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Interaction of lanthanide atoms with 4-pentyl-4′-cyanobiphenyl in low-temperature condensates

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The complexes Ln·2L are formed from metal atoms at 4–30 K, whereas an increase in the metal concentration (M/Ar > 10^{-4}) and temperature (80–210 K) results in the complexes 2Ln·2L (Ln = Sm, Eu; L = 4-pentyl-4′-cyanobiphenyl).

A number of complexes of lanthanide(0) atoms with aromatic ligands have been obtained cryochemically.[1,2] These complexes have sandwich structures. This study expands the scope of such compounds using a non-traditional ligand, 4-pentyl-4′-cyanobiphenyl (5CB), which has functional groups capable of complexing. In addition, this compound has mesogenic properties, *i.e.*, possesses a nematic liquid crystalline mesophase.

The following mesogenic compounds containing lantanides are known: complexes with Shiff bases, phthalocyanines, porphyrins and diketones.[3] Such compounds differ from other metal mesogens in high magnetic susceptibility and high magnetic susceptibility anisotropy due to the high spins of lanthanide atoms. However, the complexes of mesogenic molecules with lanthanide atoms in zero oxidation state have not been known.

Low-temperature co-condensation of vapours makes it possible to obtain complexes of mesogenic compounds with metals. For example, the existence of $M(5CB)_2$ and $M_2(5CB)_2$ complexes with the mesogenic 5CB ligand was shown by spectroscopic methods for samarium and europium (M); the structures of these complexes contain one and two metal atoms, respectively.[4–7] In order to reveal the mechanism of formation of these complexes, we carried out this study using matrix isolation of ligand molecules and metal particles in argon in the temperature range 4–30 K.

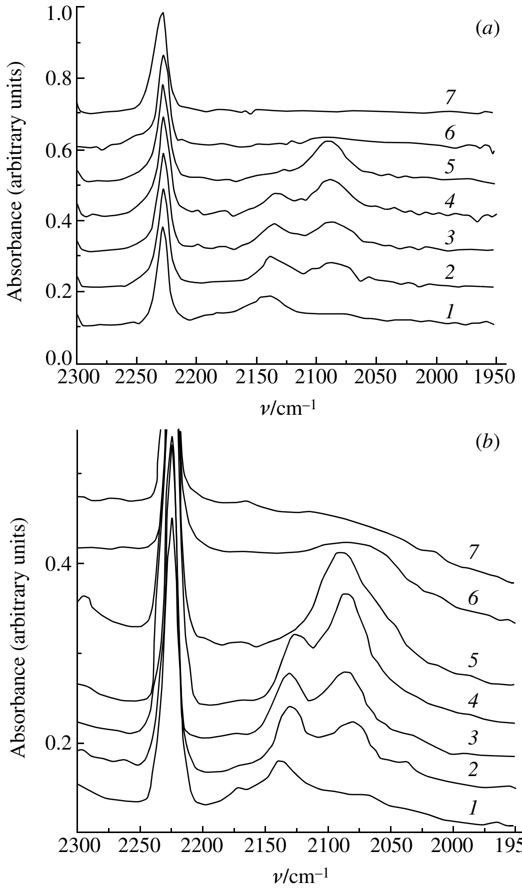

Figure 1 IR spectra of Ln/5CB co-condensates (1:10 mol/mol) at different temperatures. (*a*) Sm/5CB (*1*) 95, (*2*) 183, (*3*) 193, (*4*) 203, (*5*) 213, (*6*) 223 and (*7*) 273 K. (*b*) Eu/5CB (*1*) 80, (*2*) 163, (*3*) 183, (*4*) 203, (*5*) 223, (*6*) 243 and (*7*) 273 K.

