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Journal of Luminescence 91 (2000) 49–58

JOURNAL OF LUMINESCENCE

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Chemiluminescence of praseodymium (III), neodymium (III) and ytterbium (III) β-diketonates in solution excited from 1,2-dioxetane decomposition and singlet–singlet energy transfer from ketone to rare-earth β-diketonates

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Received 27 December 1999; accepted 4 January 2000

Abstract

This work is concerned with the chemiluminescence (CL) of Nd^{3+}, Yb^{3+} and Pr^{3+} β-diketonates in solution. Chemiluminescent reaction of adamantylideneadamantane-1,2-dioxetane (AAD) decomposition generating singlet ($Ad{=}O_S^*$) and triplet ($Ad{=}O_T^*$) excited adamantanone was used as a source of excited species. AAD chemiluminescence due to emission from $Ad{=}O_S^*$ is quenched by Ln^{3+} β-diketonates: (a) by intermolecular singlet-singlet (S-S) energy transfer from $Ad{=}O_S^*$ to β-diketonate ligand levels of $Ln(TTA)_3 \cdot 2H_2O$ and $Ln(BTFA)_3 \cdot 2H_2O$; (b) by complex formation between AAD and $Pr(FOD)_3$ or $Pr(DPM)_3$. Corresponding Stern–Volmer quenching constants or stability constants of the complex were measured. Chemiluminescence spectra of Ln^{3+} β-diketonates were recorded and relative luminescence quantum yields compared. Yb^{3+} chelates show higher luminescence yields compared to Nd^{3+}, due to a different efficiency of non-radiative energy degradation. Chemiexcitation of Ln^{3+} ions in the systems studied occurs by: (a) intermolecular singlet–singlet energy transfer: $Ad{=}O_S^* \rightarrow L_S^* \rightarrow L_T^* \rightarrow Ln^{3+*}$ (where L_S^* and L_T^* are the first singlet and triplet excited states of the β-diketonate ligand); (b) intermolecular triplet–triplet energy transfer: $Ad{=}O_T^* \rightarrow L_T^* \rightarrow Ln^{3+*}$; (c) intracomplex energy transfer from the decomposition of AAD in the complex with Ln^{3+} β-diketonate. Efficiency of chemiexcitation pathways is different for each Ln^{3+} β-diketonate and Ln^{3+} ion. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Energy transfer; Chemiluminescence; Lanthanide ions; β-diketonate complexes

1. Introduction

Chemiluminescence (CL) of rare-earth ions has attracted considerable attention [1–18], being observable: (a) in redox reactions when Ln^{3+} is formed from Ln^{4+} or Ln^{2+} [4–7]; (b) when highly exothermic reaction occurs in the inner coordination sphere of Ln^{3+}, and the Ln^{3+} ion takes active part in it [1,2]; (c) when Ln^{3+} serves only as acceptor of energy of an excited product and takes no part in the reaction [1,11–13]. Chemiluminescence of Ln^{3+} was observed from its inorganic [4–9,16],

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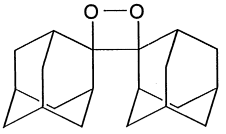
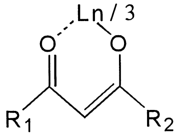
PII: S0022-2313(00)00199-X

organic [1–3,10,11] and organometallic [17,18] compounds. Brightly luminescent Eu^{3+} and Tb^{3+} β-diketonates [19,20] are commonly used to study mechanisms and quantitative characteristics of chemiluminescent reactions and for enhancement of CL intensity in those systems where the primary excited product formed does not emit but can transfer its excitation energy to a Ln^{3+} complex [11–13]. Lanthanide compounds are used to enhance chemiluminescence arising from oxidation of biological substrates [12–15].

Herein, we present an investigation of chemiluminescence of Nd^{3+}, Yb^{3+} and Pr^{3+} β-diketonates ($Ln(L)_3 \cdot nH_2O$) arising from the decomposition of adamantylideneadamantane-1,2-dioxetane (AAD). Singlet–singlet energy transfer from ketone-adamantanone (Ad = O) formed from the AAD decomposition to β-diketonates of Ln^{3+} is studied by a chemiluminescence method. Luminescence efficiencies of different Ln^{3+} β-diketonates are compared and chemiexcitation mechanisms of Ln^{3+} are discussed.



AAD



$Ln(L)_3\ nH_2O$
Ln: Nd^{3+}; Yb^{3+}; Pr^{3+}
L:
TTA: $R_1=C_4H_4S$; $R_2=CF_3$; **n** = 2
BTFA: $R_1=C_6H_5$; $R_2=CF_3$; **n** = 2
AA: $R_1= R_2=CH_3$; **n** = 3
FOD: $R_1= tC_4H_9$; $R_2= C_3H_7$; **n** = 0
DPM: $R_1= R_2= tC_4H_9$; **n** = 0

It should be noted that luminescence of Nd^{3+}, Yb^{3+} and Pr^{3+} ions in solutions is very weak with quantum yields $< 10^{-3}$. Luminescence of Nd^{3+} and Yb^{3+} ions in solutions was studied recently [21–27] while their chemiluminescence was observed from the oxidation of Yb^{3+} organometallics by O_2 and O_2^- [17] and from the decomposition of AAD melted with Nd^{3+} or Yb^{3+} perchlorates [16]. Luminescence of Pr^{3+} in solutions was studied only for its inorganic compounds [28–32] while its chemiluminescence was observed from the oxidation of CO by O_2 on ThO_2 doped with Pr^{3+} [8,9] and from the reduction of Pr^{4+} in mineral acid solutions [4,5].

2. Experimental

2.1. Materials

AAD was synthesized as in Ref. [33]. Benzoyltrifluoroacetone (BTFA) and thenoyltrifluoroacetone (HTTA) were used as received, acetylacetone (HAA) was distilled. Toluene was dried by boiling over metallic sodium and distilled.

