ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2022, Vol. 48, No. 4, pp. 224–232. © Pleiades Publishing, Ltd., 2022.
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Synthesis and Crystal Structure of $\{Eu_2^{III}Cd_2\}$, $\{Tb_2^{III}Cd_2\}$ and $\{Eu_2^{III}Zn_2\}$ Complexes with Pentafluorobenzoic Acid Anions and Acetonitrile

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Received June 10, 2021; revised October 30, 2021; accepted November 1, 2021

Abstract—Methods for the synthesis were developed and new homo- and heterometallic cadmium ($[Eu_2Cd_2(MeCN)_4(C_6F_5COO)_{10}]$ (**I**), $[Tb_2Cd_2(MeCN)_6(C_6F_5COO)_{10}]\cdot4MeCN$ (**II**)) and zinc ($[Zn(H_2O)(C_6F_5COO)_2]$ (**III**), $[Eu_2Zn_2(MeCN)_4(C_6F_5COO)_{10}]$ (**IV**)) complexes were characterized. These complexes can be used as precursors for the synthesis of compounds with N-donor ligands. Complexes **I** and **II** differ in the coordination of the MeCN molecule, which is coordinated in **II** by each Tb^{3+} ion. Also, additional coordination of MeCN induces a greater distortion of the $\{Tb_2Cd_2\}$ metal core of **II**. The crystal packing in **I**–**IV** is stabilized by numerous intermolecular O...H, F...F, C–H...F, and C–H...O contacts. The new compounds were characterized by single crystal X-ray diffraction (CCDC no. 2076524 (**I**), 2082731 (**II**), 2082803 (**III**), 2076525 (**IV**)), IR spectroscopy, C,H,N elemental analysis, and powder X-ray diffraction.

Keywords: cadmium, zinc, europium, terbium, pentafluorobenzoic acid, X-ray diffraction

DOI: 10.1134/S1070328422040042

INTRODUCTION

The interest in heterometallic complexes of transition metals and lanthanides is caused by the possibility of obtaining brightly luminescent compounds, which can be used, for example, for the design of optical amplifiers and sensor materials based on luminescent films [1–5]. The polynuclear metal cores in molecular heterometallic compounds can be used as ready blocks for metal-organic frameworks [6–8], in which the properties of molecular complexes with the same composition are either retained or altered.

Halogenated organic ligands are widely used in the synthesis of compounds possessing photoluminescent properties, because the absence of C–H bonds may enhance the efficiency of luminescence of the complexes due to the absence of quenching [9, 10], while the presence of non-covalent contacts (π...π, C–H...Hal, Hal...Hal, and C–Hal...π) results in the formation of unusual structures [11–16]. The role of non-covalent interactions between arene and perfluoroarene aromatic systems was repeatedly noted in our studies addressing the structure and crystal packing of transition metal complexes with fluorinated benzoic acid anions [11, 17, 18]. First of all, mention should be made of the formation of homo- and heterometallic metal-organic-frameworks and molecular complexes with unusual composition and structure (2,3,4,5-tetrafluorobenzoate dimers and heteroanionic polymers) [17, 19].

Most of heterometallic M^{2+}–Ln^{3+} complexes (M = Ni, Co, Cu, Zn, Cd) were obtained by replacement of inorganic anions in M and Ln salts via reactions with potassium carboxylates [18–29]. However, in some cases, the preparation of complexes by this procedure is accompanied by coordination of inorganic anions by metal ions, which may have an adverse effect on the luminescent properties and the structure of products [30]. The presence of additional competing anions in the reaction medium can be avoided by using, as the starting compounds, pre-synthesized heterometallic carboxylate complexes containing coordinated labile solvent molecules. The solvent molecules incorporated in the coordination sphere of metal ions can later be easily replaced by N- and O-donor ligands during the synthesis of target products.

Previously, we synthesized cadmium–lanthanide and zinc–lanthanide polymeric complexes with pentafluorobenzoic acid anions and 1,10-phenanthroline (Phen) $[Ln_2Cd_2(C_6F_5COO)_{10}(Phen)_2]_n$ and $[Ln_2Zn_2(C_6F_5COO)_{10}(Phen)_2]$ [17]; the synthesis started with the reaction of *d*- and *f*-metal pentafluorobenzoates.

This communication describes the synthesis and study of the structure of $\{Ln_2Cd_2\}$ and $\{Ln_2Zn_2\}$ compounds with pentafluorobenzoate anions and coordinated acetonitrile molecules, which were obtained under conditions similar to the first step of the synthesis of $[Ln_2Cd_2(C_6F_5COO)_{10}(Phen)_2]_n$ and $[Ln_2Zn_2(C_6F_5COO)_{10}(Phen)_2]$ and can be considered as the precursors of these complexes.

EXPERIMENTAL

All operations involved in the synthesis of complexes were carried out in air using MeCN (≥99.5%), EtOH (96%), $Zn(NO_3)_2{\cdot}4H_2O$ (99+%, Acros Organics), KOH (reagent grade), and Phen (99%, Alfa Aesar). The compounds $[\{Cd(C_6F_5COO)(H_2O)_4^+\}_n{\cdot}n(C_6F_5COO)^-]$, $[Eu_2(C_6F_5COO)_6(H_2O)_8]{\cdot}2H_2O$ [11], and $[Tb_2(C_6F_5COO)_6(H_2O)_8]$ [31] were synthesized by known procedures. $Zn(OH)_2$ was obtained by the reaction of stoichiometric amounts of KOH and $Zn(NO_3)_2{\cdot}4H_2O$ in water.

