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# Synthesis and Photoluminescence of Eu(III) and Tb(III) Complex Compounds Containing Anions of 4-$CF_3C_6F_4COOH$ and 4-$(CF_3)_2CFC_6F_4COOH$ Acids

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**Abstract**—Hydrates of Eu(III) and Tb(III) salts with anions (L) 4-$CF_3C_6F_4COO^-$ and 4-$(CF_3)_2CFC_6F_4COO^-$, and also mixed-ligand complexes Ln(phen)$(L)_3$ were obtained. The compounds show red and green photoluminescence characteristic of $Eu^{3+}$ and $Tb^{3+}$ ions, respectively, in the visible region of spectrum. The intensity of the photoluminescence of the complexes containing 1,10-phenanthroline is much higher than that of compounds containing water. It is connected with sensitizing properties of phen in relation to $Eu^{3+}$ and $Tb^{3+}$ ions.

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Complexes of lanthanides (Ln) with organic ligands possessing photo- and electroluminescent properties are among intensively studied types of coordination compounds [1–5]. It is caused by the prospects of their use in molecular photonics and electronics engineering. Complex salts with anions of aliphatic perfluorocarboxylic acids are among luminescent Ln compounds [6–10]. There is only limited information on Ln luminescent complexes with fluorinated aromatic monocarboxylic acids, including pentafluorobenzoic acid $C_6F_5COOH$ ($L^1H$), and mixed-ligand complexes on their basis. The compounds $Eu(L^1)_3\cdot H_2O$, Eu(4-$CF_3C_6F_4COO)_3\cdot 2H_2O$ [10] possessing photoluminescence, and also $Gd(L^1)_3\cdot 2H_2O$, $Tb(L^1)_3\cdot 2H_2O$, and $Dy(L^1)_3\cdot 2H_2O$ were synthesized [11]. A salt of Tb(III) with the anion 2-$FC_6H_4COO^-$, and also its complexes with 1,10-phenanthroline (phen) and 2,2'-bipyridyl, exhibiting luminescence [12] were obtained. Compounds Ln(phen)$(L^1)_3$ were synthesized (Ln = Tb, Eu) and the photoluminescence of these mixed-ligand complexes and of hydrates of the salts $Eu(L^1)_3\cdot 2H_2O$ and $Tb(L^1)_3\cdot 2H_2O$ obtained earlier was investigated [13]. It has turned out that complexes Ln(phen)$(L^1)_3$ possess a bright photoluminescence, and the replacement of phen by water reduces its intensity. These data show the promise in the synthesis of Ln compounds with pentafluorobenzoic acid derivatives and of studying their luminescent properties.

We have synthesized Eu(III) and Tb(III) salts with anions of perfluoro-4-methylbenzoic 4-$CF_3C_6F_4COOH$ ($L^2H$) and perfluoro-4-isopropylbenzoic 4-$(CF_3)_2CF$ $C_6F_4COOH$ ($L^3H$) acids and mixed-ligand complexes of these metals containing the above-stated anions and molecules of phen and also have studied their photoluminescence. For comparison we have investigated in addition the photolumi-nescence of analogous complexes of these elements with $L^1H$ and phen synthesized earlier.

Freshly-prepared Ln hydroxides and nonaqueous media were used for obtaining the compounds. Elemental analysis of the synthesized products covered not only C, H, N, but also F (see the table). Salts of Eu(III) and Tb(III) with anions of $L^2H$ and $L^3H$ acids **VII–X** were isolated in the form of crystal hydrates containing one or two (complex **VIII**) water molecules. The compound of Eu(III) with $L^2H$ was obtained earlier in the form of dihydrate [10], however we dried salt **VII** in a vacuum. Salts of Eu(III) and

