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Synthesis of 3-Trifluoroacetamidobenzoyltrifluoroacetone and Its Luminescent Europium Complexes

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Abstract—Reaction of 3-aminoacetophenone with excess of methyl trifluoroacetate proceeds in two stages and leads to the formation of 3-trifluoroacetamidobenzoyltrifluoroacetone 3-$CF_3C(O)NHC_6H_4C(O)CH_2C(O)CF_3$ instead of the expected 3-aminobenzoyltrifluoroacetone 3-$NH_2C_6H_4C(O)CH_2C(O)CF_3$. The cause is the readily proceeding reaction of CF_3COOCH_3 with amine group of the source 3-aminoacetophenone and the initial formation of 3-trifluoroacetamidoacetophenone. On the basis of the synthesized β-diketone the luminescent complexes were synthesized: europium(III) tris(3-trifluoroacetamidobenzoyltrifluoroacetonate) trihydrate and europium(III) tris(3-trifluoroacetamidobenzoyltrifluoroacetonate)(phenanthroline). The trifluoroacetylamide group is converted into the primary amine by treatment the solutions of the europium complexes with aqueous alkali. The molecular and crystal structures of 3-trifluoroacetamidoacetophenone were investigated.

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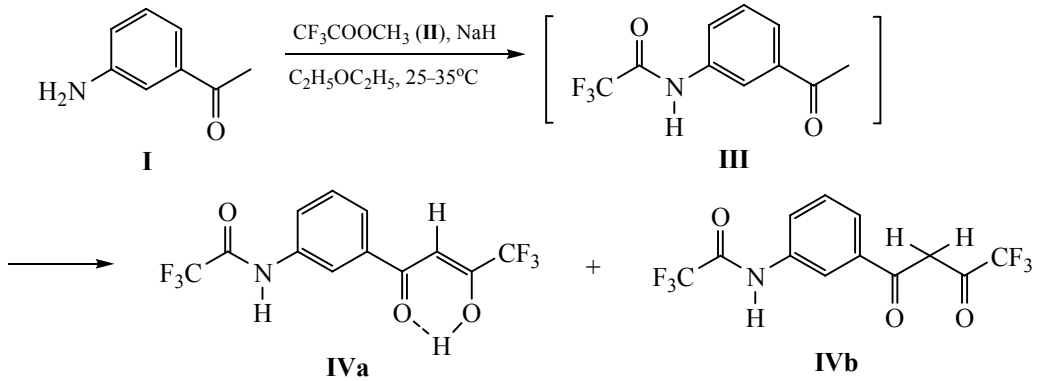
Europium and terbium complexes with functional ligands are used as fluorescent labels for time-resolved fluoroimmunoassay [1, 2, 3]. Covalent binding of a coordination compound by a protein molecule is usually achieved by introducing into the ligand molecule of the $–SO_2Cl$ or –CNS groups interacting with the terminal NH_2 group of the polypeptide chain [4]. The coordination compound having a primary amino group at the periphery can be linked using the bifunctional glutaric aldehyde $H(O)C(CH_2)_3C(O)H$. Our efforts to synthesize a ligand with a primary amino group by the reaction of 3-aminoacetophenone with excess methyl trifluoro-acetate and sodium hydride led to the formation of 3-trifluoro-acetamidobenzoyltrifluoroacetone instead of the expected 3-aminobenzoyltrifluoroacetone (Scheme 1). The reaction proceeds rapidly in ether with weak heat release. According to elemental analysis and ^1H NMR spectroscopy data, the β-diketone **IV** obtained after reprecipitation with hexane contains one ether molecule. The sublimation in a vacuum removes the associated $(C_2H_5)_2O$ molecule.

Scheme 1.



Intermediate compound in this process is 3-trifluoroacetamidoacetophenone (**III**). This is confirmed by the following observations. Compound **III** is formed readily and with high yield in the reaction of 3-aminoacetophenone with methyl trifluoroacetate in the absence of sodium hydride. The fact that the reactions of esters of organofluorine acids with primary amines proceed readily and quantitatively has been observed earlier [5] by the example of the reaction of diethyl perfluoroadipate with 3-aminopropyltriethoxysilane.

