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Thermochemical Properties of New N,O-Chelate Sc, Eu, and Tb Complexes for OLED-Devices

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Abstract—A new class of Sc, Eu, and Tb complexes with N,O-chelate ligands was synthesized for the first time. The mass spectra, thermogravimetric analysis, differential scanning calorimetry data, as well as the data on the saturated vapor pressure of the compounds were obtained. The main thermochemical parameters of the compounds were calculated.

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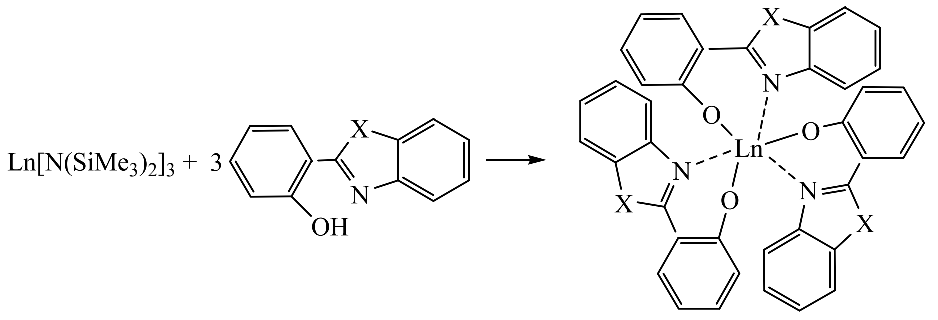
Coordination compounds of rare earth elements (Ln) possessing luminescent properties belong to a promising class of chemical compounds that can be used as emissive layers of light-emitting diode (OLED) [1]. The advantage of this class of complexes as potential materials is due to their optical properties, namely, the ability to achieve a highly monochromic emission and increased quantum efficiency. The Ln(III) ions exhibit unique optical properties, which include the luminescence due to the *f–f* transition, whose efficiency was found to depend on the nature of both the ligand and the metal itself. In [2] a set of Ln(III) complexes was described suitable for the development of efficient OLED devices. Currently β-diketonate [3], carboxylate [3], pyrazolonate [4], 8-oxyquinolinate [4, 5], amidinate [6], imidodiphosphnate [7] and other complexes of rare earth elements are known that possess electroluminescent properties. Nevertheless, the search for new Ln-complexes with organic ligands having electroluminescent properties, as well as creation of effective OLED devices based on them is a promising area of research.

Electroluminescent material is a part of the OLED included as a nano-sized thin film, commonly obtained by the vapor deposition (MO CVD). For each vapor-deposited compound its thermochemical characteristics and composition should be known.

This paper is a continuation of the investigation of thermochemical characteristics [8], such as temperature dependence of vapor pressure, melting and decomposition temperatures, as well as the data of mass spectral studies, of some new stable scandium, europium and terbium complexes coordinated with the heterocyclic 2-(2-benzothiazol-2-yl), 2-(2-benzoxazol-yl-2-yl)- and 2-(2-benzoimidazol-2-yl)phenoxide ligands. All the investigated compounds were obtained by the method described in [9], in the reactions of the rare earth elements silylamides with the corresponding heterocyclic phenols. This method is one of the most convenient and simple for the targeted synthesis of organometallic lanthanide complexes.

The compounds composition and structure were confirmed by XRD, IR and ^{1}H NMR spectroscopy. The thermal properties of new N,O-chelate terbium, europium, and scandium complexes were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

Differential scanning calorimetry. The study of phase transitions of the samples **III–VIII** in the region of 30–550ºC was performed using a differential scanning calorimeter DSC204F1. Within the sensitivity of the method, the substance under investigation is an individual phase. In the above temperature range the samples of compounds **III, IV, VI** and **VII**



I–VIII

I, Ln = Sc, X = S; **II**, Ln = Sc, X = N; **III**, Ln = Eu, X = S; **IV**, Ln = Eu, X = O; **V**, Ln = Eu, X = N; **VI**, Ln = Tb, X = S; **VII**, Ln = Tb, X = O; **VIII**, Ln = Tb, X = N.

underwent a phase transition due to melting. By the DSC of the samples temperature and thermodynamic parameters of the complexes melting were determined (Figs. 1, 2, Table 1). For compounds **V** and **VIII** at the temperatures 460 and 475ºC, respectively, a sharp change was observed in the heat flow value, but the shape of the peaks and their irreversibility indicate the occurrence of the irreversible phase transformation. According to the data of the thermogravimetric analysis, this corresponds to the process of decomposition (degradation) of compounds at further heating.

