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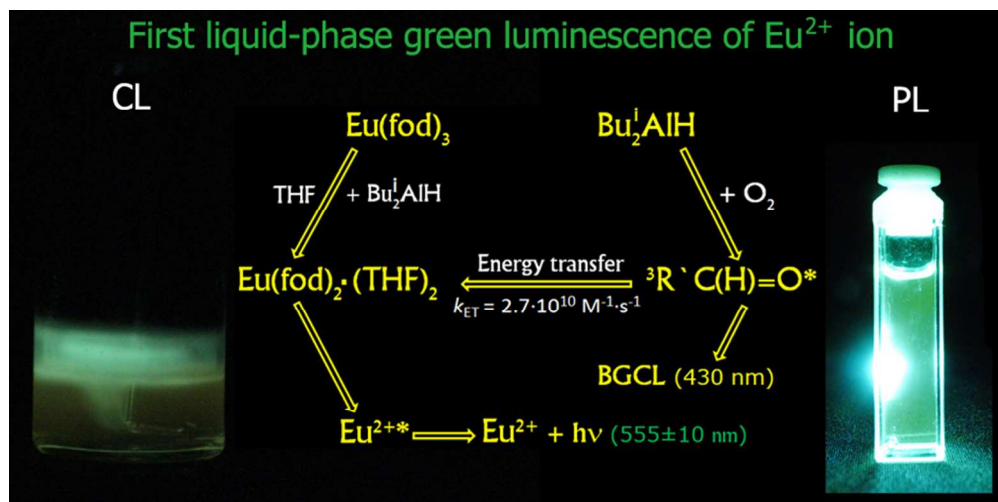
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The first registration of a green liquid-phase chemiluminescence of the divalent Eu²⁺* ion in interaction of β-diketonate complexes Eu(acac)₃·H₂O, Eu(dpm)₃, Eu(fod)₃ and Eu(CH₃COO)₃·6H₂O with Buⁱ₂AlH in THF with the participation of oxygen

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The first liquid-phase green chemiluminescence (CL) of the divalent europium Eu²⁺* at the study of interactions in the systems EuL₃·(H₂O)ₓ-THF-Buⁱ₂AlH-O₂ (L = acac, dpm, fod, and CH₃COO; x = 0, 1, 6; Buⁱ = iso-C₄H₉) was discovered. The attack of Buⁱ₂AlH on the water of crystallization of complexes EuL₃·(H₂O)ₓ affords aluminoxane (Buⁱ₂Al)₂O, hydrogen, and isobutane. The reaction of Buⁱ₂AlH and EuL₃-moiety of the initial Eu³⁺ complexes leads to the previously no synthesized divalent europium complexes EuL₂·(THF)₂, which were isolated and characterized by elemental and spectral analysis in the present work. In the reaction solutions, these complexes are associated in a bulky complexes with an excess of diisobutylaluminum hydride EuL₂·(THF)₂-Buⁱ₂AlH. The measured spectra of CL and photoluminescence (PL) of yellow-green reaction solutions in both cases consist of one broad band with λ_{max} = 555±10 nm due to the emission of the electron-excited state of the Eu²⁺* ion (4f⁶5d¹→4f⁷ transition), a part of the bulky complex EuL₂·(THF)₂-Buⁱ₂AlH. The lifetime of the excited states, PL, and CL quantum yields of the Eu²⁺* ion in the EuL₂·(THF)₂-Buⁱ₂AlH complexes were determined. A mechanism ("indirect CL") is proposed to explain the generation of the green CL. The primary emitter triplet-excited isobutyric aldehyde ³ŔC(H)=O* (Ŕ = iso-C₃H₇) is formed in the disproportionation reaction of peroxyl radicals – intermediates of Buⁱ₂AlH oxidation by oxygen. The exited ³ŔC(H)=O* molecules transfer energy to Eu²⁺ ion converting it into the electronically exited state Eu²⁺*, which is then deactivated by emitting quanta of green light due to the 4f⁶5d¹→4f⁷ transition. It was found that for a divalent Eu²⁺ unlike to trivalent Ln³⁺ ions, replacement of the inorganic anion-ligand Cl⁻ (complex EuCl₂·(THF)₂-Buⁱ₂AlH) with organic one L (complex EuL₂·(THF)₂-Buⁱ₂AlH) decreases the CL and PL intensity and leads to the green-shift of the luminescence maximum of Eu²⁺* from the blue (λ_{max} = 465 nm) to the green (λ_{max} = 555 nm) region. The high brightness and duration of the CL, visible to the naked eye in the system Eu(fod)₃-THF-Buⁱ₂AlH-O₂, make it promising as a chemical source of green light.

Introduction

Phenomenon of chemiluminescence (CL) is widely applied to analytical chemistry, studying mechanisms of chemical and biochemical reactions, identification of intermediate and final reaction products, estimation of antioxidant activity in chemistry and medicine, and creation of chemical light sources.[1-11] In numerous studies, trivalent lanthanide ions have been successfully registered as emitters and enhancers of CL. These ions emit light from the UV to near infrared region and spectrally manifest itself as narrow maximums, corresponding to the spin-forbidden f-f transitions.[2-7,10,12 and references therein] At the same time, divalent lanthanide ions were not known as emitters and enhancers of CL in liquid-phase reactions before

our studies[13,14], although some of them, especially Eu²⁺, exhibit blue easily detected d-f photoluminescence.[15-23] Only two years ago, we have found very bright blue CL of the divalent Eu²⁺* ion, which was observed by the naked eye in the interaction of crystalline hydrate EuCl₃·6H₂O and diisobutylaluminum hydride Buⁱ₂AlH in THF in presence of oxygen.[13] It was the first example of a divalent lanthanide ion action as an emitter of liquid-phase CL. The aim of the present study is to explore the possibility of CL generation in interaction of another Eu³⁺ compounds with Buⁱ₂AlH in present of oxygen in THF solution. On the one hand, unlike to EuCl₃·6H₂O, the Eu³⁺ ion in complexes, which we have chosen to examine (three Eu³⁺ ß-dicetonates and one acetate hydrate), is more shielded by bulky ligands that could complicate the reducing of Eu³⁺ to Eu²⁺. Previously, interaction complexes Eu(acac)₃·H₂O (acac = acetylacetonate), Eu(dpm)₃ (dpm = 2,2,6,6-tetramethyl-3,5-heptanedionato), Eu(fod)₃ (fod = 1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octandionato), and Eu(CH₃COO)₃·6H₂O with Buⁱ₂AlH in THF has not been studied. This study is also interesting because successful reducing of

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Eu^{3+} opens a new approach to the preparation new luminescent complexes of Eu^{2+} (and possibly Yb^{2+}, Sm^{2+}) with different bulky ligands, using Bu$^i_2$AlH as a reducing agent. However, it should be pointed out that β-diketonate complexes Ln(dpm)$_2$·(dme)$_2$ of divalent lanthanide (Ln = Eu and Sm, dme = dimethoxyethane) were first obtained by Evans et al. in reaction of Kdpm with LnI$_2$·(THF)$_2$ in THF, followed by addition of dimethoxyethane.[24] As can be seen, in contrast to our approach, Evans' group used complexes of divalent lanthanides as starting compounds whereas but trivalent lanthanides are more available compounds.