Compound **IV** exists in acetone-d_6 and chloroform-*d* solutions as a mixture of enol and ketone forms in a 15:1 ratio. The presence of enol **IVa** is confirmed by the signal at 6.91 ppm (C–H). The existence of diketone follows from the singlet signal of two protons of CH_2 group at 4.81 ppm. In addition, in the ^{1}H NMR spectrum there is a broad signal of the hydrogen atoms of the amide group at 10.46 ppm and a series of signals of protons of the phenyl group in the range of 7.6–8.6 ppm. The effect of electronegative CF_3 group is reflected in a marked downfield shift of the proton signals relative to the non-fluorinated analogs.

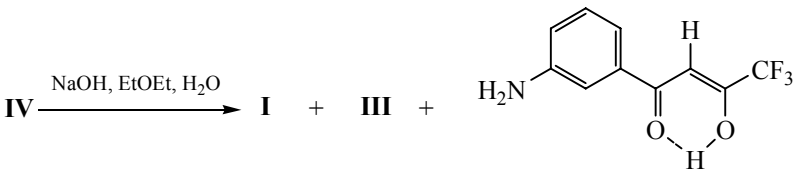
The HPLC method allowed us to confirm the existence of the two forms of β-diketone **IV**. The separation is achieved on a column Separon Si C18 with acetonitrile as the eluent.

In the mass spectrum of compound **IV** the most intense peaks are those of fragment ions with the masses 69.6, 216.2, 240.4, 258.3, and 307.1. The peak of molecular ion with *m*/*e* 327.0 has a low intensity. The masses 69.6, 258.3 and 307.1 indicate that the fragmentation of the molecule of β-diketone **IV** begins with the cleavage of HF (*m*/*e* 20) and the CF_3 radical (*m*/*e* 69.3).

It is known that protection of a primary amino group can be achieved by transformation it into amide [6]. The trifluoroacetamidate protection with the formation of $CF_3C(O)NHR$ is the most convenient, since to recover the amine group by the treatment of the amide with the alkaline alcohol or potassium carbonate solutions proceeds under milder conditions compared with the non-fluorinated analog, $CH_3C(O)NHR$.

$$RNH_2 \xrightarrow[[CF_3C(O)]_2O]{CF_3COOCH_3} RNHC(O)CF_3 \xrightarrow{NaOH,CH_3OH,H_2O} RNH_2$$

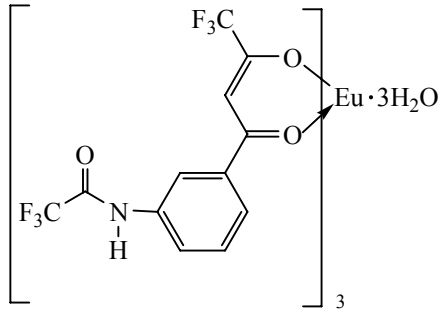
Our attempt to synthesize 3-aminobenzoyltrifluoroacetone **V** resulted (according to ^{1}H NMR, IR, HPLC and chromato-mass spectrometry) in obtaining the target compound in only 25% yield. Processing the solution of compound **IV** in diethyl ether with sodium hydroxide caused cleavage of the β-diketone in two parallel directions, to the parent 3-aminobenzoylacetone **I** and 3-trifluoroacetamidoacetophenone **III**.



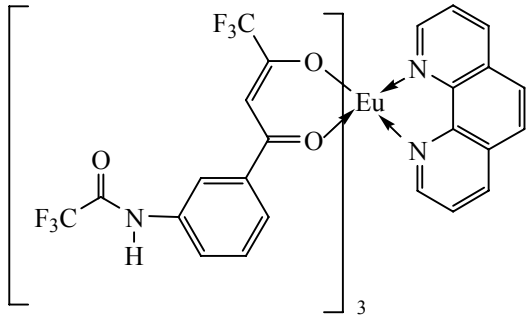
In the ^{1}H NMR spectrum of the reaction mixture two singlet signals belonging to the protons of methyl groups in compounds **I** (2.47 ppm) and **III** (2.59 ppm) were observed. In the IR spectrum there are two bands of stretching vibrations of the NH bond of the primary amine group at 3370 and 3466 cm^{-1}.The coordination compounds **VI** and **VII** were obtained from the sodium β-diketonate, europium chloride, and phenanthroline (Phen) in a water–alcohol solution.

