Synthesis, structure and luminescent properties of lanthanide fluoroalkoxides†

D. M. Kuzyaev,†a T. V. Balashova,a,b M. E. Burin,a,b G. K. Fukin,a,b R. V. Rumyantcev,a A. P. Pushkareva,b V. A. Ilicheva,b I. D. Grishin,b D. L. Vorozhtsovb and M. N. Bochkareva,b

Alkoxides [Ln(OR)3(DME)]2 (R = CH(CF3)2, Ln = Sm (1), Yb (2)), [Ce(OR)3(Phen)]2 (3) (Phen = 1,10-phenanthroline), [Ce(OR)3(DME)]2 (R = C(CF3)2) (4), (Gd(OR)3(DME)]2 (5), (Ln3O(CF3)2C=C(CF3)2O3)]2(Phen)2 (8), and (Ce(OR)3(C=C(CF3)2O)[O(CF3)2][C(CF3)2OH] (Phen)2)3 (9) were synthesized by the reactions of silylamides Ln[N(SiMe3)2]3 with respective fluorinated alcohols. The heterovalent trinuclear complex (Sm2(μ2-OR)3(μ2-OR)2Sm(OR)2(THF)2.5(ET2O)(S)3) (10) was obtained by treatment of SmI2(THF)2 with ROK. The reaction of europium(III) and yttrium(II) silylamides with ROH afforded the heterobimetallic alkoxide (Eu2(μ2-OR)3(μ2-OR)2Y(OR)(DME)2) (11) containing divalent europium. The molecular structures of 1, 2, 3, 9, 10 and 11 were determined by X-ray analysis. All the prepared cerium derivatives as well as the europium–yttrium isopropoxide upon UV excitation exhibited photoluminescence in the regions of 370–425 (for Ce3+) and 485 nm (for Eu2+) which was assigned to 4d→5f transitions.

INTRODUCTION

Luminescent materials attract great attention because of their wide application in light sources and color displays, such as cell phones, computer and TV screens. In particular, organolanthane emitters have inspired vigorous research activities owing to their long luminescence lifetimes and narrow characteristic emission bands originated from f–f transitions, which cover the entire visible and near-infrared region.1 Besides, organic derivatives of cerium(III), gadolinium(III), europium(II), and ytterbium(II) can exhibit metal-centered emission in the UV-blue area and are attractive due to their potential application in the design of the excitation sources for chemical sensing devices, lithography, optical data recording and biomedicine.2 The short-wave metal-centered luminescence of Ce3+, Eu2+ and Yb2+ occurs due to f–d transitions, which are parity-allowed, so the complexes of these metals have higher light outputs compared to f–f emitters.3 The luminescence of f–d transitions can be observed as well for the Sm2+ and Tm3+ ions but in this case, the emission wavelength is above 650 nm.4 Despite the attraction of these phosphors from the academic point of view and plausible application, the publications devoted to organolanthane UV-blue emitters are scarce. Among the organocerium derivatives the UV luminescence was detected for the complexes of CeCl3 with crown ethers5 and bipyrinide,6 and for the pyrazinecarboxylate7 and phosphors, we have synthesized a set of new fluorinated organic derivatives of cerium(III), gadolinium(III), europium(II), and ytterbium(III). Fluorinated alkoxide ligands were chosen because: (i) eliminating of C-H groups (which are well known luminescence quenchers) facilitates emitting efficiency,13 (ii) fluorine substituents improve the hydrolytic

†G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Tropinina Street 49, 603137 Nizhny Novgorod, Russia. E-mail: mboch@iomc.ras.ru, kuzyaev@iomc.ras.ru
‡Nizhny Novgorod State University, Gagarina Avenue 23/2, 603950 Nizhny Novgorod, Russia
§Electronic supplementary information (ESI) available: Details of X-ray experiments, crystallographic, collection and refinement data for the complexes 1–3, 9–11. CCDC 1437190–1437395. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt04636j

Cite this: Dalton Trans., 2016, 45, 3464–3472

This journal is © The Royal Society of Chemistry 2016
Experimental section

All experiments were performed in evacuated tubes using standard Schlenk techniques, thus excluding traces of air and water. The solvents were purified by distillation from sodium/benzophenone ketyl (THF, DME, diethyl ether) and sodium (hexane, toluene). MeCN for electron spectroscopy, ROH, R’OH, HO(CF3)2C=C(CF3)2OH, 1,10-phenanthroline, and Ln[N(SiMe3)2]3 (Ln = Ce, Gd, Sm, Yb, Dy, Y) were prepared according to the published procedures.15,16 IR spectra were recorded on a Perkin Elmer Lambda-25. Registration of absorption and emission spectra of the product is analogous to that of complex [{Ce2(O(CF3)2C=O)}3(Phen)2} (8). Magnetic susceptibility measurements were performed by using the Vario El cube CHNS elemental analyzer (Nizhny Novgorod State University). Yttrium and lanthanide contents were analysed by complexometric titration. Magnetic susceptibility measurements were carried out according to the procedure.17 Absorption spectra were recorded on a UV/VIS instrument “PerkinElmer Lambda-25” from 200 to 800 nm. Emission spectra were registered from 220 to 700 nm on a fluorescent spectrometer “Perkin Elmer LS-55”. Registration of absorption and emission spectra were performed in a 1 cm fluorescent quartz cuvette.