Experimental

The β-diketonate complexes Eu(acac)$_3$·H$_2$O, Eu(dpm)$_3$, Eu(fod)$_3$, and hexahydrate Eu(CH$_3$COO)$_3$·6H$_2$O were used as received from Aldrich Chemical Co. Dialkylhydride Bu$^i_2$AlH, 73% solution in toluene was distilled according to [25]. THF was distilled under argon from sodium benzophenone ketyl before use. Argon and air were purified as in [25]. The CL, PL spectra and decay lifetimes were recorded on a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer (model FL-3-22) equipped with double-grating monochromators, dual lamphousing with 450W Xenon lamp and pulsed solid state laser-diode NanoLED, photomultiplier tube detector (Hamamatsu R928 PMT). Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard instrument correction, provided in the instrument software. Lifetime measurements were carried out using for excitation the Xenon flash lamp (500 Hz repetition rate) in the case of Eu^{3+} and 370 nm NanoLED (1 MHz repetition rate) in the case of Eu^{2+}. PL quantum yields (ϕ$_{PL}$) of the Eu^{2+} complexes in THF were determined by ratio value of integrated area under corrected luminescence spectra with using 2.0·10^{-5} M solution of anthracene (scintillation pure grade) in EtOH as a reference sample (ϕ$_{PL}$ = 0.28).[26] As a result, the PL quantum yields were calculated by Eq.1.

$$\frac{\phi_x}{\phi_{st}} = \frac{A_{st} \cdot n_x^2 \cdot D_x}{A_x \cdot n_{st}^2 \cdot D_{st}} \qquad (1)$$

where ϕ$_{st}$ and ϕ$_x$ are the PL quantum yields of the sample and standard; A$_x$ and A$_{st}$ are absorbances at the excitation wavelength for the sample and standard; n$_x$ and n$_{st}$ are the refractive indexes of solvents: 1.4050 for THF and 1.3611 for EtOH;[27] D$_x$ and D$_{st}$ are the areas under the PL spectra of the sample and standard. CL quantum yields (in Einstein·mol^{-1}) were calculated based on the ratio S/[Me$_2$CHC(H)=O], where S is a light sum (in photon·mL^{-1}), defined as the integrated area under the CL kinetic curves in coordinates CL intensity (I$_{CL}$, in photon·s^{-1}·mL^{-1}) *versus* time (s), [Me$_2$CHC(H)=O] ≈ 4·10^{-4} M is a concentration of isobutyric aldehyde, which is formed by complete oxidation of Bu$^i_2$AlH by oxygen and calculated using data.[28]

The kinetics of Eu^{3+}→Eu^{2+} reduction was monitored by an increase in the PL intensity of Eu^{2+} at 560 nm (λ$_{exc}$ = 445 nm) with an instrument Fluorolog-3 spectrofluorimeter using a time mode «Kinetics Acquisition». The integration time for all experiments was 10 s. The kinetics of CL was carried out in the original

chemiluminometer[28] in cylindrical Pyrex CL-cell (reactor) closed with a penicillin cap. As a light detector was photomultiplier tube "FEU-39". Calibration of the chemiluminometer was carried out as in [13].

In a typical experiment, transparent the CL-cell was charged with Eu^{3+} complex (0.02 mmol), purged with argon for 20 min for removal of O$_2$ from the gas space, and then 2 ml freshly distilled THF, saturated by air at stirring, was injected by syringe. After that, avoiding falling into the chemiluminescent chamber light of day, Bu$^i_2$AlH (0.2 mL, 0.8 mmol) was injected by syringe through the penicillin stopper with continuous stirring. In separate experiments, gaseous products (Bu^{i}H and H$_2$) contained in the reaction solution and the gaseous phase above that were analyzed by GLC according to [13,25]. To explore the possibility of CL generating under anaerobic conditions, the reaction was carried out in a quartz reactor made up with two cylindrical ampoule-like parts where the solutions of Eu(fod)3 and Bu^{i}2AlH were placed. The solutions were mixed after oxygen degassing by three freeze–evacuate–thaw cycles at 300 K in a CL chamber. Isolation of Eu^{2+} complex from the yellow-green reaction solution was effected according to the modified method of [29] by removing excess THF solvent with vacuum (1 torr) and heating (75°C). At achievement of this temperature, THF was completely removed with formation of the orange precipitate and small volume of liquid (excess Bu$^i_2$AlH and its oxidation products). Then, reactor was cooled under argon and 2 ml of hexane was added to remove excess Bu$^i_2$AlH and its conversion products. This operation was performed 5 times. As a result, dark yellow Eu^{2+} complexes were isolated. The molecular formulas of the resulting Eu^{2+} complexes were determined using complexometric titration, elemental analysis, and IR spectroscopy. The UV-visible absorption spectra were recorded by spectrophotometer Perkin Elmer Lambda 750 instrument in argon atmosphere using 1 cm quartz cells fitted with hermetic stoppers.

IR spectra were recorded in solid state (KBr tablet) using «Bruker Vertex 70V» instrument. Elemental analysis of Eu^{2+} complexes were performed in the elemental analyzer CHNS with an error: ±0.3%.

Spectral and other characteristics of the complexes obtained are presented below.

Eu(fod)$_2$·(THF)$_2$. Yield (19.2 mg, 44.8 %) Found (%): Eu, 17.7; F, 31.2; C, 37.8; H, 4.2; O, 9.1. Calculated for EuC$_{28}$H$_{36}$F$_{14}$O$_6$ (%): Eu, 17.2; F, 30.0; C, 37.9; H, 4.1; O, 10.80. IR absorptions (KBr), ν$_{max}$/cm^{-1}: 840 (C-O, THF), 1034 (C-O, THF), 1228 (C-F), 1380-1425 (-C(CH$_3$)$_3$), 1460 (-CH$_2$-), 1702 (-CH$_2$-, -CH$_3$), 1735 (C=0), 1804 (-CF$_2$-CH-C=0).

Eu(dpm)$_2$·(THF)$_2$. Yield (15.3 mg, 31.3 %) Found (%): Eu, 22.9; C, 54.3; H, 8.7; O, 14.1. Calculated for EuC$_{30}$H$_{54}$O$_6$ (%): Eu, 23.0; C, 54.4; H, 8.1; O, 14.5. IR absorptions (KBr), ν$_{max}$/cm^{-1}: 798 (C-O, THF), 1029 (C-O, THF), 1406 (-CH$_2$-), 1467 (-CH$_2$-), 1528 (-CH=), 1745 (C=O), 2873 (-CH$_2$-), 2929 (-CH$_2$-), 2959 (-CH=).

