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Study of Thermochemical Properties of Lanthanides Pentafluorophenolates with Coordination Ligands

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Abstract—Saturated vapor pressure of lithium pentafluorophenolate and the lanthanide complexes as a function of temperature has been determined by the Knudsen effusion method. Processing of the pressure data allowed the calculation of thermodynamic parameters of the compounds sublimation. Mass spectra and differential scanning calorimetry data are presented.

Keywords: rare-earth element, pentafluorophenolate complex, Knudsen method, pressure, sublimation enthalpy

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Lanthanides perfluorophenolates are sufficiently stable compounds exhibiting high volatility; their ability to be sublimated in a vacuum without decomposition is important in view of their practical application [1]. The absence of the C–H bonds (well known luminescence quenchers) can enhance the intensity of the complexes emission. In view of the special features of the pentafluorophenolate ligand, organic light-emitting diode (OLED) devices have been manufactured via evaporation–condensation of these compounds in a vacuum, and their electroluminescent properties have been studied [1].

In order to develop the methods of preparation of emission layers via the vapor phase deposition, the quantitative data on the volatility and thermal stability of the complexes are required. However, thermochemical properties of the said compounds have not been studied so far.

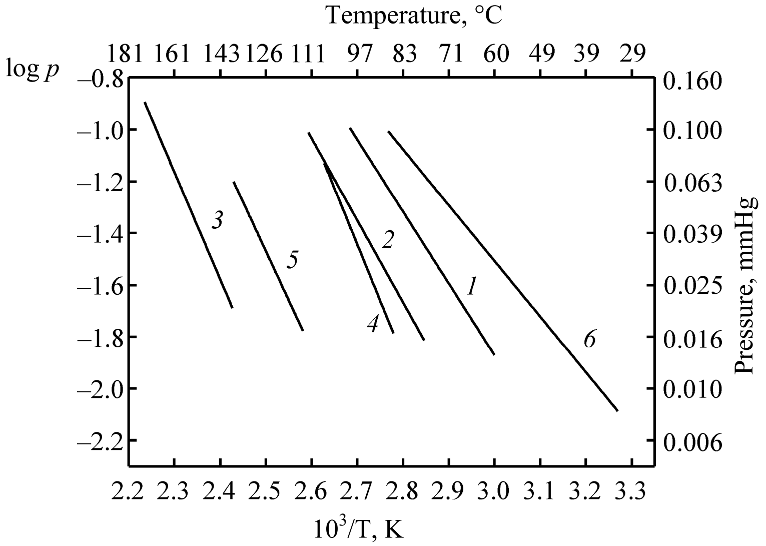
Here we present the results of the study of the saturated vapor pressure as a function of temperature, the gas phase composition, and thermodynamic parameters of melting and sublimation for monodentate lithium pentafluorophenolate $LiOC_6F_5$ and $Ln(OC_6F_5)_3(A)_x(B)_y$ (Ln = Pr, Eu, Tb, Er, Dy) complexes containing neutral (A) phenanthroline (Phen) (in the praseodymium, europium, and erbium complexes) or bipyridyl (bpy) (in the terbium complex) ligand and diethyl ether (B) (in the dysprosium complex).

Pentafluorophenolate complexes of lanthanides $Ln(OC_6F_5)_3(Phen)_x$ [Ln = Pr, $x = 1$ (**1**); Eu, $x = 1$ (**2**); Er, $x = 3$ (**2**)], $Tb(OC_6F_5)_3(bpy)_2$ (**5**) were prepared via the interaction of amides $Ln[N(SiMe_3)_2]_3$ with pentafluorophenol in benzene or toluene medium in the presence of 1,10-phenanthroline or 2,2'-bipyridyl, in the absence of air and moisture. Lithium pentafluorophenolate $LiOC_6F_5$ (**6**) was prepared similarly, but no phenanthroline or bipyridyl was added. The $Dy(OC_6F_5)_3\cdot(Phen)(Et_2O)_2$ complex (**4**) was prepared via the interaction of amide $Dy[N(SiMe_3)_2]_3$ with pentafluorophenol and 1,10-phenanthroline in the presence of diethyl ether. The preparation methods have been described in detail elsewhere [1, 2].