Elemental analysis of compounds **III–X**

| Comp. no. | Found, % | | | | Formula | Calculated, % | | | |
|---|---|---|---|---|---|---|---|---|---|
| | C | H | N | F | | C | H | N | F |
| **III** | 39.0 | 0.9 | 2.7 | 35.8 | $C_{36}H_8N_2F_{21}O_6Eu$ | 38.8 | 0.7 | 2.5 | 35.8 |
| **IV** | 38.3 | 0.75 | 2.45 | 35.1 | $C_{36}H_8N_2F_{21}O_6Tb$ | 38.5 | 0.7 | 2.4 | 35.5 |
| **V** | 35.9 | 0.5 | 2.2 | 43.8 | $C_{42}H_8N_2F_{33}O_6Eu$ | 35.6 | 0.6 | 2.0 | 44.3 |
| **VI** | 36.6 | 1.0 | 2.5 | 43.8 | $C_{42}H_8N_2F_{33}O_6Tb$ | 35.5 | 0.6 | 2.0 | 44.1 |
| **VII** | 31.1 | 0.15 | | 41.3 | $C_{24}H_2F_{21}O_7Eu$ | 30.2 | 0.2 | | 41.8 |
| **VIII** | 30.4 | 0.6 | | 40.9 | $C_{24}H_4F_{21}O_8Tb$ | 29.5 | 0.4 | | 40.8 |
| **IX** | 30.2 | 0.4 | | 49.5 | $C_{30}H_2F_{33}O_7Eu$ | 28.8 | 0.15 | | 50.0 |
| **X** | 28.9 | 0.5 | | 50.0 | $C_{30}H_2F_{33}O_7Tb$ | 28.6 | 0.15 | | 49.8 |

Tb(III) with the $C_6F_5COO^-$ anions synthesized earlier also contained one and two water molecules, respectively [10, 11]. Mixed-ligand complexes **III–VI**, as well as complexes Ln(phen)$(L^1)_3$ [13], contain one phen molecule. We were not able to grow single crystals of compounds **III–X** suitable for X-ray structural analysis. Published data show that structures of Ln compounds with fluorobenzoic acids are diverse. For example, $Pr(2,6\text{-}F_2C_6H_3COO)_3\cdot H_2O$ is a coordination polymer compound [14]. According to X-ray structural analysis, the $[Tb_2(H_2O)_8(L^1)_6]$ [13] and $[Nd_2(H_2O)_8(L^1)_6]\cdot 2H_2O$ compounds [15] have binuclear structures, $Ln^{3+}$ coordinating $C_6F_6COO^-$ anions and water molecules. According to X-ray data, the $[Tb(2\text{-}FC_6H_4COO)_3(2\text{-}FC_6H_4COOH)(H_2O)]_2$ compound is a dimer, where $2\text{-}FC_6H_4COO^-$ ions and $2\text{-}FC_6H_4COOH$ and water molecules are coordinated [12]. Coordination of these ligands in the binuclear Tb(III) compound containing $2\text{-}FC_6H_4COO^-$ ions and phen molecules was determined by X-ray structural analysis [12].

The IR spectra of $L^2H$ and $L^3H$ acids contain wide intensive bands with maxima at 2957 and 2925 $cm^{-1}$, respectively, which can be assigned to the stretching vibration of OH groups participating in the H-bond between molecules of the acids. Intensive bands at 1734 and 1750 $cm^{-1}$ correspond to ν(C=O) of carboxy groups. In the IR spectra of compounds **VII–X** containing water molecules, there is a group of bands in the region of 3675–3340 $cm^{-1}$ belonging to ν(OH). In the region of 1618–1575 $cm^{-1}$ intensive bands corresponding to $\nu_{as}$ of coordinated $COO^-$ groups are observed. They are split in the case of compounds **VII, VIII, X**.

Absorption bands in the region of 3700–3150 $cm^{-1}$ are absent from the IR spectra of complexes **III–VI**. It points to the absence of water molecules from the composition of the complexes, which agrees with the elemental analysis data. The $\nu_{as}$ bands of coordinated $COO^-$ are observed in the region of 1710–1716 $cm^{-1}$ of the spectra, these bands being displaced in the high-frequency region with respect to similar bands in the spectra of hydrates **VII–X**. In the region of 1620–1640 $cm^{-1}$ there is an intensive ν(C=N) band of the phen molecule. This band is displaced in the low-frequency range with respect to the ν(C=N) band in the spectrum of phen·$H_2O$ (ν 1643 $cm^{-1}$), which points to the coordination of the phen molecule.