Eu(acac)$_2$·(THF)$_2$. Yield (4.1 mg, 16.4 %) Found (%): Eu, 30.7; C, 43.6; H, 6.5; O - 19.2. Calculated for EuC$_{18}$H$_{30}$O$_6$ (%): Eu, 30.8; C, 43.7; H, 6.1; O, 19.4. IR absorptions (KBr), ν$_{max}$/cm^{-1}: 797 (C-O, THF), 1026 (C-O, THF), 1386 (-CH$_2$-), 1461 (-CH$_3$), 1528 (-CH), 1745 (C=O), 2855 (-CH$_2$-), 2925 (CH$_3$), 2956 (-CH=).

Eu(CH$_3$COO)$_2$·(THF)$_2$. Yield (6.3 mg, 39.9 %) Found (%): Eu, 36.9; C, 35.1; H, 5.6; O, 22.4. Calculated for EuC$_{12}$H$_{22}$O$_6$ (%): Eu, 36.7; C, 34.8; H, 5.3; O, 23.2. IR absorptions (KBr), ν$_{max}$/cm^{-1}: 789 (C-O, THF),

1030 (C-O, THF), 1386 (-CH$_2$-), 1423 (CH$_2$), 1745 (C=0), 2855 (-CH$_2$-), 2925 (-CH$_3$).

Results and discussion

The Eu(fod)$_3$ and Eu(acac)$_3\cdot$H$_2$O complexes are readily dissolve in THF and after Bu$^i_2$AlH addition their solutions retain their homogeneity. In contrast, the Eu(CH$_3$COO)$_3\cdot$6H$_2$O and Eu(dpm)$_3$ complexes are very poorly soluble in THF. However, when Bu$^i_2$AlH was added to a slurry of Eu(CH$_3$COO)$_3\cdot$6H$_2$O in THF, a homogeneous solution was also formed. In the case of Eu(dpm)$_3$, the addition of Bu$^i_2$AlH resulted in formation of a homogeneous solution but a small part (~4%) of the complex remained in solid form.

The fairly bright CL was initiated by the injecting of the Bu$^i_2$AlH in the reactor with solution of Eu(fod)$_3$ and Eu(acac)$_3\cdot$H$_2$O or suspension of Eu(CH$_3$COO)$_3\cdot$6H$_2$O and Eu(dpm)$_3$ (Fig. 1).
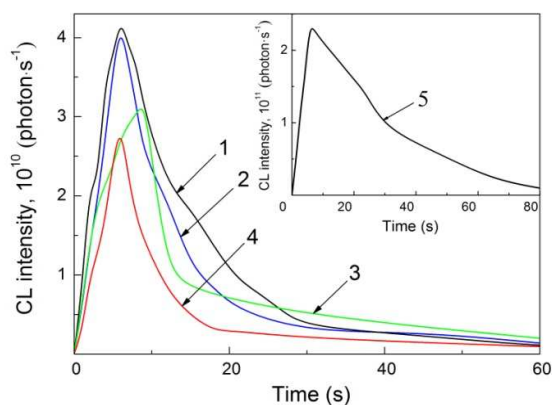

Fig. 1 CL kinetics arising in the reactions of Eu^{3+} complexes with Bu$^i_2$AlH in THF at 300 K; CL was measured with chemiluminometer. [Eu^{3+}]$_0$ = 1·10^{-2} M, [Bui$_2$AlH]$_0$ = 4·10^{-1} M, V(THF) = 2.0 mL. 1 - Eu(CH$_3$COO)$_3\cdot$6H$_2$O, 2 - Eu(acac)$_3\cdot$H$_2$O, 3 - Eu(dpm)$_3$, 4 – BGCL, the intensity was scaled up to 2·10^4 time, 5 - Eu(fod)$_3$.

Simultaneously, the reaction solutions turned yellow-green color. The decay time of the CL for all complexes was approximately the same ~1 h (for Eu(fod)$_3$ somewhat longer), and, apparently, determined by the of oxidation duration Bu$^i_2$AlH as for the previously studied CL of EuCl$_3\cdot$6H$_2$O.[13] The brightest CL was observed for Eu(fod)$_3$ complex (Fig. 1). At the same time, its intensity was much lower than the blue CL arising under the same conditions in the case of EuCl$_3\cdot$6H$_2$O. However, its brightness was sufficient to facilely observe the CL of Eu(fod)$_3$ with the naked eye in a darkened room in the form of a beautiful persistent glow having the salad color. The high brightness and duration of the CL, visible to the naked eye, in the system Eu(fod)$_3$-THF-Bu$^i_2$AlH-O$_2$ make it promising as a chemical source of green light. Although the CL is observed even at very low oxygen concentrations, it was absent if oxygen degassing by three freeze–evacuate–thaw cycles was carried out before Bu$^i_2$AlH is added to Eu(fod)3 in THF. Earlier the same experience with the same result were obtained for EuCl$_3\cdot$6H$_2$O suspension in THF.[13] Less bright CL in the case of the Eu(acac)$_3\cdot$H$_2$O complex can also be seen with the naked eye but in a more strongly darkened room and some adaptation of the eyes.

In the absence of lanthanide complexes, background CL (BGCL) was observed due to the emission occurs from the triplet-excited

isobutyric aldehyde ^{3}RC(H)=O*, generated in oxidation of Bui$_2$AlH by oxygen.[4,13] The intensity of the BGCL was many times smaller than the CL with lanthanide complexes. However, the shapes of kinetic curves in both cases for BGCL and CL were the same (Fig. 1). The combination of the mentioned factors is characteristic of the enhanced (or co-called activated) CL.[5,6,8,10,28]
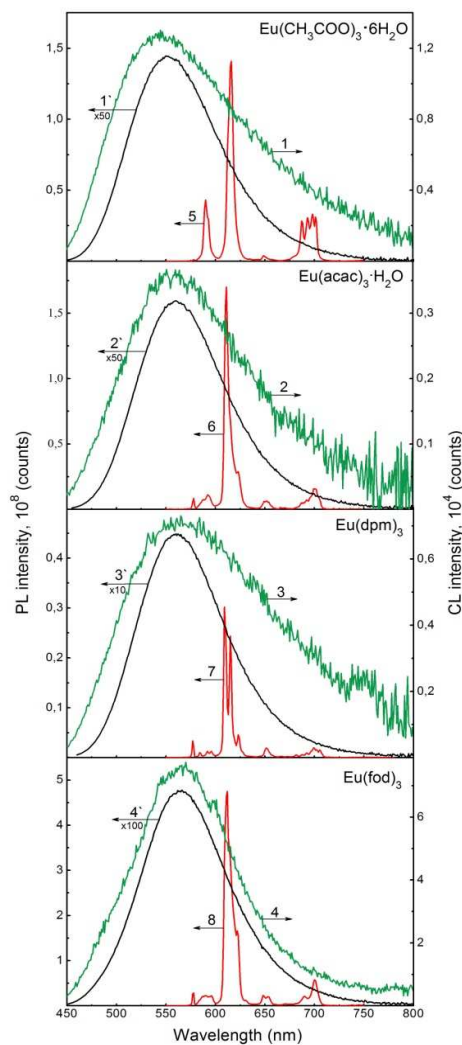
Fig. 2 CL (1-4) and PL (1'-4') spectra of the reaction solutions formed at interaction of the Eu^{3+} complexes with Bu$^i_2$AlH in THF in presence of oxygen. 5,7 – PL spectra of crystalline samples of the Eu^{3+} complexes; 6,8 – PL spectra of solutions of the Eu^{3+} complexes in THF. [Eu^{3+}]$_0$ = 10^{-2} M; V(THF) = 2 ml, [Bu$^i_2$AlH]$_0$ = 4·10^{-1} M, 300 K.

