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Luminescence Properties of Complexes $Ln(Phen)(C_6F_5COO)_3$ (Ln = Tb, Eu) and $Ln(C_6F_5COO)_3 \cdot nH_2O$ (Ln = Tb, n = 2; Ln = Eu, n = 1). Structures of the $[Tb_2(H_2O)_8(C_6F_5COO)_6]$ Complex and Its Isomer in the Supramolecular Compound $[Tb_2(H_2O)_8(C_6F_5COO)_6] \cdot 2C_6F_5COOH$

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Abstract—Complexes $Ln(Phen)(C_6F_5COO)_3$ (Ln = Tb, Eu; Phen = 1,10-phenanthroline) (**I**, **II**) are synthesized. At 300 K these complexes and compounds $Ln(C_6F_5COO)_3 \cdot nH_2O$ (Ln = Tb, n = 2; Ln = Eu, n = 1) (**III**, **VI**) possess photoluminescence (bright in the case of **I** and **II**). In the spectrum of compound **I** the line at 545 nm (transition $^5D_4 \longrightarrow {}^7F_5$) is most intense, whereas in the spectrum of compound **II** the most intense is the line at 613 nm (transition $^5D_0 \longrightarrow {}^7F_2$). The replacement of Phen by water decreases the luminescence intensity. The compound $[Tb_2(H_2O)_8(C_6F_5COO)_6] \cdot 2C_6F_5COOH$ (**IV**) is synthesized. According to the X-ray diffraction data, in structure **IV** the molecules of the binuclear Tb(III) complex with the C_6F_5COOH molecules form a supramolecular ensemble due to hydrogen bonding. The $C_6F_5COO^-$ ligands perform the monodentate and bidentate bridging function, resulting in the opening of the eight-membered cycle $Tb_2C_2O_4$. The TbO_8 polyhedron is a distored tetragonal antiprism. The crystals of the binuclear complex $[Tb_2(H_2O)_8(C_6F_5COO)_6]$ (**V**) are obtained in which the $C_6F_5COO^-$ ligands are monodentate and tridentate bridging cyclic, which results in the closure of two four-membered cycles TbO_2C and one four-membered cycle Tb_2O_2. The TbO_9 polyhedron is a distorted monocapped tetragonal antiprism.

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INTRODUCTION

Synthesis of lanthanide (**Ln**) complexes with organic ligands having a laser effect and luminescence properties is an urgent direction of coordination chemistry [1, 2]. Among the methods enhancing luminescence is the introduction of F atoms into the organic ligand [3–6] and the use of heteroligand complex formation of Ln chelates with heterocyclic nitrogen-containing ligands, especially 1,10-phenanthroline (**Phen**) [2]. Therefore, it is reasonable that Ln compounds with anions of perfluorocarboxylic acids are among the luminescent complexes. The luminescence of the Ln compounds with anions of aliphatic trifluoroacetic and pentafluoropropionic acids has been studied most completely [1, 7–11]. The Eu(III) compounds with heptafluorobutyrate and nanofluorovalerate anions were synthesized, and their luminescence was studied [11]. The Ln complexes with aromatic perfluorocarboxylic acids were studied to less extent. For example, the Eu(III) [11], Gd(III), Tb(III), and Dy(III) [12] compounds with pentafluorobenzoate anions were obtained. Compound $Eu(C_6F_5COO)_3 \cdot H_2O$ exhibits luminescence [11]. The Tb(III) complex with 2-fluorobenzoic acid and heteroligand compounds of this complex with Phen, 2,2'-Bipy, and 4,4'-Bipy have recently been synthesized, and their structures and luminescence were studied [13].

The purpose of the present work is to synthesize heteroligand complexes $Ln(Phen)(C_6F_5COO)_3$ (Ln = Tb, Eu) and to study their photoluminescence in comparison with that of earlier synthesized $Eu(C_6F_5COO)_3 \cdot H_2O$ [11] and $Tb(C_6F_5COO)_3 \cdot 2H_2O$ [12]. In addition, data on the structures of compounds of these lanthanides containing $C_6F_5COO^-$ ligands are of interest.

EXPERIMENTAL

The following reagents were used in the syntheses of the complexes: $TbCl_3 \cdot 6H_2O$, $Eu(NO_3)_3 \cdot 6H_2O$, propan-2-ol, an aqueous solution of NH_3, acetone, metha-

nol (reagent grade), and Phen · H_2O (analytical grade). Acid C_6F_5COOH was synthesized according to a described procedure [14].

Synthesis of Tb(Phen)(C_6F_5COO)$_3$ (I). A concentrated aqueous solution of NH_3 (6 ml) was added to a solution of $TbCl_3 \cdot 6H_2O$ (0.64 g, 1.7 mmol) in water (40 ml). The mixture was stirred for 30 min and left to stand in air. After a day, a precipitate of $Tb(OH)_3$ was filtered off on a glass filter with suction and washed with hot and cold waters until the pH of the washing waters became neutral. The wet precipitate was placed in a beaker, C_6F_5COOH (1 g, 4.7 mmol) was added, and the mixture was stirred with a glass stick. An acetone–CH_3OH (3 : 1) mixture (20 ml) was added, and stirring was continued for 30 min. A hydroxide excess was filtered off on a dense paper filter and washed with an acetone–CH_3OH mixture (2 × 10 ml). A solution of Phen · H_2O (0.34 g, 1.7 mmol) in propan-2-ol (10 ml) was added to the filtrate with stirring. A white precipitate was formed after several minutes. The mixture was stirred for 30 min, and then the precipitate was filtered off on a glass filter with suction, washed with acetone, and dried in air and in vacuo. The yield was 1.1 g (67%).

For $C_{33}H_8N_2F_{15}O_6Tb$				
anal. calcd, %:	C, 40.8;	H, 0.8;	N, 2.9;	F, 29.3.
Found, %:	C, 41.7;	H, 0.9;	N, 2.8;	F, 29.7.