The composition and structure of the prepared compounds were confirmed by the data of elemental analysis, IR spectroscopy, and X-ray diffraction (XRD) analysis.

Prior to further studies, the prepared compounds were purified via sublimation in a vacuum (10^{-3} Topp at 437 K).

Phase transitions of compounds **1**–**6** were studied by means of differential scanning calorimetry at 30–350°C. The studied compounds were single-phase,



Plots of saturated vapor pressure of compounds **1**–**6**. (*1*) $Pr(OC_6F_5)_3(Phen)$; (*2*) $Eu(OC_6F_5)_3(Phen)$; (*3*) $Er(OC_6F_5)_3(Phen)$; (*4*) $Dy(OC_6F_5)_3(Phen)_3(Et_2O)_2$; (*5*) $Tb(OC_6F_5)_3(bpy)_2$; and (*6*) Li (OC_6F_5).

within the experimental accuracy limits. Compounds **1**–**6** underwent the phase transition (melting) in the specified temperature range.

The composition of the gas phase had to be determined in order to find the saturated vapor pressure of crystalline compounds **1**–**6**. To do so, we performed mass spectroscopy experiments over the 50–450°C temperature range. The first stage of the compounds ionization consisted in the elimination of phenanthroline (complexes **1**–**4**) or bipyridyl (complex **5**) ion. Further fragmentation of the studied compounds under the electron impact conditions was similar. Molecular ions of the complexes decomposed with the elimination of the pentafluorophenolate ligand. The strongest peaks in the mass spectra of compounds **1**–**4** and **6** were those of the molecular and metal-containing ions, *m*/*z* (I_{rel}, %): **1**, 522.6 (18) $[PrL_2OH]^+$, 686.5 (52) $[PrL_3]^+$, 866.5 (15) $[PrL_3Phen]^+$; **2**, 537.1 (5) $[EuL_2OH]^+$, 695.5 (5) $[EuL_3]^+$, 878 (4) $[EuL_3Phen]^+$; **3**, 546.7 (17) $[ErL_2OH]^+$, 713.5 (31) $[ErL_3]^+$, 893.5 (28) $[ErL_3Phen]^+$; **4**, 542.6 (9) $[DyL_2OH]^+$, 709.2 (16) $[DyL_3]^+$, 889.5 (12) $[DyL_3Phen]^+$; **6**, 197.1 (99) $[LiL]^+$ ($L = OC_6F_5$).

The appearance of the $[ML_2OH]^+$ peaks was likely owing to the background water present in the mass analyzer trap (i.e. the feature of the mass spectrometer construction). The processes of hydrolysis and ion-molecular reaction involving the formed ions have been discussed in detail in [4].

Analysis of mass spectra of compounds **1**–**4** and **6** revealed the absence of other ions (including those heavier than the molecular ones) in the saturated vapor. Hence, it was concluded that the gas phase contained exclusively the corresponding monomeric molecular forms.

Thermodynamic parameters of vaporization and sublimation to the monomeric vapor were calculated basing on the mass spectrometry data of the studied compounds in the vapor phase.

