Effect of 4f-shell excitation of Eu(fod)$_3$ on its complex formation with alicyclic ketones

V. P. Kazakov,* S. S. Ostakhov, and A. S. Alyab´ev

Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences,
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.
Fax: +7 (347 2) 35 6066. E-mail: chemlum@ufanet.ru

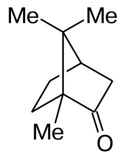
The complex formation of alicyclic ketones, *viz.*, camphor, cyclohexanone, menthone, and cytisine, with the Eu(fod)$_3$ chelate (fod is 7,7-dimethyl-1,1,1,2,2,3,3-heptafluorooctane-4,5-dione) in the ground and excited states was studied by chemiluminescence and kinetic luminescence spectroscopy, respectively. The stability constants and thermodynamic parameters of complex formation were determined. An increase in the stability of the electron-excited complexes [Eu(fod)$_3^*$ • Ketone] is explained by the enhancement of the acceptor ability of the Eu^{3+} chelate due to an increase in the fraction of the covalent component caused by the involvement of 4f-orbitals. The results obtained give direct evidence for the effect of the 4f-shell excitation of Eu(fod)$_3$ on complex formation due to the involvement of f-electrons in the chemical bonds.

Key words: fluorescence, chemiluminescence, complex formation, Eu(fod)$_3$, ketones.

The participation of 4f-orbitals of lanthanides (Ln^{3+}) in the formation of coordination bonds remains disputable until presently. A ponderable argument in favor of involvement of the f-electrons of Ln^{3+} in the formation of a chemical bond could be a considerable increase in the stability of the complexes upon excitation, because luminescence of these complexes is caused by the f—f-transitions only inside the deeply lying 4f-shell shielded by the external orbitals.

The luminescence kinetic method provides wide possibilities for studying kinetically labile lanthanide complexes in the excited state.[1—3] The application of this method made it possible to determine the parameters of complex formation of the Ln^{3+} and UO$_2^{2+}$ salts in the excited state with organic substrates[3] and inorganic ions[4,5] in solutions. In studying complex formation in the excited state, it is promising to use the Ln^{3+} tris-β-diketonate complexes, which found wide use in NMR spectroscopy as paramagnetic shift reactants.[6] We have previously found that the electron excitation of the f—f-transitions of the Eu(fod)$_3$ chelate (fod is 7,7-dimethyl-1,1,1,2,2,3,3-heptafluorooctane-4,5-dione) results in a sharp (by more than an order of magnitude) increase in the stability constants of its complexes with aromatic[7,8] and aliphatic[9—11] ketones, sulfoxides,[12,13] and sulfones[14,15] due to the involvement of the 4f-electrons in the chemical bonds.

In this work, we studied the effect of excitation of the 4f-shell in the Eu(fod)$_3$ complex on the formation of the coordination bond with alicyclic ketones, *viz.*, camphor (**1**), cyclohexanone (**2**), D(+)-menthone (**3**), and L(−)-cytisine (**4**), in benzene solutions.



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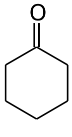

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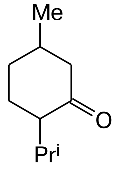

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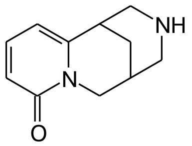

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Experimental

The lifetime (τ) of electron-excited Eu(fod)$_3^*$ was measured with a LIF-200 impulse laser fluorimeter. The absorption spectra were recorded with a Specord M-40 spectrophotometer. The fluorescence (FL) spectra and intensity ($I_{\rm fl}$) were recorded with a Hitachi MPF-4 fluorimeter. The optical rotation dispersity (ORD) was studied using a Perkin—Elmer 241 MC spectropolarimeter. The chemiluminescence (CL) intensity ($I_{\rm cl}$) was measured using a setup described previously.[16]

Cytisine was purified by double recrystallization from toluene. Camphor was purified by sublimation. Cyclohexanone was distilled and dried over molecular sieves 4A. Menthone was purified using column chromatography. Dispiro[tri-

