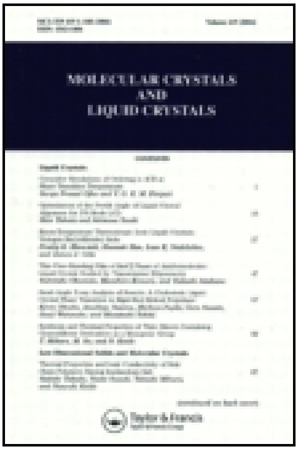

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Metastable Lanthanide Complex Formation and their Thermal Behavior in the Solid State with Alkylcyanobiphenyls

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The formation of two metastable complexes ($M/L = 1/2$ and 1/1) is shown for low temperature co-condensates of europium and samarium vapors with mesogenic ligand 4-penthyl-4′-cyanobiphenyl (5CB). The DFT-calculations based on hybrid B3LYP potential have been carried out to study the equilibrium structures of complexes. The model structures including one and two metal atoms with antiparallel disposition of ligand molecules are considered. The spectral shifts for ligand CN-group stretching vibrations and the relative thermal stability of the complexes are discussed.

Keywords: cryosynthesis; lanthanides; low temperature; metal-mesogens

INTRODUCTION

The interaction of metals with mesogenic compounds is of both fundamental and practical interest. Recently a number of works devoted to synthesis of lanthanide complexes with liquid crystal properties have appeared [1–3]. One of the approaches to the production of new hybrid metal-mesogenic systems containing metal atoms, clusters and their complexes, is cryochemical synthesis. This method allows researchers to include metal atoms directly within mesogenic matrices [4–6]. For

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the directed cryochemical synthesis of such systems the study of specific interactions of metal atoms with mesogenic molecules is important. The objective of this work is spectral study and theoretical modeling of the structure of low temperature complexes of samarium and europium obtained as solid co-condensates with the mesogenic ligand 4-pentyl-4′ -cyanobiphenyl (5CB).

EXPERIMENTAL

The samples were obtained by the co-condensation of reagent vapors under vacuum (10^{-4} torr) on the spectroscopic glass (CaF_2) in a special cryostat [5,6]. Using CaF_2 allows IR and UV spectra to be recorded. The co-condensation was carried out under molecular beam conditions. The condensation rate was 8×10^{-10} mole/s for the mesogenic ligand 4-pentyl-4-cyanobiphenyl (5CB) and $8 \div 16 \times 10^{-11}$ mole/s for europium and samarium. The reagents were evaporated by resistive heating at 850–900 for Eu, 900–950 K for Sm, and 380–390 K for 4-pentyl-4′-cyanobiphenyl (5CB).

The co-condensate samples were investigated using IR and UV spectroscopy over the temperature range 90–300 K. The metal to ligand ratio (M/L) was varied from 1/5 to 1/100 mole/mole, the warm-up rate was equal to 0.3 K/s. The IR-spectra of the film samples were registered on a “SPECORD M-80” spectrometer (Carl Zeiss Jena, Germany) in the wavenumber range 2300–1900 cm^{-1}, and UV-vis. spectra on a “Specord M-40” spectrometer (Carl Zeiss Jena, Germany), using a special cryostat for optical spectroscopy in the wavelength range 300–900 nm.

RESULTS AND DISCUSSION

The IR-spectra of Eu/5CB co-condensates were recorded at 80–300 K in the range of stretching vibrations of the CN group (2300–2000 cm^{-1}). Figure 1 shows that there are two new bands with maxima at $\nu_1 = 2135\,cm^{-1}$ and $\nu_2 = 2095\,cm^{-1}$ in comparison with the neat 5CB film. The shifts of these bands are 95 and 135 cm^{-1} to lower frequencies relative to the stretching vibration band of the CN group of 5CB (2230 cm^{-1}). Heating the sample up to 203 K leads to the absorption ν_1 decreasing and ν_2 increasing (Fig. 1). At temperatures above 223 K these bands disappear indicating the decomposition of both complexes.

IR-spectra of the Sm/5CB co-condensate showed two new bands relative to the spectrum of the pure ligand (Fig. 2). The absorption peaks are 2135 and 2085 cm^{-1} respectively. By heating of the film

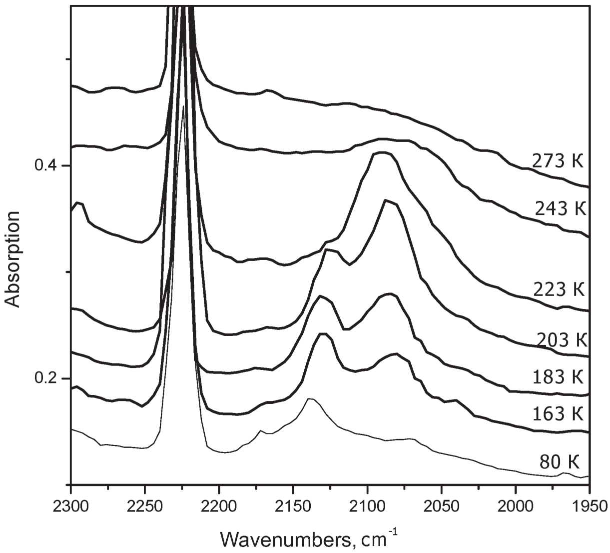


FIGURE 1 IR spectra of co-condensate Eu/5CB at the different temperatures.