$Ln(TTA)_3 \cdot 2H_2O$: 0.8 g of HTTA (3.6×10^{-3} mol) was dissolved in water (650 ml) at 60°C at intense stirring. Solution pH was adjusted to 6–6.5 with NH_4OH. To the obtained HTTA solution was added 9×10^{-4} mol of $LnCl_3 \cdot 6H_2O$ in 3 ml of water. A fine precipitate of $Ln(TTA)_3 \cdot 2H_2O$, formed immediately, was stirred for 30 min until flocculation took place and was filtered. Large flakes of $Ln(TTA)_3 \cdot 2H_2O$ were not formed if the pH of the initial HTTA solution was > 7, complicating the filtration.

$Ln(BTFA)_3 \cdot 2H_2O$: 6×10^{-3} mole of HBTFA and 6×10^{-3} mol of NaOH were dissolved in 10–15 ml of 95% ethanol under heating. Then, 2×10^{-3} mole of $LnCl_3 \cdot 6H_2O$ in 3 ml of water was added. Under evaporation, the $Ln(BTFA)_3 \cdot 2H_2O$ separates as an oil that crystallizes when mixed with water. Both complexes were washed with water to remove NaCl, and with heptane to remove unreacted β-diketone. $Ln(AA)_3 \cdot 3H_2O$: obtained as in Ref. [34] with Nd^{3+} and Pr^{3+} acetylacetonates contaminated by ≈5% admixture of $LnOH(AA)_2 \cdot nH_2O$ insoluble in toluene. All chelates were dried at normal pressure in a dessicator. It should be noted that anhydrous $Ln(L)_3$ could not be obtained by drying $Ln(TTA)_3 \cdot 2H_2O$, $Ln(BTFA)_3 \cdot 2H_2O$ and $Ln(AA)_3 \cdot 3H_2O$ in vaccum under heating due to destruction of the complexes [34,35]. The $Ln(L)_3 \cdot nH_2O$ composition was checked by C,H-analysis, with a deviation from calculated values $< 0.5\%$, and by IR spectra (KBr, 4000–200 cm^{-1}) [36]. $Pr(FOD)_3$ and $Pr(DPM)_3$ were sublimed and dried for 30 min in vacuum at 90°C just prior to use. All chelates (except $Pr(FOD)_3$) are slightly soluble in toluene at room temperature ($< 5 \times 10^{-3}$ M), although they could be dissolved up to 7×10^{-2} M on heating forming transparent and stable solutions.

2.2. Equipment and procedures

Spectrophotometers “Specord M-40” (200–900 nm) and “Specord M-80” (4000–200 cm^{-1}) were used to obtain the absorption spectra. A spectrofluorimeter MPF-4 “Hitachi” was used to obtain the fluorescence spectra in the 200–700 nm range. Photomultiplier tubes used for luminescence measurements were FEU-140 (360–700 nm) or liquid-nitrogen-cooled FEU-83 (up to 1300 nm with Cs–O–Ag cathode).

Infrared photoluminescence spectra were registered at 180° relative to the excitation light. Solutions were optically thick at the excitation wavelength.

Quenching of AAD chemiluminescence by β-diketonates $Ln(L)_3 \cdot nH_2O$ and β-diketones was performed at 75–92°C, with AAD decomposition rate $< 10^{-6}\,s^{-1}$, and conversion level $< 0.5\%$ in experiment. Quenching of CL intensity was registered in the spectral region $\lambda > 450$ nm to avoid inner filter. Quenching by Pr^{3+} β-diketonates was registered at $450 < \lambda < 470$ nm, since Pr^{3+} chemiluminesce at $\lambda > 480$ nm [1,2].

The dependence of the infrared CL intensity of Nd^{3+} and Yb^{3+} on the $Ln(L)_3 \cdot nH_2O$ concentration was registered at 82°C by placing a filter (800–1050 nm) between FEU-83 and a reactor to remove thermal emission. The concentration dependence of the Pr^{3+} CL intensity was measured in the range 550–700 nm.

Weighted amounts of Ln^{3+} β-diketonates or β-diketones were added to a 10^{-3} M solution of AAD (1–4 ml) to change the additive concentration in the 5×10^{-3}–4×10^{-2} M range when studying the quenching of the AAD CL or increase of the Ln^{3+} CL.

3. Results and discussion

3.1. Quenching of AAD chemiluminescence by Ln^{3+} β-diketonates

Adamantylideneadamantane-1,2-dioxetane is an energy-rich cyclic peroxide. It neatly decomposes in solution to form singlet ($Ad{=}O^*_S$) and triplet ($Ad{=}O^*_T$) excited adamantanone states with corresponding yields (Eq. (1)) [33]

$$\mathrm{AAD} \xrightarrow{k_1} 1.83\,\mathrm{Ad} = \mathrm{O} + 0.15\,\mathrm{Ad} = \mathrm{O}^*_{\mathrm{T}} + 0.02\,\mathrm{Ad}{=}\mathrm{O}^*_{\mathrm{S}}$$

$$\mathrm{Ad}{=}\mathrm{O}^*_{\mathrm{S}} \rightarrow \mathrm{Ad}{=}\mathrm{O} + h\nu, \quad \lambda_{\max} = 420\,\mathrm{nm}. \qquad (1)$$

Reaction (1) can be considered as a stationary source of excited species since the rate of AAD decompositon k_1 is $< 10^{-6}\,s^{-1}$ up to 100°C [33]. The chemiluminescence spectrum observed from the AAD decomposition coincides with the fluorescence spectrum of $Ad{=}O$ (Fig. 1). Emission bands of Ln^{3+} appear in the CL spectrum of AAD in the presence of the lanthanide β-diketonates studied.