$$\mathbf{IV} \xrightarrow[(2)\ EuCl_3\cdot 6H_2O]{(1)\ NaOH,\ EtOH,\ H_2O} \mathbf{VI} \xrightarrow{Phen,\ EtOH} \mathbf{VII}$$

The compounds obtained are fine orange (**VI**) and red (**VII**) powders.



VI



VII

Comparison of IR spectra of ligand **IV** with those of the complexes **VI** and **VII** indicates that the amide group is not involved in the coordination with the europium cation. The absorption band of stretching vibrations of the N–H (3300), as well as the bands amide I and amide II (1716 and 1590 cm^{-1}, respectively) are not practically displaced at the transition from the original ligand to the complexes **VI** and **VII**.

In the ^1H NMR spectrum of compound **VI** the multiple signals of the protons of phenyl group are shifted upfield relative to the original ligand by 0.7 ppm, and the singlet signal of the hydrogen atom of the central methine group,by at 0.3 ppm. This indicates that the Eu^{3+} cation withdraws the electron density from the ligand to a lesser extent as compared with the proton H^+ in the compound **IVa**.

Analysis of the mass spectra shows that the fragmentation of compounds **VI** and **VII** proceeds along the path of splitting off β-diketone **IV**, compound **III** and phenanthroline. Thus, in the mass spectrum of compound **VI** the most intense peaks are those of the β-diketone molecular ion (*m*/*e* = 327) and the products of cleavage from the molecules of HF (*m*/*e* = 307) and CF_3 radical (*m*/*e* = 258). The second series of intense peaks, with *m*/*e* 140, 168, 188, 216, 231, is identical to the peaks of fragment ions of compound **III**. The mass spectrum of complex **VII** contains a series of peaks from β-diketone **IV**, compound **III**, phenanthroline (*m*/*e* = 180), and fragment ions resulting from the splitting off β-diketone (*m*/*e* = 985) and then the radical CF_3 (*m*/*e* = 915), two molecules of β-diketone, HF, and CF_3 (*m*/*e* = 569).

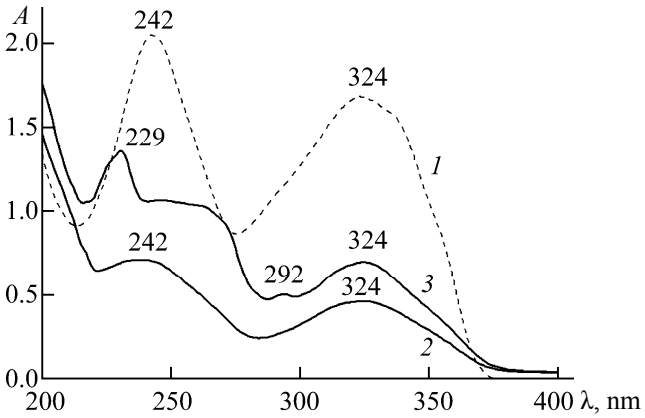


Fig. 1. EAS of acetonitlile solutions (*1*) of ligand **IV** (*c* 1.8×10^{-4} M) and (*2*) complexes **VI** (*c* 6.8×10^{-6} M.) and (*3*) **VII** (*c* 3.7×10^{-6} M).