The position of $\nu_s$ bands of $COO^-$ groups in the spectra of compounds **III–X** is difficult to determine, as in the region of 1410–1490 $cm^{-1}$ there are intensive ν(C=C) bands, which only slightly differ in frequencies from the ν(C=C) bands in the spectra of the acids $L^2H$ (1487, 1423 $cm^{-1}$) and $L^3H$ (1491, 1411 $cm^{-1}$), and also of phen·$H_2O$ (1500 and 1419 $cm^{-1}$). In the case of mixed-ligand complexes **III–VI** the situation becomes complicated owing to the presence of the ν(C=N) band. By analogy with the data [12, 13−15] we can assume that compounds **III–X** are binuclear or polynuclear. For example, the compound $Eu(L^2)_3\cdot 2H_2O$ in acetone solution is a binuclear complex [10].

The excitation of luminescence of the acid $L^1H$ with $\lambda_{max}$ 280 nm is observed in the region of 235–315 nm (Fig. 1). Bands in the photoluminescence excitation of the acids $L^2H$ and $L^3H$ are slightly displaced in the longwave range (235–345 nm). For this reason we have chosen exciting light with λ 290, 310, and 313 nm for recording photoluminescence spectra of the acids $L^1H$, $L^3H$, and $L^2H$, respectively. These acids possess a sufficiently bright photoluminescence in the UV spectral range at 300 K. Bands in the spectrum of $L^1H$ acid with $\lambda_{max}$ 336 nm are observed in the region of 300–420 nm (half-width of the bands 55 nm). Bands in the spectra of the $L^2H$ and $L^3H$ acids are in the region of 310–420 nm and are slightly displaced in the long-wave range with respect to the $L^1H$ spectrum ($\lambda_{max}$ 342 and 343 nm, respectively, the half-width of the bands ≈40 nm) (Fig. 1). Photoluminescence intensity (*I*) decreases in the series $L^1H > L^3H > L^2H$. The red shift of bands in the spectra of the $L^2H$ and $L^3H$ acids with respect to $L^1H$, and also a decrease in the photoluminescence intensity seem to be connected with the presence of perfluoroalkyl groups in molecules of these acids.

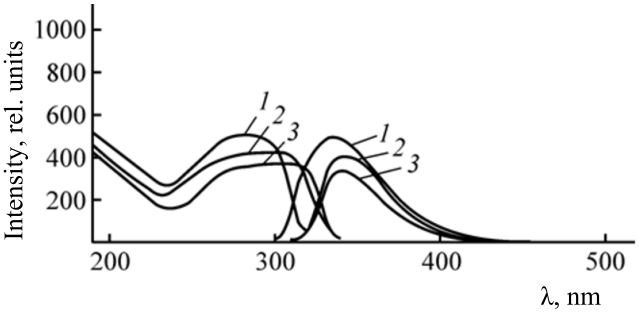

**Fig. 1.** Luminescence and photoluminescence excitation spectra of: (*1*) $C_6F_5COOH$, (*2*) 4-$(CF_3)_2CFC_6F_4COOH$, (*3*) 4-$CF_3C_6F_4COOH$. *V* = 500 V, slit 5 nm, $\lambda_{exc}$ = 290 ($L^1H$), 310 ($L^3H$), 313 nm ($L^2H$).

Luminescence excitations of mixed-ligand complexes **I–VI** are equal for the compounds containing a molecule of phen and anions of acids, they appear in a wider (compared to the acids) ranges of 230–360 nm (Figs. 2 and 3). For the bands in the excitation spectra of Eu(III) complexes $\lambda_{max}$ is 290–300 nm (Fig. 2). Maxima of bands in the excitation spectra of Tb(III) complexes are at 305 nm (**II, IV**) and 285 nm (**VI**) (Fig. 3). A red shift and broadening of bands as compared to the acids are observed in the region of excitation of mixed-ligand complexes **I–VI**, therefore we have chosen the wavelength of excitation light of 330 nm for recording photoluminescence spectra of these complexes.