Synthesis of Eu(Phen)(C_6F_5COO)$_3$ (II). A solution of $Eu(NO_3)_3 \cdot 6H_2O$ (0.35 g, 0.8 mmol) in water (5 ml) was added to a solution of KOH (0.2 g, 3.5 mmol) in water (5 ml). A precipitate of $Eu(OH)_3$ that formed was filtered off, washed with water to the neutral pH of the washing waters, and placed in a beaker with a solution of C_6F_5COOH (0.52 g, 2.45 mmol) in propan-2-ol (7 ml). The mixture was stirred, and the solution formed was filtered through a glass filter with suction. A solution of Phen · H_2O (0.16 g, 0.8 mmol) in propan-2-ol (5 ml) was added with stirring to the filtrate. After several minutes, a white precipitate was formed. The mixture was stirred for 10 min and left to stand in air to evaporate to a half of the solvent volume. The precipitate was filtered off on a dense paper filter, washed with ethanol, and dried in air and then in vacuo. The yield was 0.11 g (12%).

For $C_{33}H_8N_2F_{15}O_6Eu$				
anal. calcd, %:	C, 41.1;	H, 0.8;	N, 2.9;	F, 29.5.
Found, %:	C, 41.7;	H, 0.9;	N, 2.8;	F, 29.7.

Polycrystals of the $Tb(C_6F_5COO)_3 \cdot 2H_2O$ (**III**) complex were prepared by the reaction of $Tb(OH)_3$ with C_6F_5COOH according to a described procedure [12]. The crystals appropriate for X-ray diffraction analysis precipitated during the slow evaporation of the mother liquor, which contained acetone, propan-2-ol, and hexane as solvents and was obtained in the synthesis after a precipitate of complex **III** was separated. According to the elemental analysis data for this phase, the following content of elements was found (%): C, 29.6; H, 1.2; F, 33.9. The atomic ratio is C : F = 1.39, which corresponds to a ratio of 1.4 calculated for the empirical formulas $Tb(C_6F_5COO)_3 \cdot 4H_2O \cdot 0.5C_6F_5COOH$ and $Tb(C_6F_5COO)_3 \cdot 4H_2O \cdot C_6F_5COOH$. The X-ray diffraction data presented below indicate in favor of the second formula: compound $[Tb_2(H_2O)_8(C_6F_5COO)_6] \cdot 2C_6F_5COOH$ (**IV**) was obtained.

IR, cm^{-1}: 3635, 3533, 3382, 2924, 2854, 1689, 1627, 1576, 1495, 1434, 1399, 1379, 1121, 992, 770, 753, 724.

To obtain single crystals of terbium(III) pentafluorobenzoate hydrate, polycrystals of complex **III** were dissolved in water, and the solution was left to stand in air. The crystals suitable for X-ray diffraction analysis of the $[Tb_2(H_2O)_8(C_6F_5COO)_6]$ complex (**V**) stable in air were formed by slow evaporation.

Polycrystals of $Eu(C_6F_5COO)_3 \cdot H_2O$ (**VI**) were obtained using a described procedure [11].

Elemental analyses were carried out according to known procedures [11]. IR spectra were recorded on a Scimitar FTS 2000 spectrometer in the interval from 4000 to 400 cm^{-1} in Nujol and fluorinated oil. Photoluminescence spectra were obtained on an SDL-1 spectrometer. A DRSh-250 mercury lamp with the filter for 365 nm was used for luminescence excitation. The spectra were recorded using a FEU-62 photoelectron multiplier. Samples were prepared as pellets of equal surface areas using triturated polycrystals of the complexes. Photoluminescence spectra were measured at room temperature under standard conditions for all samples.

X-ray diffraction analysis. The unit cell parameters and reflection intensities for compounds **IV** and **V** were measured on a Bruker X8 APEX CCD automated diffractometer equipped with a two-coordinate detector (MoK_α-radiation, graphite monochromator, φ-scan mode for narrow frames) using a standard procedure at room temperature. The experimental details and crystallographic characteristics of compounds **IV** and **V** are given in Table 1. The structures were determined by a direct method and refined by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms (SHELX-97) [15]. The hydrogen atoms of the water molecules in the structures of compounds **IV** and **V** were located from the difference electron density synthesis and refined in the isotropic approximation together with non-hydrogen atoms. The full tables of coordinates of basal atoms, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (nos. 714786 and 714787; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) and are available from the authors. Selected interatomic distances and bond angles for compounds **IV** and **V** are listed in Table 2.

Table 1. Crystallographic characteristics and details of experiment and refinement for structures **IV** and **V**

Parameter	Value	
Empirical formula	$C_{56}H_{18}F_{40}O_{24}Tb_2$	$C_{42}H_{16}F_{30}O_{20}Tb_2$
Crystal system	Triclinic	Triclinic
a, Å	7.5860(2)	7.7216(7)
b, Å	12.9638(5)	9.5332(8)
c, Å	16.8846(6)	17.5243(16)
α, deg	79.312(1)	92.744(3)
β, deg	86.487(1)	97.279(2)
γ, deg	83.749(1)	99.797(2)
V, Å^3	1620.55(10)	1257.75(19)
Z; ρ(calcd), g/cm^3	1; 2.206	1; 2.282
μ, mm^{-1}	2.363	2.981
Crystal sizes, mm	0.08 × 0.08 × 0.04	0.26 × 0.12 × 0.07
Scan range, θ, deg	1.84–30.00	1.17–25.67
Number of measured reflections	14928	7469
Number of independent reflections	9168	4117
R_{int}	0.0150	0.0218
Number of reflections with $I > 2\sigma(I)$	8409	3570
Number of refined reflections	586	456
Goodness-of-fit for F^2	1.065	1.102
R factor, $I > 2\sigma(I)$		
R_1	0.0188	0.0331
wR_2	0.0439	0.0857
R factor (for all I_{hkl})		
R_1	0.0229	0.0460
wR_2	0.0455	0.1023
Residual electron density (min/max), e Å^{-3}	1.071/–0.805	1.663/–1.361