In our case, it means that the generation of the CL emitter occurs by energy transfer from the primary exited emitter ^{3}RC(H)=O* to Eu^{2+} ion. CL spectra match with the PL spectra of yellow-green reaction solutions (Fig. 2). For easy comparison, the PL spectra were increased on the ordinate: 100 times for Eu(fod)$_3$, 50 times for Eu(CH$_3$COO)$_3\cdot$6H$_2$O, Eu(acac)$_3\cdot$H$_2$O and 10 times for Eu(DPM)$_3$ (Fig. 2).

Thus, the CL and PL spectra are caused by emission of the same emitter glow. Based on the results presented below, we consider

that the emitter of the CL and PL is the electronically excited state of divalent europium $Eu^{2+}*$.

First of all, in favor of this identification indicates significant difference between the PL spectra of the starting Eu^{3+} complexes and the CL and PL spectra of the yellow-green solutions formed in the reaction. Indeed, the PL spectra of crystalline samples and solutions of the initial Eu^{3+} complexes contain narrow maxima and are located in red region with a variation of the dominant peak in the range 610-615 nm (Fig. 2, Table 1). Thus, these maxima are due to $^5D_0$-$^7F_2$ transitions and coincide with literature data.[30-39] The position of the most intense peaks of the PL for solid samples and solutions of the Eu^{3+} complexes are almost the same. However, it is interesting to note that the lifetimes of the excited states of the Eu^{3+} complexes in solution and a solid substantially differ although in both cases, these lie in the microsecond range. The lifetimes of the Eu^{3+} excited states in THF solutions for $Eu(fod)_3$ and $Eu(acac)_3 \cdot H_2O$ measured by us (Table 1) were close to those previously obtained for solutions in CH_3CN (τ = 510 and 180 μs, respectively)[33]. Significant decrease in the lifetime of the $Eu^{3+}*$ in the crystalline sample $Eu(dpm)_3$ (τ = 40 μs), we measured, is correlated with τ = 22.8 μs that previously obtained and caused by the unusually strong temperature quenching of $Eu(dpm)_3$ luminescence even at room temperatures.[32] In contrast to the above data, CL and PL spectra of the reaction solutions consist of one broad band located at shorter wavelengths. The shape of these spectra are very similar to the PL spectra of inorganic compounds and organic complexes of divalent europium in solutions.[13,15-23] The lifetimes of the excited states of the PL emitters of the yellow-green reaction solutions are much shorter (ns timescale) than that for Eu^{3+} (μs timescale) in the original crystals or solutions of complexes

(Table 1). Registration lifetime in the nanosecond region is characteristic of Eu^{2+} d-f luminescence, for example, Eu^{2+} complexes with 15-crown-5 and its derivatives.[17]

CL and PL spectra due to the emissive deactivation of the electronically excited $Eu^{2+}*$ ion from $5d^1$ level (the allowed $4f^6 5d^1 \rightarrow 4f^7$ transition),[17-19] which (unlike 4f-levels of the $Eu^{3+}*$ ion) is not shielded by fully filled $5s^2$ and $5p^6$ orbitals. Therefore, the $5d^1$ exited level of the $Eu^{2+}*$ ion is more readily available to environment influence. Due to this influence $4f^6 5d^1$ exited states of Eu^{2+} have the broad range, which is manifested in CL and the PL spectra as broad bands. The fact that this broad band green luminescence precisely belongs to the $Eu^{2+}*$ ion is evident from the following experiment. After bubbling of air through the reaction solution, the broad band disappears and instead of it narrow PL peaks of the Eu^{3+} ion in the red region of the spectrum appear (see below experiments with $Eu(acac)_3 \cdot H_2O$). The subsequent addition of excess Bu^i_2AlH leads to the regeneration of the broad "green" band. Besides the $4f^6 5d^1 \rightarrow 4f^7$ interconfiguration transition, luminescence of the Eu^{2+} ion may be caused only by the intraconfiguration (within $4f^7$) transition, which manifests as a narrow peak.[17] However, the last one is covered by the levels of the $4f^6 5d^1$ configuration, so that usually this narrow peak is not observed, especially in a solution.

Thus, it is obvious that the exited divalent europium $Eu^{2+}*$ is the emitter of CL and PL in interaction of Eu^{3+} complexes with Bu^i_2AlH in THF with involvement of oxygen. Monitoring the kinetics of the interaction of Eu^{3+} with Bu^i_2AlH by increase the intensity of the PL maximum Eu^{2+} showed that the reduction of Eu^{3+} to Eu^{2+} is fully completed in about 12.5 min (Fig. 3).
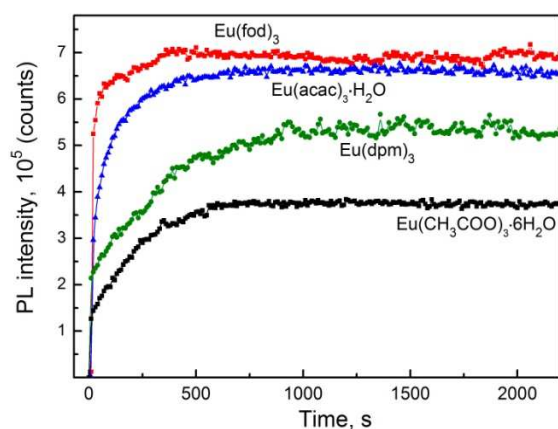
Fig. 3 Kinetics of reduction of Eu^{3+} to Eu^{2+} in the reaction of Eu^{3+} complexes with Bu^i_2AlH in THF, monitored by changes of intensity in PL maxima of Eu^{2+} at 560 nm (λ_{exc} = 450 nm), [Eu^{3+} complex]$_0$ = 10^{-2} M, [Bu^i_2AlH]$_0$ = $4 \cdot 10^{-1}$ M, V(THF) = 2 ml.
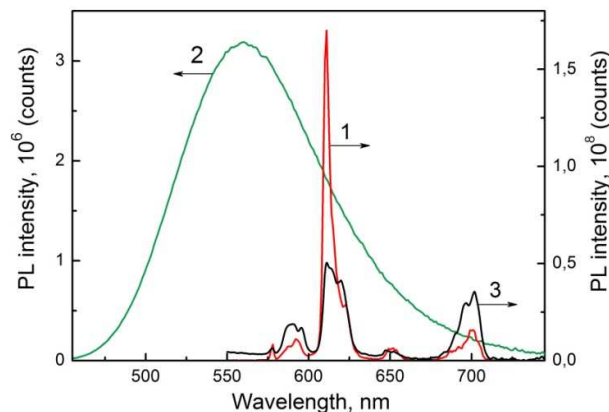
Fig. 4 PL spectra before (1) and after (2) reaction of $Eu(acac)_3 \cdot H_2O$ and Bu^i_2AlH in THF. 3 − PL spectrum after air bubling through the yellow-green reaction solution, λ_{exc} = 394 (1,3), 443 (2) nm, [$Eu(acac)_3 \cdot H_2O$]$_0$ = 10^{-2} M, [Bu^i_2AlH]$_0$ = $4 \cdot 10^{-1}$ M, V(THF) = 2 ml.

