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Heterometallic Ln(III)–Cd(II) Complexes with Anions of Monocarboxylic Acids: Synthetic Approaches and Analysis of Structures and Photoluminescence Properties

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Abstract—The results of studying heterometallic complexes Ln(III)–Cd(II) with anions of aromatic and aliphatic monocarboxylic acids are generalized. A number of substantial features is observed in complexes Ln(III)–Cd(II), but they are not characteristic of compounds Ln(III)–M(II) with 3*d*-metal ions (M = Co, Ni, Cu, Zn). A tendency of the cadmium(II) complexes to form coordination polymers at the compositions typical of the molecular 3*d*-metal complexes is shown. The effect of the substituent in benzoic acid on the structures and photoluminescence properties of the heterometallic Ln(III)–Cd(II) complexes is revealed.

Keywords: cadmium, lanthanides, heterometallic complexes, photoluminescence, crystal structure

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INTRODUCTION

The lanthanide compounds are known to have unique physicochemical properties: magnetic, optical, and catalytic [1–8]. The luminescence of the Ln compounds covers the whole spectral range: ultraviolet (UV) (Gd), visible (Sm, Eu, Tb, Dy), or infrared (IR) (Pr, Nd, Ho, Er, Tm, Yb) wavelength ranges, and the narrow lines of transitions in the luminescence spectra corresponding to the $f \rightarrow f$ transitions make it possible to obtain "pure colors." When preparing photoluminescent materials based on rare-earth elements (REE), the necessary condition is to achieve high luminescence efficiencies, which is provided, in particular, by a high extinction coefficient of the exciting light. The use of the "antenna effect" is one of the methods for enhancing the luminescence efficiency, when the luminescence quantum yields and molar absorption coefficients can increase considerably due to the insertion of molecules of aromatic organic ligands, for example, monocarboxylic acids, into the coordination environment of the REE [9]. The efficiency of the intramolecular energy transfer to the REE ion depends on both the distance between the ligand molecule and Ln ion [10] and the difference in energies between the triplet level of the organic ligand and resonance level of the metal ion. Since the position of the triplet level depends on the organic ligand nature, their variation during the synthesis makes it possible to affect the luminescence properties of the formed complexes.

However, the insertion of carboxylate anions into the coordination environment of the REE does not always result in the efficient energy transfer to the lanthanide metal center. According to Latva's rule [11], for an efficient energy transfer the difference between the triplet level of the antenna and resonance level of the Ln^{3+} ion should lie in a range of 2500–3500 cm^{-1} for Eu^{3+} and 2500–4000 cm^{-1} for Tb^{3+}. A violation of this condition leads to energy losses because of nonradiative intrasystem transitions. For instance, the benzoate anion (T_1 = 23200 cm^{-1}) is capable of sensitizing both Tb^{3+} and Eu^{3+} ions, the 2-naphthoic acid anion (T_1 = 22000 cm^{-1}) sensitizes only Eu^{3+} ion, whereas a single luminescence band of the ligand is observed in the emission spectrum in the case of the Tb^{3+} ion [10].

Another method for the variation of the energy of the triplet level of the antenna is the insertion of the d^{10} block into the carboxylate complex. The d^{10}-block structure contains the transition metal with the completely filled *d* shell (Cd^{2+}, Zn^{2+}, Ag^{+}) having the ligand environment that provides exciting radiation absorption. The efficiency of this approach was demonstrated [12, 13]. The authors [12] synthesized a series of homo- and heterometallic complexes with anions of benzoic acid (Bnz^{-}) and 1,10-phenanthroline (Phen) and showed that the luminescence intensity decreased in the order $[Tb_2Zn_2(Phen)_2(Bnz)_{10}]$ > $[Tb(Phen)_2(Bnz)_3]$ > $[Tb(Bnz)_3]$. A similar effect was observed for the complexes with 2-furancarboxylic acid anions (Fur^-): $[Tb_2Zn(H_2O)_2(Fur)_8]_n$ and $[Tb(Fur)_3]$ [13].

There are available published data on many heterometallic complexes in which REE and Zn^{2+} ions are combined. According to the Cambridge Structural Database (CSD) (5.42, Nov. 2020 + 3 upd), 1269 structures with various O- and N-donor ligands were described (Schiff bases [14–16], mono- and polycarboxylic acids [17–19], and other polydentate organic ligands [20, 21]), and of them 137 compounds had the molecular, anionic, and polymer structures, where the structure forming role is played by monocarboxylic acid anions characterized by the bi- [22–24], tri- [25, 26], and tetranuclear complexes [27, 28], as well as the complexes of higher nuclearity [29, 30]. The chemistry of the Ln(III)–Cd(II) compounds is poorly studied. The total number of the described complexes is 264 of which only 57 compounds contain anions of monocarboxylic acids. At the same time, the high coordination number of the Cd^{2+} ion and a long covalent radius make it possible to synthesize compounds with specific structural features and physicochemical properties. The heterometallic compounds $\{Ln\text{-}d^{10}\}$ exhibit the properties of monomolecular and monoionic magnets [31, 32] and photocatalytic activity [33] and demonstrate the luminescence sensitive to the polarization and concentration of metal cations [34], antibiotics [35, 36], and other organic compounds [37, 38]. In addition, the triplet level energy changes, as a rule, on going from zinc(II) to cadmium(II) in the d^{10}-block composition resulting in an additional possibility of selecting an optimum correspondence with the energy of the resonance level of the REE ion aimed at enhancing the photoluminescence efficiency [31].

The ligand environment of the metals and crystal packing of the molecules considerably contribute to the photophysical properties. The study of the role of these parameters allows one to elucidate structure–property relationships, which are used when planning syntheses of substances with required photoluminescence characteristics.

The data on the synthesis, structures, and luminescence properties of the Ln(III)–Cd(II) complexes with monocarboxylic acid anions and N-donor ligands (Scheme 1) are generalized and analyzed in the present review. The structural formulas of the ligands are shown in Scheme 1.

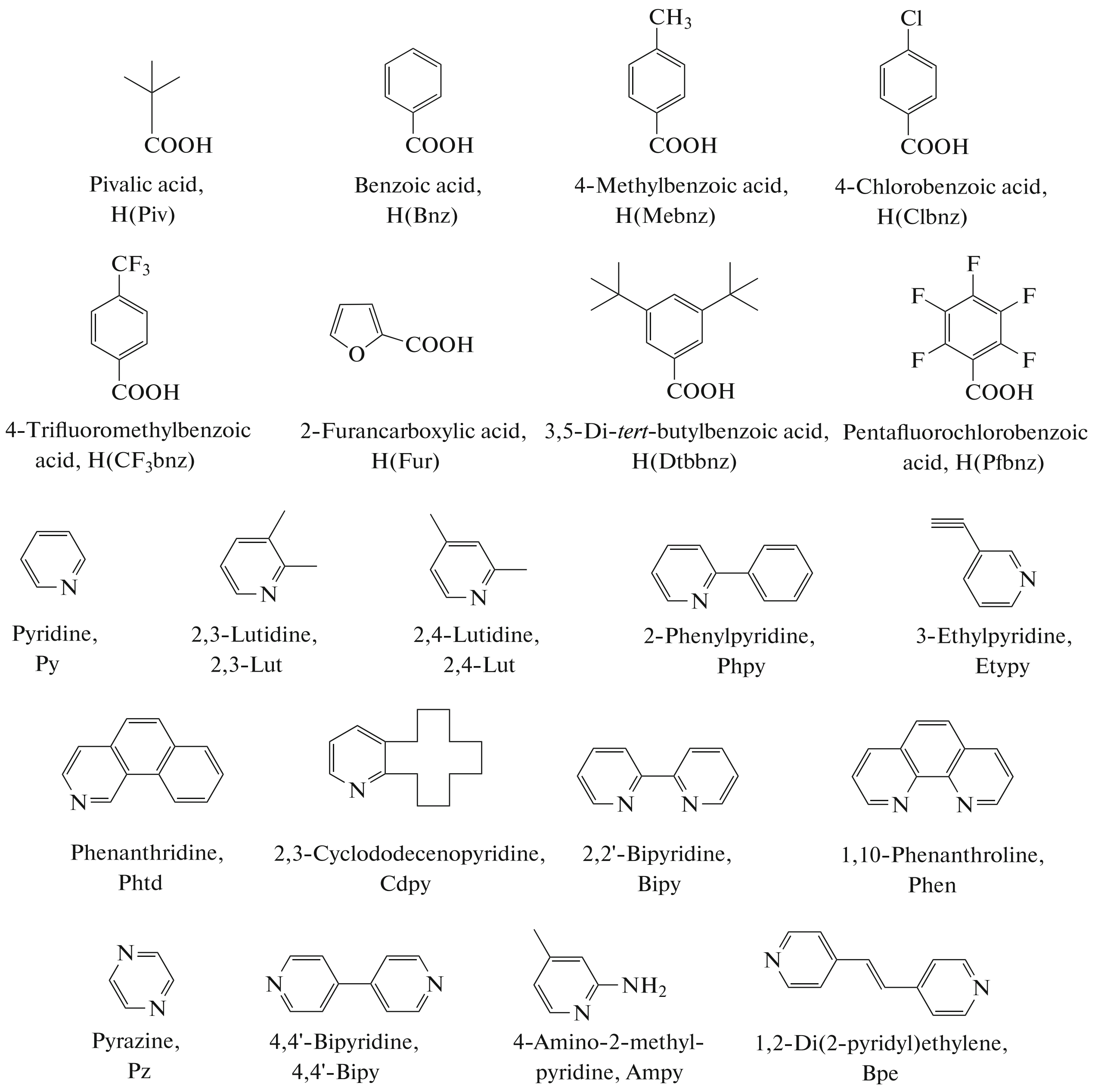
Synthesis of heterometallic complexes Ln(III)–Cd(II) (hereinafter Ln–Cd). Three different approaches are known to the synthesis of polynuclear carboxylate Ln–Cd complexes with anions of monocarboxylic acid anions. Y. Chi and coauthors [39–41] succeeded to obtain the heterometallic complexes by the hydrothermal synthesis when an aqueous solution of salts of a *d* metal and REE with a high excess of organic ligands are placed in an autoclave and hold at 90–120°C for several days, after which the autoclave is slowly cooled to room temperature to form crystals of heterometallic complexes suitable for X-ray diffraction analysis (XRD). A drawback of the method is high labor intensiveness and poor reproducibility of the results.

We described the synthesis without using autoclaves and other special equipment. The most general procedure includes the preliminary synthesis of the starting *d*- and *f*-element carboxylates, for example, from the corresponding metal hydroxides and acids. The reaction is carried out in organic solvents with the addition of an N-donor ligand, after which the crystals of the heterometallic complex are obtained by the evaporation of the solution [42–45].