{[Sm(OR)3(DME)]2} (1)
Propanol ROH (0.094 g, 0.56 mmol) was condensed to the solution of Sm[N(SiMe3)2]3 (0.123 g, 0.19 mmol) in 10 ml of DME. The reaction mixture was stirred for 3 h. The solvent was removed by condensation in vacuo and the residue was recrystallized from the mixture PhCH3–Et2O. Yield of the product is 0.18 g (77%). Anal. calcd (%) for C20H20GdF27O7: C, 23.04; H, 1.93; Gd, 13.66. Found (%): C, 22.91; H, 1.93; Gd, 13.66. IR (ν, cm⁻¹): 3684 (w), 1238 (s, br), 1052 (w), 936 (m), 872 (m), 759 (w), 739 (m), 720 (m), 704 (w), 674 (w), 542 (w).

{[Yb(OR)3(DME)]2} (2)
Complex 2 was prepared similarly to 1 from Yb[N(SiMe3)2]3 (0.272 g, 0.42 mmol) and ROH (0.215 g, 1.28 mmol). Yield of the product is 0.213 g (66%). Mp: 158–160 °C. Anal. calcd (%) for C28H31GdF4O3Sm2: C, 20.64; H, 1.71; Yb, 22.64. Found (%): C, 20.71; H, 1.95; Yb, 22.76. The IR spectrum of the product is analogous to that of complex 1.

{[Ce(OR)3(Phen)]2} (3)
A solution of ROH (0.209 g, 1.24 mmol) and 1,10-phenanthroline (0.071 g, 0.39 mmol) in 10 ml of PhCH3 was added to a solution of Ce[N(SiMe3)2]3 (0.238 g, 0.38 mmol) in 10 ml of PhCH3. The reaction mixture was stirred at 70 °C for 4 h. The precipitated yellow crystals were filtered off and washed with cold PhCH3 (2 × 10 ml). Drying of the crystals gave 0.219 g (70%) of complex 3. Mp: 147–148 °C (dec.). Anal. calcd (%) for C42H22Ce2F36N4O6: C, 31.70; H, 1.33; Ce, 16.81; N, 3.36. Found (%): C, 31.82; H, 1.35; Ce, 16.84; N, 3.47. IR (ν, cm⁻¹): 3658 (w), 3456 (w), 1628 (w), 1593 (w), 1580 (w), 1521 (m), 1499 (w), 1428 (w), 1286 (s), 1260 (m), 1213 (s), 1183 (s), 1126 (w), 1095 (s), 887 (m), 864 (w), 855 (m), 845 (s), 771 (w), 741 (m), 731 (m), 687 (s), 644 (w), 521 (w).

{[Ce(OR)3(DME)]2} (4)
Complex 4 was prepared similarly to 1 from butanol R’OH (0.266 g, 1.13 mmol) and Ce[N(SiMe3)2]3 (0.167 g, 0.27 mmol). Yield of the product is 0.197 g (72%). Mp: 171 °C (dec.). Anal. calcd (%) for C40H20Ce2F36O14: C, 23.43; H, 1.97; Ce, 13.66. Found (%): C, 23.24; H, 1.78; Ce, 13.42. IR (ν, cm⁻¹): 3691 (w), 3606 (w), 3403 (w), 1231 (s), 1097 (m), 1050 (s), 1017 (w), 966 (s), 858 (s), 768 (m), 726 (s), 708 (m), 569 (w), 536 (m).

{[Gd(OR)3(DME)]2} (5)
Complex 5 was prepared similarly to 1 from butanol R’OH (0.173 g, 0.73 mmol) and Gd[N(SiMe3)2]3 (0.149 g, 0.23 mmol). Yield of the complex 5 is 0.162 g (67%). Mp: 152 °C (dec.). Anal. calcd (%) for C42H22Gd2F36O14: C, 23.04; H, 1.93; Gd, 15.08. Found (%): C, 22.91; H, 2.05; Gd, 15.43. The IR spectrum of the product is analogous to that of 4.