Synthesis of $[Eu_2Cd_2(MeCN)_4(C_6F_5COO)_{10}]$ (I). $[Eu_2(C_6F_5COO)_6(H_2O)_8]{\cdot}2H_2O$ (0.146 g, 0.083 mmol) was added to a solution of $[\{Cd(C_6F_5COO)(H_2O)_4^+\}_n{\cdot}n(C_6F_5COO)^-]$ (0.100 g, 0.166 mmol) in MeCN (5 mL). The reaction mixture was stirred for 20 min at 70°C, and the resulting colorless solution was allowed to slowly evaporate in air. The colorless crystals suitable for X-ray diffraction, which formed after 10 days, were separated from the mother liquor by decantation and washed with cold MeCN ($T = {\sim}5$°C). The yield of compound **I** was 0.169 g (72.4% based on $[\{Cd(C_6F_5COO)(H_2O)_4^+\}_n{\cdot}\,n(C_6F_5COO)^-]$.

For $C_{78}H_{12}O_{20}N_4F_{50}Cd_2Eu_2$

Anal. calcd.,	C, 33.2	H, 0.2	N, 1.8
Found, %	C, 33.4	H, 0.4	N, 2.0

IR (ATR; ν, cm^{-1}): 3661 w, 2988 w, 2304 w, 2277 w, 1653 m, 1607 s, 1584 s, 1526 m, 1491 s, 1392 s, 1296 s, 1261 m, 1108 s, 990 s, 934 m, 830 m, 768 s, 753 m, 742 s, 696 s, 626 w, 584 w, 508 w.

Synthesis of $[Tb_2Cd_2(MeCN)_6(C_6F_5COO)_{10}]{\cdot}4MeCN$ (II) was carried out similarly to the synthesis of **I** using $[Tb_2(C_6F_5COO)_6(H_2O)_8]$ (0.143 g, 0.083 mmol) instead of $[Eu_2(C_6F_5COO)_6(H_2O)_8]{\cdot}2H_2O$. The obtained colorless solution was allowed to slowly evaporate in air. The colorless crystals suitable for X-ray diffraction, which formed after 9 days, were separated from the mother liquor by decantation and washed with cold MeCN ($T = {\sim}5$°C). The yield of **II** was 0.160 g (62.9% based on $[\{Cd(C_6F_5COO)(H_2O)_4^+\}_n{\cdot}n(C_6F_5COO)^-]$.

For $C_{90}H_{30}O_{20}N_{10}F_{50}Cd_2Tb_2$

Anal. calcd., %	C, 35.3	H, 1.0	N, 4.6
Found, %	C, 35.4	H, 0.9	N, 4.2

IR (ATR; ν, cm^{-1}): 3663 w, 2988 w, 2303 w, 2278 w, 1653 m, 1602 s, 1586 s, 1526 m, 1495 s, 1389 s, 1298 s, 1261 m, 1108 s, 990 s, 935 m, 830 m, 768 s, 751 m, 750 s, 699 s, 621w, 592w, 508 w.

Synthesis of $[Zn(H_2O)(C_6F_5COO)_2]_n$ (III). A solution of potassium pentafluorobenzoate C_6F_5COOK (0.323 g, 1.346 mmol) in EtOH (15 mL), obtained by the reaction of KOH with C_6F_5COOH, was added to a solution of $Zn(NO_3)_2{\cdot}6H_2O$ (0.200 g, 0.673 mmol) in EtOH (15 mL). The reaction mixture was stirred for 30 min at 70°C and cooled to room temperature, and the white precipitate of KNO_3 was filtered off. The filtrate was kept at room temperature with slow evaporation of the solvent for 2 days. The colorless crystals suitable for X-ray diffraction, which formed during this period, were separated from the mother liquor by decantation, washed with cold EtOH ($T = {\sim}5$°C), and dried in air. The yield of **III** was 0.293 g (86.1% based on $Zn(NO_3)_2{\cdot}6H_2O$).

For $C_{24}H_2O_5F_{10}Zn$

Anal. calcd., %	C, 33.3	H, 0.4
Found, %	C, 33.7	H, 0.1

IR (ATR; ν, cm^{-1}): 1989 w, 1945 w, 1793 w, 1727 w, 1645 m, 1617 s, 1567 s, 1526 s, 1486 s, 1396 s, 1119 s, 993 s, 942 m, 811 w, 774 m, 746 m, 712 w, 614 w, 586 w, 529 w, 442 m.

Synthesis of $[Eu_2Zn_2(MeCN)_4(C_6F_5COO)_{10}]$ (IV). *Procedure A.* C_6F_5COOH (0.314 g, 1.485 mmol) was added to freshly precipitated $Zn(OH)_2$ (0.075 g, 0.742 mmol) in water (20 mL), and the mixture was stirred at 80°C for 2 h, until $Zn(OH)_2$ completely dissolved, and then evaporated to dryness. The resulting precipitate was dissolved in MeCN (15 mL), and $[Eu_2(C_6F_5COO)_6(H_2O)_8]{\cdot}2H_2O$ (0.651 g, 0.371 mmol) was added. The reaction mixture was kept at room temperature with slow evaporation. The colorless crystals suitable for X-ray diffraction, which formed after 10 days, were separated from the mother liquor by decantation and dried in air. The yield of **IV** was 0.827 g (82.1% based on $Zn(OH)_2$).