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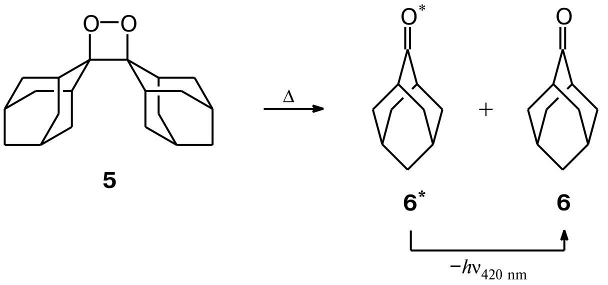
cyclo[3.3.1.1^{3,7}]decane-2,3′-[1,2]dioxetane-4′,2″-tricyclo[3.3.1.1^{3,7}]decane] (**5**) was synthesized using a known procedure.[17] Anhydrous Eu(fod)$_3$ (Aldrich) was prepared by heating at 370 K *in vacuo* for 4 h. Benzene was refluxed over metallic sodium and recrystallized.

Results and Discussion

Complex formation of ketones (L) with Eu(fod)$_3$ in the ground state

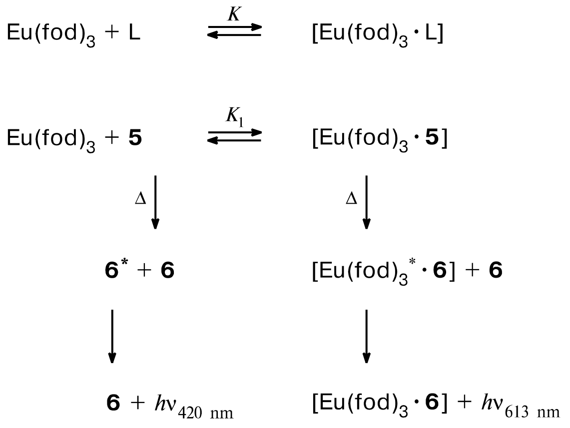
The authors of the work[18] proposed a method for determination of the stability constants of the [Eu(fod)$_3$ · L] complexes based on CL quenching during thermolysis of dioxetane **5** (Scheme 1).

Scheme 1



In the presence of Eu(fod)$_3$, dioxetane **5** is decomposed simultaneously with processes involving the formation of the [Eu(fod)$_3$·**5**] and [Eu(fod)$_3$·**6**] complexes, decomposition of dioxetane in a complex with excited Eu^{3+}, and light irradiation.[18] When a complex-forming agent, *viz*., ketone, is added, the latter competes with dioxetane **5** for the site in the coordination sphere of the Eu(fod)$_3$ chelate (Scheme 2).

Scheme 2



Since CL is mainly determined by the decomposition of dioxetane **5** in the complex with Eu(fod)$_3$, the CL intensity decreases due to the formation of the [Eu(fod)$_3$ · L] complex. In this case, the CL intensity obeys the equation[18]

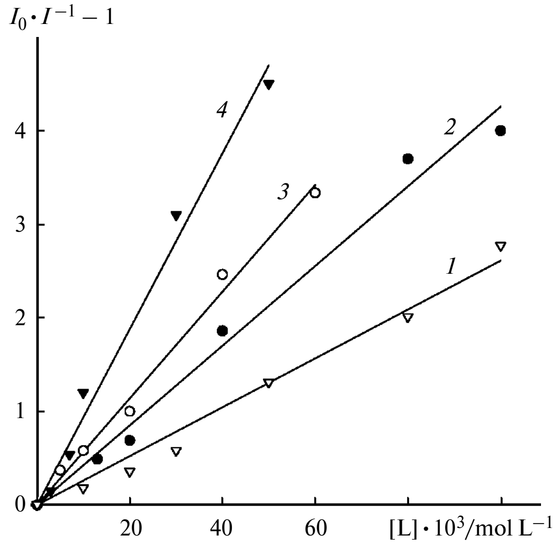


Fig. 1. Plots for the CL intensity ($I_0 \cdot I^{-1} - 1$) of dioxetane **5** (10^{-3} mol L^{-1}) in the presence of Eu(fod)$_3$ (10^{-2} mol L^{-1}) *vs*. concentration of ketones **1** (*1*), **2** (*2*), **3** (*3*), and **4** (*4*) in the coordinates of Eq. (1) (benzene, 300 K).

$$I_0/I = 1 + \{K[\mathrm{L}]_0/(1 + K_1[\mathrm{Eu(fod)_3}]_0)\}, \qquad (1)$$

where I and I_0 are the CL intensities in the presence and absence of L, respectively; [Eu(fod)$_3$]$_0$ and [L]$_0$ are the initial concentrations of the reactants; K_1 and K are the stability constants of the [Eu(fod)$_3$ · **5**] and [Eu(fod)$_3$ · L] complexes, respectively.