{[Ce2(O(CF3)2C=O)3-C(CF3)2O)3]} (6)
Butanediol HO(CF3)2C=C(CF3)2OH (0.120 g, 0.36 mmol) was added by condensation in vacuo to a solution of Ce[N(SiMe3)2]3 (0.140 g, 0.23 mmol) in 10 ml THF. The reaction mixture was stirred for 3 h. The solvent was removed by condensation in vacuo. Recrystallization of the residue from the mixture THF–Et2O gave colorless crystals of complex 6 (0.109 g, 76%). Mp: 110–112 °C (dec.). Anal. calcd (%) for C18Ce2F36O6: C, 16.94; Ce, 21.96. Found (%): C, 16.79; Ce, 21.68. IR (ν, cm⁻¹): 3684 (w), 1238 (s), 1052 (w), 936 (m), 872 (m), 739 (w), 739 (m), 720 (m), 704 (w), 674 (w), 542 (w).

{[Gd2(O(CF3)2C=C(CF3)2O)]3} (7)
Complex 7 was prepared similarly to 1 from butanediol HO(CF3)2C=C(CF3)2OH (0.130 g, 0.39 mmol) and Gd[N(SiMe3)2]3 (0.156 g, 0.24 mmol). Yield of the product is 0.137 g (86%). Mp: 142 °C (dec.). Anal. calcd (%) for C18Gd2F36O12: C, 16.50; Gd, 24.00. Found (%): C, 16.71; Gd, 23.76. The IR spectrum of the product is analogous to that of 6.

{[Ce2(O(CF3)2C=C(CF3)2O)(Phen)]2} (8)
A solution of Ce[N(SiMe3)2]3 (0.243 g, 0.39 mmol) and 1,10-phenanthroline (0.075 g, 0.42 mmol) in 10 ml of THF was added to a solution of HO(CF3)2C=C(CF3)2OH (0.207 g, 0.62 mmol) in 5 ml of THF. The reaction mixture was stirred for 3 h. The solvent was removed by condensation in vacuo. The resulting pale-brown solid was washed with hexane (3 × 15 ml) and dried. Recrystallization of the residue from the mixture DME–PhCH3 gave orange crystals of complex 9.
(0.022 g, 5%) which were isolated via decantation of the supernatant solution. After evaporation of the solvent from the mother liquor in vacuo and washing of the residue with hexane (2 × 10 ml), alkoxide 8 was obtained as a pale-brown solid. Yield of the product was 0.266 g (83%).

A solution of Ce[N(SiMe3)2]3 (0.100 g, 0.16 mmol) and 1,10-phenanthroline (0.110 g, 0.64 mmol) in 10 ml of THF was added to a solution of SmI2(THF)2 (0.351 g, 0.64 mmol) in 10 ml of THF. The reaction mixture was stirred for 3 h. The solvent was removed by condensation in vacuo. The resulting pale-brown solid was washed with hexane (3 × 15 ml) and dried. Recrystallization of the product from the mixture DME–PhCH3 gave complex 9 as orange crystals (0.110 g, 59%). Mp: 180−183 °C (dec.).

A solution of Ce[N(SiMe3)2]3 (0.100 g, 0.16 mmol) and 1,10-phenanthroline (0.110 g, 0.64 mmol) in 10 ml of THF was added to a solution of Ho(CF3)2C(OH)(Phen)2 (0.022 g, 5%) which were isolated from the ether (4 × 10 ml). After concentrating and cooling of the resulting solution (0.115 g, 55%). Mp: 208−209 °C (dec.).

A solution of Ce[N(SiMe3)2]3 (0.168 g, 0.26 mmol) and Y[O(CF3)2C(OH)](Phen)2 (0.058 g, 0.32 mmol) in 10 ml of THF was added slowly to a solution of SmI2(THF)2 (0.351 g, 0.64 mmol) in 10 ml of THF. The reaction mixture was stirred for 3 h. The precipitate of KI was filtered off and the solvent from the resulting solution was removed by condensation in vacuo. The residue was extracted with diethyl ether (4 × 10 ml). After concentrating and cooling of the extract, dark red crystals of 10 (0.155 g, 40%) were obtained. ρeff = 2.91 mg. Anal. calcld (%) for C33H32F42O10Sm3: C, 19.99; H, 1.56. Found (%): C, 21.29; H, 1.70; Sm, 24.55. The IR spectrum of the product is similar to that of 1.

