Influence of the steric properties of pyridine ligands on the structure of complexes containing the $\{LnCd_2(bzo)_7\}$ fragment*

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The reaction of $Cd(NO_3)_2 \cdot 4H_2O$ and $Eu(NO_3)_3 \cdot 6H_2O$ or $Tb(NO_3)_3 \cdot 6H_2O$ with potassium 3,5-di-*tert*-butylbenzoate (Kbzo) and *N*-donor ligands (1,10-phenanthroline (phen), 2,4-lutidine (2,4-lut), 3,4-lutidine (3,4-lut), phenanthridine (phtd), 2,3-cyclododecenopyridine (cdpy), acridine (acr)) afforded heterometallic $LnCd_2$ complexes: $[EuCd_2(bzo)_7(EtOH)_2(phen)]$ (**2**), $[LnCd_2(bzo)_7(2,4\text{-lut})_4]$ (Ln = Eu (**3**), Tb (**4**)), $[EuCd_2(bzo)_7(H_2O)_2(2,4\text{-lut})_2] \cdot MeCN$ (**5**), $[EuCd_2(NO_3)(bzo)_6(EtOH)_2(2,4\text{-lut})_2]$ (**6**), $[EuCd_2(bzo)_7(H_2O)(EtOH)(3,4\text{-lut})_2] \cdot 5EtOH$ (**7**), $3[EuCd_2(bzo)_7(H_2O)_2(phtd)_2] \cdot 4phtd$ (**8**), $[EuCd_2(bzo)_7(EtOH)_3(cdpy)]$ (**9**), $2[EuCd_2(bzo)_2(EtOH)_4] \cdot acr$ (**10**). The structures of complexes **2**, **3**, and **5—10** were determined by single-crystal X-ray diffraction. The isostructurality of complexes **3** and **4** was confirmed by powder X-ray diffraction. The structure of the trinuclear $\{Ln_2Cd\}$ metal core is stable and independent of the type of peripheral ligands coordinated to cadmium atoms. Photoluminescent properties of compounds **3** and **4** were studied.

Key words: cadmium, lanthanides, 3,5-di-*tert*-butylbenzoic acid, luminescence, X-ray diffraction.

Variations of geometric parameters of ligands involved in the heterometallic chain structural units $\{M_2X_n(O_2CR)_k\}$ (M = Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}; X = Li ($n = 2$, $k = 6$), Mg ($n = 1$, $k = 6$), Ca ($n = 1$, $k = 6$), Ln ($n = 1, 2$, $k = 7, 10$)), in which 3d metals or cadmium are combined with lithium, magnesium, calcium, or lanthanide atoms,[1—12] can be employed to get knowledge on conformational flexibility of these metal cores. These data are useful for the analysis of the structures of more complex polynuclear compounds, particularly metal-organic frameworks based on related heterometallic units and structurally similar metal cores. This heterometallic unit is composed of two peripheral metal-containing moieties $\{M(O_2CR)_3\}$ structurally similar to scorpionate ligands. In the latter moieties, a group consisting of three carboxylate anions coordinated to a M atom acts as a chelating ligand for the heterometal X. The coordination environment of triply charged lanthanide ions is completed by additional carboxylate anions or carboxylate and nitrate anions to form the $\{LnM_2(O_2CR)_7\}$, $\{LnM_2(NO_3)(O_2CR)_6\}$, $\{Ln_2M_2(NO_3)_2(O_2CR)_8\}$, or $\{Ln_2M_2(O_2CR)_{10}\}$ units. In these systems, the coordination environment of M can be completed by neutral monodentate or chelating ligands to form molecular complexes and also by neutral bridging ligands to form coordination polymers.[7,10,12,13] The coordination environment of 3d metals is completed by a monodentate or chelating, generally *N*-donor, ligand regardless of the type of the heterometallic complex. The 3d metal atom coordinated by a monodentate *N*-donor ligand has a tetrahedral or distorted trigonal-bipyramidal coordination

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* Dedicated to Academician of the Russian Academy of Sciences A. M. Muzafarov on the occasion of his 70th birthday.

† Deceased.

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environment; the 3d metal atom coordinated by chelating ligands has an octahedral geometry.

Related complexes of cadmium exhibit specific features due to the larger coordination number of this metal and longer bonds of the coordination polyhedron. In this case, complexes with somewhat different structures can be synthesized. In such complexes, the coordination environment of cadmium is completed *via* the coordination of additional ligands, *e.g.*, by small solvent molecules.[10] Besides, bridging carboxylate groups mediate the spin exchange coupling between metal centers, which is important for the preparation of magnetic materials. The presence of an aromatic moiety in the carboxylate anion can give rise to ligand-centered luminescence or efficient energy absorption or transfer to the lanthanide ion and, as a consequence, lead to enhancement of its emission.[14—16]

The aim of this work is to examine the coordination to a cadmium atom involved in the heterometallic unit $\{EuCd_2(bzo)_7\}$ (bzo is the 3,5-di-*tert*-butylbenzoate anion) of monodentate pyridine derivatives with bulky α-substituents and 1,10-phenanthroline in coordinating solvents, the molecules of which can compete for a coordination site in the environment of the metal ion. 3,5-Di-*tert*-butylbenzoic acid is a readily available aromatic acid containing bulky alkyl substituents bonded to an aromatic moiety. Two *tert*-butyl substituents provide high solubility of the resulting carboxylate complexes in non-aqueous media, making it possible to isolate crystals suitable for X-ray diffraction. Besides, these substituents ensure the formation exclusively of the $\{LnM_2(O_2CR)_7\}$ or $\{LnM_2(NO_3)(O_2CR)_6\}$ units, which were required for our study. In almost all cases, we used 96% ethanol as the solvent. Compact water and ethanol molecules allowed us to efficiently examine the coordinative unsaturation of cadmium atoms under varying conditions of the synthesis.

Results and Discussion

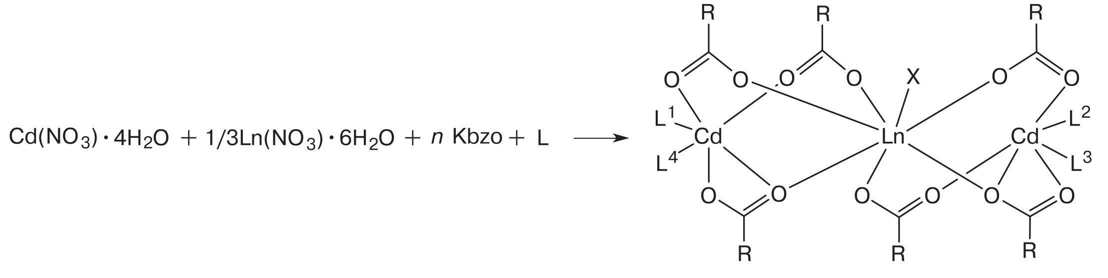
The heterometallic complex of the composition $[TbCd_2(NO_3)(bzo)_6(phen)_2]\cdot 2MeCN$ (**1**) was synthesized previously[12] by the reaction of cadmium 3,5-di-*tert*-butylbenzoate with $Tb(NO_3)_3\cdot 6H_2O$ and 1,10-phenanthroline (Kbzo : Tb : phen = 3 : 1 : 3). The centrosymmetric structure of complex **1** and the octahedral environment of cadmium atoms indicate that the metal atom is efficiently shielded by its coordination environment, thereby preventing the coordination of small solvent molecules. Here we showed that the replacement of $Ln(NO_3)_3\cdot 6H_2O$ by $\{Ln(bzo)_3\}$, which was prepared *in situ* by the reaction similar to that used to synthesize **1**, gave an asymmetric linear complex of the composition $[EuCd_2(bzo)_7(EtOH)_2(phen)]$ (**2**, Scheme 1). The reactions utilizing 2,4-lutidine (2,4-lut) as the ligand (L) afford heterometallic trinuclear complexes, in which coordinated solvent molecules are completely or partially replaced depending on the Cd : L ratio. The reaction with a tenfold excess of 2,4-lut (Cd : Eu : L = 3 : 1 : 30) gives the compounds $[LnCd_2(bzo)_7(2,4\text{-lut})_4]$ (Ln = Eu (**3**), Tb (**4**), see Scheme 1). The tenfold excess of 2,4-lut was required to completely prevent the coordination of water or ethanol molecules to cadmium atoms because the use of a smaller amount of the ligand (Cd : L = 1 : 5) resulted in the formation of complexes, in which cadmium atoms are coordinated by water or ethanol molecules (see Scheme 1): $[EuCd_2(bzo)_7(H_2O)_2(2,4\text{-lut})_2]\cdot MeCN$ (**5**) and $[EuCd_2(NO_3)(bzo)_6(EtOH)_2(2,4\text{-lut})_2]$ (**6**). Under similar conditions, the reaction with 3,4-lutidine (3,4-lut) at Cd : Eu : L = = 3 : 1 : 15 afforded the molecular complex $[EuCd_2(bzo)_7(H_2O)(EtOH)(3,4\text{-lut})_2]\cdot 4EtOH$ (**7**). The reaction with bulkier phenanthridine (phtd) (Cd : Eu : L = 3 : 1 : 9) gave the complex $3[EuCd_2(bzo)_7(H_2O)_2(phtd)_2]\cdot 4phtd$ (**8**). The reactions with 2,3-cyclododecenopyridine (cdpy) and acridine (acr) (Cd : Eu : L = 3 : 1 : 9) produced the asymmetric complex $[EuCd_2(bzo)_7(EtOH)_3(cdpy)]$ (**9**) and the complex $2[EuCd_2(bzo)_2(EtOH)_4]\cdot acr$ (**10**) containing the outer-sphere *N*-donor molecule, respectively (see Scheme 1).

It is worth noting that in the known heterometallic 3d-metal Ln complexes with monocarboxylic acids, only one α-substituted pyridine molecule is coordinated to each 3d metal atom, while water, ethanol, or other solvent molecules are not involved in the coordination; a large excess of *N*-donor ligands is not required.[1,2,17,18]

In the trinuclear metal core of compound **2**, the central Eu atom is linked to the terminal cadmium atoms *via* one chelating bridging and two bridging bzo anions (Fig. 1). The Cd(1) atom (CdO_4N_2) is coordinated by the chelating *N*-donor ligand. The coordination environment of the Cd(2) atom (CdO_6) is completed by two EtOH molecules. The coordination environment of the cadmium atoms can be described as a distorted octahedron. The environment of the Eu(1) atom (EuO_8) is completed to a trigonal dodecahedron by two O atoms of the chelating bzo^- anion, as opposed to compound **1**, in which the environment of the terbium atom (TbO_8) is completed by a NO_3^- anion. Selected bond lengths and bond angles of complex **2** are given in Table 1.