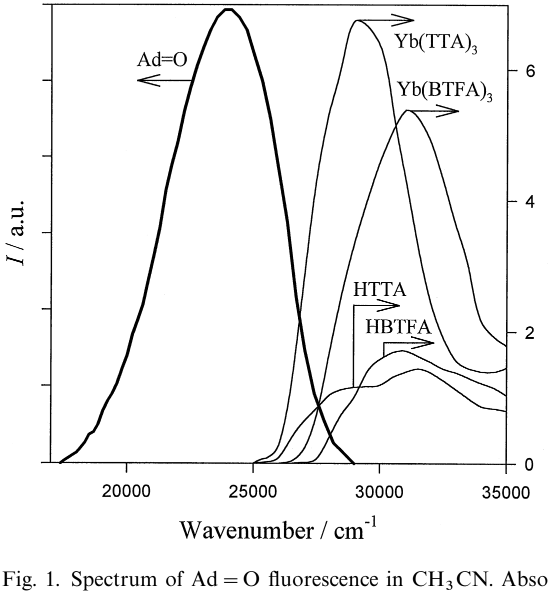


Fig. 1. Spectrum of $Ad{=}O$ fluorescence in CH_3CN. Absorption spectra of Yb^{3+} β-diketonates in CH_3CN and of β-diketones in n-C_6H_{14}.

However, emission bands of Ad$=$O and Ln^{3+} do not overlap and changes in CL intensity of both emitters can be studied.

The AAD chemiluminescence is quenched in the presence of $Ln(TTA)_3 \cdot 2H_2O$, $Ln(BTFA)_3 \cdot 2H_2O$, $Pr(DPM)_3$ and β-diketones HTTA, HBTFA. Quenching obeys the Stern-Volmer equation (Eq. (2)), where I^0_{CL} and I_{CL} stand for the AAD CL intensity in the absence and presence of the quencher, respectively, K_{SV} is the Stern–Volmer quenching constant and [Q] is the quencher concentration (Fig. 2). Calculated values of K_{SV} are listed in Tables 1 and 2. The efficiency of quenching by the chelates is only slightly dependent on the Ln^{3+} ion, which is determined largely by the β-diketonate ligand with K_{SV} decreasing in the order: $Ln(TTA)_3 \cdot 2H_2O > Ln(BTFA)_3 \cdot 2H_2O > Pr(DPM)_3$ (Fig. 2). Similar change of K_{SV} values is observed for the corresponding β-diketones: HTTA > HBTFA, although their quenching efficiency is less than that for the chelates. Both $Ln(AA)_3 \cdot 3H_2O$ and HAA do not quench AAD CL, while quenching by $Pr(FOD)_3$ could not be observed due to a bright CL of Pr^{3+}.

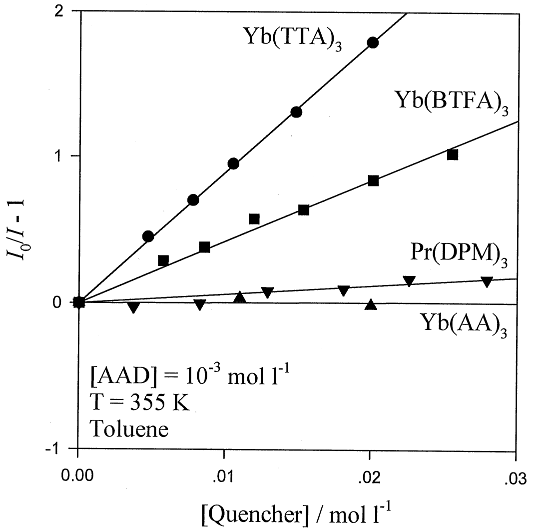


Fig. 2. Stern–Volmer AAD chemiluminescence quenching by Yb^{3+} and Pr^{3+} β-diketonates.

$$I^0_{CL} I^{-1}_{CL} = 1 + K_{SV}[Q]. \qquad (2)$$

Quenching of AAD chemiluminescence by Ln^{3+} β-diketonates can occur either by intermolecular energy transfer from $Ad=O^{*}_{S}$ to the chelate (Eq. (3)) and/or by formation of the complex $AAD \cdot Ln(L)_3$ that lowers the concentration of free AAD and thus decreases the CL intensity (Eq. (4)). Obviously, Ln^{3+} in $AAD \cdot Ln(L)_3$ is coordinated

Table 1
Quenching of the AAD chemiluminescence by Nd^{3+} and Yb^{3+} β-diketonates and by β-diketones and growth of Nd^{3+} and Yb^{3+} chemiluminescence in toluene[a]

Quencher	K_{SV} ($l\,mol^{-1}$)	$k_q \times 10^{-9}$ ($l\,mol^{-1}\,s^{-1}$)	$J \times 10^{15}$ ($cm^4\,M^{-1}$)	R_0 (Å)	r (Å)	K_{CL} ($l\,mol^{-1}$)
HTTA	56	6.1	1.1	9.3	4.8	—
$Nd(TTA)_3 \cdot 2H_2O$	79	7.9	4.7	11.9	5.8	90 ± 10
$Nd(TTA)_3 + Ad=O$	82	8.7	4.7	11.9	5.7	45 ± 7
$Yb(TTA)_3 \cdot 2H_2O$	90	9.0	4.6	11.9	5.6	44 ± 2
$Yb(TTA)_3 + Ad=O$	88	9.7	4.1	11.6	5.5	26 ± 2
HBTFA	20	2.2	0.093	6.2	3.8	—
$Nd(BTFA)_3 \cdot 2H_2O$	36	4.0	0.96	9.1	5.0	> 90
$Nd(BTFA)_3 + Ad=O$	45	4.9	0.84	8.9	4.7	55 ± 5
$Yb(BTFA)_3 \cdot 2H_2O$	42	4.6	0.71	8.7	4.7	45 ± 7
$Yb(BTFA)_3 + Ad=O$	48	5.3	0.61	8.5	4.5	16 ± 2

[a] Errors: K_{SV} – 10%, J – 30%. K_{SV}, k_q and K_{CL} measured at 355 K. For the calculation of J were used: absorption spectra of $Ln(L)_3 \cdot nH_2O$ in CH_3CN and β-diketones in n-C_6H_{14} and luminescence spectrum of Ad = O in CH_3CN at 290 K. In the experiments with Ad = O, the ratio $[Ad=O]:[Ln(L)_3 \cdot nH_2O]$ is 5.