Thermogravimetric study. The data of thermogravimetric analysis of the compounds **III–V** and **VI–VIII** are shown in Figures 3 and 4, respectively. The results of TGA revealed that the europium complexes **III–V** are stable compounds up to temperatures of 362.8, 373.6, 391.9ºC, respectively. The terbium compounds **VI–VIII** are resistant to temperatures of 408.6, 429.2 and 476ºC, respectively. Above these temperatures there is a marked weight loss, which may be associated with the decomposition processes after passing by the compounds the above mentioned temperatures. The scandium complexes **I** and **II** are thermally stable up to temperatures of 400 and 450ºC, respectively. The TGA data for **I** and **II** are not given here, since the nature of the curves is similar to that of **VI–VIII.**

Mass spectrometric investigation. The presence of molecular ions in the mass spectra of complexes **I–VIII** indicates existence of these molecules in the vapor phase. The absence of the ligand ions in the mass spectrum of Eu complex **VI** with X=N indicates its thermal decomposition at heating. Table 2 contains the characteristics of the main peaks in the mass spectra.

Saturated vapor pressure. The temperature dependence of the vapor pressure of the complexes was measured by the Knudsen's effusion method with the registration of the amount of material sublimated in

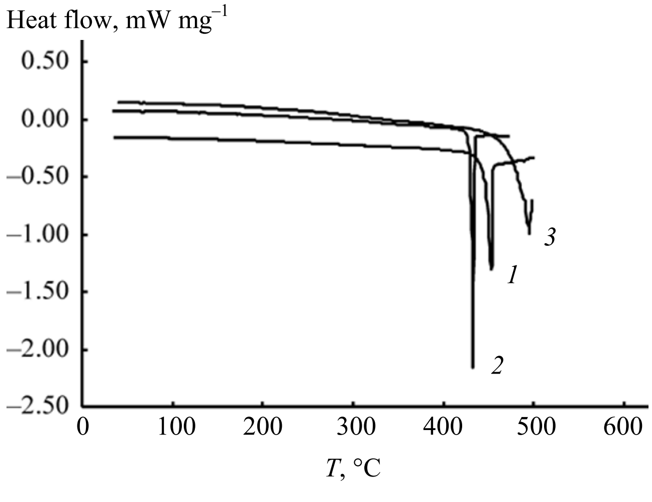


Fig. 1. Differential scanning calorimetry curves for the europium complexes: (*1*) **III,** (*2*) **IV,** (*3*) **V.**

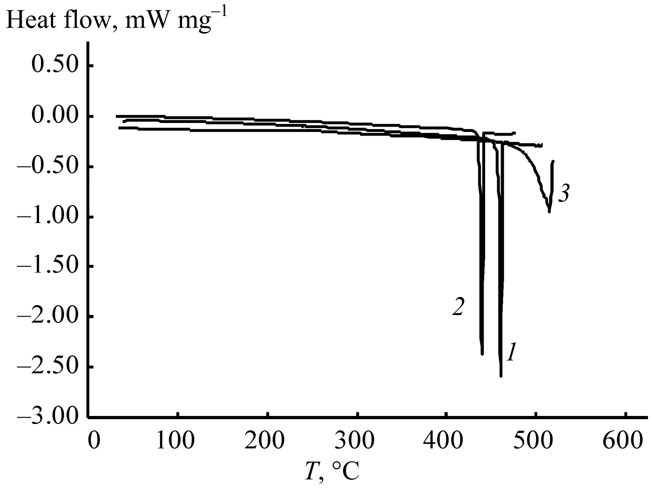


Fig. 2. Differential scanning calorimetry curves for the terbium complexes: : (*1*) **VI,** (*2*) **VII,** (*3*) **VIII**.