The third published procedure assumes the synthesis of metal carboxylates and the use of them in the reaction without preliminary isolation in the solid state. They are synthesized by the exchange reaction between metal nitrates and potassium carboxylate in ethanol due to which KNO_3 precipitates and only the required salt remains in the solution. An N-donor ligand is added to the resulting reaction mixture, and the mixture is left to evaporate to obtain crystals of the demanded compounds [31, 32, 46, 47]. A drawback of this procedure is that nitrate anions do not always precipitate completely from the reaction mixture leading to the formation of heteroanionic nitratocarboxylate compounds $\{Ln_2(NO_3)CdL_4(RCOO)_6\}$ or $\{Ln_2(NO_3)_2Cd_2L_4(RCOO)_8)\}$, which exerts a negative effect on the luminescence properties.

STRUCTURES AND PHOTOLUMINESCENCE PROPERTIES OF THE Ln(III)–Cd(II) COMPLEXES

Complexes Ln(III)–Cd(II) with anions of aliphatic monocarboxylic acids. The complexes of this type were described to date only for pivalic acid: $[LnCd_2(H_2O)_2(Piv)_7]_n \cdot nMeCN$ (Ln^{3+} = Sm (**I(Sm)**), Eu (**I(Eu)**), Tb (**I(Tb)**), Dy (**I(Dy)**), Ho (**I(Ho)**), Er (**I(Er)**) Yb (**I(Yb)**); Piv is pivalic acid anion) [32] and $[Eu_2Cd(H_2O)(DMF)(CH_3COOO)(Piv)_7]_n$ (**II(Eu)**, DMF is dimethylformamide) [48]. In the structures of compounds **I**, the trinuclear monomeric fragments $\{LnCd_2\}$ are linked into a zigzag 1D polymer chain by the bridging and chelate bridging Piv^- anions (Fig. 1). In complexes **I**, the geometry of the LnO_8 polyhedron changes from a two-capped trigonal prism for Ln = Sm and Eu to a triangular dodecahedron for Ln = Tb, Dy, Er, and Yb, whereas the coordination environment of the cadmium ion and the structure of the $\{LnCd_2\}$ metal cage remain unchanged.



Scheme 1.

Unlike complexes **I**, compound **II(Eu)** (Fig. 2) is built of the monomeric fragments {Eu_2Cd} bound to each other due to the bridging Piv^- and CH_3COO^- anions with the formation of a zigzag polymer chain (EuEuCd angle is 114.5(1)°). In the structure of the trinuclear metal cage, the central Cd^{2+} ion is bound to each Eu^{3+} ion via one chelate bridging and two bridging Piv^- anions or bridging and chelate bridging Piv^- anions and chelate bridging CH_3COO^- anion. The coordination environment of the Cd^{2+} ion corresponds to the distorted octahedron (CdO_6). The Eu(1) ion builds up its environment to a one-capped square antiprism ($Eu(1)O_9$) by the coordination of the water and DMF molecules. The coordination environment of Eu(2) corresponds to a dodecahedron with the triangular faces $Eu(2)O_8$. The polymer chain of **II(Eu)** is additionally stabilized by hydrogen bonds between the oxygen atoms of the carboxyl groups of Piv and hydrogen atoms of the coordinated water molecule (O(13)...O(6) 2.951(8) Å, O(6)–H(6B)...O(13) 2.105(5) Å, O(6)H(6B)O(13) angle 163.4(7)°; O(6)...O(18) 2.866(8) Å, O(6)–H(6A)....O(18) 2.011(5) Å, O(6)H(6*A*)O(18) angle 167.5(4)°).

Interestingly, molecular complexes $[LnM(L)(Piv)_5]$, $[LnM_2(L)_2(Piv)_7]$, $[Ln(NO_3)M_2(L)_2(Piv)_6]$, or $[Ln_2M_2(L)(Piv)_{10}]$ are formed in the case of the heterometallic pivalate complexes

Ln(III)–M(II) (M = Co, Ni, Cu, Zn) in the presence of monodentate and chelating N-donor ligands (L = pyridine (Py), 2,2'-bipyridine (Bipy), Phen, 2-phenylpyridine, 2,3-lutidine, 2,4-lutidine (2,4-Lut), quinolone, pyrazino[2,3-f][1,10]phenanthroline, or 1,3,5-trimethylhexahydrotriazine) [24, 49–52]. Possibly, a reason for the formation of pivalate coordination polymer **I** and **II(Eu)** is that the "head-to-tail" binding of the trinuclear fragments $\{LnCd_2(L)_2(Piv)_7\}$ into a coordination polymer is thermodynamically more favorable than the stabilization of these fragments by the N-donor ligands in the form of molecular complexes as in the case of 3*d* metals. Probably, in this case, as in the case of the homometallic coordination polymers of cadmium with the whole series of monocarboxylic acid anions, the formation of the polymer structure is favored by a longer (than in the case of 3*d* metals) Cd–O bond [53].

It is shown that the heterometallic polymers Ln–Cd_2 with pivalic acid anions can be used as precursors for the synthesis of metal-organic frameworks. It was demonstrated that the trinuclear metal cage $\{LnCd_2\}$ underwent no rearrangement upon the replacement of the pivalate anion by the 1,4-naphthalenedicarboxylic acid dianion [54].

The luminescence properties of compounds **I(Eu)** and **I(Tb)** were studied. The absence of groups capable of efficiently quenching luminescence in the nearest coordination environment of the REE results in a higher intrinsic luminescence quantum yield for **I(Eu)** than that of $Eu(NO_3)_3{\cdot}6H_2O$ and comparable with the values for the Eu(III) complexes with aromatic monocarboxylic acids. The lifetime of the excited state for **I(Eu)** and **I(Tb)** is close to the values for the heterometallic carboxylate compounds Ln–Zn and Ln–Cd, for example, pentafluorobenzoate complexes $[Eu_2Cd_2(Phen)_2(Pfbnz)_{10}]_n{\cdot}3n$MeCN and $[Eu_2Zn_2(Phen)_2(Pfbnz)_{10}]{\cdot}2$MeCN [32].

Attempts to isolate the Ln–Cd complexes combining anions of aliphatic monocarboxylic acids and N-donor ligands were unsuccessful so far. Only the starting compound **I(Eu)** was isolated upon the addition of a stoichiometric amount of 2,4-Lut to complex **I(Eu)**. The use of chelating N-donor ligands Phen and Bipy led to the destruction of the heterometallic metal cage and formation of complexes $[Eu_2(Bipy)_2(Piv)_6]$ and $[Eu_2(Phen)_2(Piv)_6]$, the structures of which were determined earlier [55].

Complexes Ln(III)–Cd(II) with anions of aromatic monocarboxylic acids. The authors succeeded to isolate the heterometallic complexes with benzoic acid (HBnz) of different nuclearity due to the variation of the REE ions under similar synthesis conditions [39].

The reaction of Na(Bnz), $Er(NO)_3{\cdot}5H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$, and Phen (at the molar ratio Na(Bnz) : $Ln(NO)_3$: $Cd(NO_3)_2$: Phen = 4 : 1 : 1 : 1) in a medium of H_2O and EtOH affords binuclear complex $[ErCd(H_2O)(Phen)(Bnz)_5]$ (**III(Er)**, Fig. 3). Under the conditions similar to the synthesis conditions of **III(Er)**, the replacement of $Er(NO_3)_3$ by $Ho(NO_3)_3$ results in the formation of the pentanuclear centrosymmetric linear structure $[Ho_2Cd_3(Phen)_2(Bnz)_{12}]$ (**IV(Ho)**) (Fig. 4), whereas tetranuclear compounds $[Ln_2Zn_2(Phen)_2(Bnz)_{10}]$ are formed in the case of compounds Er–Zn and Ho–Zn under the conditions identical to those of the synthesis of **III(Er)** and **IV(Ho)** [39]. The presence of $Eu(NO_3)_3$ as the starting compound leads to the formation of trinuclear compound $[EuCd_2(Phen)_2(Bnz)_7]$ (**V(Eu)**, Fig. 5a). The replacement of Phen by Bipy and the use of the exchange reaction of K(Bnz), $Eu(NO)_3{\cdot}6H_2O$, and $Cd(NO_3)_2{\cdot}4H_2O$ result in the crystallization of tetranuclear complex $[Eu_2(NO_3)_2Cd_2(Bipy)_2(EtOH)_2(Bnz)_{10}]$ (**VI(Eu)**, Fig. 5b), where the REE ions build up their environment due to the coordination of the nitrate anion [43].

The formation of different complexes upon the variation of lanthanide is an unexpected result, since Eu^{3+}, Ho^{3+}, and Er^{3+} ions form, as a rule, isostructural compounds [32, 56–68]. Probably, in this case, the complexes are energetically very close and, hence, some variation of the synthesis and crystallization conditions gives compounds of various compositions.

In the structure of compound **III(Er)**, the metal ions are linked with each other by three bridging acid anions and the Cd^{2+} ion additionally coordinates two N atoms of the Phen molecule (coordination number (CN) is 5). Erbium(III) builds up its environment due to the coordination of four O atoms of two acid anions bound via the chelate mode and one O atom of the water molecule (CN = 8).

The packing of complex **III(Er)** exhibits joining of two binuclear fragments due to the formation of intermolecular hydrogen bonds between the coordinated water molecule and the O atom of the acid anion bound via the chelate mode (O(11)–H···O(1), O(11)–H···O(3)) (Fig. 3). The aromatic fragments Phen of two adjacent molecules of the complex are involved in intermolecular π–π interactions.

In the structure of complex $[Ho_2Cd_3(Phen)_2(Bnz)_{12}]$ (**IV(Ho)**), the central Cd^{2+} ion (CN = 6) is linked with each Ho^{3+} ion (CN = 8) by one bridging and two chelate bridging Bnz^- anions, whereas the terminal Cd^{2+} ions are bound to the REE by two bridging and one chelate bridging acid anions. Each terminal Cd^{2+} ion (CN = 6) additionally coordinates the Phen molecule bound via the chelate mode. The aromatic Phen fragments of two adjacent molecules of the complex are involved in intermolecular π–π interactions.

