Luminescent properties of europium carboxylates

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Abstract

Mixed-ligand europium carboxylates with nitrogen- and phosphorus-containing neutral ligands having polymer or island structure were studied by the luminescent and X-ray photoelectron spectroscopy methods. In similar groups of the compounds, the value of Stark splitting of the $^7F_1 \rightarrow$ level decreased with decrease of the electron density transfer from europium ion to ligand (covalence of metal-ligand bond increases) and the relative intensity of electro-dipole $^5D_0 \rightarrow ^7F_4$ transition raised.

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1. Introduction

Such properties of the lanthanide compounds at tendency to complexing and sublimation, ability to intensive absorption and luminescence depend directly on the lanthanide electron structure and the nature of the chemical bond in the mixed-ligand complexes. It is known that substitutes, even distant from reaction centers of ligand molecules, change distribution of the electron density in these molecules and therefore influence on the physico-chemical and analytical properties of the compounds: strength of Ln-ligand bond, its character, and optic characteristics of the compounds. The change of the atom change may be a measure of the change of electron distribution [1–5].

For an accurate estimation of influence of the nature of the environmental on the spectral – luminescence properties of the rare-earth complexes one should have knowledge on peculiarities of their electron structure. Wide use of the lanthanide compounds [6,7] is a cause of increased interest to study of their electron structure nature of chemical bond.

The literature analysis testifies to insufficient investigation of correlation of the Ln$^{3+}$ luminescent parameters with the characteristics of its electron structure determined by the photo- and X-ray electron spectroscopy methods [1–3,8–10]. The mixed-ligand europium(III) compound with β-diketones were studied by the luminescent and X-ray spectroscopy methods [11,12] while the rare-earth compounds with carboxylic acids were not practically investigated [13,14].

2. Experimental

2.1. Materials

For synthesis of the compounds the following reagents were used:
2.2. Synthesis

Europium complexes were obtained by interaction of europium trifluoroacetate and trichloroacetate hydrates and neutral ligand (in the 1: 2 M ratio). Mixed-ligand compounds with meta-methylbenzoic and cinnamic acids were prepared by interaction of a europium salt, sodium salt of the acid, and a neutral ligand (in the molar ratio 1: 3: 2). The method was described in detail in Refs. [15–17].

2.3. Chemical elemental analysis

The elemental contents of complexes were measured with EURO EA 3000.

2.4. Luminescence measurements

The luminescence spectra were registered on a SDL-1 diffraction spectrometer at 300 K and 77 K. The resolution of the diffraction spectrometer ~1 nm. In order to estimate intensity of luminescence we carried out integration of the areas of the luminescence bands which positions were determined to an approximation of ± 2–3 cm⁻¹.

The luminescence excitation spectra were recorded on the installation assembled on the basis of a SDL-1 spectrometer and a MPD-23 monochromator; a Tungsram 2500 W xenon lamp served
as an excitation source. Measurements were carried out at 300 and 77 K.

2.5. X-ray electron measurements

The X-ray photoelectron spectra of carbon, oxygen, and nitrogen and europium were recorded on a ES-2401 spectrometer (Russia) at the room temperature using nonmonochromatic AlKα-radiation. Due to suggestion of the binding energies (Eb) of the electrons of functional groups atoms to be constant [18], the scale of the bond energies equaled 0.1 eV. The X-ray photoelectron spectra of carbon, oxygen, and nitrogen were recorded on a ES-2401 spectrometer (Russia) at the room temperature using nonmonochromatic AlKα-radiation. Meta-methylbenzoic and cinnamic spectra were calibrated against (687.9 eV). Meta-methylbenzoic and cinnamic spectra were calibrated against (687.9 eV). Meta-methylbenzoic and cinnamic spectra were calibrated against (687.9 eV).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Found (%)</th>
<th>Calculated (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(C8H7O2)3·3H2O</td>
<td>10.41</td>
<td>10.38</td>
</tr>
<tr>
<td>Eu(C9H7O2)3·2C10H8N2·H2O</td>
<td>32.50</td>
<td>32.18</td>
</tr>
<tr>
<td>Eu(C9H7O2)3·2C12H8N2·H2O</td>
<td>35.21</td>
<td>35.38</td>
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</table>