The stability constants for the Eu(fod)$_3$ complex in the ground state with ketones **1—4** (Table 1) were determined from the slope of the linear anamorphosis in the coordinates of Eq. (1) (Fig. 1) using the known K_1 values (ΔH_0 = 19±2 kJ mol^{-1}, ΔS_0 = −3.5±4 J mol^{-1} K^{-1}).[19] The thermodynamic parameters of formation of the [Eu(fod)$_3$ · L] complexes were determined from the plots of the stability constants *vs*. $1/T$ (Fig. 2). The data presented in Table 2 show that the stability of the Eu(fod)$_3$ complexes with ketones **1—3** is determined by the positive change in the entropy, while the enthalpy contribution predominates in the case of cytisine. The high stability constants and exothermicity of complex formation for cytisine are likely related to the presence of two functional groups and the possibility of coordination at both the oxygen and nitrogen atoms.

The plots for ORD of chiral molecules **3** and **4** *vs*. concentration of Eu(fod)$_3$ were also obtained. In the presence of the Eu^{3+} chelate, the absolute value of the rotation angle (α) increases (Fig. 3) due to the formation of the [Eu(fod)$_3$ · L] complex. As found previously,[20,21] the optical activity is induced during the formation of adducts

Table 1. Stability constants of the Eu(fod)$_3$ complexes in the ground and excited states with ketones **1—4** and the lifetime of Eu(fod)$_3$*

T /K	τ_0 /μs	**1**			**2**			**3**			**4**		
		K	K^*	τ_1 /μs	K	K^*	τ_2 /μs	K	K^*	τ_3 /μs	K	K^*	τ_4 /μs
		L mol^{-1}			L mol^{-1}			L mol^{-1}			L mol^{-1}		
280	220	9.0	180	420	9.5	120	440	31.0	430	330	1990	2170	480
290	180	11.5	250	410	13.5	180	425	36.0	810	320	1060	1860	480
300	140	15.0	360	400	18.5	310	400	41.0	930	310	590	1450	485
310	110	19.0	450	370	25.0	360	370	47.0	1010	290	340	1180	485
320	90	23.5	530	320	33.0	500	310	53.5	1140	260	200	960	490
330	70	29.0	650	260	43.5	620	260	60.0	1230	210	130	810	495