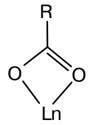
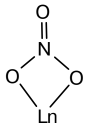
A comparison of the molecular structures of complexes **1** and **2** determined by X-ray diffraction shows that the geometry of the {Cd—Ln—Cd} metal core remains unchanged regardless of the ligand occupying two coordination sites in the environment of the Cd atom (Fig. 2). Only slight changes are observed in the bond and torsion angles and, as a consequence, in the Cd—Ln—Cd angle (173.87° in complex **1** and 171.44° in complex **2**). The geometry of the coordination polyherdra and the conformations of all bridging carboxylate groups remain unchanged. The largest difference is observed, as expected, in the positions of NO_3^- and bzo^- anions, which is reflected in the change

Scheme 1

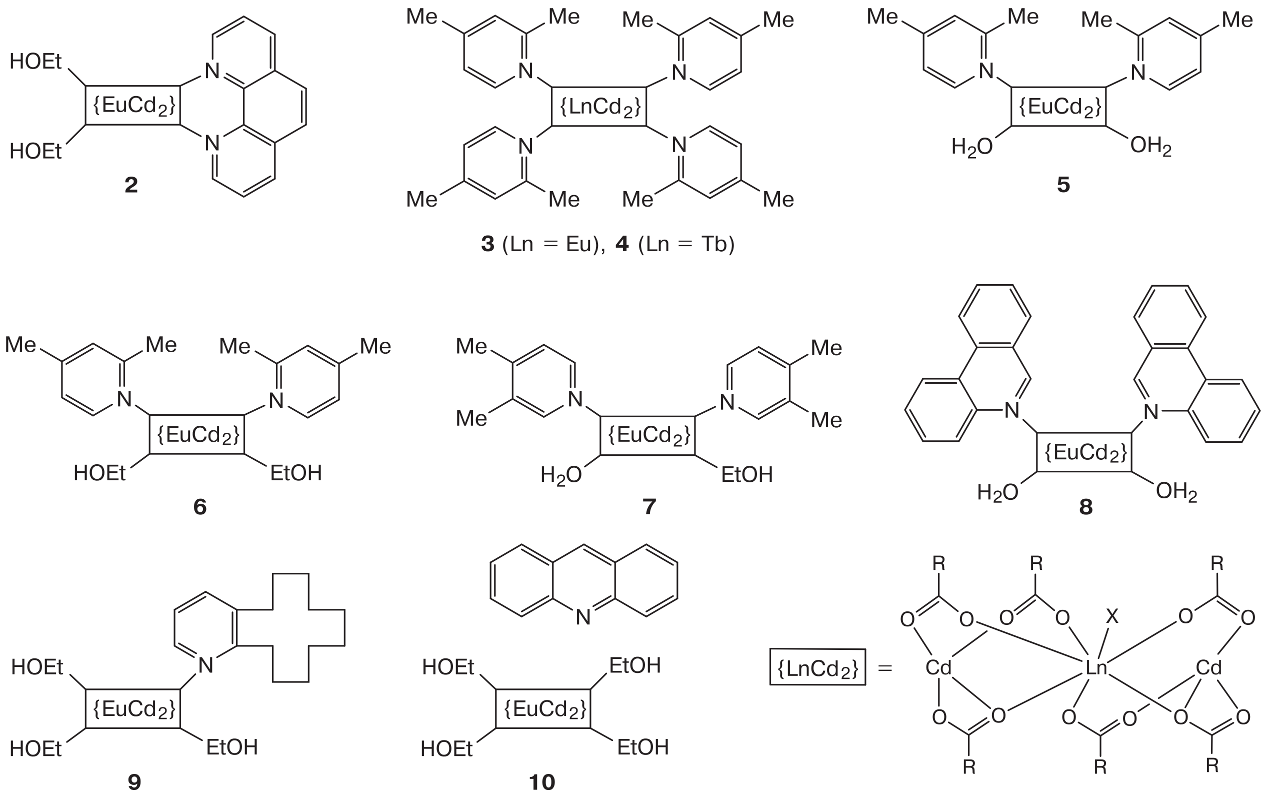


$Cd(NO_3)\cdot 4H_2O + 1/3Ln(NO_3)\cdot 6H_2O + n$ Kbzo + L →

2—10

n = 2, 3; R = 3,5-$Bu^tC_6H_3$; LnX =  (**2**—**5**, **7**—**10**),  (**6**); Ln = Eu (**2**, **3**, **5**—**10**), Tb (**4**)

L	Cd : L	Product	Ln	L^1	L^2	L^3	L^4
phen	1 : 1	**2**	Eu	EtOH	phen		EtOH
2,4-lut	1 : 10	**3**	Eu	2,4-lut	2,4-lut	2,4-lut	2,4-lut
2,4-lut	1 : 10	**4**	Tb	2,4-lut	2,4-lut	2,4-lut	2,4-lut
2,4-lut	1 : 5	**5**	Eu	2,4-lut	2,4-lut	H_2O	H_2O
2,4-lut	1 : 5	**6**	Eu	2,4-lut	2,4-lut	EtOH	EtOH
3,4-lut	1 : 5	**7**	Eu	3,4-lut	3,4-lut	EtOH	H_2O
phtd	1 : 3	**8**	Eu	phtd	phtd	H_2O	H_2O
cdpy	1 : 3	**9**	Eu	EtOH	cdpy	EtOH	EtOH
acr	1 : 3	**10**	Eu	EtOH	EtOH	EtOH	EtOH



2

3 (Ln = Eu), **4** (Ln = Tb)

5

6

7

8

9

10

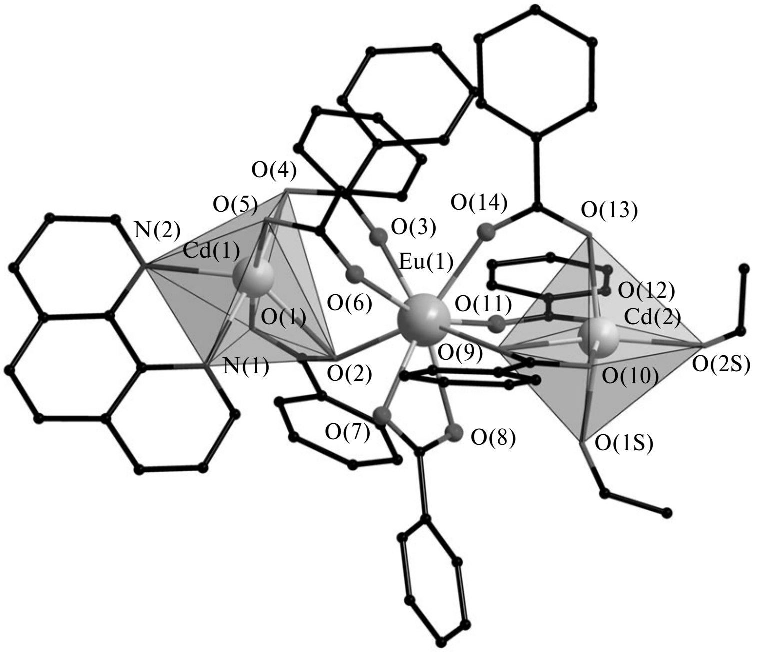


Fig. 1. Molecular structure of compound **2**. Hydrogen atoms, solvent molecules, and a part of *tert*-butyl substituents are omitted for clarity.

of the angle between the M—O—C(N) and O—C(N)—C(O) planes. The corresponding M—O—C(N)—C(O) torsion angles are 180° and 169.8° in complexes **1** and **2**, respectively. An analysis of intramolecular non-covalent interactions in complex **2** shows that a decrease in the torsion angle is apparently attributed to an intramolecular CH···π interaction between the methylene hydrogen atom of coordinated ethanol and the π system of the bzo⁻ anion.

The presence of bulky conjugated 1,10-phenanthroline moieties in both complexes is apparently responsible for a considerable contribution of π···π interactions to the crystal packing of the compounds. However, the crystals

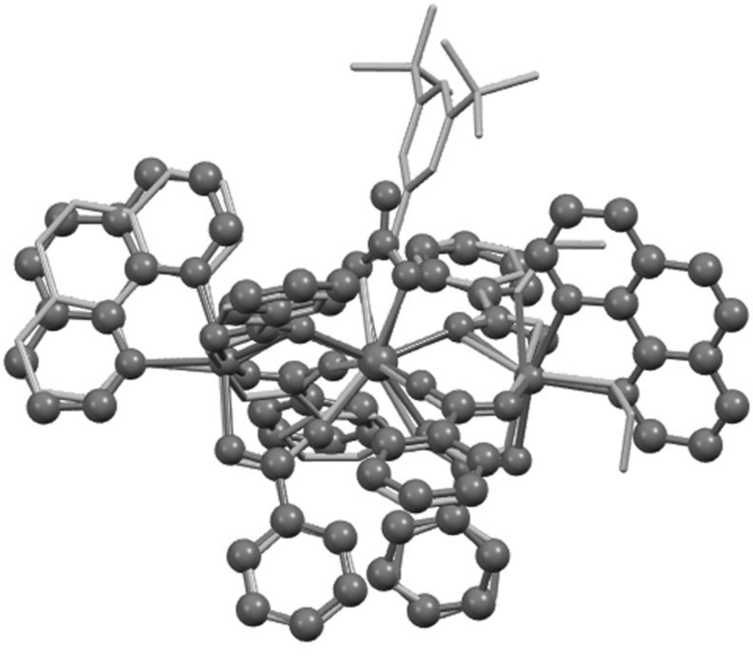


Fig. 2. Superposition of the molecular structures of complexes **1** and **2** (atoms of complex **1** are represented by spheres). Hydrogen atoms, solvent molecules, and a part of *tert*-butyl substituents are omitted for clarity.

Table 1. Selected geometric parameters of complexes **2**, **3**, **5**, and **6**

Parameter	**2**	**3**	**5**	**6**
Bond		d/Å		
Cd—N (L)	2.332(3), 2.353(3)	2.376(7), 2.384(10)	2.315(4)	2.21(2), 2.377(9)
Cd—O (solv)	2.250(3), 2.344(3)	—	2.362(3)	2.392(4)
Cd—O (bzo)	2.206(3)—2.634(3)	2.205(6)—2.734(7)	2.225(3)—2.610(3)	2.234(4)—2.721(4)
Eu—O (bzo)	2.314(3)—2.506(3)	2.327(8)—2.504(5)	2.311(4)—2.511(4)	2.401(4)—2.479(4)
Eu—O (NO_3)	—	—	—	2.620(5)
Cd···Eu	3.743(2), 3.745(2)	4.024(9)	3.815(4)	3.927(6)
Angle		ω/deg		
Cd—Eu—Cd	171.44	166.65	172.74	170.01

of **1** and **2** exhibit different degrees of overlap between the π systems, which is reflected in different geometric parameters of interactions. Thus, the distances between the centroids of the phenanthroline moieties are 4.192(3) Å in **1** and 5.682(2) Å in **2**; the centroid—plane distances are 3.316 and 3.547 Å, respectively. This significant difference in the strength of interactions is apparently attributed to the presence of EtOH molecules in **2**, which form competing hydrogen bonds with both coordinated (O(8)···O(1S), 2.753(4) Å) and ethanol solvent molecules that are disordered in the crystal (for this reason, the structure refinement of **2** was performed using the SQUEEZE procedure). The crystal structure of **1** is stabilized by only weak CH···N contacts involving acetonitrile solvent molecules.

