Chemiluminescence in the reaction of LnI$_2$ (Ln = Dy, Nd) with water

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Chemiluminescence (CL) upon the reaction of crystalline LnI$_2$ (Ln = Dy, Nd) with water was found. The CL emitters are the Ln^{3+}* electron-excited ions (Dy^{3+}*, λ_{max} = 470, 570 nm; Nd^{3+}*, λ = 700—1200 nm) generated by the electron transfer from the Ln^{II} ions to the H$_2$O molecules. The identified reaction products are H$_2$, dissolved LnI$_3$, and insoluble LnI(OH)$_2$ (49—51% and 48—50% yield for DyI$_2$ and NdI$_2$, respectively). The treatment of NdI$_2$ with an H$_2$O solution in THF gives the NdI$_2$OH(thf)$_2 \cdot$3H$_2$O complex and hydrogen.

Key words: dysprosium, neodymium, diiodides, chemiluminescence, hydrolysis, photoluminescence.

Chemiluminescence (CL) involving Ln^{II} compounds, unlike Ln^{III} compounds, was studied to less extent. The CL is known for the EuCl$_2$ complexes with organic ligands[1—3] and Cp$_2$Yb,[4] Cp$_2$Sm, and Cp$_2$Eu lanthanidocenes (see Refs 5 and 6) upon oxidation with hydrogen peroxide and molecular oxygen. In all cases, the CL emitters are the excited Ln^{3+}* ions: Eu^{3+}*, Yb^{3+}*, and Sm^{3+}*. The Eu^{II}, Yb^{II}, and Sm^{II} compounds are rather stable, ($E°$(Ln^{3+}/Ln^{2+}) = −(0.34—1.50 V)[7,8]), whereas the compounds of other Ln^{II} (Ln = Nd, Dy, and Tm) with very low oxidation potentials ($E°$(Ln^{3+}/Ln^{2+}) = −(2.22—2.62 V)[7,8]) are extremely unstable; they have been synthesized rather recently.[9—11] The properties of these compounds were studied to less extent, and their CL has not recently been examined. Therefore, investigation of the physicochemical properties of the labile Nd^{II} and Dy^{II} compounds is urgent.

In this work, we studied for the first time the ability of DyI$_2$ (**1**) and NdI$_2$ (**2**) to enter chemical reactions and generate radiative excited states Ln^{3+}*. The interaction of compounds **1** and **2** with water was chosen as this reaction. The reaction has not been studied earlier: CL was not detected and no stable products were identified.

Experimental

Crystalline samples **1** and **2** (content of the main substance 95 and 93%, respectively) were synthesized according to earlier described procedures.[9,10] Bidistilled water was used; THF was purified by reflux over NaOH and metallic sodium and prior to use it was kept for 15 min over compound **1** or **2** for the additional purification from water traces.

For recording IR spectra, the samples were prepared as a suspension in Nujol and placed between NaCl plates. Photoluminescence (PL) spectra were recorded on a home-made spectrofluorimeter designed on the basis of an MDR-23 double monochromator. Absorption spectra were measured on Specord M-40 (UV-visible region) and Specord M-40 (IR region) spectrophotometers.

Chemiluminescence measurements. To measure the CL kinetics, a powder of compound **1** (18.20 mg, 0.04 mmol) or **2** (15.92 mg, 0.04 mmol) was placed under argon on the bottom of a glass cell mounted in a light-tight chamber of the chemiluminescence setup.[12] Water (2 mL) was added for 3 s from a doser to the cell, and CL was detected. The spectra of CL arisen upon the hydrolysis of compounds **1** (91.40 mg, 0.22 mmol) and **2** (87.60 mg, 0.22 mmol) were measured using a set of cut-off color filters according to a known procedure[13] with FEU-39 (for **1**) and FEU-83 (for **2**) photomultipliers cooled with liquid nitrogen as light receivers. When measuring the CL spectra, an aliquot of water (2 mL) was added to compound **1** (or **2**) or argon containing water vapor, which was obtained by purging argon through a bottle filled with water, was supplied.