Procedure B. $[Eu_2(C_6F_5COO)_6(H_2O)_8]{\cdot}2H_2O$ (0.348 g, 0.198 mmol) was added to a solution of compound **III** (0.100 g, 0.198 mmol)) in MeCN (25 mL). The reaction mixture was stirred for 60 min at 70°C, and the resulting colorless solution was allowed to slowly evaporate in air. The colorless crystals suitable for X-ray diffraction, which formed after 7 days, were separated from the mother liquor by decantation and washed with cold MeCN ($T = \sim 5°C$). The yield of **IV** was 0.206 g (76.9% based on compound **III**).

For $C_{78}H_{12}N_4O_{20}F_{50}Zn_2Eu_2$

Anal. calcd., %	C, 34.6	H, 0.4	N, 2.7
Found, %	C, 34.4	H, 0.5	N, 2.3

IR (ATR; ν, cm^{-1}): 3675 w, 2988 w, 2901 w, 2303 w, 2277 w, 1652 m, 1609 m, 1584 m, 1525 m, 1490 s, 1396 s, 1296 m, 1264 w, 1108 m, 1077 w, 1066 w, 1046 w, 991 s, 935 m, 826 m, 773 m, 742 s, 703 w, 653 w, 624 w, 584 w, 508 w.

Heterometallic compounds **I**, **II**, and **IV** were used for the synthesis of 1,10-phenanthroline complexes obtained in our previous study: $[Eu_2Cd_2(Phen)_2(C_6F_5COO)_{10}]_n \cdot 3n$MeCN, $[Tb_2Cd_2(Phen)_2(C_6F_5COO)_{10}]_n \cdot 3n$MeCN, and $[Eu_2Zn_2(C_6F_5COO)_{10}(Phen)_2] \cdot 4$MeCN [17].

Synthesis of $[Eu_2Cd_2(Phen)_2(C_6F_5COO)_{10}]_n \cdot 3n$MeCN. A weighed portion of Phen (0.007 g) was added to a solution of complex **I** (0.100 g) in MeCN (20 mL). The reaction mixture was stirred for 40 min at 70°C, and the resulting colorless solution was allowed to slowly evaporate in air. The colorless crystals suitable for X-ray diffraction, which formed after 3 days, were separated from the mother liquor by decantation and washed with cold MeCN ($T = \sim 5°C$). The yield of the product was 0.086 g (76.1% based on compound **I**).

For $C_{50}H_{12.5}N_{3.5}O_{10}F_{20}CdEu$

Anal. calcd., %	C, 38.5	H, 0.8	N, 3.1
Found, %	C, 38.4	H, 0.6	N, 2.8

IR (ATR; ν, cm^{-1}): 1651 m, 1625 m, 1589 s, 1573 m, 1519 m, 1488 s, 1450 m, 1432 w, 1381 s, 1348 s, 1285 m, 1220 w, 1136 m, 1102 s, 996 s, 927 m, 863 m, 846 w, 830 s, 760 s, 723 s, 699 s, 651 m, 637 m, 618 m, 559 m, 544 m, 500 w.

Synthesis of $[Tb_2Cd_2(Phen)_2(C_6F_5COO)_{10}]_n \cdot 3n$MeCN. A weighed portion of Phen (0.006 g) was added to a solution of complex **II** (0.100 g) in MeCN (20 mL). The reaction mixture was stirred for 40 min at 70°C, and the resulting colorless solution was allowed to slowly evaporate in air. The colorless crystals suitable for X-ray diffraction, which formed after 2 days, were separated from the mother liquor by decantation and washed with cold MeCN ($T = \sim 5°C$). The yield of the product was 0.070 g (68.2% based on compound **II**).

For $C_{50}H_{12.5}N_{3.5}O_{10}F_{25}CdTb$

Anal. calcd., %	C, 38.3	H, 0.8	N, 3.1
Found, %	C, 38.5	H, 0.6	N, 2.9

IR (ATR; ν, cm^{-1}): 1648 m, 1629 m, 1589 s, 1576 m, 1516 m, 1488 s, 1447 m, 1435 w, 1383 s, 1346 m, 1285 m, 1219 m, 1138 m, 1102 s, 989 m, 929 m, 862 w, 845 m, 829 m, 762 s, 726 s, 697 m, 648 m, 643 m, 622 w, 560 m, 543 w, 502 m.

Synthesis of $[Eu_2Zn_2(C_6F_5COO)_{10}(Phen)_2] \cdot 4$MeCN. A weighed portion of Phen (0.007 g) was added to a solution of complex **IV** (0.100 g) in MeCN (25 mL). The reaction mixture was stirred for 80 min at 70°C, and the resulting colorless solution was allowed to slowly evaporate in air. The colorless crystals suitable for X-ray diffraction, which formed after 8 days, were separated from the mother liquor by decantation and washed with cold MeCN ($T = \sim 5°C$). The yield of the product was 0.063 g (55.6% based on compound **IV**).