The structure of complex **3** was determined by X-ray diffraction (Fig. 3). The isostructurality of complexes **3** and **4** was confirmed by powder X-ray diffraction (Fig. 4). Complex **3** is the first example of compounds, in which two 2,4-lutidine molecules containing a substituent in the α position are coordinated to one metal center involved in a polynuclear complex and having an octahedral coordination geometry (CdO_4N_2). A search of the Cambridge Structural Database showed that only mononuclear carboxylate complexes with two coordinated α-substituted pyridine molecules were synthesized and characterized.[19,20]

The coordination modes of the bzo$^-$ anions and the structures of the trinuclear metal cores of complexes **3**, **5**, and **6** are similar to those of compounds **1** and **2** (Figs 5 and 6). The coordination environment of the Cd atoms is completed to an octahedron by the oxygen atom of the solvent molecule (EtOH or H_2O) and the nitrogen atom of the 2,3-lut molecule (compounds **5** and **6**) or by two N atoms of lut molecules (compound **3**). The coordination of two solvent molecules instead of 2,4-lutidine results in

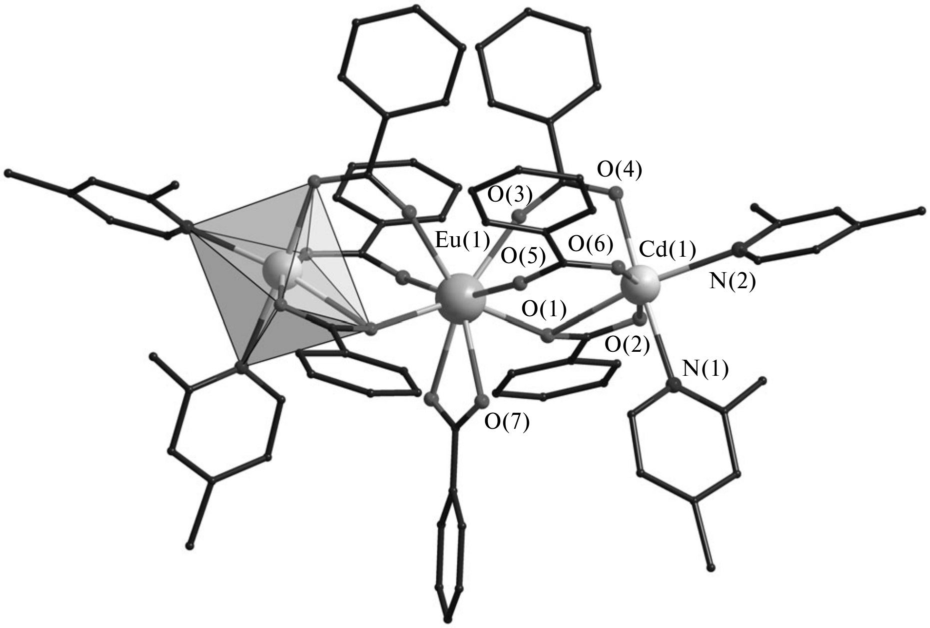


Fig. 3. Molecular structure of complex **3**. Hydrogen atoms and *tert*-butyl substituents are omitted for clarity.

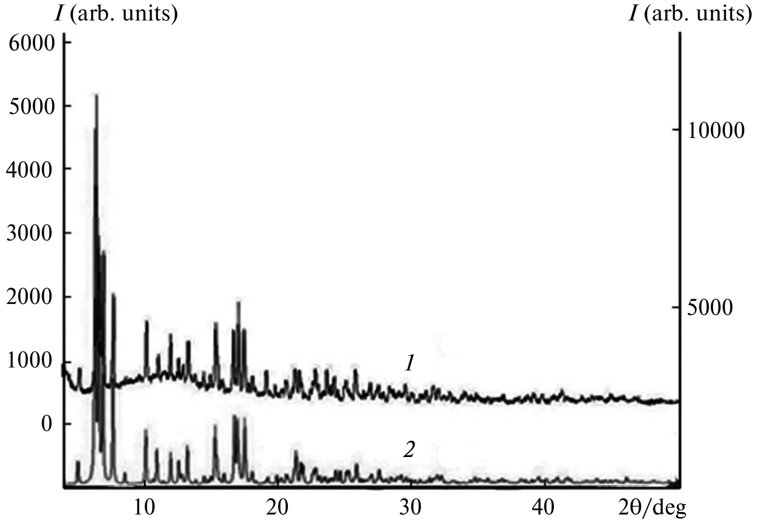


Fig. 4. Comparison of the experimental powder X-ray diffraction pattern of complex **4** (*1*) and the simulated diffraction pattern of complex **3** (*2*).

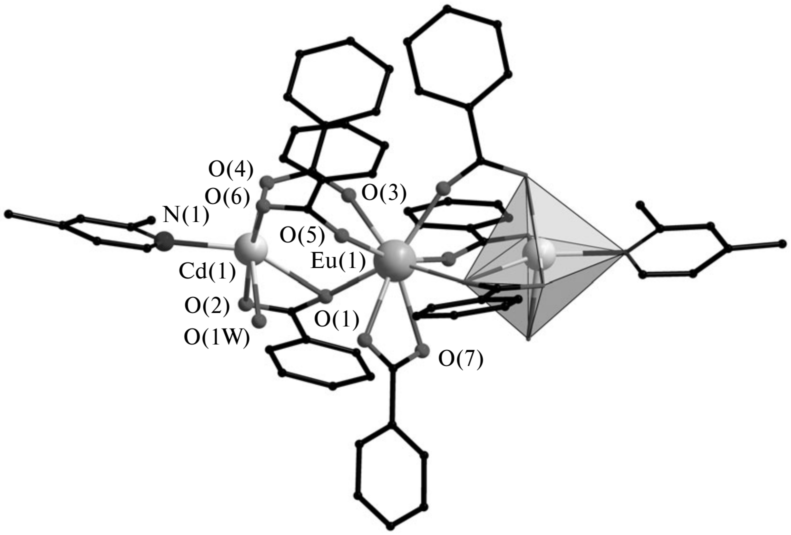


Fig. 5. Molecular structure of complex **5**. Hydrogen atoms, *tert*-butyl substituents, and solvent molecules are omitted for clarity.

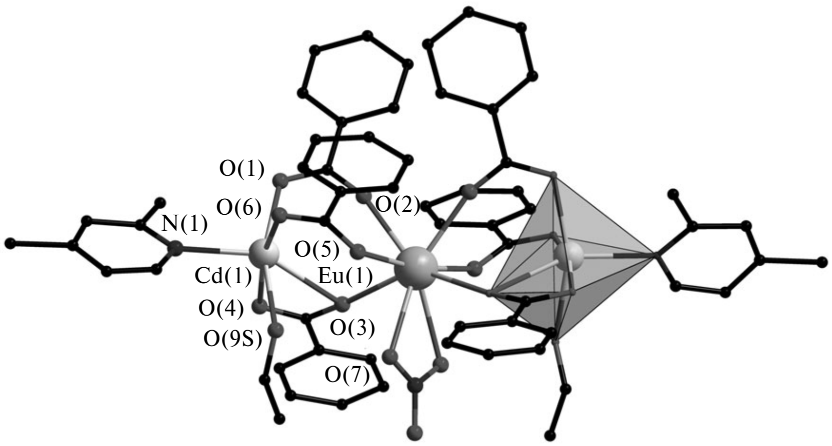


Fig. 6. Molecular structure of complex **6**. Hydrogen atoms, *tert*-butyl substituents, and solvent molecules are omitted for clarity.

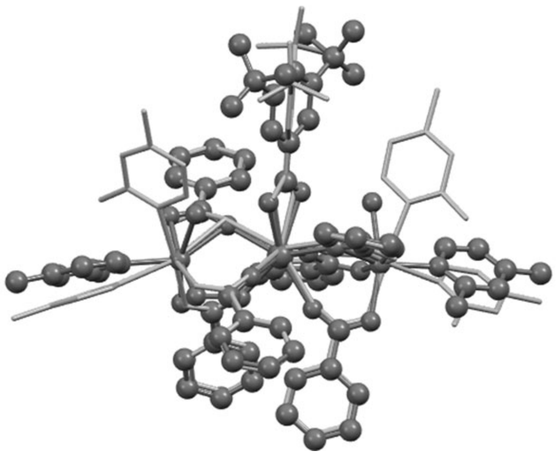


Fig. 7. Superposition of the molecular structures of complexes **3** and **6**. Atoms of complex **3** are represented by spheres.

a change of the Cd—Eu—Cd angle from 166.65° in complex **3** to 176.12° and 170.02° in compounds **5** and **6**, respectively. Selected bond lengths and bond angles of complexes **3**, **5**, and **6** are given in Table 1.

Compounds **3**, **5**, and **6** have very similar molecular and crystal structures (Fig. 7). Moreover, the unit cell parameters of the crystals of **3** and **5** are also similar. These complexes crystallize in space group *C*2/*c*, and the molecules occupy a special position on a twofold axis passing through the Eu(1) atom and the carbon or nitrogen atom of the bzo or NO_3 anions, respectively. A comparison of the geometric parameters of the molecules shows that the main, although very small, difference is observed in the region of lutidine substituents. It should be noted that the positions of the coordinated water and ethanol molecules in complexes **5** and **6** are the same and are stabilized by identical intramolecular hydrogen bonds (O(7)···O(1W), 2.859(4) Å in the structure of complex **5**; O(7)···O(9S), 3.024(6) Å in complex **6**). The presence of additional hydrogen bonds with O atoms of coordinated solvent molecules in the structures of **5** and **6** has no significant effect on the molecular packing in the crystals. Thus, in all the three structures, the packing consists of chains running along the 0*a* axis and is stabilized mainly *via* CH···O interactions. Only the structure of **5** contains a hydrogen bond with the MeCN solvent molecule; however, this interaction does not give rise to supramolecular chains (N(1S)···O(1W), 2.915(7) Å).