{Ce[O(CF3)2C–C(CF3)2O]2[O(CF3)2C–C(CF3)2OH]}[(Phen)3] (9)

A solution of Ce[N(SiMe3)2]3 (0.100 g, 0.16 mmol) and 1,10-phenanthroline (0.110 g, 0.64 mmol) in 10 ml of THF was added to a solution of Ho(CF3)2C–C(CF3)2OH (0.108 g, 0.32 mmol) in 5 ml of THF. The reaction mixture was stirred for 3 h. The solvent was removed by condensation in vacuo. The resulting pale-brown solid was washed with hexane (3 × 15 ml) and dried. Recrystallization of the product from the mixture DME–PhCH3 gave complex 9 as orange crystals (0.110 g, 59%). Mp: 180−183 °C (dec.).

{Sm3[μ2-OR]3[μ1-OR]2Sm(OR)8(THF)2,3(ET2O)0,3} (10)

A solution of SmI2(THF)2 (0.351 g, 0.64 mmol) in 10 ml of THF was added to a solution of ROK (prepared from 0.050 g (1.25 mmol) of KH and 0.236 g (1.40 mmol) of ROH according to the known procedure) in 10 ml of THF. The reaction mixture was stirred for 5 h. The precipitate of KI was filtered off and the solvent from the resulting solution was removed by condensation in vacuo. The residue was extracted with diethyl ether (4 × 10 ml). After concentrating and cooling of the extract, dark red crystals of 10 (0.155 g, 40%) were obtained. ρeff = 2.91 mg. Anal. calcld (%) for C50H54F60O20Sm3 (1837.61): C, 21.57; H, 1.76; Sm, 24.84. The IR spectrum of the product is similar to that of complex 1.

Device fabrication

The three-layer device of structure ITO/TPD (30 nm)/complex 3 (50 nm)/BATH (20 nm)/Yb, consisting of triphenylamine derivative (TPD) as a hole transport layer, 4,7-diphenyl-1,10-phenanthroline (BATH) as an electron-transporting and hole-blocking layer and the lanthanide complex as an emission layer, was fabricated in a vacuum chamber (10−6 mbar) with different resistive heaters for organic and metal layers. A commercial ITO on a glass substrate with 5 Ω sq.−1 was used as the anode material (Luminescence Technology Corp.) and commercial Yb, 99.9% trace metal basis (Sigma-Aldrich) as the cathode material. The deposition rate for the organic compounds and metallocomplex was 1 nm s−1. The active area of the device was 5 × 5 mm. The EL spectra and current–voltage characteristics were measured using an Ocean Optics USB-2000 fluorimeter, the computer controlled GW Instek PPE 3323 power supply and a GW Instek GDM 8246 digital multimeter under ambient conditions.

Results and discussion

Synthesis

Isopropoxides 1 and 2 were prepared by reactions of respective silylamides Ln[N(SiMe3)2]3 (Ln = Sm, Yb) and hexafluoroisopropanol in DME solution. To synthesize cerium isopropoxide 3 in the reaction mixture phenanthroline was added. Note that complexes 1 and 2 have been prepared earlier, but their structures and luminescent properties have not been studied.

The products were isolated from the ether–toluene mixture as microcrystalline powders soluble in THF, diethyl ether, and DME. Unlike hydrolyzed and nonsublimable 1 and 2, cerium isopropoxide 3, due to the presence of the shielding phenanthroline at the metal center, is relatively stable in air and can be sublimed in vacuo without decomposition which made it possible to design the OLED device on its base and study the EL properties (vide infra).

X-ray analysis revealed that complexes 1 and 2 are centrosymmetrical, and isoelectronic dimeric compounds (Fig. 1) and have the arrangement quite analogous to that of the Ce and Tm isopropoxides reported earlier. In alkoxides 1 and 2 two lanthanide ions are linked via two bridging μ2-OR groups, each ion is bonded with two terminal isopropoxide groups and one DME molecule. The terminal Ln–O distances (2.130(5)−2.182(4) Å in 1 and 2.068(3)−2.092(3) Å in 2) are notably shorter compared to the bridging ones (2.368(4)−2.408(3) Å in 1 and 2.279(3)−2.284(3) Å in 2). The Yb–Yb distance in 2 is equal to
3.7294(4) Å that is shorter than the Sm⋯Sm one in 1 (3.9452 Å).

It is interesting to note that there are close intramolecular contacts Sm(1)⋯F(12A) (Sm(1A)⋯F(12)) in 1 whereas the analogous interactions in 2 are absent. Really, the Yb(1)⋯F(12A) distance in 2 is 3.0564 Å and notably exceeds the analogous one in 1 (2.8524 Å). According to the literature data,21,22 typical interval values for intramolecular Yb⋯F and Sm⋯F interactions are 2.48(1)–2.726(9) Å and 2.537(2)–2.813(3) Å respectively. Besides, the intramolecular Sm(1A)⋯F(12) interaction leads to elongation of the C(6A)⋯F(12A) (1.364(7) Å) bond length compared to other distances in this CF3 group (1.317(8)–1.329(8) Å). In order to understand why the intramolecular Yb(1A)⋯F(12) interactions are absent in 2, we have analyzed the saturation of the metal coordination sphere (G-parameter)23 in these complexes. According to our calculations the saturation of the metal coordination sphere by ligands in 2 is 97.3 (2)% that markedly exceeds the analogous one in 1 (94.9 (2)%). Thus, there is insufficient room around the metal in 2 to realize an additional Yb⋯F interaction. In other words, steric factors inhibit realization of the intramolecular Yb⋯F contact in 2.

