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$4f^n$–$4f^{n-1}d$–transitions in the optical spectra of tris (1,2,4-triphenylcyclopentadienyl) complexes of the lanthanide ions

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Tris complexes of Ln^{3+} ions ($Ln = La, Ce, Pr$), with triphenyl-substituted cyclopentadienyl ligands were studied by optical spectroscopy. Emission of both $5d$–$4f$ and $4f$–$4f$ transitions was observed for Pr^{3+} complex. It was found that the strength of the crystal field formed by triphenyl-substituted cyclopentadienyl ligands in tris complexes is comparable to the case of sulfides, and as a result, red luminescence is observed for the Ce^{3+} compound. The quantum yield of photoluminescence is 20% for the latter.

Keywords: $5d$–$4f$-luminescence, ligand field, quantum yield of photoluminescence, Ln^{3+} ions, cyclopentadienyl ligand.

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Introduction

The last two decades have been marked by a significant increase in the use of rare earth elements (REE) in new technologies in almost all sectors of the economy [1]. Inorganic compounds, activated by Ln^{3+} ions, as well as molecular complexes of lanthanides, are used for various applications. In particular, intraconfigurational $4f$–$4f$ transitions are used in luminescent devices based on inorganic compounds, such as fluorescent lamps, cathode ray tubes, and lasers [2], while molecular complexes are used in biology, medicine, catalysis, optics and materials science [3]. The luminescence decay time of emitting $4f$ levels is usually in the range of 10–50 ns in case of Ce^{3+} and Pr^{3+} ions and in the range of 0.2–2 ms in case of Eu^{3+} and Tb^{3+} ions. The energies of numerous $4f$-levels of lanthanides can be found on the Dicke diagram [4] up to energies of $40\,000\,cm^{-1}$. This diagram has recently been extended to the vacuum ultraviolet area [5]. However, if we look at the amount of data on $5d$–$4f$ interconfigurational transitions, we can find much less information and very little information in the case of $5d$–$4f$ interconfigurational transitions for lanthanide molecular complexes. Despite a deep understanding of the nature of $4f$–$4f$-transitions, knowledge about $4f^n$–$4f^{n-1}d$-transitions is not enough.

Cyclopentadienyl (Cp) ligands are among the most common in organometallic chemistry due to their active use in the preparation of lanthanide complexes acting as catalysts, but the photophysical properties of lanthanide complexes with Cp derivatives are practically not studied. One of the reasons for this is the predominance of the traditional approach in the design of brightly luminescent lanthanide compounds — the use of various σ-coupled „antenna“ ligands.

Over the past few years, we have been actively engaged in target design of the lanthanide complexes containing π-coupled „antenna“ ligands based on cyclopentadienyl derivatives, together with a detailed analysis of the energy transfer processes in them [6–8]. Previously, using quantum chemical calculations, it was shown that the crystal field formed by three diphenyl-substituted Cp ligands leads to a strong decrease in the energy of the $5dz^2$-orbital of Ln ions [6]. Such a significant decrease in the energy of the $5d$ level and, as a consequence, the participance of the allowed interconfigurational $5d$–$4f$ transitions in the processes of luminescence sensitization of the lanthanide ion should lead to unexpected optical properties. Indeed, for the terbium bis-complex containing diphenyl-substituted Cp ligands, a high photoluminescence (PL) quantum yield (50%) was obtained, while the lifetimes for $4f$–$4f$ transitions turned out to be short (0.35 ms). Therefore, we chose the triphenyl-substituted Cp ligand as a system that provides a further decrease in the energy of the $4f^{n-1}5d$ levels.

Since the energies of the $5d$ states are extremely sensitive to the environment of the ion, a sufficiently strong field Cp of the ligand can be an effective tool for increasing the efficiency of luminescence sensorialization of the Ln ion due to $f-d$ transitions.