sample up to 213 K the intensity of the first peak (2135 cm^{-1}) decreases and the intensity of the second one (2085 cm^{-1}) increases. These new bands also disappear at higher temperatures. Thus the thermal

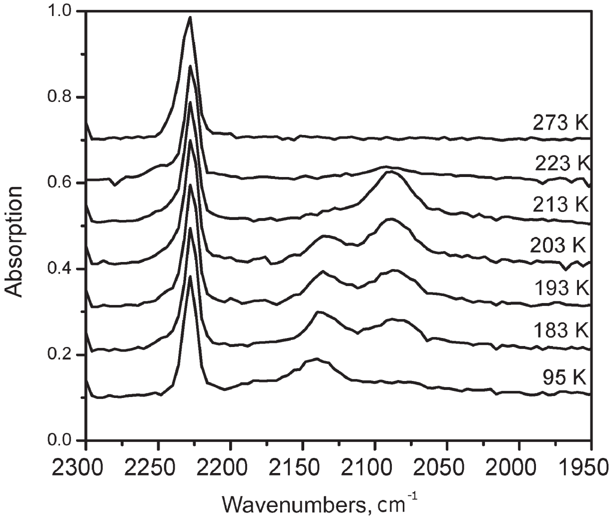


FIGURE 2 IR spectra of co-condensate Sm/5CB at the different temperatures.

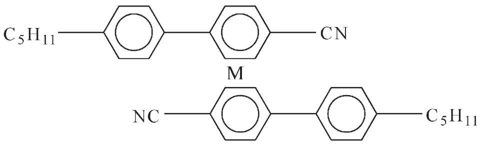
behavior of new IR bands for two complexes of samarium and europium co-condensates with 5CB is similar.

The frequency red shift is typical for π-complex formation of transition metals with unsaturated compounds [7]. Consequently new bands can be related to two different π-complexes distinguished by their thermal stability. The composition of the complexes has been determined in the work [8] and conforms to stoichiometric formulas M•2L (ν_1) and M2•L2 (ν_2). The combination of the spectral data at different temperatures and the time dependence of absorption [9] allows us to propose the existence of transformation of the complex M•2L into the complex M2•L2 over the temperature range 95–223 K.

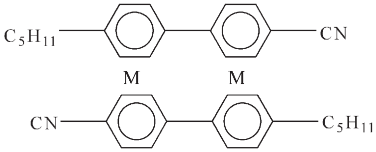
The electronic spectra of the systems Eu/5CB and Sm/5CB also revealed two new bands existing at low temperatures but which disappeared at 220–240 K [8]. This is in accord with IR spectroscopic study data and provides additional confirmation of the existence of the complexes.

The calculations of the equilibrium geometry complex configurations (Fig. 3) were carried out at DFT level with the exchange-correlating potential B3LYP using the NWCHEM program [10]. For all heavy atoms Stuttgart's pseudo-potentials were used [11]. For hydrogen atoms the 6-31G basis set was chosen.

The C_2 and C_{2h} symmetries have been used along the geometry optimization of complex I [$Eu(5CB)_2$] and complex II [$Eu_2(5CB)_2$] respectively:



(I)



(II)

Thus, the atom (or atoms) of europium is disposed between the benzene rings of the 5CB dimer with an antiparallel arrangement of the ligand molecules. For each complex there are several electronic states with different multiplicity. The complex I can have multiplicity equal to 8 and 10, and the multiplicity of complex II can be equal to 15, 17

