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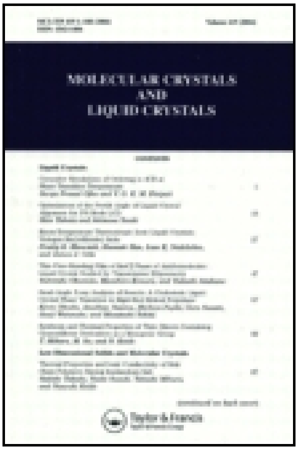

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The ESR-Study of Chemical Interactions in Triple Solid 'Ag-CCl_4-5CB' Co-Condensate Mesogenic System

Tatyana I. Shabatina [a] , Yurii N. Morosov [a] , Vadim A. Timoshenko [a] & Gleb B. Sergeev [a]

[a] Lomonosov Moscow State University, Department of Chemistry, Moscow, Russia

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The ESR-Study of Chemical Interactions in Triple Solid ‘Ag-CCl_4-5CB’ Co-Condensate Mesogenic System

Tatyana I. Shabatina
Yurii N. Morosov
Vadim A. Timoshenko
Gleb B. Sergeev
Lomonosov Moscow State University, Department of Chemistry,
Moscow, Russia

The possibilities of new metal-mesogenic complex formation and their solid phase chemical reactions have been demonstrated using low temperature co-condensation techniques and ESR-spectroscopy for a solid triple system, containing silver, the mesogenic ligand 4-pentyl-4-cyanobiphenyl (5CB) and an alternative electron-acceptor ligand or the third reactive component carbon tetrachloride (CCl_4). It was shown by ESR-spectroscopy that the existence of four paramagnetic products were stabilised in the system at low temperatures: silver atom π-complex with two cyano-biphenyl molecules, silver atom σ-complex with cyanobiphenyl molecule stabilised by CCl_4 co-ligand, $AgCl^- CCl_3\bullet$ and silver nanoclusters, formed by silver atom aggregation in the mesogenic matrix. The relative thermal stability of these silver species and their thermal behavior are discussed.

Keywords: carbon tetrachloride; ESR spectroscopy; metal mesogens; silver complexes; three-phase solid

INTRODUCTION

Nowadays the possibilities of the use of supramolecular organised systems for production of highly ordered nanosystems are an attractive root for investigators in the fields of nanochemistry and nanotechnologies [1–5]. The mesogenic matrices possessing diversely molecular organised phases in the solid and liquid crystalline states are of great

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Address correspondence to Tatyana I. Shabatina, Lomonosov Moscow State University, Department of Chemistry, 119992 Moscow, Russia. E-mail: tsh@kinet.chem.msu.ru

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interest for synthesis of anisotropic metal nanoparticles and their highly ordered assemblies [6–7]. In the present work, the specific features of mesogenic ordering effects on the processes of metal atom aggregation and on the chemical interactions of metal species of different aggregation size were studied for the example of silver atoms and silver nanoclusters interacting with carbon tetrachloride in the low temperature mesogenic matrix of 4-pentyl-4-cyanobiphenyl.

EXPERIMENTAL

Triple silver and carbon tetrachloride (CCl_4) containing 4-pentyl-4-cyanobiphenyl (5CB) samples ($l = 20–50\,\mu m$) were obtained by low temperature co-condensation of reagent vapors and the mesogenic component on the cooled surface of a quartz tube under molecular beam conditions. The component ratio ($Ag/CCl_4/5CB$) was varied from 1:1:100 to 1:10:100. The metal content in the sample was determined by photometry analysis. Condensation rates of the silver and cyanobiphenyl components were chosen at 5×10^{13} and 4×10^{15} molecule/cm^2 s values, respectively, in order to minimize metal atom aggregation. The condensation rate of CCl_4 was determined by the value of its saturated vapor pressure at a given temperature and was varied from 1×10^{14} to 1×10^{15} molecule/cm^2 s.

The ESR-spectroscopic studies of the samples obtained in the temperature range 77–350 K were made *in situ* under vacuum conditions using a specially constructed cryostat supplied with reagent inlets and a vacuum moving connection [8]. The construction of this cryostat allows us to record ESR-spectra of the samples both during the co-condensation process and during the sample warm up to room temperature. The cryostat was also supplied by sample temperature maintaining set up within ±1 K interval. The ESR spectra of the samples obtained were recorded using a digital 3-cm band ESR spectrometer “Rubin” SEPR-1307 with 100 kHz modulation and a modified electronic scheme. All equipment was operated under a computer program suite in OS-2 WARP 4.0 operating system.

