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Synthesis of Coordination Polymers from the Heterometallic Carboxylate Complexes with Chelating N-Donor Ligands

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Abstract—New trinuclear Cd–Ln molecular complexes $[EuCd_2(O_2CC_6F_5)_6(NO_3)(Bipy)_2]$ (**I**, Bipy is 2,2'-bipyridine) and $[LnCd_2(Bzo)_6(NO_3)(Phen)_2] \cdot 4MeCN$ (Ln = Tb (**II**), Eu (**III**), Bzo is anion of 3,5-di-*tert*-butylbenzoic acid, Phen is 1,10-phenanthroline) are studied. Their structures are determined by X-ray structure analysis (CIF files CCDC nos. 1938125 (**I**), 1938124 (**II**)) or by X-ray diffraction analysis (**III**), and the photoluminescence properties are studied. The reactions of complexes **I** and **II** with terephthalic acid (H_2Bdc) are accompanied by the destruction of the heterometallic molecules to form 2D coordination polymers $[Cd_3(Bbdc)_3(Bipy)_2]_{3n} \cdot 4n MeCN \cdot nH_2O$ (**IV**) and $[Cd_2(Bdc)_2(Phen)_2]_n \cdot 2n DMF$ (**V**) (CIF files CCDC nos. 1938126 and 1937492, respectively).

Keywords: cadmium, terephthalic acid, coordination polymers, lanthanides, 3,5-di-*tert*-butyl benzoate, pentafluorobenzoate, luminescence, X-ray structure analysis

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INTRODUCTION

Interest in 4*f*-metal complexes is evoked by the possibility to obtain brightly luminescent compounds with a wide range of application, for example, as components of LED and OLED devices and fluorescent labels in biochemistry and medicine [1–5]. The efficiency of emission of the lanthanide complexes is high compared to inorganic materials, since they contain aromatic ligands capable of absorbing external radiation and transmitting energy to the luminescing levels of the 4*f* ion due to intrasystem transitions [6, 7]. Chemical "complementarity" and electronic optical characteristics of the aromatic ligand, such as the molar absorption coefficient, absorption range, and energy of the triplet state, play a special role in processes of excitation and emission of the complexes of 4*f*-element ions [8, 9]. The carboxylate complexes of 4*f* metals can be distinguished among compounds with high quantum yields of photoluminescence [10–16]. The photoluminescence properties of lanthanide carboxylates can be controlled due to the variation of the substituent at the carboxylate group of the anion of acid (^-O_2CR), introduction of an additional aromatic ligand (L) into the coordination sphere of the metal ion, and preparation of heterometallic complexes with diamagnetic transition metal (M) ions in addition to the aforementioned methods [10, 15]. The last approach allows one to form a stable metallic framework, $\{L–M–(O_2CR)_x–Ln\}$ or $\{L–M–(O_2CR)_x–Ln–(O_2CR)_x–M–L\}$, in which the coordination sphere of the 4*f* ion can be blocked from water molecules and the organic moiety can be replaced. Such heteronuclear *d*–4*f* molecules are of interest as precursors for the target synthesis of metal-organic frameworks (MOF), since all carboxylate ligands can be replaced by anions of polycarboxylic aromatic acids and neutral molecules can be substituted by N-donor bridging ligands.

It has previously been shown that the substitution of the trimethylacetate anions (Piv) in the molecular complexes $[Co_2Gd(NO_3)(Piv)_6(Py)_2]$ and $[Li_2M_2$-

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† Deceased.

$(Piv)_6(Py)_2]$ (M = Co, Zn; Py is pyridine) by terephthalate (Bdc) or biphenyldicarboxylate (Bpdc) ligands and the replacement of pyridine (bound via the monodentate mode) by its bidentate bridging derivatives result in the formation of Li–3*d* or 3*d*–Ln 2D or 3D coordination polymers, which partially or completely retain their heterometallic frameworks [16–18]. At first glance, it seems more simply to substitute only some ligands with retention of the structure of the metallic framework. This is confirmed by examples of the 1D and 2D coordination polymers $[Fe_2NiO(Piv)_6(L)]_n$ (Piv^- is anion of pivalic acid; and L is tris(4-pyridyl)triazine, 2,6-bis(3-pyridyl)-4-(4-pyridyl)pyridine, *N*-(bis-2,2-(4-pyridyloxymethyl)-3-(4-pyridyloxy)propyl)pyridone-4, and 4-(*N*,*N*-diethylamino)phenylbis-2,6-(4-pyridyl)pyridine) or $[\{Fe_2NiO(Piv)_6\}_8\{L^2\}_{12}]$ (L^2 is 4-(*N*,*N*-dimethylamino)phenyl-2,6-bis(4-pyridyl)pyridine), which were synthesized earlier due to the replacement of the monodentate N-donor ligands by the bidentate bridging ligands in the $[Fe_2NiO(Piv)_6(HPiv)_3]$ complex [19, 20]. The examples for the retention of the metallic framework during the substitution of the pivalate anions in compound $[Cu_2(Piv)_4(HPiv)_2]$ by the β-naphthoate anions to form the $[Cu_2(\beta\text{-Naph})_4(MeCN)_2]$ complex are known [21]. The bi-, tri-, or tetranuclear molecular heterometallic complexes with the linear metallic framework contain from 5 to 10 anions of monocarboxylic acids. Thus, the substitution of these anions by bridging anions of dicarboxylic acid can result in the formation of a pentabonded metal fragment. This number of bridging ligands is already enough for the formation of 3D polymer structures.

The purpose of this work is to synthesize new molecular heterometallic Cd–Ln complexes soluble in organic solvents and to study their stability in the synthesis of MOF with dicarboxylic (terephthalic) acid. The Cd–Ln carboxylate complexes are of interest, because they are poorly studied. On the one hand, it is evident that photoluminescent materials can be prepared on the basis of these compounds. On the other hand, only single examples for the Cd–Ln complexes with anions of monocarboxylic acids are known at the moment [22–25]. The solubility of the compounds in organic solvents can be achieved due to the use of anions of 3,5-di-*tert*-butylbenzoic or pentafluorobenzoic acids [14, 26, 27]. Additional N-donor bridging ligands were not used in this work for the synthesis of MOF, because the obtained molecular Cd–Ln complexes contained the chelating ligands, 2,2'-dipyridyl (Bipy) or 1,10-phenanthroline (Phen), which can participate in the enhancement of luminescence of 4*f* ions if the metallic framework is retained.

EXPERIMENTAL

All procedures related to the synthesis of new complexes were carried out in air using dimethylformamide (DMF, high-purity grade), acetonitrile (≥99.5%), and ethanol (reagent grade). The following reagents were used for the synthesis of new compounds: $Cd(NO_3)_2 \cdot 4H_2O$ (99+%, Acros Organics), $Eu(NO_3)_3 \cdot 6H_2O$ (99.99%, Lankhit), $Tb(NO_3)_3 \cdot 6H_2O$ (99.99%, Lankhit), KOH (analytical grade), 3,5-di-*tert*-butylbenzoic acid (HBzo, 99%, Alfa Aesar), pentafluorobenzoic acid ($HO_2CC_6F_5$, 99%, P&M Invest), terephthalic acid (H_2Bdc, 99%, Acros Organics), Bipy (99%, Alfa Aesar), and Phen (99%, Alfa Aesar).

The IR spectra of the compounds were recorded on a Spectrum 65 FTIR spectrophotometer (Perkin Elmer) using the attenuated total reflection (ATR) method in a frequency range of 4000–400 cm^{-1}. Luminescence spectra were measured using a Fluorolog FL3-22 spectrofluorimeter (Horiba-Jobin-Yvon) equipped with a xenon lamp (power 450 W) and a PMT R-928 standard photomultiplier. A xenon flash lamp was used for measuring the kinetic dependences of the luminescence decay. All spectra were corrected taking into account the apparatus function of the instrument. Elemental analysis was conducted on a EuroEA 3000 CHNS analyzer (EuroVector). X-ray diffraction analysis (XRD) was carried out on a Bruker D8 Advance diffractometer (CuK_α, $\lambda = 1.54060$ Å, Ni filter, LYNXEYE detector, reflection geometry).