According to X-ray data complex 3 has a centro-symmetrical, dimeric structure (Fig. 2a) which is close to that of 1 and 2.

Fig. 1 Molecular structures of 1 (Ln = Sm) and 2 (Ln = Yb). Thermal ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity. Selected distances [Å] and angles [°] in 1: Sm(1)⋯O(5) 2.130(5), Sm(1)⋯O(4) 2.182(4), Sm(1)⋯O(2) 2.368(4), Sm(1)⋯O(2A) 2.408(3), Sm(1)⋯O(5) 2.459(4), Sm(1)⋯O(4) 2.514(4), Sm(1)⋯F(12A) 2.852(4), Sm(1)⋯Sm(1A) 3.9452(9), O(3)⋯Sm(1)⋯O(1) 101.43(16), O(3)⋯Sm(1)⋯O(2) 106.75(17), O(1)⋯Sm(1)⋯O(2) 85.29(14), O(3)⋯Sm(1)⋯O(2A) 100.55(15), O(1)⋯Sm(1)⋯O(2A) 149.75(15), O(2)⋯Sm(1)⋯O(2A) 68.59(15), O(3)⋯Sm(1)⋯F(12A) 75.66(15), O(1)⋯Sm(1)⋯F(12A) 146.17(13), O(2)⋯Sm(1)⋯F(12A) 128.20(11), O(2A)⋯Sm(1)⋯F(12A) 60.40(12); in 2: Yb(1)⋯O(3) 2.068(3), Yb(1)⋯O(1) 2.092(3), Yb(1)⋯O(2) 2.277(3), Yb(1)⋯O(2A) 2.284(3), Yb(1)⋯O(4) 2.356(4), Yb(1)⋯O(5) 2.388(4), Yb(1)⋯F(12A) 3.056(4), Yb(1)⋯Yb(1A) 3.7294(4), O(3)⋯Yb(1)⋯O(1) 100.84(13), O(3)⋯Yb(1)⋯O(2) 105.48(13), O(1)⋯Yb(1)⋯O(2) 87.84(13), O(3)⋯Yb(1)⋯O(2A) 99.36(12), O(1)⋯Yb(1)⋯O(2A) 153.56(13), O(2)⋯Yb(1)⋯O(2A) 70.38(12), O(3)⋯Yb(1)⋯F(12A) 69.49(11), O(1)⋯Yb(1)⋯F(12A) 145.07(13), O(2)⋯Yb(1)⋯F(12A) 126.93(11), O(2A)⋯Yb(1)⋯F(12A) 59.30(10). Symmetry transformations were used to generate equivalent atoms: −x + 1, −y + 1, −z + 1 in 1 and 2.

The main difference of complex 3 from 1 and 2 lies in coordination phenanthroline molecules instead of the DME ones. Cerium ions are linked by two μ2-bridged OR ligands. Each metal ion is bound to two terminal isopropoxide groups and one phenanthroline molecule. The distance Ce⋯Ce(1A) (4.1305(2) Å) is slightly longer than that in the complex Ce2(OR)6(DME)3 (4.064 Å).12 As in 1 the intramolecular Ce⋯F interactions in 3 are realized. The Ce(1)⋯F(16) distance (2.9182(14) Å) exceeds the analogous distances in 1 and lies within the interval of values for published data (2.6248(16)–2.9206(13) Å).14,25 As one should expect that such an interaction leads to elongation of the C(21)⋯F(16) bond length (1.362(2) Å) compared to other distances in this CF3 group (1.330(3)–1.339(3) Å). The steric saturation of the metal coordination sphere by ligands in 3 is 90.5 (2)% that is less than in 2. Thus, the steric factors do not prevent the realization of the intramolecular Ce⋯F interaction in 3 as it is distinct from 1. Due to the presence of phenanthroline containing extensive π-systems, in a crystal of 3, intermolecular π⋯π interactions are realized which combine the molecules in couples (Fig. 2b). The distances between centers of six-membered rings are 3.665 Å and satisfy the geometric criterion for the existence of π⋯π interactions (3.8 Å)19 between phenanthroline molecules in neighboring complexes.