Reactions of compounds 1 and 2 with liquid water. The reactions were carried out in an ampule filled with argon and connected to a gas burette. Water (5 mL) was added dropwise at 0 °C to compound **1** (1.39 g, 3.34 mmol). After gas evolution ceased completely, more water (15 mL) was added to the reaction mixture, the mixture was centrifuged, and a light blue solution was separated from the precipitate by decantation. The precipitate was washed with MeOH (10 mL) and dried *in vacuo*. The yield of DyI(OH)$_2 \cdot$H$_2$O was 0.494 g (82.4%). Found (%): Dy, 47.03; I, 38.26. H$_4$IDyO$_3$. Calculated (%): Dy, 47.59; I, 37.17.

The reaction of compound **2** with water was carried out similarly. Diiodide **2** (1.28 g, 3.22 mmol) gave NdI(OH)$_2 \cdot$H$_2$O (0.425 g, 74%). Found (%): I, 38.26; Nd, 45.74. H$_4$INdO$_3$.

Calculated (%): I, 39.27; Nd, 44.63. IR, ν/cm^{-1}: 3250, 1600. As found by complexonometry, the solution contained 0.84 g (100%) of NdI$_3$.

Reaction of compound 2 with water vapor. An argon flow bubbled through a water layer was purged above a layer of powder **2** (0.549 g, 1.38 mmol) with periodical shaking. After 20 min, the substance turned gray from dark violet. Water (10 mL) was added to the powder, and no gas evolution was observed. A gray suspension formed was centrifuged, and a precipitate was washed with water (10 mL) and MeOH (10 ml) and dried. The yield of NdI(OH)$_2$·H$_2$O was 0.141 g (67%). Found (%): I, 28.28; Nd, 45.29. H$_4$INdO$_3$. Calculated (%): I, 39.27; Nd, 44.63.

Reaction of compound 2 with liquid water in THF. The reaction was carried out in an ampule *in vacuo*. A water solution in THF (1.17 mol L^{-1}) was added dropwise with ice-cooling to compound **2** (0.559 g, 1.40 mmol). The vigorous reaction accompanied by gas evolution was observed for the first seconds. A dark violet solution was formed on heating to room temperature and stirring. After centrifuging, the solution was decanted, and the solvent was removed *in vacuo*. Hydroxydiiodide NdI$_2$OH(thf)$_2$·3H$_2$O as a pale blue solid was obtained in a yield of 0.763 g (88.62%). Found (%): I, 19.91; Nd, 23.81. C$_8$H$_{23}$I$_2$NdO$_6$. Calculated (%): I, 20.69; Nd, 23.53. IR, ν/cm^{-1}: 3250, 1600, 1072, 1034, 1003, 915, 850.

The content of Dy^{III} or Nd^{III} in the products was determined by complexonometric titration according to an earlier described procedure[14] (Xylenol Orange as indicator), and the content of iodide ions was determined by the Volhard method.[14] Hydrogen was analyzed by GLC on a Tsvet-800 chromatograph.

Results and Discussion

Individual inorganic compounds of bivalent lanthanides Sm, Eu, and Yb in solutions at room temperature possess no PL.[15—17] However, at 77 K the bright blue PL appears in aqueous acidic solutions of EuCl$_2$ and Eu(ClO$_4$)$_2$.[17] At the same time, the EuCl$_2$ complexes with crown ethers[18] and chlorides LnCl$_2$ (Ln = Sm, Eu, Yb) doped into inorganic matrices of NaCl, BaCl$_2$, and SrCl$_2$ exhibit the PL at room temperature as well.[15] Published data on the PL of compounds **1** and **2** and other iodides LnI$_2$ are lacking. We either found no PL for solid samples of compounds **1** and **2** (300 and 77 K).