Synthesis of $[EuCd_2(O_2CC_6F_5)_6(NO_3)(Bipy)_2]$ (I). A solution of $KO_2CC_6F_5$ (0.163 g, 0.649 mmol) in ethanol (10 mL), which was prepared by the reaction of KOH (0.036 g, 0.649 mmol) with $HO_2CC_6F_5$ (0.138 g, 0.649 mmol) was added to a solution of $Cd(NO_3)_2 \cdot 4H_2O$ (0.100 g, 0.324 mmol) in ethanol (10 mL). The reaction mixture was stirred at 70°C for 10 min and filtered from a formed white precipitate of KNO_3. A solution of $Eu(NO_3)_3 \cdot 6H_2O$ (0.049 g, 0.108 mmol) in MeCN (10 mL) and a weighed sample of Bipy (0.051 g, 0.324 mmol) were added to the resulting filtrate, and the obtained mixture was stirred at 70°C for 10 min. The resulting colorless solution was kept at room temperature. Colorless crystals formed in 6 days suitable for X-ray structure analysis were separated from the mother liquor by decantation, washed with cold acetonitrile ($T \approx 5$°C), and dried in air. The yield of compound **I** was 0.128 g (58.8% based on $Eu(NO_3)_2 \cdot 6H_2O$).

For $C_{62}H_{16}N_5O_{15}F_{30}Cd_2Eu$

Anal. calcd., %	C, 36.88	H, 0.80	N, 3.47
Found, %	C, 37.12	H, 0.92	N, 3.52

IR (ATR; ν, cm^{-1}): 3188 s, 1653 m, 1593 w, 1519 w, 1488 w, 1477 w, 1442 w, 1397 w, 1367 w, 1318 m, 1286 m, 1181 s, 1161 m, 1121 s, 1101 w, 1062 s, 1043 s, 1018 m, 989 w, 932 w, 828 w, 763 w, 734 w, 698 w, 649 w, 627 w, 582 m, 479 m, 458 s, 442 s, 425 s.

Synthesis of $[TbCd_2(Bzo)_6(NO_3)(Phen)_2] \cdot 4MeCN$ (II). A solution of KBzo (0.176 g, 0.649 mmol) in ethanol (10 mL), which was prepared by the reaction of KOH (0.036 g, 0.649 mmol) with HBzo (0.151 g, 0.649 mmol), was added to a solution of $Cd(NO_3)_2 \cdot 4H_2O$ (0.100 g, 0.324 mmol) in ethanol (10 mL). The reaction mixture was stirred at 70°C for 10 min and filtered from a formed white precipitate of KNO_3. A solution of $Tb(NO_3)_3 \cdot 6H_2O$ (0.050 g, 0.108 mmol) in MeCN (10 mL) and a weighed sample of Phen (0.058 g, 0.324 mmol) were added to the obtained filtrate, and the mixture was stirred at 70°C for 10 min. The resulting colorless solution was kept at room temperature. Colorless crystals formed in 3 days suitable for X-ray structure analysis were separated from the mother liquor by decantation, washed with cold acetonitrile ($T \approx 5$°C), and dried in air. The yield of compound **II** was 0.185 g (78.1% based on $Tb(NO_3)_3 \cdot 6H_2O$).

For $C_{122}H_{154}N_9O_{15}Cd_2Tb$

Anal. calcd., %	C, 61.77	H, 6.49	N, 5.32
Found, %	C, 62.02	H, 6.32	N, 5.42

IR (ATR; ν, cm^{-1}): 1622 w, 1607 w, 1591 w, 1556 s, 1541 s, 1531 s, 1496 w, 1477 m, 1461 m, 1429 s, 1375 vs, 1361 vs, 1344 m, 1284 m, 1246 m, 1223 w, 1201 m, 1160 w, 1147 m, 1125 w, 1103 m, 1089 m, 1049 m, 994 m, 969 w, 950 w, 922 w, 896 m, 890 m, 864 m, 855 m, 847 s, 822 s, 792 s, 780 w, 748 m, 740 m, 726 s, 707 s, 641 m, 603 w, 578 m, 547 m, 534 m, 510 w, 489 m, 473 m, 420 m, 414 m, 406 s.

Synthesis of $[EuCd_2(Bzo)_6(NO_3)(Phen)_2] \cdot 4MeCN$ (III) was carried out according to the procedure similar to that for complex **II** using $Eu(NO_3)_3 \cdot 6H_2O$ (0.049 g, 0.108 mmol) instead of $Tb(NO_3)_3 \cdot 6H_2O$. The yield of compound **III** was 0.200 g (84.5% based on $Eu(NO_3)_3 \cdot 6H_2O$).

For $C_{122}H_{154}N_9O_{15}Cd_2Eu$

Anal. calcd., %	C, 62.01	H, 6.52	N, 5.33
Found, %	C, 62.38	H, 6.40	N, 5.41

IR (ATR; ν, cm^{-1}): 1629 w, 1608 w, 1595 w, 1557 m, 1539 s, 1531 s, 1515 w, 1499 w, 1477 w, 1458 m, 1429 m, 1391 s, 1361 s, 1342 s, 1288 m, 1247 w, 1223 w, 1203 m, 1159 w, 1150 m, 1125 w, 1101 w, 1086 w, 1048 m, 993 m, 969 w, 951 w, 925 w, 895 w, 863 w, 845 w, 821 w, 791 m, 747 w, 730 s, 702 s, 639 w, 578 m, 532 w, 488 w, 469 w, 434 w, 426 m, 419 w, 403 s.

Synthesis of $[Cd_3(Bdc)_3(Bipy)_2]_{3n} \cdot 4n$MeCN $\cdot$ nH_2O (IV). A solution of H_2Bdc (0.0027 g, 0.0163 mmol) in DMF (2 mL) was added to a solution of complex **I** (0.0109 g, 0.0046 mmol) in DMF (3 mL). The obtained reaction mixture was placed in an autoclave with a Teflon bush, gradually heated to 110°C with a heating rate of 5°C/h, kept at 110°C for 24 h, and gradually cooled down to 40°C with a cooling rate of 1°C/h. The formed colorless crystals were filtered off and dried in air. The yield of compound **IV** was 0.004 g (42.1% based on complex **I**).

For $C_{140}H_{98}N_{16}O_{37}Cd_9$

Anal. calcd., %	C, 46.57	H, 2.72	N, 6.21
Found, %	C, 47.18	H, 2.17	N, 5.89

IR (ν, cm^{-1}): 2819 w, 2546 w, 1676 m, 1648 m, 1597 s, 1576 m, 1520 m, 1487 s, 1441 m, 1424 m, 1376 s, 1366 m, 1282 s, 1174 w, 1156 w, 1105 s, 1063 w, 1019 m, 1017 m, 991 s, 928 m, 880 m, 824 m, 782 m, 700 m, 674 w, 661 m, 647 m, 565 m, 529 m, 506 m, 470 m, 451 m, 418 w.

Synthesis of $[Cd_2(Bdc)_2(Phen)_2]_n \cdot 2n$DMF (V). A solution of H_2Bdc (0.0031 g, 0.0185 mmol) in DMF (2 mL) was added to a solution of complex **II** (0.0126 g, 0.0053 mmol) in DMF (3 mL). The resulting reaction mixture was placed in an autoclave with a Teflon bush, gradually heated to 100°C with a heating rate of 4°C/h, kept at 100°C for 48 h, and gradually cooled down to 30°C with a cooling rate of 1°C/h. The formed colorless crystals were filtered off and dried in air. The yield of compound **V** was 0.003 g (58.7% based on complex **II**).