Perfluorinated tert-butoxides 4, 5 and diolates 6, 7, 8 were prepared similarly to 1–3. In the reactions with the diol, the molar ratio 2:3 was used. The butoxides contain two molecules of DME whereas diolates have no coordinated solvent at all. LDI-TOF analysis revealed that cerium tert-butoxide is a
dimer while the gadolinium counterpart has a monomeric structure.

\[
\begin{align*}
2 \text{Ce}^3\{\text{NSiMe}_3\}_2 + 6 \text{ROH} & \rightarrow \{\text{Ce}^3\{\text{OR}\}_3\}_2\{\text{DME}\}_2; \\
\text{Gd}^3\{\text{NSiMe}_3\}_2 + 3 \text{ROH} & \rightarrow \{\text{Gd}^3\{\text{OR}\}_3\}_2\{\text{DME}\}_2.
\end{align*}
\]

Besides the pale brown product 8 in the last reaction, a negligible amount of mononuclear diolate \(\{\text{Ce}^3\{\text{O(CF}_3)_2\text{C}(\text{C}_2\text{F}_5)_2\}_{\cdot}\text{O}\}_2\}_{\cdot}(\text{OH})_2\}_{\cdot}(\text{phen})_2\} \) \(9\) was isolated as orange crystals. Change of the cerium amide : diol ratio to 1 : 2 resulted in an increase of the yield of 9 up to 59%. Probably, the reason for formation of such a product is due to a slight excess of alcohol and phenanthroline in the reaction mixture.

According to X-ray analysis complex 9 (Fig. 3a) has a monomeric structure in which the cerium ion is linked to one butanediolate ligand (2.311(4) and 2.344(4) Å) are significantly longer than the length of the cerium–oxygen bond of the hydroxybutane-

\[
\begin{align*}
\text{Ce}(1) & – \text{O}(2) 75.95(16), \text{O}(2) – \text{Ce}(1) 2.311(4), \\
\text{Ce}(2) & – \text{O}(3) 2.258(5), \text{Ce}(1) – \text{Ce}(2) 3.7253(12).
\end{align*}
\]

diolate group (2.258(5) Å). Such differences in the bond lengths can be caused by steric effects in the coordination sphere of cerium. In complex 9 as for 3 there is an intramolecular Ce(1)–F(1) (2.950 (4) Å) interaction which leads to the elongation of the bond C(3)–F(1) (1.353(9) Å) length compared to analogous ones (1.337(9)–1.341(9) Å). The steric saturation of the metal coordination sphere by ligands in 3 is 87.7(2)%. It should be noted that phenanthroline molecules neighboring complexes 9 in the crystal have offset disposition to each other but the distance between the centers of the six-membered rings of these ligands (3.875 Å) slightly exceeds the geometric criterion for the existence of the \(\pi–\pi\) interaction (Fig. 3b).

The general properties of alkoxides 4–9 are similar to those of isoproxides 1 and 3: they are slowly hydrolyzed in air, soluble in common organic solvents and do not sublime \textit{in vacuo} which prevents their application as an emitting material in OLED devices.

As it has been mentioned, f-d emission of lanthanide complexes is of considerable interest because of their wide application potential. In an effort to obtain samarium(i) the f-d emitter, interaction of SmI\(_2\) with potassium isopropoxide KOR was carried out. However, the reaction afforded the complex \(\{\text{Sm}_3\{\mu_3\text{OR}\}_6\{\mu_3\text{OR}\}_2\text{Sm}(\text{OR})_2\{\text{THF}\}_2\{\text{Et}_2\text{O}\}_{0.5}\} \) (Fig. 4) containing one Sm\(^{3+}\) and two Sm\(^{2+}\) cations.

\[
\begin{align*}
\text{Fig. 3} & \quad \text{Molecular structure of 9 (a) and the dimeric structure of 9 in crystal (b). Thermal ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity. Selected distances [Å] and angles [°] in 9: Ce(1)–Ce(1) 3.259(8), Ce(1)–O(2) 2.311(4), Ce(1)–O(1) 2.344(4), Ce(1)–N(2) 2.648(5), Ce(1)–N(1) 2.653(6), Ce(1)–N(4) 2.679(6), Ce(1)–N(3) 2.741(6), Ce(1)–F(1) 2.950(4); O(3)–Ce(1)–O(2) 136.86(17), O(3)–Ce(1)–O(1) 75.95(16), O(2)–Ce(1)–O(1) 66.80(15), O(3)–Ce(1)–N(2) 139.64(18), O(2)–Ce(1)–N(2) 83.17(16), O(1)–Ce(1)–N(2) 131.94(16), O(3)–Ce(1)–F(1) 115.54(16), O(2)–Ce(1)–F(1) 62.61(15), O(1)–Ce(1)–F(1) 59.63(14), N(1)–Ce(1)–F(1) 64.77(15), N(3)–Ce(1)–F(1) 137.70(17).
\end{align*}
\]