Table 2
Quenching of the AAD chemiluminescence by Pr^{3+} β-diketonates and growth of Pr^{3+} chemiluminescence in toluene[a]

Chelate	K_{SV} ($l\,mol^{-1}$)	$k_q \times 10^{-9}$ ($l\,mol^{-1}\,s^{-1}$)	$J \times 10^{15}$ ($cm^4\ M^{-1}$)	R_0 (Å)	r (Å)	K_{CL} ($l\,mol^{-1}$)
$Pr(TTA)_3 \cdot 2H_2O$	104	11	5.4	12.2	5.6	$\gg 100$
$Pr(BTFA)_3 \cdot 2H_2O$	36	4	0.79	8.9	4.9	$\gg 100$
$Pr(FOD)_3$		—	0	—	—	42[b]
$Pr(DPM)_3$	≈ 6	—	0	—	—	≈ 11

[a] Errors: K_{SV} – 10%, J – 30%. K_{SV}, k_q and K_{CL} measured at 355 K. For the calculation of J were used: absorption spectra of $Ln(L)_3 \cdot nH_2O$ and luminescence spectrum of Ad = O in CH_3CN at 290 K.

[b] At 344 K.

by oxygen atoms of peroxide.

$$Ad{=}O_S^* + Ln(L)_3 \cdot nH_2O \overset{k_q}{\rightarrow} Ad{=}O + Ln(L)_3 \cdot nH_2O^*, \tag{3}$$

$$AAD + Ln(L)_3 \overset{K}{\leftrightarrow} AAD \cdot Ln(L)_3 \overset{k_2}{\rightarrow} \phi_{Ln}^*[Ln(L)_3^* \cdot 2Ad{=}O] + (1 - \phi_{Ln}^*) \times [Ln(L)_3 \cdot 2Ad{=}O], \tag{4}$$

It will be shown below that mechanism (3) is operative for $Ln(TTA)_3 \cdot 2H_2O$ and $Ln(BTFA)_3 \cdot 2H_2O$, while mechanism (4) for $Pr(DPM)_3$ and $Pr(FOD)_3$.

3.1.1. Quenching by singlet-singlet energy transfer from adamantanone to ligand levels in $Ln(TTA)_3 \cdot 2H_2O$ and $Ln(BTFA)_3 \cdot 2H_2O$

Charactersitic coordination number of Ln^{3+} is 8 or 9 and thus formation of $AAD \cdot Ln(L)_3$ in the case of $Ln(TTA)_3 \cdot 2H_2O$, $Ln(BTFA)_3 \cdot 2H_2O$ and $Ln(AA)_3 \cdot 3H_2O$ (Eq. (4)) requires that H_2O be substituted by the AAD molecule, since all coordination sites of the Ln^{3+} ion in these β-diketonates are occupied. Since the composition of $Ln(L)_3 \cdot nH_2O$ is preserved in toluene solution and since it was used in 5–25 excess relative to AAD concentration, it should be expected that only a small part of AAD will coordinate to Ln^{3+} to form $AAD \cdot Ln(L)_3$ due to a competition with H_2O molecules. Moreover, adamantanone added in the ratio $[Ad{=}O]:[Ln(L)_3 \cdot nH_2O] = 5$ to prevent formation of $AAD \cdot Ln(L)_3$ does not change the values of K_{SV} (Table 1). Adamantanone being in large excess expels both AAD and H_2O from the inner coordination sphere of Ln^{3+} to form $Ln(L)_3 \cdot nAd{=}O$ ($n = 1, 2$) and if CL quenching occurred by mechanism (4), the presence of Ad = O should have altered the K_{SV} values, but no such change is observed and reaction (4) is considered to be insignificant in the system studied. It should be noted that Ad = O itself does not influence the CL intensity of AAD.

We think that the observed quenching of AAD CL occurs by intermolecular singlet–singlet energy transfer (S–S) from $Ad{=}O_S^*$ to singlet levels of the β-diketonate ligand (L_S^*) in the $Ln(TTA)_3 \cdot 2H_2O$ and $Ln(BTFA)_3 \cdot 2H_2O$ chelates (Eq. (3)). The energy transfer is exothermic since $Ad{=}O_S^*$ lies at 29 000 cm^{-1}, while L_S^* in $Ln(TTA)_3$ is at 26 000 cm^{-1}, and in $Ln(BTFA)_3 \cdot 2H_2O$ at 27 000 cm^{-1}, as determined from the absorption spectra (Figs. 1 and 3). Both β-diketones – HTTA ($L_S^* = 26000\ cm^{-1}$) and HBTFA ($L_S^* = 27500\ cm^{-1}$) also quench CL of AAD thus indicating intermolecular S–S energy transfer since complex formation (Eq. (4)) cannot take place with them.