RESULTS AND DISCUSSION

The specific interactions in the binary mesogenic silver – 4-pentyl-4-cyanobiphenyl (Ag-5CB) system were studied by us previously [8,9]. It was shown that the formation of a paramagnetic π-complex of silver atoms (^{107}Ag and ^{109}Ag) with $J = 1/2$, was revealed in the spectra as two doublet lines. The structure was proposed to include two cyanobiphenyl molecules arranged in a head-to-tail manner [10]. The spectra

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of co-condensate samples showed also a central singlet line of complex shape with g-factor close to the free electron value of $g_e = 2{,}0032$, and that this belonged to the conducting electrons spin resonance signal (CEPR) for silver nanoclusters also formed in the system. Such signals were detected also for silver and copper co-condensates with different inert matrix compounds [11–12]. There was a distribution in cluster sizes for such systems and the singlet line represents the superposition of a number of CEPR-signals with isotropic Lorentz line shape belonging to metal clusters of a definite size.

Typical ESR-spectra of triple Ag-CCl$_4$-5CB solid co-condensates with different composition at 77 K are presented in Figure 1. The spectra possess complex line shapes, which changed by varying the CCl$_4$ content of the sample. This fact indicates the existence of ESR signals of several types. First, one can see two doublet lines and a central singlet line, which are characteristic of binary Ag-5CB systems and their relative intensities do not depend upon the CCl$_4$ content. One of these paramagnetic species belongs to silver atoms included in the Ag-5CB complex structure and the other to metal nanoclusters. The relative intensity of doublet lines of the metal atom complexes decreases in the triple Ag-CCl$_4$-5CB system by on increase of the CCl$_4$ content in the sample.

The nature of the other paramagnetic centers can be clarified by the experiments on the cyclic annealing of the samples. Each sample was heated up to a definite temperature and then cooled down to 77 K. ESR-spectra of the system were recorded at each step of the process. Typical spectra for the three systems with different CCl$_4$ content are presented in Figures 2–4. The analysis of the data obtained allowed us to identify four main components. Two of them, both existing in triple and binary systems, have been mentioned in the previous section. Two doublet lines at higher and lower magnetic fields with $g_{iso} = 1.9995$ and $A_{iso}(Ag^{109}) = 641\,G$, $A_{iso}(Ag^{107}) = 558\,G$, belonged to silver atoms included in the Ag-5CB complex structure and disappeared at 150 K due to complex thermal degradation. The other is a central signal with g-factor close to the free electron value of $g_e = 2{,}0032$ due to metal nanocluster formation. The line shape of this signal is less anisotropic, and that can be due to the narrower size distribution in the case of the triple system. Its relative intensity grew over the temperature range 90–150 K due to effective aggregation of metal atoms escaping into the mesogenic matrix free volume during complex degradation. The integral intensity of this signal did not change on heating of the system up to 200 K, and then abruptly drops at 210 K due to the further aggregation of silver nanoclusters and formation of higher metal particles not detected by the ESR technique.

