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Role of alkyl substituents in the structure and luminescence properties of discrete terbium(III)-lithium(I) B-Diketonates



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1. Introduction

Metal complexes based on trivalent lanthanide (Ln) ions are regarded as highly luminescent materials combining the characteristic spectral range, narrow-band emission and long lifetimes [1-10]. However, to optimize the luminescent properties of Ln (III) complexes it is often necessary to fine-tuning the molecular structure of organic ligands. Therefore, the use of ligands, which can be readily modified, is a platform for identifying more specific characteristics affecting the properties of molecular complexes of rare earth metals. In this context, 1,3-diketones are among the most versatile and extensively used structural units in coordination chemistry. The variation of substituents in 1,3-dicarbonyl fragment as well as the co-ligands participating in the formation of metal complexes allows the "structure-property" relationships to be controlled efficiently [11,12].

Incorporation of polyfluoroalkyl groups in 1,3-dicarbonyl moiety significantly changes the properties of both the ligands and coordination compounds based on them [13]. Replacing a hydrocarbon substituent by fluorocarbon one is reported to result in better crystallization of metal complexes from the organic solvents [14-18]. As compared to C–H bonds, C-F bonds decrease the vibrational relaxation processes, which dramatically influence the photophysical

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ABSTRACT

Functionalized perfluoroalkyl lithium β -diketonates LiL react with terbium (III) salts in methanol to give heterobimetallic complexes of general formula [(TbL₃)(LiL)(MeOH)]. The length of both fluoroalkyl and hydrocarbon substituents in ligand was found to affect the crystal packing of metal complexes. Photoluminescence of heterobimetallic β -diketonates in the solid state is reported.

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properties of luminescent materials [12]. The elongation of fluorocarbon chain in the series of Eu (III) β -diketonates was shown to be an efficient approach to increase the fluorescence lifetimes [19]. Moreover, fluorine atoms or polyfluoroalkyl groups often participate in intra- and intermolecular interactions thereby providing the special organization of crystal structure in metal complexes. Short F...X contacts (where X = H, F, π -system, etc.) can modify not only the geometry of a molecule, but the crystal packing as well [20].

Previously we have reported on the synthesis of heterobimetallic complexes with general formulas $[LnL_3 \cdot LiL \cdot (sol)]$ (Ln = Eu(III), Tb (III), Dy (III), sol = MeOH, H_2O and $[LiLnL_4(CH_3CN)]$ (Ln = Eu (III), Tb(III)) based on the original functionalized lithium $CF_3-\beta$ -diketonate (LiL) (Fig. 1) [21,22]. These coordination compounds were the first examples of Ln-Li heterobimetallic β diketonates for which the crystal structure were identified by XRD analysis. Interestingly, the structure of [LnL₃·LiL·(sol)] differed from the well-known Ln(III) tris- and tetrakis- β -diketonates. Moreover, a number of [LnL₃·LiL·(MeOH)] complexes exhibited bright (mechano)luminescence [21]. In this work, we have studied the effect of the substituents in the dicarbonyl moiety on the structure and luminescent properties of bimetallic Tb(III)-Li β -diketonates. Increasing the length of the fluoroalkyl group or hydrocarbon chain provokes a change in both the geometry of molecules and intermolecular interactions - two main factors responsible for the "structure-property" relationships.



Fig. 1. Diketonate-anions used for the synthesis of Tb(III) complexes.

2. Experimental

2.1. Materials

All procedures associated with the synthesis of new ligands and complexes were carried out in air using commercial reagents (TbCl₃·6H₂O (99.99%), lithium hydride (97%) and 1,2-dimethoxyethane (99%) (Alfa Aesar); Tb(OAc)₃·xH₂O (99.99%), methanol (99.9%) (Sigma Aldrich); ethyl trifluoroacetate CF₃CO₂Et (99%) and ethyl pentafluoropropionate C₂F₅CO₂Et (98% min) (P&M Invest)).