For $C_{102}H_{28}N_8O_{20}F_{50}Zn_2Eu_2$

Anal. calcd., %	C, 39.9	H, 0.9	N, 3.7
Found, %	C, 40.2	H, 0.7	N, 3.5

IR (ATR; ν, cm^{-1}): 1724 m, 1698 w, 1651 s, 1612 s, 1518 w, 1492 s, 1426 m, 1395 s, 1313 m, 1227 m, 1145 m, 1100 s, 987 s, 933 m, 849 w, 845 m, 830 m, 765 m, 740 s, 725 s, 700 s, 645 m, 588 m, 506 w.

The IR spectra of the compounds were measured on a Spectrum 65 (PerkinElmer) Fourier transform IR spectrometer with the attenuated total reflection (ATR) method in the 4000–400 cm^{-1} frequency range. Elemental analysis was carried out on a EuroEA 3000 (EuroVector) CHNS analyzer.

Single crystal X-ray diffraction stidy was carried out on Bruker Apex II (**I** and **IV**) and Bruker D8 Venture (**II**, **III**) diffractometers equipped with a CCD array detector (MoK_{α}, $\lambda = 0.71073$ Å, graphite monochromator) [32]. Semiempirical absorption corrections were applied for all compounds using the SADABS software [33]. The structures were solved by direct methods and refined by full-matrix least squares method in the anisotropic approximation for all nonhydrogen atoms. The hydrogen atom positions were generated geometrically. All hydrogen atoms were refined in the isotropic approximation in the riding model. The calculations were carried out by the SHELX program package [34] using OLEX2 software [35]. The geometry of metal atom polyhedra was determined by the SHAPE 2.1 program [36, 37]. The crystallographic parameters of structures **I**–**IV** are summarized in Table 1 and selected bond lengths and angles are given in Table 2.

The atom coordinates and other characteristics of compounds **I**–**IV** are deposited with the Cambridge Crystallographic Data Centre (CCDC no. 2076524 (**I**), 2082731 (**II**), 2082803 (**III**), 2076525 (**IV**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Table 1. Crystallographic parameters and structure refinement details for **I–IV**

Parameter	Value			
	I	**II**	**III**	**IV**
M	2803.64	3063.88	505.53	2709.58
T, K	296	100	150	296
System	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$C2/c$	Pc	$P\bar{1}$
a, Å	14.3259(7)	27.1874(7)	15.2692(14)	13.1947(3)
b, Å	23.8579(11)	13.8375(4)	5.9656(6)	13.6509(3)
c, Å	14.8740(7)	28.3728(8)	8.7070(8)	13.9538(4)
α, deg	90	90	90	65.0930(10)
β, deg	117.9260(10)	109.229(1)	104.938(3)	89.9450(10)
γ, deg	90	90	90	75.2480(10)
V, Å^3	4491.7(4)	10078.5(5)	766.32(13)	2188.21(10)
Z	2	4	2	1
ρ(calcd.), g/cm^3	2.073	2.019	2.191	2.056
μ, mm^{-1}	2.020	1.970	1.749	2.135
θ_{max}, deg	25.038	26.000	30.49	27.536
T_{min}/T_{max}	0.674/0.739	0.589/0.827	0.547/0.746	0.5769/0.7461
Number of measured reflections	50595	54800	7782	21901
Number of unique reflections	8629	9831	4026	8571
Number of reflections with $I > 2\sigma(I)$	6673	8584	3674	7431
R_{int}	0.0933	0.0454	0.0386	0.0389
Number of refined parameters	711	783	4391	8785
GOOF	1.044	1.019	0.998	1.061
R_1 ($I > 2\sigma(I)$)	0.0588	0.0267	0.0280	0.0362
wR_2 ($I > 2\sigma(I)$)	0.1506	0.0624	0.0636	0.0684
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	–1.545/1.829	–0.891/0.658	–0.700/0.532	–1.292/0.522

Table 2. Selected geometric characteristics of complexes **I–IV**

Bond	d, Å			
	I M = Cd; Ln = Eu	**II** M = Cd; Ln = Tb	**III** M = Zn	**IV** M = Zn; Ln = Eu
M–N (MeCN)	2.271(5)–2.363(10)	2.275(3), 2.326(3)		2.069(4), 2.254(4)
Ln–N (MeCN)		2.643(3)		
M–O (H_2O)			1.978(4)	
M–O ($C_6F_5COO^-$)	2.224(6)–2.517(6)	2.247(2)–2.550(2)	1.928(3)–1.972(3)	1.990(3)–2.082(3)
Ln–O ($C_6F_5COO^-$)	2.280(9)–2.534(13)	2.370(2)–2.710(2)		2.298(3)–2.681(2)
M...M	7.560(5)	7.501(8)	4.548(1)	9.280(1)
M...Ln	4.040(8)	3.925(1)		4.023(1)
Ln...Ln	4.045(9)	4.069(1)		3.957(1)
Angle	ω, deg			
MLnLn	171.4(1)	161.2(1)		166.8(1)