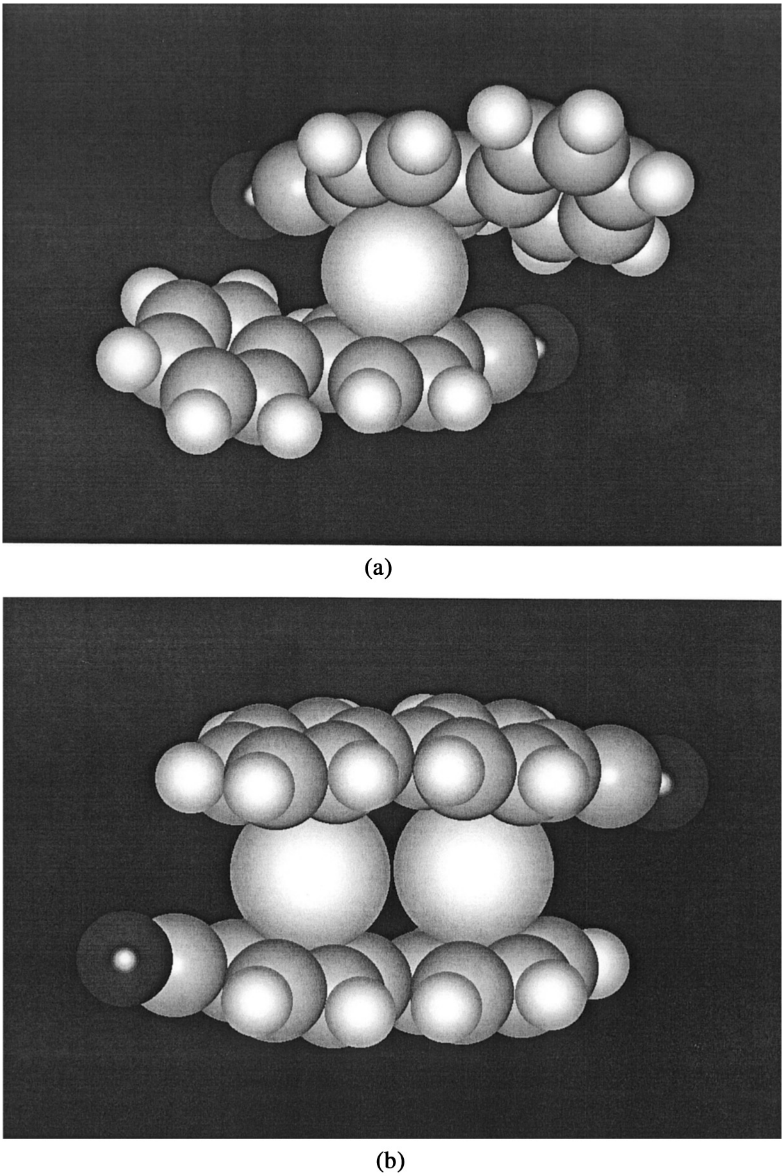


FIGURE 3 Calculated structures of the complexes 2Eu●2(5CB) and Eu●2(5CB).

TABLE 1 Some Equilibrium Geometry Parameters for Complex $Eu(5CB)_2$

	$Eu(5CB)_2$	
Multiplicity	8	10
r_{CN},Å	1.179	1.179
r_{CC},Å	1.412	1.412
r_{EuC},Å (average)	2.812	2.843
r_{CC},Å (average)	1.419	1.423
r_{CH},Å (average)	1.084	1.084
ϕ_1, degrees	23	22
ϕ_2, degrees	57	41
ϕ_3, degrees	23	45

φ_1, – the torsion angle between benzene ring planes of the same ligand
φ_2, – the angle between benzene ring planes of different ligands
φ_3, – the angle between the axis of the ligands

and 19. Some calculated geometry characteristics of both complexes with different multiplicity are presented in the Tables 1, 2. The pilot calculations for the complex $Eu(5CB)_2$ have shown that the state with multiplicity 10 lies lower by 4.4 kcal/mole than the one with multiplicity 8. Analogously for the complex II, the states with multiplicity 17 and 19 are higher by 3.3 and 24.2 kcal/mole, respectively, than for the state with lowest multiplicity (15).

For the complex I the change of multiplicity weakly influences the ligand equilibrium geometry. Only the angle between benzene rings of the same ligand molecule (φ_2) is different at varying multiplicity. This parameter is 57° and 41° for multiplicity 8 and 10, respectively. Analogously the angle between the ligand molecule axis (φ_3) varies from 23° (multiplicity 8) to 45° (multiplicity 10). The change of other geometric characteristics is insignificant. It should be noted that the geometry of molecule 5CB in the complex I is similar to that of free

TABLE 2 Some Equilibrium Geometry Parameters for Complex $Eu_2(5CB)_2$

	$Eu_2(5CB)_2$		
Multiplicity	15	17	19
R_{CN},Å	1.177	1.178	1.178
R_{CC},Å	1.414	1.414	1.414
r_{EuEu},Å	3.785	3.816	4.106
r_{EuC},Å (average)	2.930	2.944	3.027
r_{CC},Å (average)	1.420	1.420	1.420
r_{CH},Å (average)	1.082	1.082	1.082
φ_1, degrees	13	12	7

molecule 5CB, with the exception of φ_1. According to DFT/B3LYP calculations the latter is equal almost to 40° for the individual ligand.

The rotation of one benzene ring relatively to another one in the complex $Eu_2(5CB)_2$ is impossible. The shift of one 5CB molecule relative to another molecule is also impossible. So the benzene rings buckle and the molecule 5CB becomes nonlinear. The angle between the planes of the benzene rings (φ_2) decreases from the state with multiplicity 15 (13°) to the state with multiplicity 19 (7°). Moreover the increase of multiplicity gives rise to an increase in the distance between the europium atom and the nearest carbon atoms. It appears that the state with maximal multiplicity has the least metal-ligand interaction energy.

The stabilization energies for the complexes I (multiplicity 10) and II (multiplicity 15) are equal to 11 and 31 kcal/mole, respectively. Thus, complex II is more stable than complex I and this fact conforms with the spectral data. It is important that these values are comparable with the experimentally estimated activation energy for thermal degradation of the Sm•5CB complex which is equal to 7 kcal/mole [9].

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