The Sm/5CB interaction in an argon matrix was studied by FT-IR spectroscopy using an FS-01 Fourier spectrometer (Russia). The main features of the set-up and the low-temperature experiment in the 4–30 K range were considered previously.[8–10] In this work, spectroscopic measurements were carried out with a resolution of 0.4 cm^{-1} in the range 4000–400 cm^{-1}. Argon and reagents were sputtered onto copper mirrors at 6 and 10 K. The effect of thermal radiation of the metal vaporizer on cryogenic matrices was minimised by water-cooled screens. The pressure in the vaporising block was $(1–2)\times10^{-4}$ Pa. The absolute intensities of the molecular flows of Sm, 5CB and Ar were determined using a low-temperature differential quartz microbalance.[8] The deposition rate of the metal was about $(1–7)\times10^{-7}$ mol s^{-1} m^{-2}, that of 5CB was $(4–7)\times10^{-6}$ mol s^{-1} m^{-2}, and that of argon was $(2.8–14)\times10^{-4}$ mol s^{-1} m^{-2}. Argon of 99.99% purity was used. The co-condensation time was 2400 s in all experiments.

Samples for studies at 77–300 K were obtained by co-condensation of reagent vapours onto CaF_2 glass cooled with liquid nitrogen in a special cryostat[4] in a vacuum (~10^{-2} Pa). In order to perform the interaction of reagent molecules on a cold surface and to exclude the reaction in the gas phase, condensation was carried out in the molecular beam mode.[4] The condensation rate was 4×10^{-6} mol s^{-1} m^{-2} for the ligands (L) and $(4–8)\times10^{-7}$ mol s^{-1} m^{-2} for europium and samarium. The condensation time was 300–3600 s. The evaporation temperatures were 850–900 K for Eu, 900–950 K for Sm and 380–390 K for 5CB. The Ln:5CB molar ratio was 1:5 to 1:20. The sample heating rate was 0.3 K s^{-1}. The IR spectra were recorded using Specord M80 and Specord 75 IR instruments in the range 2300–1900 cm^{-1}.

The formation and transformations of complexes were studied at various temperatures and metal/ligand ratios. In the general case, the interaction of a metal and a ligand in cryocondensates consists of competition between metal aggregation processes and complexation with the ligand.[11,12]

The IR spectra of Sm/5CB and Eu/5CB co-condensates with a molar ratio of ~1:10 at different temperatures are presented in Figure 1. The region of stretching vibrations of the CN group of 5CB contains two new bands (2135 and 2085 cm^{-1}) in comparison with the spectrum of the ligand. These bands were assigned to

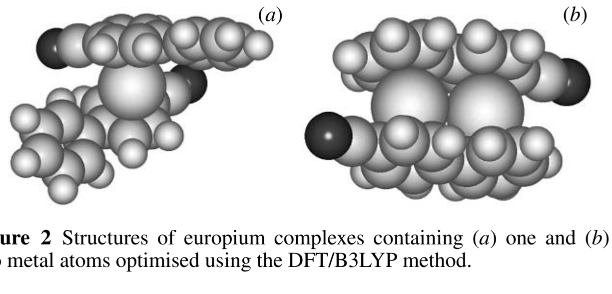

Figure 2 Structures of europium complexes containing (*a*) one and (*b*) two metal atoms optimised using the DFT/B3LYP method.

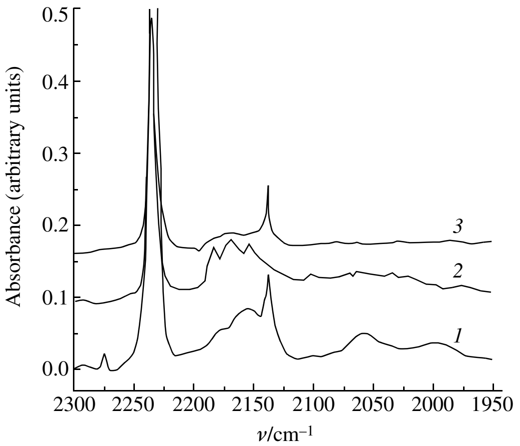

Figure 3 IR spectra of Sm/5CB/Ar co-condensates with different molar ratios at liquid helium temperatures. (*1*) 1:10:400, 6.5 K; (*2*) 1:24:5000, 10.5 K; (*3*) 1:33:10000, 10.5 K.

the low-temperature π-complexes of samarium and europium with 5CB: Ln·2L (complex I) and 2Ln·2L (complex II),[4] respectively. At 170–210 K, band I decreases, whereas band II simultaneously increases. Thus, the conversion of complex I to complex II was observed in the temperature range 95–210 K. When the temperature is further increased, both complexes decompose. The similarity of the spectral data and the temperature ranges of existence of bands for the Eu/5CB and Sm/5CB systems suggests that coordination mechanisms in the Eu/5CB and Sm/5CB systems are identical.