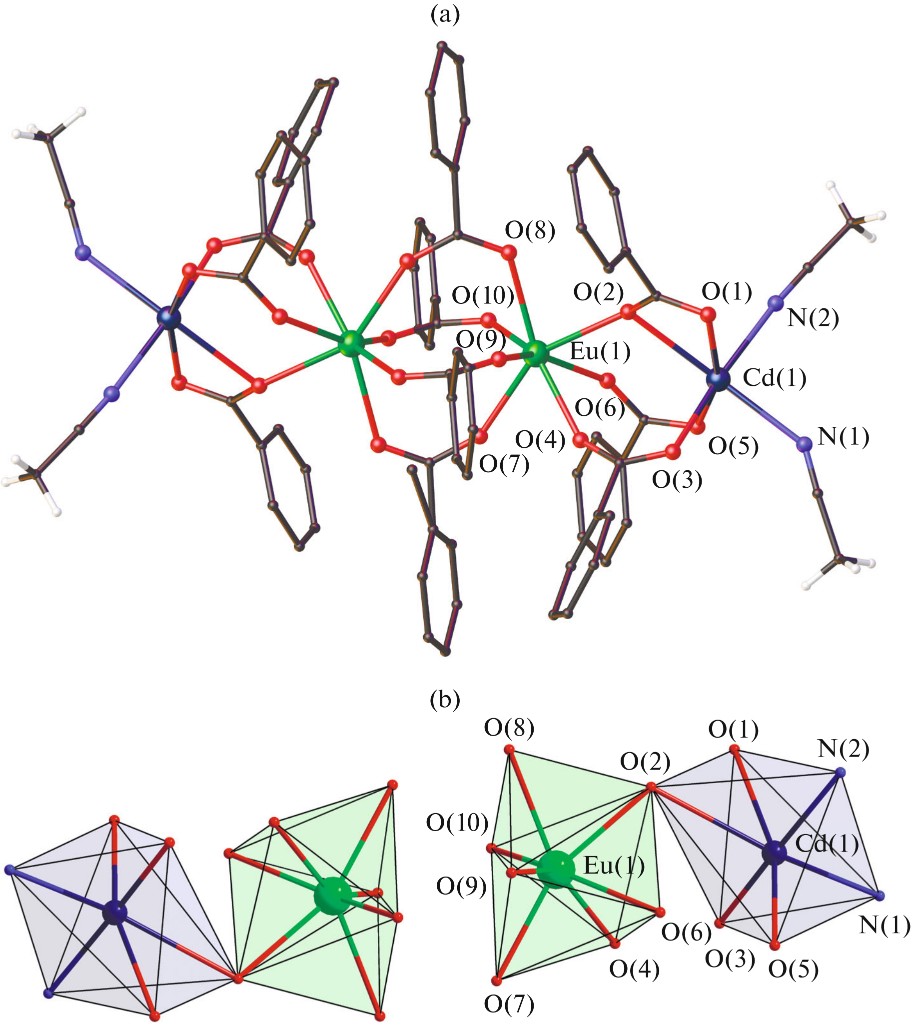

Fig. 1. (a) Molecular structure and (b) metal coordination polyhedra of complex **I**. The fluorine atoms in (a) are omitted.

Powder X-ray diffraction study of sample **I** was carried out on a Bruker D8 Advance diffractometer. The measurement step was 0.02° 2θ and the measurement range was 5°–40° 2θ (CuK_α, $\lambda = 1.54060$ Å, Ni filter, LYNXEYE detector, reflection geometry). Comparison of the experimental and theoretical X-ray diffraction patterns was carried out by means of TOPAS 4 software.

RESULTS AND DISCUSSION

The reaction of cadmium(II) and europium(III) pentafluorobenzoates [11] in MeCN resulted in isolation of crystals of $[Eu_2Cd_2(MeCN)_4(C_6F_5COO)_{10}]$ (**I**, Fig. 1). When Eu^{3+} pentafluorobenzoate in reaction **I** was replaced by a similar Tb^{3+} salt [31], the compound that crystallized was $[Tb_2Cd_2(MeCN)_6(C_6F_5COO)_{10}]\cdot 4MeCN$ (**II**, Fig. 2); unlike **I**, in this product, each lanthanide ion was additionally coordinated to an acetonitrile molecule. The phase purity of the polycrystalline sample of **I** was confirmed by powder X-ray diffraction (Fig. 3). Examples of coordination of solvents molecules by lanthanide ions in heterometallic carboxylate complexes are known from the literature [38–41].

It should be noted that additional ligand coordination in pentafluorobenzoate complexes of this type with retained structure of the metal core can also be observed in other cases. For example, we obtained the $[Eu_2Cd_2(Phen)_2(C_6F_5COO)_{10}]_n$ heterometallic complex, in which the metal core structure of a monomer unit was typical of d^{II}–f^{III} element benzoates, and the $[Eu_2Cd_2(Phen)_4(C_6F_5COO)_{10}]$ complex, in which the Eu^{3+} atoms, which was at the center of the linear metal core coordinated also 1,10-phenanthroline molecules, apart from the carboxylate anions [17].