For $C_{46}H_{38}N_6O_{10}Cd_2$

Anal. calcd., %	C, 51.91	H, 3.58	N, 7.91
Found, %	C, 51.82	H, 3.39	N, 7.83

IR (ν, cm^{-1}): 1662 s, 1592 s, 1550 s, 1517 m, 1504 m, 1433 m, 1381 s, 1282 m, 1144 m, 1089 m, 1019 m, 1018 w, 986 s, 929 m, 864 m, 832 s, 745 s, 724 s, 695 s, 661 m, 639 m, 521 m, 437 w, 428 m, 418 s.

The X-ray structure analyses of single crystals of compounds **I**, **II**, and **IV** were carried out on a Bruker Apex II diffractometer equipped with a CCD detector (MoK_α, λ = 0.71073 Å, graphite monochromator) [28]. A semiempirical absorption correction was applied for all compounds using the SADABS program [29]. The structures were solved by direct methods and refined by full-matrix least squares in the anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms at the carbon atoms of the organic ligands were generated geometrically and refined in the riding model. The calculations were performed using the SHELX program package [30]. The geometry of the metal polyhedra was determined using the SHAPE 2.1 program [31–33].

The XRD data for complex **V** were obtained on the X-ray beam of the Belok station of the Kurchatov Center of Synchrotron Radiation at the Kurchatov

Table 1. Crystallographic parameters and structure refinement details for compounds **I**, **II**, **IV**, and **V**

Parameter	Value			
	I	**II**	**IV**	**V**
FW	2017.56	2370.25	3607.94	1059.62
T, K	150(2)	150(2)	120(2)	100(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2/n$	$P2_1/n$	$P2_1/c$
a, Å	11.9120(12)	15.9414(11)	14.9097(18)	11.905(2)
b, Å	15.7124(16)	13.5408(10)	31.816(4)	19.283(4)
c, Å	18.3125(19)	27.531(2)	15.8052(19)	18.462(4)
α, deg	84.631(2)	90	90	90
β, deg	79.311(2)	94.9220(10)	111.911(2)	98.60(3)
γ, deg	77.053(2)	90	90	90
V, Å^3	3277.5(6)	5920.9(7)	6955.9(15)	4190.6(15)
Z	2	2	2	4
ρ_{calc}, g/cm^3	2.044	1.330	1.723	1.680
μ, mm^{-1}	1.746	1.011	1.432	1.460
θ_{max}, deg	28.26	28.68	25.999	30.98
T_{min}/T_{max}	0.622/0.903	0.580/0.746	0.780/0.945	0.779/0.892
Number of measured reflections	34568	41028	44079	69367
Number of independent reflections	16145	15104	13686	9551
Number of reflections with $I > 2\sigma(I)$	13035	9975	6933	8372
R_{int}	0.0318	0.0735	0.152	0.0484
Number of refined parameters	1036	692	916	578
GOOF	1.078	1.000	1.003	1.063
R_1 ($I > 2\sigma(I)$)	0.0338	0.0629	0.0534	0.0339
wR_2 ($I > 2\sigma(I)$)	0.0808	0.1610	0.0878	0.0945

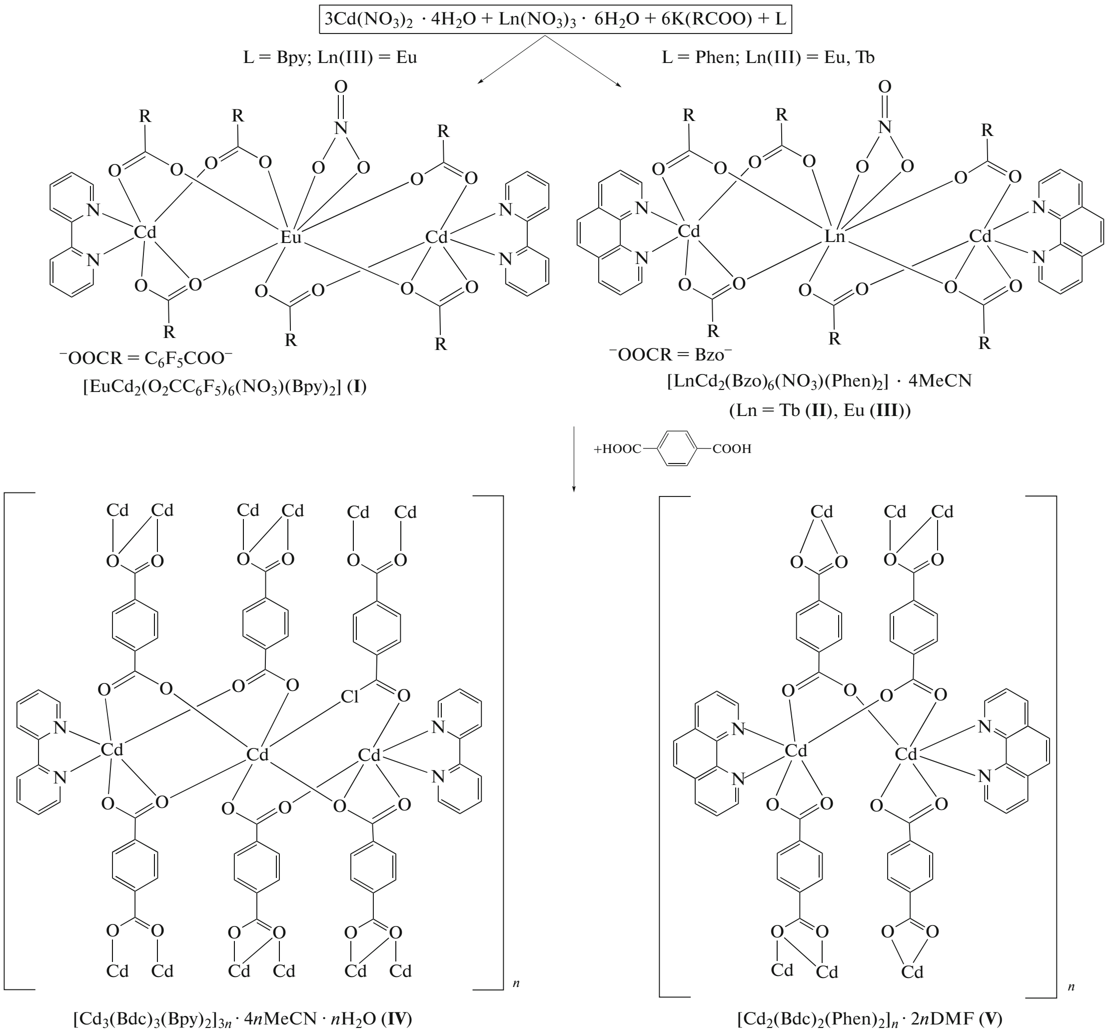
Institute Russian Research Center in the φ scan mode using a Rayonix SX165 CCD detector at 100 K (λ = 0.79373 Å). The primary indexing, refinement of the parameters, integration of reflections, and absorption correction application were performed using the XDS program package [34, 35]. The structure was solved by direct methods and refined by full-matrix least squares for F^2 with the anisotropic approximation parameters for all non-hydrogen atoms. Hydrogen atoms were placed in the calculated positions and refined in the riding model with $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl groups and $1.2U_{eq}(C)$ for other hydrogen atoms. The calculations were performed using the SHELXTL program package [30].

The crystallographic parameters and structure refinement details for compounds **I**, **II**, **IV**, and **V** are presented in Table 1. The structural data for compounds **I**, **II**, **IV**, and **V** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1938125, 1938124, 1938126, and 1937492, respectively); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The reactions of potassium salts of $HO_2CC_6F_5$ or HBzo and cadmium(II) and lanthanide(III) (Eu, Tb) nitrates in the presence of the chelating N-donor ligand L, as well as Bipy or Phen ($KO_2CR : Cd : Ln : L = 6 : 3 : 1 : 3$), afforded molecular trinuclear heterometallic compounds $[EuCd_2(O_2CC_6F_5)_6(NO_3)(Bipy)_2]$ (**I**) and $[LnCd_2(Bzo)_6(NO_3)(Phen)_2] \cdot 4MeCN$ (Ln = Tb (**II**), Eu (**III**)) (Fig. 1, Scheme 1).

