Triboluminescence of lanthanide acetylacetonates

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Triboluminescence of $Ln(acac)_3 \cdot H_2O$ (Ln = Tb, Eu, Pr, Ce, Gd) was found. The UV radiation was detected for the first time as narrow bands caused by the emission of the adsorbed N_2^* molecules (transitions $^3\Pi_u \rightarrow {}^3\Pi_g$) in the study of triboluminescence of lanthanide compounds. The emission of Ln^{3+*} (ionic triboluminescence) was observed only for Tb^{3+*} (λ_{max}/nm: 490 ($^5D_4$—$^7F_6$), 545 ($^5D_4$—$^7F_5$), 580 ($^5D_4$—$^7F_4$)) and Eu^{3+*} (λ_{max}/nm: 613, 614 ($^5D_2$—$^7F_3$)). The generation of N_2^* occurs due to the energy of electric fields appeared upon the destruction of crystalline samples of $Ln(acac)_3 \cdot H_2O$. The Tb^{3+*} and Eu^{3+*} ions are formed due to the energy transfer from the triplet level of the ligand ($acacT_1$), which is excited by the light emitted from the N_2^* molecule.

Key words: lanthanide acetylacetonates, triboluminescence, luminescence of molecular nitrogen.

An interest in triboluminescence (TL), which is an emission produced by crystal destruction, is caused by a search for routes of conversion of mechanical energy into light and prospects for practical use of TL in various areas of science and technology.[1] In studies of lanthanides, TL has been detected only for a limited number of inorganic salts and heteroligand β-diketonates,[2—9] whereas TL of the complexes $Ln(acac)_3 \cdot H_2O$ (**1**) has not been described in the literature.[1] The mechanism of Ln^{3+} excitation during TL is not presently interpreted unambiguously.[2,6,8] For example, a study of the mechanism of TL of the europium dibenzoylmethanate complexes[2] allowed the conclusion that Eu^{3+*} is formed due to the intramolecular energy transfer from the excited ligand to the resonance level of the lanthanide. However, the mechanism of triplet generation from the ligand remained unclear. The authors[2] only succeeded to exclude the possibility of ligand excitation due to an electric discharge between surfaces of a fracture in crystals, because no influence of a high vacuum or the nature of the gas surrounding the crystals was observed. In the later works,[6,8] the authors concluded that the TL of the europium phenanthroline complexes is excited due to electron bombardment or charge recombination that are generated by the electric field appeared between the unlikely charged crystal surfaces. The authors[6,8] did not refine whether they implied the direct excitation of Ln^{3+} or energy transfer from the excited ligand.

In this work, we report the first observation of TL of the $Ln(acac)_3 \cdot H_2O$ complexes and discuss the mechanism of its appearance.

Experimental

Complexes $Ln(acac)_3 \cdot H_2O$ (Ln = Tb, Eu, Pr, Ce, Gd) (**1**) were synthesized and recrystallized as described previously.[10] The compositions of the complexes were determined by the complexonometric titration of Ln^{3+} using a known procedure,[11] and the concentrations of C, H, O, and water were determined by elemental analysis and Fischer titration, respectively.[11] For example, for $Tb(acac)_3 \cdot H_2O$ found (%): Tb, 33.63; C, 37.89; H, 4.81; O, 23.67. $Tb(C_5H_7O_2)_3 \cdot H_2O$. Calculated (%): Tb, 33.54; C, 37.98; H, 4.85; O, 23.63. Complexes **1** (0.56 mmol) were placed at the bottom of a glass cell (diameter 35 mm) in a light-tight chamber of a spectrofluorimeter designed on the basis of an MDR-23 monochromator. Complexes **1** were destructed at 300 K by an electromotively driven three-blade fluoroplastic stirrer (1000—2000 rpm). The plastic blades of the stirrer softly triturated complex **1** over the cell bottom. The TL from the cell bottom was monitored by an FEU-39 photoelectron multiplier. The triboluminescence and photoluminescence (PL) spectra were recorded on the same spectrofluorimeter with a resolution of 2 nm.

Results and Discussion

The brightest TL is observed visually in the case of $Tb(acac)_3 \cdot H_2O$ even in a weakly shaded room as a green glow rim in the site of contact of the stirrer with the cell bottom or as flashes when the crystals are stirred in a beaker with a glass stick. The integral intensity of TL, which is equal to the sum of surface areas of bands in the TL spectra (in arb. units) recorded at 300—620 nm, depends on the lanthanide nature and decreases in the series Tb (100) > Pr (1.37) > Gd (1.19) > Eu (0.95) > Ce (0.32).