In this paper we present the results obtained for tris complexes containing triphenyl-substituted Cp ligands, for which $4f^n$–$4f^{n-1}d$ transitions were detected for the first time by optical spectroscopy. It was also shown that the crystal field formed by three triphenyl-substituted Cp ligands, in terms of its effect on $4f^{n-1}5d$-levels of lanthanide ions, is comparable to one of the strongest crystal fields known for inorganic compounds, namely sulfides.

Objects and methods

Polycrystalline samples of the composition $[\{Ph_3C_5H_2\}_3LnCl]^-[Li(THF)_4]^+$, Ln = La (**1**), Ce (**2**), Pr (**3**), $Ph_3C_5H_2$ — 1,2,4-triphenylcyclopentadienyl, THF — tetrahydrofuran (Diagram 1) were synthesized according to [6].

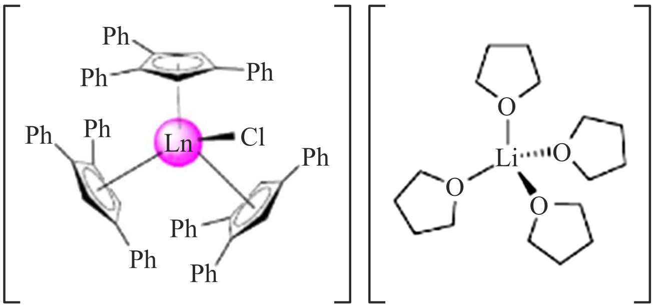

Diagram1

The sterically overloaded tris(1,2,4-triphenylcyclopentadienyl)-complexes of lanthanides are characterized by the local symmetry C_3 of the complex anion. The third order axis passes through the Ln–Cl bond line, and the three ligands are actually equivalent. Meanwhile, the $Li(THF)_4^+$ cation is completely shielded by tetrahydrofuran molecules, and there are not shortened cation-anion contacts in the crystal.

Luminescence and luminescence excitation spectra were measured on a Fluorolog FL3-22 spectrofluorimeter manufactured by Horiba-Jobin-Yvon. For optical excitation, a xenon lamp with a power of 450 W, emitting in the range 250–800 nm, was used. The R-928 photomultiplier is sensitive in the 250–850 nm spectral range and operates in the photon counting mode. The required excitation and registration wavelengths of luminescence were selected by the corresponding monochromators, the bandwidth of which could be set in the range 0.1–14 nm. The resulting compounds are hygroscopic and unstable in air, so they were placed in quartz ampoules and sealed. The diameter of the used ampoules is 0.5 cm. For low-temperature measurements (77 K), the ampoule with the sample was placed in a quartz nitrogen cryostat.

Time-resolved luminescence measurements were also performed on a Fluorolog FL3-22 instrument. A xenon flash lamp with a pulse duration on the order of several microseconds was used as a source of pulsed optical excitation. The typical decay time of the instrumental function, which has the form of a single decreasing exponent, is approximately 10 ms. To measure the kinetic dependences, the time gating method was chosen, which allows to measure lifetimes with a duration of approximately from 10 ms to seconds. We also used a set of short-pulse diode light sources (DeltaLED, spectral range 260–400 nm with a step of 20 nm). The range of measured luminescence lifetimes is 5 ns–0.5 s, the implementation by the time-correlated single photon counting methods (TCSPC) and direct observation of the decay of the luminescence intensity.

The absolute PL quantum yield was measured by the absolute Wrigton [9–11] method using a G8 integrating sphere manufactured by GMP (General microtechnology & photonics, Switzerland) mounted on a Fluorolog FL3-22 spectrofluorimeter. This configuration of the device allows to measure the PL quantum yield of samples at room temperature in the spectral range of excitation 300–800 nm and luminescence 360–850 nm using an R-928 photomultiplier. The inner surface of the sphere is covered with a diffusely reflective material — Spectralon SRS-99, which reflects 99% of the incident light in the spectral range 400–1700 nm. The calibration of the spectral dependence of the diffuse reflectance of the sphere and the sensitivity of the photomultiplier was carried out using a calibrated quartz halogen incandescent lamp with a power of 45 W manufactured by Oriel. Each sample was measured three times under slightly different experimental conditions. Experimental error was ±10%.