Upon the addition of liquid water to solid samples of LnI$_2$ under an argon flow, we found the rapidly decaying PL (Figs 1 and 2), whose intensity was I_{max} = 5.4·10^8 and 6·10^7 photon s^{-1} mL^{-1} for compounds **1** and **2**, respectively. Since the emission intensity was low, the CL spectra were measured using boundary light filters. The CL spectrum of hydrolysis of compound **1** lies at 400—600 nm and has maxima at 470 and 570 nm, whose positions (within the measurement error ±20 nm) coincide with those of the maxima in the PL spectra of salts DyCl$_3$·6H$_2$O (see Ref. 19) and DyCl$_3$·3(BuO)$_3$PO,[20] *i.e.*, the excited Dy^{3+*} ion is the emitter of this CL. It was found using the SZS-9, KS-19, and FS-6 cut-off color filters that the CL for the hydrolysis of compound **2** lies in
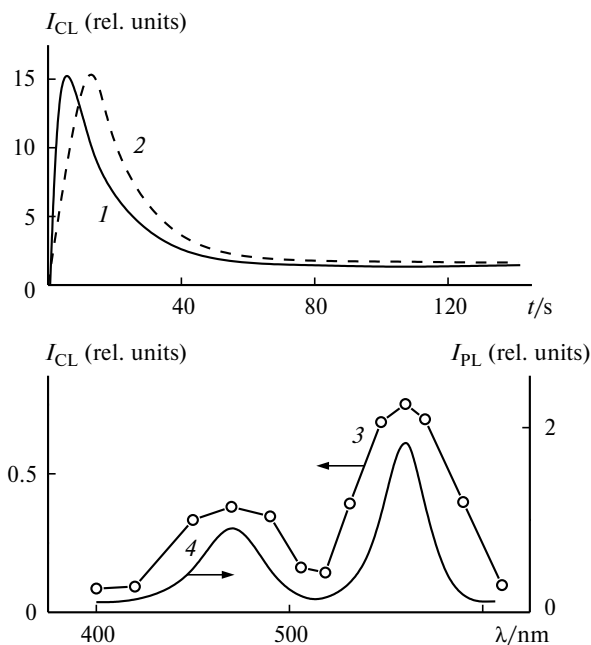

Fig. 1. Kinetics (*1*, *2*) and the CL spectrum (*3*) for the reaction of DyI$_2$ (18.20 mg, 0.04 mmol) with H$_2$O (*1*, upon the addition of 2 mL of H$_2$O; *2*, upon the supply of an argon flow containing H$_2$O vapor) and the PL spectrum of a solution of DyCl$_3$·3(BuO)$_3$PO in toluene (*4*), λ_{exc} = 352 nm (according to published data[20]).

a longer-wavelength spectral region (700—1200 nm) characteristic[20] of the emission of the Nd^{3+*} ion. The SZS-9 color filter absorbs completely the CL, whereas the KS-19 and FS-6 color filters weaken the CL by 5 and 50%, respectively (see Fig. 2). These results indicate that Nd^{3+*} is the CL emitter in the hydrolysis of compound **2**.