The reaction of zinc(II) and europium(III) pentafluorobenzoates [11] in MeCN gave crystals of the $[Eu_2Zn_2(MeCN)_4(C_6F_5COO)_{10}]$ complex (**IV**, Fig. 4), structurally similar to **I**. When Eu^{3+} pentafluoroben-

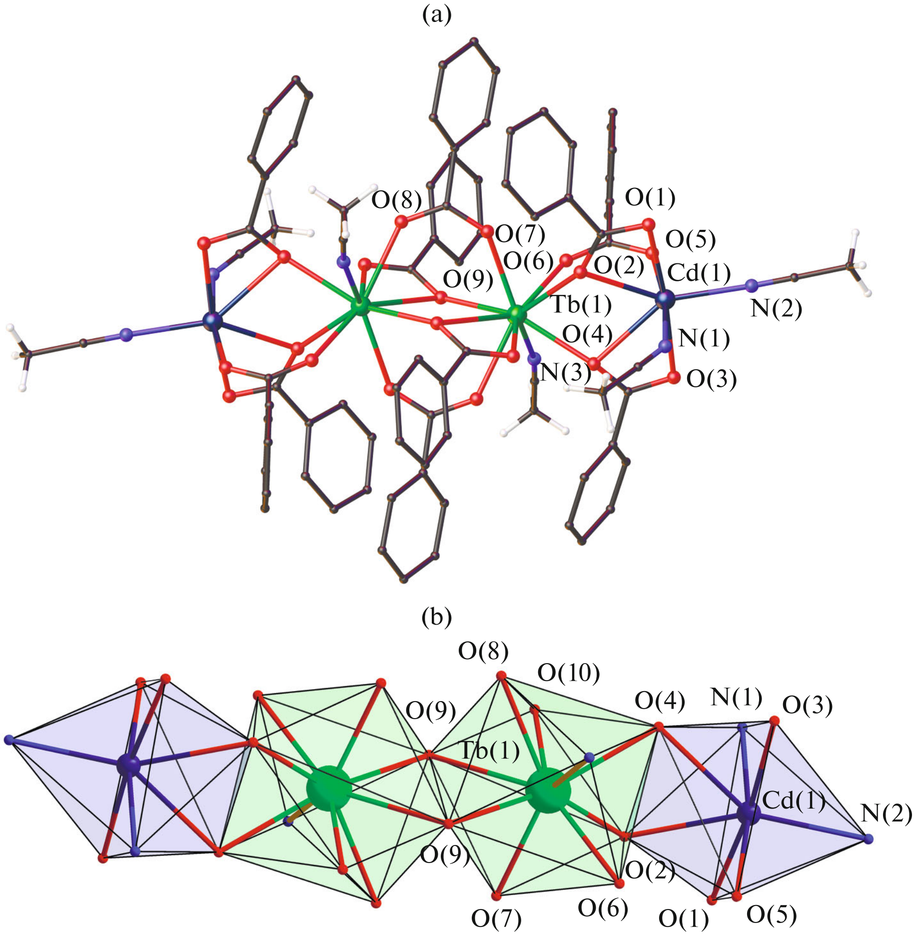

Fig. 2. (a) Molecular structure and (b) metal coordination polyhedra of complex **II**. The fluorine atoms and solvent molecules in (a) are omitted.

zoate in reaction **IV** was replaced by analogous Tb^{3+} salt, no crystals suitable for X-ray diffraction were obtained so far, and the polycrystalline precipitate thus formed did not correspond to the structure of **IV**, according to powder X-ray diffraction data. Apparently, this is due to the instability of many complexes with coordinated solvent molecules [42, 43]. However, this is not a drawback as regards the convenience of synthesis of heterometallic complexes from starting compounds such as **I**, **II**, and **IV**.

Complexes **I**–**IV** crystallize in the following space groups: monoclinic $P2_1/c$ (**I**), $C2/c$ (**II**), and Pc (**III**) and triclinic $P\overline{1}$ (**IV**). The inversion center in **I**, **II**, and **IV** is located between the Ln(1) and Ln(1A) central atoms. In the linear tetranuclear metal core of compounds **I** (Fig. 1), **II** (Fig. 2), and **IV** (Fig. 4), the two central lanthanide ions are linked by four bridging (**I**) or two bridging and two chelating bridging (**II**, **IV**) $C_6F_5COO^-$ anions. The terminal d^{10} metal ions are bound to the lanthanide metal centers by one chelating bridging and two bridging (**I**, **IV**) or one bridging and two chelating bridging (**II**) $C_6F_5COO^-$ anions. Each transition metal ion coordinates two MeCN molecules, thus completing the environment to an octahedron (**I**, CdO_4N_2; **IV**, ZnO_4N_2) or to a pentagonal bipyramid (**II**, CdO_5N_2). The Eu^{3+} coordination environment in **I** is a one-capped trigonal prism (EuO_7), while that in **IV** is a dodecahedron with triangular faces. The Tb^{3+} environment in **II** is completed to a “muffin” nine-vertex polyhedron by binding an acetonitrile molecule (TbO_8N). The coordination of acetonitrile to Tb^{3+} affects the geometry of the tetranuclear metal core, which is reflected as a distortion of the metal core linrarity (the CdEuEu angle in **I** is 171.4(1)° and the CdTbTb angle in **II** is 161.2(1)°). According to the CCDC, in the previously synthesized tri- and tetranuclear $\{LnZn_2\}$, $\{LnNi_2\}$, and $\{Ln_2Co_2\}$ complexes with monocarboxylate anions, unlike complexes **I**, **II**, and **IV**, only one MeCN molecule is coordinated to each transition metal atom [44–47].