Table 1 Luminescence properties of europium ion before and after reaction of Eu^{3+} complexes with Bu^i_2AlH in THF at 300 K.

Initial Eu^{3+} complexes	Crystalline samples of Eu^{3+} complexes		Solutions of Eu^{3+} complexes in THF		Yellow-green reaction solutions of Eu^{2+} complexes		
	λ_{max}, nm	τ, μs	λ_{max}, nm	τ, μs	λ_{max}, nm	τ, ns	ϕ_{PL}
$Eu(acac)_3 \cdot H_2O$	610^a	273	611^a	180.4	560	359.4	0.21
$Eu(fod)_3$	612^a	144	612^a	603.4	565	316.4	0.29
$Eu(CH_3COO)_3 \cdot 6H_2O$	615^a	404	$-^b$	$-^b$	560	308.2	0.19
$Eu(DPM)_3$	610^a	40	$-^b$	$-^b$	550	336.8	0.28

^{a} - dominant maxima the Eu^{3+} luminescence are given, ^{b} – not soluble in THF.

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Nature of the organic ligand in the initial Eu^{3+} complex has a little effect on the PL quantum yield of yellow-green solutions. The PL quantum yield of the Eu^{2+} complexes is decreased in the following series $Eu(fod)_2 \cdot (THF)_2$ (ϕ_{PL} = 0.29) > $Eu(dpm)_2 \cdot (THF)_2$ (ϕ_{PL} = 0.28) > $Eu(acac)_2 \cdot (THF)_2$ (ϕ_{PL} = 0.21) > $Eu(CH_3COO)_2 \cdot (THF)_2$ (ϕ_{PL} = 0.19).

A large excess of Bu^i_2AlH stabilizes the divalent state of europium in solution because Bu^i_2AlH reacts very vigorously with impurity of oxygen and moisture – known oxidants of Eu^{2+}. However, Eu^{2+} can be oxidized back to Eu^{3+} when Bu^i_2AlH is completely oxidized by oxygen. For example, as follows from Table 1, the lifetime of the excited state of Eu^{2+} in the yellow-green reaction solution (τ_2= 359.4 ns) is considerably less than τ_1= 180.4 μs of the initial solution $Eu(acac)_3 \cdot H_2O$ in THF. However, bubbling a yellow-green solution with air discolors it and the lifetime of the PL emitter is significantly increased (to τ_3= 199.3 μs). The latter value is close to the value of τ_1= 180.4 μs that indicates that Eu^{2+} was oxidized to Eu^{3+}. The small difference $\tau_3 - \tau_1$ = 18.9 μs is possibly due to the different ligand environment of the Eu^{3+} ion in the initial complex $Eu(acac)_3 \cdot H_2O$ and the compounds formed after oxidation of Eu^{2+} and Bu^i_2AlH by oxygen. At air bubbling, along with the fall of the value of τ the disappearance of the green broad band at 560 nm in the PL spectrum and the appearance of narrow red peak at 611 nm were observed (Fig. 4).

It should be noted that it was surprising for us that these CL and PL spectra are located in the green region (Fig. 2). Indeed, firstly, the spectral maximum of CL generated in the reaction $EuCl_3 \cdot 6H_2O$ with Bu^i_2AlH in THF in presence of oxygen lies in the blue region (λ_{max} = 465 nm).[13] Secondly, the location of the luminescence maximum in the blue region is more characteristic for the Eu^{2+} ion. For example, the broad band of the bright PL ($4f^65d \rightarrow 4f^7$) at 77 K of frozen acidic aqueous solutions $EuCl_2$ was observed at 450 nm (in 2 M $HClO_4$) or 463 nm (in 0.65 M HCl) [15]. The very weak PL of $EuCl_2$ in MeOH at room temperature peaks at 489 nm [16] and maxima of more bright PL solutions of complexes Eu^{2+} with crown ethers, cryptands, and polyethylene glicoles (total 21 compounds) in MeOH manifest in interval 417-488 nm ($4f^65d \rightarrow 4f^7$).[16-19] A solution of EuI_2 in THF has PL maximum at 442 nm (300 K).[20] The solution of the complex hydride $NaEu(BH_4)_4 \cdot (DME)_n$ in THF emits with λ_{max} = 465 nm,[21] and another one but very similar solid hydride $Eu(BH_4)_2 \cdot (THF)_2$ radiates at 490 nm.[23] The frozen solution of $(C_5H_5)_2Eu$ in THF (77 K) shows PL as a broad band at 430-450 nm.[22] Since the green CL found by us is observed in solutions, then the above data were taken from where the PL of divalent europium was studied in liquid phases, except the solid complex $Eu(BH_4)_2 \cdot (THF)_2$. Thus, numerous data on the PL of Eu^{2+} in solid matrices were excluded from consideration. However, we take into account that the radiative transition $4f^65d^1 \rightarrow 4f^7$ from the Eu^{2+*} excited of state in composition of the diverse compounds in solid matrices may be

accompanied by the emission of blue (~440 nm), green (586 nm), and even red (612 nm) light.[40,41] So, it should not be theoretically excluded that similar of the Eu^{2+*} emission colour change from blue through green to red can be also found in the solution. To the best of our knowledge, in the literature, there is only one example[42] where the PL of divalent europium in solution is observed in the green region. This green PL of Eu^{2+} as a broad maximum at ~525-540 nm (300 K) was observed after reducing of $EuCl_3$ in dimetylformamide (DMFA) under UV radiation.[42] However, in this case, the formation of the Eu^{2+} complex emitting green PL was carried out photochemically rather than by purely chemical reactions as in our case. With regard to the green liquid-phase CL, such examples are non-existent.
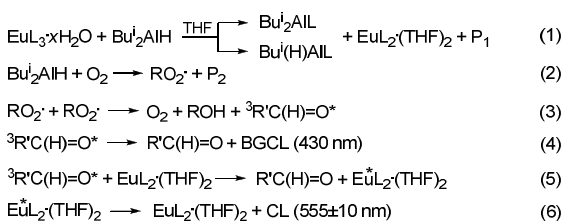
Using GC analysis, we found that at interaction of Bu^i_2AlH with the Eu^{3+} complexes containing water of crystallization ($Eu(acac)_3 \cdot H_2O$ and $Eu(CH_3COO)_3 \cdot 6H_2O$) the same gases isobutane and hydrogen were formed, which have previously been identified as products in the reaction $EuCl_3 \cdot 6H_2O$ with Bu^i_2AlH.[13,29] Proceeding from composition of the $Eu(L)_2 \cdot (THF)_2$ complexes obtained by us, it is clear that at interaction of the Eu^{3+} complexes with Bu^i_2AlH, water of crystallization was completely removed whereas the organic ligand does not undergo destruction and only its amount is decreased by one and becomes equal to two.