RESULTS AND DISCUSSION

Heteroligand compounds **I** and **II** were obtained by the reactions of Tb(III) and Eu(III) pentafluorobenzoates with Phen in organic solvents. Polycrystals of complex **III** were isolated according to a described procedure [12]. The X-ray diffraction results for a single crystal of the solid phase isolated by the slow evaporation of the mother liquor, which was obtained after a precipitate of complex **III** was separated, indicates the formation of compound **IV**: $[Tb_2(H_2O)_8(C_6F_5COO)_6] \cdot 2C_6F_5COOH$. The experimental diffraction pattern of the crystals of the solid phase is consistent with that calculated from the X-ray diffraction data. The presence of the $[Tb_2(H_2O)_8(C_6F_5COO)_6]$ complex in compound **IV** stimulated us to grow crystals of this complex from an aqueous solution of compound **III**. The X-ray diffraction data for the single crystal confirmed a possibility to obtain individual complex **V**.

Structure **IV** is formed from symmetric molecules of the binuclear complex $[Tb_2(H_2O)_8(C_6F_5COO)_6]$ and C_6F_5COOH molecules (Fig. 1a), whereas structure **V** is built of molecules of the complex of analogous composition (Fig. 1b).

In the binuclear complex in compound **IV**, the coordination number of Tb^{3+} ions is eight. Each Tb^{3+} ion coordinates two O atoms of the bidentate bridging ligand-anions $C_6F_5COO^-$, two O atoms of the monodentate ligands $C_6F_5COO^-$, and four O atoms of the water molecules. The appreciably different Tb–O bond lengths in the bridging ligands are 2.304(1) and 2.424(1) Å. The bridging function of two $C_6F_5COO^-$ ligands produces the eight-membered cycle $Tb_2C_2O_4$ (Tb···Tb 4.812(2) Å). The coordination polyhedron of the Tb atom can be presented as a distorted tetragonal antiprism. The average deviation of the atoms in the quadrilateral faces of the prism formed by the O(2)O(3)O(11)O(12) and O(1)O(4)O(13)O(23) atoms is 0.105 and 0.209 Å, respectively. The distortion of the antiprism is that these faces arranged at an angle of 2.8° to each other are not planar but have inflections at the O(3)–O(11) and O(13)–O(23) edges to form dihedral angles of 12.6° and 21.4°. The C_6F_5 cycles of three independent $C_6F_5COO^-$ ligands are nearly planar: the average deviation of the C and F atoms from their planes (**Δ**) is 0.037(2), 0.006(2), and 0.013(2) Å. The C_6F_5 cycle of pentafluorobenzoic acid is also planar (Δ = 0.013(2) Å). The carboxy group of this acid is joined with the H atoms of two water molecules and the noncoordinated O atom of the monodentate $C_6F_5COO^-$ ligand by a strong hydrogen bond O(5)–H···O(21) and weaker hydrogen bonds O(4)–H···O(6) and O(2)–H···O(6) (O(5)···O(21) 2.543(2), O(4)···O(6) 2.877(2), and O(2)···O(6) 2.895(2) Å). The character of bonding between the $[Tb_2(H_2O)_8(C_6F_5COO)_6]$ and C_6F_5COOH molecules in crystal **IV** makes it possible to ascribe this structure to the supramolecular ensemble [16]. The maximum size of the molecule of the binuclear complex in the ensemble is 1.97 nm, which corresponds to the F(52)···F(52)' distance.

The IR spectrum of C_6F_5COOH contains very intense band at 1713 cm^{-1} attributed to ν(C=O). The spectrum of complex **IV** exhibits no band at this frequency, but the band at 1689 cm^{-1} is observed. It is most likely that this band corresponds to the stretching vibration of the C=O group connected to the water molecule by the strong hydrogen bond. The high-frequency bands are assigned to stretching vibrations of the OH groups of the water and acid molecules.

The molecular packing of $[Tb_2(H_2O)_8(C_6F_5COO)_6]$ and C_6F_5COOH in structure **IV** (projection to the plane

Table 2. Selected interatomic distances and bond angles in the structures of compounds **IV** and **V***