As opposed to the above-considered complexes with 2,4-lutidine, complex **7** contains 3,4-lutidine as the *N*-donor ligand. This ligand has approximately the same volume and exhibits only slightly different electron density distribution. Complex **7** crystallizes in space group $P2_1$ and, unlike molecules **3**, **5**, and **6**, occupies a general position. This is attributed to the fact that the cadmium atoms in complex **7** are coordinated by asymmetric ligands. Thus, one cadmium atom is coordinated, apart from 3,4-lutidine, by a water molecule, and another cadmium atom is coordinated by an ethanol molecule, which completes the coordination environment of cadmium to an octahedron. An analysis of the molecular structure of complex **7** (Fig. 8) shows that its structure is very similar to that of complex **5** and, in general, differs slightly from the structures of the complexes with 2,4-lutidine. The crystal packing is also composed of chains running along

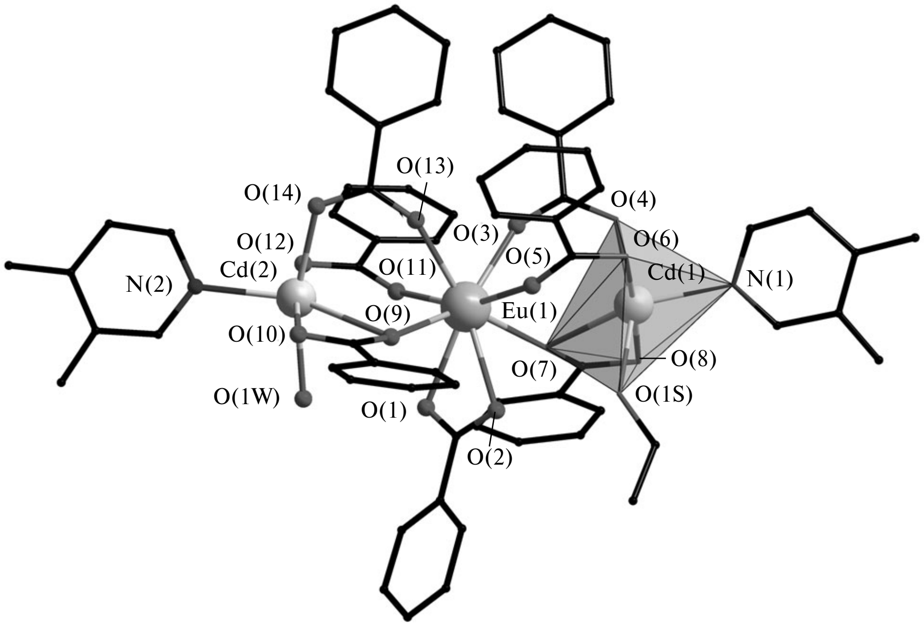


Fig. 8. Molecular structure of complex **7**. Hydrogen atoms and solvent molecules are omitted for clarity.

Table 2. Selected geometric parameters of complexes **7—10**

Parameter	**7**	**8**	**9**	**10**
Bond		d/Å		
Cd—N (L)	2.259(6), 2.262(5)	2.29(2), 2.38(2)	2.339(3)	—
Cd—O (solv)	2.334(4) (H_2O), 2.333(3) (EtOH)	2.322(4)—2.355(5)	2.265(3)—2.424(3)	2.26(1)—2.349(7)
Cd—O (bzo)	2.220(4)—2.694(4)	2.242(3)—2.650(5)	2.202(2)—2.659(2)	2.182(10)—2.613(6)
Eu—O (bzo)	2.309(4)—2.568(4)	2.305(4)—2.538(4)	2.328(2)—2.524(2)	2.323(6)—2.551(6)
Cd···Eu	3.735(4), 3.778(4)	3.707(5), 3.751(6), 3.808(5)	3.706(3), 3.852(3)	3.740(8), 3.763(8)
Angle		ω/deg		
Cd—Eu—Cd	176.11	172.91, 173.09	170.81	179.32

the 0*a* axis. A hydrogen bonding system is somewhat more extensive due to the presence of four ethanol solvent molecules per complex **7**. However, as in the structure of **5**, these interactions do not give rise to supramolecular chains (O(1W)···O(1), 2.745(6) Å; O(1S)···O(2), 2.771(6) Å; O(1W)···O(2S), 2.645(7) Å; O(3S)···O(4S), 2.70(1) Å; O(1W)···O(4S), 2.901(6) Å; O(5S)···O(12), 2.88(1) Å). Selected bond lengths and bond angles of complex **7** are given in Table 2.

The replacement of lutidine by bulky phenanthridine (phtd) resulted in the crystallization of complex **8** (Fig. 9), which retains the structure of the trinuclear metal core {CdEuCd} observed in the above complexes. The solvent molecules coordinated to the Cd atoms are only partially replaced. Thus, each metal center (Cd) is coordinated by the N atom of only one phtd molecule and a water O atom, thereby completing the coordination environment to a distorted octahedron ($CdNO_5$). The coordination polyhedron of Eu(1) can be described as a trigonal dodecahedron (EuO_8). Selected bond lengths and bond angles of complex **8** are given in Table 2.

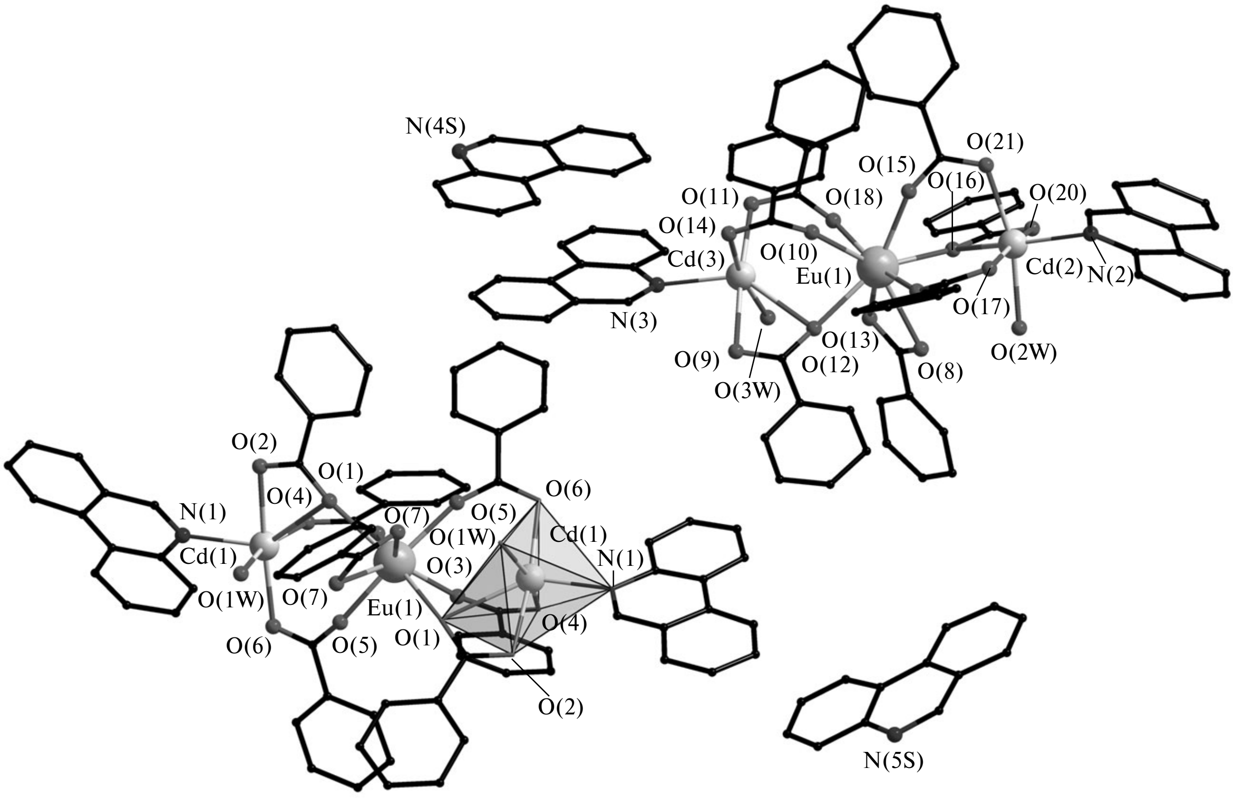


Fig. 9. Fragment of the crystal packing of complex **8**. Hydrogen atoms and *tert*-butyl substituents are omitted for clarity.

Due to steric hindrance created by the phtd molecule, the coordination of the second phtd molecule to the same metal center is energetically and sterically less favorable than the coordination of a water molecule present in the reaction mixture. Only one example of the coordination of two phtd molecules to one Cd atom in a mononuclear complex of the composition [Cd(phtd)I_2], in which cadmium has the coordination number 4, was described in the literature.[21]

The investigation of homometallic cadmium pivalates demonstrated that 2,3-cyclododecenopyridine ensures the formation of a paddle-wheel binuclear complex, whereas binuclear complexes only with two bridging anions crystallize in the presence of 2,4-lutidine and phenanthridine.[22] In the series of the heterometallic complexes with the pyridine derivatives under consideration, 2,3-cyclododecenopyridine contains the largest conformationally flexible aliphatic substituent. Despite the presence of an excess of cdpy in the reaction solution, only one cadmium atom, Cd(1), in complex **9** (Fig. 10, Table 2) is coordinated by a cdpy molecule and, additionally, by an EtOH molecule, as opposed to lutidine- and phenanthridine-containing compounds **2—8**. The coordination environment of the Cd(2) atom is completed to an octahedron by two EtOH molecules. It cannot be ruled out that a complex, in which a pyridine ligand is coordinated to each Cd atom, is generated in solution, but this apparently would lead to a significant increase in its solubility, resulting in the precipitation of the least soluble compound among those present in equilibrium in the reaction solution.

Complexes **8** and **9** are distinguished from compounds **2—7** by much bulkier *N*-donor ligands. An analysis of the geometry of complexes **8** and **9** suggests that the region of the molecules, where the bulky *N*-donor ligand and the small solvent molecule are coordinated, does not undergo changes compared to complexes **2—7**. However, the region of the molecule of complex **9**, where only two ethanol molecules are coordinated, is significantly different. In particular, one EtOH molecule occupies a coordination site, which belongs to the carboxylate group in the other complexes, and the O atom of the bridging bzo group occupies the site of the solvent molecule (the Eu—O—C—O and Cd—O—C—O torsion angles of the corresponding 3,5-di-*tert*-butylbenzoate moiety are 128.69(2)° and −4.23(3)° in complex **8**; −108.02(3)° and 66.24(3)° in complex **9**, respectively).

Interestingly, the asymmetric unit of the crystal structure of compound **8** contains 1.5 molecules of the complex and two phtd molecules. It should be noted that the geometry of two independent molecules **8** is the same within experimental error.