The conditions chosen for the synthesis of the MOF based on the initial compounds **I** and **II** and terephthalic acid (variation of the reaction temperature *T* from 50 to 130°C, cooling and heating rates from 1 to 20°C/h, and storage time at the maximum *T* from 12 to 80 h) did not allow us to isolate heterometallic products: the precursor complexes underwent destruction and the layered coordination polymers of Cd(II), $[Cd_3(Bdc)_3(Bipy)_2]_{3n} \cdot 4nMeCN \cdot nH_2O$ (**IV**) and $[Cd_2(Bdc)_2(Phen)_2]_n \cdot 2nDMF$ (**V**), crystallized (Scheme 1).



Scheme 1.

Compounds **I–III** are characterized by similar structures of the trinuclear molecule, where the central Ln atom is bound to each terminal Cd(II) atom by one chelate bridging and two bridging carboxylate anions $^{-}O_2CR$ (Eu–O 2.353(3)–2.433(2), Cd–O 2.212(3)–2.529(2), Cd(1)···Eu(1) 3.903(5), Cd(2)···Eu(1) 3.933(6), and Cd···Cd 7.546(8) Å for **I**; Tb–O 2.284–2.482, Cd–O 2.208(5)–2.543(4), Cd(1)···Tb(1) 3.7805, Cd(2)···Tb(1) 3.7805, and Cd···Cd 7.550(8) Å for **II**). The cadmium atoms in compounds **I–III** build up their environments to a distorted octahedron due to the coordination of two N atoms of the chelating ligand (Cd–N 2.268(3)–2.305(4) Å in **I**; Cd–N 2.354(5)–2.376(5) Å in **II**). The central rare-earth metal builds up its environment to a distorted tetragonal antiprism due to binding two O atoms of the nitrate anion (Eu–O 2.469(3)–2.478(2) Å in **I**; Tb–O 2.482 Å in **II**). The XRD data confirmed that complexes **II** and **III** were isostructural.

A significant distortion of the linear geometry of the metallic framework is observed in the molecule of compound **I**, whereas the Cd–Ln–Cd metallic framework of complex **II** is nearly linear (the CdLnCd angle is 148.65(7)° and 173.87(10)° in compounds **I** and **II**, respectively). The planes of the coordinated aromatic ligands in one molecular fragment of compounds **I** and **II** are turned relative to each other at an angle of 55.67° and 41.00°, respectively.

The orientation of the aromatic moieties in the N-donor ligands of the adjacent molecules of the complexes in the crystals of compounds **I** and **II** is close to parallel, which possibly indicates in favor of π-stacking interactions (Fig. 2) (the distance between the planes of the N-donor ligand and the dihedral angle between them are 3.56–3.70 Å and 0.23°–2.34° for compound **I** and 3.30 Å and 0.0° for compound **II**).

Only one example for the trinuclear Cd–Ln carboxylate resembling compounds **I–III** and combining anions of benzoic acid and Phen was described [24]. A similar structure is stable for the 3*d*-metal com-

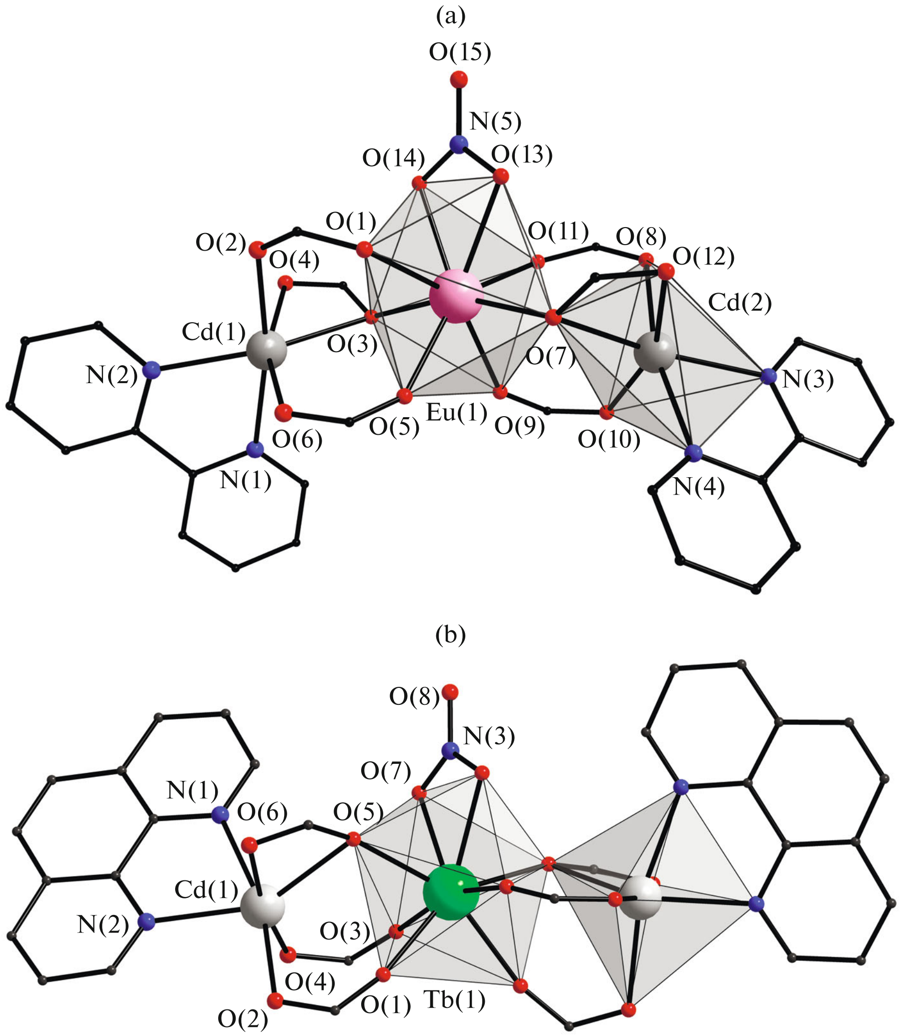


Fig. 1. Structures of complexes (a) **I** and (b) **II** (pentafluorophenyl and di-*tert*-butylphenyl substituents, hydrogen atoms, and solvate molecules are omitted).

pounds, and many molecular complexes with the {M_2Ln} metallic framework were synthesized for a wide range of metals: M = Zn(II) [15, 36, 37], Co(II) [38, 39], Ni(II) [38], and Cu(II) [38].

The crystal structure of compound **IV** is a metal-organic framework based on the hexabonded linear trinuclear node {$Cd_3(Bdc)_3Bipy_2$} (Fig. 3). The structure of compound **IV** contains two crystallographically independent trinuclear fragments, one of which (Cd(1)–Cd(2)–Cd(3)) is in the general position and the second fragment $(Cd(4)–Cd(5)Cd(4)_{1-x, 1-y, 1-z})$ occupies the partial position on the inversion center. In both fragments, the central Cd atom is bound to the terminal Cd atoms by one chelate bridging and two bridging carboxylate groups of three terephthalate anions (Cd–O 2.164(6)–2.551(6) Å). The terminal Cd atoms build up their environments to distorted octahedra due to the coordination of the N-donor ligand molecule bound via the chelate mode (Cd–N 2.313(8)–2.357(7) Å). The metal atoms in the trinuclear fragments lie on one line (the Cd(1)Cd(2)Cd(3) and $Cd(4)Cd(5)Cd(4)_{1-x, 1-y, 1-z}$ angles are 172.28(3)° and 180.0°, respectively) with the Cd···Cd distances equal to 3.547(1)–3.656(1) Å, indicating the absence of metal–metal interactions.