In the structure of trinuclear complex $[EuCd_2(Phen)_2(Bnz)_7]$ (**V(Eu)**), the terminal Cd^{2+} ions are bound to the central Eu^{3+} ion by one chelate

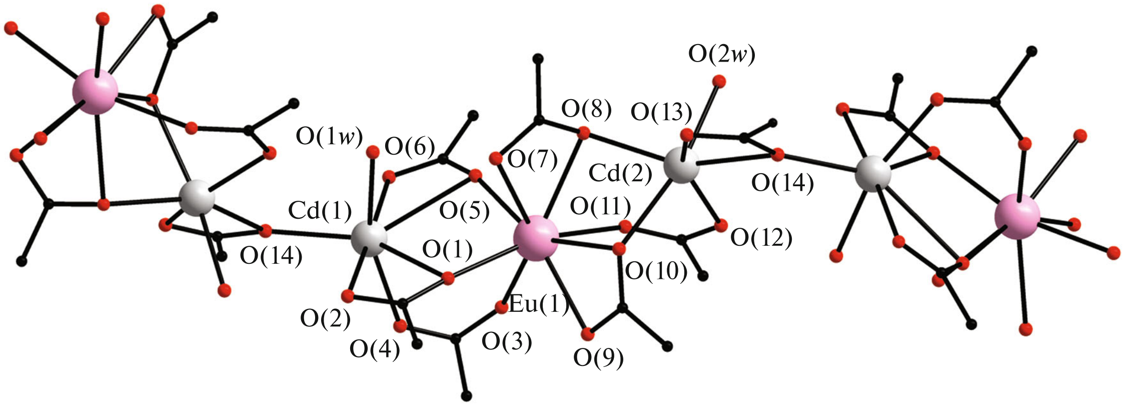


Fig. 1. Fragment of the polymer chain in complex **I(Eu)**. Hydrogen atoms and *tert*-butyl substituents are omitted.

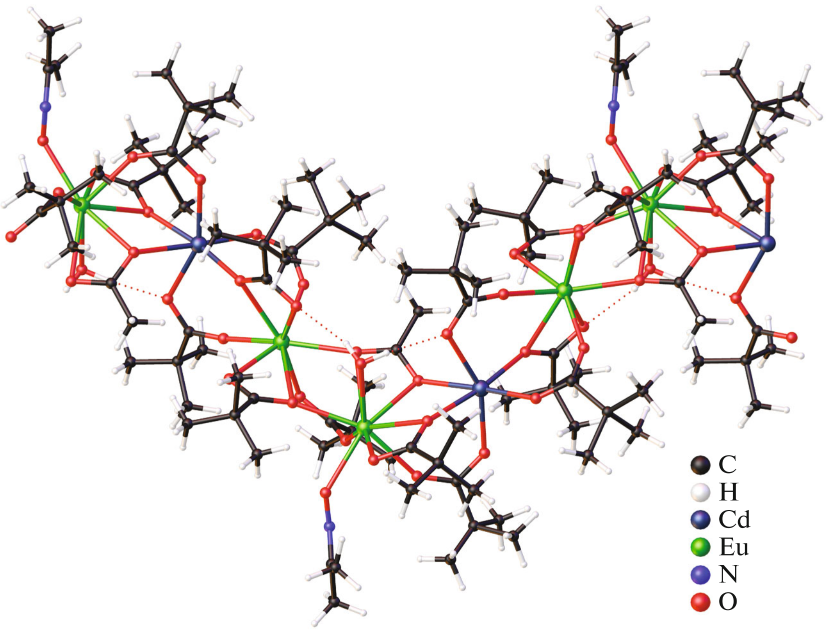


Fig. 2. Fragment of the polymer chain in complex **II(Eu)**.

bridging and two bridging acid anions. Each Cd^{2+} ion additionally coordinates two nitrogen atoms of the Phen molecule (CN = 6), whereas the central Eu^{3+} ion builds up its environment due to the coordination of the benzoate anion bound via the chelate mode (CN = 8). The aromatic Phen fragments of two adjacent molecules of the complex are involved in intermolecular π–π interactions.

In tetranuclear complex $[Eu_2(NO_3)_2Cd_2(Bipy)_2(EtOH)_2(Bnz)_{10}]$ (**VI(Eu)**), the metal ions are linked with each other by the bridging and chelate bridging Bnz^- anions. Each Cd^{2+} ion builds up its octahedral environment (CdO_4N_2) by two nitrogen atoms of the Bipy molecule bound via the chelate mode. The Eu^{3+} ion builds up its environment (EuO_8) to a distorted two-capped trigonal prism due to the coordination of the oxygen atoms of the ethanol molecule and chelate-bound NO_3^- anion from the starting inorganic salt.

It was shown for the benzoate complexes [39] that the presence of a d^{10} block favored a decrease in the energy of the triplet level, shortens the difference in energies with the resonance levels of Ln^{3+} ions, and

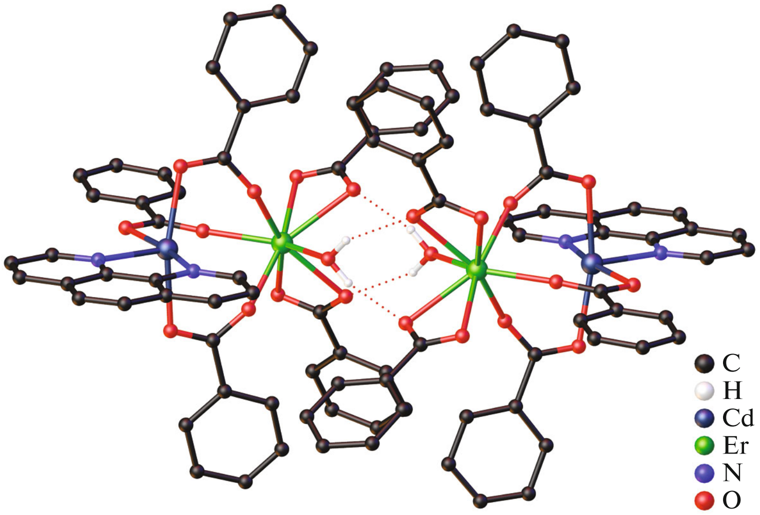


Fig. 3. Fragment of the crystal packing in complex **III(Er)**. Only hydrogen atoms involved in hydrogen bonding are shown.

can facilitate a more efficient energy transfer to the Ln^{3+} ion.

The emission spectra of compounds **III(Er)** and **IV(Ho)** in the near-IR range exhibit bands characteristic of transitions of Ho^{3+} and Er^{3+} ions. However, splitting and shifts of the characteristic bands compared to the published data are observed, which is explained [39] by the influence of the Cd^{2+} ions entered the d^{10}-block structure on the 4*f* orbitals of the REE and the crystalline field effect. The visible range contains the bands corresponding to the luminescence of the d^{10} block indicating an incomplete energy transfer from the triplet level to the Ln^{3+} ion. The luminescence intensity of complex **III(ErCd)** is much lower than that of the zinc-containing analog $[Er_2Zn_2(Phen)_2(Bnz)_{10}]$, which was attributed by the authors to vibrational luminescence quenching due to the water molecule present in the coordination sphere of the REE ion in the structure of compound **III(Er)**.

The emission spectrum of complex **V(Eu)** exhibits the bands characteristic of transitions of the Eu^{3+} ion, whereas the bands corresponding to intraligand transitions are nearly absent. This can indicate an efficient energy transfer to the REE ion. The intensity of the $^5D_0$–$^7F_0$ transition is higher than that of the $^5D_0$–$^7F_1$ transition, indicating the asymmetric environment of the Eu^{3+} ion.

A series of the tetranuclear and binuclear complexes was synthesized using the benzoic acid derivatives with a substituent in the *para*-position. The following tetranuclear compounds Ln_2–Cd_2 (**VII–IX**) of similar structures are formed in the case of 4-methylbenzoic (H(Mebnz)), 4-trifluoromethylbenzoic ($H(CF_3bnz)$), and 4-chlorobenzoic (H(Clbnz)) acids: $[Ln_2Cd_2(Phen)_2(Mebnz)_{10}]$, ($Ln^{3+}$ = Nd (**VII(Nd)**), Pr (**VII(Pr)**), Sm (**VII(Sm)**) [65] (Fig. 6), $[Ho_2Cd_2(Phen)_2(Clbnz)_{10}]$ [65], (**VIII(Ho)**), and $[Ln_2Cd_2(Bipy)_2(CF_3bnz)_{10}]$ [43], (Ln^{3+} = Eu (**IX(Eu)**), Tb (**IX(Tb)**).

Compounds **VII–IX** with $Mebnz^–$, $Clbnz^–$, and $CF_3bnz^–$ anions are tetranuclear complexes with the linear metal cage {Cd...Ln...Ln...Cd} in which the terminal cadmium(II) ions coordinate the chelate-bound molecule of the N-donor ligand (Phen in the case of **VII** and **VIII(Ho)** or Bipy in the case of **IX(Er)**). The main distinction in structures of complexes **VII**, **VIII(Ho)**, and **IX(Er)** is the character of binding of Cd^{2+} and Ln^{3+} ions. For instance, in compounds **VII** and **VIII(Ho)**, the central REE ions are linked between each other by four bridging carboxylate groups and with the terminal cadmium(II) ions by two bridging and one chelate bridging carboxyl groups, whereas the central REE ions in complex **IX(Er)** are bound to each other by two bridging and two chelate bridging carboxyl groups, and with the terminal cadmium(II) ions they are linked by the bridging and chelate bridging carboxyl groups.

In the packing of complexes **VII** and **VIII(Ho)**, the Phen molecules are involved in intermolecular π–π interactions between the aromatic fragments of the N-donor ligands and acid anions of two adjacent molecules of the complex (distances between the centers of interacting species and angles between planes are 3.57 Å and 0.00°, 3.71 Å and 6.00°, respectively (**VII(Nd)**); 3.58 Å and 0.00°, 3.71 Å and 6.03°, respectively (**VII(Pr)**); 3.56 Å and 0.00°, 3.69 Å and 6.66°, respectively (**VII(Sm)**); 3.56 Å and 0.00°, 3.71 Å and 6.36°, respectively (**VIII(Ho)**). On the contrary, only intramolecular π–π interactions between two pairs of

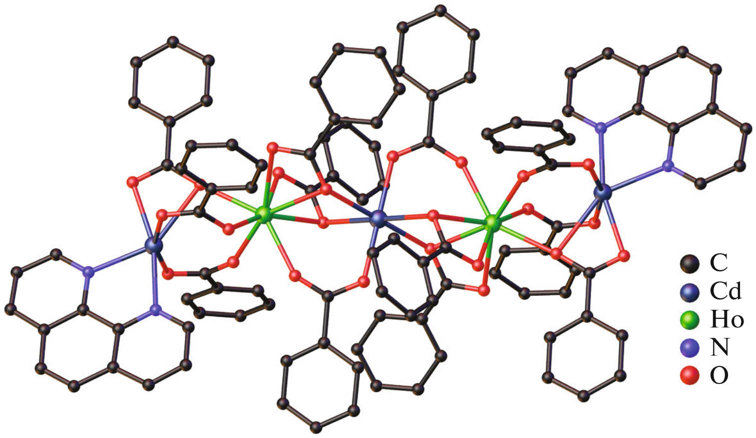


Fig. 4. Structure of complex **IV(Ho)**. Hydrogen atoms are omitted.