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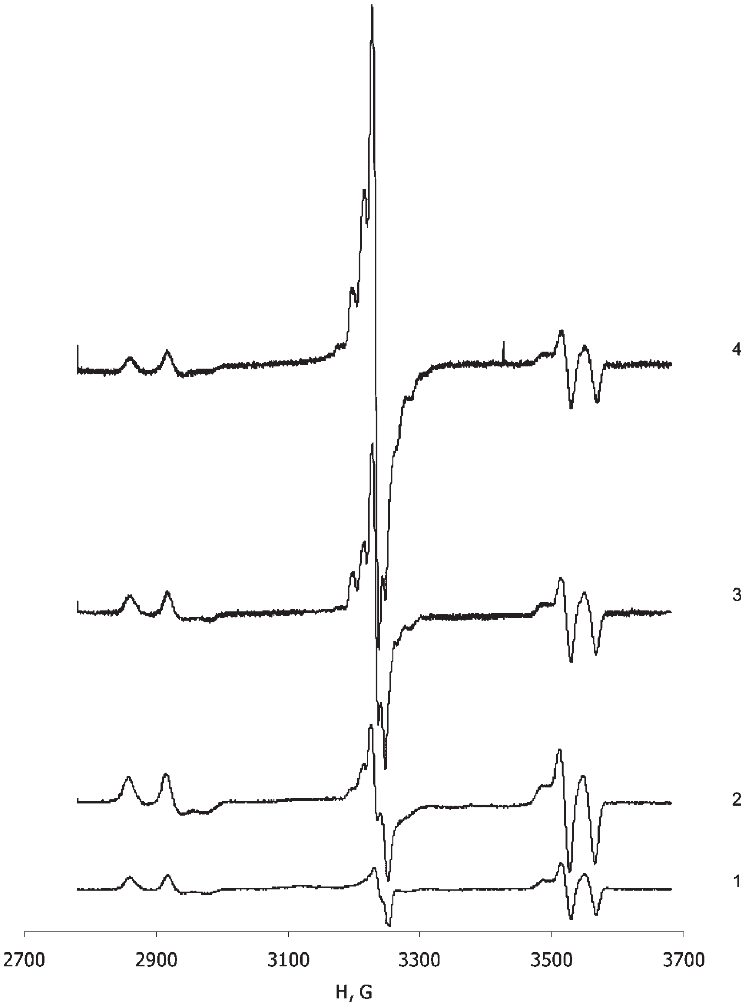

FIGURE 1 The ESR spectra of the samples of triple system Ag-CCl_4 – 4-n-pentyl-4′-cyanobiphenyl obtained during low temperature vacuum cocondensation, containing different proportion of the components: 1-1:0:100, 2-1:1:100, 3-1:3:100, 4-1:10:100.

There are two new signals in the triple Ag-CCl_4-5CB system not detected in the binary Ag-5CB system. One is an anisotropic doublet line with g-factor close to 2,0025. The intensity of this signal increased as the CCl_4 concentration rose in the sample and by increasing the temperature of the sample up to 120 K. The same signal was detected

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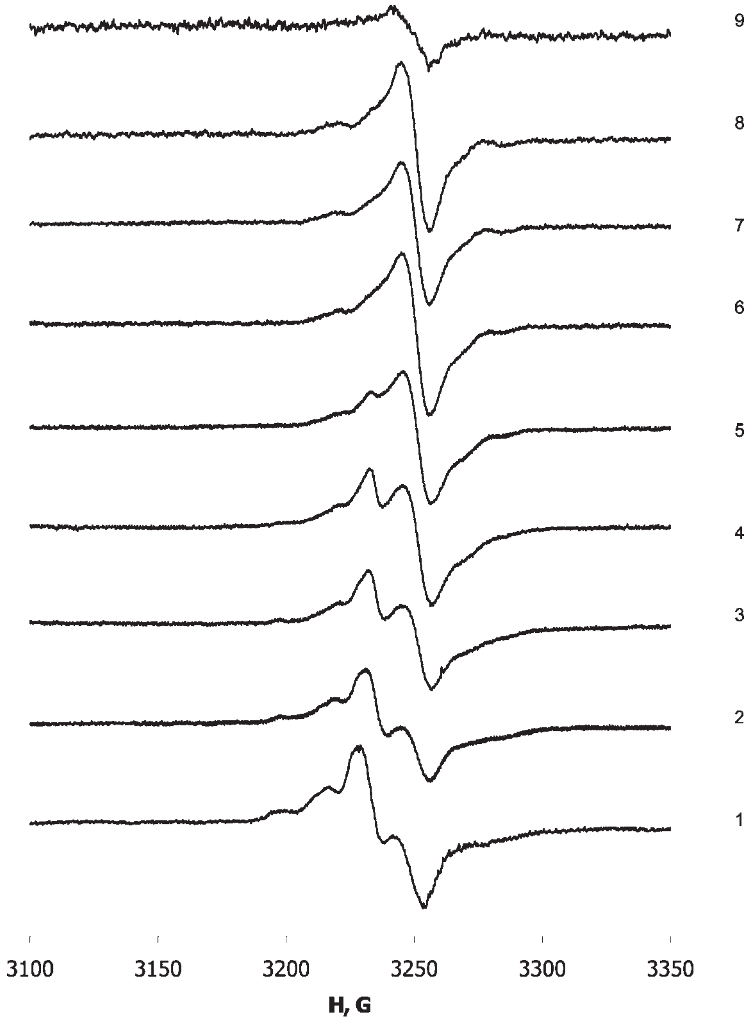