2.2. Physicochemical measurements

¹H, ¹⁹F and ¹³C NMR spectra were recorded on AVANCE-500 spectrometer in DMSO– d_6 using Me₄Si and C₆F₆ as internal standards. In ¹H NMR spectra the solvent residual signals observed at δ 2.52 (DMSO) and 3.43 (water) ppm. IR diffuse-reflectance spectra

Crystal	structure	data	for	terbium(III)	complexes.
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were recorded with a Perkin-Elmer Spectrum One FTIR instrument in the range 400–4000 cm⁻¹ at a resolution of 4 cm⁻¹ (32 scan collected). Elemental analysis was performed using a Perkin Elmer PE 2400 Series II analyzer.

The UV-Visible transmittance spectrum was performed with UV-2600 Shimadzu spectrometer from 200 to 800 nm. Photoluminescence properties were analyzed by a Varian Cary Eclipse fluorescence spectrophotometer with mutually perpendicular beams. Phosphorescence was measured in the solid state, quartz glass with the crystals of complex was turned 50° away from the detector window to avoid reflections. The spectrophotometer was equipped with a 15 W xenon pulse lamp, Czerny-Turner monochromators, photomultiplier tube. The photomultiplier detector voltage was 600 V and the instrument excitation and emission slits were set at 5 and 5 nm, respectively. The lifetime were measured on a Varian Cary Eclipse fluorescence spectrophotometer with a microsecond flash lamp (pulse length: 2 μ s).

X-ray diffraction studies of the single crystals of **3** and **4** were carried out on an Xcalibur 3 diffractometer (Oxford Diffraction, UK) with CCD detector according to standard procedure [monochromatized Mo K α radiation; ω -scanning with a step 1° at 295(2) K]. A correction for absorption was applied empirically. The structures were solved by the direct statistical method and refined by fullmatrix least-squares method (with F^2) in an anisotropic approximation for all non-hydrogen atoms except those for the disordered fragments. Hydrogen atoms were added in calculated positions and refined in an isotropic approximation in the "riding" model. All calculations were performed using Olex shell [23] and SHELX program package [24]. The main crystallographic data and experimental details are collected in Table 1.

2.3. Synthesis of the ligands and the complexes

3,3-Dialkoxybutane-2-ones were prepared from 2,3butanedione (97%, Alfa Aesar) and the corresponding trialkyl orthoformate. Lithium β -diketonates **1**, **2** were synthesized by following the reported literature procedures [25,26].

	3	4	
	[IbL' ₃ ·LiL'·(MeOH)]	[IbL ² ₃ ·LiL ² ·(MeOH)]	[IDL ₃ ·LIL·(MeOH)]*
Chemical formula	C37H44F20LiO17Tb	C41H60F12LiO17Tb	C33H44F12LiO17Tb
Formula wt. (g/mol)	1306.58	1218.75	1106.54
Crystal size (mm)	$0.41\times0.33\times0.24$	$0.47\times0.38\times0.26$	$0.25\times0.20\times0.15$
Crystal system	Triclinic	Orthorombic	Monoclinic
Space group	PĪ	$P2_12_12_1$	Pn
a (Å)	11.1998(5)	13.7132(7)	12.1678(6)
b (Å)	11.5161(5)	15.4941(12)	12.1989(3)
c (Å)	22.8908(8)	26.5653(16)	15.8643(5)
α (°)	75.995(3)	90	90
β (°)	77.089(3)	90	94.541(4)
γ(°)	70.763(4)	90	90
Volume (Å ³)	2671.22(19)	5644.4(6)	2347.41(15)
Z	2	4	2
d (calc., g/cm³)	1.624	1.434	1.566
Abs. coeff. (mm ⁻¹)	1.455	1.352	1.443
Theta range (deg.)	3.63 to 25.56	3.77 to 26.70	1102
Reflections collected	26,295	24,986	13,147
Data/restraints/param.	14,280/396/1032	13,658/184/773	6641/134/707
R(int) [indep. refl.]	0.054	0.0464	0.030
R1, wR2 [($I > 2\sigma(I)$]	0.0626, 0.1309	0.0490, 0.1041	0.0344, 0.0792
R1, wR2 (all data)	0.1179, 0.1763	0.0810, 0.1385	0.0453, 0.0871
Goodness of fit	1.019	1.005	1.002
Largest diff. peak/hole (eÅ ⁻³)	1.042/-1.271	1.177/-1.295	1.09/-0.693
CCDC deposition no.	2,011,088	2,011,089	1,855,392