In compound **I**, the CdO_4N_2 coordination polyhedron shares a vertex with the EuO_7 polyhedron of the neighboring lanthanide; the lanthanide coordination polyhedra do not share vertices or edges (Fig. 1b). In

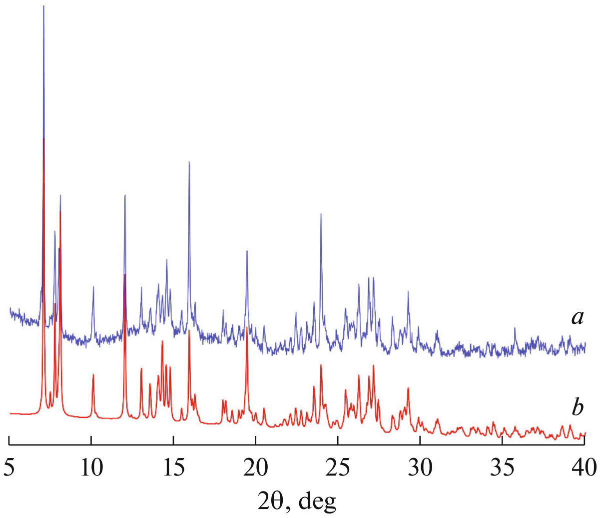

Fig. 3. Comparison of the (*a*) calculated and (*b*) experimental X-ray diffraction patterns for complex **I**.

compound **IV** (Fig. 4b), the ZnO_4N_2 coordination polyhedron shares a vertex with EuO_8N, while the coordination polyhedra of lanthanides share an edge. The polyhedra of **II** are packed much more closely, because all neighboring metal polyhedra have a common edge, unlike those of compound **I** (Fig. 2b).

In the structure of **III** (Fig. 5), the Zn^{2+} ions are connected to form a 1D polymer chain via bridging $C_6F_5COO^-$ anions. The metal environment is completed to a tetrahedron (ZnO_4) by coordination of the O atoms of the monodentately coordinated $C_6F_5COO^-$ anion and a water molecule.

The packing of complexes **I**, **II**, and **IV** contains numerous F...F (2.686 Å) and C–F...π (F...π 3.010(9)–3.509(3) Å) contacts between the pentafluorobenzoate anions and the C–H...F, C–F...π, and C–H...O contacts (C...O, 3.171(5)–3.310(5); F...π, 2.865(4)–3.191(9); C...F, 3.068(15)–3.465(4) Å) between the acetonitrile molecules and the pentafluorobenzoate anions, which stabilize the molecular packing in the crystals.

In the packing of complex **III**, the coordinated water molecule is involved in the hydrogen bonding with two O atoms of two monodentate $C_6F_5COO^-$ anions, thus forming a supramolecular polymer layer (O(1*w*)...O(4), 2.774(3); O(4)...H(1*w*B), 1.927(3) Å; O(4)H(1*w*A)O(1*w*), 163.6(2)°. O(1*w*A)...O(4A), 2.731(4); O(4A)...H(1*w*B), 1.884(3) Å; O(4A)H-(1*w*B)O(1*w*A), 163.5(2) °).

In relation to the previously synthesized pentafluorobenzoate $[Eu_2Cd_2(C_6F_5COO)_{10}L_x]$ complexes with pyridine (Py) and 2-phenylpyridine (2-Phpy), it was shown that the geometry of the {Cd–Eu–Eu–Cd} metal core is retained irrespective of the ligand that occupies coordination sites in the Cd environment [11], whereas the coordination of Phen induces a considerable distortion of the linearity of the $\{Eu_2Cd_2\}$ moiety and formation of polymers [17] (L = MeCN: Cd...Eu, 3.925(1); Eu...Eu, 4.069(1) Å; CdEuEu, 161.2(1)°; L = Py: Cd...Eu, 3.892(1); Eu...Eu, 3.920(2) Å; CdEuEu, 172.8(1)°; L = 2-Phpy: Cd...Eu, 4.079(1); Eu...Eu, 3.926(1) Å; CdEuEu, 168.4(1)°; L = Phen: Cd...Eu, 3.987(1); Eu...Eu, 4.178(1) Å; CdEuEu, 115.2(1)°).

The synthesized compounds proved to be convenient precursors for the synthesis of heterometallic complexes with aromatic N-donor ligands. Indeed, reactions of compounds **I**, **II**, and **IV** with 1,10-phenanthroline made it possible to isolate previously described heterometallic complexes $[Ln_2Cd_2(C_6F_5COO)_{10}(Phen)_2]_n \cdot 3n MeCN$ (Ln = Eu, Tb) and $[Eu_2Zn_2(C_6F_5COO)_{10}(Phen)_2] \cdot 4MeCN$ [17] (see Experimental).