Mixed-ligand complexes of $Eu^{3+}$ (**I, III, V**) at 300 K possess a bright photoluminescence characteristic of this ion [16]. The bands with $\lambda_{max}$ 592, 614, and 700 nm corresponding to the transitions $^5D_0 \rightarrow {}^7F_1, \rightarrow {}^7F_2, \rightarrow {}^7F_4$ in the $Eu^{3+}$ ion are highly intensive. Spectral bands

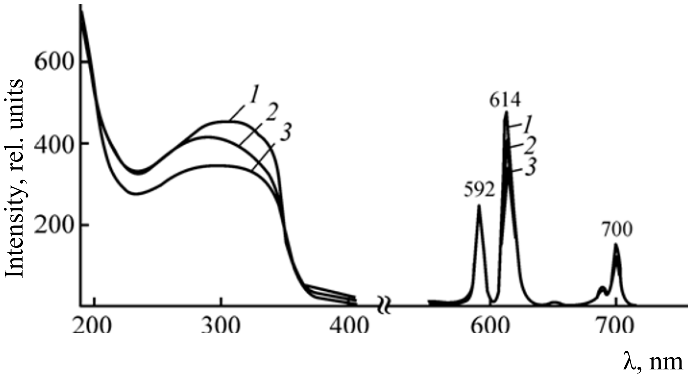

**Fig. 2.** Luminescence and photoluminescence excitation spectra of: (*1*) Eu(phen)(4-$CF_3C_6F_4COO)_3$, (*2*) Eu(phen)$(C_6F_5COO)_3$, (*3*) Eu(phen)[4-$(CF_3)_2CFC_6F_4COO]_3$. *V* = 600 V, slit 5 nm, $\lambda_{exc}$ = 330 nm.

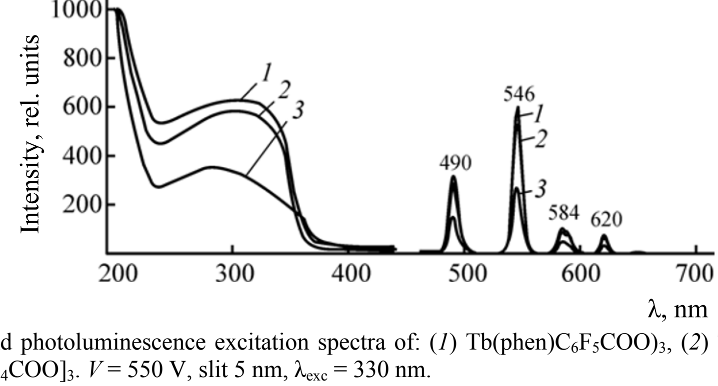

**Fig. 3.** Luminescence and photoluminescence excitation spectra of: (*1*) Tb(phen)$C_6F_5COO)_3$, (*2*) Tb(phen)(4-$CF_3C_6F_4COO)_3$, (*3*) Tb(phen)[4-$(CF_3)_2CFC_6F_4COO]_3$. *V* = 550 V, slit 5 nm, $\lambda_{exc}$ = 330 nm.

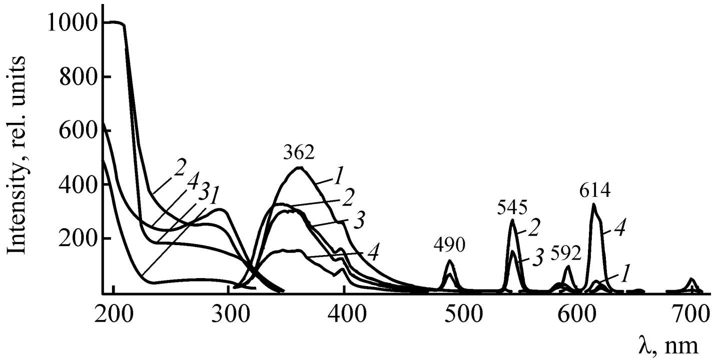

**Fig. 4.** Luminescence and photoluminescence excitation spectra of: (*1*) $Eu[4\text{-}(CF_3)_2CFC_6F_4COO]_3\cdot H_2O$, (*2*) $Tb(4\text{-}CF_3C_6F_4COO)_3\cdot 2H_2O$, (*3*) $Tb[4\text{-}(CF_3)CFC_6F_4COO]_3\cdot H_2O$, (*4*) $Eu(4\text{-}CF_3C_6F_4COO)_3\cdot 2H_2O$. $V = 600$ V, slit 5 nm, $\lambda_{exc} = 290$ nm.