Figure 1 shows the electron absorption spectra of ligand **IV** and complexes **VI** and **VII**. The spectra of compounds **IV** and **VI** are similar, they consist of two absorption bands with peaks at 242 and 324 nm. The similarity is due to the existence of both the ligand and the complex as chelates. In the enol form of the ligand, the proton bound to an oxygen atom of carbonyl group through the intramolecular hydrogen bond plays the role of the metal cation. The presence of neutral phenanthroline ligand in the compound **VII** causes a significant change in the spectrum, but it actually represents a superposition of the spectra of compound **IV** and phenanthroline. It is known [7] that phenanthroline spectrum contains two peaks, at 229 and 265 nm, and both occur in the spectrum of compound **VII**. The position of the long-wave band (324 nm) due to the ligand **IV** remains unchanged.

Removing the trifluoroacetyl protection to obtain the europium complexes **VIII** and **IX** with amino group was carried out under the conditions similar to those used in the reaction of the ligand **IV** with NaOH. The complexes **VI** and **VII** are moderately resistant to the alkaline reagent. The appearance of amino group in the reaction products **VIII** and **IX** is clearly traced by infrared spectroscopy. The spectral region 4000–3000 cm^{-1} in the spectra of the parent compound **VI** and the product of reaction with NaOH is shown in Fig. 2. The disappearance is seen of the absorption band ν(NH) at 3300 cm^{-1} of the amide group and the appearance of two bands, at 3364 and 3455 cm^{-1}, belonging to the primary amine group.

Compounds **VI**, **VII**, **VIII**, and **IX** possess intense cationic photoluminescence (PL) in dilute acetonitrile solutions (*c* = 10^{-6}–10^{-7} M). Emission spectra in general are identical (Figs. 3 and 4), while the photoluminescence excitation spectra (PLE) can vary significantly (Fig. 3). At λ_{reg} = 615 nm the PLE spectrum of the amide complex **VI** a single band is observed at the excitation wavelength 370 nm, in the spectrum of obtained from amino derivative **VIII** it is shifted to longer wavelengths region 400 nm (Fig. 3). The PLE spectra of complexes **VII** and **IX** contain two bands, at 300 and 350 nm (Fig. 4). In the PL spectra of all com-

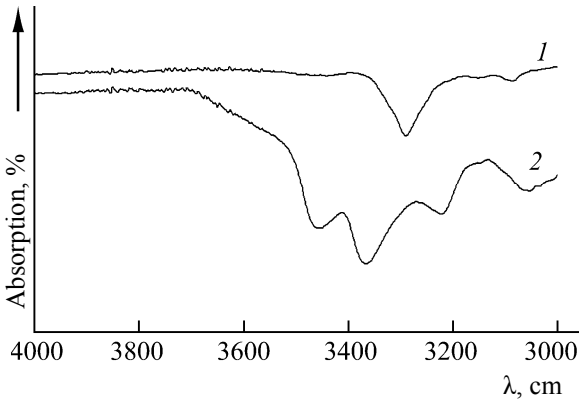


Fig. 2. IR spectra of compounds (*1*) **VII** and (*2*) **VIII** in the region of stretching vibrations of N–H bond.

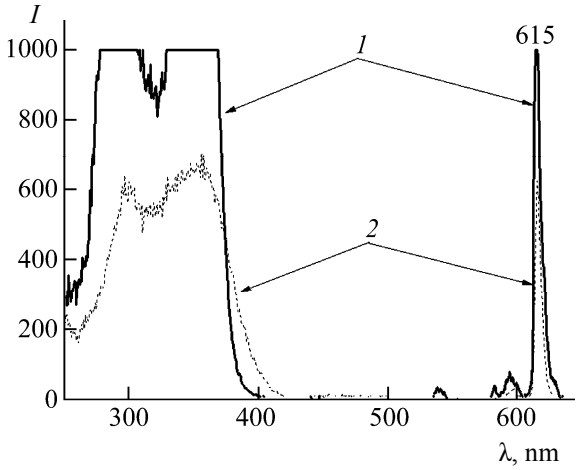


Fig. 4. Excitation spectra (λ_{reg} 615 nm) and photoluminescence spectra of complexes **VII** (*1*, λ_{ex} 340 nm, *c* 1.9×10^{-6} M) and **IX** (*2*, λ_{ex} 360 nm, *c* 1.4×10^{-5} M) in acetonitlile solution.