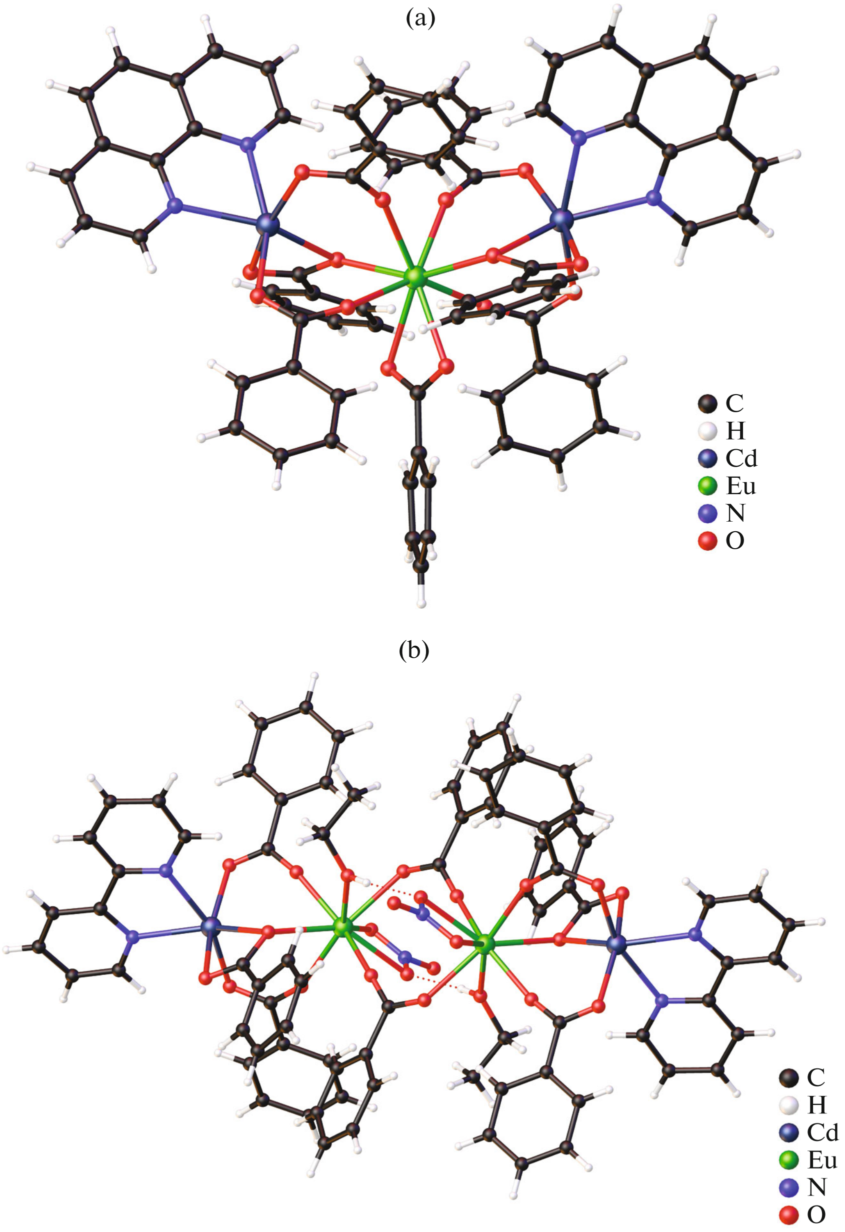


Fig. 5. Structures of complexes (a) **V(Eu)** and (b) **VI(Eu)**.

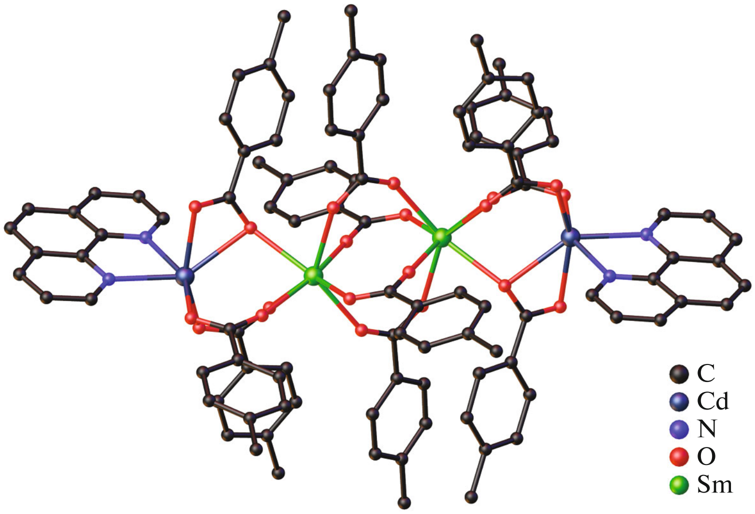


Fig. 6. Molecular structure of complex **VII(Sm)**. Hydrogen atoms are omitted.

the CF_3bnz anions are observed in the case of complex **IX(Eu)** (distances between the centers of interacting species and angles between planes are 3.72 Å and 4.61°, respectively).

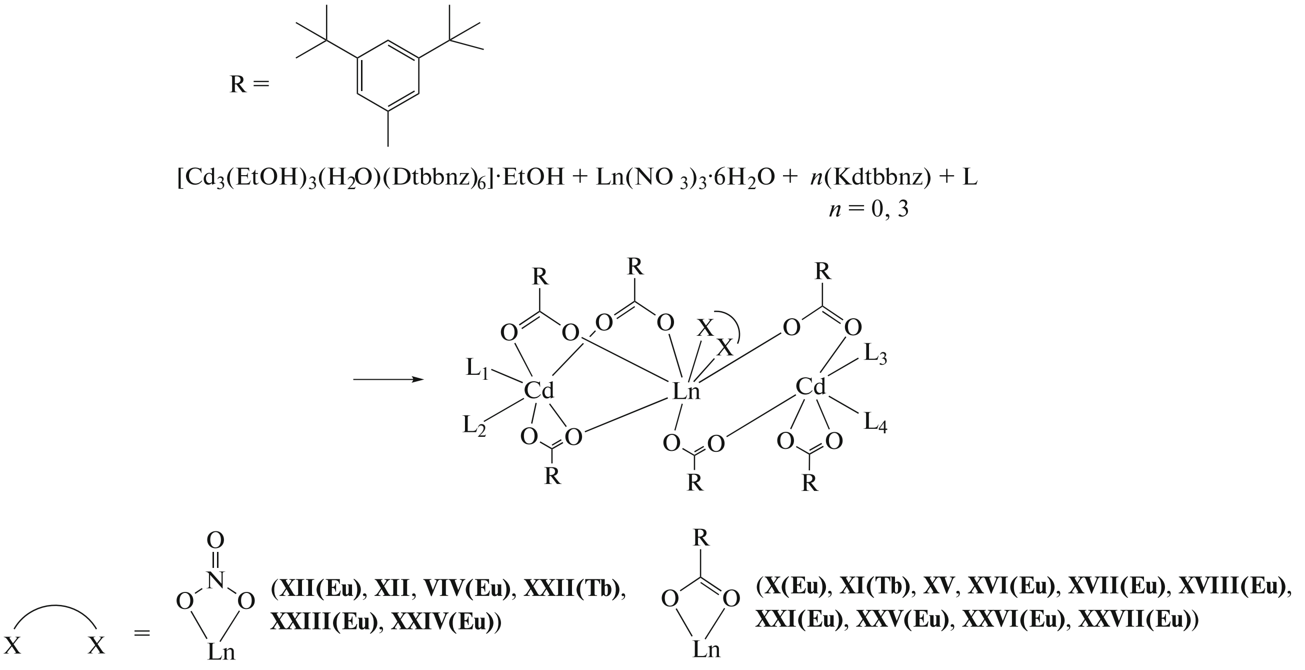
The photophysical properties of complexes **VII**–**IX** were studied for the solid samples at room temperature. The emission spectra of compounds **VII(Nd)**, **VII(Pr)**, and **VIII(Ho)** in the near-IR range exhibit bands characteristic of transitions of Nd^{3+}, Pr^{3+}, and Ho^{3+} ions. The visible spectral range contains intense bands corresponding to the luminescence of the d^{10} block, which indicates an incomplete energy transfer from the triplet level to the lanthanide ion. The study of the luminescence properties of complex **VII(Sm)** showed a very intense band at 370–420 nm in the emission spectrum. This band is attributed to the intraligand transition of the d^{10} block, whereas the intensity of the bands corresponding to transitions of the Sm^{3+} ion is very low, which indicates an inefficient energy transfer from the triplet level of the d^{10} block to the REE ion.

Upon UV excitation, samples **IX(Eu)** and **IX(Tb)** demonstrate the metal-centered luminescence characteristic of Eu^{3+} and Tb^{3+} ions, respectively. The $^5D_0 \rightarrow {}^7F_0$ transition is presented in the luminescence spectrum by the single symmetric band indicating that the coordination environment is the same for both Eu^{3+} ions in the molecule. This is also confirmed by the monoexponential character of quenching of the Eu^{3+} luminescence in the studied complex (τ_{obs} = 1.8 ms). The ratio of integral intensities of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions for complex **IX(Eu)** is 5.54, which is consistent with the absence of an inversion center of the coordination environment of Eu^{3+}.

The internal luminescence quantum yield in the visible spectral range of complex **IX(Eu)** is 81%, which indicates the luminescence efficiency of the Eu^{3+} ion in this matrix and the absence of luminescence quenchers in the nearest environment of the ion, for example, high-frequency oscillators O–H and C–H [69], whereas the absolute luminescence quantum yields are low (13 and 7% for **IX(Eu)** and **IX(Tb)**, respectively). It is most likely that the low absolute luminescence quantum yield is related to the inefficient energy transfer from the d^{10} block to the central ion. The broad bands in a wavelength range of 310–440 nm in the luminescence spectra of complexes **IX(Eu)** and **IX(Tb)** assigned to radiative transitions of the d^{10} block to the ground state also indicate a low efficiency of energy transfer.

Complexes Ln(III)–Cd(II) with 3,5-di-*tert*-butylbenzoic acid anions. In the case of the complexes with 3,5-di-*tert*-butylbenzoic acid (H(Dtbbnz)), a substantial restriction of conformational mobility of the metal cage is observed because of steric hindrances of two bulky *tert*-butyl substituents in $Dtbbnz^-$, which allows one to obtain rather rigid metal cage. This makes it possible to substitute various neutral ligands in the complex without noticeable changes in the geometric parameters of the carboxylate metal fragment. The reactions of $[Cd_3(EtOH)_3(H_2O)(Dtbbnz)_6]\cdot EtOH$ with $Ln(NO_3)_3\cdot 6H_2O$ or in situ obtained {Ln(Dtbbnz)$_3$} (Ln^{3+} = Eu, Tb) [69]) afforded the heterometallic complexes based on $\{Ln(NO_3)Cd_2(Dtbbnz)_6\}$ or $\{LnCd_2(Dtbbnz)_7\}$ fragments (**X–XXVII**). The coordination of the additional nitrate or carboxylate anion on the REE ion depends on the choice of the starting lanthanide compound. When nitrate is used, this ligand enters the coordination sphere of the REE.