Each trinuclear node {$Cd_3(Bdc)_3(Bipy)_2$} in compound **IV** is bound to six adjacent similar fragments by six terephthalate bridges, which results in the formation of a layered structure parallel to the crystallographic plane (1 0 –1) with the abundant topological motif of the hexagonal lattice ***hxl*** [40–43] (Fig. 4). A combination of the hexabonded coordination of the nodes with triangular rings makes the network dense and resistant toward distortions to a wavy shape. The terminal Bipy molecules simultaneously fill the triangular rings and shift from the polymer layer restricting the permeability of an individual layer and bringing the layers together. The thickness of the layer corre-

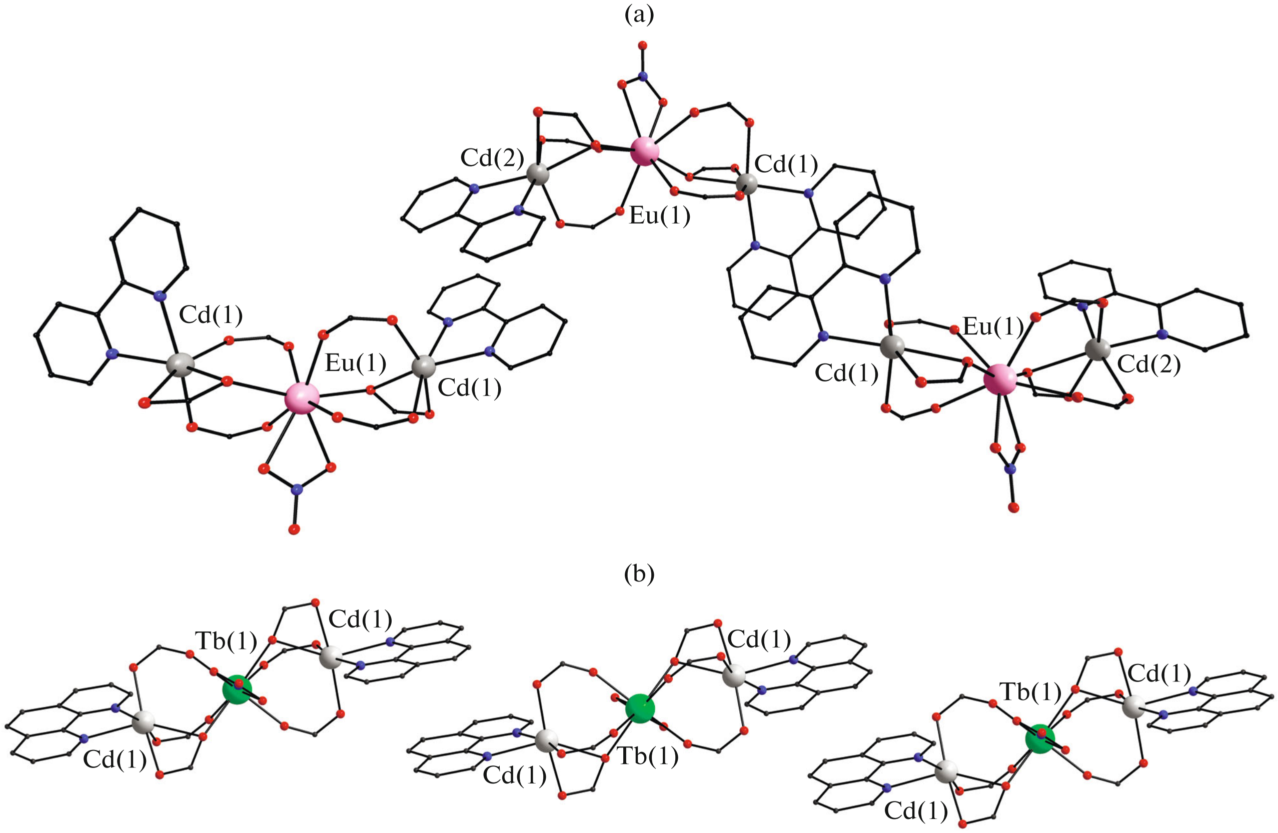


Fig. 2. Fragment of the crystal packing of compounds (a) **I** and (b) **II** (pentafluorophenyl and di-*tert*-butylphenyl substituents, hydrogen atoms, and solvate molecules are omitted).

sponds to the length of the $\{Cd_3(Bdc)_3(Bipy)_2\}$ fragment. Two solvate molecules of acetonitrile (one of which is disordered over two positions) and the solvate water molecule with a halved population are located between the polymer layers in the packing of the structure of compound **IV**.

Coordination polymers based on the hexabonded block $\{M_3(Bdc)_3(Bipy)_2\}$ and topology ***hxl*** were described only for Mn(II) [44, 45] and Ni(II) [46], and these MOF were synthesized using inorganic salts of the corresponding metals. The Cd coordination polymers with terephthalic acid and 2,2'-bipyridyl are characterized by the formation of polymers of various dimensionality on the basis of the mononuclear fragment $\{Cd(Bdc)(H_2O)(Bipy)\}$ [47–49] or $\{Cd(Bdc)(Bipy)\}$ [50], which were synthesized by the direct

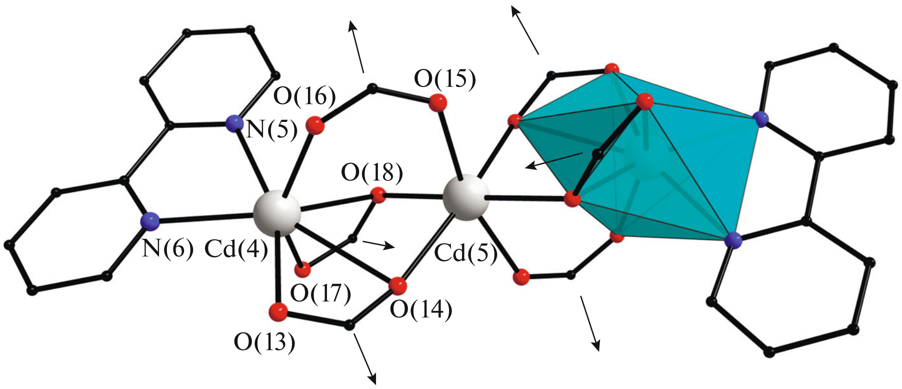


Fig. 3. Structure of the hexabonded fragment $\{Cd_3(Bdc)_3(Bipy)_2\}$ in compound **IV** (arrows show directions of polymerization during the bridging coordination of Bdc; hydrogen atoms, phenylene substituents, and solvate molecules are omitted).

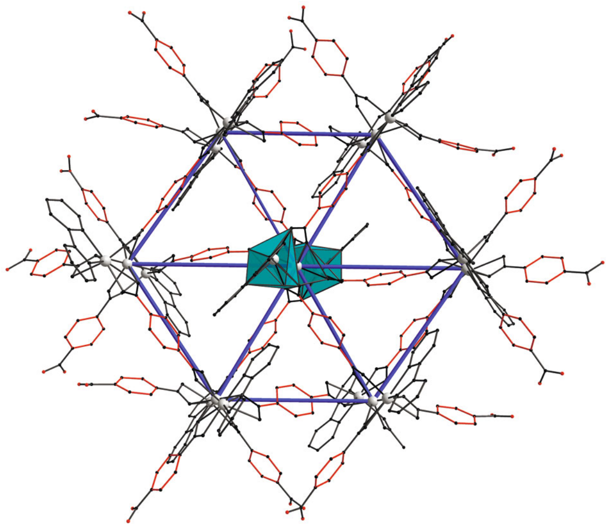


Fig. 4. Projection of the fragment of the polymer layer of compound **IV** along the plane (1 0 −1) (phenyl fragments Bdc^- are red-colored, cadmium atoms are gray, the network of topology ***hxl*** is shown by blue, and hydrogen atoms and solvate molecules are omitted for clarity).

reactions of the cadmium salts with Bipy and H_2Bdc. The coordination polymers based on the $\{Cd_3(Bdc)_3(L)_2\}$ fragment were synthesized for a series of monodentate, bridging, and chelating ligands: DMF [51, 52], bromide anion [53], and 2-methylbenzimidazole in combination with DMF [54], 4,4'-bipyridyl [55], 1-(1-methylnaphthyl)imidazole [56]), 2,2'-diimidazole [57], and *N*-methyl-2,2'-diimidazole [58].