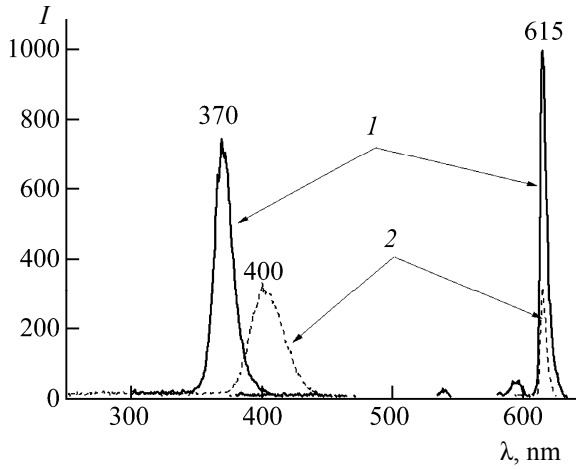


Fig. 3. Photoluminescence excitation spectra (λ_{reg} 615 nm) and photoluminescence spectra of complexes **VI** (*1*, λ_{ex} 340 nm, *c* 6.8×10^{-6} M) and **VIII** (*2*, λ_{ex} 440 nm, *c* 3×10^{-3} M.) in acetonitlile solution.

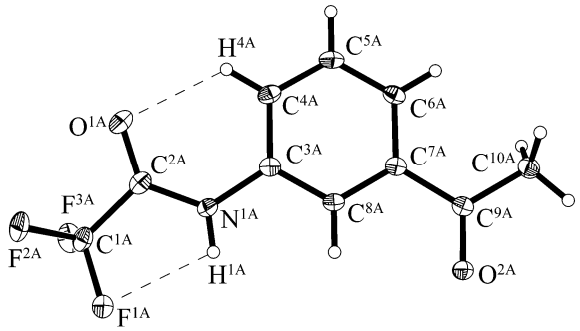


Fig. 5. Molecular structure of 3-trifluoroacetamidoacetophenone (**III**). The thermal ellipsoids are presented in 30% probability.

plexes the most intense transition corresponds to $^5D_0 \rightarrow {}^7F_2$ transition in the Eu^{3+} cation with λ_{max} 615 nm.

Molecular structure of compound **III** was determined by XRD investigation (Fig. 5). In an independent region of the cell there are two molecules, whose geometric characteristics are close to each other, so we report the geometric structure of only one of them (the main bond lengths and bond angles are listed in the table). The O^{1A}–C^{2A} and O^{2A}–O^{9A} distances fall in a narrow range 1.214(1)–1.223(1) Å, which corresponds to the length of a typical C=O double bond [8]. The N^{1A}–C^{2A} [1.346(1) Å] and N^{1A}–C^{3A} [1.419(1) Å] distances are appreciably different in keeping with the electron-acceptor nature of the O^{1A} atom and which is characteristic of amide fragments of the R(C=O)NHAr type [9–11].

The 3-trifluoroacetamidoacetophenone molecule is virtually flat, the maximum deviation of atom O^{1A} is 0.25(1) Å. The angle between the aromatic ring and $C^{1A}C^{2A}O^{1A}$ planes is 13(1)°. The intramolecular distance $F^{1A}\cdots H^{1A}$ is 2.29(2) Å, the $F^{1A}H^{1A}N^{1A}$ angle is 107.7(7)°. These geometric characteristics can be interpreted as intramolecular F···H interactions (2.25 Å [12]). Somewhat greater length of C^{1A}–F^{1A} bond [1.343(1) Å] compared with C^{1A}–F^{2A} and C^{1A}–F^{3A} bonds [1.329(1)–1.334(1) Å] confirms this assumption. In addition, in molecule **III** an intramolecular $O^{1A}\cdots H^{4A}$ interaction occurs [the O^{1A}–H^{4A} bond length is 2.25(3) Å, the $C^{4A}H^{4A}O^{1A}$ bond angle is 121.7(6)°]. In the crystal, the molecules of **III** are packed in stacks along the *a* axis (Fig. 6). The packing also includes the intermolecular F···H [2.43(1)–2.49(1) Å] and O···H [2.14(1)–2.46(1) Å] interactions [12]. The distance between the centers of the aromatic rings in the stack is 4.823(5) Å.