When {Ln(Dtbbnz)$_3$} is inserted as the starting compound, the lanthanide builds up its environment due to the O atoms of the carboxylate anion coordinated via the chelate mode [42, 44, 45, 70].



Scheme 2.

The central Ln^{3+} ion is surrounded by eight oxygen atoms, two O atoms of which belong to the chelate-coordinated nitrate or carboxylate anion and six O atoms belong to the bridging carboxylate anions binding the central ion to the peripheral Cd^{2+} ions. The coordination environments of the Cd^{2+} and Ln^{3+} ions correspond to a distorted octahedron and a dodecahedron with triangular faces, respectively.

The study of the complexes with the Dtbbnz anion showed a possibility of inserting into the heterometallic Ln–Cd$_2$ compounds of monodentate, bridging, and chelating ligands, including ligands bearing sterically hindered substituents with both partial and complete substitution of coordinated solvent molecules and retention of the geometry of the trinuclear metal cage and coordination polyhedra of the metals (Table 1).

The addition of stoichiometric amounts of the monodentate ligands (Py, 2,4-Lut, phenanthridine (Phtd)) to the reaction mixture of **X(Eu)**, **XI(Tb)**, or **XII(Eu)** in ethanol affords crystals of compounds **X(Eu)**, **XI(Tb)**, or **XII(Eu)** containing no molecules of the N-donor ligand, which is associated with the competition in the reaction mixture between the ligand and coordinating solvent molecules.

Analogous trinuclear compounds {Ln(NO$_3$)-Zn$_2$(MeCN)$_2$(Piv)$_6$} and {Ln(NO$_3$)Co$_2$(MeCN)$_2$-(Piv)$_6$} (Piv is pivalic acid anion) are formed upon the reaction of transition metal pivalate with Ln(NO$_3$)$_3$·xH$_2$O in acetonitrile. However, each transition metal atom binds only one solvent molecule, whereas in the structures of compounds **X(Eu)**, **XI(Tb)**, and **XII(Eu)** each cadmium(II) atom builds up its environment by the coordination of two solvent molecules [24, 52].

The reactions of a 3–5-fold excess of 2,4-Lut, 2,3-cyclododecenopyridine (Cdpy), and Phtd afford complexes [Eu(NO$_3$)Cd$_2$(2,4-Lut)$_2$(EtOH)$_2$(Dtbbnz)$_6$] (**XIV(Eu)**), [EuCd$_2$(Cdpy)(EtOH)$_3$(Dtbbnz)$_7$] (**XVII(Eu)**), and 3[Eu-Cd$_2$(Phtd)$_2$(H$_2$O)$_2$(Dtbbnz)$_7$]·4Phtd (**XVI(Eu)**) in which only one molecule of the N-donor ligand is coordinated to each Cd^{2+} ion and Cd^{2+} builds up its environment by binding the solvent molecule. At the same time, the use of a tenfold excess of 2,4-lutidine or pyridine made it possible to completely substitute the coordinated solvent molecules by molecules of N-donor ligands with the formation of compounds **XIII(Eu)**, **XV(Eu)**, and **XV(Tb)**.

The coordination of two molecules of α-substituted pyridine to one metal atom in the heterometallic carboxylate complex was observed for the first time for [LnCd$_2$(2,4-Lut)$_4$(Dtbbnz)$_7$] (**XV(Eu)**, (**XV(Tb)**) (Fig. 7). No complexes similar in structure to compound **XV** are known for 3*d* elements. Examples for binding to one metal atom of only one molecule of lutidine or other α-substituted pyridine was reported for the binuclear and linear trinuclear carboxylate complexes of these metals [72–74], which is related to a smaller (compared to the cadmium(II) atom) ion radius and a greater role of steric hindrances created by α-substituents in the case of coordination of two N-donor ligand molecules. The 3*d*-element atoms are in the distorted tetrahedral environment, which is often supplemented to a distorted trigonal bipyramid by a longer M–O bond. However, in several cases, Cd^{2+} manifests low coordination bonds to form analogs of 3*d*-metal compounds [39, 75–77].

A high excess of monodentate N-donor ligands required for the substitution of coordinated solvent molecules indicates stability and an appreciably higher inertness of the cadmium(II) complexes compared to the 3*d*-element compounds. Probably, the formation of products with different ratios of coordinated N-donor ligand and solvent molecules allows one to speak about the stepwise mechanism of the ligand substitution reaction.

A stoichiometric amount of the reagents was enough for the complete substitution of coordinated solvent molecules in the case of chelating ligands (Bipy, Phen).

The binding of the bridging ligands (pyrazine (Pz), 4,4'-bipyridine (4,4'-Bipy), 1,2-di(2-pyridyl)ethylene (Bpe), 2-amino-4-methylpyridine (Ampy)) affords chain zigzag (Pz) (**XXIII(Eu)**) or linear (4,4'-Bipy, Bpe) (**XXV(Eu)**, **XXVI(Eu)**) coordination polymers based on the indicated heterometallic fragments or molecular complexes with the monodentate coordination of the N-donor ligands (**XXIV(Eu)**, **XXVII(Eu)**).

A specific feature of the synthesis of the coordination polymers considered in this review is the necessity to use a significant excess of pyrazine for its binding with the Cd^{2+} ion. The use of a stoichiometric amount of the ligand leads to the isolation of molecular complex $[Eu(NO_3)$-$Cd_2(MeCN)_2(THF)_2(Dtbbnz)_6]\cdot 2EtOH$ (**XII(Eu)**) with the solvent molecules coordinated to the Cd^{2+} ion. The use of an eightfold excess of Pz makes it possible to substitute 50% solvent molecules in the trinuclear $\{LnCd_2\}$ fragment and leads to the crystallization of 1D polymer $[Eu(NO_3)$-$Cd_2(Pz)(H_2O)_2(Dtbbnz)_6]_n$ (**XXIII(Eu)**), where the pyrazine molecules bind the trinuclear fragments to form zigzag chains (Eu(1)Eu(1)Eu(1) angle between the metal ions of three adjacent $\{EuCd_2\}$ fragments of the chain is 112.9°). The further increase in the amount of pyrazine to a 15-fold excess results in the coordination of the second Pz molecule to the heterometallic $\{EuCd_2\}$ fragment due to the decomposition of the polymer structure rather than substitution of the coordinated solvent molecules. As a result, molecular complex $[Eu(NO_3)Cd_2(Pz)_2(EtOH)_2(Dtbbnz)_6]$ (**XXIV(Eu)**) is formed in which the Pz molecules are coordinated by only one nitrogen atom.

The luminescence properties of compounds **X(Eu)**, **XI(Tb)**, **XII(Eu)**, **XIII**, **XV(Eu)**, **XV(Tb)**, **XIX(Eu)**, **XX(Tb)**, **XXII(Tb)**, **XXIII(Eu)**, **XXIV(Eu)**, **XXV(Eu)**, and **XXVI(Eu)** were studied (Table 2). The emission spectra of the complexes exhibit characteristic bands of the following electronic transitions: $^5D_0 \rightarrow {}^7F_J$, J = 0–4 for the Eu^{3+} ion and $^5D_4 \rightarrow {}^7F_J$, J = 6–3 in the case of Tb^{3+}. The $^5D_4 \rightarrow {}^7F_J$, J = 2–0 bands are expectedly low in intensity. The excitation spectra represent a set of broad bands caused by the energy transfer from the d^{10} block to the REE and low lines of *f–f* transitions, whose intensity is comparable with the absorption of the organic ligands, indicating an inefficient sensitization of metal-centered luminescence by the environment of the ligand.

The luminescence spectra contain broad bands in a range of 340–450 nm attributed to the radiative transitions in the d^{10} block. These bands indicate the presence of undesirable channels of energy loss. The observed lifetimes of complexes **XIII(Eu)**, **XXIV(Eu)**, and **XXVI(Eu)** are fairly long (>2 ms) and close to the values for free Eu^{3+} ions in the absence of quenchers. Interestingly, the removal of water or ethanol molecules from the coordination sphere of Cd^{2+} ions favors an increase in the overall quantum yield from 2.5 to 14%. The replacement of Bipy by Phen or 4,4'-Bipy insignificantly affects the quantum yield.

Complexes Ln(III)–Cd(II) with pentafluorobenzoic acid anions. We gave attention to the known systems of organic compounds combining perfluorinated and nonfluorinated aromatic fragments. These systems are typical of the parallel arrangement of all aromatic cycles and their bringing together at the distances approximately to 3.4–3.6 Å. For instance, the crystal packings of benzene and hexafluorobenzene are characterized by the same “ladder” motif, whereas their cocrystallizate $C_6H_6\cdot C_6F_6$ has the layered dense packing [78]. This effect was studied in detail for the organic fluorine-containing and unsubstituted aromatic molecules [78–80]. Halogen-substituted organic ligands are actively used in the synthesis of the compounds with the photoluminescence properties, since the absence of C–H bonds exerts a positive effect on the luminescence properties due to the absence of a quenching effect [9]. In addition, numerous noncovalent interactions (π...π, C–H...Hal, Hal...Hal, C–Hal...π) in the crystal packing result in the formation of unusual structures and also exert a positive effect on the photoluminescence properties [28]. We used the pentafluorobenzoate Ln–Cd compounds and pyridine or its derivatives as aromatic N-donor ligands to study a possibility of binding the fragments of the complex between each other in the crystalline lattice for the synthesis of polymer structures.