*From ref. [21].

2.3.1. General synthesis of lithium β -diketonates 1, 2

To a solution of $F(CF_2)_nCO_2Et$ (0.1 mol) and the corresponding 3,3-dialkoxybutane-2-one (0.1 mol) in 1,2-dimethoxyethane (70 mL) LiH powder (0.1 mol) was added. The resulting suspension was stirred for 4 h under reflux. After 4 h, the reaction mixture was concentrated, the residue was filtered, washed with cold diethyl ether (2 × 30 mL) and air-dried to afford colorless solid.

Lithium 1,1,1,2,2-*pentafluoro*-6,6-*dimethoxy*-5-*oxohept*-3-*en*-3*olate LiL*¹ (**1**). Yield 23.87 g (84%), m.p. 201–203°C (sublimation). Calc. for C₉H₁₀F₅LiO₄: C, 38.05; H, 3.55. Found: C, 37.88; H, 3.41. IR (ATR, ν/cm^{-1}): 2997, 2942, 2839 (C–H); 1645 (*C* = 0); 1517 (C=C); 1479 (CH₃); 1325–1139 (C–F). ¹H NMR: δ/ppm 1.25 (s, 3H, Me), 3.09 (s, 6H, 2 MeO), 5.93 (s, 1H, CH). ¹⁹F NMR: δ/ppm 41.49 (br s, 2F, CF₂), 81.00 (br s, 3F, CF₃). ¹³C NMR: δ/ppm 20.95 (s), 48.82 (s), 89.52 (s), 101.44 (s), 108.78 (tq, *J* = 262, 35 Hz), 118.79 (qt, *J* = 286, 37 Hz), 170.86 (q, *J* = 21 Hz), 192.82 (s).

Lithium 1,1,1-trifluoro-5,5-diethoxy-4-oxohex-2-en-2-olate LiL² (**2**). Yield 23.07 g (88%), m.p. 262–263°C (sublimation). Calc. for $C_{10}H_{14}F_3LiO_4$: C, 45.82; H, 5.38. Found: C, 45.73; H, 5.29. IR (ATR, ν/cm^{-1}): 2984, 2940, 2894 (C–H); 1636 (C = 0); 1515 (C=C); 1478 (CH₃); 1309–1131 (C–F). ¹H NMR: δ/ppm 1.10 (t, ³J_{HH} = 7.1 Hz, 6H, 2Me), 1.26 (s, 3H, Me), 3.28–3.47 (m, 4H, 2 CH₂), 5.93 (s, 1H, CH). ¹⁹F NMR: δ/ppm 87.75 (s, 3F, CF₃). ¹³C NMR: δ/ppm 15.32 (s), 21.92 (s), 56.51 (s), 88.03 (s), 101.15 (s), 119.10 (q, J = 289.3 Hz), 170.06 (q, J = 29.4 Hz), 193.93 (s).

2.3.2. General synthesis of the complexes [(TbL₃)·(LiL)·(MeOH)] 3, 4

To a solution of the corresponding lithium β -diketonate LiL (4 mmol) in methanol (15 mL) terbium(III) chloride hydrate [or terbium(III) acetate hydrate] (1 mmol) was added and the mixtre was stirred under reflux until a clear solution was obtained. After cooling to room temperature, the resulting solution was slowly evaporated to afford crystalline colorless complexes **3** and **4**.