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
IV							
Tb(1)–O(11)	2.293(1)	Tb(1)–O(13)	2.424(1)	C(11)–C(21)	1.509(3)	O(23)–C(13)	1.241(2)
Tb(1)–O(23)	2.304(1)	Tb(1)–O(4)	2.444(1)	O(12)–C(12)	1.251(2)	C(13)–C(23)	1.513(2)
Tb(1)–O(12)	2.389(1)	Tb(1)–O(1)	2.473(1)	O(22)–C(12)	1.244(2)	O(5)–C(1)	1.290(2)
Tb(1)–O(3)	2.392(1)	O(11)–C(11)	1.246(2)	C(12)–C(22)	1.517(2)	O(6)–C(1)	1.224(2)
Tb(1)–O(2)	2.415(1)	O(21)–C(11)	1.248(2)	O(13)–C(13)	1.245(2)	C(1)–C(2)	1.496(3)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(11)Tb(1)O(23)	147.49(5)	O(12)Tb(1)O(2)	122.06(5)	O(23)Tb(1)O(4)	72.97(5)	O(3)Tb(1)O(1)	139.01(5)
O(11)Tb(1)O(12)	77.09(5)	O(3)Tb(1)O(2)	77.60(6)	O(12)Tb(1)O(4)	135.95(5)	O(2)Tb(1)O(1)	137.26(5)
O(23)Tb(1)O(12)	77.54(5)	O(11)Tb(1)O(13)	86.11(5)	O(3)Tb(1)O(4)	76.03(5)	O(13)Tb(1)O(1)	69.78(5)
O(11)Tb(1)O(3)	106.99(6)	O(23)Tb(1)O(13)	102.15(5)	O(2)Tb(1)O(4)	70.77(5)	O(4)Tb(1)O(1)	128.46(5)
O(23)Tb(1)O(3)	81.50(5)	O(12)Tb(1)O(13)	142.38(5)	O(13)Tb(1)O(4)	76.56(5)	C(11)O(11)Tb(1)	163.9(1)
O(12)Tb(1)O(3)	67.76(5)	O(3)Tb(1)O(13)	149.86(5)	O(11)Tb(1)O(1)	76.30(5)	C(12)O(12)Tb(1)	139.0(1)
O(11)Tb(1)O(2)	70.42(5)	O(2)Tb(1)O(13)	81.76(5)	O(23)Tb(1)O(1)	77.29(5)	C(13)O(13)Tb(1)	115.1(1)
O(23)Tb(1)O(2)	141.47(5)	O(11)Tb(1)O(4)	139.26(5)	O(12)Tb(1)O(1)	73.60(5)		
V							
Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Tb(1)–O(11)	2.326(5)	Tb(1)–O(3)	2.423(4)	O(12)–C(12)	1.255(7)	C(11)–C(21)	1.511(9)
Tb(1)–O(12)	2.341(4)	Tb(1)–O(23)	2.490(4)	O(13)–C(13)	1.224(8)	C(12)–C(22)	1.510(8)
Tb(1)–O(4)	2.393(5)	Tb(1)–O(1)	2.516(4)	O(21)–C(11)	1.231(8)	C(13)–C(23)	1.514(8)
Tb(1)–O(13)'	2.401(5)	Tb(1)–O(13)	2.765(4)	O(22)–C(12)	1.253(8)		
Tb(1)–O(2)	2.395(5)	O(11)–C(11)	1.258(8)	O(23)–C(13)	1.252(8)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(11)Tb(1)O(12)	108.8(2)	O(11)Tb(1)O(3)	75.9(2)	O(11)Tb(1)O(4)	72.8(2)	O(12)Tb(1)O(3)	68.6(2)
O(12)Tb(1)O(4)	139.3(2)	O(4)Tb(1)O(3)	72.8(2)	O(11)Tb(1)O(13)'	145.6(2)	O(13)'Tb(1)O(3)	77.1(2)
O(12)Tb(1)O(13)'	80.4(2)	O(2)Tb(1)O(3)	118.1(2)	O(4)Tb(1)O(13)'	79.0(2)	O(11)Tb(1)O(23)	84.1(2)
O(11)Tb(1)O(2)	69.6(2)	O(12)Tb(1)O(23)	140.8(1)	O(12)Tb(1)O(2)	76.0(2)	O(4)Tb(1)O(23)	79.5(2)
O(4)Tb(1)O(2)	135.8(2)	O(13)'Tb(1)O(23)	110.1(2)	O(13)'Tb(1)O(2)	143.6(2)	O(2)Tb(1)O(23)	74.5(2)
O(3)Tb(1)O(23)	149.5(2)	O(4)Tb(1)O(13)	66.6(2)	O(11)Tb(1)O(1)	137.6(2)	O(2)Tb(1)O(13)	115.6(2)
O(12)Tb(1)O(1)	72.9(2)	O(3)Tb(1)O(13)	126.1(2)	O(4)Tb(1)O(1)	134.2(2)	O(1)Tb(1)O(13)	67.3(2)
O(13)'Tb(1)O(1)	76.7(2)	O(11)Tb(1)C(13)	103.0(2)	O(2)Tb(1)O(1)	70.1(2)	O(12)Tb(1)C(13)	141.1(2)
O(3)Tb(1)O(1)	136.3(2)	O(4)Tb(1)C(13)	71.3(2)	O(23)Tb(1)O(1)	73.3(2)	O(3)Tb(1)C(13)	142.5(2)
O(11)Tb(1)O(13)	121.1(1)	C(13)O(23)Tb(1)	100.7(4)	O(12)Tb(1)O(13)	129.8(2)	O(21)C(11)O(11)	124.3(6)
O(1)Tb(1)C(13)	68.6(2)	O(11)C(11)C(21)	116.6(6)	O(2)Tb(1)C(13)	95.4(2)		

* The C–C and C–F bond lengths vary in the intervals 1.367(4)–1.393(3) and 1.328(3)–1.341(3) Å for **IV** and 1.357(9)–1.396(9) and 1.324(8)–1.351(9) Å for **V**.