Since the refinement of both experimental data sets was performed using the SQUEEZE procedure to account

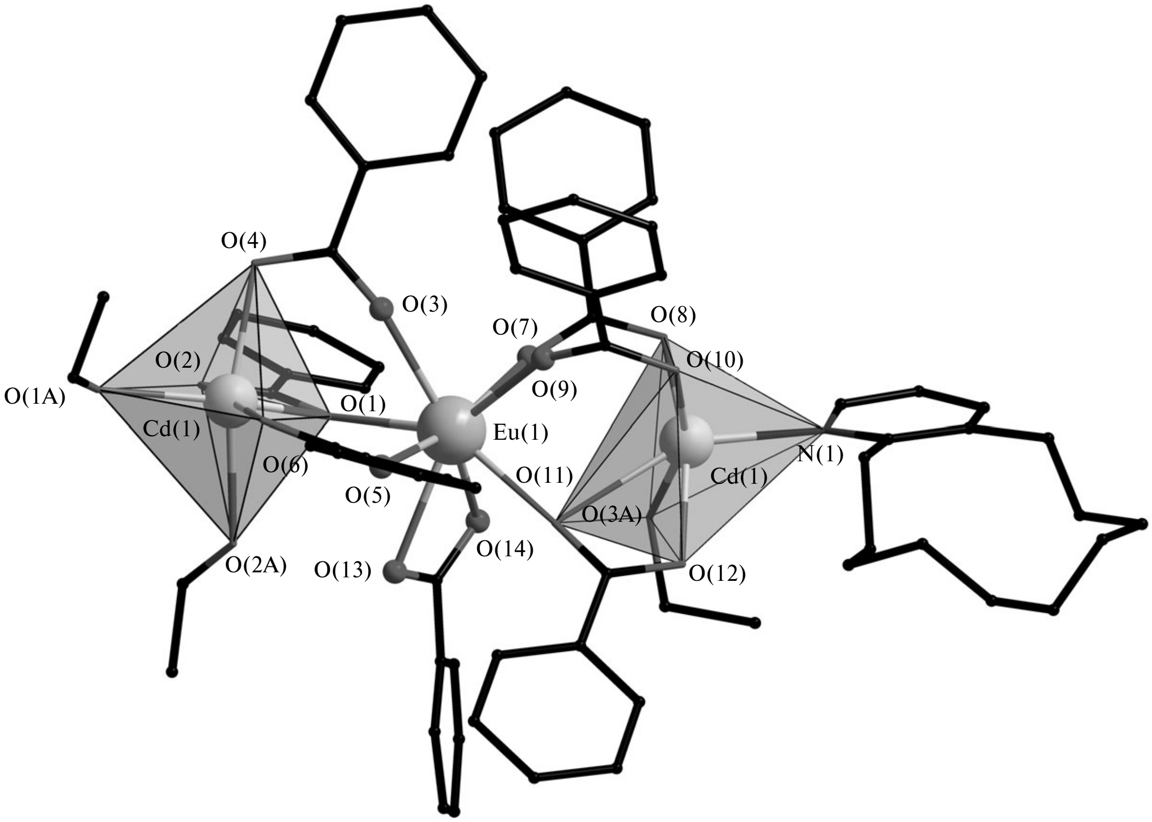


Fig. 10. Molecular structure of complex **9**. Hydrogen atoms and *tert*-butyl substituents are omitted for clarity.

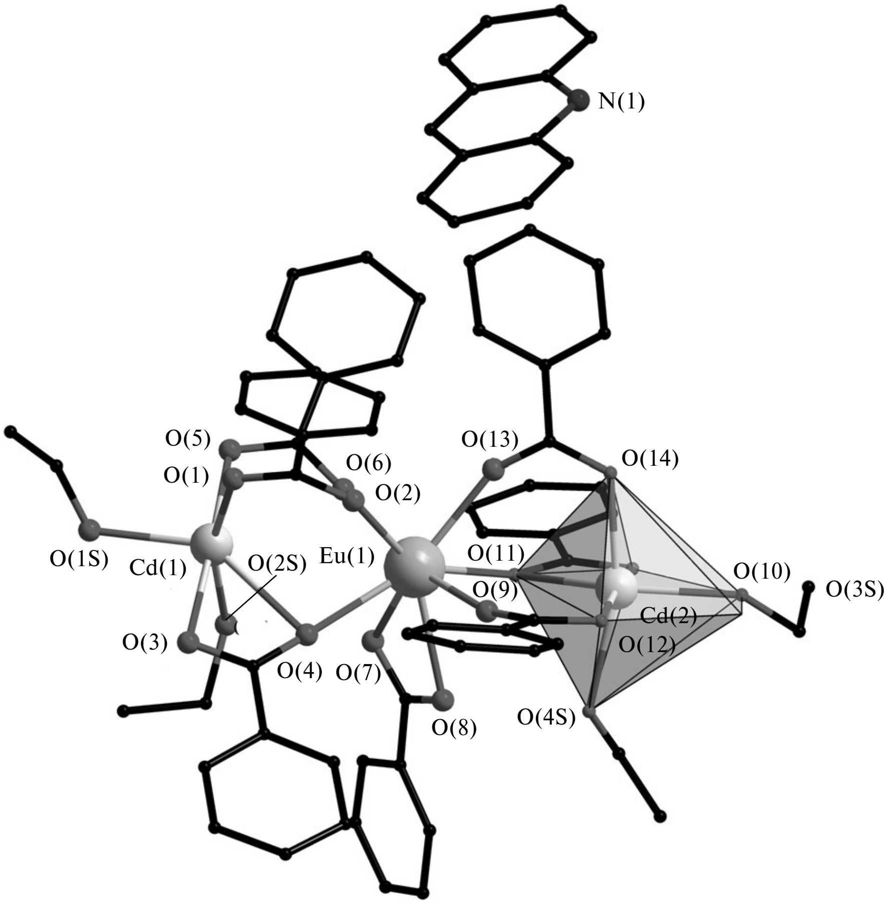


Fig. 11. Molecular structure of complex **10**. Hydrogen atoms, solvent molecules, and *tert*-butyl substituents are omitted for clarity.

for disordered ethanol solvent molecules, it is difficult to discuss a hydrogen bonding system in the crystal. In general, the system of non-covalent bonds in complex **8** is somewhat more complex due to the presence of the phenanthridine solvent molecule involved both in the hydrogen bonding (O(1W)···O(7), 2.842(7) Å; O(1W)···N(5S), 2.81(1) Å; O(2W)···O(8), 2.792(6) Å; O(2W)···N(4S), 2.807(7) Å; O(3W)···O(13), 2.749(6) Å in the structure of complex **8**; O(1A)···O(13), 2.822(5) Å; O(3A)···O(14), 2.825(3) Å in **9**) and π···π overlap (Table 3).

To evaluate the degree of influence of coordinated bulky *N*-donor ligands on the geometry of the metal core in the compounds under consideration, it was interesting to compare these compounds with a related system lacking *N*-donor ligands. For this purpose, we synthesized and structurally characterized a complex with acridine (acr) of the composition 2[EuCd$_2$(bzo)$_2$(EtOH)$_4$]·acr (**10**, Fig. 11, Table 2). Low solubility and steric hindrance did not allow acridine to be involved in the complex, and the *N*-donor in the crystal of **10** is present as a solvent molecule. The molecular structure of trinuclear complex **10** is similar to those of complexes **2—9** (Fig. 12). The coordination sites in the environment of both cadmium atoms are occupied by ethanol molecules. As can be seen in Fig. 12, which presents the superposition of complexes **10** and **3**, the metal core remains almost unchanged. Hence, it can

Table 3. π···π Interactions in the crystal packing of complexes **2** and **8**

Interaction	Cg—Cg	Cg—Perp	α /deg
	Å		
		Complex **2**	
phen—phen	2.934	1.660	0.00
		Complex **8**	
phtd(N(1A))—phtd(N(1A))	3.443	3.389	5.696
phtd(N(1A))—phtd(N(1B))	3.480	3.426	1.537
phtd(N(1B))—phtd(N(1B))	3.538	3.472	4.818
phtd(N(2A))—phtd(N(4S))	3.541	3.491	4.698
phtd(N(2B))—phtd(N(4S))	3.536	3.489	2.698
Phtd(N(3))—phtd(N(4S))	3.595	3.497	3.001

Note. Cg is the centroid of aromatic rings, Perp is the perpendicular to the ring plane, α is the angle between the planes of aromatic moieties.

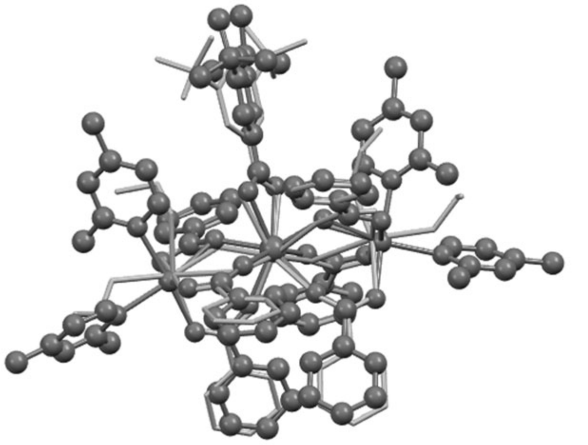


Fig. 12. Superposition of the molecular structures of complexes **3** (atoms in the structure of complex **3** are represented by spheres) and **10**. Hydrogen atoms, solvent molecules, and *tert*-butyl substituents are omitted for clarity.

be concluded that the $\{LnCd_2(O_2CR)_7\}$ metal core weakly depends on the type of peripheral ligands coordinated to cadmium atoms.

The luminescence properties of solid samples of complexes **3** and **4** were studied at room temperature. These compounds were chosen because their syntheses are well reproducible and phase-pure samples can easily be prepared.

Figure 13 displays the luminescence spectrum of complex **3** showing characteristic $^5D_0{\to}^7F_J$, $J = 0$—4, electronic transitions of the Eu^{3+} ions. At the wavelength of 537 nm, the spectrum has a weak $^5D_1{\to}^7F_1$ transition indicative of the partial internal conversion $^5D_1{\to}^5D_0$. The most intense band corresponds to the $^5D_0{\to}^7F_2$ transition, which is very sensitive to the coordination environment of the europium ion. This is indicative of the absence of a center of inversion. On the contrary, the probability of the $^5D_0{\to}^7F_1$ magnetic dipole transition in the first approximation is constant and independent of the geometry of the complex. The integrated intensity ratio of $^5D_0{\to}^7F_J$, J = 0, 2, 4, transitions to $^5D_0{\to}^7F_1$ are 0.05, 4.29, and 0.97, respectively and are indicative of low symmetry of the Eu^{3+} coordination environment.

The luminescence spectrum of complex **4** (Fig. 14) shows intense bands assigned to $^5D_4{\to}^7F_J$, $J = 6$—3, transitions. The $^5D_4{\to}^7F_J$, $J = 2$—0, transitions have expectedly low intensity.

The optical excitation spectra of complexes **3** and **4** (Fig. 15) display narrow f—f transition lines of lanthanide ions and broad bands associated with ligand absorption. The broadband excitation appears as two closely spaced bands I and II with maxima at wavelengths of 282 and 295 nm, respectively, which are apparently assigned to $S_0{\to}S_1$ transitions of the 2,4-lut (I) and bzo (II) ligands.[23] It should be noted that terbium complexes **3** and **1** exhibit similar excitation spectra (see Ref. 12), whereas the excitation spectra of related europium complexes are significantly different. This may be attributed to the contribution of the 1,10-phenanthroline molecule to sensitization of the Eu^{3+} ion in complex **1**. Therefore, despite the remoteness of 1,10-phenanthroline from the emission center, this ligand is actively involved in the excitation of the central lanthanide ion. In the isostructural terbium complex, this pathway of luminescence excitation of the central ion is less efficient. Apparently, in both Tb^{3+} complexes, the bzo

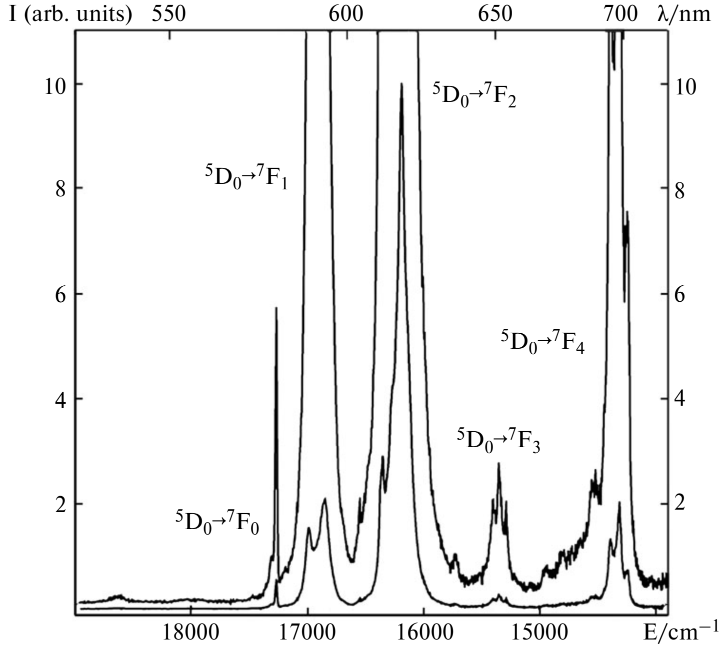


Fig. 13. Luminescence spectrum of complex **3** at λ_{ex} = 300 nm and T =300 K.