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The triboluminescence spectra contain the long- and short-wave components (Fig. 1). The long-wave maxima in the TL spectra of the $Tb(acac)_3 \cdot H_2O$ and $Eu(acac)_3 \cdot H_2O$ complexes and in the PL spectra of toluene solutions of these complexes coincide (see Fig. 1), *i.e.*, the long-wave TL is caused by the characteristic f—f luminescence of Ln^{3+}* (hereinafter ionic TL).

The short-wave TL of all complexes, regardless of the lanthanide nature, contains maxima at 337, 357, 375, 380, 393, 401, 405, and 429 nm, which are not typical of the emission of Ln^{3+}*. The short-wave TL is not either the emission of the ligand, because the position of diffuse maxima (394, 412 nm) of the ligand phosphorescence spectrum in the $Gd(acac)_3 \cdot H_2O$ complex (77 K)[10,12] differs substantially from the position of narrow maxima in the short-wave region of the TL spectrum. No fluorescence of the acac ligand was observed for the photoexcitation of solutions of complexes **1**.[10,12] The short-wave maxima of TL correlate well with the emission maxima of N_2* (transitions between two triplet-excited states $^3\Pi_u$—$^3\Pi_g$) detected in the TL spectra of salt $Li_2SO_4 \cdot H_2O$ [13] and aniline hydrochloride[14] (see Fig. 1). The TL spectra of complexes **1** contain no earlier observed emission maximum of N_2* molecules at 316 nm,[13,14] which can be explained by the effect of internal filter caused by light absorption of the glass cell (55% transmission at $\lambda_{max} = 316$ nm) and complexes **1** having the maximum absorption at 293 nm.

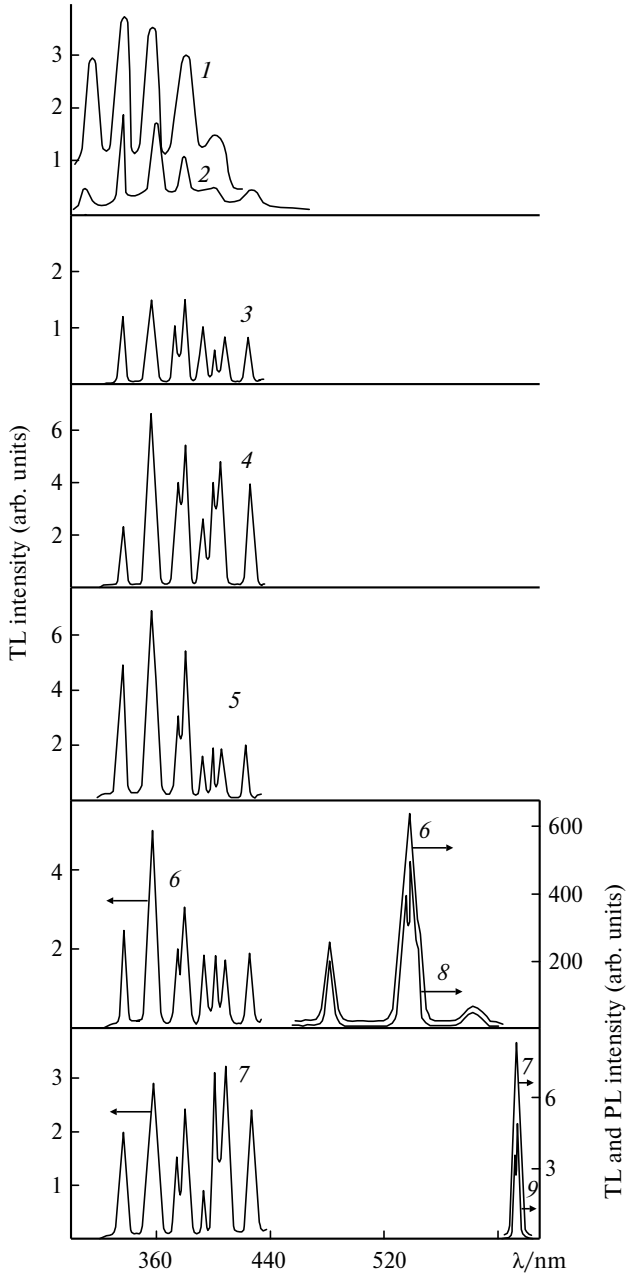

Fig. 1. Triboluminescence spectra of the complex $Li_2SO_4 \cdot H_2O$ [13] (*1*), aniline hydrochloride[14] (*2*), and complexes $Ln(acac)_3 \cdot H_2O$ (*3*, Ce; *4*, Pr; *5*, Gd; *6*, Tb; *7*, Eu) and the photoluminescence spectra of $Ln(acac)_3 \cdot H_2O$ in toluene: *8*, Tb and *9*, Eu; $T = 298$ K; $\lambda_{exc} = 290$ nm.