Coefficients of the vapor pressure equation $\log p = A - B/T$ and sublimation enthalpies of the studied compounds

Compound	*M*	ΔT, K	*A*	*B*	R^{2a}	$\Delta_s H_T$, kJ/mol
Li OC_6F_5	190	305.9–353.4	2.1513	4.9467	0.997	41.08
$Pr(OC_6F_5)_3$Phen	867.3	333.4–372.7	2.7724	6.4457	0.996	53.08
$Eu(OC_6F_5)_3$Phen	867.3	351.4–385.7	3.2102	7.3079	0.998	60.56
$Dy(OC_6F_5)_3(Phen)(Et_2O)_2$	977.7	359.9–380.6	3.7986	8.0277	0.995	72.71
$Tb(OC_6F_5)_3(bpy)_2$	1034	384.6–411.7	4.1319	8.3391	0.998	79.08
$Er(OC_6F_5)_3(Phen)_3$	1254	412.1–447.5	3.5243	8.1102	0.998	83.02

The saturated vapor pressure of the sublimated complexes as a function of temperature (30–180°C) was measured using the effusion Knudsen method (see the Figure). The obtained data were described by the $\log p = A - B/T$ equation (p being the vapor pressure in Pa) with the correlation coefficient R above 0.995. Parameters A and B (see the table) were found using the least-squares method, the accuracy being of at least ±5%. The obtained data were then used to calculate thermodynamic parameters of sublimation. Temperature range of the vaporization was chosen according to DSC data.

The table shows the values of the sublimation enthalpies at the midpoint of the temperature range. The volatility of the studied compounds was decreased in the series of the corresponding metals (lithium to erbium). Molecular mass of the compounds made the major contribution to their volatility, the heat of sublimation growing with the increase in the compound molecular mass.

EXPERIMENTAL

DSC studies were performed using a DSC204F1 Phoenix calorimeter as described elsewhere. The experiments were performed under argon atmosphere at the heating rate of 5 deg/min. Mass spectra were registered using a Polaris Q mass spectrometer equipped with a direct injection system.

Saturated vapor pressure was measured using a stainless steel effusion chamber with the evaporation area to the effusion hole (l = 0.050 mm, d = 0.35 mm) area ratio of 660. The experimental conditions have been described elsewhere [7, 8]. The Klausing coefficient reflecting the resistance of the hole to the vapor flux was calculated according to Eq. (1) ($0 < l/r \leq 1.5$).

$$K = 1/[1 + 0.5(l/r)]. \quad (1)$$

Hence, the product of K and the effusion hole area was of 8.14×10^{-4} cm^2.

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REFERENCES

1. Fagin, A.A., Ilichev, V.I., Pushkarev, A.P., Maleev, A.A., Marygin, A.V., Mensov, S.N., and Bochkarev, M.N., *Russ. Chem. Bull*., 2012, vol. 61, no. 11, p. 2190. DOI: 10665285/12/61112190.
2. Maleev, A.A., Fagin, A.A., Ilichev, V.A., and Lopatin, M.A., *J. Organomet. Chem*., 2013, vol. 747, p. 126. DOI: 10.1016/j.jorganchem.2013.03.052.
3. Pushkarev, A.P., Ilichev, V.A., Maleev, A.A., Fagin, A.A., Konev, A.N., Lopatin, M.A., Samsonov, M.A., and Fukin, G.K., *J. Mater. Chem*., 2014, vol. 2, p. 1532. DOI: 10.1039/c3tc32054e.
4. Mitin, A.S., Faerman, V.I., and Lopatin, M.A., *Mass-Spektrometr*., 2008, vol. 5, no. 2, p. 147.
5. Hohne, G.W.H., Hemminger, W.F., and Flammersheim, H.F., *Differential Scanning Calorimetry*, Berlin; Heidelberg: Springer-Verlag, 2003.
6. Drebushchak, V.A., *J. Therm. Anal. Cal*., 2005, vol. 79, p. 213.
7. Lebedev, Yu.A. and Miroshnichenko, E.A., *Termokhimiya paroobrazovaniya organicheskikh veshchestv* (Thermochemistry of Vaporization of Organic Substances), Moscow: Nauka, 1981.
8. Efimova, Yu.A., Abakumov, G.A., Petrov, B.I., Pochekutova, T.S., and Khamylov, V.K., *Russ. J. Phys. Chem.,* 2008, vol. 82, no. 11, p. 1792. DOI: 10.1134/S0036024408110010.