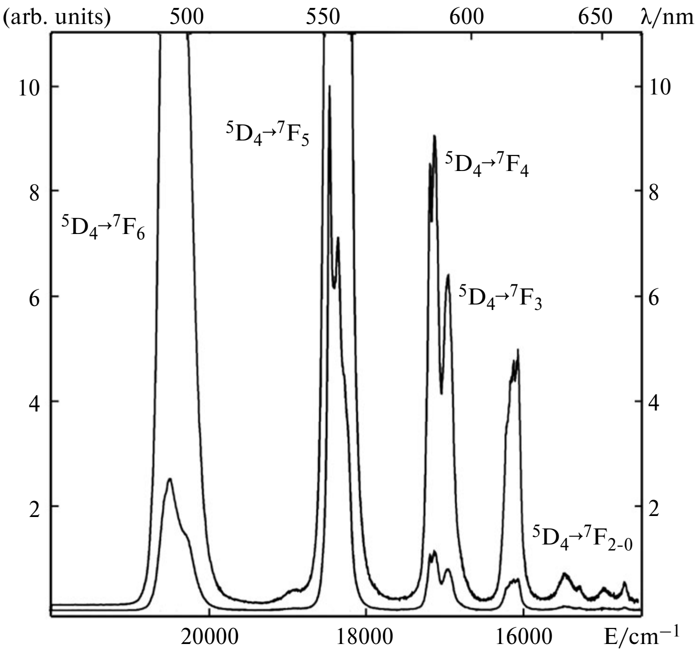


Fig. 14. Luminescence spectrum of complex **4** at λ_{ex} = 300 nm and T = 300 K.

ligand makes the major contribution to the energy transfer to the emission center.

The intensity of direct f—f excitation lines of the terbium ion is much weaker than the intensity of ligand excitation, which is indicative of efficient sensitization of excitation of the lanthanide ion in complex **4** through the *d* block. The probability of energy transfer from the ligand to the lanthanide ion greatly depends on the energy dif-

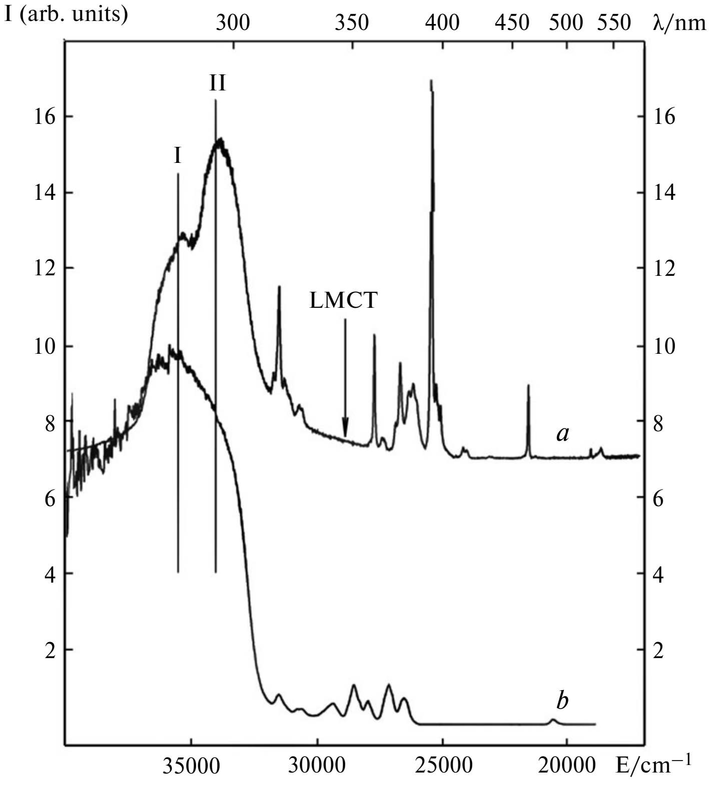


Fig. 15. Optical excitation spectra of complexes **3** (a, λ_{em} = 615 nm) and **4** (b, λ_{em} = 545 nm) at T = 300 K.

ference ΔE between the triplet level of the ligand and the emission state of the lanthanide ion. According to the empirical rule for the efficient energy transfer from the ligand to Eu^{3+} and Tb^{3+} ions, ΔE should be in the ranges of 2000—2500 and 2000—4000 cm^{-1}, respectively.**[24,25]** As follow from the intensities of the ligand and f—f transitions, the antenna effect in complex **3** is much less pronounced compared to complex **4** due to the large value of ΔE. In these complexes, ΔE with respect to the triplet levels of 2,4-lut (*ca.* 28700 cm^{-1}) and bzo (26800 cm^{-1})**[23]** are larger than 6000 cm^{-1} for **4** and 9000 cm^{-1} for **3**, *i.e.*, this value for the europium complex is significantly larger than the optimal value. Hence, the quantum yield of luminescence of complex **3** (10%) is much lower compared to complex **4** (24%). The band II in the excitation spectrum of complex **3** is more intense than the band I, which may be attributed to more efficient energy transfer from the ligand with slightly lower energy S_1 and T_1 levels due to approaching to the optimal energy values. Besides, the excitation spectrum of complex **3** exhibits a weak broad band in the spectral range of 310—350 nm, which is absent in the excitation spectrum of **4**. This band can be assigned to the charge transfer from the ligand to the europium(III) ion (ligand-to-metal charge transfer, LMCT). Since the LMCT state lies lower than the singlet S_1 state, the charge transfer can compete with the intrasystem $S_1 \rightarrow T_1$ transfer and lead to a decrease in the quantum yield of luminescence of complex **3**.**[26]**

In summary, we synthesized a series of complexes of similar composition $[LnCd_2(bzo)_7L_{3/4}]$ or $[LnCd_2(NO_3)(bzo)_6L_4]$, in which monodentate and chelating ligands of different nature can act as L. The competition between *N*-donor molecules and water or ethanol molecules for two sites in the Cd coordination environment was shown for the complex with 2,4-lutidine. Due to an increase in the volume of the α-substituent in pyridine, the coordination of the second *N*-donor in the complexes with phtd and cdpy is highly improbable. The coordination of the acr molecule to the cadmium atom in $\{LnCd_2(bzo)_7\}$ is not observed. The variation of *N*-donor ligands has only a slight effect on the geometric characteristics of the $LnCd_2$ metal core. According to the photoluminescence spectra, samples **3** and **4** exhibit weak metal-centered emission. The efficiency of luminescence enhancement of Tb and Eu by aromatic organic ligands is low due to the large energy difference ΔE between the triplet level of the ligands and the excited state (>6000 cm^{-1}) and the charge transfer from the ligand to the europium(III) ion.

Experimental

All manipulations for the synthesis of new complexes were performed in air using EtOH (96%), MeCN (⩾99.5%), and THF (99%). New compounds were synthesized using the following reagents: $Cd(NO_3)_2 \cdot 4H_2O$ (99+%, Acros Organics), $Eu(NO_3)_3 \cdot 6H_2O$ (99.99%, Lanhit), $Tb(NO_3)_3 \cdot 6H_2O$ (99.99%, Lanhit), KOH (chemical purity grade, Reakhim), 3,5-di-*tert*-butylbenzoic acid (>98%, Sigma-Aldrich), 1,10-phenanthroline (99%, Alfa Aesar), 2,4-lutidine (99%, Sigma-Aldrich), 3,4-lutidine (98%, Sigma-Aldrich), phenanthridine (97%, Sigma-Aldrich), 2,3-cyclododecenopyridine (98%, Sigma-Aldrich), and acridine (98%, Sigma-Aldrich). Potassium 3,5-di-*tert*-butylbenzoate (Kbzo) was prepared *in situ* by the reaction of stoichiometric amounts of KOH and Hbzo in EtOH or an EtOH—MeCN mixture. Attenuated total internal reflection IR spectra were recorded on a Spectrum 65 Fourier-transform infrared spectrometer (Perkin Elmer) in the frequency range of 4000—400 cm^{-1}. Elemental analysis was performed on a EuroEA 3000 CHNS analyzer (EuroVector).

(3,5-Di-*tert*-butylbenzoato-$\varkappa^2 O,O'$)bis(μ-3,5-di-*tert*-butylbenzoato-$\varkappa^3 O,O,O'$)tetrakis(μ-3,5-di-*tert*-butylbenzoato-$\varkappa^2 O,O'$)-(1,10-phenanthroline)diethanoleuropium(III)dicadmium(II), $[Eu(bzo\text{-}\varkappa^2 O,O')Cd_2(\mu\text{-}bzo\text{-}\varkappa^3 O,O,O')_2(\mu\text{-}bzo\text{-}\varkappa^2 O,O')_4(EtOH)_2(phen)]$ (2). A solution of Kbzo (0.175 g, 0.649 mmol) in EtOH (10 mL) was added to a solution of $Cd(NO_3)_2 \cdot 4H_2O$ (0.100 g, 0.325 mmol) in EtOH (15 mL). The reaction mixture was stirred with heating (t = 70 °C) for 15 min. The white precipitate of KNO_3 that formed was filtered off, and a suspension, which was prepared by the reaction of $Eu(NO_3)_3 \cdot 6H_2O$ (0.048 g, 0.108 mmol) with Kbzo (0.088 g, 0.325 mmol) in EtOH (5 mL) and MeCN (5 mL), was added to the filtrate. The resulting reaction mixture was stirred at 75 °C for 30 min, the precipitate of KNO_3 was filtered off, and phen (0.059 g, 0.325 mmol) was added to the filtrate. The reaction mixture was stirred at 75 °C for 5 min, cooled to room temperature, and kept to allow slow evaporation for 7 days. Colorless crystals of complex **2** suitable for X-ray diffraction that precipitated were separated from the mother liquor by decantation, washed with cold acetonitrile (5 °C), and dried in air. The yield of **2** was 0.109 g (43.4% with respect to $Eu(NO_3)_3 \cdot 6H_2O$). Found (%): C, 63.7; H, 7.7; N, 1.5. $C_{121}H_{167}Cd_2EuN_2O_{16}$. Calculated (%): C, 63.7; H, 7.4; N, 1.2. IR, ν/cm^{-1}: 3277 w, 2962 m, 2903 s, 2865 w, 1603 m, 1531 s, 1464 s, 1434 m, 1396 s, 1362 m, 1289 m, 1251 m, 1247 m, 1209 m, 1151 w, 1127 w, 1115 w, 1016 m, 923 m, 874 m, 842 m, 790 s, 763 m, 725 s, 704 s, 655 m, 582 m, 550 w, 531 m, 507 m, 477 m, 440 m, 426 s, 418 s, 412 s.