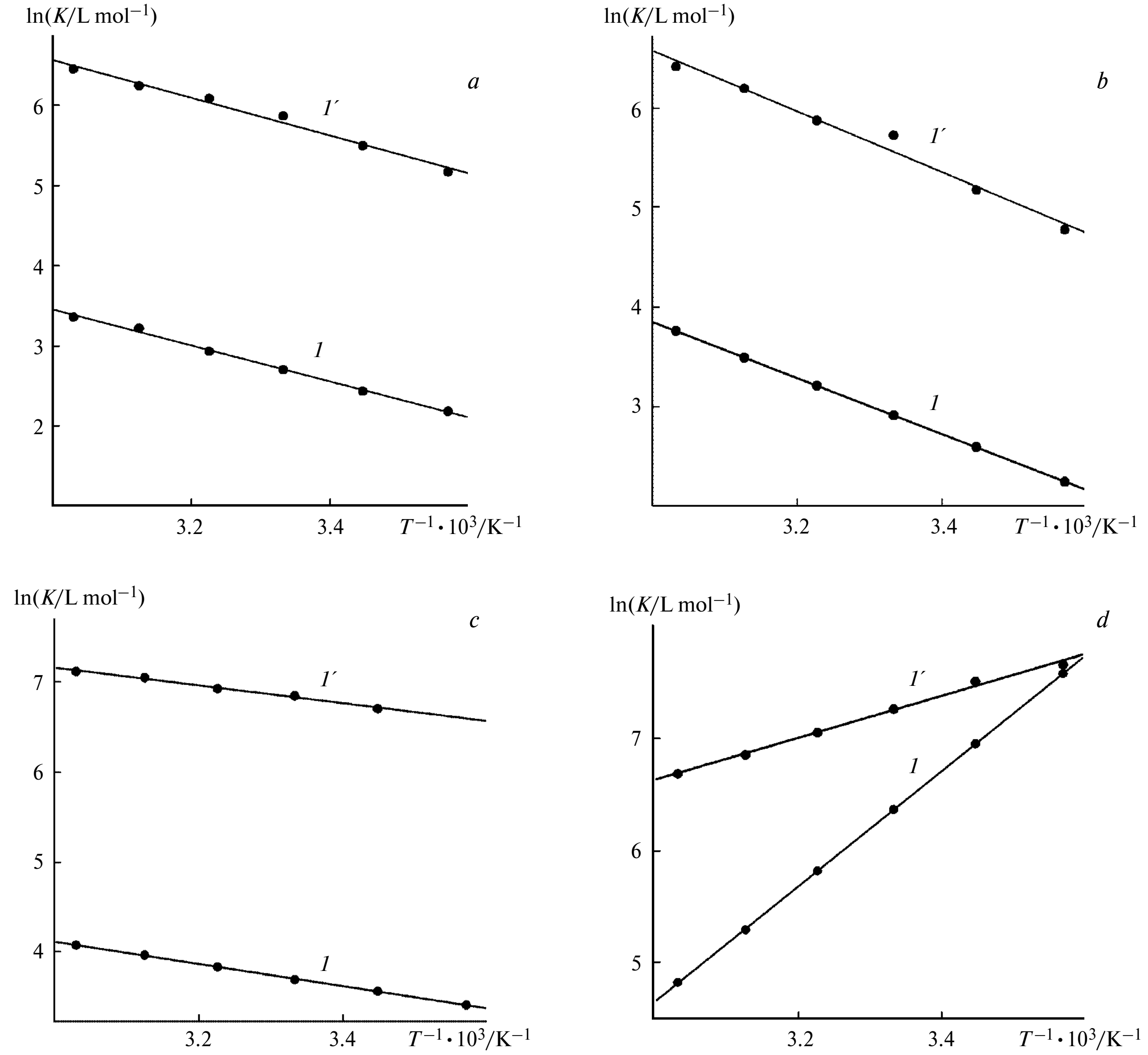


Fig. 2. Temperature plots for the stability constants of the Eu(fod)$_3$ complex in the ground (*1*) and excited (*1′*) states with ketones **1** (*a*), **2** (*b*), **3** (*c*), and **4** (*d*).

Table 2. Changes in the enthalpy and entropy of complex formation of $Eu(fod)_3$ with ketones **1—4**

Ketone	ΔH	ΔH^*	ΔS	ΔS^*
	kJ mol^{-1}		J mol^{-1} K^{-1}	
1	18.6	20.0	84	114
2	23.4	25.0	102	130
3	10.2	8.4	65	85
4	−42.6	−15.9	−89	8

Note. The average error of measurements is ±10%.

of the chiral substrate with achiral Ln^{3+} β-diketonates. A maximum at the equimolar ratio of the Eu^{3+} chelate to the ligand is observed in the curves of the plots of the rotation angle *vs.* ligand concentration, indicating the formation of the 1 : 1 complexes.

Complex formation of ketones with Eu(fod)$_3$ in the excited state

The addition of ketones **1—4** to a solution of $Eu(fod)_3$ ($5 \cdot 10^{-3}$ mol L^{-1}) in benzene increases τ and I_{fl} of the $Eu(fod)_3{}^*$ complex in the excited state (Fig. 4) due to both shielding of $Eu(fod)_3{}^*$ by the L molecules from the quenching effect of the solvent and an increase in the covalent component of the Eu^{3+}—L bonds caused by the involvement of the 4f-orbitals.[22] The positions of the bands in the absorption and FL spectra of $Eu(fod)_3{}^*$ in the presence of ketones remain unchanged, but an insignificant redistribution of the FL intensities is observed at 580 and 613 nm. At the $Eu(fod)_3$ and L concentrations used ($5 \cdot 10^{-3}$ and $3 \cdot 10^{-3}$—$8 \cdot 10^{-2}$ mol L^{-1}, respectively), the formation of the two-ligand complexes $[Eu(fod)_3 \cdot L_2]$ can be neglected.[23] The processes occurring upon the photoexcitation of a solution in which the 1 : 1 $Eu(fod)_3{}^*$ complexes with ketones are formed can be presented by Scheme 3.