To study the mechanism of CL generated in the reaction of LnI$_2$ with water, we identified the composition and yield of the stable hydrolysis products of compounds **1** and **2** in particular experiments using larger amounts of the reactants than those in CL measurements. Upon the dropwise addition of water to LnI$_2$, hydrogen evolved vigorously for several seconds (84—100%) and light precipitates and pale yellow (color characteristic of Dy^{3+} ions) or pale blue (color characteristic of Nd^{3+} ions) were formed. Due to the hydrolysis of LnI$_2$, a portion of lanthanides is transformed into a precipitate and a portion goes to the solution. The presence in the solutions of triiodides DyI$_3$ and NdI$_3$, whose molar yield is 49—51%, was established by titration. The corresponding lanthanides and iodine in a ratio of 1 : 1 were found in the precipitates. The IR spectrum of the precipitate contains intense bands at 3200—3550 and 1600 cm^{-1} assigned to vibrations of the hydroxy groups in the molecule of water of crystallization.[21] Against the broad absorption band of water, the stretching vibrations of the hydroxy group in the Ln—OH groups are observed[21] as a weakly resolved shoulder at 3565 cm^{-1}. These results indicate that the
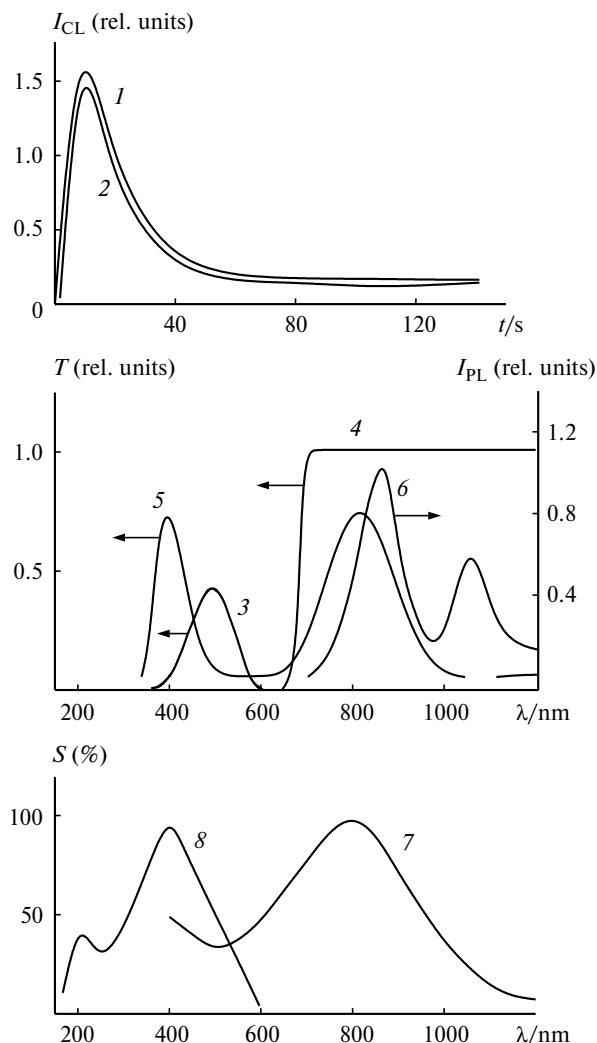
Fig. 2. Kinetics in the absence (*1*) and presence of the KS-19 light filter (*2*) and CL spectral parameters (*3—5*) for the reaction of NdI_2 (15.92 mg, 0.04 mmol) with H_2O (*3*, *4*, and *5*, transmittance of the SZS-9, KS-19, and FS-6 color filters, respectively), the PL spectrum of a solution of $NdCl_3 \cdot 3(BuO)_3PO$ in toluene (*6*) (λ_{exc} = 337.1 nm, according to published data[20]), and the spectral sensitivity (*S*) of FEU-83 (*7*) and FEU-39 (*8*).

precipitate composition corresponds to the formula $LnI(OH)_2 \cdot H_2O$.

Thus, the product composition of the reaction of compounds **1** and **2** with water differs from the expected one (LnI_2OH and H_2) and corresponds to the equation

$$2\, LnI_2 + 2\, H_2O \longrightarrow LnI_3 + LnI(OH)_2 + H_2.$$

The formation of triiodide NdI_3 and monoiodide $NdI(OPh)_2$ instead of the NdI_2OPh diiodide complex has previously been observed[22] in the reactions of compound **2** with phenol in THF at −90 °C. These results were explained by the disproportionation of the starting diiodide or primary product NdI_2OPh. Under the same condi-

tions, dysprosium salt **1** gives only the $DyI_2(OPh)$ diiodide complex.[22] It can be assumed that in water with much higher solvating and donating ability than that of THF[23] the processes of substituent redistribution at the metal ion accelerate. As a result, the disproportionation products are formed in an aqueous medium under the action of even less reactive reducing agent **1**. For the reactions with water (as with phenol) it seems impossible to conclude certainly about the starting compound of this process, *i.e.*, attribute it to LnI_2 or LnI_2OH.
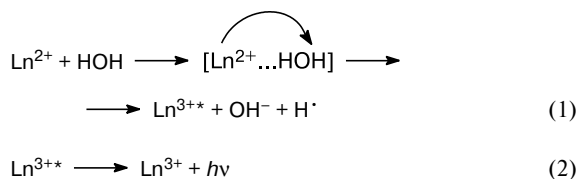
Another reaction occurs when a solution of water in THF (1.17 mol L^{-1}) interacts with compound **2**. In this case, no precipitation was observed, but hydrogen evolved vigorously (for several seconds) and the solution turned dark violet. The solution contained neodymium and iodine in a ratio of 1 : 2. The IR spectrum of the precipitate isolated from this solution exhibits, in addition to the absorption bands of water, bands at 1072, 1034, 1003, 915, and 850 cm^{-1} attributed to vibrations of molecules of coordinately bound THF.[21] Based on the results obtained, the composition of the precipitate can be described by the formula $NdI_2OH(thf)_2 \cdot 3H_2O$. The yield of the substance was 88.62%. Thus, the composition of the products of the reaction of compound **2** with water in THF corresponds to the equation

$$NdI_2 + H_2O \xrightarrow{\text{THF}} HONdI_2(thf)_2 + 0.5\, H_2.$$

The $NdI_2OH(thf)_2 \cdot 3H_2O$ complex in water remains unchanged, indicating in favor of LnI_2 (rather than LnI_2OH) as the disproportionating substance during diiodide hydrolysis in the absence of THF.