In turn, an assumption made allowed us to calculate the equilibrium geometry of complexes for europium as an example.[7] The 6-31G basis was selected for hydrogen atoms; effective core potentials (ECP) were used for all heavy atoms (Stuttgart RSC 1997 ECP for europium atoms and Stuttgart RLC 1997 ECP for carbon and nitrogen atoms), the corresponding basis was selected for each of the atoms.[7] The calculation confirmed the formation of two sandwich complexes, *viz.*, $Eu(5CB)_2$ and $Eu_2(5CB)_2$ (Figure 2). In optimised structures, one or two europium atoms, respectively, are included between the benzene rings of different 5CB molecules. The complexes have positive stabilization energies of 44.5 and 131.5 kJ mol^{-1}, respectively. According to published data,[7] the vibration frequency of the CN group in the IR spectrum shifts to the low-frequency region in the case of such complexation; this fact is in agreement with experimental data [Figure 1(*b*)].

Experiments at liquid nitrogen temperature did not give unambiguous information on particles responsible for the formation of 1:2 complexes (complex I). The use of liquid helium temperatures made it possible to obtain data on the formation mechanism of complex I. Figure 3 shows the IR spectra of the Sm/5CB/Ar co-condensate with different molar ratios at 6–10 K. It is known that samarium clusters are absent from the matrix if the metal is diluted with argon in a 1:10000 molar ratio.[13] The corresponding spectrum [Figure 3, curve *3*] contains a structured band at 2160 cm^{-1}, which is new in comparison with the spectrum of individual 5CB. In our opinion, this band belongs to complex I, while its splitting into three components is probably caused by the existence of the molecules of complex I in different conformations or by stabilization in different local environments of the argon matrix. The band is shifted relative to its position in 5CB matrix not diluted with argon, that is, 2135 cm^{-1} (the sharp peak at 2137 cm^{-1} corresponds to the CO admixture). The band of complex II is absent. Thus, under conditions of high dilution with the matrix gas, where no metal aggregation occurs, samarium atoms can react with 5CB molecules to give complex I. Furthermore, the formation of the complex at ~10 K suggests that this process occurs almost without activation.

With the Sm:Ar ratio of about 1:400, not only samarium atoms but also clusters exist in the matrix.[13,14] The corresponding spectrum of Sm:5CB:Ar (1:10:400) [Figure 3, curve *1*] contains not only the band at 2160 cm^{-1} but also a band at 2060 cm^{-1}, which was assigned to complex II. Thus, variation of the reagent ratio by dilution makes it possible to control complex formation. This is an additional confirmation that the composition of complex II is $Ln_2(5CB)_2$. In our opinion, such complexes can be formed either in the reaction of a samarium atom with a molecule of complex I [$Ln + Ln(5CB)_2 \rightarrow Ln_2(5CB)_2$] or in the reaction of a samarium dimer with 5CB molecules [$Ln_2 + 2(5CB) \rightarrow$ $\rightarrow Ln_2(5CB)_2$].

Thus, the formation of low-temperature complexes in Sm-5CB and Eu-5CB co-condensates was found. Based on calculated data, sandwich structures of $Ln(5CB)_2$ and $Ln_2(5CB)_2$ were proposed. The $Ln(5CB)_2$ complex is converted to $Ln_2(5CB)_2$ in the temperature range 170–210 K. The $Ln(5CB)_2$ complex is formed in the reaction of lanthanide atoms with 4-pentyl-4′-cyanobiphenyl molecules.

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