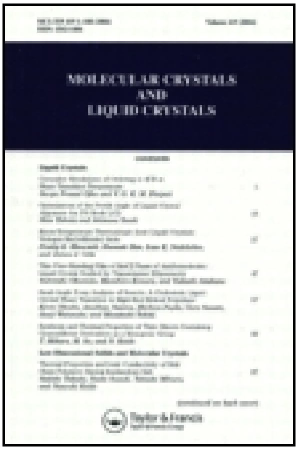

Molecular Crystals and Liquid Crystals

Formation and Solid Phase Transformation of Sm(0) Complexes with Mesogenic4-Penthyl-4″-Cyanophenylpiridine

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FORMATION AND SOLID PHASE TRANSFORMATION OF SM(0) COMPLEXES WITH MESOGENIC 4-PENTHYL-4′-CYANOPHENYLPIRIDINE

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The IR-spectroscopic study of samarium – mesogenic 4-pentyl-4′-cyanophenylpiridine (5Py) low temperatures solid co-condensates was made in temperature range 90–300 K. The formation of two metastable complexes has been found. The kinetics of transformation of one complex to another is discussed.

Keywords: solid phase reactions; kinetics; metallmesogens; lanthanides

INTRODUCTION

The problem of interactions of transition metals with mesogenic ligands is of both fundamental and practical interest. At present time a lot of metalmesogenic compounds are known [1]. This fact is due to large perspective applications of metalmesogenic supramolecular systems in molecular electronics and catalysis [2]. Mesogenic compounds of lanthanides are of special interest by their unique magnetic properties – magnetic sensibility and anisotropy of magnetic sensibility [3]. On the other hand at present time there is no works devoted to synthesis of mesogenic compounds of zerovalent lanthanides. However both stable and labile complexes of zerovalent lanthanides with conventional ligands – CO [4], C_2H_4 [5] and some bulk substituted benzene [6] ligands were described. This work extends the class of zero-valent compounds of lanthanides and is attempt to receive novel metallomesogenic systems using low temperature co-condensation of lanthanide metal and mesogenic compound vapors on the cooled surface.

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EXPERIMENTAL

Preparation of samples was made via joint co-condensation of reagents vapors on the spectroscopic glass (CaF_2) in the special cryostat (10^{-4} Torr) [7], [8]. Using CaF_2 allows recording of both IR- and UV-spectra in situ under vacuum conditions. Condensation was carried out under the molecular beam conditions. The rate of condensation is about $8*10^{-10}$ mol /s for 5Py and $(8 \div 16)*10^{-11}$ mol/s for samarium. Time of co-condensation is about 1 h. Evaporation of reagents was realized by outer resistive heating. Evaporation temperature for Sm is about 900–950 K and for 5Py is about 430–440 K. During co-condensation temperature of support cooled by liquid nitrogen was 80–90 K and then samples were heated with the rate of 0.3 K/s. The film samples were studied by IR-spectroscopy in temperature range 80–300 K. IR-spectra were recorded using the "SPECORD M80" in the range 4000–400 cm^{-1} and more carefully in CN-stretching vibration region at 2300–1900 cm^{-1}. Spectra were treated on the computers "IBM PC" using standard program package "Origin 5.0".

RESULTS AND THEIR DISCUSSION

The IR-spectra of co-condensates Sm/5Py (Fig. 1) contain two new (relatively the spectrum of individual 5Py) bands $-2150\ cm^{-1}$ and