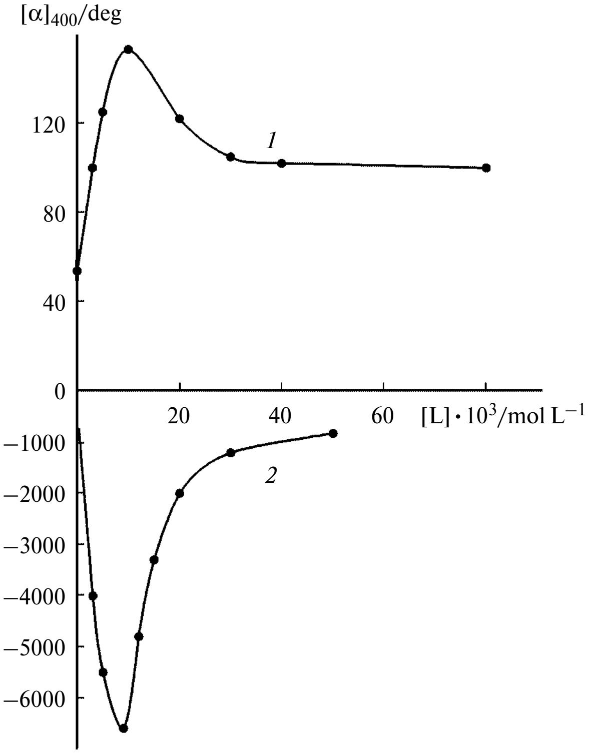


Fig. 3. Specific rotation angle of the $[Eu(fod)_3{}^* \cdot L]$ complex as a function of the concentration of D(+)-menthone (*1*) and L(−)-cytisine (*2*) ($[Eu(fod)_3] = 5 \cdot 10^{-3}$ mol L^{-1}; benzene, 295 K).

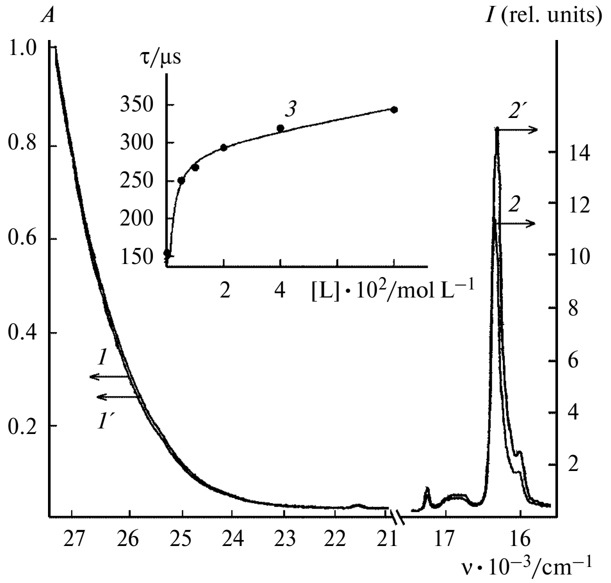
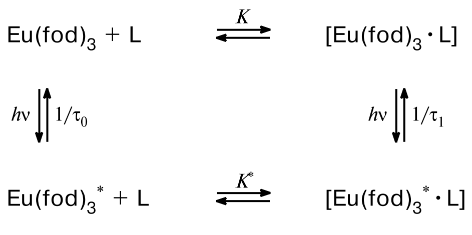


Fig. 4. Absorption spectra of $Eu(fod)_3$ (0.01 mol L^{-1}) (*1*, *1′*) and FL spectra of $Eu(fod)_3$ ($5 \cdot 10^{-3}$ mol L^{-1}) (*2*, *2′*) in the absence (*1*, *2*) and presence (*1′*, *2′*) of ketone **1** (10^{-2} mol L^{-1}). The plot of τ of $Eu(fod)_3{}^*$ ($5 \cdot 10^{-3}$ mol L^{-1}) (*3*) *vs.* concentration of ketone **1** (benzene, 295 K).

Scheme 3



Here τ_0 and τ_1 are the lifetimes of $Eu(fod)_3{}^*$ and $[Eu(fod)_3{}^* \cdot L]$, respectively; K and K^* are the stability constants of the $Eu(fod)_3 \cdot L$ complexes in the ground and excited states.