\[
\begin{align*}
\text{Fig. 4} & \quad \text{Molecular structure of 10. Thermal ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity. Selected distances [Å] and angles [°] in 10: Sm(1A)–O(3A) 2.486(11), Sm(1A)–O(1A) 2.555(10), Sm(1A)–O(2A) 2.460(11), Sm(1A)–F(10A) 2.720(11), Sm(1A)–F(4A) 2.728(10), Sm(1A)–Sm(2A) 3.7253(12), Sm(1A)–Sm(3A) 3.8026(12), Sm(2A)–O(7A) 2.155(11), Sm(2A)–O(6A) 2.201(11), Sm(2A)–O(3A) 2.410(12), Sm(2A)–O(5A) 2.519(10), Sm(3A)–O(25A) 2.590(11), Sm(3A)–O(2A) 2.617(11), Sm(3A)–O(1A) 2.663(10), Sm(3A)–F(28A) 2.894(11); O(3A)–Sm(1A)–O(1A) 71.8(3), O(3A)–Sm(1A)–O(4A) 136.0(3), \text{O}(1A)–Sm\text{-}1\text{A}–O(4A) 76.0(4), \text{O}(3A)–Sm\text{-}1\text{A}–O(2A) 69.0(3), \text{O}(1A)–Sm\text{-}1\text{A}–O(2A) 64.5(3), \text{O}(4A)–Sm\text{-}1\text{A}–O(2A) 70.5(4), \text{O}(3A)–Sm\text{-}1\text{A}–F(10A) 85.0(4), \text{O}(1A)–Sm\text{-}1\text{A}–F(10A) 125.6(3), \text{O}(4A)–Sm\text{-}1\text{A}–F(10A) 90.2(4), \text{O}(2A)–Sm\text{-}1\text{A}–F(10A) 61.3(3), \text{O}(1A)–Sm\text{-}1\text{A}–F(4A) 60.5(3), \text{O}(4A)–Sm\text{-}1\text{A}–F(4A) 104.8(4), \text{O}(2A)–Sm\text{-}1\text{A}–F(4A) 124.0(3). Sm(2A)–Sm(1A)–O(3A) 59.86(2).
\end{align*}
\]
Formation of heterovalent product can be stipulated by the reaction of the formed at initial stage samarium(III) isopropanoxide with ROH which remains after the synthesis of potassium salt and its excess cannot be removed from the reaction solution without decomposition of this salt.

According to the X-ray analysis, the metal atoms in 10 are linked to each other via μ₂- and μ₁-isopropanoxide ligands. Two terminal OR groups are bonded to the Sm⁴⁺ ion. The μ₁-oxygen atoms (O(1) and O(2)) are disposed over and under the plain Sm₁Sm₂Sm₃ forming the trigonal-bipyramidal skeleton. Note that there are two independent molecules of 10 in the asymmetric unit cell. The Sm³⁺ cations in one of the independent molecules of 10 are coordinated by three THF molecules whereas in other molecules they are coordinated by one Et₂O and two THF molecules. Additionally, there are four close contacts between samarium(II) ions and fluorine atoms of μ₂-OR ligands in the complex.

Another potential f-d emitter – heterobimetallic alkoxide of divalent europium [Eu₂(μ₂-OR)₃(μ₁-OR)₂Y(OR)₂(DME)₂] (11) was synthesized by the reaction of Y[N(SiMe₃)₂]₃ and Eu[N(SiMe₃)₂]₃] with isopropanol in Et₂O solution. Yttrium was chosen as a sensitizer of europium emission because it can form high-lying ligand-to-metal charge transfer state (LMCT) from which transfer of absorbing energy to resonance levels of Eu(II) may occur.² It should be noted that compound 11 is the first structurally characterized heterobimetallic complex, which contains yttrium and europium ions (Fig. 5).

