexes and shows the electron density donnation from silver atom to the π*-orbital of ligand molecule. There was also the central wide anisotropic singlet line with g-factor close to 2.003 in the experimental spectra, that could be reffered to non-valent silver atoms aggregates or small clusters complexes.

UV-vis spectroscopic study of silver/CB and silver/CB/decane systems at 80 K showed (Figure 3, curve 1) the appearance of new absorbance band with maximum at 340 nm due to pale-yellow colour of co-condensate films.

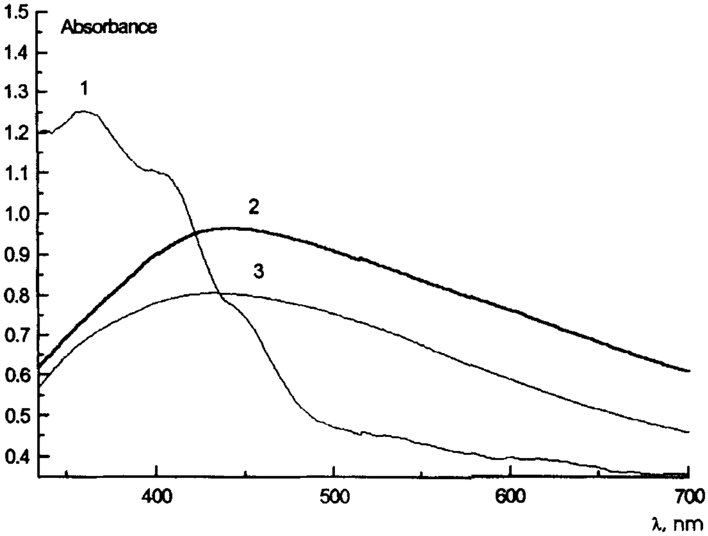

FIGURE 3. UV-vis spectra of Ag/ 5CB/n-decane (1:1:10 w/w/w) co-condensate film: 1 - T=80K, 2- T=200 K, 3- T=300 K (l=2.μm)

This band disappeared at 200 K (Figure3, curve2) and the new wide band with maximum at 440 nm was detected . It could be caused by the aggregation of silver atoms and/or small clusters via complexes decomposition and formation of silver nanosize metal particles. Further heating of the film samples led to red shift of this band maximum (Figure3, curve 3), that could be connected as with rising of the size of metal particles and also with producing of the anisotropic metal particles in liquid-crystalline mesophase at room temperatures. Silver-5CB samples encapsulated in poly-para-xylylene polymeric films were obtained under vacuum conditions using special cryostat supplied with the inlet for xylylene monomer injecting into the system. TEM picture of the samples obtained show two kinds of metal particles stabilized in the matrix: globes of about 15-30 nm in size and anisotropic rod-like particles of more than 100 nm in length. UV-Vis spectra of the film samples at room temperature showed the broad absorbance at 450-600 nm. Thus silver atoms/small clusters stabilized at low temperatures via π-interactions with CB molecules can aggregate at higher temperatures in anisotropic matrix.

CONCLUSIONS

Silver-containing cyanobiphenyl mesogenic systems were obtained by low temperature co-condensation of metallic and mesogenic component vapours under molecular beam conditions.The combination of the results of IR-, UV-vis. and ESR-spectroscopic study of silver-cyanobiphenyl co-condensate films and triple co-condensates with inert matrix component – decane (iso-octane) showed the formation of labile silver-CB π-complexes at low temperatures. Thermal degradation of the complexes by annealing of the samples at 200-300 K led to the formation of nanosize (15-30 nm) silver particles and to their further aggregation in anisotropic matrices resulted in production of anisotropic metal-mesogenic nanostructures.

ACKNOWLEDGEMENTS

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