The $\{Cd_3(Bipy)_2(CO_2)_6\}$ fragment has been observed previously in the framework coordination polymer $[Cd_3(Bipy)_2(Cpt)_2]_n \cdot 2nH_2O$ (Cpt^{3-} is (4-carboxylphenoxy)terephthalate anion) [59]; layered structures $[Cd_3(Bipy)_2(H_2O)_2(Tst)_2] \cdot 2H_2O$ (Tst^{3-} is 2,2',2"-(1,3,5-triazine-2,4,6-triyltrisulfanediyl)triacetate anion) [60], $[Cd_3(Bipy)_2(Me_3Btc)_2]$ (Me_3Btc^{3-} is 2,4,6-trimethylbenzene-1,3,5-tricarboxylate anion) [61] with the motif of the 3,6-coordinated network ***kgd***, and $[Cd_3(Bipy)_2(Hcpmb)_2]$ ($Hcpmb^{6-}$ is 1,2,3,4,5,6-hexakis(3-carboxylatophenoxymethyl)benzene anion) with the topology of the 4-coordinated network ***sql*** [62]; and chains $[Cd_3(Bipy)_2(HSdb)(Sdb)]$ (Sdb^{2-} is 4,4'-sulfonyldibenzoate anion) and $[Cd_3(Bipy)_2(Cpp)_2]$ (Cpp^{3-} is 3-(2-carboxylatophenoxy)phthalate anion) [63]. Of isocrosslinked structures with the ***hxl*** topology and $\{M_3(Bipy)_2(CO_2)_6\}$ fragment, only $[Mn_3(Bipy)_2(2\text{-}NH_2Bdc)_3]$ [64] and $[Zn_3(Bipy)_2(Pdsda)_3]$ (Pdsda is 2,2'-(1,4-phenylenedisulfanediyl)diacetate anion) [65] were observed, whereas the $\{Cd_3(L)_2(CO_2)_6\}$ fragments (L is water, dimethylamine, DMF, and diethylformamide) were found in a series of isocrosslinked layers with the following anions: 2-aminoterephthalate [66], biphenyl-4,4'-dicarboxylate [67], 4,4'-(2,3,6,7-tetramethoxyanthracene-9,10-diyl)benzoate [68], and 4,4'-diazine-1,2-diyldibenzoate [69]. Thus, compound **IV** can be named the first representative of the isocrosslinked series with the ***hxl*** topology and nodal fragment $\{Cd_3(Bipy)_2(CO_2)_6\}$.

An analog of compound **V** was described [70], but the refinement of the unit cell parameters revealed the doubling of parameter *b* (9.668(2) → 19.283(4) Å)

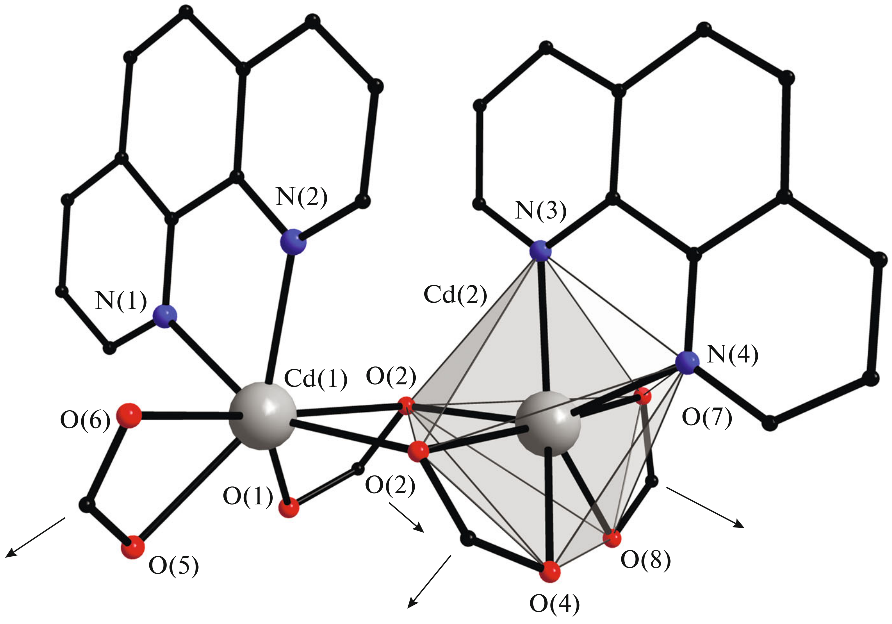


Fig. 5. Structure of the tetrabonded molecular fragment $\{Cd_2(Bdc)_2(Phen)_2\}$ in compound **V** (arrows show directions of polymerization during the bridging coordination of Bdc; hydrogen atoms, phenylene substituents, and solvate molecules are omitted).

accompanied by an increase in the unit cell volume over that published earlier (2134.0(9) → 4190.6(15) $Å^3$), which is induced by the disordering of molecules of the crystallization solvent (DMF) and leads the structure to the space group $P2_1/c$.

Complex **V** is based on the binuclear fragment $\{Cd_2Bdc_2Phen_2\}$ (Fig. 5) bound by four anions of terephthalic acid into a layer (Fig. 6). Each Cd atom coordinates five O atoms of three terephthalate anions and two N atoms of the Phen molecule. In the dimeric $\{Cd_2Bdc_2Phen_2\}$ fragment, two Phen molecules are close to each other and involved into π–π interactions to form the wavy profile of the coordination layers in the crystal packing of compound **V**.

The wavy shape of the layers makes impossible their absolutely dense packing and, hence, channels (radius from 1.17 to 1.82 Å) filled with DMF molecules are observed between the layers along the crystallographic axis *a* in the crystal packing of polymer **V** [71].

The motif of binding of the binuclear fragments by the bridging anions of terephthalic acid in the coordination layers obeys the topology ***sql*** (Fig. 6), which is the first in abundance among the layered coordination polymers with the 4-coordinated tetragonal network [41–43, 71]. On the whole, the series of isocrosslinked compounds with the nodal binuclear fragment $\{Cd_2((O_2C)_2R)_2Phen_2\}$ and ligands of various lengths (from the anion of succinic acid to that of 1,2-ethylenebis(4-benzoic acid)) acting as nearly direct bridges includes 11 examples [72] (Table 2), which were found using the ToposPro topological collections (https://topcryst.com/). The following features of this series of earlier undescribed compounds are of interest. Two compounds of the series (FIPGUH and JAYYIS) have the same ligand composition as compound **V**. Nevertheless, JAYYIS is a geometric isomer of compounds **V** and FIPGUH: the Phen ligands in the dimeric fragment are remote from each other at a maximum distance and fill rectangular windows of adjacent layers due to which the channels accessible for migration are absent between them. Interestingly, for a similar configuration of the Phen ligands of the dimeric fragment in [Cd(Pba)(Phen)] (MATJEY, MATJEY01), the longer size of the ligand provides the channels accessible for migration but in the cross direction toward the layers.

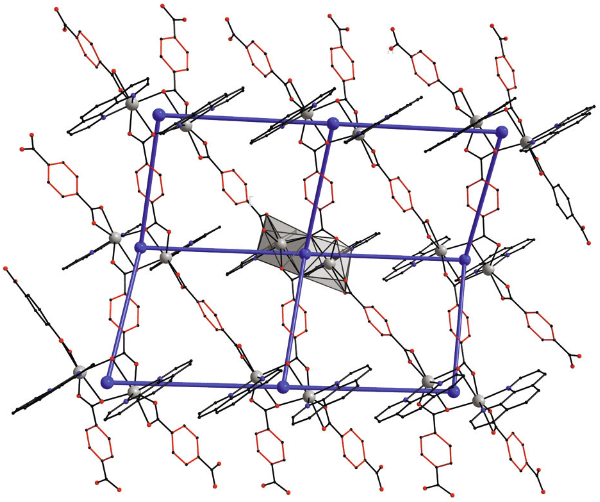


Fig. 6. Projection of the fragment of the polymer layer of compound **V** along the plane *ac* (phenyl fragments Bdc^- are red-colored, cadmium atoms are gray, the network of topology ***hxl*** is shown by blue, and hydrogen atoms and solvate molecules are omitted for clarity).