The observed $Ad{=}O_S^* \rightarrow L_S^*$ energy transfer might be either due to a long-range dipole–dipole or short-range exchange interaction [37]. We assumed that the energy transfer $Ad{=}O_S^* \rightarrow L_S^*$ occurs by dipole–dipole mechanism since the transitions in both the donor and acceptor are allowed [37]. In that case the energy transfer efficiency is directly proportional to the overlap integral (J) between the luminescence spectrum of the donor and absorption spectrum of the acceptor as given in Eq. (5), where $I_D(v)$ is the luminescence intensity of the donor, satisfying $\int I_D(v)\,dv = 1$, and $\varepsilon_A(v)$ is the molar extinction coefficient of the acceptor [37]. Only intense β-diketonate ligand absorption was taken for the calculation of J while weak

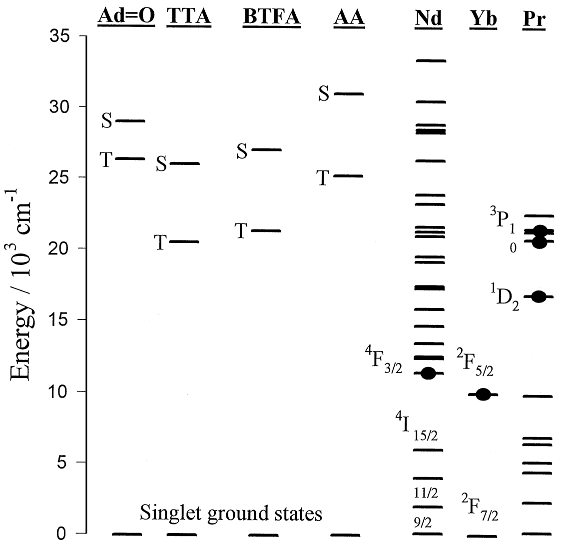


Fig. 3. Energy levels of Ad = O [11] and β-diketonate ligands in $Ln(L)_3 \cdot nH_2O$ [19,41], and ff-states of Ln^{3+} [45]. Luminescence is observed from the Ln^{3+} levels marked with (●).

ff-absorption by the Ln^{3+} ion was neglected. Calculated values of J are listed in Tables 1 and 2 and actually K_{SV} is proportional to J. If intermolecular energy transfer is the sole quenching mechanism, then the bimolecular rate constants of AAD CL quenching (k_q) can be calculated from $k_q = K_{SV} \cdot \tau_D^{-1}$, where $\tau_D = 9.12$ ns is the fluorescence lifetime of Ad = O in hexane in the absence of the quencher [38] (Tables 1 and 2).

$$J = \int I_D(\nu)\varepsilon_A(\nu)\nu^{-4}\, d\nu. \tag{5}$$

Assuming dipole–dipole energy transfer we calculated the actual distances between the donor and acceptor – r (Eq. (6)), and the critical energy transfer distances – R_0 (Eq. 7) [37]. In Eqs. (6) and (7) the $k^2 = \frac{2}{3}$ is a geometric factor, n is the refraction index of toluene, $\phi_D = 0.0052$ is the photoluminescence quantum yield of Ad = O [39]. The R_0 is a distance when $k_q = \tau_D^{-1}$. The values of R_0 and r are listed in Tables 1 and 2.

$$r = 9.79 \times 10^3 (k_q \tau_D)^{-1/6} (k^2 n^{-4} \phi_D J)^{1/6}, \tag{6}$$

$$R_0 = 9.79 \times 10^3 (k^2 n^{-4} \phi_D J)^{1/6}. \tag{7}$$

We consider values of J and consequently of R_0 and r as lower estimates of actual ones due to experimental errors in the J determination. However, it should be noted, that energy transfer $Ad{=}O_S^* \rightarrow L_S^*$ might be partially due to exchange mechanism since the obtained distances of r around 4 or 5 Å (Tables 1 and 2) are short enough for this mechanism to be operative too.

Lanthanide β-diketonates have higher molar extinction coefficients (Fig. 1) and overlap integrals, and, thus, higher K_{SV} values as compared to β-diketones (Table 1). Additional evidence for the S–S energy transfer quenching mechanism is that both HAA ($L_S^* = 32\,000\,cm^{-1}$) and $Ln(AA)_3 \cdot 3H_2O$ ($L_S^* = 31\,000\,cm^{-1}$) do not quench the AAD CL, since their absorption spectra do not overlap with the AAD CL spectrum and $J \approx 0$. The K_{SV} values for $Ln(TTA)_3 \cdot 2H_2O$ and $Ln(BTFA)_3 \cdot 2H_2O$ increase by 5–15% in the range 345–360 K.

Quenching of triplet excited organic molecules by metal β-diketonates has been studied in detail [40,41] while quenching of singlet states is not so thoroughly studied [42]. Investigation of S–S energy transfer from adamantanone to $Ln(L)_3 \cdot nH_2O$ using photoexcitation of ketone is complicated since Ad = O cannot be excited selectively. Thus, ε_{max} of Ad = O at 295 nm is only 17 $(M\,cm)^{-1}$ [39], while that for $Ln(L)_3 \cdot nH_2O$ it is $\approx 10^4$ $(M\,cm)^{-1}$ (Fig. 1). Thus, chemiluminescence proves to be a convenient approach to study the interaction of singlet excited states of organic molecules with metal β-diketonates, since donor excited state is populated through the energy released in chemical reaction and not by irradiation with light.

3.1.2. Quenching due to complex formation of AAD with Pr(FOD)₃ and Pr(DPM)₃

Singlet–singlet energy transfer to the β-diketonates $Pr(DPM)_3$ ($L_S^* = 32\,000\,cm^{-1}$) and $Pr(FOD)_3$ ($L_S^* = 29\,500\,cm^{-1}$) cannot take place since their absorption spectra do not overlap with the fluorescence spectrum of Ad=O and thus $J \approx 0$. Contrary to the Ln^{3+} β-diketonates considered above, only six coordination bonds of Pr^{3+} ion are occupied in $Pr(DPM)_3$ and $Pr(FOD)_3$ and these two chelates readily form complexes with compounds that have oxygen atoms [43] including AAD [1,2]. Thus, quenching of the AAD CL through complex formation becomes feasible with these chelates (Eq. (4)). If only mechanism (4) is operative, then the observed K_{SV} should be equal to the stability constant of the $AAD \cdot Ln(L)_3$ complex, $K_{SV} = K$.