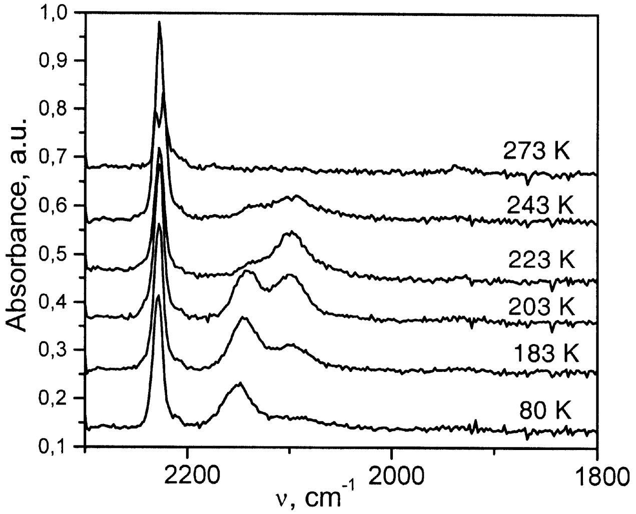

FIGURE 1 IR-spectra of co-condensate Sm/5Py (1/10 mol/mol) at the different temperatures.

2100 cm^{-1} – in the field of stretching vibration of CN-group (2230 cm^{-1} for neat ligand film). The shift of about 100 cm^{-1} to lower frequencies is similar to π-complexes of zerovalent transition metal complexes with π-ligands [9]. However only one band (2150 cm^{-1}) is revealed at the 80 K. The absorbance of the band at 2100 cm^{-1} increases and the absorbance of the band at 2150 cm^{-1} decreases simultaneously by annealing of the sample from 80 up to 273 K. Similar changes in spectra of co-condensates Sm with mesogenic 4-pentyl-4′-cyanobiphenyl (5CB) have been related to two π-complexes of different composition –M/L = 1:2 and 1:1 [8]. According these results the band 2150 cm^{-1} can be belong to the higher (I) and one 2100 cm^{-1} – to lower (II) Sm/5Py complexes.

The kinetic curves for Sm/5Py complexes transformation in the solid state of Py matrix at different temperatures 183, 193, 203 K are presented in (Figs. 2, 3, 4). At first, the initial part (up to 500 s) of kinetics of thermal transformation for complex I possess weak maximum. This fact is likely to be connecting with the supplementary formation of complex I from atoms and clusters of Sm. Secondly, at the time above

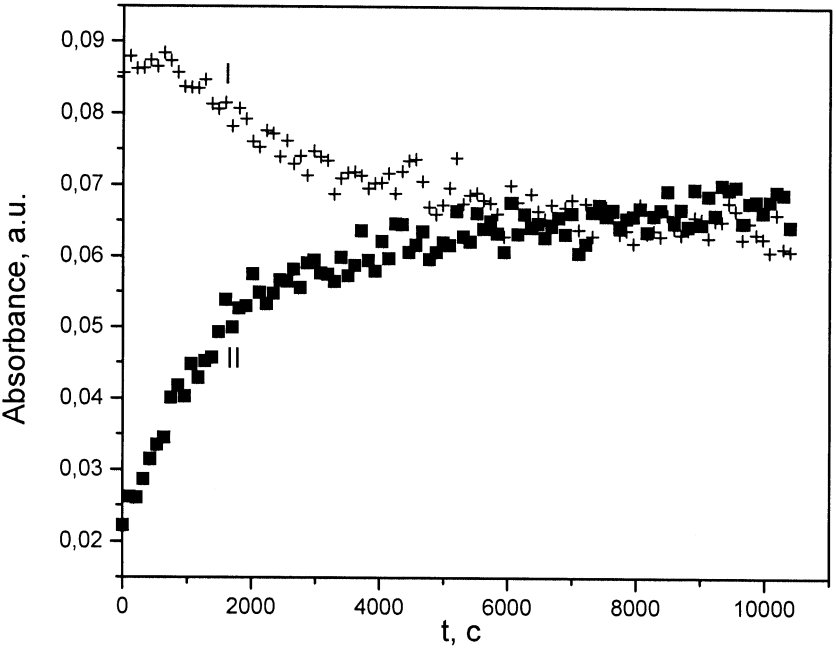

FIGURE 2 Kinetic curves of solid state transformation of complexes Sm(5Py)$_2$ (2150 cm^{-1}, I) and Sm(5Py) (2100 cm^{-1}, II) at 183 K, Sm/5Py = 1/5 mol/mol.