The photoluminescence spectra of cadmium–europium complexes **I** and **III** detected at room temperature (Fig. 7) are characteristic of the radiation of the Eu^{3+} ion during the transition from the $^5D_0$ level to

Table 2. Isocrosslinked compounds of the ***sql*** topology with the nodal binuclear $\{Cd_2((O_2C)_2R)_2Phen_2\}$ fragment

Compound	Refcode in CSD	Literature
Cd(Adp)(Phen) · $3H_2O$	QETCIC	73
Cd(Bdc)(Phen) · $0.5H_2O$	JAYYIS	74
Cd(Bdc)(Phen) · DMF	FIPGUH	70
Cd(Cmf)(Phen) · $C_2H_4(OH)_2$	KADHEE	75
Cd(Fmr)(Phen)	JEFTOE	76
Cd(Ndc)(Phen)	WEWLOB	77
Cd(Ndc)(Phen) · $0.5H_2O$	WUHZAC	78
Cd(Pba)(Phen)	MATJEY	79
Cd(Pba)(Phen) · $2H_2O$	MATJEY01	80
Cd(Suc)(Phen)	DIFFAA	81
$[Cd_2(Bpea)(Bdc)(Phen)_2][Cd(Bdc)(Phen)] \cdot 2H_2O$	WAFKUK	82

H_2Adp is adipic acid, H_2Cmf is (1*R*,3*S*)-(+)-camphoric acid, H_2Fmr is fumaric acid, H_2Ndc is naphthalene-2,6-dicarboxylic acid, H_2Pba is 3,3'-(1,4-phenylene)bis(acrylic acid), H_2Bpea is 1,2-ethylenebis(4-benzoic acid), and H_2Suc is succinic acid.

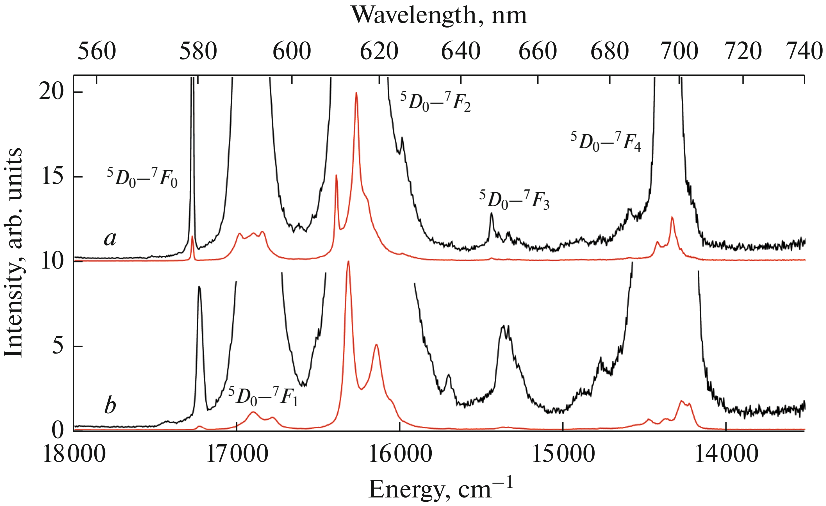


Fig. 7. Photoluminescence spectra of complexes (a) **I** and (b) **III** (λ_{exc} = 280 nm, T = 300 K).

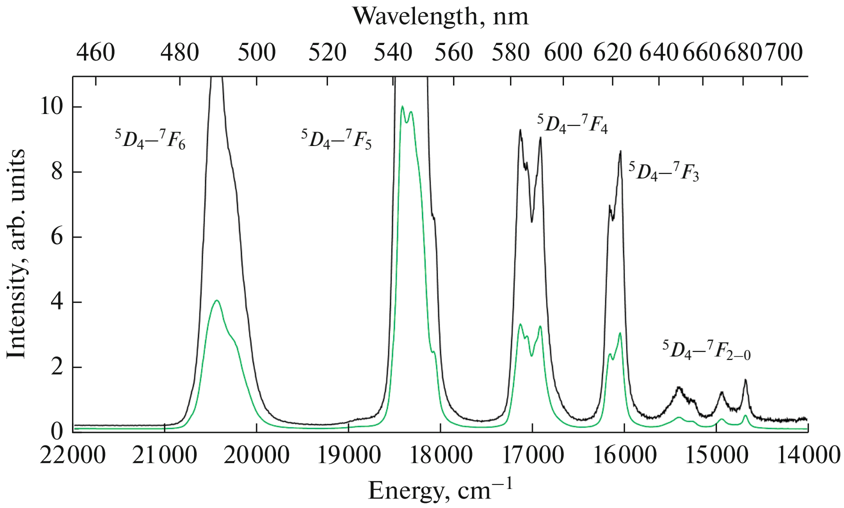


Fig. 8. Photoluminescence spectrum of complex **II** (λ_{exc} = 280 nm, T = 300 K).

the ^7F_J (J = 0–4) levels. The single symmetric line of the singlet transition $^5D_0$–$^7F_0$ and the monoexponential behavior of the luminescence decay curves indicate that compounds **I** and **III** contain luminescing metal centers of only one type. The rate of the radiative transition of the magnetic dipole $^5D_0$–$^7F_1$ is nearly independent of the coordination environment of the europium(III) ion. On the contrary, the most intense transition $^5D_0$–$^7F_2$ is very sensitive to distortions of the geometry of the coordination polyhedron of europium(III). In complexes **I** and **III**, the ratios of integral intensities of the $^5D_0$–$^7F_2$ transition to the magnetic dipolar transition $^5D_0$–$^7F_1$ equal to 3.4 and 7.6, respectively, indicate a slight deviation of the symmetry of the Eu^{3+} metal center from the inversion center, which is consistent with the X-ray structure data [83].

Emission lines that can be ascribed to the $^5D_0$–^7F_J transitions (J = 0–6) of the terbium(III) ion are detected in the luminescence spectra of a sample of compound **II** at room temperature (Fig. 8). The $^5D_0$–$^7F_{2-0}$ transitions demonstrate a very low intensity, whereas the $^5D_0$–$^7F_5$ transition is the most intense one, being 52% of the total integral intensity.

The excitation spectra of samples of complexes **I**–**III** obtained when recording the luminescence of the lanthanide ions exhibit broad bands corresponding to the excitation of the organic ligands and narrow bands attributed to the f–f transitions of the lanthanide ions (Fig. 9).

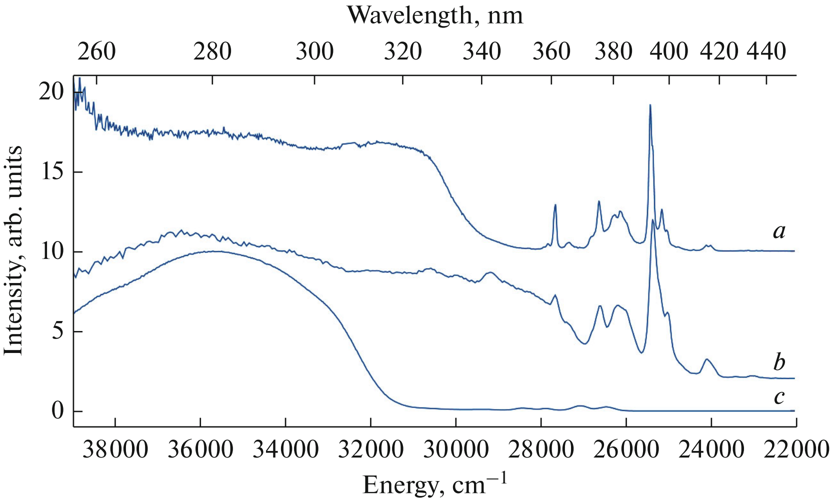


Fig. 9. Excitation spectra of complexes (a) **I**, (b) **III**, and (c) **II** (λ_{emis} = 615, 615, and 545 nm, respectively; T = 300 K).