In spite of the fact that complexes 10 and 11 were prepared by different reactions, the molecular structures of these compounds are very similar. Moreover, arrangement of the prepared earlier complexes Eu₃(OR)₂(DME)₂ and Yb₃(OR)₂(THF)Et₂O¹² appeared to be analogous to that of complexes 10 and 11. In both complexes one trivalent and two divalent metal cations are linked to each other via three μ₂- and two μ₁-isopropanoxide ligands. Two terminal OR groups are bonded to Sm³⁺ (in 10) and Y³⁺ (in 11) ions. Two coordination sites around each of divalent ions are occupied by Et₂O and THF molecules in samarium isopropanoxide and by DME in europium-yttrium complex. The μ₁-oxygen atoms (O(1), O(2) in 10 and O(10), O(11) in 11) are disposed over and under the plain Sm₁Sm₂Sm₃(Y(1)Eu(1)Eu(2)) forming the trigonal-bipyramidal skeleton. Six-membered metallacycle Ln₃O₃ in 10 and 11 is essentially flat. The largest deviation from the plane of atom metallacyle is 0.112 Å in 10 and 0.191 Å in 11.
It is interesting to note that among the prepared alkoxides 1, 3, and 9–11 where intramolecular Ln⋯F interactions are observed, the steric saturation of the metal coordination sphere varies in the range of 87.7(2)–94.9(2)%. In turn, in complex 2 where such interactions are absent, the G-parameter (97.3 (2)%) significantly exceeds the analogous values for the complexes with close Ln–F contacts.

**Luminescent properties**

Among the prepared complexes, PL was observed for the europium–yttrium isopropoxide and all the cerium derivatives. Acetonitrile solutions of cerium compounds 4 and 6 showed emission in the region of 370–400 nm (Fig. 6). These bands exhibit multimodal character and each of them can be decomposed into two Gaussian peaks with maxima at 343, 373 and 392, 425 nm respectively. The energy difference between these peaks is close to 2000 cm⁻¹, in good agreement with the characteristic splitting of the two Ce³⁺ 4f ground levels induced by the spin–orbit interaction. Therefore, the PL of 4 and 6 is attributed to the electric-dipole 4d→5f transitions in the cerium ion from the lowest excited state ⁵D₃/₂ to the ground states ⁷F₅/₂ and ⁷F₇/₂.

Besides, the f–d emission of the Ce³⁺ ion was observed for complexes 3, 8 and 9 (Fig. 7). Comparison of the PL spectra of 6 and 8 shows that insertion of the phenanthroline ligand in the cerium butanediolate caused slight blue shifting of the emission maximum from 410 to 405 nm and decreasing PL intensity.

Heterobimetallic complex 11 revealed blue PL with a maximum at 485 nm (Fig. 8). As the compound does not contain chromophore ligands and the band of emission lies in the range of Eu²⁺ luminescence, so the observed peak was attributed to 4f⁶5d¹→4f⁷ transition in the europium(II) ion.

Interestingly, complexes 3 and 11 did not reveal luminescence in MeCN solution in contrast to THF medium probably because of differences in the symmetry of the crystal field at cerium atoms in these solvents.

As noted above, due to low volatility and thermal stability of the majority of the prepared complexes, the only OLED device based on isopropoxide 3 was fabricated. A simple three-layered device of structure ITO/TPD/complex 3/BATH/Yb was prepared by the vacuum evaporation method. The diode displayed weak orange luminescence, the spectrum of which contained a single broad band with the maximum at 620 nm (Fig. 9). The EL efficiency did not exceed 2 cd m⁻² at 30 V.
The observed EL can be ascribed to the emission of the electroplex formed at the TPD/3 interface. Confirmation of the supposition is the absence of PL of the double layer and blend TPD-3 samples. Similar EL of electroplex was registered previously for the OLED devices based on the lanthanide pentafluorophenolates.\textsuperscript{29}

### Conclusions

A set of Ce(III), Sm(III), Eu(III), Gd(III) and Yb(III) complexes with fluorinated isopropoxide, tert-butoxide and butanediolate ligands was prepared. X-ray and LDI-TOF analysis revealed that Ln(III) isopropoxides as well as Ce tert-butoxide have binuclear arrangement whereas gadolinium butoxide is mononuclear probably due to a smaller radius of the Gd\(^{3+}\) ion. Isosctructural alkoxides 10 and 11 are trinuclear clusters in which two Ln\(^{2+}\) cations are bonded via bridging RO ligands to the Sm\(^{3+}\) cation (in 10) or the Y\(^{3+}\) cation (in 11). All the prepared cerium complexes upon UV excitation showed short-wavelength emission at the region of 370–425 nm as broadened bands, which is characteristic for 5d→4f transitions in the cerium ion.\textsuperscript{30} Heterobimetallic alkoxide 11 revealed blue PL with a maximum at 485 nm which was assigned to f-d emission of the europium(III) ion. Attempts to prepare OLED devices using the synthesized alkoxides as emitter layers for investigation of their EL properties failed because of low thermal stability of the compounds. The only complex, on the basis of which we were able to design a diode, was cerium compound 3 but this device displayed the electroplex luminescence and not the metal-centered emission.

### Acknowledgements

This work was supported by the Russian Foundation for Basic Research (projects 13-03-00097, 14-03-31043, 15-33-20296).

### Notes and references