The stability constant of the $AAD \cdot Pr(DPM)_3$ complex determined from quenching of the AAD CL is $K \approx 61\,l\,mol^{-1}$ at 355 K, which is significantly lower than that for AAD $Pr(FOD)_3$: $K = 57\,l\,mol^{-1}$ as determined from decomposition kinetics of AAD $Pr(FOD)_3$ [1]. The difference in stability constants might be explained by steric crowding of bulky tret-butyl substituents of $Pr(DPM)_3$ and less Lewis acidity of non-fluorinated $Pr(DPM)_3$ as compared to fluorinated $Pr(FOD)_3$ [43]. Quenching by $Pr(FOD)_3$ could not be registered due to intense background chemiluminescence of Pr^{3+}.

3.2. Spectra and efficiency of luminescence of Ln^{3+} β-diketonates

In β-diketonates of luminescent Ln^{3+} ions, excitation into the ligand absorption band results in ff-luminescence of Ln^{3+} [19,20]. Population of excited ff-levels of Ln^{3+} occurs by energy transfer from ligand triplet state (L_T^*), formed by fast intersystem crossing $L_S^* \rightarrow L_T^*$. Direct excitation of Ln^{3+} ion also results in Ln^{3+} emission.

Energy transfer from $Ad{=}O^*$ to $Ln(L)_3 \cdot nH_2O$ (Eqs. (3) and (4) forms excited Ln^{3+} β-diketonate and we have observed ff-chemiluminescence of Nd^{3+}, Yb^{3+} and Pr^{3+} ions in the $Ln(L)_3 \cdot nH_2O$-AAD system. For Nd^{3+}, the maxima in the CL spectrum (λ_{max}) are observed at 860 ± 20 nm ($^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition) and 1060 ± 20 nm ($^4F_{3/2} \rightarrow {}^4I_{11/2}$), while for Yb^{3+} at 980 ± 20 nm ($^2F_{5/2} \rightarrow {}^2F_{7/2}$) (Fig. 4). The CL spectra of Nd^{3+} and Yb^{3+} coincide with their PL spectra. Relative photoluminescence (ϕ_{Ln}) and chemiluminescence (ϕ_{CL}) quantum yields of Nd^{3+} and Yb^{3+} were calculated with correction made for spectral sensitivity of the photomultiplier tube (Table 3). Thus comparison of ϕ_{Ln} and ϕ_{CL} between Nd^{3+} and Yb^{3+} compounds is possible. Observed luminescence yields for Yb^{3+} were always higher than those for the corresponding Nd^{3+} chelate (Table 3), since the Yb^{3+} ion has a larger energy gap between the radiative and lower lying levels than the Nd^{3+} ion. For Yb^{3+}, the energy difference between the $^2F_{5/2}$ and $^2F_{7/2}$ levels is 10 000 cm^{-1}, while that for Nd^{3+} between $^4F_{3/2}$ and $^4I_{15/2}$ levels, it is 5390 cm^{-1} (Fig. 3), leading to efficient non-radiative energy losses of Nd^{3+} through high vibrational modes of C–H and O–H bonds present in its surroundings [44].

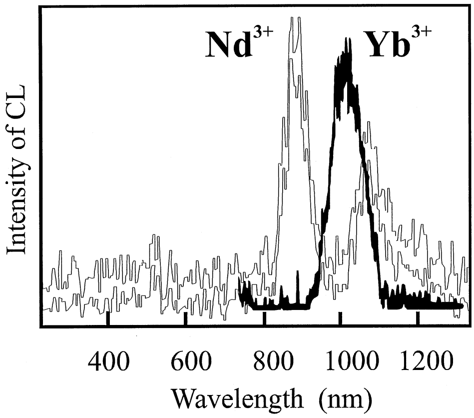


Fig. 4. Chemiluminescence spectra of Yb^{3+} and Nd^{3+}. $[Ln(L)_3 \cdot nH_2O] = 3 \times 10^{-2}$ M, $[AAD] = 10^{-2}$ M, $T = 368$ K in toluene. The broad band in the Nd^{3+} spectrum at 1100–1250 nm is an artefact. The CL spectra are not corrected for the spectral sensitivity of the photomultiplier tube and intensities cannot be compared.

Table 3
Relative luminescence efficiencies of Nd^{3+} and Yb^{3+} β-diketonates[a]

Chelate	ϕ_{Ln}[b] toluene	ϕ_{Ln}[b] CH_3CN	ϕ_{CL}[c]	ϕ_{CL}[d] $Ad{=}O$
$Nd(TTA)_3 \cdot 2H_2O$	35	84	39	33
$Yb(TTA)_3 \cdot 2H_2O$	100	100	100	154
$Nd(BTFA)_3 \cdot 2H_2O$	31	70	36	25
$Yb(BTFA)_3 \cdot 2H_2O$	80	90	42	88
$Nd(AA)_3 \cdot 3H_2O$	—	18	<3	<4
$Yb(AA)_3 \cdot 3H_2O$	—	21	3	4

[a] Errors – 20%.

[b] Relative photoluminescence yields of 10^{-3} M solutions of $Ln(L)_3 \cdot nH_2O$ in toluene ($\lambda_{exc} = 365$ nm) or CH_3CN (($\lambda_{exc} = 315$ nm) at 300 K.

[c] Relative chemiluminescence yields of $Ln(L)_3 \cdot nH_2O$: 3 ml of toluene solution $[Ln(L)_3 \cdot nH_2O] = 3 \times 10^{-2}$ M, $[AAD] = 10^{-2}$ M at 368 K.

[d] As in footnote c with $[Ad{=}O] = 0.15$ M.