with $\lambda_{max}$ 580 ($^5D_0\rightarrow{}^7F_0$ transition) and 650 nm ($^5D_0\rightarrow{}^7F_3$) are weak (Fig. 2). The "red" band, $\lambda_{max}$ 614 nm, has the highest *I* value. The intensity of this band for complex **III** is approximately 2 and 3.3 times higher than *I* of the bands with $\lambda_{max}$ at 592 nm and 700 nm, respectively. The intensity of photoluminescence of mixed-ligand complexes decreases in the series: **III** > **I** > **V**. The complex containing an anion of the $L^3H$ acid with the greatest number of F atoms has the least intensity.

Mixed-ligand $Tb^{3+}$ complexes **II, IV, VI** at 300 K possess a bright photoluminescence characteristic of this ion [16]. Bands with $\lambda_{max}$ 490, 546, 584, and 620 nm corresponding to the transitions $^5D_4\rightarrow{}^7F_6$, $\rightarrow{}^7F_5$, $\rightarrow{}^7F_4$, $\rightarrow{}^7F_3$ in the $Tb^{3+}$ ion have the greatest intensity (Fig. 3). Band positions differ only slightly from that in the spectrum of the Tb(III) complex containing $2\text{-}FC_6H_4COO^-$ ions and phen molecules [12]. The "green" band with $\lambda_{max}$ 546 nm is the most intensive. The intensities of bands with $\lambda_{max}$ 490, 584, and 620 nm for complex **II** are 53, 16 and 13% of the "green" band intensity, respectively. Bands with $\lambda_{max}$ 650 and 670 nm corresponding to the $^5D_4\rightarrow{}^7F_2$, $\rightarrow{}^7F_1$ transitions are of low-intensity. The intensity of photoluminescence of Tb(III) complexes decreases in the series: **II** > **IV** > **VI**. Similarly to Eu(III) complexes, the photoluminescence intensity of complex **VI** containing the $L^3H$ acid anion is essentially less (Fig. 3).

The excitation of photoluminescence of hydrates **VII–X** is observed in the range of 230–340 nm, which is close to the range of excitation of the $L^2H$ and $L^3H$ acids (Fig. 4). Spectra of complexes **VII** and **IX** with the acid $L^2H$ anion contain clearly expressed bands with $\lambda_{max}$ 280 and 290 nm, respectively. To record the spectra, we have chosen the wave length of exciting light equal to 290 nm. The measurements have shown that hydrates **VII–X** possess a photoluminescence, however its intensity is essentially lower than that of mixed-ligand complexes **III–VI** containing a phen molecule. It agrees with the data for complexes containing $C_6F_5COO^-$ anions [13]. For example, the intensity of the "red" band in the photoluminescence spectrum of hydrate **VII** is 1.6 times lower than that of the analogous band of mixed-ligand complex **III**, and the intensity of the "green" band in the hydrate **VIII** spectrum is 5.5 times lower than the *I* value of the analogous band of mixed-ligand complex **IV** (Figs. 2, 3, and 4). In the UV regions of the spectra of the hydrates there are wide bands caused by the photoluminescence of organic ligands. Intensities of the bands of terbium compounds **VIII, X** being close to each. In the case of europium compounds the intensity of the band of ligands containing $(CF_3)_2CF$ group in complex **IX** is much higher than the intensity of the analogous band in complex **VII** with ligands containing the $CF_3$ group. The following regularity is observed for these complexes: the higher is the intensity of photoluminescence of anion ligand, the weaker is the intensity of $Eu^{3+}$ ion bands (Fig. 4). It suggests that the effectiveness of exciting light conversion in the $Eu^{3+}$ ion in complexes **VII, IX** depends on the substituent nature. It is obvious that the effectiveness of the conversion increases on the substitution of $CF_3$ group for $(CF_3)_2CF$. It agrees with a higher intensity of the bands of the $Eu^{3+}$ ion in complex **VII** as compared with the intensity of bands in the compound **IX** spectrum.