The exponential character of the FL decay kinetics of $Eu(fod)_3{}^*$, indicating fast ligand exchange in the first coordination sphere of the europium complex due to which an equilibrium between concentrations of different complex forms is maintained, makes it possible to use Eq. (2) [7,24] for the determination of the stability constants (K^*) of the [Eu(fod)$_3$* • L] complexes.

$$\frac{\tau\tau_0}{\tau-\tau_0} = \frac{\tau_1\tau_0}{\tau_1-\tau_0} + \frac{\tau_1\tau_0}{\tau_1-\tau_0}\cdot\frac{1}{K^*[\mathrm{L}]_{\mathrm{eq}}}, \qquad (2)$$

where τ is the apparent luminescence lifetime of the solution after the equilibration between different complexes in the excited states, τ_0 is the lifetime of Eu(fod)$_3$* in the absence of the ligand, τ_1 is the lifetime of the [Eu(fod)$_3$* • L] complex, and $[\mathrm{L}]_{\mathrm{eq}}$ is the equilibrium concentration of the ligand. The plot for $\tau\tau_0(\tau-\tau_0)^{-1}$ *vs.* $[\mathrm{L}]_{\mathrm{eq}}^{-1}$ is a straight line with the $\tau_1\tau_0(\tau_1-\tau_0)^{-1}$ section cut in the ordinate and the slope ratio $\tau_1\tau_0(\tau_1-\tau_0)^{-1}(K^*)^{-1}$. The equilibrium concentrations of the ligand for each initial concentration of ketone were determined from the stability constants of the [Eu(fod)$_3$ • L] complex in the ground state (see Table 1). The plots for τ *vs.* equilibrium concentration $[\mathrm{L}]_{\mathrm{eq}}$ in the coordinates of Eq. (2) are presented in Fig. 5. Using these plots, we calculated the stability constants K^* and lifetimes τ_1 of the [Eu(fod)$_3$* • L] complex in the excited state (see Table 1). The thermodynamic parameters of complex formation of ketones with Eu(fod)$_3$* (see Table 1) were determined using the temperature dependences of K^* (see Fig. 2).

The data presented in Table 1 show that the stability of the chelate Eu(fod)$_3$ complexes with ketones at the excitation of the f—f-transitions of the Eu^{3+} ion increases in the whole temperature interval studied ($K^*/K \approx 24$, 17, 23, and 2.5 at 300 K for ketones **1—4**, respectively). We attribute this fact to the enhancement of the acceptor ability of Eu(fod)$_3$ due to an increase in the fraction of the covalent component caused by the involvement of the 4f-orbitals. The transition of the Eu(fod)$_3$ complex to the excited state is accompanied by an increase in the contribution of the entropy factor to complex formation with ketones **1—3** and that of the enthalpy factor to complex formation with ligand **4** (see Table 1). At ΔH_0 and $\Delta S_0 > 0$, the complex formation of ketones **1—3** with Eu(fod)$_3$ in both the ground and excited states is likely preceded by the close approach of the reacting species with liberation of the solvent molecules, which increases the entropy. The negative ΔH_0 values and ΔS_0 close to zero for cytisine indicate that the formation of the [Eu(fod)$_3$* • **4**] complexes, regardless of excitation, occurs probably without changing the number of solvent molecules in the coordination sphere of Eu(fod)$_3$.

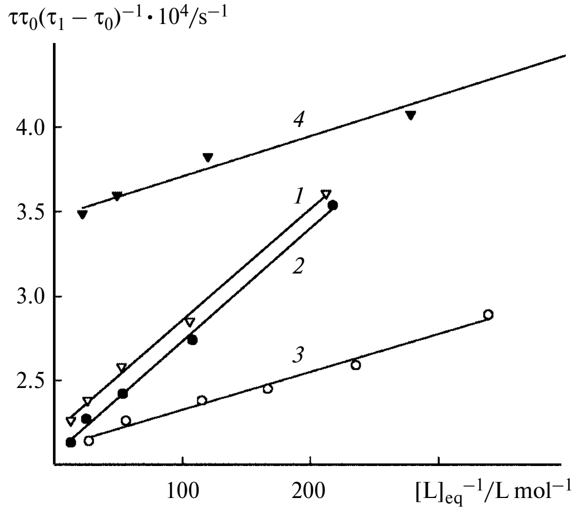


Fig. 5. Plots for τ of FL of Eu(fod)$_3$* ($5\cdot10^{-3}$ mol L^{-1}) *vs.* concentration of ketones **1** (*1*), **2** (*2*), **3** (*3*), and **4** (*4*) in the coordinates of Eq. (2) (benzene, 338 K).

