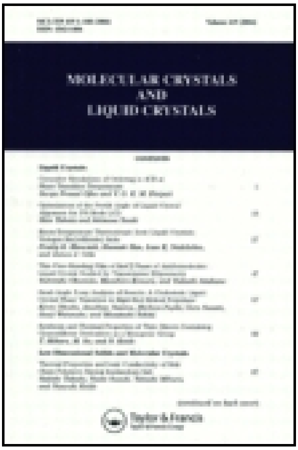

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Solid Phase Transformations of Labile Samarium-Cyanobiphenyl Complexes

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Solid Phase Transformations of Labile Samarium-Cyanobiphenyl Complexes

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Samarium containing cyanobiphenyl(CB) solid phase samples were obtained by low temperature co-deposition of the reagent vapors under the molecular beam conditions using special vacuumed cryostats. Film samples were studied by IR- and UV-visible spectroscopy in the temperature range 80–300 K. The formation of two Sm-CB complexes of different compositions. The kinetics of solid phase transformations in the system was discussed.

Keywords: solid phase kinetics; low temperature spectroscopy; metallo-mesogenic systems

INTRODUCTION

Metal containing mesogenic systems are of great interest due to their fundamental importance for the theory of liquid crystalline state and also due to their future applications for molecular electronics. In present work we discribe the results on the interactions of metallic samarium with mesogenic 4-pentyl-4'-cyanobiphenyl (5CB) in solid phase co-condensates obtained via joint atomic/molecular beams deposition on the cooled surfaces.

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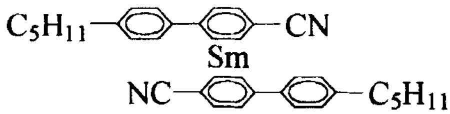
EXPERIMENTAL

Experiment was carried out by co-condensation of reagents in vacuum 10^{-4} Torr on the spectroscopic glass (CaF_2) cooled by liquid nitrogen. Scheme of vacuumed cryostat is presented in [1]. IR-spectra were registered on the instrument "Specord M80" at the temperature range 95-300 K in the region of CN-group stretching vibrations [1].

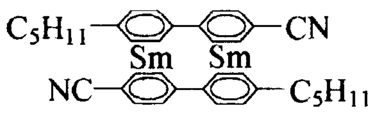
RESULTS AND DISCUSSION

The new band shifted on 95 cm^{-1} to low frequencies relatively to this vibration for pure 5CB (2230 cm^{-1}) appears in the co-condensates Sm-5CB (1/10 mol/mol) at 95 K. Annealing of co-condensates up to 183-203 K led to the appearance of new band at 2085 cm^{-1} (II). The both vibrations were corresponded to Sm π-complexes [2]. The temperature dependence of the intensities of the absorption bands of these complexes are presented in Figure1.

The composition of complex at 2135 cm^{-1} is 1:2 [$Sm(5CB)_2$] and the one at 2085 cm^{-1} is 1:1 [$Sm_2(5CB)_2$] [2]. Suggested structures of these complexes are presented here.



(I)



(II)

For investigation of solid state kinetics of transition $Sm(5CB)_2$ to $Sm_2(5CB)_2$ kinetic dependencies of complexes absorbance were registered

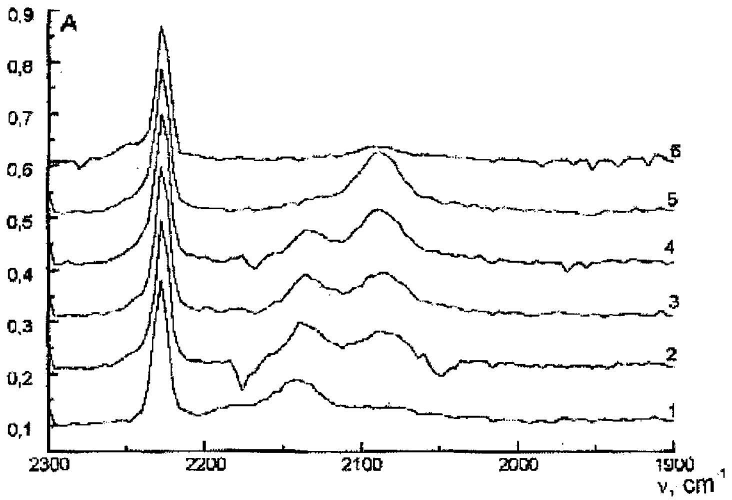


FIGURE 1. IR-spectra of co-condensate Sm/5CB (1/10 mol/mol) at the different temperatures: 1 - T=95 K, 2 - T=183 K, 3 - T=193 K, 4 - T=203 K, 5 - T=213 K, 6 - T=223 K.

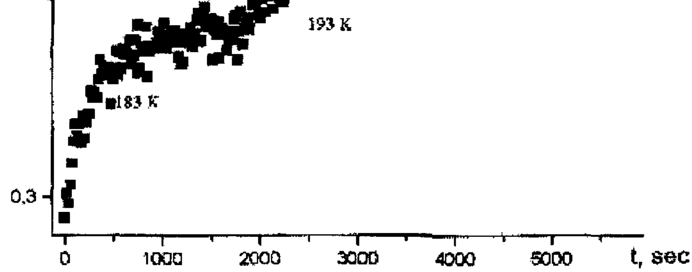


FIGURE 2. Kinetic absorbance dependence of complex II (2085 cm^{-1}) at the temperatures 183, 193, 203 K.