All the above features of occurrence of the green CL lead to the conclusion that this CL is generated by the same mechanism (Scheme 1) as the blue CL arising in the system $EuCl_3 \cdot 6H_2O$-THF-Bu^i_2AlH-O_2, which was studied in[13]. In the cases of hydrates $Eu(acac)_3 \cdot H_2O$ and $Eu(CH_3COO)_3 \cdot 6H_2O$, as well for $EuCl_3 \cdot 6H_2O$, the interaction beginning with the reaction of Bu^i_2AlH with water of crystallization, which is removed from coordination sphere of Eu^{3+} with formation a mixture of products (P_1), consisting of aluminoxane $(Bu^i_2Al)_2O$, isobutene, and hydrogen (1) according to our present GLC analysis and the previous data.[4,29,43] At the same time, Bu^i_2AlH taken in a big excess reacts with Eu^{3+} (1) and oxygen (2-3), as result Eu^{3+} is reduced to Eu^{2+}. Ligand L, removed from the coordination sphere of europium, is attached to the aluminum atom to form Bu^i_2AlL (1, top arrow) or $Bu^i(H)AlL$ (1, lower arrow), and possibly both of these compounds. The choice between these compounds is difficult because in the literature there is no information on the reactions of metal complexes with dialkylaluminum hydrides. At the same time, compound Bu^i_2AlL were L = acac had repeatedly been identified[44-46] in reactions of acetylacetonate complexes of transition metals with aluminum alkyls. It should be also noted that the choice between Bu^i_2AlL and $Bu^i(H)AlL$ is not essential for elucidating the CL mechanism. This follows from the fact that during the reaction of the Eu^{3+} complexes with Bu^i_3Al (instead of Bu^i_2AlH), green CL having the same characteristics (Fig. S2, S3 in ESI†) also occurs. The only difference is

in a slower reduction process from Eu^{3+} to Eu^{2+} (Fig. S4 in ESI†). Note that only Bu^i_2AlL may formed when Bu^i_3Al is used.

Oxidation of Bu^i_2AlH by oxygen affords as key intermediates peroxyl radicals (2), disproportionation reaction of which generates the triplet-exited state of isobutyric aldehide $^3R\acute{C}(H)=O*$ (3).[4,25]

In Scheme 1, the oxidation of Bu^i_2AlH is reflected in its simplest form (2-3). In more detail, it is shown in our previous publications.[4,13,25] The exited $^3R\acute{C}(H)=O*$ molecules transfer energy to Eu^{2+} converting it into the electronically exited state $Eu^{2+}*$ (5), which is deactivated by emitting the green CL (6). When the europium complex is absent in the reaction system (not loaded into the reactor), we observed only very weak BGCL caused by emission of the triplet-excited aldehyde[4,25,13] in a much shorter wavelength 430 nm (6). In Scheme 1, P_2 denotes molecular oxidation products, among which $(Bu^iO)_2Al(OH)$ is the main one.[47]

$$EuL_3 \cdot xH_2O + Bu^i_2AlH \xrightarrow{THF} \begin{array}{c} Bu^i_2AlL \\ Bu^i(H)AlL \end{array} + EuL_2 \cdot (THF)_2 + P_1 \quad (1)$$

$$Bu^i_2AlH + O_2 \longrightarrow RO_2^\cdot + P_2 \quad (2)$$

$$RO_2^\cdot + RO_2^\cdot \longrightarrow O_2 + ROH + {}^3R'C(H)=O* \quad (3)$$

$$^3R'C(H)=O* \longrightarrow R'C(H)=O + BGCL\ (430\ nm) \quad (4)$$

$$^3R'C(H)=O* + EuL_2 \cdot (THF)_2 \longrightarrow R'C(H)=O + Eu\overset{*}{L}_2 \cdot (THF)_2 \quad (5)$$

$$Eu\overset{*}{L}_2 \cdot (THF)_2 \longrightarrow EuL_2 \cdot (THF)_2 + CL\ (555\pm10\ nm) \quad (6)$$

L = fod, dpm, acac, CH_3COO; x = 0, 1, 6; R = Bu^i; R' = Pr^i;
$P_1 = (Bu^i_2Al)_2O$, Bu^iH, H_2; P_2 - molecular products.

Scheme 1 The scheme of reactions occurring in the systems $EuL_3 \cdot (H_2O)_x$-THF-Bu^i_2AlH-O_2, leading to the green CL of Eu^{2+}.

The position of the Eu^{2+} PL maxima and their shape in the isolated complexes $EuL_2 \cdot (THF)_2$ (Fig. S6 in ESI†) and in the yellow-green solutions (Fig. 2) do not differ significantly. At the same time, the Eu^{2+} PL quantum yields in the composition of the isolated complexes $EuL_2 \cdot (THF)_2$ is much lower than in the yellow-green solution, formed after the interaction in the systems $EuL_3 \cdot (H_2O)_x$-THF-Bu^i_2AlH-O_2. For example, the ratio of PL quantum yields of the pairs $\phi[(Eu(dpm)_2 \cdot (THF)_2) \cdot Bu^i_2AlH]/\phi[Eu(dpm)_2 \cdot (THF)_2)]$, $\phi[Eu(acac)_2 \cdot (THF)_2 \cdot Bu^i_2AlH]/\phi[Eu(acac)_2 \cdot (THF)_2]$ and $\phi[Eu(CH_3COO)_2 \cdot (THF)_2 \cdot Bu^i_2AlH]/\phi[Eu(CH_3COO)_2 \cdot (THF)_2]$ are equal to 28.0, 7.0, and 3.2, respectively. This means that in the reaction solutions, the form of europium complex is another than $EuL_2 \cdot (THF)_2$. We believe that $EuL_2 \cdot (THF)_2$ in the yellow-green solution is associated to more bulky complex with Bu^i_2AlH loaded in large excess $([Eu]/[Bu^i_2AlH] = 1/40)$. The formation of such complexes is confirmed also by the fact that even after the complete removal of THF from yellow-green reaction solutions, complexes $EuL_2 \cdot (THF)_2$ did not precipitate out though their concentration in this case becomes equal to $1.0 \cdot 10^{-1}M$, and precipitating them requires the addition of heptane and heating. These complexes in their most general form can be represented as $EuL_2 \cdot (THF)_2$-Bu^i_2AlH. At present, we have no data on the composition and structure of such complex and it is a task for future work. We can only assume that it has bridge-type four-center structure, in which the Eu^{2+} ion bonded to aluminum of Bu^i_2AlH through Bu^i radical (giving unit Eu^{2+}–Bu^i–Al) and the oxygen atom of the organic ligand (giving unit Eu^{2+}–O–Al). Our assumption is based on the fact

that such bridged-type four-centered structures have been detected in reactions of both trivalent[48] and divalent[49] lanthanide complexes with alkyl aluminum compounds and their hydrides, respectively.