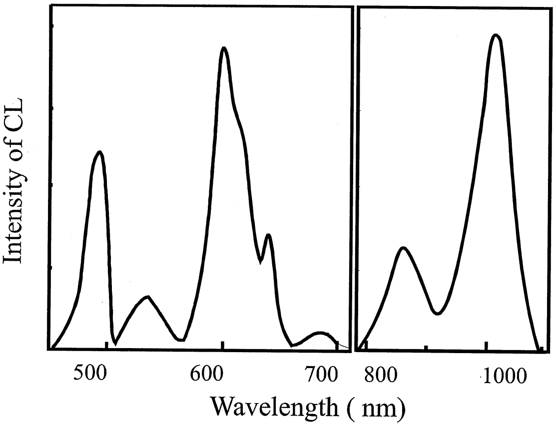


Fig. 5. Chemiluminescence spectrum of Pr^{3+} $[Pr(FOD)_3] = 7 \times 10^{-2}$ M, $[AAD] = 10^{-2}$ M, $T = 368$ K in toluene (spectral slit $\Delta\lambda = 7$ nm). The CL spectrum is not corrected for the spectral sensitivity of the photomultiplier tube and intensities between visible and IR regions cannot be compared.

The chemiluminescence spectrum of Pr^{3+} in visible and infrared regions is shown in Fig. 5. It should be noted that its luminescence is observed from three excited states: $^3P_1$, $^3P_0$ and $^1D_2$ with comparable quantum yields [29] while both Nd^{3+} and Yb^{3+} emit from resonant states only (Fig. 3). It is a curious fact since luminescence of lanthanide ions in solutions from resonant state usually predominates [44]. In CL spectrum of Pr^{3+} transitions from upper $^3P_1$, $^3P_0$ levels prevail in visible region, while infrared CL is due mainly to transitions from resonant $^1D_2$ level (Fig. 5). For discussion of Pr^{3+} chemiluminescence spectrum, the reader is referred to Refs. [1,2]. Relative photoluminescence yield of Pr^{3+} was estimated by measuring the emission intensity at 1000 nm ($^1D_2 \rightarrow {}^3F_4$ transition) while chemiluminescence yield by measuring the emission intensity in the range $550 < \lambda < 700$ nm (transitions from $^3P_1$, $^3P_0$ and $^1D_2$ levels) (Table 4).

3.3. Chemiexcitation mechanisms of Ln^{3+}

A brief review of known chemiexcitation mechanisms of Ln^{3+} ions has been given in the Introduction. Elucidation of the chemiexcitation mechanism of Ln^{3+} in the $Ln(L)_3 \cdot nH_2O$-AAD system comes from comparison of the relative luminescence yields of Ln^{3+} (Tables 3 and 4) and photophysical parameters of energy donor and acceptor (Fig. 3).

Table 4
Relative luminescence efficiencies of Pr^{3+} β-diketonates[a]

Chelate	ϕ_{Ln}[b] C_2H_5OH	ϕ_{CL}[c]	ϕ_{CL}[d] Ad = O
$Pr(TTA)_3 \cdot 2H_2O$	100	100	48
$Pr(BTFA)_3 \cdot 2H_2O$	103	91	36
$Pr(AA)_3 \cdot 3H_2O$	80	< 6	< 6
$Pr(FOD)_3$	110	2000	57
$Pr(DPM)_3$	89	64	51

[a] Errors – 10%.

[b] Relative photoluminescence yields of 10^{-3} M solutions of $Ln(L)_3 \cdot nH_2O$ in 95% C_2H_5OH ($\lambda_{exc} = 315$ nm) at 290 K.

[c] Relative chemiluminescence yields of $Ln(L)_3 \cdot nH_2O$: 2 ml toluene solution of $[Ln(L)_3 \cdot nH_2O] = 2 \times 10^{-2}$ M, $[AAD] = 10^{-3}$ M at 363 K.

[d] As in footnote c with $[Ad=O] = 0.1$ M.

Chemiexcitation of Ln^{3+} in the β-diketonates studied might occur by intermolecular singlet–singlet energy transfer from $Ad=O_S^*$ to the L_S^* level of the β-diketonate ligand and subsequently to the lanthanide ion: $Ad=O_S^* \rightarrow L_S^* \rightarrow L_T^* \rightarrow Ln^{3+*}$ (Eq. (3)). This process is energetically possible only for $Ln(TTA)_3 \cdot 2H_2O$ and $Ln(BTFA)_3 \cdot 2H_2O$ since their L_S^* states lie lower in energy than $Ad=O_S^*$ (Fig. 3).

Secondly, Ln^{3+} might be excited by intermolecular triplet–triplet (T–T) energy transfer from $Ad=O_T^*$ to the triplet level of the β-diketonate ligand: $Ad=O_T^* \rightarrow L_T^* \rightarrow Ln^{3+*}$, since triplet excited molecules are effectively quenched by lanthanide β-diketonates sensitizing their luminescence [40,41]. $Ad=O_T^*$ lies at 26 300 cm^{-1} [11] and energy transfer $Ad=O_T^* \rightarrow L_T^*$ is exothermic for $Ln(TTA)_3 \cdot 2H_2O$ ($L_T^* = 20\,500$ cm^{-1}), $Ln(BTFA)_3 \cdot 2H_2O$ ($L_T^* = 21\,300$ cm^{-1}) and $Ln(AA)_3 \cdot 3H_2O$ ($L_T^* = 25\,200$ cm^{-1}) (Fig. 3) [19,41]. The L_T^* energy for $Pr(DPM)_3$ and $Pr(FOD)_3$ should be lower than that for $Ln(AA)_3 \cdot 3H_2O$ and thus energy transfer $Ad=O_T^* \rightarrow L_T^*$ will also be possible. The efficiency of intermolecular energy transfer from $Ad=O_T^*$ is determined by its unusually short lifetime estimated to be 0.06 ns at 90°C [33] and 4 ns at 65°C

[3]. However, the T–T excitation pathway cannot be neglected, since $Ad=O_T^*$ is a major excited product formed from the AAD decomposition.