It is noteworthy that the complex formation of Eu(fod)$_3$ with ketones **1—3** substantially decreases the efficiency of temperature quenching of FL of [Eu(fod)$_3$* • L], while for bidentate cytisine **4** τ_1 of [Eu(fod)$_3$* • **4**] is virtually temperature-independent (see Table 1). The temperature plots of τ_0 for Eu(fod)$_3$* and τ_1 for [Eu(fod)$_3$* • L] are satisfactorily described by the equation[25]

$$\ln(1/\tau_i - 1/\tau_e) = \ln A^i - E_a{}^i/RT, \qquad (3)$$

where τ_i are the current τ_0 and τ_1 values at the temperature T, τ_e is the emissive lifetime of Eu^{3+} (4.8 μs),[26] and A^i and $E_a{}^i$ are the pre-exponential factor and activation energy of the non-emissive deactivation of FL for Eu(fod)$_3$* and [Eu(fod)$_3$* • L], respectively. The activation parameters of the temperature plots of τ_0 and τ_1 for Eu(fod)$_3$* and the Eu(fod)$_3$* complexes with ketones **1—3** are the following: $E_a{}^0 = 18.4\pm1.2$ kJ mol^{-1} ($\log A^0 = 7.0\pm0.5$); $E_a{}^1 = 15.6\pm1.3$ kJ mol^{-1} ($\log A^1 = 6.0\pm0.5$); $E_a{}^2 = 10.8\pm1.0$ kJ mol^{-1} ($\log A^2 = 5.7\pm0.3$), and $E_a{}^3 = 14.6\pm1.2$ kJ mol^{-1} ($\log A^3 = 5.9\pm0.4$), respectively ($E_a{}^0$ is the activation energy of non-emissive degradation of the energy of excited Eu$^{\mathrm{III}}$ in the absence of ketones, and $E_a{}^1$, $E_a{}^2$, and $E_a{}^3$ are the activation energies for the Eu$^{\mathrm{III}}$ complexes with ketones **1—3**). A decrease in dissipation losses of the excitation energy in the [Eu(fod)$_3$* • L] complexes compared to that for Eu(fod)$_3$* ($E_a{}^0 > E_a{}^i$) is a result, most likely, of shielding of Eu(fod)$_3$ by molecules **1—4** from the quenching effect of the solvent.

A helpful information can be obtained from analysis of the temperature plots of the apparent (averaged over different types of complexes) lifetime τ of the [Eu(fod)* • L] complex. It has previously been mentioned[27] that for lanthanides a sharp change in the FL parameters occurs in the 290—310 K temperature interval, which is critical for the shift of the chemical equilibrium in complex formation reactions. As can be seen from the data in Fig. 6, the temperature dependences of τ of Eu(fod)* in the presence of menthone are described by the sum of two exponents

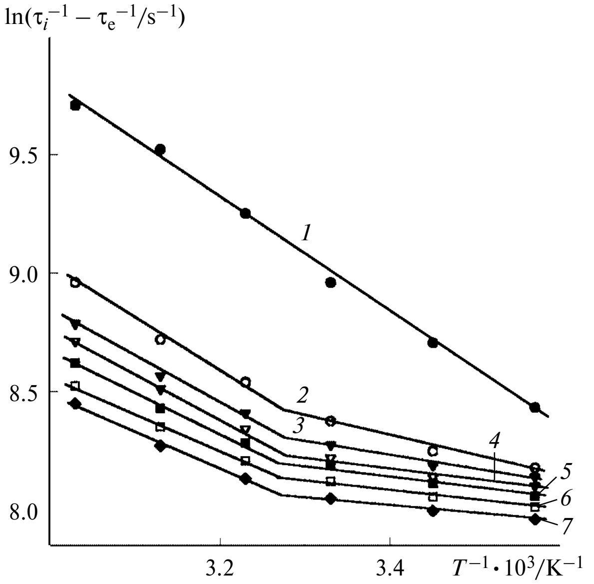


Fig. 6. Temperature plots for τ of Eu(fod)* ($5 \cdot 10^{-3}$ mol L^{-1}) at the concentrations of menthone **3**: 0 (*1*), $3.5 \cdot 10^{-3}$ (*2*), $5 \cdot 10^{-3}$ (*3*), $7 \cdot 10^{-3}$ (*4*), $1 \cdot 10^{-2}$ (*5*), $2 \cdot 10^{-2}$ (*6*), and $4 \cdot 10^{-2}$ mol L^{-1} (*7*).