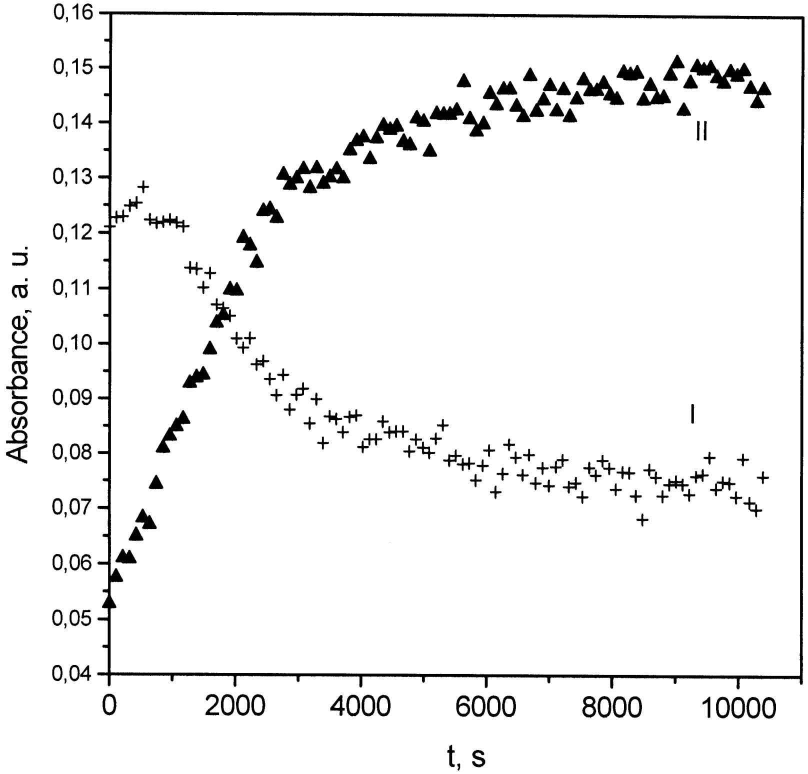

FIGURE 3 Kinetic curves of solid state transformation of complexes Sm(5Py)$_2$ (2150 cm^{-1}, I) and Sm(5Py) (2100 cm^{-1}, II) at 193 K, Sm/5Py = 1/5 mol/mol.

500 s absorption of complex I decreases and simultaneously the absorption of complex II increases. Similar picture takes place for the Sm/5CB co-condensates and points out to transformation of complex 1:2 to complex 1:1 [9]. It is shown that kinetic curves of complex I do not come to zero for given temperature from 183–203 K range and they have anomalous retarded behavior similar to some reactions in the solid phase [11]. This fact can be connected with a wide distribution of complex reaction rate constants [12], that is each assembly of reagent's molecules has their own free activation energy (ΔG^*) and reacts with the appropriate rate constant (k_i).

For quantitative description of kinetic curves on the descending region the model of square distribution of molecules on ΔG^* [11] have been used. According to [11] the kinetic curves can be treated in coordinates A/A_0 (ln t) – (1).