Thirdly, Ln^{3+} chemiexcitation with an efficiency ϕ_{Ln^*} might occur by intracomplex energy transfer from $Ad=O^*$ formed from the decomposition of the $AAD \cdot Ln(L)_3$ complex (Eq. (4)). The intracomplex excitation mechanism seems to be dominant for the $Pr(DPM)_3$ and $Pr(FOD)_3$ chelates [1,2]. Although complex formation is not a major mechanism of AAD chemiluminescence quenching by $Ln(TTA)_3 \cdot 2H_2O$, $Ln(BTFA)_3 \cdot 2H_2O$ and $Ln(AA)_3 \cdot 3H_2O$, chemiexcitation of Ln^{3+} in these chelates from decomposition of minute quantities of $AAD \cdot Ln(L)_3$ might determine the observed CL yield. In fact, the rate constant for the $AAD \cdot Ln(L)_3$ decomposition (k_2 in Eq. (4)) exceeds that of AAD (k_1 in Eq. (1)) by 2–3 orders of magnitude [1]. The high efficiency of intracomplex chemiexcitation is demonstrated by $Pr(FOD)_3$, which has relative CL yield >20 times higher than that for coordination saturated Pr^{3+} chelates (Table 4). The ϕ_{CL} of $Pr(DPM)_3$ is lower than for $Pr(FOD)_3$ due to different stability constants of $AAD \cdot Ln(L)_3$.

Addition of $Ad=O$ into the $Ln(L)_3 \cdot nH_2O$-AAD system, to prevent the formation of $AAD \cdot Ln(L)_3$, enhances ϕ_{CL} of Yb^{3+} chelates and lowers ϕ_{CL} of Nd^{3+} and Pr^{3+} (Tables 3 and 4). At the same time $Ad=O$ enhances the photoluminescence yield of Ln^{3+} β-diketonates in toluene to a similar extent due to formation of $Ln(L)_3 \cdot nAd=O$. Thus, chemiexcitation of Ln^{3+} is not only due to the intracomplex mechanism (Eq. (4)), since in that case adamantanone expelling AAD from $AAD \cdot Ln(L)_3$ would decrease the ϕ_{CL} of Ln^{3+}. However, for the Nd^{3+} and Pr^{3+} chelates intracomplex excitation is more efficient than the intermolecular one, resulting in a decrease of ϕ_{CL} in the presence of $Ad=O$, while for Yb^{3+} – intermolecular excitation prevails over the intracomplex one.

The constants of chemiluminescence growth of Ln^{3+} (K_{CL} in Tables 1 and 2) were calculated from the concentration dependence of its CL intensity by Eq. (8), where I_{CL} is the CL intensity of Ln^{3+} and γ is a constant parameter [41].

$$I_{CL}^{-1} = \gamma^{-1}(1 + (K_{CL}[Ln^{3+}])^{-1}). \tag{8}$$

For $Pr(DPM)_3$ the calculated values of $K_{CL} = 11\,l\,mol^{-1}$ and $K_{SV} \approx 61\,l\,mol^{-1}$ are close to each other. For $Pr(FOD)_3$ the value of $K_{CL} = 42\,l\,mol^{-1}$ coincides with the stability constant of $AAD \cdot Pr(FOD)_3$: $K = 40\,l\,mol^{-1}$, determined from its decomposition kinetics [1]. Such coincidence suggests that for $Pr(FOD)_3$ and $Pr(DPM)_3$ both the quenching of the AAD chemiluminescence and chemiexcitation of Pr^{3+} ion occur from the decomposition of $AAD \cdot Ln(L)_3$. On the contrary, K_{SV} and K_{CL} generally do not coincide for $Ln(TTA)_3 \cdot 2H_2O$ and $Ln(BTFA)_3 \cdot 2H_2O$, suggesting that all Ln^{3+} chemiexcitation pathways are operative, including S–S, T–T and intracomplex energy transfer.

The extremely small value of ϕ_{CL} for $Ln(AA)_3 \cdot 3H_2O$ precluded the calculation of K_{CL}. In fact, for $Ln(AA)_3 \cdot 3H_2O$ the S–S energy transfer is endothermic while T–T energy transfer might be complicated by the back transfer process $L_T^* \rightarrow Ad=O_T^*$ due to a small energy gap $\approx 1100\,cm^{-1}$ separating L_T^* and $Ad=O_T^*$. At the same time nonfluorinated $Ln(AA)_3 \cdot 3H_2O$ is expected to show weak Lewis acidity [43] precluding formation of $AAD \cdot Ln(AA)_3$.

Comparison between the chemiluminescence yields of Pr^{3+} β-diketonates in the *presence* of $Ad=O$ shows that the highest ϕ_{CL} is observed for $Pr(DPM)_3$ and $Pr(FOD)_3$. Since for both of these chelates the S–S energy transfer is endothermic, it might be concluded that in that case the observed CL of Pr^{3+} is due to intermolecular T–T energy transfer: $Ad=O_T^* \rightarrow L_T^* \rightarrow Ln^{3+*}$. However, one cannot rule out that even in the presence of $Ad=O$ minute quantities of the $AAD \cdot Ln(L)_3$ or $AAD \cdot Ad=O \cdot Ln(L)_3$ complexes might be formed which determine the observed CL of Pr^{3+}. Thus, at present neither can we definitely prove nor rule out the participation of $Ad=O_T^*$ in intermolecular energy transfer involving $Ln(L)_3 \cdot nH_2O$.

4. Conclusions

Chemiluminescence serves as a convenient tool to study singlet–singlet energy transfer from ketone to rare-earth β-diketonates. The chemiluminescence of Nd^{3+}, Yb^{3+} and Pr^{3+} β-diketonates observed from dioxetane decomposition is excited by either a physical mechanism including singlet–singlet and triplet–triplet energy transfer from the ketone, or a chemical route involving decomposition of the $AAD \cdot Ln(L)_3$ complex. The efficiciency of each mechanism is determined by the β-diketonate ligand and the availability of free coordination sites in Ln^{3+} β-diketonate.

Acknowledgements

This work was supported by RFFI (grant 99-03-32140). N.M.Sh. acknowledges financial support from George Soros (ISSEP grant a99-408).

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