When a water molecule is replaced by a phen molecule (complexes **III–VI**), the bands caused by anions of acids are not observed, whereas the intensity of photoluminescence bands of lanthanide ions sharply increases (Figs. 2 and 3). It is known that phen is a sensibilizer of europium(III) photoluminescence [4, 12, 17], which results in essential increase in the intensity of the $Eu^{3+}$ ion photoluminescence. In fact, the intensity of the band with $\lambda_{max}$ of 614 nm in the spectrum of mixed-ligand complex **III** is 1.6 times higher than *I* of the analogous band in the spectrum of hydrate **VII**. According to [4], phen also can be a sensitizer of photoluminescence of $Tb^{3+}$ ions, as the triplet level of excited phen molecules is located a little higher than the resonance $^5D_4$ level of $Tb^{3+}$ ions. It can result in an effective energy transfer from excited phen molecules to $Tb^{3+}$ ions and to strengthening the photoluminescence of these latter. Our data on the photoluminescence of mixed-ligand terbium(III) complexes containing a phen molecule confirm the sensibilization possibility. Thus, the intensity of the band with $\lambda_{max}$ 546 nm in the spectrum of mixed-ligand complex **IV** is 5.5 times higher than the intensity of the analogous band in the spectrum of hydrate **VIII**. The effect of phen on the photoluminescence intensity in mixed-ligand complex **IV** of the $Tb^{3+}$ ion is 3.4 times stronger than the effect of phen in complex **III** of the $Eu^{3+}$ ion.

## EXPERIMENTAL

In the synthesis of complexes we used chemically pure grade $TbCl_3\cdot6H_2O$, $Eu(NO_3)_3\cdot6H_2O$, 2-propanol, 25% aqueous solution of $NH_3$, KOH, acetone, methanol, toluene, and hexane, and also analytical grade phen·$H_2O$. The acids $C_6F_5COOH$ ($L^1H$) and 4-$CF_3C_6F_4COOH$ ($L^2H$) were synthesized by the procedure [18]. Analogously from 4-$(CF_3)_2CFC_6F_4CF_3$ we obtained the acid 4-$(CF_3)_2CFC_6F_4COOH$ ($L^3H$), mp 115−116°C (sublimation in a vacuum at 110°C, 15 mm Hg); mp 110−111°C (petroleum ether) [19]. The compounds Eu(phen)$(L^1)_3$ (**I**) and Tb(phen)$(L^1)_3$ (**II**) were prepared by the procedures [13].

Elemental analysis for C, H, N, and F was carried out by procedures [10]. The IR spectra were recorded on a Scimitar FTS 2000 spectrometer in mineral and fluorinated oils. The excitation and photoluminescence spectra of solid-phase samples were taken on a Cary Eclipse Varian fluorescent spectrophotometer at 300 K under equal conditions for all samples.

**Eu(phen)(4-$CF_3C_6F_4COO)_3$ (III).** A solution of 0.35 g (0.8 mmol) of $Eu(NO_3)_3\cdot6H_2O$ in 5 ml of water was added to a solution of 0.2 g (3.56 mmol) of KOH in 5 ml of water. Precipitated $Eu(OH)_3$ was filtered off on a glass filter, washed by hot water, then by water of room temperature to a neutral reaction of washings. The wet precipitate was introduced in a solution of 0.64 g (2.45 mmol) of $L^2H$ in 10 ml of 2-propanol. The mixture was stirred for 1 h and filtrated through a glass filter. A solution of 0.16 g (0.8 mmol) of 1,10-phenanthroline hydrate in 5 ml of 2-propanol was added to the filtrate with stirring. In a few minutes a colorless precipitate was formed. The mixture was stirred for 30 min, then the precipitate was filtered off on a glass filter, washed by 2-propanol, and dried first in air then in a vacuum. Yield 0.64 g (72%). IR spectrum, ν, $cm^{-1}$: 2920, 1710, 1622, 1486, 1410, 1377, 1336, 1210, 1185, 1136, 993, 867, 841, 747, 726, 715, 459.

**Tb(phen)(4-$CF_3C_6F_4COO)_3$ (IV)** was synthesized by an analogous procedure using $TbCl_3\cdot6H_2O$. Yield of the colorless complex 0.43 g (48%). IR spectrum, ν, $cm^{-1}$: 2920, 1715, 1630, 1486, 1464, 1411, 1377, 1338, 1211, 1183, 1134, 994, 867, 841, 746, 729, 714, 460.