and exhibit a break just in the region of 300 K. For the activation parameters of temperature quenching of τ of Eu(fod)* in the presence of menthone **3** (concentration interval $3.5 \cdot 10^{-3}$—$4 \cdot 10^{-2}$ mol L^{-1}) determined in the temperature intervals $\Delta T_1 < 300$ K and $\Delta T_2 > 300$ K, the following kinetic compensation dependences are fulfilled[28]:

$$\log A = (0.2 \pm 0.02) \cdot 10^{-3} E_a + (3.5 \pm 0.3) \quad \Delta T_1 < 300 \text{ K}, \qquad (4)$$

$$\log A = (0.2 \pm 0.02) \cdot 10^{-3} E_a + (3.2 \pm 0.3) \quad \Delta T_2 > 300 \text{ K}. \qquad (5)$$

The $\log A$ and E_a values determined for the temperature quenching of τ_0 of Eu(fod)* fall on the plot (4), whereas τ_1 of [Eu(fod)$^* \cdot$**3**] lies on the plot (5). Based on these data, we can assume that at the temperatures >300 K the temperature quenching processes of the [Eu(fod)$^* \cdot$**3**] complex prevail; this agrees with the endothermic character of the complex formation of menthone with Eu(fod)*.

The substantial differences in the thermodynamics of complex formation of Eu(fod)$_3$ in the ground and excited states with ketones are also emphasized by the characteristic dependences between the entropy and enthalpy of complex formation. The relationship between ΔH_0 and ΔS_0 (thermodynamic compensation effect[27,29]) (Fig. 7) obeys satisfactorily the linear correlation $\Delta S_0 = \nu \Delta H_0 + \alpha$ ($r = 0.999$).

In the ground state of Eu(fod)$_3$,

$$\Delta S_0 = (2.9 \pm 0.2) \cdot 10^{-3} \cdot \Delta H_0 + (34 \pm 5), \qquad (6)$$

and in the excited state,

$$\Delta S_0^* = (3.0 \pm 0.4) \cdot 10^{-3} \cdot \Delta H_0^* + (56 \pm 7). \qquad (7)$$

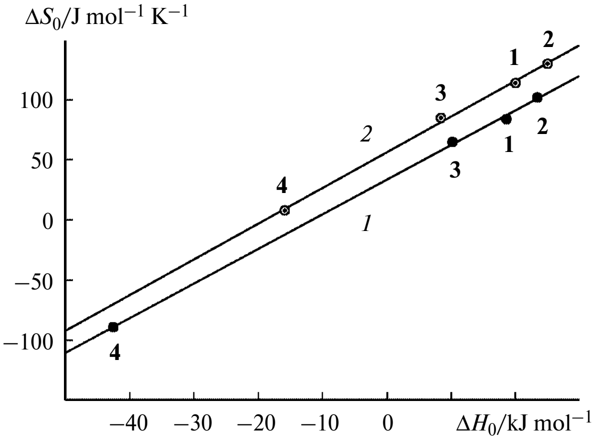


Fig. 7. Compensation dependences of the thermodynamic parameters of complex formation of Eu(fod)$_3$ in the ground (*1*) and electron-excited (*2*) states with ketones **1—4** in benzene.

Correspondingly, at the reversal temperatures ($T_0 = 1/\nu$) $T_0 = 345$ K, $T_0^* = 333$ K ($\Delta G = -\alpha T$) $\Delta G_0 = -11.6 \pm 1.2$ kJ mol^{-1} and $\Delta G_0^* = -18.7 \pm 1.9$ kJ mol^{-1}. In the region of these temperatures, the stability constants are independent of the enthalpy of complex formation and amount to $K = 60 \pm 10$ L mol^{-1} and $K^* = 870 \pm 80$ L mol^{-1} in the ground and excited states of Eu(fod)$_3$, respectively.

The thermodynamic compensation effect is applicable only to reactions of the same class, which is determined by the complex-forming metal ion capable of coordinating a series of ligands. Since for the compensation dependences considered the coordination center is identical and $\alpha^* \neq \alpha$, then it can be assumed that the electron excitation of the 4f-orbitals of Eu^{3+} is also a factor determining the "homology" of several complex formation reactions.

The results obtained indicate the effect of electron excitation of the 4f-shell of Eu(fod)$_3$ on an increase in the fraction of the contribution of the f-electrons to the formation of the coordination bond.

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