(3,5-Di-*tert*-butylbenzoato-$\varkappa^2 O,O'$)bis(μ-3,5-di-*tert*-butylbenzoato-$\varkappa^3 O,O,O'$)tetrakis(μ-3,5-di-*tert*-butylbenzoato-$\varkappa^2 O,O'$)-tetrakis(2,4-lutidine)europium(III)dicadmium(II), $[Eu(bzo\text{-}\varkappa^2 O,O')Cd_2(\mu\text{-}bzo\text{-}\varkappa^3 O,O,O')_2(\mu\text{-}bzo\text{-}\varkappa^2 O,O')_4(2,4\text{-}lut)_4]$ (3). Compound **3** was synthesized as described for **2** using 2,4-lut (0.375 mL, 3.251 mmol, Cd : L = 1 : 10) instead of phen. Colorless crystals suitable for X-ray diffraction that formed within 3 days were separated from the mother liquor by decantation and washed with cold acetonitrile (t ≈ 5 °C). The yield of **3** was 0.168 g (62.3% with respect to $Eu(NO_3)_3 \cdot 6H_2O$). Found (%): C, 65.2; H, 7.3; N, 2.2. $C_{133}H_{183}Cd_2EuN_4O_{14}$. Calculated (%): C, 65.5; H, 7.6; N, 2.3. IR, ν/cm^{-1}: 3675 w, 2964 m, 2901 m, 1609 m, 1566 s, 1477 m, 1436 m, 1394 s, 1361 s, 1290 s, 1248 m, 1203 w, 1164 w, 1066 s, 1048 s, 922 m, 892 m, 818 s, 790 s, 737 s, 703 s, 599 w, 533 m, 473 m, 440 m, 419 m, 414 m, 407 m.

(3,5-Di-*tert*-butylbenzoato-$\varkappa^2 O,O'$)bis(μ-3,5-di-*tert*-butylbenzoato-$\varkappa^3 O,O,O'$)tetrakis(μ-3,5-di-*tert*-butylbenzoato-$\varkappa^2 O,O'$)-tetrakis(2,4-lutidine)terbium(III)dicadmium(II), $[Tb(bzo\text{-}\varkappa^2 O,O')Cd_2(\mu\text{-}bzo\text{-}\varkappa^3 O,O,O')_2(\mu\text{-}bzo\text{-}\varkappa^2 O,O')_4(2,4\text{-}lut)_4]$ (4). Compound **4** was synthesized as described for complex **3** using

Tb(NO$_3$)$_3$·6H$_2$O (0.049 g, 0.108 mmol) instead of Eu(NO$_3$)$_3$·6H$_2$O. Colorless crystals suitable for X-ray diffraction that formed within 5 days were separated from the mother liquor by decantation and washed with cold acetonitrile ($t \approx 5$ °C). The yield of **4** was 0.149 g (56.9% with respect to Tb(NO$_3$)$_3$·6H$_2$O). Found (%): C, 65.0; H, 7.3; N, 2.1. $C_{133}H_{183}Cd_2TbN_4O_{14}$. Calculated (%): C, 65.3; H, 7.5; N, 2.3. IR, ν/cm^{-1}: 3675 w, 2962 m, 2901 m, 1609 m, 1568 m, 1475 m, 1436 m, 1396 s, 1360 s, 1290 s, 1248 m, 1204 m, 1164 w, 1066 s, 1048 s, 922 m, 893 m, 816 s, 789 s, 736 s, 705 s, 599 w, 535 m, 473 m, 441 m, 418 m, 414 m, 406 m.

Diaqua(3,5-di-*tert*-butylbenzoato-ϰ^2*O*,*O*′)bis(μ-3,5-di-*tert*-butylbenzoato-ϰ^3*O*,*O*,*O*′)tetrakis(μ-3,5-di-*tert*-butylbenzoato-ϰ^2*O*,*O*′)bis(2,4-lutidine)europium(III)dicadmium(II), solvate with acetonitrile, [Eu(bzo-ϰ^2*O*,*O*′)Cd$_2$(μ-bzo-ϰ^3*O*,*O*,*O*′)$_2$(μ-bzo-ϰ^2*O*,*O*′)$_4$(H$_2$O)$_2$(2,4-lut)$_2$]·MeCN (5). Compound **5** was synthesized as described for complex **2** using 2,4-lut (0.188 mL, 1.625 mmol, Cd : L = 1 : 5) instead of phen. Colorless crystals suitable for X-ray diffraction that formed within 3 days were separated from the mother liquor by decantation and washed with cold acetonitrile ($t \approx 5$ °C). The yield of **5** was 0.107 g (42.3% with respect to Eu(NO$_3$)$_3$·6H$_2$O). Found (%): C, 63.1; H, 7.1; N, 2.4. $C_{123}H_{175}Cd_2EuN_4O_{16}$. Calculated (%): C, 63.1; H, 7.5; N, 2.4. IR, ν/cm^{-1}: 3675 w, 2962 m, 2902 m, 1608 w, 1524 m, 1475 m, 1438 m, 1392 s, 1362 s, 1317 m, 1289 m, 1248 m, 1202 m, 1163 w, 1128 w, 1079 m, 1067 m, 1047 m, 923 m, 894 m, 823 m, 816 s, 791 s, 742 m, 703 s, 674 m, 593 w, 531 m, 474 m, 457 w, 445 m, 419 m, 406 m.

Bis(μ-3,5-di-*tert*-butylbenzoato-ϰ^3*O*,*O*,*O*′)tetrakis(μ-3,5-di-*tert*-butylbenzoato-ϰ^2*O*,*O*′)bis(2,4-lutidine)(nitrato-ϰ^2*O*,*O*′)-diethanoleuropium(III)dicadmium(II), [Eu(NO$_3$-ϰ^2*O*,*O*′)Cd$_2$(μ-bzo-ϰ^3*O*,*O*,*O*′)$_2$(μ-bzo-ϰ^2*O*,*O*′)$_4$(EtOH)$_2$(2,4-lut)$_2$] (6). A solution of Kbzo (0.175 g, 0.649 mmol) in EtOH (10 mL) was added to a solution of Cd(NO$_3$)$_2$·4H$_2$O (0.100 g, 0.325 mmol) in EtOH (15 mL). The reaction mixture was stirred with heating (t = 70 °C) for 15 min. The white precipitate of KNO$_3$ that formed was filtered off, Eu(NO$_3$)$_3$·6H$_2$O (0.048 g, 0.108 mmol) was added to the filtrate, and the mixture was stirred for 10 min at 80 °C. Then 2,4-lut (0.188 mL, 1.625 mmol, Cd : L =1 : 5) was added to the reaction mixture, and the mixture was stirred for 10 min. The resulting transparent solution was kept at room temperature for 7 days. Crystals suitable for X-ray diffraction that precipitated were separated from the mother liquor by decantation, washed with cold acetonitrile ($t \approx 5$ °C), and dried in air. The yield of **6** was 0.089 g (38.6% with respect to Eu(NO$_3$)$_3$·6H$_2$O). Found (%): C, 60.1; H, 7.1; N, 1.8. $C_{108}H_{156}Cd_2EuN_3O_{17}$. Calculated (%): C, 60.5; H, 7.3; N, 1.9. IR, ν/cm^{-1}: 3675 w, 2962 m, 2902 m, 1608 w, 1524 m, 1475 m, 1438 m, 1392 s, 1362 s, 1317 m, 1289 m, 1248 m, 1202 m, 1163 w, 1128 w, 1079 m, 1067 m, 1047 m, 923 m, 894 m, 823 m, 816 s, 791 s, 742 m, 703 s, 674 m, 593 w, 531 m, 474 m, 457 w, 445 m, 419 m, 406 m.

Aqua(3,5-di-*tert*-butylbenzoato-ϰ^2*O*,*O*′)bis(μ-3,5-di-*tert*-butylbenzoato-ϰ^3*O*,*O*,*O*′)tetrakis(μ-3,5-di-*tert*-butylbenzoato-ϰ^2*O*,*O*′)di(3,4-lutidine)ethanoleuropium(III)dicadmium(II), solvate with five ethanol molecules, [Eu(bzo-ϰ^2*O*,*O*′)Cd$_2$(μ-bzo-ϰ^3*O*,*O*,*O*′)$_2$(μ-bzo-ϰ^2*O*,*O*′)$_4$(H$_2$O)(EtOH)(3,4-lut)$_2$]·5EtOH

Table 4. Crystallographic parameters and the structure refinement statistics for compounds **2**, **3**, and **5**

Parameter	2	3	5
Molecular formula	$C_{121}H_{167}Cd_2EuN_2O_{16}$	$C_{133}H_{183}Cd_2EuN_4O_{14}$	$C_{123}H_{175}Cd_2EuN_4O_{16}$
M	2282.32	2438.58	2342.42
T/K	150(2)	123(2)	120(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$C2/c$
a/Å	17.370(19)	26.9463(18)	26.956(2)
b/Å	18.346(11)	22.9817(15)	22.4576(19)
c/Å	21.352(14)	20.7788(13)	20.5806(17)
α/deg	81.600(11)	90	90
β/deg	88.36(3)	97.718(2)	98.809(2)
γ/deg	84.373(19)	90	90
V/Å^3	6699(9)	12751.2(14)	12312.0(18)
Z	2	4	4
d_{calc}/g cm^{-3}	1.132	1.270	1.264
μ/mm^{-1}	0.830	0.876	0.906
θ_{max}/deg	26.000	25.999	26.000
T_{min}/T_{max}	0.658/0.811	0.872/0.924	0.856/0.912
Number of reflections			
measured	59215	38271	60115
unique	26221	12340	12116
with $I > 2\sigma I$	20010	5388	9479
(R_{int})	(0.0297)	(0.1471)	(0.0845)
Number of refined parameters	4856	3218	3865
GOOF	1.023	0.968	1.055
R_1 ($I > 2\sigma(I)$)	0.0338	0.0755	0.0458
wR_2 ($I > 2\sigma(I)$)	0.0887	0.2096	0.1178
Residual electron density ($\Delta\rho_{min}/\Delta\rho_{max}$)/e Å^{-3}	−0.628/1.104	−1.835/2.274	−1.026/1.989

(7). Compound **7** was synthesized as described for complex **2** using 3,4-lut (0.187 mL, 1.625 mmol, Cd : L = 1 : 5) instead of phen. Colorless crystals suitable for X-ray diffraction that formed within 5 days were separated from the mother liquor by decantation and washed with cold acetonitrile ($t \approx 5$ °C). The yield of **7** was 0.130 g (47.7% with respect to $Eu(NO_3)_3 \cdot 6H_2O$). Found (%): C, 62.9; H, 8.0; N, 1.3. $C_{131}H_{203}Cd_2EuN_2O_{21}$. Calculated (%): C, 62.5; H, 8.1; N, 1.1. IR, ν/cm^{-1}: 3665 w, 3021 w, 2947 w, 2958 m, 2902 m, 1596 s, 1524 m, 1490 m, 1438 m, 1392 s, 1362 s, 1317 m, 1296 m, 1241 m, 1202 m, 1170 w, 1128 w, 1079 m, 1067 m, 1049 m, 923 m, 894 m, 823 m, 816 s, 791 s, 742 m, 703 s, 674 m, 593 w, 522 m, 457 w, 445 m, 419 m, 406 m.