The reactions of cadmium(II) and europium(III) pentafluorobenzoates in the presence of pyridine (Cd : L = 1 : 2) or 2-phenylpyridine (Phpy, Cd : L = 1 : 10) lead to the crystallization of linear tetranuclear complexes with similar structures $[Eu_2Cd_2(Py)_4(Pfbnz)_{10}]$ (**XXVIII(Eu)**, Fig. 8) and $[Eu_2Cd_2(Phpy)_2(MeCN)_2$-$(Pfbnz)_{10}]\cdot 5MeCN$ (**XXIX(Eu)**) [71]. Attempts to syn-

Table 1. Compositions of complexes **I–XXXIV**

L	Complex	Literature
H_2O	$[LnCd_2(H_2O)_2(Piv)_7]_n\cdot n$MeCN (**I(Sm)**, **I(Eu)**, **I(Tb)**, **I(Dy)**, **I(Ho)**, **I(Er)**, **I(Yb)**)	[32]
H_2O	$[Eu_2Cd(H_2O)(DMF)(CH_3COOO)(Piv)_7]_n$ (**II(Eu)**)	[38]
Phen, H_2O	$[ErCd(H_2O)(Phen)(Bnz)_5]$ (**III(Er)**)	[39]
Phen	$[Ho_2Cd_3(Phen)_2(Bnz)_{12}]$ (**IV(Ho)**)	[39]
Phen	$[EuCd_2(Phen)_2(Bnz)_7]$ (**V(Eu)**)	[39]
Bipy, EtOH	$[Eu_2(NO_3)_2Cd_2(Bipy)_2(EtOH)_2(Bnz)_{10}]$ (**VI(Eu)**)	[43]
Phen	$[Ln_2Cd_2(Phen)_2(Mebnz)_{10}]$ (**VII(Nd)**, **VII(Pr)**, **VII(Sm)**)	[65]
Phen	$[Ho_2Cd_2(Phen)_2(Clbnz)_{10}]$ (**VIII(Ho)**)	[65]
Bipy	$[Ln_2Cd_2(Bipy)_2(CF_3bnz)_{10}]$ (**IX(Eu)**, **IX(Tb)**)	[43]
H_2O, EtOH	$[EuCd_2(H_2O)_2(EtOH)_2(Dtbbnz)_7]\cdot 3EtOH$ (**X(Eu)**)	[45]
H_2O, EtOH	$[TbCd_2(H_2O)(EtOH)_3(Dtbbnz)_7]\cdot 2EtOH\cdot 2.7H_2O$ (**XI(Tb)**)	[45]
MeCN, THF	$[Eu(NO_3)Cd_2(MeCN)_2(THF)_2(Dtbbnz)_6]\cdot 2EtOH$ (**XII(Eu)**)	[44]
Py	$[Ln(NO_3)Cd_2(Py)_4(Dtbbnz)_6]\cdot 1.5MeCN$ (**XIII(Eu)**, **XIII(Tb)**)	[45]
2,4-Lut	$[Eu(NO_3)Cd_2(2,4\text{-}Lut)_2(EtOH)_2(Dtbbnz)_6]$ (**XIV(Eu)**)	[70]
2,4-Lut	$[LnCd_2(2,4\text{-}Lut)_4(Dtbbnz)_7]$ (**XV(Eu)**, **XV(Tb)**)	[70]
Phtd	$3[EuCd_2(Phtd)_2(H_2O)_2(Dtbbnz)_7]\cdot 4Phtd$ (**XVI(Eu)**)	[70]
Cdpy	$[EuCd_2(Cdpy)(EtOH)_3(Dtbbnz)_7]$ (**XVII(Eu)**)	[70]
Acridine (Acr)	$2[EuCd_2(EtOH)_4(Dtbbnz)_7]\cdot Acr$ (**XVIII(Eu)**)	[70]
Bipy	$[EuCd_2(Bipy)_2(H_2O)(Dtbbnz)_7]\cdot MeCN\cdot 2THF\cdot 3H_2O$ (**XIX(Eu)**)	[45]
Bipy	$[TbCd_2(Bipy)_2(H_2O)(Dtbbnz)_7]$ (**XX(Tb)**)	[45]
Phen	$[EuCd_2(Phen)(EtOH)_2(Dtbbnz)_7]$ (**XXI(Eu)**)	[42]
Phen	$[Tb(NO_3)Cd_2(Phen)_2(Dtbbnz)_6]\cdot MeCN$ (**XXII(Tb)**)	[42]
Pz	$[Eu(NO_3)Cd_2(Pz)(H_2O)_2(Dtbbnz)_6]_n$ (**XXIII(Eu)**)	[44]
Pz	$[Eu(NO_3)Cd_2(Pz)_2(EtOH)_2(Dtbbnz)_6]$ (**XXIV(Eu)**)	[44]
4,4'-Bipy	$[EuCd_2(4,4'\text{-}Bipy)(H_2O)_2(Dtbbnz)_7]_n$ (**XXV(Eu)**)	[44]
Bpe	$[EuCd_2(Bpe)(H_2O)_2(Dtbbnz)_7]_n$ (**XXVI(Eu)**)	[44]
Ampy	$[EuCd_2(Ampy)_2(EtOH)(H_2O)(Dtbbnz)_7]$ (**XXVII(Eu)**)	[44]
Py	$[Eu_2Cd_2(Py)_4(Pfbnz)_{10}]$ (**XXVIII(Eu)**)	[71]
Phpy, MeCN	$[Eu_2Cd_2(Phpy)_2(MeCN)_2(Pfbnz)_{10}]\cdot 5MeCN$ (**XXIX(Eu)**)	[71]
Etypy, H_2O	$[Eu_2Cd(Etypy)(H_2O)_2(Pfbnz)_8]_n\cdot 3n(MeCN)\cdot n(Etypy)$ (**XXX(Eu)**)	[71]
Bipy	$[Eu(NO_3)Cd_2(Bipy)_2(Pfbnz)_6]$ (**XXXI(Eu)**)	[42]
Phen	$[Ln_2Cd_2(Phen)_2(Pfbnz)_{10}]_n\cdot 3n$MeCN (**XXXII(Eu)**, **XXXII(Gd)**, **XXXII(Tb)**, **XXXII(Dy)**)	[31]
Phen	$[Tb_2Cd_2(Phen)_2(Pfbnz)_{10}]$ (**XXXIII(Tb)**)	[31]

thesize heterometallic pentafluorobenzoate Ln–Cd complexes with 2,4-lutidine, isoquinoline, 7,8-benzoquinoline, and 2,2'-biquinoline resulted in the crystallization of only homometallic complexes [71].

In the structures of compounds **XXVIII(Eu)** and **XXIX(Eu)**, the Eu^{3+} ions are linked with each other via two bridging and two chelate bridging Pfbnz anions. The peripheral Cd^{2+} ions are bound to the Eu^{3+} ions via one bridging and two chelate bridging Pfbnz anions in compound **XXVIII(Eu)** and via one chelate bridging and two bridging Pfbnz anions in complex **XXIX(Eu)**. In complex **XXVIII(Eu)**, the Cd^{2+} ion coordinates two Py molecules thus building up its environment (CdO_5N_2) to a pentagonal bipyramid. In compound **XXIX(Eu)**, the environment of the Cd^{2+} ion (CdO_4N_2) is built up to an octahedral environment by the coordination of the N atoms of the Phpy molecule and MeCN. It is most likely that the presence of

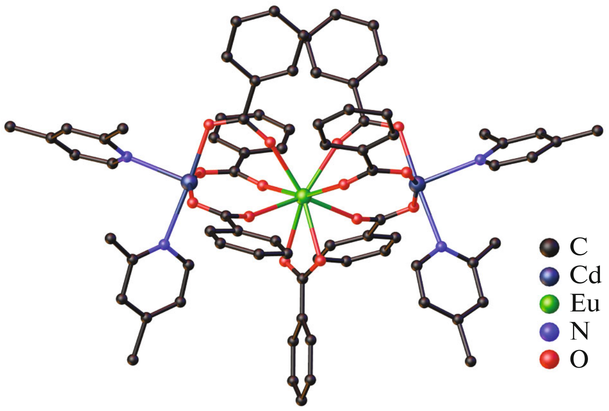


Fig. 7. Structure of complex **XV(Eu)**. Hydrogen atoms are omitted.

the bulky phenyl substituent in the α-position of the Phpy molecule prevents the coordination of the second Phpy molecule, and a more compact MeCN molecule enters the coordination sphere of Cd^{2+}. The main contribution to the stabilization of the crystal packing of complexes **XXVIII(Eu)** and **XXIX(Eu)** is made by intra- and intermolecular interactions C–H...F, C–F...π, and F...F.

Unlike 3,5-di-*tert*-butylbenzoate $Ln–Cd_2$ complexes, complex **XIII** needs a tenfold pyridine excess for the complete substitution of coordinated solvent molecules, a stoichiometric amount of the ligand is sufficient in the case of the pentafluorobenzoate compounds, and a pyridine excess (Cd : L = 1 : 10) induces the destruction of the heterometallic metal cage and formation of the mononuclear $[Cd(Py)_3(Pfbnz)_2]$ complex. This effect of a pyridine excess was quite unexpected. Numerous literature examples show that the heterometallic carboxylate complexes in which lanthanide, lithium, magnesium, or alkaline-earth atoms are combined with 3*d*-metal atoms are fairly stable and can retain the heterometallic cage even under the action of an excess of chelating N-donor ligands [81, 82].

The use of a 3-ethynylpyridine excess (Etypy, Cd : L = 1 : 6) results in the formation of 1D polymer $[Eu_2Cd(Etypy)(H_2O)_2(Pfbnz)_8]_n \cdot 3n(MeCN) \cdot n(Etypy)$ [71] (**XXX(Eu)**, Fig. 9). The polymer chain of **XXX(Eu)** is built of the trinuclear $\{Eu_2Cd\}$ fragments bound by two $\mu_3\kappa^1\kappa^2\kappa^1$ and two bridging Pfbnz anions. In the structure of the trinuclear metal cage $\{Eu_2Cd\}$, the central Cd^{2+} ion is linked with each Eu^{3+} ion by one bridging Pfbnz anion and one bridging oxygen atom of the carboxyl group of the $\mu_3\kappa^1\kappa^2\kappa^1$ anion. In molecule **XXX(Eu)**, one $\mu_3\kappa^1\kappa^2\kappa^1$ anion of pentafluorobenzoic acid binds the central cadmium(II) ion with two europium(III) ions and the peripheral europium(III) ions are bound to each other via this anion. However, the tetranuclear $\{Ln_2Cd_2\}$ fragments observed in complexes **XXVIII(Eu)** and **XXIX(Eu)** can also be distinguished in the polymer chain of complex **XXX(Eu)**. However, each cadmium(II) ion in the polymer chain simultaneously enters two adjacent $\{Ln_2Cd_2\}$ fragments.

The packing of complex **XXX(Eu)** exhibits π–π interactions between the coordinated and solvate Etypy molecules of the adjacent polymer chains and also between the Pfbnz fragments inside one polymer chain. The hydrogen atoms of the acetylene fragment and pyridine ring of the coordinated and solvate Etypy molecules participate in the C–H...F interactions with the fluorine atoms of the Pfbnz anions inside the same chain or between adjacent polymer chains.

Unlike molecular complexes **XXVIII(Eu)** and **XXIV(Eu)**, a significant deviation of the metal cage geometry from linearity is observed for polymer **XXX(Eu)** (CdEuEu angles are 110.85° and 111.45° for **XXX(Eu)**, 172.80° for **XXVIII(Eu)**, and 168.37° for **XXIV(Eu)**). It is most likely that the intra- and intermolecular π–π interactions lead to a distortion of the metal cage geometry of compound **XXX(Eu)**, whereas no π–π interaction is observed in the crystals of close to linear compounds **XXVIII(Eu)** and **XXIV(Eu)**.