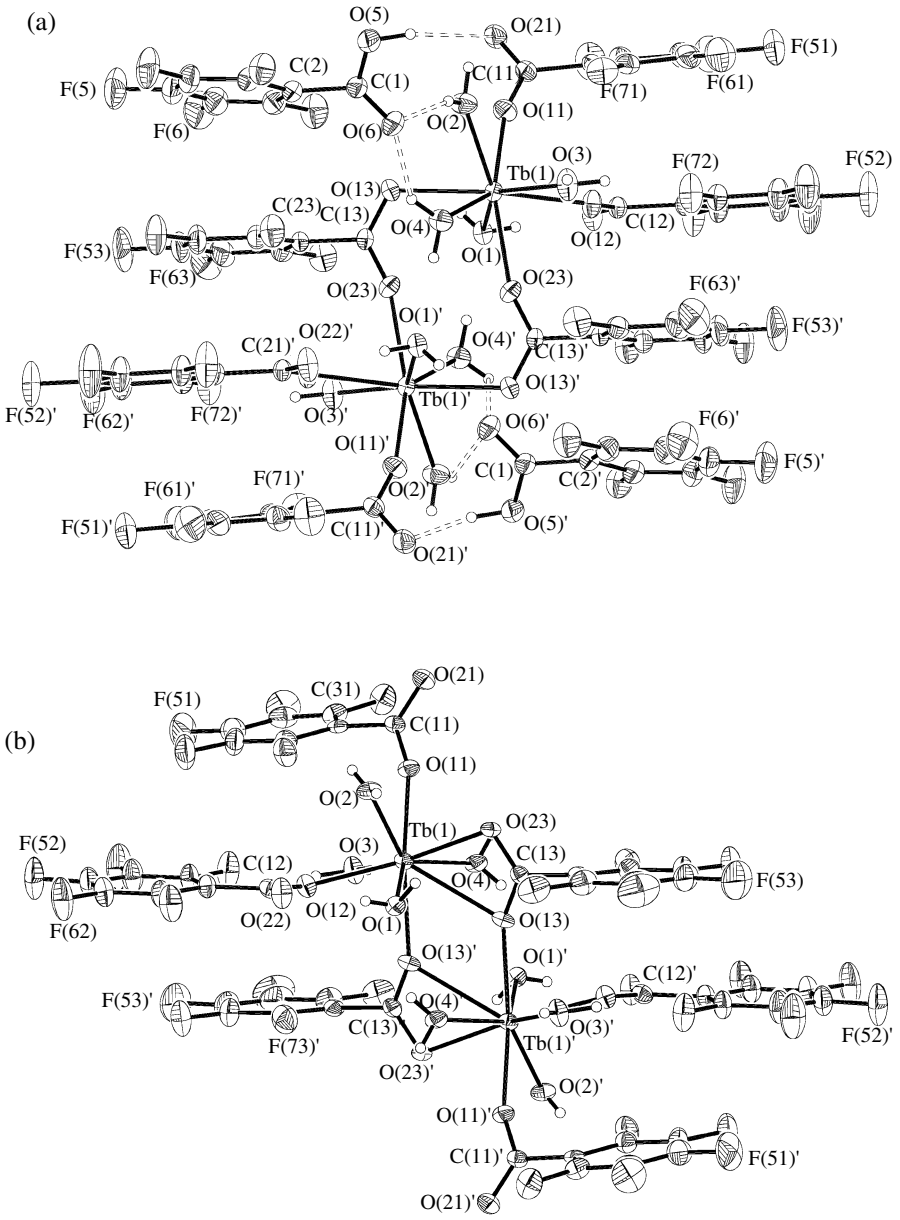

Fig. 1. Structures of the (a) supramolecular ensemble in the structure of compound **IV** and (b) binuclear molecule of complex **V** with designations of non-hydrogen atoms. The thermal ellipsoids are shown with the 40% probability.

(100)) is shown in Fig. 2a. The molecules are arranged in the layer parallel to the plane (001). It is seen that both the considered above C_6F_5 cycles in compound **IV** and the C_7F_5 fragments including the C atom of the carboxy group are also planar. We analyzed a possibility of the appearance of π–π interactions between the adjacent C_7F_5 fragments. The results of calculations of the parameters characteristic of these interactions [17] are given in Table 3. Their analysis showed that the π–π interactions can occur only between some sufficiently overlapped C_7F_5 fragments (given by bold in Table 3). In other cases, these fragments are overlapped at the peripheral part, which creates conditions only for closer contacts between atoms of the fragments. Selected data from Table 3 for compound **IV** are illustrated in Fig. 3.

In complex **V** the Tb^{3+} ion coordinates four O atoms of the water molecules, two O atoms of two monodentate ligands, and three O atoms of two tridentate bridging cyclic $C_6F_5COO^-$ ligands (Fig. 1b). The coordination results in the formation of two four-membered TbO_2C chelate cycles and the four-membered Tb_2O_2 metallocycle rather than the formation of one cycle as in compound **IV**. The shortest bonds of the Tb atoms with the O atoms of the monodentate $C_6F_5COO^-$