[TbL¹₃·LiL¹·(MeOH)] (**3**). Yield 0.84 g (64%), m.p. 142–143°C. Calc. for $C_{37}H_{44}F_{20}LiO_{17}$ Tb: C, 34.01; H, 3.39. Found: C, 33.83; H, 3.29. IR (ATR, ν/cm^{-1}): 3428 (br) (O–H); 2997, 2947, 2840 (C–H); 1650, 1632 (*C* = 0); 1519 (C=C); 1468 (CH₃); 1331–1124 (C–F). ¹⁹F NMR: δ /ppm 40.2–42.8 (br s, CF₂, LiL), 55.1–57.7 (br s, CF₂, [TbL₃]), 61.0–64.0 (br s, CF₂, [TbL₄]⁻), 79.7–82.3 (br s, CF₃, LiL), 97.7–100.5 (br s, CF₃, [TbL₄]⁻), 103.1–105.5 (br s, CF₃, [TbL₃]). The ratio of [LiL]:[TbL₃]:[TbL₄]⁻ = 2:1:4.

[TbL²₃·LiL²·(MeOH)] (**4**). Yield 0.66 g (54%), m.p. 74–75°C. Calc. for C₄₁H₆₀F₁₂LiO₁₇Tb: C, 40.41; H, 4.96. Found: C, 40.23; H, 4.79. IR (ATR, ν/cm^{-1}): 3536, 3465 (br) (O–H); 2983, 2940, 2900 (C–H); 1651, 1634 (*C* = 0); 1523 (C=C); 1473 (CH₃); 1317–1137 (C–F). ¹⁹F NMR: δ /ppm 86.0–88.6 (br s, CF₃, LiL), 109.7–112.7 (br s, CF₃, [TbL₃]), 115.7–120.2 (br s, CF₃, [TbL₄]⁻). The ratio of [LiL]:[TbL₃]:[TbL₄]⁻ = 1:0.8:2.4.

3. Results and discussion

Lithium β -diketonates **1**, **2** were obtained according to the reported procedure [25,26] by Claisen condensation of the corresponding fluoroalkylated esters and 3,3-dialkoxybutane-2-ones in the presence of lithium hydride.

Scheme 1

The reaction of lithium $R^F-\beta$ -diketonates **1**, **2** with terbium(III) salts {TbCl₃·6H₂O or Tb(OAc)₃·xH₂O} in methanol resulted in heterobimetallic complexes [TbL¹₃·LiL¹·(MeOH)] **3** and [TbL²₃·LiL²·(MeOH)] **4** (Eq. (1)).

$$\underbrace{\text{LiL}}_{1,2} + \underbrace{\text{TbX}_3 \cdot xH_2O}_{X=CI,OAc} \xrightarrow{\text{MeOH}} \left\lfloor (\text{TbL}_3)(\text{LiL})(\text{MeOH}) \right\rfloor + 3\text{LiX} + xH_2O$$
(1)

3.1. ¹⁹F NMR spectroscopic studies

The significant broadening of signals in the ¹H NMR spectra of complexes **3**, **4** registered in DMSO- d_6 made them uninformative for identifying the paramagnetic metal species. However, the behavior of Ln(III) diketonates in solution was properly investigated by ¹⁹F NMR spectroscopy [27-29]. In the ¹⁹F NMR spectrum of complex 4 there are three signals corresponding to different types of diketonates existing in equilibrium in the solution of DMSO- d_6 . The value of the highest field signal at $\delta_F = 87.7$ ppm is comparable to that observed for the initial lithium β -diketonate 2, but in contrast with the ligand, the complex has this singlet broadened ($\Delta \delta_{\rm F} = 1.2$ ppm). Two broadened signals at $\delta_{\rm F} = 111.5$ and 117.7 ppm indicate [TbL₄]⁻ and [TbL₃] metal species, respectively [30]. The same behavior was observed for C₂F₅-substituted β -diketonate **3**, but its ¹⁹F NMR spectrum contained a doubled number of fluorine atoms signals. A similar set of signals in the ¹⁹F NMR spectra was registered for *tetrakis*- β -diketonates M[TbL₄] (M = Na, K, Cs), and the chemical shift of the high field singlet varied depending on the alkali metal ion [30]. Therefore, ¹⁹F NMR spectroscopy has proved to be a valuable tool in the qualitative analysis of Ln(III) R^{F} - β -diketonates and can also be used in the complexes purity determination, as well as in the identification of the metal ions nature. We have found that the change of substituents from Me to Et in the acetal fragment of functionalized $CF_3-\beta$ -diketonates and the nature of alkali metals [30] do not affect the equilibrium of Ln(III) tris- and tetrakis-diketonates in solution.