According to the CSD data, no analogous polymer complexes $\{Ln_2M\}$ (M is transition metal atom) with monocarboxylic acid anions and N-donor aromatic

Table 2. Lifetimes (τ_{obs}) and internal $\left(Q_{Ln}^{Ln}\right)$ and overall $\left(Q_{L}^{Ln}\right)$ quantum yields of the complexes

Complex	λ_{exc}, nm	τ_{obs}, ms	Q_{Ln}^{Ln}, %	Q_{Ln}^{L}, %	Complex	λ_{exc}, nm	τ_{obs}, ms	Q_{Ln}^{Ln}, %	Q_{Ln}^{L}, %
X(Eu)	450	1.31	56	2.5	**XIX(Eu)**	440	1.36	60	14
XI(Tb)		1.21			**XX(Tb)**		1.59		14.5
XII(Eu)	440	1.04	46	1	**XXII(Tb)**		1.63		13
XIII(Eu)	445			17	**XXIII(Eu)**	480	0.85	41	7
XIII(Tb)		1.76	26		**XXIV(Eu)**	320	2.05	66	7
XV(Eu)	360			10	**XXV(Eu)**	415	1.58	65	11
XV(Tb)				24	**XXVI(Eu)**	355	2.33	93	1

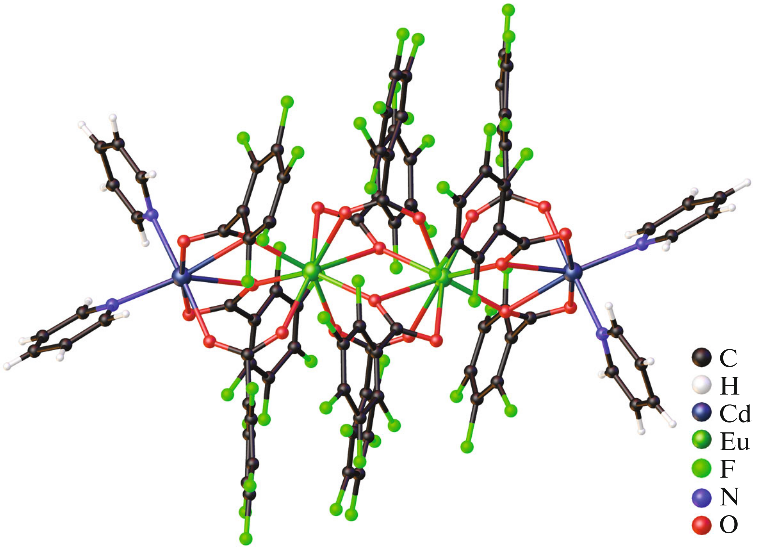


Fig. 8. Structure of complex **XXVIII(Eu)**.

ligands were described, but a series of polymer complexes {Ln_2M} without aromatic N-donor ligands, where the bridging function is performed by the carboxylate anions $[Ln_2Zn(H_2O)_2(Fur)_8]_n$ (Fur is 2-furancarboxylic acid anion) [13, 83] and $[Ln_2Mn(H_2O)_4(CH_3COO)_8]$ [84, 85], was synthesized.

The reaction of $Cd(NO_3)_2{\cdot}4H_2O$, $Eu(NO_3)_3{\cdot}6H_2O$, KPfbnz, and Bipy afforded trinuclear complex $[Eu(NO_3)Cd_2(Bipy)_2(Pfbnz)_6]$ **(XXXI(Eu))**, whose structure is similar to $[EuCd_2(Bipy)_2(H_2O)(Dtbbnz)_7]{\cdot}MeCN{\cdot}2THF{\cdot}3H_2O$ **(XIX(Eu))**. The hydrogen atoms of the coordinated Bipy molecules are involved in the formation of C–H...F contacts with the fluorine atoms of the Pfbnz anions of the adjacent molecules of the complex.

An analysis of the luminescence of complexes **XIX(Eu)** and **XXXI(Eu)** shows that the replacement of the 3,5-di-*tert*-butylbenzoic acid anion in complex **XIX(Eu)** by the pentafluorobenzoic acid anion in complex **XXXI(Eu)** results in a twofold increase in the quantum yield from 14 to 25% and in the lifetime from 1360 to 2150 μs. Possibly, this effect is caused by a more appropriate in energy triplet level of the Pfbnz anion (E_T = 22000 cm^{-1}) [86], which makes the energy transfer from the ligand to the luminescing levels of the metal ion (${}^JD_0$) more efficient.

We inserted Phen to increase the probability of intra- and intermolecular interactions to occur in the crystals of the complexes, since a higher tendency for its participation in π–π interactions compared with 2,2'-bipyridine is observed [28].

The reactions between cadmium(II) and lanthanide(III) pentafluorobenzoates in the presence of Phen in MeCN at room temperature afforded a series of 1D coordination polymers $[Ln_2Cd_2(Phen)_2(Pfbnz)_{10}]_n{\cdot}3n$MeCN, (Ln = Eu (**XXXII(Eu)**), Gd (**XXXII(Gd)**), Tb (**XXXII(Tb)** (Fig. 10a), Dy (**XXXII(Dy)**). It was found that increasing synthesis and crystallization temperature to 75°C led to the formation of molecular complex $[Tb_2Cd_2(Phen)_2(Pfbnz)_{10}]$ (**XXXIII(Tb)**, Fig. 10b) [31] isostructural to the Zn(II) complexes.

The polymer chains of compound **XXXII** are built of the tetranuclear chain fragments {Ln_2Cd_2} in which, as in the molecular Ln_2–Cd_2 complexes, the cadmium(II) ions are peripheral and the lanthanide(III) ions are central. In compound **XXXII**, one of the pentafluorobenzoate anions is bound to each metal ion via the chelate mode, one of the oxygen atoms of this anion provides the bridging binding with the lanthanide(III) ion of “its” tetranuclear {Ln_2Cd_2} fragment, and the second oxygen atom is coordinated by the cadmium(II) ion of the adjacent {Ln_2Cd_2} fragment. Since the fragments are equivalent and centrosymmetric, they are linked with each other by two bridging oxygen atoms of two carboxylate anions. Each cadmium(II) ion builds up its environment to a pentagonal bipyramid (CdO_5N_2) via the coordination of two N atoms of the Phen molecule and O atoms of one bridging, one $\mu_3\kappa^1\kappa^2\kappa^1$-, and one $\mu_3\kappa^1\kappa^1\kappa^1$-Pfbnz anions. The Ln(III) ions build up their coordination environment to a nine-vertex polyhedron (LnO_9) by the coordination of two O atoms of the chelating Pfbnz anion and O atoms of one bridging, two $\mu_3\kappa^1\kappa^2\kappa^1$-, and one $\mu_3\kappa^1\kappa^1\kappa^1$-Pfbnz anions.

The structure of molecular complex **XXXIII(Tb)** is similar to the {Ln_2M_2} structure of isle compounds **XXVIII(Eu)** and **XXIX(Eu)**, where the central metal ions are linked with each other by two bridging and

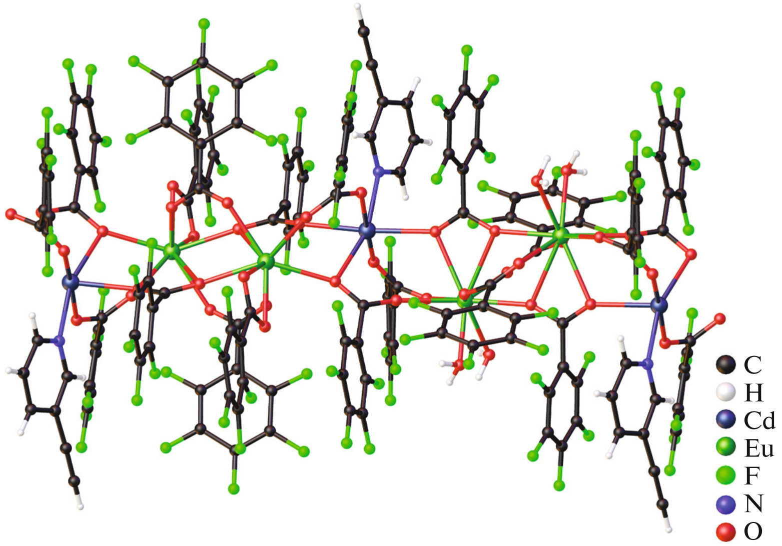


Fig. 9. Structure of complex **XXX(Eu)**. Solvate molecules are omitted.

two chelate bridging Pfbnz anions. The peripheral cadmium(II) ions are bound to the bridging REE and two chelate bridging Pfbnz anions. The coordination environment of the cadmium(II) ions corresponds to the octahedron (CdO_4N_2).

We experimentally detected both the molecular and polymer forms of the same composition for compounds **XXXII(Tb)** and **XXXIII(Tb)** as examples. The structures of the tetranuclear heterometallic fragments $\{Tb_2Cd_2(Phen)_2(Pfbnz)_{10}\}$ differ substantially in polymer **XXXII(Tb)** and molecular complex **XXXIII(Tb)**. The metal ions in **XXXIII(Tb)** lie nearly on one line. The flattened structural motif described for polymer complex **XXX(Eu)** is observed in the tetranuclear fragment of polymer $\{Ln_2Cd_2(Phen)_2(Pfbnz)_{10}\}$. As a result, the aromatic fragments are brought together and the zigzag arrangement of the metal ions is observed (CdLnLn angle in the tetranuclear fragments changes from ~172° to 115° compared to molecular compounds **XXVIII(Eu)**, **XXIX(Eu)**, and **XXXIII(Tb)**).

It is most likely that the stabilization of the polymer structure is related to the intramolecular interactions π...π, C–H...F, F...F, and F...π, which provides the close to parallel arrangement of all pentafluorophenyl substituents of the carboxylate anions and coordinated Phen molecules of the polymer chain and eliminates the blocking of the metal center that is necessary for polymerization. In the structure of molecular complex **XXXIII(Tb)**, the pentafluorobenzoate anions are involved only in the C–H...F interactions.

According to the CSD data, all other known heterometallic complexes Ln–M, where M is the transition metal, with monocarboxylic acid anions and molecules of 1,10-phenanthroline or its substituted analogs (55 compounds are described) are molecular complexes.

The replacement of cadmium(II) by zinc(II) and variation of the synthesis and crystallization temperature from 25 to 80°C showed the crystallization of only one product under these conditions: molecular tetranuclear complexes $[Ln_2Zn_2(Phen)_2(Pfbnz)_{10}]\cdot 2MeCN$ (Ln = Eu, Gd, Tb, Dy). The system with zinc(II) ions is indifferent to temperature variation, which is likely due to a smaller radius of the zinc(II) ion compared to the cadmium(II) ion preventing the coordination of the carboxylate groups of the adjacent molecule of the complex.