Excitation mechanism of CL due to energy transfer from the primary emitter $^3R\acute{C}(H)=O*$ to Eu^{2+}, besides the above-mentioned arguments, confirms enhancement of CL with increasing concentration of the energy acceptor Eu^{2+} ion. It should be noted that $[Eu^{2+}]$ assumed equal to $[Eu^{3+}]_0$. Thus, green CL registered in the present study refers to the so-called "indirect CL".[5,6,50] As is known,[51,52] the enhanced CL intensity is given by Eq. 2.

$$\left(\frac{I}{I_0} - 1 \right)^{-1} = \left[\frac{\alpha_2}{\alpha_1} \left(\frac{\phi^2_{PL}}{\phi^1_{PL}} - 1 \right) \right]^{-1} + \left[\frac{\alpha_2}{\alpha_1} \left(\frac{\phi^2_{PL}}{\phi^1_{PL}} - 1 \right) \right]^{-1} \frac{1}{K_{SV}[Eu^{2+}]} \quad (2)$$

were I and I_0 are CL intensities with and without enhancer Eu^{2+}, respectively; α^1, α^2 are photomultiplier sensitivity in the spectral region of the emission of primary emitter $^3R\acute{C}(H)=O*$ and enhancer $Eu^{2+}*$, respectively; ϕ^1_{PL} и ϕ^2_{PL} are luminescence quantum yields of $^3R\acute{C}(H)=O*$ and Eu^{2+}, respectively; $K_{SV} = k_{ET} \cdot \tau_0$ is the Stern-Volmer constant.

Characteristics of the CL enhancement have been studied on the example of $Eu(acac)_3 \cdot H_2O$-THF-Bu^i_2AlH-O_2 system, in which the Eu^{2+} ion in the bulky complex $Eu(acac)_2 \cdot (THF)_2$-Bu^i_2AlH, formed at interaction in this system, acts as an enhancer. As seen in Fig. 5 (curve 1), CL intensity increases with increasing Eu^{2+} concentration, and there is a linear (R = 0.99146) dependence (line 2), in the coordinates $(I/I_0-1)^{-1}$ – $[Eu^{2+}]^{-1}$. According to the Eq. 2, the intercept of ordinate by straight line 2 A = $[\alpha_2/\alpha_2 \cdot (\phi^2_{PL}/\phi^1_{PL} -1)]^{-1}$ and its slope B = $[\alpha_2/\alpha_2 \cdot (\phi^2_{PL}/\phi^1_{PL} -1)]^{-1} \cdot [K_{SV}]^{-1}$ are equal to A = $5.765 \cdot 10^{-5}$ L mol^{-1} and B = = $1.543 \cdot 10^{-8}$ L mol^{-1} for the CL enhancement by Eu^{2+}, respectively. Calculation of the bimolecular rate constant of energy transfer (k_{ET}) need to know real lifetime (τ_0) of the primary emitter $^3R\acute{C}(H)=O*$ under the experimental conditions.
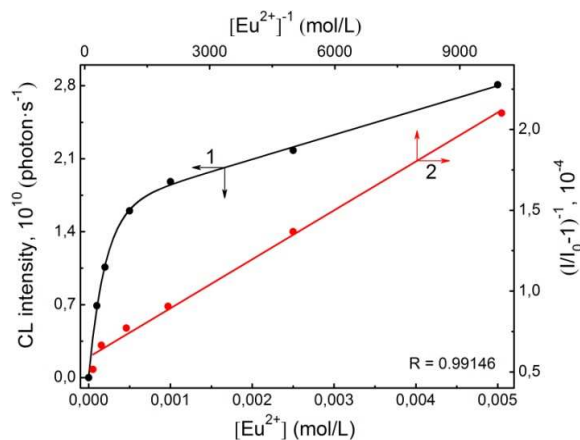
Fig. 5 The dependence of the CL intensity on the concentration of Eu^{2+} assumed to be equal $[Eu(acac)_3 \cdot 6H_2O]_0$ (1) and its linear anamorphosis in coordinates Eq. 2 (2). $[Eu(acac)_3 \cdot 6H_2O]_0 = 10^{-4} - 5 \cdot 10^{-3}$ M, $[Bui_2AlH]_0 = 4 \cdot 10^{-1}$ M, V(THF) = 2.0 mL.

To determine τ_0, enhancement of CL occurring during the oxidation Bu^i_2AlH by oxygen was measured using the known enhancer 9,10-dibromoanthracene (DBA), which activates CL due to the triplet-

singlet energy transfer with the known rate constant $(1.0\pm0.5)\cdot10^9$ $M^{-1}\cdot s^{-1}$.[53,54] As a result, linear anamorphosis (R = 0.99983) was found in coordinates $(I/I_0-1)^{-1}$–$[DBA]^{-1}$ from intercept and slope of which were defined $\tau_0 = 1.4\cdot10^{-7}$ s. Using the value τ_0 from Eq. $K_{SV} = k_{ET}\cdot\tau_0$ the rate constant $k_{ET} = (2.7\pm1.4)\cdot10^{10}$ $M^{-1}\cdot s^{-1}$ was determined for system $Eu(acac)_3\cdot H_2O$-THF-Bu^i_2AlH-O_2. The k_{ET} value obtained clearly characterizes the energy transfer in the system under study as a diffusion-controlled process.

The classic studies of the enhanced CL notes that a necessary condition for excitation of energy transfer from donor to acceptor is a higher energy level position of the donor.[6, 55-59] The important condition for the energy transfer is also the overlap of the luminescence spectrum of the energy donor and the absorption spectrum of the energy acceptor.[43,60] In our case, the triplet excited isobutyric aldehyde $^3\acute{R}C(H)=O^*$ is an energy donor. As potential energy acceptors can act the Eu^{2+} ion, in the bulk $EuL_2\cdot(THF)_2$-Bu^i_2AlH complex and organic ligand L, coordinated with the Eu^{2+} ion (Fig. S5 in ESI†) demonstrates good agreement of the phosphorescence spectrum of $^3\acute{R}C(H)=O^*$ (donor) and spectrum of BGCL, recorded during the oxidation of Bu^i_2AlH by oxygen in the absence of the europium complex. Fig. S5 (ESI†) also shows the absorption spectra of Eu^{2+} (acceptor) in the yellow-green reaction solutions. As seen from Fig. S5 (ESI†), the luminescence spectra of $^3\acute{R}C(H)=O^*$ (donor) and absorption spectra of Eu^{2+} (acceptor) have some overlap, which is a favourable factor for the possibility of energy transfer from $^3\acute{R}C(H)=O^*$ to Eu^{2+}.