3.2. X-Ray crystallographic studies

According to XRD analysis, dinuclear heterometallic complexes **3**, **4** are neutral β -diketonates, which crystallize in centrosymmetric space groups of triclinic P1 (**3**) and orthorhombic P2₁2₁2₁ (**4**) systems (Fig. 2, 3, Table 1). The structure of **3**, **4** consists of two metal-containing parts: Tb(III) *tris*-diketonate TbL¹⁽²⁾₃ and the initial lithium β -diketonate LiL¹⁽²⁾ serving as a coligand. Central Tb(III) ion is octa-coordinated by oxygen atoms of diketonate-anions, which form three six-membered 4f-metal chelate cycles (coordination mode A) (Fig. 1, 4a,c), as well as methoxy group and bridging μ_2 -O atom of LiL¹⁽²⁾, which form five-membered 4f-metal chelate cycle (coordination mode B) (Fig. 1, 4b,d). Lithium ion is additionally coordinated with one molecule from the *tris*-diketonate fragment via mode B. Methanol solvent molecule saturates the penta-coordinated sphere around Li ion (Fig. 4b,d).



i: CH(OR)₃, *p*-toluenesulfonic acid (cat.), reflux; *ii*: R^FCO₂Et, 1,2-dimethoxyethane, reflux. 1: R^F = C₂F₅, R = Me; 84%. 2: R^F = CF₃, R = Et; 88%

Scheme 1. Synthesis of lithium R^{F} - β -diketonates.



Fig. 2. Crystal structure of terbium(III) complex $[TbL^1_3\text{-}LiL^1\cdot(\text{MeOH})]$ 3. Hydrogen atoms are omitted.

However, the structure of Tb(III) *tris*-diketonate fragments is different in these complexes: all diketonate anions in $[TbL_3]$ of **3** are in the *cis*-form (Fig. 4a), while the isomerization of one diketonate anion into the *trans*-form occurs in the complex **4** (Fig. 4c).

The Tb-Li distance in complex **3** is equal to 3.48 Å and similar to that found in $[TbL_3 \cdot LiL \cdot (MeOH)]$ [25]. But the replacement of



Fig. 3. Crystal structure of terbium(III) complex $[{\rm TbL}^2_3 \cdot {\rm LiL}^2 \cdot ({\rm MeOH})]$ 4. Hydrogen atoms are omitted.



 $[TbL^{2}_{3}\cdot LiL^{2}\cdot (MeOH)]$ 4

Fig. 4. Terbium(III) tris-diketonate fragments and heterobimetallic core organization in the complexes 3 (a, b) and 4 (c, d). Hydrogen atoms are omitted.



Fig. 5. The view of heterobimetallic β -diketonates forming the crystal packing of terbium(III) complexes 3 (*a*) and 4 (*b*) with the shortest intermolecular Tb...Tb distances. Only hydrogens participating in the intermolecular H...F interactions (blue dashed lines) are shown.

the alkyl substituents in the acetal group from Me to Et leads to an increase in the distance between metal ions up to 3.52 Å in complex **4**, which is closer to that obtained from the *tetrakis*-diketonate [LiTbL₄·(CH₃CN)] [22].