An attempt to synthesize heterometallic compound Ln_2–Cd_2 in the presence of zinc(II) pentafluorobenzoate resulted in the crystallization of complex $[Eu_2Cd_2(Phen)_4(Pfbnz)_{10}]\cdot 4MeCN$ (**XXXIV(Eu)**, Fig. 11). A more “loose” tetranuclear metal cage is formed in the structure of compound **XXXIV(Eu)**, where the metal ions are linked by the bridging Pfbnz anions only, which elongates the Cd...Ln distance over that in tetranuclear molecular complex **XXXIII(Tb)** and each metal ion coordinates the chelate-bound Phen molecule. The coordination environment of Eu^{3+} corresponds to the square antiprism (EuO_7N_2), and the cadmium(II) atom builds up its environment to a trigonal prism by the coordination of the chelating Pfbnz anion (CdO_4N_2). We failed to find in the CSD any examples of heterometallic REE complexes with transition metals and monocarboxylic acid anions, where the molecule of an N-donor chelating ligand would be coordinated to each metal atom.

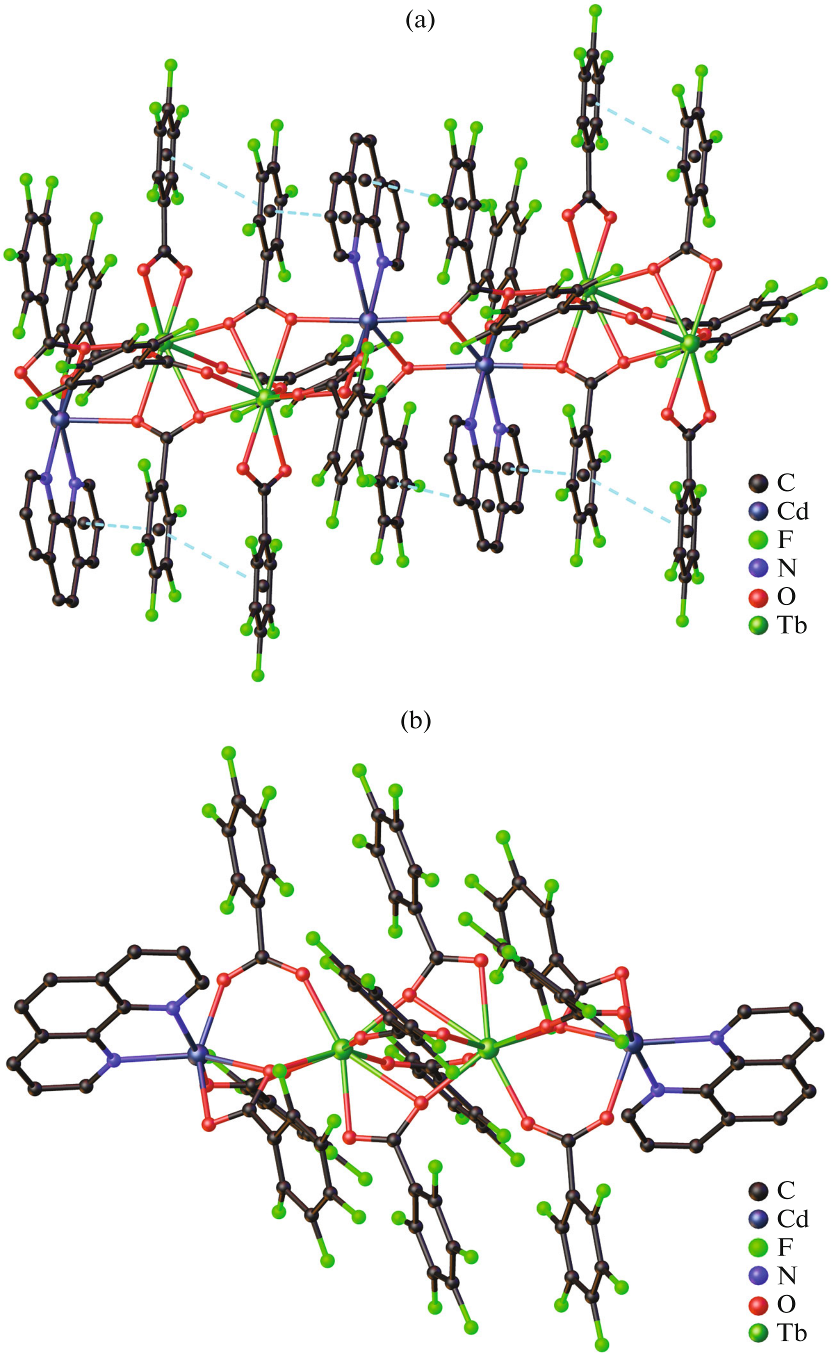


Fig. 10. Structures of complexes (a) **XXXII(Tb)** and (b) **XXXIII(Tb)**. Hydrogen atoms and solvate molecules are omitted.

The photophysical properties of complexes **XXXII(Eu)**, **XXXII(Tb)**, and **XXXIII(Tb)** were studied for the solid samples at room temperature. The long luminescence decay times were elucidated for the europium(III)- and terbium(III)-containing complexes comparable with the times for free europium(III) and terbium(III) ions, indicating an insignificant contribution of the ligand environment to the deactivation of the excited states of the lanthanide ions.

The luminescence quantum yields for $[Eu_2Cd_2(Phen)_2(Pfbnz)_{10}]_n \cdot 3n$MeCN (**XXXII(Eu)**), $[Tb_2Cd_2(Phen)_2(Pfbnz)_{10}]_n \cdot 3n$MeCN (**XXXII(Tb)**), and $[Tb_2Cd_2(Phen)_2(Pfbnz)_{10}]$ (**XXXIII(Tb)**) equal to 39, 63, and 45%, respectively, turned out to be rather high compared to the yields of the previously studied heterometallic Ln–Cd complexes. It was revealed that the luminescence quantum yield and lifetime of Tb^{3+}-containing polymer complex **XXXII(Tb)** exceeded the

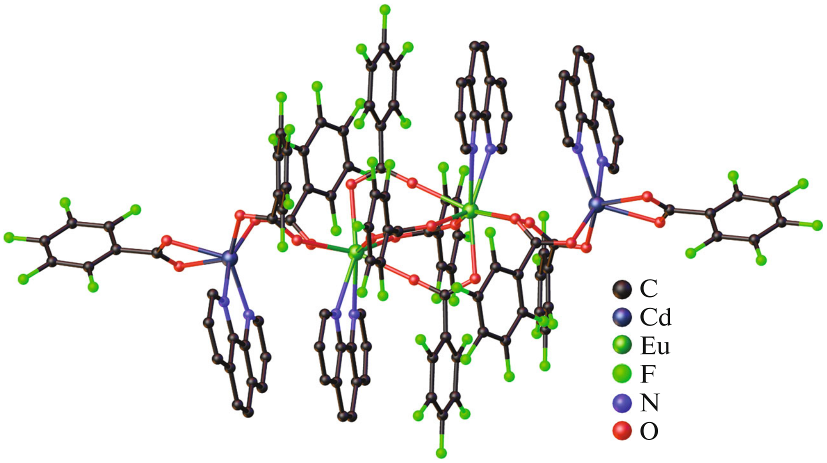


Fig. 11. Structure of complex **XXXIV(Eu)**. Hydrogen atoms and solvate molecules are omitted.

values for molecular complex **XXXIII(Tb)** of a similar composition. The lifetime of the excited state and sensitization efficiency (η = 58%) also increase for $[Eu_2Cd_2(Phen)_2(Pfbnz)_{10}]_n \cdot 3n$MeCN (**XXXII(Eu)**) compared to the earlier synthesized homometallic europium(III) complex $[Eu_2(Phen)_2(H_2O)_2(Pfbnz)_6]$ [87]. The lower sensitization efficiency can be related to luminescence quenching by vibrational oscillations of the water molecule coordinated by the Eu^{3+} ion. A comparison of the quantum yields for complex **XXXII** and polymer $[Ln(H_2O)(Pfbnz)_3]_n$ [88] showed values of Q lower by ~3.6 and ~1.7 times for the homometallic complexes and europium- and terbium-containing compounds, respectively, which can be due to the presence of water molecules in the $[Ln(H_2O)(Pfbnz)_3]_n$ complexes and many ligand-antennas based on one Ln(III) atom in $[Eu_2Cd_2(Phen)_2(Pfbnz)_{10}]_n \cdot 3n$MeCN (**XXXII(Eu)**).

To conclude, the presented review of the data on the structures and synthesis conditions of the heterometallic compounds shows a series of substantial features, which are observed for the Ln(III)–Cd(II) complexes but are not characteristic of the similar in composition and structure compounds Ln(III)–M(II) with 3*d*-metal atoms (M^{2+} = Co, Ni, Cu, Zn). In the case of 3*d* metals, the stable molecular complexes correspond to the heterometallic compositions $\{LnM_2(L)_2(OOCR)_7\}$, $\{LnM_2(L)_2(NO_3)(OOCR)_6\}$, $\{Ln_2M_2(L)_2(OOCR)_{10}\}$, and $\{Ln_2M_2(L)_2(NO_3)_2(OOCR)_8\}$ (M^{2+} = Co, Ni, Cu, Zn, and Cd; L is N-donor heterocyclic monodentate or chelating ligand). Note that the compounds isostructural to the 3*d*-metal complexes can also be obtained for the Ln(III)–Cd(II) systems.

The ability of the heterometallic cadmium(II) complexes to form coordination polymers at the compositions typical of molecular complexes of 3*d* metals with aromatic N-donor heterocyclic monodentate or chelating ligands was also found for the heterometallic pentafluorobenzoate complexes. The 1D coordination polymers can correspond to the compositions $\{Ln_2Cd_2(Phen)_2(C_6F_5COO)_{10}\}$ and $\{Ln_2Cd_2(Phen)_2(NO_3)_2(C_6F_5COO)_8\}$.

The coordination environment of cadmium(II) can be built up by solvent molecules with the formation of isle structures for all listed heterometallic compounds. The high coordination numbers of cadmium(II) and formation of its longer bonds with donor atoms favor an increase in the “friability” of the ligand environment of the heterometallic metal fragments. As a result, the solvent molecules can build up the coordination environment of both cadmium(II) atoms and lanthanide(III) atoms.

The tendency found in the Ln(III)–Cd(II) complexes to build up the coordination environment of the lanthanide(III) atoms by additional solvent molecules is brightly manifested for compound **XXXIV(Eu)** in which the lanthanide(III) atoms bind the Phen molecules via the chelate mode (in the case of a high excess of Phen in the reaction mixture, Cd^{2+} : Phen = 1 : 10). Note that the possibility of binding solvent molecules by lanthanide atoms allows one to consider their effect on the photophysical properties of the compounds making the Ln(III)–Cd(II) complexes to be promising for the detection of molecules in the reaction mixture.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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