Results and discussion

Fig. 1 shows the PL spectra measured upon excitation with a UV lamp with $\lambda_{exc} = 370$ nm at 77 K. In the presented spectra, broad bands are observed with maxima 480 and 505 nm/20 833 and 19 800 cm^{-1} (compound **1**), 430 and 450 nm/23 256 and 22 222 cm^{-1} (compound **2**) and 540 and 610 nm/18 520 and 16 393 cm^{-1} (compound **3**). The bands observed in the case of the compound **1** (ion La^{3+}) are caused by the fluorescence of the triphenyl-substituted Cp ligand. The bands observed in the region 420–460 nm of the PL spectrum for the compound **2** (Pr^{3+}ion) are assigned to interconfigurational $5d$–$4f$ transitions [12,13]. They are transitions from the lowest excited $4f^15d^1$-state to ^3H_J- and ^3F_J-multiplets of the basic $4f^2$ -electron configuration ($4f^15d^1 \rightarrow 4f^2$) of Pr^{3+} ions. In addition, narrow bands associated with intraconfigurational $4f$–$4f$ transitions of the Pr^{3+} ion were also registered in this compound. The identification of the observed $4f^2 \rightarrow 4f^2$ transitions was carried out on the basis of the well-known Dicke diagram

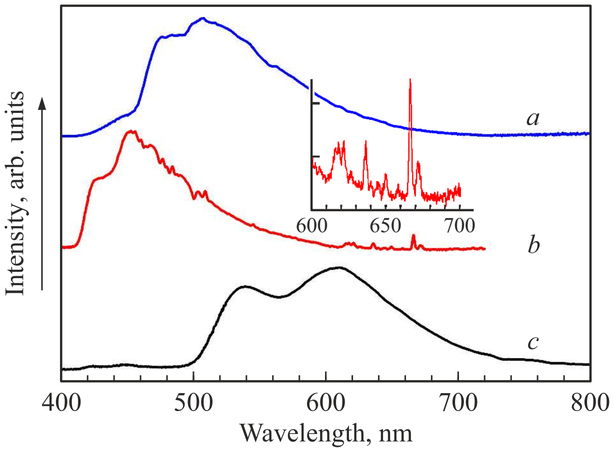

Figure 1. PL spectra of polycrystalline samples of compounds **1** (La^{3+}, a), **2** (Pr^{3+}, b) and **3** (Ce^{3+}, c), measured with $\lambda_{exc} = 270$ nm excitation at a temperature of 77 K. The insert shows a part of the luminescence spectrum obtained at a higher spectral resolution.

(Fig. 1, inset). It should be noted that the intensity of transitions from the $^3P_0$ level (485 nm) is lower than one of the transitions from the $^1D_2$ level (600 nm), which is probably due to the multiphonon relaxation processes on the $^1D_2$ multiplet.

There is two bands with maxima at 560 and 610 nm in the luminescence spectrum of the compound **3**. These two maxima correspond to the main doublet of the Ce^{3+} ion, namely, the $5d^1$–$4f^1$ ($^2F_{5/2}$) and $5d^1$–$4f^1$ ($^2F_{7/2}$) transitions. The energy difference between these two levels $\sim 1500\,\text{cm}^{-1}$ is due to the spin-orbit interaction in the crystal field [14]. A similar broad luminescence band of the cerium ion with a maximum at 620 nm was observed in complexes with azolyl-substituted theophenolates [15]. It is known from the literature that in Lu_2S_3 sulfide, activated by Ce^{3+} ions, these transitions are at similar energies ($600\,\text{nm}/16\,600\,\text{nm}^{-1}$), while in compounds of $LiYF_4$ composition the energy of this doublet is 310 nm ($32\,300\,\text{cm}^{-1}$) [16]. Thus, the the crystal field formed by three triphenyl-substituted Cp ligands is comparable to one of the strongest crystal fields known for inorganic compounds, the field in sulfides, in its strength of influence on the $4f^{n-1}5d$ levels of lanthanide ions.