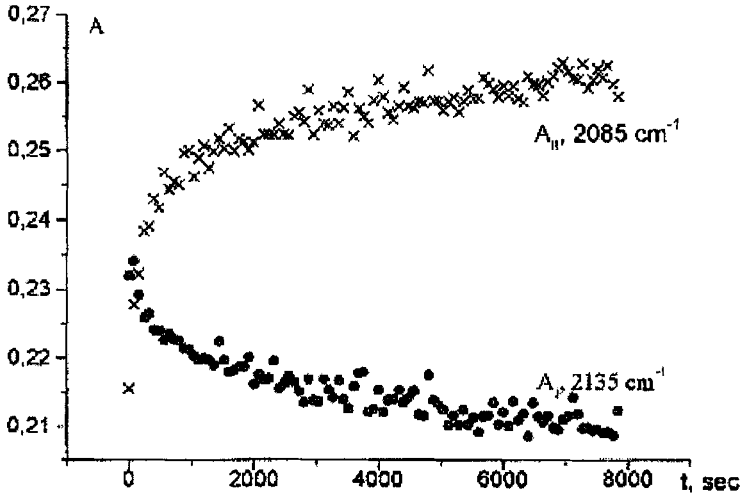


FIGURE 3 Kinetic curves of absorbance of complexes I (2135 cm^{-1}) and II (2085 cm^{-1}) at the temperature 193 K.

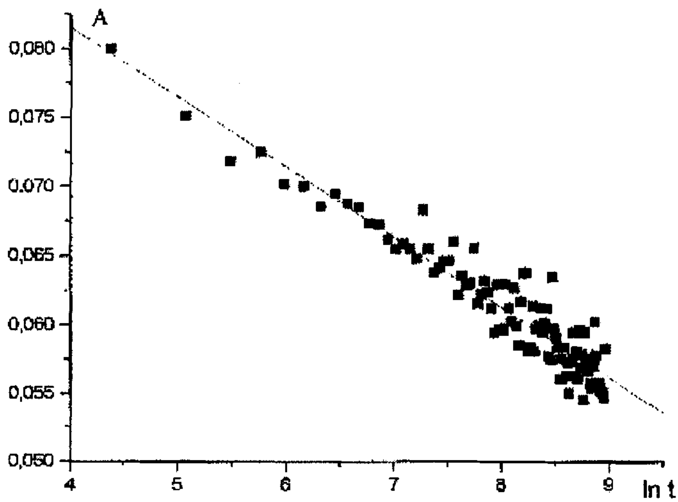


FIGURE 4. Absorbance dependence of the complex I (2135 cm^{-1}) on logarithm of time at the temperature 193 K

at the temperatures 183, 193, 203 K. Kinetics of this transformation has stepwise character (see Figure 2).

Symbate increasing absorbance of $Sm_2(5CB)_2$ at 2085 cm^{-1} and decreasing absorbance of $Sm(5CB)_2$ at 2135 cm^{-1} are supplementary prove of transition $Sm(5CB)_2$ to $Sm_2(5CB)_2$ (see Figure 3).

Kinetic curves can be linearized in coordinates of dependence of absorbance on logarithm of time (refer to Figure 4). This fact indicates that there is a wide distribution in activation free energy of reactive particles. Maximal and minimal values of reaction rate constants and the width of activation free energy distribution obtained from the kinetic data (see Table 1) were determined using following equations [3,4]:

TABLE 1. Kinetics of solid phase transitions $Sm(5CB)_2$ to $Sm_2(5CB)_2$

T, K	**k_{min}, sec^{-1}**	**k_{max}, sec^{-1}**	**$\Delta(\Delta G)$, kJ/mol**
183	$3.1*10^{-17}$	$6.4*10^{-3}$	50
193	$1.9*10^{-9}$	$8.9*10^{-3}$	25
203	$3.2*10^{-5}$	$7.1*10^{-3}$	10

$$A/A_0|_1 = -\ln k_{min}/\Delta(\ln k) - [1/\Delta(\ln k)]*\ln t \quad (1)$$
$$\Delta(\ln k) = \ln k_{max} - \ln k_{min} \quad (2)$$
$$k = (k_B*T/h)*\exp[-\Delta G/(R*T)] \quad (3)$$

The value of activation energy estimated using initial reaction rates is equal to E≅30 kJ/mol.

CONCLUSIONS

In present work we made the IR-and UV-Vis spectroscopic study of the thermal behavior of two labile Sm-5CB complexes of metal to ligand ratio 1:1 and 1:2. It was shown that in temperature 183-200 K the solid phase transformation of 1:2 complex to 1:1 complex took place. The kinetics of the process can be considered as retarded with a wide rate constant distribution. The effective value of the activation energy of the process was estimated as $E_{exp}=(30\pm7)$kJ/mole.

Acknowledgments
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