Since the short-wave TL of complexes **1** does not disappear under argon, it can be assumed that the emission from N_2* molecules occurs from the crystal layer in which nitrogen is adsorbed rather than from the gas phase. According to the published data,[5] the adsorbed nitrogen is strongly linked with the crystalline matrix and is not removed when air is replaced by helium. Note that the short-wave TL found for complexes **1** is the first example when the N_2* discrete spectrum was detected for TL of lanthanide compounds.[2—9] Only one study[6] reports the emission of N_2* molecules in the TL spectrum of the europium tris(2-thenoyltrifluoroacetonato)phenanthroline complex. However, the corresponding TL spectrum was not presented in this work, and the assignment was made only on the basis of authors´ observation of a continuous emission at 280—380 nm separated by one light filter.

Taking into account the experimental results and analysis of published data, we can propose a mechanism for the appearance of TL of the complexes under study (Scheme 1).

Scheme 1

$$[Ln^{3+}(acac)_3 \cdot H_2O]_{cr} \cdot (N_2)_{ads} \xrightarrow{\text{Destruction}} [Ln^{3+}(acac)_3 \cdot H_2O]_{cr} \cdot N_2^*{}_{ads} \quad (1)$$

$$[Ln^{3+}(acac)_3 \cdot H_2O]_{cr} \cdot N_2^*{}_{ads} \longrightarrow [Ln^{3+}(acac)_3 \cdot H_2O]_{cr} \cdot (N_2)_{ads} + h\nu_1 \quad (2)$$

$$Ln^{3+}(acac)_3 \cdot H_2O + h\nu_1 \longrightarrow Ln^{3+}(acac^*S_1)_3 \cdot H_2O \quad (3)$$

$$Ln^{3+}(acac^*S_1)_3 \cdot H_2O \longrightarrow Ln^{3+}(acac^*T_1)_3 \cdot H_2O \longrightarrow Ln^{3+*}(acacS_0)_3 \cdot H_2O \quad (4)$$

$$Ln^{3+*}(acacS_0)_3 \cdot H_2O \longrightarrow Ln^{3+}(acacS_0)_3 \cdot H_2O + h\nu_2 \quad (5)$$

$h\nu_1$ and $h\nu_2$ are photons of short-wave and ionic TL, respectively

We attribute the short-wave TL to the excitation and emission of molecular nitrogen adsorbed by complexes **1** (see Scheme 1, reactions (1) and (2)). According to the published data,[1] the excited molecules N_2* are generated by the electric field appeared upon crystal destruction. In addition, the emission from N_2* is absorbed by the ligand to convert the latter to a singlet state acac*S_1 (see Scheme 1, reaction (3)), which is transformed[15] due to intersystem crossing into a triplet state acac*T_1 (reaction (4)). Then the energy of acacT_1 is transferred to a resonance level of Ln^{3+}, converting this ion to an excited state that deactivates with ionic TL emission (reactions (4) and (5)).

The mechanism proposed for the generation of ionic TL can be named "photoluminescence", because the ligand is excited due to the absorption of photons emitted by N_2* molecules. In this case, Ln^{3+} is excited, as well as in the case of PL of complexes **1**, due to energy transfer from the excited ligand. This interpretation of the TL mechanism is confirmed by ionic TL observed only for Tb^{3+}* and Eu^{3+}*, whose radiative levels[12,15] are lower than the acacT_1 level and, correspondingly, by the absence of radiation from Gd^{3+} (f—f) and Ce^{3+}, Pr^{3+} (d—f), whose radiative levels[12,15] are higher than the acacT_1 level.

The ultraviolet f—d emission of Pr^{3+}* is absent because of the energy deficient of the acacT_1 level, whereas the absence of the f—f luminescence of Pr^{3+}* from the $^3P_1$, $^3P_0$, and $^1D_2$ levels in the visible and IR regions of the TL spectrum (480—1000 nm) cannot be explained from the same point of view. These radiative levels have a lower energy compared to that of the acacT_1 level. To explain this fact, we can use the data[15] relating the absence of the f—f PL of Pr^{3+}* induced by the energy transfer (see Scheme 1, reactions (4) and (5)) to the fact that the energy of Pr^{3+}* obtained from acacT_1 is rapidly consumed to nonradiative transitions inside the closely lying radiative levels of Pr^{3+}*.

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