FIGURE 2 The ESR spectra of sample of triple system Ag-CCl$_4$ – 4-n-pentyl-4′-cyanobiphenyl (1:1:100), obtained during vacuum cocondensation, registered after heating to a new temperature: 1–77 K, 2–100 K, 3–120 K, 4–140 K, 5–160 K, 6–180 K, 7–190 K, 8–200 K, 9–210 K.

in the experiments on co-condensation of silver with CCl$_4$. The identity of this spectrum for binary and triple systems, and its axial symmetry, allows us to refer it as superposition of CCl$_3$• radical and the ion-radical pair AgCl$^-$ CCl$_3$•. The signal disappeared at 150–160 K.

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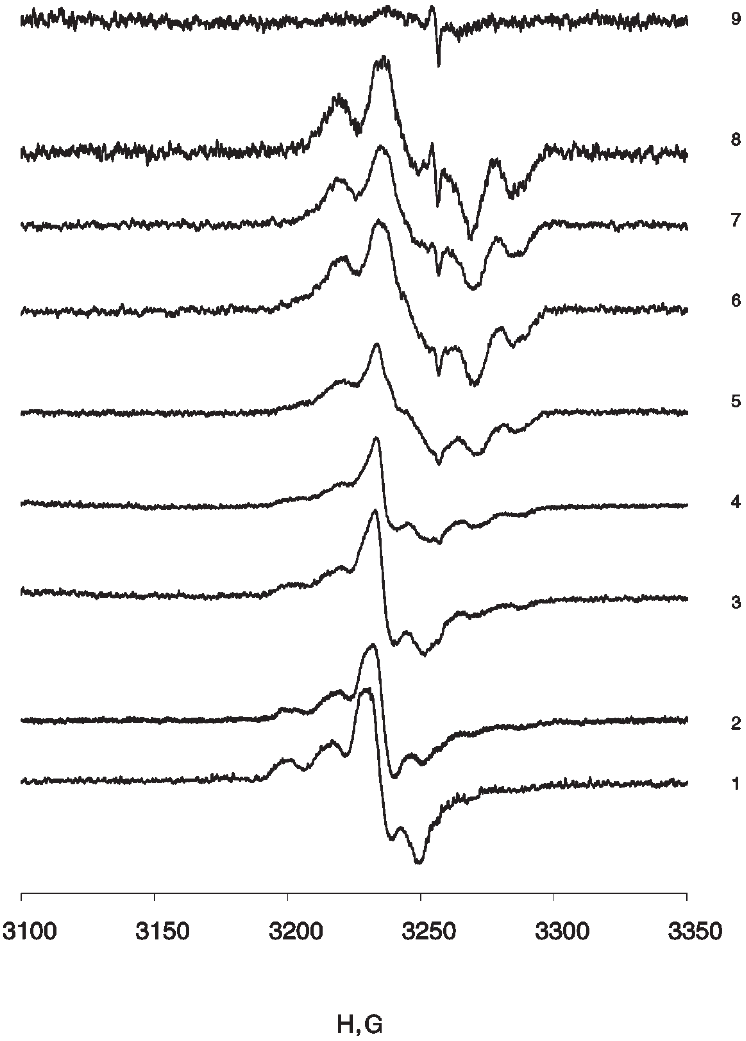

FIGURE 3 The ESR spectra of sample of triple system Ag-CCl_4 – 4-n-pentyl-4′-cyanobiphenyl (1:3:100), obtained during vacuum cocondensation, registered after heating to a new temperature: 1–77 K, 2–100 K, 3–120 K, 4–140 K, 5–160 K, 6–180 K, 7–190 K, 8–200 K, 9–210 K.