EXPERIMENTAL

IR spectra of compounds were taken from liquid films between KBr plates or from suspensions in mineral oil on a FTIR spectrometer FSM 1201. The ^1H

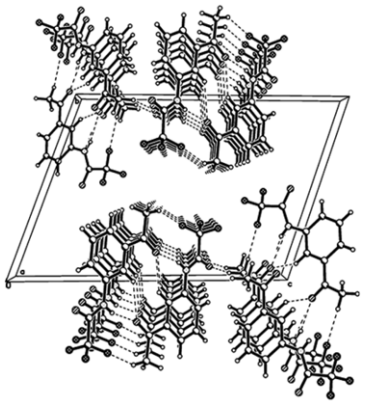


Fig. 6. Crystal structure of 3-trifluoroacetamidoacetophenone (**III**).

NMR spectra were recorded on a Bruker Avance DPX-200 instrument (200 MHz) at 25°C, internal reference TMS. Fluorescence and excitation fluorescence spectra were measured on a Perkin-Elmer LS-55 spectrofluorimeter from solutions in acetonitrile. Electron absorption spectra were recorded on a Perkin Elmer Lambda 25 spectrophotometer.

The mass chromatograms were obtained with a gas chromatography-mass spectrometer Polaris Q/Trace GC Ultra. We used a capillary chromatographic column TR-5MS, 60 m long and of 0.25 mm diameter. The flow rate of carrier gas (helium M 60 grade) was 1.2 ml min^{-1}, column temperature was raised from 40 to 200°C at 10 deg min^{-1}. Mass chromatograms were recorded at ionizing electron energy 70 eV in the range of mass numbers 40–400. To identify the detected substances NIST 2005 library was used.

The products of reaction of compound **IV** with NaOH were analyzed on a Knauer liquid chromatograph equipped with UV spectrophotometric detector, column 6×100 mm with a sorbent Separon Si C18. 5 μm, eluent 60% acetonitrile in water. Detection was performed at 230 nm wavelength.

The XRD data of compound **III** were obtained using a Smart APEX diffractometer (λ = 0.71073 Å, T = 100 K): empirical formula $C_{10}H_8F_3NO_2$, M 231.17; a 4.8230(2), b 12.4654(5), c 17.4706(7) Å; α 69.869(1), β 84.520(1), γ 81.000(1)°; space group P-1, Z 4, d_{calc} 1.578 g cm^{-3}, μ 0.148 mm^{-1}, $2\theta_{max}$ 52°; a = 4.82301)°, steric group P-1, Z = 4, d_{calc} = 1.578 g cm^{-3} , μ = 0.148 mm^{-1}, $2\theta_{max}$ = 52°; 8450 reflections were measured, of which 3778 were independent (R_{int} = 0.0123), R_1 (with respect to F for the reflections with $I > 2\sigma(I)$ = 0.0327, wR_2 (with respect to F^2 over all reflections) is 0.0878. The structure was solved by the direct method and refined by least-squares with respect to F^2_{hkl} anisotropically for nonhydrogen atoms and the hydrogen atom of the amide group. All other hydrogen atoms were located in the geometrically calculated positions and refined using the *rider* model. The calculations were carried out within the software package SHELXTL v. 6.10 [13]. The extinction was accounted for using the SADABS program [14].