According to the calculations performed in the SHAPE 2.1 program [31,32], the geometry of the octa-coordinated Tb(III) ion can be best described as a distorted triangular dodecahedron (TDD-8), and the penta-coordinated Li(I) ion has a distorted square pyramidal (SPY-5) environment.

The elongation of the carbon chain in acetal or perfluoroalkyl groups of ligands **1**, **2** resulted in the different crystal packing of complexes **3** and **4**. In **3**, the molecules are stacked to produce square packing with the shortest intermolecular Tb...Tb distance equal to 11.200 Å (Figs. 5a, and 6). Between molecules in neighboring stacks, short C-H...F contacts are observed with H...F distances of 2.61–2.96 Å (Fig. 5a).

As compared to **3**, heterobimetallic Tb(III) β -diketonate **4** has a shorter intermolecular Tb...Tb distance of 10.994 Å (Fig. 5b). The mutual orientation of two diketonate anions of neighboring

molecules is realized through the intermolecular C–H…F interactions (2.61–2.79 Å) between trifluoromethyl group and alkyl substituents (Fig. 5b). Molecules with the shortest Tb…Tb distance are arranged in chains to form zigzag layers' network providing crystal packing of the complex **4** (Fig. 7).

3.3. Photoluminescence studies

The solid-state luminescence properties were measured at room temperature. The UV-absorption spectra of complexes **3** and **4** showed maximum excitation at 323 and 327 nm, respectively. The photoluminescence spectra exhibited the typical Tb³⁺-centered emission bands in the 490–650 nm region corresponding to the ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ (J = 2-6) transitions (Table 2). The phosphorescence lifetimes of **3** and **4** were 569 and 237 μ s, respectively. In Table 3 we have summarized the data for a series of heterobimetallic Tb(III)-M (M is alkali metal) complexes based on the functionalized R^F- β -diketonates. Varying of both alkali metals and ligands (from L to L¹ and L²) dramatically changes the crystal structure of the



Fig. 6. Crystal packing of terbium(III) complex $[TbL_{3}^{1}.LiL^{1}.(MeOH)]$ 3 along the *b* axis. Hydrogen atoms are omitted.



Fig. 7. Crystal packing of terbium(III) complex [TbL²₃·LiL²·(MeOH)] 4 along the *a* axis. Hydrogen atoms are omitted.

Table 2		
Photophysical data for	terbium(III)	complexes.

Complex	Transition	λ [nm]	[%] of total emission	Lifetimes [µs]
3 [TbL ¹ ₃ ·LiL ¹ ·(MeOH)]	${}^{5}D_{4} \rightarrow {}^{7}F_{6}$	490	23.0	569
	$^{5}D_{4} \rightarrow ^{7}F_{5}$	548	65./	
	$^{5}D_{4} \rightarrow ^{7}F_{4}$	582	6.3	
	${}^{5}D_{4} \rightarrow {}^{7}F_{3}$	621	3.7	
	${}^{5}D_{4} \rightarrow {}^{7}F_{2}$	650	1.3	
4 [TbL ² ₃ ·LiL ² ·(MeOH)]	${}^5D_4 \rightarrow {}^7F_6$	491	17.2	237
	${}^{5}D_{4} \rightarrow {}^{7}F_{5}$	548	73.5	
	${}^5D_4 \rightarrow {}^7F_4$	582	5.1	
	${}^{5}D_{4} \rightarrow {}^{7}F_{3}$	621	3.1	
	$^5D_4 \rightarrow \ ^7F_2$	650	1.1	