Luminescence excitation spectra of compounds **1**–**3**, measured at $\lambda_{reg} = 505$, 450 and 610 nm, respectively, are shown in Fig. 2. The spectra obtained contain a number of broad bands in the region 270–500 nm. In the excitation spectrum of the **1** compound there is an intense band with a maximum at 370 nm and a low-frequency shoulder with a maximum at 410 nm. Based on the previously obtained data on the structure and optical spectra of a number of Ln^{3+} compounds containing polyphenyl-substituted Cp, the mentioned intense band is assigned to π–π^* transitions of phenyl rings while the shoulder — is the band of intraligand charge transfer — ILCT) [7]. In the excitation spectrum of the **2** compound, the above-mentioned 370 nm band can be distinguished, while for the **3** compound, in addition to the 370 nm band, ther are 420 and 480 nm bands. Thus, four groups can be distinguished in the luminescence excitation spectra. First, the highest frequency and most intense bands with a maximum of 250 nm, related to π–π^* transitions of the unsubstituted Cp ring. Secondly, the bands around 370 nm assigned to the π–π^* transitions of the phenyl groups of the Cp ring. It should be noted that the shape and intensity of the bands in this area strongly depend on the coplanarity of the phenyl rings and Cp of the ring. Thirdly, less intense bands around 420 nm caused by intraligand charge transfer state. The nature of the appearance of this charge transfer state becomes clearer when taking into account the factors that the ligands under consideration are characterized by strong steric hindrances, which lead to different rotation angles of the phenyl rings with respect to the central cyclopentadienyl ring. This, in turn, leads to different conjugation between aromatic fragments and, as a result, to the presence of intramolecular charge transfer. The fourth group is formed by the bands at 390 and 480 nm, observed in the compounds of Pr^{3+} and Ce^{3+} ions, respectively, and assigned to $4f \rightarrow 5d$ transitions. According to the literature, the energy of the $4f \rightarrow 5d$ transition for the Pr^{3+} ion is higher than for the Ce^{3+} ion [17]. Thus, in the case of

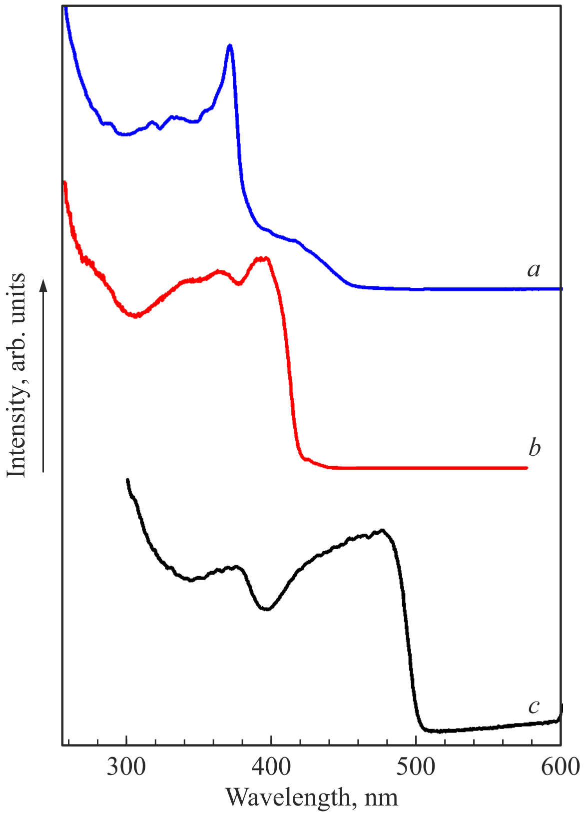

Figure 2. Luminescence excitation spectra of the compounds **1** (La^{3+}, a), **2** (Pr^{3+}, b) and **3** (Ce^{3+}, c), measured at 77 K.