The last signal is a feature only for the triple Ag-CCl_4-5CB system and does not register for binary Ag-CCl_4 or Ag-5CB co-condensates. It is a singlet with complex line shape stable up to 200 K. This signal is the only paramagnetic species for the triple systems with

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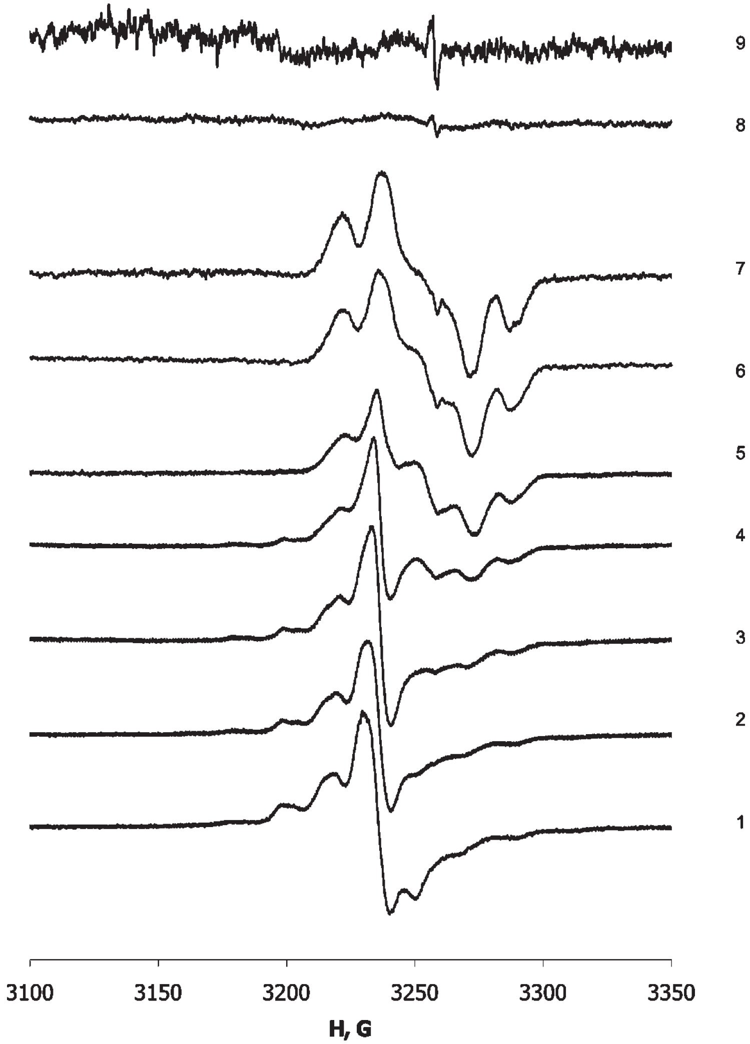

FIGURE 4 The ESR spectra of sample of triple system Ag-CCl$_4$ – 4-n-pentyl-4′-cyanobiphenyl (1:10:100), obtained during vacuum cocondensation, registered after heating to a new temperature: 1–77 K, 2–100 K, 3–120 K, 4–140 K, 5–160 K, 6–180 K, 7–190 K, 8–200 K, 9–210 K.

Ag/CCl$_4$/5CB ratio of 1:3:100 and 1:10:100 at 190 K. It can be described as an anisotropic signal with hyperfine interaction (HFI) of a single unpaired electron with silver nuclei (J = 1/2). We have proposed the formation of a σ-complex of silver atoms with two different ligands 5CB and CCl_4. Computer modeling of this spectrum allows us to obtain the parameters of the anisotropic spin-Hamiltonian: $g_{xx} = 1.9880$; $g_{yy} = 2.0063$; $g_{zz} = 2.0192$ and $A_{xx}(Ag) = 16.65$; $A_{yy}(Ag) = 13.72$; 13.72; $A_{zz}(Ag) = 18.09$. Almost axial symmetry of the g- and A-tensors allowed us to conclude the formation of a linear 5CB-Ag-CCl_4 σ-complex structure due to the interaction of a silver atom with a lone electron pair of the N-atom of the CN-group in the 5CB ligand molecule.

CONCLUSIONS

The triple Ag-CCl_4-5CB systems, of different reagent ratios varied from 1:1:100 to 1:10:100, were studied by the ESR-technique over the temperature range 77–350 K. The competitive formation of silver atom complexes of the π-type with two cyanobiphenyl molecules and the σ-type with two different ligands 5CB and CCl_4, dependent upon the concentration of the last component in the system, was demonstrated. The thermal behavior of the complexes was considered and the higher stability of the σ-complex structure was established. The formation of nanosize metal clusters and the $AgCl^- \, CCl_3\bullet$ ion-radical pair was shown also for the triple Ag-CCl_4-5CB system and also for the binary Ag-5CB and Ag-CCl_4 systems, respectively.

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