The mixed-ligand europium compounds with trifuoroacetic, trichloroacetic, m-methylbenzoic and cinnamic acids display red luminescence at both room temperature and 77 K. Their luminescence spectra (77 K) are given in Fig. 1. As it may be seen, all the compounds may be divided into two groups. In the spectra of the first group compounds, the bands corresponding to the $^5D_0 - ^7F_2$ electro-dipole transition are the most intensive that is typical for most of the luminescent Eu compounds [23,24]. Compounds [Eu(C9H7O2)3·xH2O]m and Eu(C9H7O2)3·xH2O has such spectra (Fig. 1a,b). It should be noted that the band distribution of the $^5D_0 - ^7F_j$ transition ($j = 1, 2$) in the spectra of monomer and dimeric compounds differ slightly. It may be connected with the fact that the crystal field in the homologous series studied in this work changes insignificantly. The low — temperature spectra of these compounds have linear character. In this case maximum possible number of components of the $^5D_0 - ^7F_j$ ($j = 0-4$) transitions of Stark structure is observed. The value of Stark splitting magneto-dipole transition $^5D_0 - ^7F_1$ ($\Delta F_1$) equals 150—200 cm$^{-1}$.

In the spectra of the second group compounds, the bands of the $^5D_0 - ^7F_1$ magneto-dipole transition (580—590 nm) are rather intensive. Thus, for most of carboxylates containing substituors with strong negative effect (—CCL, —CFL), intensity of the $^5D_0 - ^7F_2$ magneto-dipole transition is comparable or two time less than that of the $^5D_0 - ^7F_2$ electro-dipole transition (Fig. 1c). In the luminescence spectra of Eu(C9H7O2)3·xH2O (where D = C12H8N2, C10H8N2), relative intensity of the bands of the $^5D_0 - ^7F_2$ magneto-dipole transition is higher than for other compounds of the first group, but lower than for the complexes of the second one. Increase of intensity of the $^5D_0 - ^7F_2$ transition in the luminescence spectra of the compounds Eu(TFA)3D, where D = dipyr or phen, is explained by coordination of the most donor molecules dipyr and...
Table 2