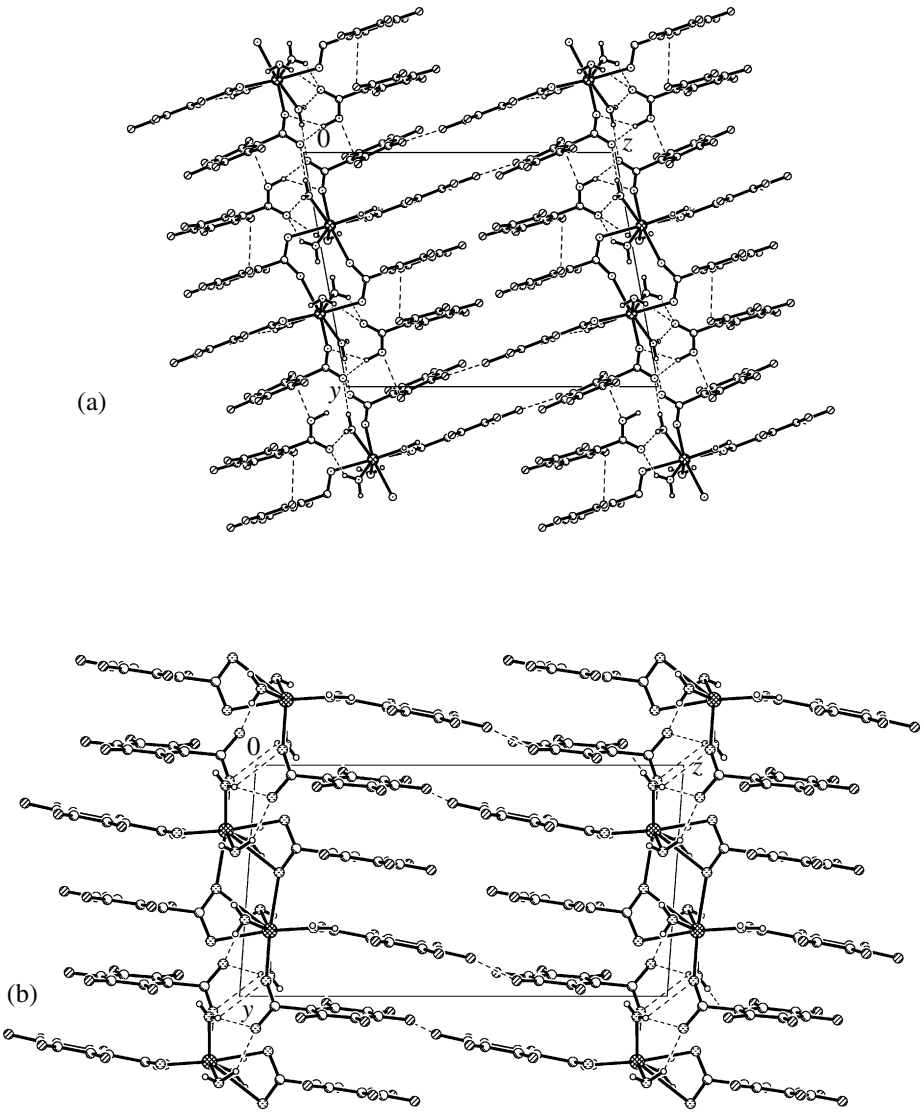

Fig. 2. Projections of crystal structures (a) **IV** and (b) **V** onto the plane (100). The hydrogen bonding system is shown by dashed lines.

ligands are Tb(1)–O(11) 2.326(5) and Tb(1)–O(12) 2.341(4) Å. The distances between the Tb atoms and the bridging O(13) and O(13)' atoms of the tridentate ligands are considerably longer and differ strongly (2.765(4) and 2.401(5) Å, Δ = 0.364 Å). The Tb(1)–O(23) and Tb(1)'–O(23)' distances are intermediate: 2.490(4) Å. An elongated distance of 2.765(4) Å should be taken into account when estimating the coordination number of the Tb^{3+} ion. The tridentate bridging cyclic function of the carboxylate ligands in the complexes with strongly different Ln–O distances is described [18]. For instance, in $(CN_3H_6)[Ce(CH_3COO)_4] \cdot H_2O$ the distances from Ce to O_{bridg} are 2.48 and 2.80 Å, indicating that the elongated bond is weak [19]. At the same time, this bond was taken into account in the determination of the coordination number of the Ce atom [19]. The considerable difference in the Tb–O bond lengths of the Tb_2O_2 metallocycle was also found for the $[Tb_2(H_2O)_2(2\text{-}FC_6H_4COOH)_2(2\text{-}FC_6H_4COO)_6]$ complex (2.316(8) and 2.668(8) Å, Δ = 0.352 Å) [13]. The authors also included the elongated bond in the estimation of the coordination number of the Tb atom equal to nine. We believe that in complex **V** synthesized by us the coordination number of the Tb^{3+} ions is 9 (8 + 1). Different coordination functions of the ligands distort the coordination polyhedron, which can be presented as a distorted monocapped tetragonal antiprism. One of the bases of the antiprism formed by the O(2)O(11)O(3)O(12) atoms is almost planar (Δ = 0.059 Å). For two coordination polyhedra in complex **V**, the O(13)···O(13)' edge is common. The Tb…Tb distance in compound **V** (4.437(2) Å) is considerably

Table 3. Characteristics of the C_7F_5 fragments and parameters of their interactions in crystal structures **IV** and **V***

No. of fragment and its constituent atoms	Δ, Å	Interacting planes	φ, deg	⟨*d*⟩, Å	*r*, Å	Δ*r*, Å
			IV			
1. C(11)–F(71)	**0.036(2)**	**1–2**	**7.77(3)**	**3.33**	**3.834**	**1.900**
2. C(12)–F(72)	0.006(2)	2–3	3.25(2)	3.28	4.845	3.566
3. C(13)–F(73)	**0.013(2)**	**3–4**	**5.22(2)**	**3.35**	**4.138**	**2.429**
4. C(1)–F(7)	0.027(2)	4–5	15.70(3)	3.12	4.957	3.852
5. C(11)'–F(71)'	0.036(2)					
			V			
1. C(12)–F(72)	0.015(7)	1–2	8.22(5)	3.36	4.858	3.509
2. C(11)–F(71)	**0.031(6)**	**2–3**	**7.26(5)**	**3.29**	**4.340**	**2.829**
3. C(13)–F(73)	0.014(7)	3–4	3.16(6)	3.24	4.974	3.771
4. C(12)'–F(72)'	0.015(7)					

* Δ is the average deviation of the atoms from the plane of the C_7F_5 fragment; φ and *d* are the angle and average distance between the planes of the fragments; *r* is the intercenter distance; and Δ*r* is the shift of the centers of the fragments relative to each other.

shorter than that in compound **IV** (Δ = 0.375 Å). It is most likely that this "compression" is caused by the formation in compound **V** of two additional relatively weak coordination bonds Tb(1)–O(13) and Tb(1)'–O(13)' in the eight-membered cycle. The C_7F_5 fragments are partially overlapped in compound **IV** and also in the structure of complex **V** (Table 3).

The mutual arrangement of molecules of binuclear complexes in crystal **V** is shown in Fig. 2b in the projection onto the plane (100). The coordinated water molecules between the complex molecules form hydrogen bonds with the O atoms of the monodentate $C_6F_5COO^-$ ligands forming layers parallel to the (001) plane (O(4)···O(21) 2.775(7), O(4)···O(1) 2.803(7) Å). One