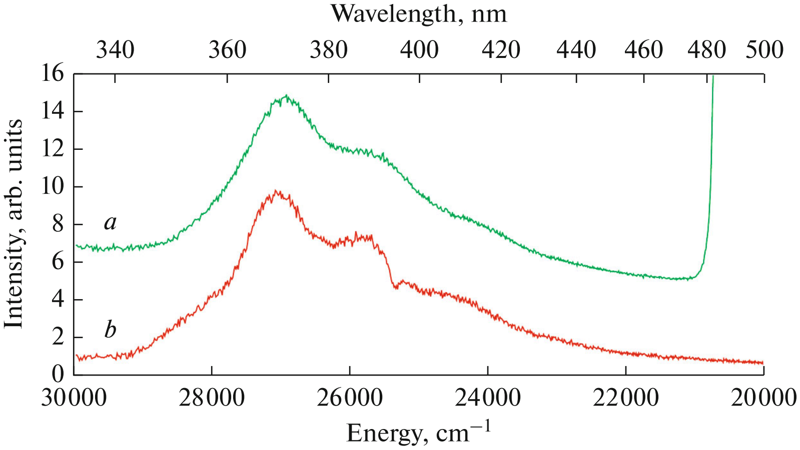


Fig. 10. Photoluminescence spectra of complexes (a) **II** and (b) **III** (λ_{exc} = 280 nm, T = 300 K). The LLCT transitions of the *d* block are shown on the spectra.

The broad-band excitation of complex **I** is extended to 330 nm and has two maxima at 280 and 315 nm related to the *n*, π–π*, and S_0–S_1 transitions of the 2,2'-bipyridyl ligands, respectively. The pentafluorobenzoic ligand can also participate in absorption and energy transfer processes. The intense *f*–*f* transitions of europium(III) indicate the inefficient ligand–metal transfer caused by the high position of the triplet level. The difference in energies between the T_1 state of the Bipy ligand [84] and the $^5D_0$ level of the Eu^{3+} ion is about 5690 cm^{-1}, whereas the optimum energy gap should lie in a range of 2000–2500 cm^{-1} according to the empirical rules [85, 86].

The direct excitation of the europium(III) ion in complex **III** is more efficient than sensitization by organic ligands. On the contrary, terbium(III)-containing complex **II** demonstrates a pronounced antenna effect. The broad-band excitation of complex **II** is possible to 310 nm with a maximum at 280 nm corresponding to the S_1 level of the Bzo anion. The excitation spectrum of compound **III** additionally exhibits a broad band with a maximum at 350 nm corresponding to the S_1 state of Phen. It is most likely that the excitation of the terbium(III) ion through the carboxylic acid anion Bzo is much more efficient than that through Phen because of the backward energy transfer to the latter.

The luminescence spectra of complexes **II** and **III** contain weak broad-band transitions caused by the ligand-to-ligand charge transfer (LLCT) in the *d* block (Fig. 10) [24]. The energy level of the LLCT state is localized between the S_1 and T_1 levels of the

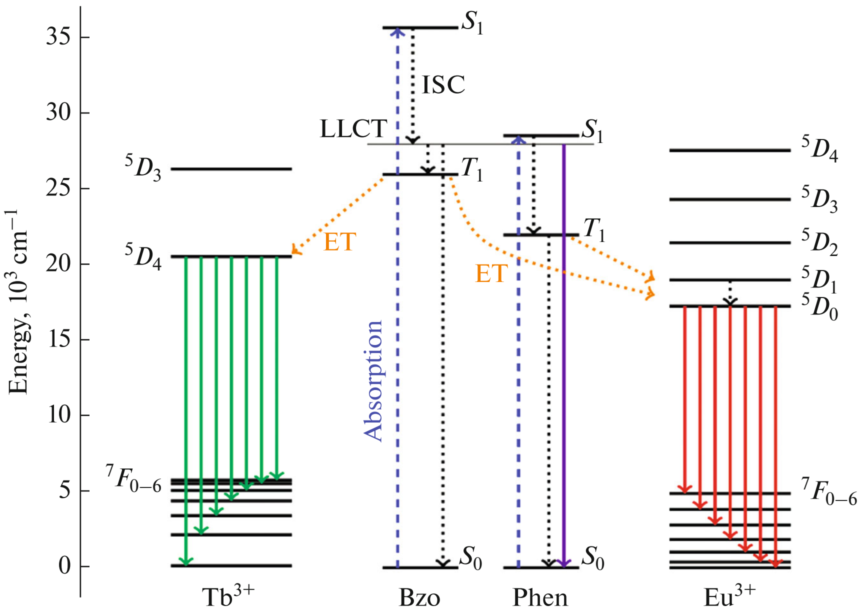


Fig. 11. Simplified diagram of the energy transfer in complexes **II** and **III**; ISC is the intrasystem transition, ET is the energy transfer from the ligand to the lanthanide ion; and LLCT is the state with the ligand-to-ligand charge transfer.

Bzo ligand, which favors a more efficient intrasystem transfer of the radiation energy (Fig. 11).

The very long luminescence lifetime τ_{obs} of the excited states of the lanthanide ions at $T = 300$ K in all complexes **I**–**III** is caused by the absence of high-frequency oscillating bonds in the internal coordination spheres of the lanthanide ions ($\tau_{obs} = 2.15 \pm 0.05$ (**I**), 1.63 ± 0.03 (**II**), and 1.41 ± 0.03 ms (**III**)). In spite of the inefficient energy transfer from the organic ligands to the europium(III) ion in complexes **I** and **III**, all compounds demonstrate bright metal-centered luminescence.

Thus, the heterometallic molecular Cd(II)–Ln(III) complexes of pentafluorobenzoic and 3,5-di-*tert*-butylbenzoic acids, $[EuCd_2(O_2CC_6F_5)_6(NO_3)(Bpy)_2]$ (**I**) and $[LnCd_2(Bzo)_6(NO_3)(Phen)_2] \cdot 4MeCN$ (Ln(III) = Tb (**II**), Eu (**III**)), were synthesized. It was shown that the metallic framework in compounds **I** and **II** underwent destruction in the reactions with terephthalic acid and the homometallic complexes $[Cd_3(Bdc)_3(Bipy)_2]_{3n} \cdot 4nMeCN \cdot nH_2O$ (**IV**) and $[Cd_2(Bdc)_2(Phen)_2]_n \cdot 2nDMF$ (**V**) were isolated as the crystalline reaction products. It can be mentioned that the described Cd–Ln complexes are less stable than Co–Gd trimethyl acetate [16], where only the partial destruction of the $[Co_2Gd(Piv)_6(NO_3)(Py)]$ complex was observed. Complexes **IV** and **V** are coordination polymers with the layered structure in which the binuclear or trinuclear monomeric fragments are linked by the bridging anions of dicarboxylic acids. The studies of luminescence showed that all compounds demonstrated bright metal-centered luminescence with a long luminescence lifetime.

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X-ray structure analysis (for compounds **I** and **II**), X-ray diffraction analysis, IR spectroscopy, and elemental analysis of the synthesized compounds were carried out using the equipment of the Center for Collective Use of Physical Methods of Investigation at the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences) in the framework of the state task of the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences) in the area of basic research. The study of the structure of complex **IV** was supported by the Ministry of Science and Higher Education of the Russian Federation using the scientific equipment of the Center of Molecular Structure Investigation at the Nesmeyanov Institute of Organoelement Compounds (Russian Academy of Sciences). The data on the structure of compound **V** were obtained on the X-ray beam of the Belok station of the Kurchatov Center of Synchrotron Radiation at the Kurchatov Institute Russian Research Center.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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