Selected bond lengths (d) and bond angles (ω) in compound **III**

Bond	d, Å	Angle	ω, deg
O^{1A}–C^{2A}	1.214(1)	$C^{2A}N^{1A}C^{3A}$	126.24(9)
O^{2A}–C^{9A}	1.223(1)	$O^{1A}C^{2A}N^{1A}$	127.7(1)
N^{1A}–C^{2A}	1.346(1)	$O^{1A}C^{2A}C^{1A}$	117.5(1)
N^{1A}–C^{3A}	1.419(1)	$N^{1A}C^{2A}C^{1A}$	114.73(9)
F^{1A}–C^{1A}	1.343(1)	$C^{8A}C^{3A}N^{1A}$	117.22(8)
F^{2A}–C^{1A}	1.329(1)	$C^{4A}C^{3A}N^{1A}$	123.0(1)
F^{3A}–C^{1A}	1.334(1)	$C^{8A}C^{7A}C^{9A}$	118.57(8)
C^{1A}–C^{2A}	1.536(2)	$C^{6A}C^{7A}C^{9A}$	121.68(9)
C^{7A}–C^{9A}	1.498(2)	$O^{2A}C^{9A}C^{7A}$	120.09(9)
C^{9A}–C^{10A}	1.502(2)	$O^{2A}C^{9A}C^{10A}$	121.1(1)
		$C^{7A}C^{9A}C^{10A}$	118.85(9)

In the syntheses sodium hydride was used as 60% suspension in mineral oil from Acros. 3-aminoacetophenone (**I**) (Acros) and methyl trifluoroacetate (**II**) (PIM-Invest) were used without purification.

3-Trifluoroacetamidoacetophenone (III) was obtained by reacting equimolar amounts of compounds **I** and **II** in ether and purified by recrystallization from toluene, yield 87%. IR spectrum, ν, cm^{-1}: 3300 (NH), 1716 (amide I), 1614, 1550 (C = O), 1590 (amide II), 1489, 1458, 1282, 1221, 1188, 1150, 1120 (CF_3), 788. ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm (*J*, Hz): 2.60 s (3H, C<u>H</u>$_3$C(O)), 7.57–7.61 t (1H$_{arom}$, *J* 8.03), 7.87–7.89 d (1H$_{arom}$) 8.00–8.02 d (1H$_{arom}$) 8.33 s (1H$_{arom}$), 10.44 s (1H, NH). Found, %: C 51.06, H 3.07. $C_{10}H_8F_3NO_2$. Calculated, %: C 51.95, H 3.49.

3-Trifluoroacetamidobenzoyltrifluoroacetone (IV). A three-necked flask equipped with stirrer, dropping funnel, and reflux condenser was charged with a solution of 3.0 g (0.075 mol) of NaH in 100 ml of unhydrous diethyl ether, and 19.2 g (0.15 mol) of compound **II** was added dropwise while stirring. Then was added a solution of 5.0 g (0.037 mol) of 3-aminoacetophenone **I** in 20 ml of anhydrous ether, the mixture was stirred for 3 h, and then to it was added by portions 10% solution of H_2SO_4 to a neutral reaction. The ether layer was separated from water and dried over Na_2SO_4. The product was recrystallized from diethyl ether–hexane. 10.1 g of **IV**·$O(C_2H_5)_2$ etherate was isolated. ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 1.06–1.13 t (6H, C<u>H</u>$_3$CH$_2$, *J* 7.03), 3.34–3.45 q (4H, CH$_3$C<u>H</u>$_2$, *J* 7.03). The final purification was performed by sublimation in a vacuum, 9.4 g (78%) of diketone **IV** was isolated. IR spectrum, ν, cm^{-1}: 3300 (NH), 3087 (C=CH), 1716 (amide I), 1614, 1550 (C=O),

1590 (amide II), 1489, 1458, 1282, 1221, 1188, 1150, 1120 (CF_3), 788. ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm (*J,* Hz): 4.81 s (2H, CH_2 diketone), 6.91 s (1H, CH enol), 7.64–7.68 t ($1H_{arom}$, *J* 8.03), 8.02–8.04 d ($1H_{arom}$), 8.08–8.1 d ($1H_{arom}$), 8.44 s ($1H_{arom}$), 10.49 s (NH). Found, %: C 43.20, H 2.15. $C_{12}H_7F_6NO_3$. Calculated, %: C 44.04, H 2.16.