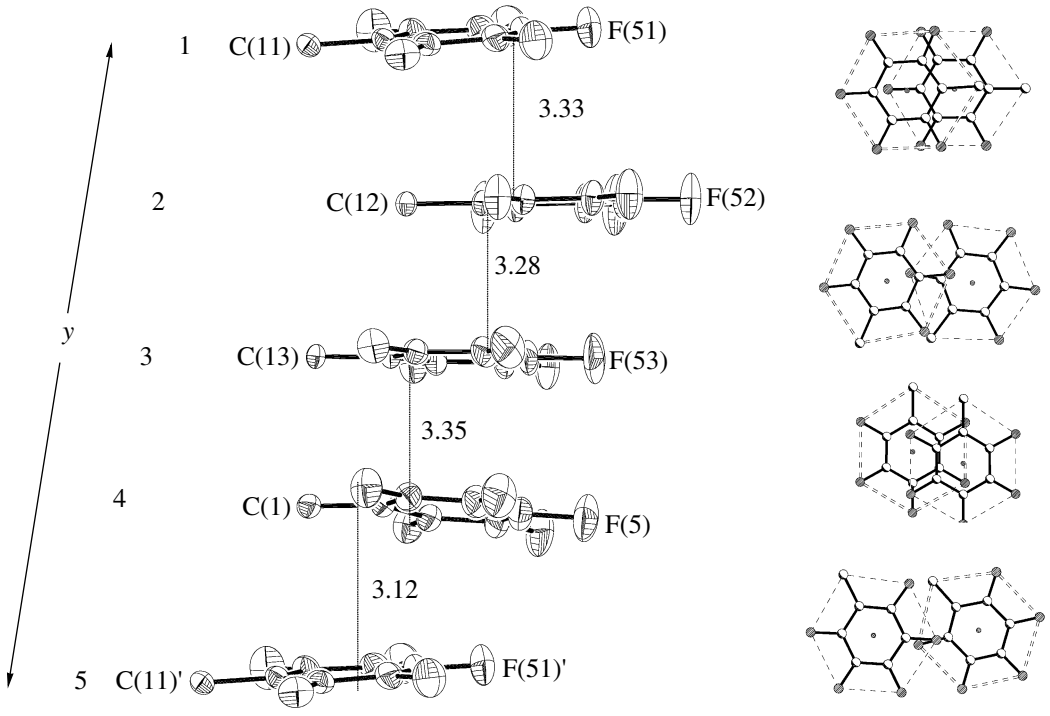

Fig. 3. Arrangement of the C_7F_5 fragments in the structure of compound **IV** in projection onto the plane (100), the average interplanar distances (Å) between them, and the degree of overlapping of the adjacent C_7F_5 fragments in projection onto the statistical mean plane.

layer falls on one unit cell (Fig. 2b), and the next layer is translationally identical. The layers are bound by nonvalent contacts F(51)···F(42) 2.663(7) and F(61)···F(52) 2.793(9) Å (doubled van der Waals radius of the F atom 2.91 Å).

The composition of the $[Tb_2(H_2O)_8(C_6F_5COO)_6]$ complex remains unchanged on going from compound **IV** to **V**. However, the X-ray diffraction data indicate that the $[Tb_2(H_2O)_8(C_6F_5COO)_6]$ molecules have different structures in complex **V** and in supramolecular compound **IV**. The formation of an ensemble of molecules of complex **V** and C_6F_5COOH results in the cleavage of two weak Tb–O bonds, which makes it possible to obtain the isomeric form of the complex as a fragment of supramolecular compound **IV**.

The IR spectra of compounds **I** and **II** exhibits no bands in the region 4000–3200 cm^{-1}, indicating that they contain no water. We failed to grow single crystals of these compounds. It is most likely that their structures are binuclear similar to those determined by the X-ray diffraction method for $[Tb_2(Phen)_2(2\text{-}FC_6H_4COO)_6]$ [13] and $[Dy_2(Phen)_2(C_6H_5COO)_6]$ [20]. In these complexes, the Phen molecules are bidentate cycle-forming ligands and the $C_6H_5COO^-$ anions perform different ligand functions.

The study of the luminescence properties of complexes **I**–**III** and **VI** showed that Phen-containing heteroligand complex **I** at 300 K and λ_{exc} = 365 nm has bright photoluminescence characteristic of Tb^{3+} ions [21]. The photoluminescence spectrum contains narrow bands (lines) corresponding to the transitions in the Tb^{3+} ions at wavelengths of 490 (transition $^5D_4 \longrightarrow {}^7F_6$), 545 ($^5D_4 \longrightarrow {}^7F_5$), 584 ($^5D_4 \longrightarrow {}^7F_4$), 620 ($^5D_4 \longrightarrow {}^7F_3$), 650 ($^5D_4 \longrightarrow {}^7F_2$), and 670 nm ($^5D_4 \longrightarrow {}^7F_1$) (Fig. 4a). The "green" line corresponding to the $^5D_4 \longrightarrow {}^7F_5$ transition is most intense. The intensity of spectral lines of the transitions $^5D_4 \longrightarrow {}^7F_6$, $^7F_4$, $^7F_3$ estimated from the maximum intensity value (I_{max}) is 30% of I_{max} of the $^5D_4 \longrightarrow {}^7F_5$ transition. The contribution to the emission of the transitions $^5D_4 \longrightarrow {}^7F_2$, $^7F_1$ is small. The position of the above listed lines in the spectrum of water-containing complex **III** does not differ from the position of lines in the spectrum of complex **I** (Fig. 4b). However, the replacement of the Phen molecule by water molecules decreased the photoluminescence intensity. The intensity of the brightest "green" line (transition $^5D_4 \longrightarrow {}^7F_5$) in the spectrum of complex **III** decreased by 18%, and the intensity of lines of the transitions $^5D_4 \longrightarrow {}^7F_6$, $^7F_4$, $^7F_3$ decreased more substantially (by 45%). This changed the ratio of the I_{max} values of these lines to I_{max} of the "green" line. For compound **III** this ratio is 0.2.