Thus, our results in favor of the CL mechanism generation due to the energy transfer (so-called "indirect chemiluminescence") can be summarized as follows.

First of all, it should be noted that an alternative "direct CL", due to the reduction of Eu^{3+} into Eu^{2+}* emitting excited state is excluded because the CL in the absence of oxygen is not observed. Secondly, there are primary $^3\acute{R}C(H)=O^*$ and secondary Eu^{2+}* emitters in the studied systems. $^3\acute{R}C(H)=O^*$ is generated by oxidation of Bu^i_2AlH by oxygen in THF and deactivated with the emission of light at 430 nm from the BGCL. In the presence of Eu^{2+} in solution, BGCL is not observed; the CL intensity increases with the concentration of Eu^{2+}, and the CL contains emission only of the Eu^{2+}* ion, i.e. Eu^{2+} is an enhancer of CL. The shape of kinetic curves of the BGCL and the enhanced CL is the same. The energy of the triplet excited radiating level of $^3\acute{R}C(H)=O^*$ is higher than energy of the emitting level $(4f^65d^1)$ of the Eu^{2+} acceptor. The absorption spectrum of the energy acceptor Eu^{2+} has an area overlapping with the luminescence spectrum of the energy donor $^3\acute{R}C(H)=O^*$. In turn, the excitation of the Eu^{2+} ion as a result of the energy acceptance from $^3\acute{R}C(H)=O^*$ in the system under study may occur due to two main mechanisms (Scheme 2). First, it is a direct intermolecular energy transfer of electronic excitation from the primary excited emitter $^3\acute{R}C(H)=O^*$ to the Eu^{2+} ion with the population of the $4f^65d^1$ excited state of Eu^{2+}*, which is deactivated with the emission of green CL (1). The second involves the energy transfer from the $^3\acute{R}C(H)=O^*$ to the lowest T_1-excited triplet level of ligand $^3L^*$, and then intramolecular energy transfer from the T_1-level of $^3L^*$ to the emitting level $4f^65d^1$ of the Eu^{2+}* ion, which subsequently results in green emission as in the way (1). The second energy transfer

mechanism is generally implemented for the Eu^{3+} β-diketonate complexes. At the same time, these data on the stepwise excitation mechanism in solutions of the Ln^{2+} complexes with organic ligands are absent in the literature.
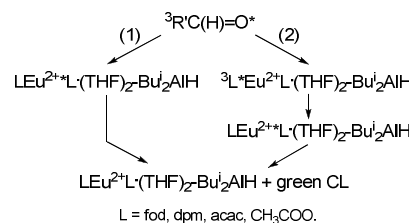
Scheme 2 Scheme generation of indirect green CL of Eu^{2+}.

Comparing the energies of the T_1-exited levels of donor $^3\acute{R}C(H)=O^*$ (λ_{max} = 430 nm, 23255.8 cm^{-1}) and potential ligand-acceptors $^3L^*$, known from the literature: acac - 412 nm, 24300 cm^{-1},[30] 415 nm, 24096 cm^{-1};[35] dpm- 413, nm, 24213;[35] fod - 444 nm, ~22500 cm^{-1},[34] shows that energy transfer from $^3\acute{R}C(H)=O^*$ to ligand coordinated with Eu^{2+} is possible only for fod-ligand. The T_1-levels of other ligands are higher in energy than $^3\acute{R}C(H)=O^*$, i.e. energy transfer to these ligands are thermodynamically impossible. We have not found the energy value of the T_1-level CH_3COO^- ligand in literature. T_1-levels of all above ligands lie above the $4f^65d^1$ excited level of Eu^{2+}* (λ_{max} = 555 nm, 18018 cm^{-1}). Therefore, the excitation of Eu^{2+}, coordinated with acac- or dpm-ligand, most likely occurs by one-step mechanism according to (1), Scheme 2. In case of $Eu(fod)_3$, the excitation of Eu^{2+} is possible through both (1) and (2). In the first case, the energy gap between the levels of the T_1 ($^3\acute{R}C(H)=O^*$) and $4f^65d^1$ (Eu^{2+}*) is 23255.8 − 18018 = 5237.8 cm^{-1}. In the second case, the energy difference between the first and second energy transfer steps is 23255.8 − 22500 = 755.8 cm^{-1}, and the difference for the second and third steps is 22500 − 18018 = 4482 cm^{-1}. It turns out that the gain in resonance between the donor and acceptor (due to very small gap) in the first step is lost at the next one (due to relatively large gap). Therefore, at this time it is difficult to give priority to one of these variants of the energy transfer for $Eu(fod)_3$.

Conclusions

Thus, in present study, we found that on going from the previously studied system[13] $EuCl_3\cdot6H_2O$-THF-Bu^i_2AlH-O_2 to the present systems $EuL_3^-(H_2O)_x$-THF-Bu^i_2AlH-O_2, a green-shift of CL and PL spectra of the reaction solutions occurs. The main difference between these systems is the nature of the anion at the Eu^{2+} cation. Interestingly, unlike to Eu^{2+}, replacement of the Cl^- anion with an organic anion-ligand at the trivalent cation Eu^{3+} does not lead to such a large shift in the dominant red maximum of luminescence at 610-615 mm due to f-f intraconfiguration transition [for example [31-33]]. Therefore, apparently, the main reason of the green-shift is a greater availability of external influence radiative configuration $4f^65d$-$4f^7$ compared to internal f-f transitions in Eu^{3+}*, which always emits as the dominant only red luminescence. As is known, one of the main reasons for the long-wavelength shift of the PL peak of the trivalent lanthanides, when changing the nature of the ligand, is nephelauxetic effect.[61-63] The red shift of the emission Eu^{2+} in solid

perovskite matrix is also associated with this effect.[64] This effect is due to the decrease in energy of the radiating Ln^{3+*} level as a result of exposure to the electron cloud of the anion-ligands on the Ln^{3+*} cation, which leads to an increase in the degree of covalency of the Ln-ligand bond.[61-64] In turn, the degree of this exposure is determined by the polarizability of the ligand, i.e. the greater polarizability, the greater the long-wavelength shift of the Ln^{3+} luminescence maximum.[61,62] Establishing a rigid dependence between the polarizability of the anion-ligand, coordinated with Eu^{2+}, and the probability of radiation from Eu^{2+*} blue or green light and its intensity is the subject of our future quantum-chemical studies.

We believe that the high brightness and duration of CL, generated in systems $EuCl_3 \cdot 6H_2O$-THF-Bu^i_2AlH-O_2 and $Eu(fod)_3$-THF-Bu^i_2AlH-O_2, opens up the prospect of using them as chemical sources of blue and green light, respectively.

Acknowledgements

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