Europium(III) tris(3-trifluoroacetamidobenzoyltrifluoroacetonate) trihydrate (VI). 0.98 g (3 mmol) of compound **IV** was dissolved in 15 ml of 95% ethanol, then at vigorous stirring 3 ml of 1 N NaOH and 5 ml of 0.2 M aqueous solution of europium chloride (1 mmol) was added. To the mixture 100 ml of water was poured, the mixture was heated to 60°C and then cooled. Orange precipitate of the compound **VI** formed was isolated and purified by recrystallization from a dichloromethane–hexane mixture. Yield 0.5 g (43%). IR spectrum, ν, cm^{-1}: 3300 (NH), 3087 (C=CH), 1716 (amide I), 1614 (C=O), 1590 (amide II), 1560, 1533, 1489, 1465, 1299, 1225, 1188, 1150, 1120 (CF_3), 788. ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm (*J,* Hz): 6.57 s (1H, CH), 6.92–7.00 t ($1H_{arom}$, *J* 8.03), 7.15–7.18 d ($1H_{arom.}$), 7.26–7.30 d ($1H_{arom}$), 10.2 s ($1H_{arom}$). Found, %: C 37.40, H 2.15. $C_{36}H_{24}Eu{\cdot}F_{18}N_3O_{12}$. Calculated, %: C 36.46, H 2.04.

Europium(III) tris(3-trifluoroacetamidobenzoyltrifluoroacetonate) (phenanthroline) (VII). To a solution of 0.38 g (0.32 mmol) of compound **VI** in 95% ethanol was added 0.06 g (0.32 mmol) of phenanthroline. The mixture was stirred for 4 h with a magnetic stirrer. The solvent was removed under vacuum and the residue was recrystallized from toluene at heating. 0.35 g (89%) of compound **VII** was isolated as a red-orange powder. IR spectrum, ν, cm^{-1}: 3300 (NH), 3087 (C=CH), 1716 (amide I), 1614, 1550 (C=O), 1590 (amide II), 1560, 1529, 1489, 1458, 1421, 1299, 1221, 1188, 1150, 1120 (CF_3), 788. ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm, (*J,* Hz): 7.31–7.51 m (8H, Phen), 8.78 s (1H, CH), 9.4–9.5 m ($1H_{arom}$) 10.22–10.25 m ($1H_{arom}$), 10.3–10.4 m ($1H_{arom}$), 12.02 s ($1H_{arom}$). Found, %: C 43.74, H 2.23. $C_{48}H_{26}Eu{\cdot}F_{18}N_5O_9$. Calculated, %: C 43.97, H 1.98.

Europium(III) tris(3-aminobenzoyltrifluoroacetonate) trihydrate (VIII). To a solution of 0.5 g (0.42 mmol) of compound **VI** in 20 ml of ethyl alcohol at stirring with a magnetic stirrer was added dropwise 2 ml of 1N NaOH. The mixture was stirred for 7 h at 25°C. The excess alkali was neutralized with acid. The solvent and water were removed in a vacuum. The dry residue was dissolved in dichloromethane and washed twice with water. The organic layer was separated from water, dried over Na_2SO_4, the solvent was removed in a vacuum. 0.25 g (70%) of compound **VIII** was isolated as a yellow powder. IR spectrum, ν, cm^{-1}: 3364, 3455 (NH_2), 3060 (C=CH), 1719, 1682 (C=O), 1614, 1580, 1529, 1492, 1316, 1292, 1259, 1191, 1137 (CF_3), 798. Found, %: C 41.06, H 2.83. $C_{30}H_{27}Eu{\cdot}F_9N_3O_9$. Calculated, %: C 40.13, H 3.03.

Europium(III) tris(3-aminobenzoyltrifluoroacetonate)(phenanthroline) (IX). Compound **IX** was synthesized from the complex **VII** similarly to **VIII**. Yield 70%. IR spectrum, ν, cm^{-1}: 3373, 3470 (NH_2), 3062 (C=CH), 1724, 1634 (C=O), 1614, 1587, 1530, 1490, 1317, 1293, 1222, 1188 , 1137 (CF_3), 778. Found, %: C 50.04, H 3.33. $C_{42}H_{29}EuF_9N_5O_6$. Calculated, %: C 49.32, H 2.84.

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