Heteroligand Phen-containing complex **II** at 300 K and λ_{exc} = 365 nm has bright photoluminescence characteristic of Eu^{3+} ions [21]. The photoluminescence spectrum exhibits lines corresponding to the transitions

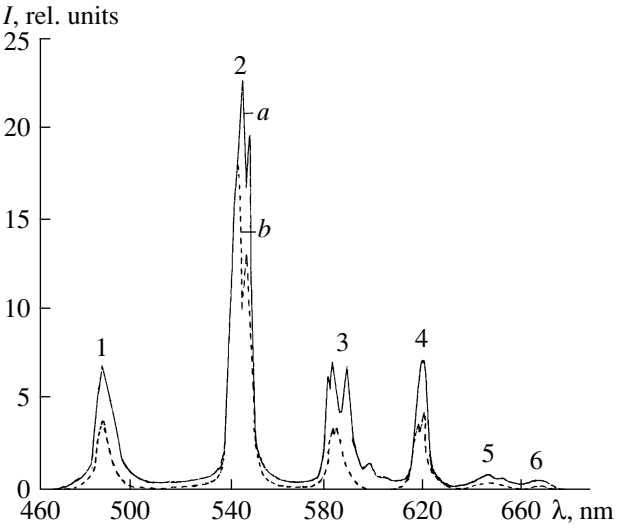

Fig. 4. Photoluminescence spectra of terbium(III) compounds (*a*) **I** and (*b*) **III** at 300 K and λ_{exc} = 365 nm. The spectral lines correspond to the radiative transitions of the Tb^{3+} ion: (1) $^5D_4 \longrightarrow {}^7F_6$, (2) $^5D_4 \longrightarrow {}^7F_5$, (3) $^5D_4 \longrightarrow {}^7F_4$, (4) $^5D_4 \longrightarrow {}^7F_3$, (5) $^5D_4 \longrightarrow {}^7F_2$, and (6) $^5D_4 \longrightarrow {}^7F_1$.

in the Eu^{3+} ions at the wavelengths 580 (transition $^5D_0 \longrightarrow {}^7F_0$), 593 (transition ($^5D_0 \longrightarrow {}^7F_1$), 613 (transition $^5D_0 \longrightarrow {}^7F_2$), 650 (transition $^5D_0 \longrightarrow {}^7F_3$), and 700 nm (transition $^5D_0 \longrightarrow {}^7F_4$) (Fig. 5a). The "red" line (transition $^5D_0 \longrightarrow {}^7F_2$) has the maximum intensity. The ratios of the I_{max} values of the lines of the $^5D_0 \longrightarrow {}^7F_2$ and $^5D_0 \longrightarrow {}^7F_4$ transitions to I_{max} of the line of the transition $^5D_0 \longrightarrow {}^7F_1$ are 4.7 and 2.6, respectively. The intensities of the lines of the transitions $^5D_0 \longrightarrow {}^7F_0$, $^7F_3$ are low. The position of the most intense lines in the spectrum of water-containing complex **VI** somewhat differs from that for complex **II**. For example, the lines of the transitions $^5D_0 \longrightarrow {}^7F_1$, $^7F_2$, $^7F_4$ are observed at λ = 590, 619, and 696 nm, respectively (Fig. 5b). As in the case of complexes **I** and **III**, the replacement of Phen by water decreases the photoluminescence intensity, this decrease being stronger. The I_{max} value of the "red" line (transition $^5D_0 \longrightarrow {}^7F_2$) of complex **II** is 12.8 times higher than I_{max} of the analogous line for compound **VI**. An increase in the photoluminescence intensity for several Eu(III) complexes upon Phen coordination was observed [22–24].

The line intensity in the photoluminescence spectrum of complex **II** is fourfold higher than that in the spectrum of complex **I** also containing Phen. It is assumed that Phen in the Eu(III) complexes behaves as a sensitizer of Eu^{3+} ion radiation [21]. In the diagram of triplet levels of Phen and excited $^5D_0$ levels of the Eu^{3+} ions, the levels of Phen lie in energy somewhat higher than the $^5D_0$ levels, which can result in the efficient

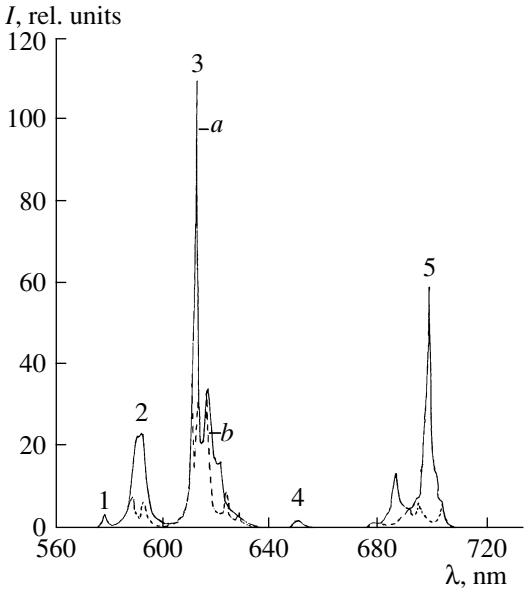

Fig. 5. Photoluminescence spectra of europium(III) compounds (*a*) **II** and (*b*) **VI** at 300 K and λ_{exc} = 365 nm. The spectral lines correspond to the radiative transitions of the Eu^{3+} ion: (1) $^5D_0 \longrightarrow {}^7F_0$, (2) $^5D_0 \longrightarrow {}^7F_1$, (3) $^5D_0 \longrightarrow {}^7F_2$, (4) $^5D_0 \longrightarrow {}^7F_3$, and (5) $^5D_0 \longrightarrow {}^7F_4$. The intensity of the spectral lines of compound **VI** is amplified by 4.2 times.

energy transfer from the Phen levels to the $^5D_0$ levels of the Eu^{3+} ions [21]. This can substantially increase photoluminescence of the Phen-containing Eu(III) complexes. The excited $^5D_4$ levels of the Tb^{3+} ions lie in energy higher than the triplet levels of the Phen molecules, decreasing the efficiency of the energy transfer from the Phen molecules to the $^5D_4$ levels of the Tb^{3+} ions. This corresponds to the lower photoluminescence intensity of complex **I** compared to that of complex **II**.

The present study indicates that the further synthesis of luminescent heteroligand Ln complexes containing pentafluorobenzoate anions and nitrogen heterocycles as ligands is promising.

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