Thus, it was shown that reactions of cadmium(II) or zinc(II) pentafluorobenzoate with lanthanide(III) pentafluorobenzoate in acetonitrile afford heterometallic compounds with Ln : Zn and Ln : Cd ratios of 1 : 1, i.e., with the same ratio as observed previously in the heterometallic molecular complexes with pyridine and 2,2'-bipyridine and 1,10-phenanthroline derivatives. It is very interesting that the Ln–Cd complex has a molecular structure, although compounds with the same metal carboxylate skeleton, but with chelating ligands crystallize, most often, as coordination polymers. This, apparently, indicates that arene–perfluoroarene interactions rather than steric factors play a crucial role in the formation of polymers, since acetonitrile occupies a very small volume in the metal inner sphere. It was shown that compounds **I**, **II**, and **IV** can be used as precursors for the synthesis of heterometallic complexes.

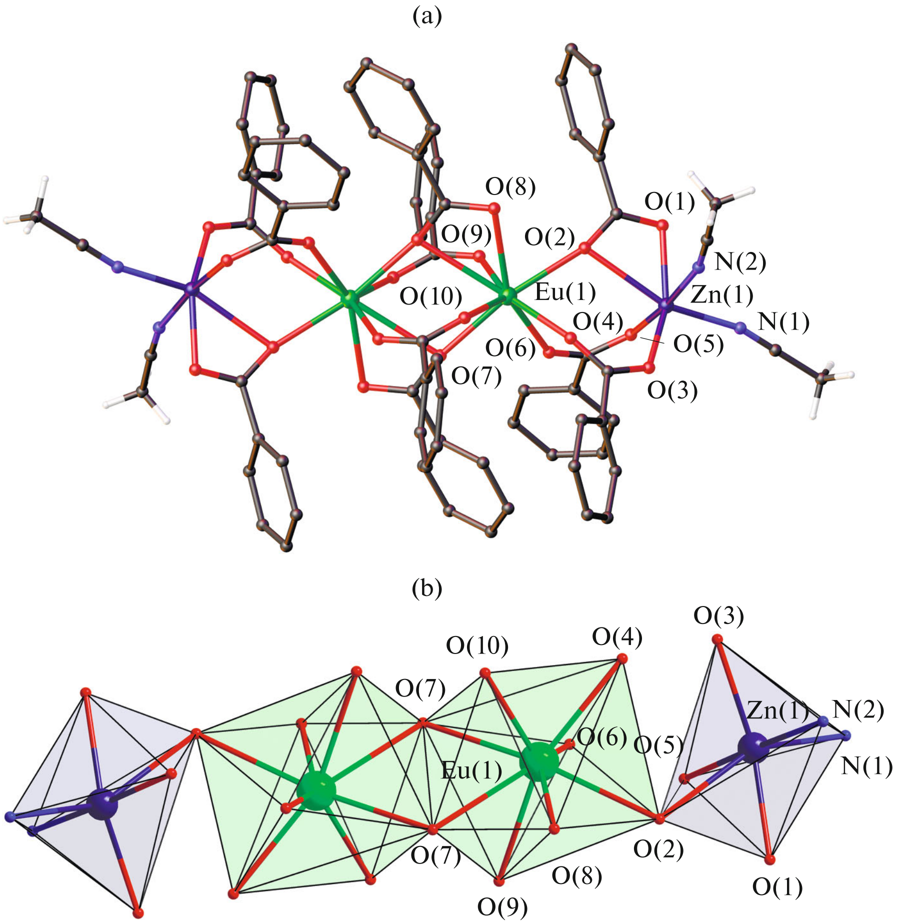

Fig. 4. (a) Molecular structure and (b) metal coordination polyhedra of complex **IV**. The fluorine atoms in (a) are omitted.

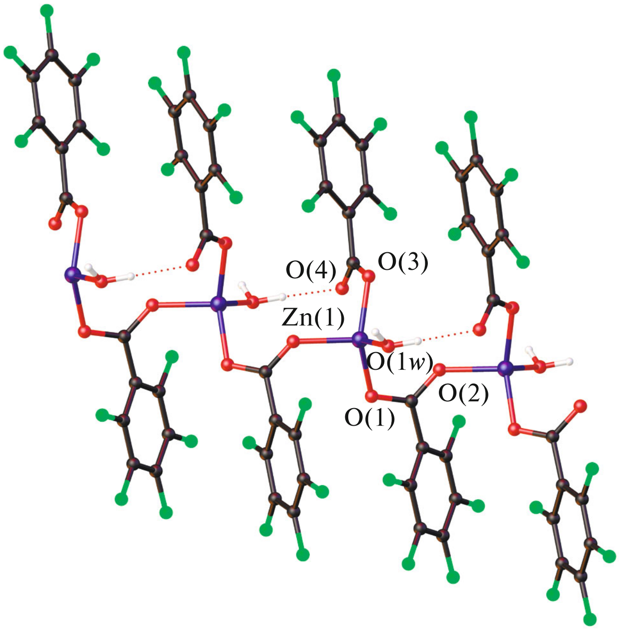

Fig. 5. Fragment of the polymer chain of **III**.

FUNDING

This study was supported by the Ministry of Education and Science of Russia within the framework of the state assignment of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences. Single crystal and powder X-ray diffraction, IR spectroscopy, and C,H,N,S analysis were carried out using the equipment of the Center for Collective Use of the Physical Investigation Methods, Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, supported by the state assignment of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, in the field of fundamental research.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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Translated by Z. Svitanko