We believe that the motive force of the hydrolysis of LnI_2 are the low oxidation potentials of the Nd^{2+}/Nd^{3+} and Dy^{2+}/Dy^{3+} pairs and the high coordinative unsaturation of the Nd^{2+} and Dy^{2+} ions. Taking into account the results obtained, we can present the mechanism of the hydrolysis of LnI_2 as Scheme 1.

Scheme 1

$$Ln^{2+} + HOH \longrightarrow [Ln^{2+}...HOH] \longrightarrow$$

$$\longrightarrow Ln^{3+*} + OH^- + H^{\cdot} \qquad (1)$$

$$Ln^{3+*} \longrightarrow Ln^{3+} + h\nu \qquad (2)$$

Ln = Dy, Nd

On contact with LnI_2 the water molecules are incorporated into the first coordination sphere of the lanthanide, then an electron transfers from Ln^{II} to the water molecule and, as a result, Ln^{II} is oxidized to Ln^{III}, and atomic hydrogen is formed. The lanthanide ion transits to the excited state Ln^{3+*} (see Scheme 1, reaction (1)), which

is deactivated with photon emission (see Scheme 1, reaction (2)).

The energy values necessary for the population of the Nd^{3+}* (1.44 eV) and Dy^{3+}* (2.68 eV) excited states were estimated from the positions of the short-wavelength maxima in the PL spectra (see Figs 1 and 2). The free Gibbs energy ($\Delta G°$) of reaction (1) (see Scheme 1) was determined by the known[24] Weller equation

$$\Delta G° \text{ (eV)} = E°(\text{Ln}^{3+}/\text{Ln}^{2+}) - E°(\text{H}_2\text{O/H}^{\bullet},\text{OH}^-) - ke^2/(\varepsilon r) - E^*(\text{Ln}^{3+}), \qquad (I)$$

where $E°(\text{Ln}^{3+}/\text{Ln}^{2+})$ and $E°(\text{H}_2\text{O/H}^{\bullet},\text{OH}^-)$ are the oxidation potential of the Ln^{II} ion and the reduction potential of water, respectively; $E^*(\text{Ln}^{3+})$ is the energy of the excited state of the CL emitter; k is the Boltzmann constant; e is the electron charge; ε is the dielectric constant of the solvent (for water 78.5)[25]; r is the distance between the Ln^{II} atom and H$_2$O (0.5 nm).[26] The substitution of the corresponding $E°(\text{Ln}^{3+}/\text{Ln}^{2+})$[8] and $E°(\text{H}_2\text{O/H}^{\bullet},\text{OH}^-)$[27] values into Eq. (I) gave the $\Delta G°$ values for the hydrolysis of compounds **1** and **2**

$$\Delta G° = E°(\text{Dy}^{3+}/\text{Dy}^{2+}) - E°(\text{H}_2\text{O/H}^{\bullet},\text{OH}^-) - ke^2/(\varepsilon r) - E^*(\text{Dy}^{3+}) =$$
$$= -2.56 - (-0.41) - 0.04 - 2.68 = -4.87 \text{ (eV)}, \qquad (II)$$

$$\Delta G° = E°(\text{Nd}^{3+}/\text{Nd}^{2+}) - E°(\text{H}_2\text{O/H}^{\bullet},\text{OH}^-) - ke^2/(\varepsilon r) - E^*(\text{Nd}^{3+}) =$$
$$= -2.62 - (-0.41) - 0.04 - 1.44 = -3.69 \text{ (eV)}. \qquad (III)$$

The resulting $\Delta G°$ values indicate that electron transfer from the both Ln^{II} atoms is an exothermic process and the amount of the evolved energy is quite sufficient for the formation of the Dy^{3+}* and Nd^{3+}* ions.

Thus, the CL accompanying the reactions of iodides DyI$_2$ and NdI$_2$ with water was found and studied for the first time, the products were identified, and the energy parameters of the process were estimated.

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