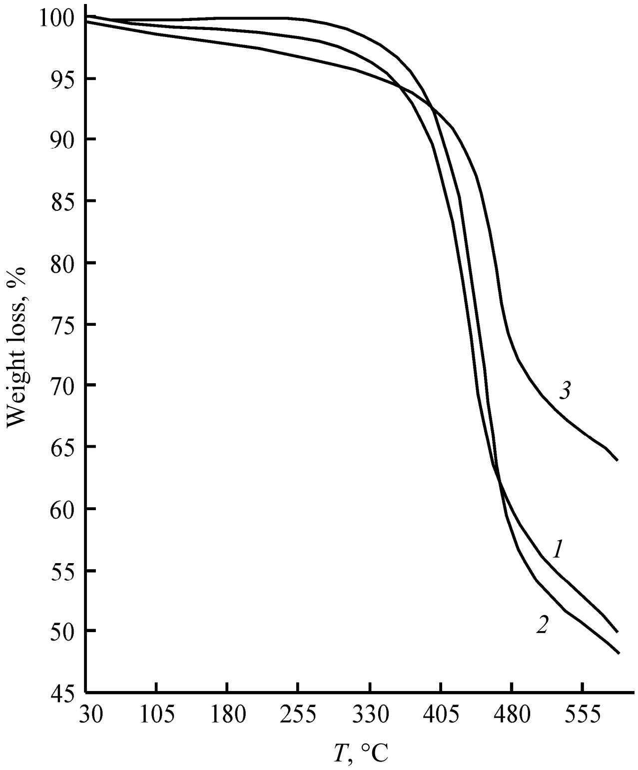


Fig. 3. TGA curves for the europium complexes: (*1*) **III**, (*2*) **IV**, (*3*) **V.**

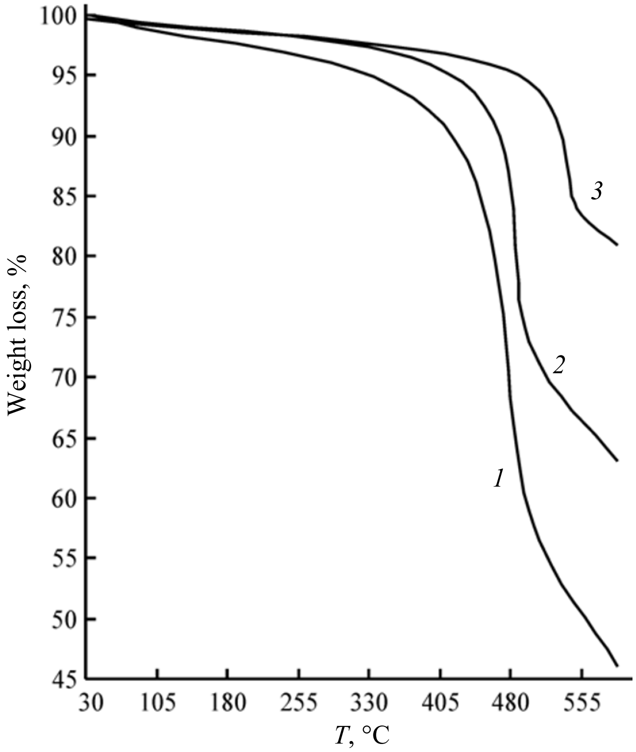


Fig. 4. TGA curves for terbium complexes: (*1*) **VI,** (*2*) **VII,** (*3*) **VIII**.

the temperature range 290–365ºC (Fig. 5), which is expressed by the equation: log p (mm Hg) = $A–B/T$. Coefficients of this equation are listed in Table 3. From the $P–T$ plot we calculated the thermodynamic parameters of sublimation. Vaporization temperature interval was chosen according to the DSC data. In the investigated temperature range only the process of vaporization occurs. In addition, according to mass spectrometry, at vaporization of compounds the molecules do not associate, so the calculation was performed for the vapor pressure of sublimation into the monomeric vapor.

EXPERIMENTAL

To study the phase transitions of the compounds a Netzsch DSC204F1 differential scanning calorimeter (Germany) was used. Measurements were carried out under argon atmosphere at a heating rate 5 K min^{-1}. The error in determining temperature of a physical transformation is ±0.2 K, error of the transition enthalpy is ±1%.