**Eu(phen)[4-$(CF_3)_2CFC_6F_4COO]_3$ (V)** was synthesized analogously using $L^3H$. Yield of the colorless complex 0.67 g (60%). IR spectrum, ν, $cm^{-1}$: 2940, 1714, 1623, 1483, 1417, 1294, 1240, 1152, 1090, 999, 971, 841, 729, 554, 446.

**Tb(phen)[4-$(CF_3)_2CFC_6F_4COO]_3$ (VI)** was synthesized analogously using $TbCl_3\cdot6H_2O$ and $L^3H$. Small amount of $Tb(OH)_3$, which has not entered in the reaction with $L^3H$ was filtered off on a dense paper filter. Yield 0.3 g (26%). IR spectrum, ν, $cm^{-1}$: 3104, 2920, 1716, 1641, 1475, 1464, 1377, 1293, 1242, 1178, 1150, 1088, 997, 970, 844, 722, 620, 552, 468.

**Eu(4-$CF_3C_6F_4COO)_3\cdot H_2O$ (VII).** Concentrated aqueous ammonia solution, 6 ml, was added to a solution of 0.7 g (1.6 mmol) of $Eu(NO_3)_3\cdot6H_2O$ in 40 ml of water. The mixture was stirred for 1 h and left in air for a day. We treated the $Eu(OH)_3$ precipitate in the same way as in the synthesis of complex **III**. The wet precipitate was transferred in a beaker, 1.28 g (4.9 mmol) of $L^2H$ was added, and the mixture was stirred. Then an acetone-methanol (3:1) mixture, 40 ml, was added and stirred for 1 h. Small amount of the hydroxide, which has not entered in the reaction, was filtered off on a dense paper filter, and then the filtrate was evaporated to a minimal volume. The formed colorless precipitate was filtered off on a glass filter, washed by hexane, and dried first in air and then in a vacuum. Yield 1.18 g (77%). IR spectrum, ν, $cm^{-1}$: 3660, 3590, 3382, 1612, 1589, 1486, 1411, 1377, 1337, 1209, 1151, 996, 869, 830, 773, 715, 554, 464.

**Tb(4-$CF_3C_6F_4COO)_3\cdot H_2O$ (VIII).** A solution of 0.31 g (0.8 mmol) of $TbCl_3\cdot6H_2O$ in 5 ml of water was added to a solution of 0.2 g (3.56 mmol) of KOH in

5 ml of water. We treated the $Tb(OH)_3$ precipitate in the same way as in the synthesis of complex **VII**, then the precipitate was transferred to a beaker with a solution of 0.64 g (2.45 mmol) of $L^2H$ in 10 ml of 2-propanol. The mixture was stirred at room temperature for 1 h. Then we proceeded in the same way as in the synthesis of complex **VII**. Yield 0.7 g (72%). IR spectrum, ν, $cm^{-1}$: 3671, 3344, 1610, 1589, 1489, 1420, 1377, 1340, 1155, 996, 871, 827, 780,751, 716, 560, 462.

**$Eu[4\text{-}(CF_3)_2CFC_6F_4COO]_3 \cdot H_2O$ (IX)** was synthesized according to the procedure of the complex **VIII** synthesis, using 0.35 g (0.8 mmol) of $Eu(NO_3)_3 \cdot 6H_2O$ and 0.89 g (2.45 mmol) of $L^3H$. Yield of colorless complex 0.66 g (66%). IR spectrum, ν, $cm^{-1}$: 3660, 3534, 1614, 1483, 1412, 1377, 1296, 1238, 1152, 1091, 999, 972, 828, 730, 447.

**$Tb[4\text{-}(CF_3)_2CFC_6F_4COO]_3 \cdot H_2O$ (X)** was synthesized analogously to complex **VIII**, using 0.89 g (2.45 mmol) of $L^3H$. A colorless precipitate was washed out by 2-propanol. Yield 0.49 g (49%). IR spectrum, ν, $cm^{-1}$: 3650, 3574, 1648, 1607, 1575, 1486, 1377, 1296, 1239, 1182, 1153, 1091, 1002, 973, 833, 817, 769, 733, 552, 449.

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