Tri[diaqua(3,5-di-*tert*-butylbenzoato-$\varkappa^2O,O'$)bis(μ-3,5-di-*tert*-butylbenzoato-$\varkappa^3O,O,O'$)tetrakis(μ-3,5-di-*tert*-butylbenzoato-$\varkappa^2O,O'$)bis(phenanthridine)europium(III)dicadmium(II)], solvate with four phenanthridine molecules, [Eu(bzo-$\varkappa^2O,O'$)-Cd_2(μ-bzo-$\varkappa^3O,O,O'$)$_2$(μ-bzo-$\varkappa^2O,O'$)$_4$(H_2O)$_2$(phtd)$_2$]$_3$ · 4phtd (8). Compound **8** was synthesized as described for complex **2** using phtd (0.174 g, 0.974 mmol, Cd : L = 1 : 3) instead of phen. Colorless crystals suitable for X-ray diffraction that formed within 5 days were separated from the mother liquor by decantation and washed with cold acetonitrile ($t \approx 5$ °C). The yield of **8** was 0.113 g (39.5% with respect to $Eu(NO_3)_3 \cdot 6H_2O$). Found (%): C, 67.4; H, 7.0; N, 1.8. $C_{445}H_{544}Cd_6Eu_3N_{10}O_{48}$. Calculated (%): C, 67.5; H, 6.8; N, 1.8. IR, ν/cm^{-1}: 3675 w, 2962 s, 2902 s, 1558 m, 1524 m, 1438 m, 1394 s, 1361 m, 1289 m, 1248 m, 1202 w, 1164 w, 1067 w, 1048 m, 923 w, 893 m, 824 m, 789 s, 746 s, 703 s, 655 s, 584 w, 531 w, 506 w, 472 m, 426 s, 419 s, 413 s.

(3,5-Di-*tert*-butylbenzoato-$\varkappa^2O,O'$)bis(μ-3,5-di-*tert*-butylbenzoato-$\varkappa^3O,O,O'$)tetrakis(μ-3,5-di-*tert*-butylbenzoato-$\varkappa^2O,O'$)-bis(2,3-cyclododecenopyridine)triethanoleuropium(III)dicadmium(II), [Eu(bzo-$\varkappa^2O,O'$)Cd_2(μ-bzo-$\varkappa^3O,O,O'$)$_2$(μ-bzo-$\varkappa^2O,O'$)$_4$-(EtOH)$_3$(cdpy)] (9). Compound **9** was synthesized as described for **2** using cdpy (0.217 g, 0.974 mmol, Cd : L = 1 : 3) instead of phen. Colorless crystals suitable for X-ray diffraction that formed within 7 days were separated from the mother liquor by decantation and washed with cold acetonitrile ($t \approx 5$ °C). The yield of **9** was 0.122 g (47.7% with respect to $Eu(NO_3)_3 \cdot 6H_2O$). Found (%): C, 64.3; H, 8.0; N, 0.6. $C_{130}H_{198}Cd_2EuNO_{19}$. Calculated (%): C, 64.0; H, 8.0; N, 0.6. IR, ν/cm^{-1}: 2952 w, 1608 s, 1562 w, 1438 w, 1395 w, 1361 w, 1290 w, 1247 m, 1203 s, 1164 s, 1044 s, 922 s, 894 m, 823 m, 790 w,742 w,704 w, 596 s, 531m, 475 m, 416 w.

Di[(3,5-di-*tert*-butylbenzoato-$\varkappa^2O,O'$)bis(μ-3,5-di-*tert*-butylbenzoato-$\varkappa^3O,O,O'$)tetrakis(μ-3,5-di-*tert*-butylbenzoato-$\varkappa^2O,O'$)-tetraethanoleuropium(III)dicadmium(II)], solvate with acridine, [Eu(bzo-$\varkappa^2O,O'$)Cd_2(μ-bzo-$\varkappa^3O,O,O'$)$_4$(μ-bzo-$\varkappa^2O,O'$)$_2$-(EtOH)$_4$] · acr (10). Compound **10** was synthesized as described for **2** using acr (0.174 g, 0.974 mmol, Cd : L = 1 : 3) instead of phen. Colorless crystals suitable for X-ray diffraction that formed within 10 days were separated from the mother liquor by decantation and washed with cold acetonitrile ($t \approx -5$ °C). The yield of **10** was 0.169 g (63.9% with respect to $Eu(NO_3)_3 \cdot 6H_2O$). Found (%): C, 63.1; H, 7.6; N, 0.4. $C_{239}H_{352}Cd_4Eu_2N_2O_{36}$. Calculated (%): C, 62.8; H, 7.7; N, 0.3. IR, ν/cm^{-1}: 3280 w, 2961 m, 2867 m, 1621 m, 1555 s, 1516 m, 1477 w, 1460 m, 1437 m,

Table 5. Crystallographic parameters and the structure refinement statistics for compounds **6**—**8**

Parameter	**6**	**7**	**8**
Molecular formula	$C_{108}H_{156}Cd_2EuN_3O_{17}$	$C_{131}H_{203}Cd_2EuN_2O_{21}$	$C_{445}H_{544}Cd_6Eu_3N_{10}O_{48}$
M	2145.11	2518.70	7931.15
T/K	120(2)	120(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1$	$C2/c$
a/Å	17.6197(12)	15.8851(9)	70.236(3)
b/Å	29.232(2)	27.3294(15)	18.5297(9)
c/Å	21.462(2)	17.8939(10)	34.9673(16)
α/deg	90	90	90
β/deg	96.3800(10)	114.5681(11)	94.1134(8)
γ/deg	90	90	90
V/Å^3	10985.8(15)	7065.0(7)	45391(4)
Z	4	2	4
d_{calc}/g cm^{-3}	1.297	1.184	1.161
μ/mm^{-1}	1.009	0.796	0.745
θ_{max}/deg	26.000	25.999	27.544
T_{min}/T_{max}	0.834/0.860	0.765/0.812	0.797/0.943
Number of reflections			
measured	87983	67971	100006
unique	10785	27696	49676
with $I > 2\sigma I$	8116	24724	27743
(R_{int})	(0.0848)	(0.0398)	(0.0633)
Number of refined parameters	3598	3697	9945
GOOF	1.045	1.010	1.017
R_1 ($I > 2\sigma(I)$)	0.0486	0.0346	0.0697
wR_2 ($I > 2\sigma(I)$)	0.1316	0.0789	0.1963
Residual electron density ($\Delta\rho_{min}/\Delta\rho_{max}$)/e Å^{-3}	−2.413/0.978	−0.587/0.582	−0.952/1.540

Table 6. Crystallographic parameters and the structure refinement statistics for compounds **9** and **10**

Parameter	**9**	**10**
Molecular formula	$C_{130}H_{198}Cd_2EuNO_{19}$	$C_{239}H_{352}Cd_4Eu_2NO_{36}$
M	2455.64	4568.71
T/K	150(2)	100(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a/Å	17.6662(8)	40.65(9)
b/Å	18.4364(8)	23.71(6)
c/Å	20.8438(9)	31.35(11)
α/deg	77.8890(10)	90
β/deg	87.0900(10)	128.04(3)
γ/deg	80.5180(10)	90
V/Å^3	6546.1(5)	23800(117)
Z	2	4
d_{calc}/g cm^{-3}	1.246	1.275
μ/mm^{-1}	0.856	0.936
θ_{max}/deg	26.000	26.000
T_{min}/T_{max}	0.897/0.919	0.742/0.885
Number of reflections		
measured	63747	75694
unique	25724	23335
with $I > 2\sigma I$	21597	14774
(R_{int})	(0.0302)	(0.0874)
Number of refined parameters	5023	4256
GOOF	1.013	1.022
R_1 ($I > 2\sigma(I)$)	0.0391	0.0536
wR_2 ($I > 2\sigma(I)$)	0.1003	0.1342
Residual electron density ($\Delta\rho_{min}/\Delta\rho_{max}$)/e Å^{-3}	−1.612/2.156	−1.723/1.799

1393 s, 1361 s, 1316 w, 1289 s, 1247 m, 1203 w, 1162 w, 1142 w, 1044 m, 922 w, 895 m, 854 w, 824 m, 789 s, 739 s, 703 s, 657 w, 600 m, 532 m, 471 m, 419 m, 414 w, 404 m.

Single-crystal X-ray diffraction studies were performed on Bruker Apex II (for **2**, **3**, **8**, and **10**) and Bruker Apex II DUO (for **5**—**7** and **9**) diffractometers equipped with a CCD detector (Mo-Kα, λ = 0.71073 Å, graphite monochromator).[27] For all the compounds, semiempirical absorption corrections were applied with the SADABS program.[28] The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for all non-hydrogen atoms. The OH hydrogen atoms of water and ethanol molecules in complexes **2**, **5**, **8**, and **9** were located in difference Fourier maps; all other hydrogen atoms were positioned geometrically. All hydrogen atoms were refined isotropically using a riding model. The solvent molecules in the structures of complexes **2** and **7**—**10** disordered over several positions were subtracted using the SQUEEZE/Platon procedure. The calculations were performed using the SHELX program suite[29] and the OLEX2 software package.[30]

Crystallographic parameters and the structure refinement statistics for compounds **2**, **3**, and **5**—**10** are given in Tables 4—6. The structural data for compounds **2**, **3**, and **5**—**10** were deposited with the Cambridge Crystallographic Data Centre (CCDC 1993446 (**2**), 1993447 (**3**), 1993448 (**5**), 1993449 (**6**), 1993450 (**7**), 1993451 (**8**), 1993561 (**9**), 1993562 (**10**)) and are available at deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif. The geometry of the polyhedra of the metal atoms was determined using the SHAPE 2.1 program.[31,32]

Single-crystal X-ray diffraction analysis (compounds **2**, **3**, **8**, and **10**), powder X-ray diffraction studies, IR spectroscopy measurements, and elemental analysis were performed using equipment of the Shared Facility Center for Physical Research Methods of the N. S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences (IGIC RAS) within the framework of the State assignment of the IGIC RAS in the field of fundamental scientific research. Complexes **5**—**7** and **9** were structurally characterized with the financial support from the Ministry of Science and Higher Education of the Russian Federation using equipment of the Center for Molecular Composition Studies of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences. We thank D. A. Makarov for help in synthesizing compounds **7** and **9**.

Complexes **2**—**5** and **8**—**10** were synthesized and characterized with the financial support from the Russian Science Foundation (Project No. 16-13-10537); complexes **6** and **7**, within the framework of the State assignment of the IGIC RAS in the field of fundamental scientific research.

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