$CsCdBr_3$ activated by Pr^{3+} and Ce^{3+} ions, the energy of the $4f \rightarrow 5d$ transition is 38250 and 26010 nm^{-1}, respectively. In the compounds under our study, this tendency is quite well carried out (25640 and 20830 cm^{-1}).

The PL decay kinetics of the cerium complex could be approximated by a monoexponential law, and the calculated luminescence decay time for the $5d{-}4f$ transition in the Ce^{3+} ion was 110 ns. The absolute PL quantum yield, measured using an integration sphere at $\lambda_{\text{exc}} = 340$ nm, was 1% for the praseodymium compound and 21% for the cerium compound.

Conclusions

It is known that the positions of the $4f^{n-1}5d$ levels depend much more on the interaction with the crystal field than the positions of the $4f^n$ levels. This is due to the strong interaction of the $5d$ electron with neighboring anionic ligands in the compound. Based on the analysis of experimental data, it is shown that the the crystal field formed by three triphenyl-substituted Cp ligands is comparable in its strength of influence on the $4f^{n-1}5d$ levels of lanthanide ions to one of the strongest crystal fields known for inorganic compounds — the crystal field in sulfides. It has long been shown that the energy of the $5d$ level of the Ce^{3+} ion in a certain compound can be used to estimate the position of the $4f^15d$ level of the Pr^{3+} ion in a similar compound [16]. Usually this energy is 12500 cm^{-1} higher in the case of the ion Pr^{3+}. In the studied compounds, there is the same tendency, but the difference between the energies of the lowest $4f^{n-1}5d$ levels of the Ce^{3+} and Pr^{3+} ions is 6900 cm^{-1}. It should be noted that the energy differences indicated in the literature are applicable for inorganic compounds activated by lanthanide ions, while in this work these differences are obtained for the first time for lanthanide molecular complexes. Moreover, a similar correlation is true for compounds activated by Tb^{3+} ions, where the first allowed $4f^8{-}4f^75d$ transition usually has higher energy by 14 000 cm^{-1} than in the corresponding compound activated by Ce^{3+} ion. Unfortunately, it is not yet possible to check this correlation, since the high steric crowding of the complexes under consideration does not allow us to obtain a compound with terbium ion due to the lanthanide compression effect.

As it was shown earlier by quantum chemical calculations, the crystal field formed by three ligands containing 1,3-diphenyl-substituted Cp leads to a strong decrease in the energy of the $5dz^2$-orbital of the lanthanide ion [6]. However, due to the strong overlap of the bands in the excitation spectra, it was not possible to single out the bands corresponding to the $4f{-}5d$ transitions unambiguously. The introduction of a third phenyl as a substituent in the Cp ligand and the preparation of the corresponding tris complex made it possible for the first time to experimentally isolate the $4f^n{-}4f^{n-1}5d$ bands in the luminescence excitation spectra of lanthanide complexes with substituted Cp and demonstrate their participation in the process of luminescence sensitization of the Ln^{3+} ion.

Thus, since the energies of the $5d$ states are extremely sensitive to the ligand surrounding relatively strong crystal field of the Cp ligand can be an effective tool for lowering the energy of interconfigurational $f{-}d$ transitions and, as a consequence, for their involvement in the process of luminescence sensitization of the lanthanide ion in order to increase the efficiency of this sensitization. This result is of great interest for the further development of lanthanide complexes based on polyphenyl-substituted Cp for various optical applications.

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Conflict of interest

The authors declare that they have no conflict of interest.

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