Luminescent features and core electrons binding energies (eV) in mixed-ligand europium carboxylates.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\eta_1$</th>
<th>$\eta_2$</th>
<th>$\Delta\eta$</th>
<th>$\nu_0$, cm$^{-1}$</th>
<th>$\Delta\nu$, cm$^{-1}$</th>
<th>$\text{Eu}^{3+}$</th>
<th>N1s</th>
<th>P2p</th>
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<tr>
<td>[Eu(C$_2$F$_5$O$_2$)$_3$]·2H$_2$O</td>
<td>0.45</td>
<td>0.10</td>
<td>0.05</td>
<td>17273.8</td>
<td>16.7</td>
<td>137.9</td>
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<td>Eu(C$_2$F$_5$O$_2$)$_3$·2C$_3$H$_7$N$_3$PO·H$_2$O</td>
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<td>0.12</td>
<td>0.12</td>
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<td>137.7</td>
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<tr>
<td>Eu(C$_2$F$_5$O$_2$)$_3$·2C$_3$H$_7$N$_3$H$_2$O</td>
<td>0.24</td>
<td>0.15</td>
<td>0.30</td>
<td>17253.8</td>
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<td>136.5</td>
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<td></td>
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<tr>
<td>Eu(C$_2$F$_5$O$_2$)$_3$·2C$_3$H$_7$N$_3$PO·H$_2$O</td>
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<td>0.19</td>
<td>0.35</td>
<td>17255.9</td>
<td>14.8</td>
<td>136.7</td>
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<tr>
<td>Eu(C$_2$F$_5$O$_2$)$_3$·2C$_3$H$_7$N$_3$H$_2$O</td>
<td>0.25</td>
<td>0.20</td>
<td>0.45</td>
<td>17256.8</td>
<td>14.8</td>
<td>136.8</td>
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<tr>
<td>Eu(C$_2$F$_5$O$_2$)$_3$·2C$_3$H$_7$N$_3$N$_2$H$_2$O</td>
<td>0.24</td>
<td>0.22</td>
<td>0.45</td>
<td>17257.8</td>
<td>14.8</td>
<td>136.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eu(C$_2$F$_5$O$_2$)$_3$·2C$_3$H$_7$N$_3$PO·H$_2$O</td>
<td>0.24</td>
<td>0.28</td>
<td>0.45</td>
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<td>14.8</td>
<td>137.0</td>
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<tr>
<td>Eu(C$_2$F$_5$O$_2$)$_3$·2C$_3$H$_7$N$_3$H$_2$O</td>
<td>0.28</td>
<td>0.28</td>
<td>0.45</td>
<td>17263.9</td>
<td>14.8</td>
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<tr>
<td>Eu(C$_2$F$_5$O$_2$)$_3$·2C$_3$H$_7$N$_3$PO·H$_2$O</td>
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<td>0.38</td>
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<tr>
<td>Eu(C$_2$F$_5$O$_2$)$_3$·2C$_3$H$_7$N$_3$H$_2$O</td>
<td>0.59</td>
<td>0.41</td>
<td>0.45</td>
<td>17265.9</td>
<td>14.8</td>
<td>137.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. EXP spectra of europium(III) compounds: a – [Eu(C$_2$F$_5$O$_2$)$_3$·3H$_2$O]$, b$ – [Eu(C$_2$F$_5$O$_2$)$_3$·3C$_3$H$_7$N$_3$N$_2$·3H$_2$O], c – Eu(C$_2$F$_5$O$_2$)$_3$·2C$_3$H$_7$N$_3$·2H$_2$O.
According to [15], it is dimmer therefore its luminescent features are given (Table 2) but are not compared with the data for the mixed-ligand compounds.

In the luminescence spectra of m-methylbenzoates, Δν and ΔF1 values decrease in the series from \([\text{Eu}(C_6H_7O_2)_3 \cdot 2H_2O]_n\), \([\text{Eu}(C_6H_7O_2)_3 \cdot C_8H_8N_2PO_2 \cdot 2H_2O]_n\), \([\text{Eu}(C_6H_7O_2)_3 \cdot C_6H_18N_3PO_2 \cdot 2H_2O]_n\), \([\text{Eu}(C_6H_7O_2)_3 \cdot C_6H_18N_2]_2 \cdot 2H_2O\), \([\text{Eu}(C_6H_7O_2)_3 \cdot C_6H_8N_2]_2\) to \([\text{Eu}(C_6H_7O_2)_3 \cdot C_6H_8N_2]_2\) (Table 2). The XPS data show that this series is characterized by the increase of the electron density on Eu4d5/2 (decrease of Ec for Eu4d5/2) that indicates to the donation of electron density from the bond energy \(N_1\) binding energy equals 400.5 eV showing to insignificant donation from nitrogen atom. It may be explained by the structure of the neutral ligand. Diphenylguanidine composition includes voluminous phenyl substitutes.

Besides analysis of the values of Stark splitting \(\Delta F_1\) and shift of the \(5D_0 - 7F_2\) transition band, calculation of ratio of the integral intensities of the bands of the \(5D_0 - 7F_j\) transition \(j = 1, 4\) to the \(5D_0 - 7F_2\) dipole transition was carried out. The ratio of intensities of the luminescent bands, splitting of the \(5D_0 - 7F_1\) magnetodipole transition \(\Delta F_1\), and charge state of the central europium atom correlate between each other: in similar series of the mixed-ligand europium carboxylates the value of Stark splitting \(\Delta F_1\) decreases with increase of electron density on the europium atom (increase of covalence of metal-ligand bond) and intensity of the \(5D_0 - 7F_4\) electrodipole transition \(\eta_2\) rise.

**Conflict of interest**

The authors declare that they have no conflict of interest.

**Acknowledgments**

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