Table 1. Standard thermodynamic parameters of melting

Comp. no.	mp, °C	$\Delta_m H$, kJ mol^{-1}	$\Delta_m S$, J mol^{-1} K^{-1}
III	432	59.6	84.5
IV	425	50.9	72.9
VI	450	61.8	85.5
VII	430	53.1	75.6

Table 2. Major peaks and relative intensities of the ions in the mass spectra of compounds **I–VIII**

Comp. no.	Complex	m/z (I_{rel}, %)
I	$Sc(SON)_3$	227 (75) $[SON]^+$, 497 (100) $[Sc(SON)_2]^+$, 723 (67) $[Sc(SON)_3]^+$
II	$Sc(NON)_3$	210 (100) $[NON]^+$, 463 (86) $[Sc(NON)_2]^+$, 672 (30) $[Sc(NON)_3]^+$
III	$Eu(SON)_3$	227 (100) $[SON]^+$, 605 (35) $[Eu(SON)_2]^+$, 831 (20) $[Eu(SON)_3]^+$
IV	$Eu(OON)_3$	211 (100) $[OON]^+$, 361 (46) $[Eu(OON)]^+$, 571 (44) $[Eu(OON)_2]^+$, 781 (18) $[Eu(OON)_3]^+$
V	$Eu(NON)_3$	210 (100) $[NON]^+$
VI	$Tb(SON)_3$	227 (100) $[SON]^+$, 611 (45) $[Tb(SON)_2]^+$, 837 (11) $[Tb(SON)_3]^+$
VII	$Tb(OON)_3$	211 (28) $[OON]^+$, 579 (100) $[Tb(OON)_2]^+$, 789 (70) $[Tb(OON)_3]^+$
VIII	$Tb(NON)_3$	210 (10) $[NON]^+$, 577 (100) $[Tb(NON)_2]^+$, 786 (30) $[Tb(NON)_3]^+$

Table 3. Vapor pressure and thermodynamic parameters of evaporation of the Sc and Eu complexes

Compound	Temperature range	A	$B\times10^{-3}$	$\Delta_{\text{subl}}H(T)$,[a] kJ mol^{-1}	$\Delta_{\text{subl}}S$, J mol^{-1} K^{-1}
$Sc(SON)_3$	292–347	8.65±0.4	5.88±0.24	112.6±3.4	110.5±2.5
$Eu(SON)_3$	313–365	8.33±0.2	6.11±0.1	116.9±4.1	104.2±2.1

[a] T is the middle of the temperature range.

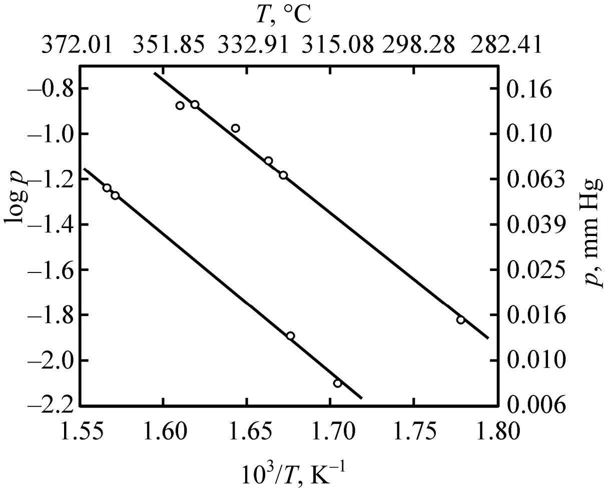


Fig. 5. Plots of saturated vapor pressure of the Sc and Eu complexes: log p (mm Hg) = $f(10^3/T)$: (*1*) **III**, (*2*) **I**.

The thermogravimetric analysis was performed on a Perkin-Elmer PYRJS6-TGA instrument in the temperature range 40–620ºC under nitrogen atomsphere, heating rate 5 deg min^{-1}.

The mass spectra of the compounds vapor were obtained on a Polaris Q mass spectrometer using direct input. The tested powder was rubbed into the inner surface of the glass crucible (DIP sample cup) in a quantity sufficient to produce an ion current 100 times exceeding the background.

The vapor pressure of the compounds was measured by the Knudsen's effusion method with the registration of the sublimed material weight. The vapor pressure values were calculated using the Hertz–Knudsen equation:

$$p = 17.14(\Delta m/\sigma_{\text{eff}}\tau)\sqrt{T/M},$$

where p is the vapor pressure to be determined, mm Hg; Δm is the amount of the evaporated substance, g; σ_{eff} is the area of the effusion hole, cm^2; τ is evaporation time, s, T is the evaporation temperature, K, and M is molecular weight of the vapor. σ_{eff} = 1.46×10^{-3} cm^2. Sensitivity of the Mack-Ben balances was 1.0156 g cm^{-1} of the scale of a KM-8 cathetometer.

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