Table 3

summary of the main structural of	characteristics and	phosphorescence	lifetimes for	a series o	f heterometallic	dinuclear	complexes.
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Nº	Complex	TbTb distance, [Å]*	[LnO ₈] geometry**	Phosphorescence lifetimes of solids, $[\mu s]$	Ref.	
Discrete struc	tures					
1	[TbL ₃ ·LiL·(MeOH)]	10.552	TDD-8	648	[21]	
2	Na[TbL ₄](MeOH)(H ₂ O)	11.658	TDD-8	640	[30]	
3	$[TbL_{3}\cdot LiL^{1}\cdot (MeOH)]$ (3)	11.200	TDD-8	569		
4	$[TbL_3 \cdot LiL \cdot (H_2O)]$	9.923	TDD-8	520	[21]	
5	$[LiTbL_4 \cdot (H_2O)](CH_3CN)$	9.545	BTRP-8	480	[22]	
6	$[TbL_{3}\cdot LiL_{\cdot}(MeOH)]$ (4)	10.994	TDD-8	237		
Polymeric structures						
7	$K[TbL_4](H_2O)$	10.455	TDD-8	292	[30]	
8	Cs[TbL ₄]	10.995	SAPR-8	48	[30]	

*The shortest intermolecular distance.

**Based on the calculations performed in the SHAPE 2.1 program [31,32] (TDD-8 – triangular dodecahedron (D_{2d} symmetry); BTRP-8 – biaugmented trigonal prism J50 (C_{2v} symmetry); SAPR-8 – square antiprism (D_{4d} symmetry)).

resulting complexes, including the geometry of the Ln(III) environment, the distances between heterometals in the molecules, and the crystal packing. Since the emission of Ln(III) ions is primarily associated with the geometry of the crystal field and the electron distribution around coordinating atoms of the ligand, these parameters were used to identify "structure-property" relationships. The longest afterglow times are exhibited by heterometallic dinuclear complexes with TDD-8 geometry of the LnO₈ coordination polyhedron. Although the use of ligand L¹ does not modify the geometry of the Ln(III) environment in complex 3, but (perfluoro)alkyl substituents in diketonate anions affect the π -electron-density distribution in metal cycles. In particular, replacing the CF₃-substituent with C₂F₅-group decreases the negative inductive effect on the oxygen atom of the adjacent carbonyl group thereby increasing the electron density at the coordinating oxygen atom and reducing the hardness of Lewis acid. However, the changes in the acetal group of L resulted in a more drastic decrease of the phosphorescence lifetimes of complexes. The reorientation of one ligand in the Tb(III) tris-diketonate fragment due to ethoxy group incorporation (Fig. 4c) provokes the significant redistribution of electron density in the LnO₈ coordination polyhedron.

In addition, the elongation of (perfluoro)alkyl groups in ligands influences the crystal packing of the corresponding complexes **3**, **4**. Despite the discrete structure, they have more close-packed crystals and, therefore, do not exhibit the mechanoluminescence typical for the heterobinuclear complexes based on the ligand L.

4. Conclusion

We have demonstrated herein how the elongation of (perfluoro)alkyl substituents in the initial functionalized R^F - β -diketonate ligand L affects the organization of the crystal packing in the resulting complexes. A bulkier ethoxy-substited acetal group modifies the Tb(III) *tris*-diketonate structure due to the isomerization of one diketonate anion into *trans*-form. The long-lived emission in the discrete Tb(III) β -diketonates is realized through both reducing the number of intermolecular C–H…F contacts and the electron effect produced by the trifluoromethyl group.

Appendix A. Supplementary data

Crystallographic data for this paper have been deposited at Cambridge Crystallogaphic Data Center (CCDC 2,011,088 for 3 and CCDC 2,011,089 for 4) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data to this article can be found online at

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Yulia S. Kudyakova: Conceptualization, Investigation, Funding acquisition, Writing - original draft. Pavel A. Slepukhin: Investigation. Marina S. Valova: Investigation. Yanina V. Burgart: Writing - review & editing. Victor I. Saloutin: Writing - review & editing. Denis N. Bazhin: Methodology, Investigation, Supervision, Writing - original draft.

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Supplementary materials

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