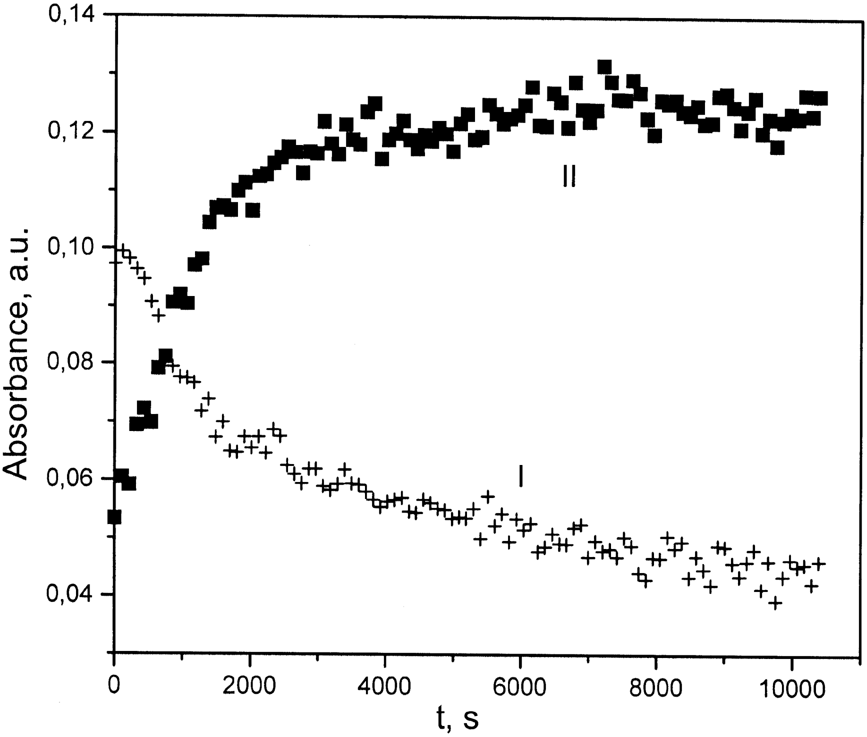

FIGURE 4 Kinetic curves of solid state transformation of complexes $Sm(5Py)_2$ ($2150\,cm^{-1}$, I) and Sm(5Py) ($2100\,cm^{-1}$, II) at 203 K, Sm/5Py = 1/5 mol/mol.

$$A/A_0 = (-\ln k_{min} - \ln t)/(\ln k_{max} - \ln k_{min}) \qquad (1)$$

Here t – reaction time, k_{min} and k_{max} – minimum and maximum rate constants, A and A_0 – running and starting absorption of complex I. In the case of the wide reaction distribution ΔG^* have been determined according Eq. (2)

$$1/A_0^* dA/d(\mathrm{In}\, t) = -RT^* \varphi(\Delta G^*), \qquad (2)$$

where T – temperature, R – universal gas constant, $\varphi(\Delta G^*)$ – function of distribution of molecules on ΔG^*. Calculated values of $\Delta(\Delta G^*)$ (width of distribution of ΔG^*), k_{min} and k_{max} are presented in Table 1.

By the increasing of the temperatures the solid phase complexes transformation kinetic curves undergo following changes. Maximum on the kinetic curve for complex I disappears (Fig. 4) and only small

TABLE 1 The Rate Constants and Distribution Width of Free Activation Energy of Transformation of Sm[5Py]$_2$ to Sm[5Py]

T, K	k_{max}, s^{-1}	k_{min}, s^{-1}	$\Delta(\Delta G^*)$, kJ/mol
183	$4{,}1 \cdot 10^{-3}$	$2{,}5 \cdot 10^{-9}$	22
193	$8{,}9 \cdot 10^{-3}$	$2{,}6 \cdot 10^{-7}$	17
203	$1{,}5 \cdot 10^{-2}$	$4{,}8 \cdot 10^{-4}$	6

induction period remains. This fact can be connected with two reasons – 1) aggregation of metal atoms and clusters and 2) increasing of the ratio of effective rate constants of complex I to complex II solid state transformation and of formation of complex I. Moreover, increasing the temperature leads to the rise of degree of decomposition of complex I at the some definite time. This can be explained by the existence of a wide distribution of rate constants of molecules in the solid phase (see above), that is at the higher temperature molecules react with higher activation energy.

CONCLUSIONS

The existence of two low temperature metastable complexes Sm-5Py was shown by IR-spectroscopy. The solid state transformation of complex 1:2 to 1:1 was revealed at the temperatures 180–230 K. The kinetics of this process was anomalously retarded and can be described in terms of square distribution on free activation energy. Maximal and minimal values of reaction rate constants for a wide of distribution of free activation energy are determined. The both complexes are unstable at relevant temperatures.

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