ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2020, Vol. 46, No. 7, pp. 493–504. © Pleiades Publishing, Ltd., 2020.
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*Dedicated to I.L. Eremenko on the occasion of his 70th birthday*

# Influence of Substituents in the Aromatic Fragment of the Benzoate Anion on the Structures and Compositions of the Formed {Cd–Ln} Complexes

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Received December 10, 2019; revised February 11, 2020; accepted February 17, 2020

**Abstract**—The reactions of $Cd(NO_3)_2 \cdot 4H_2O$ and $Eu(NO_3)_3 \cdot 6H_2O$ with potassium salts of the benzoic acid derivatives and 2,2'-bipyridine (Bipy) in ethanol, under the same synthesis conditions, afford the homo- and heterometallic complexes: $[Eu_2Cd_2(BA)_8(NO_3)_2(Bipy)_2]$ (**I**, BA is benzoic acid anion), $[Ln_2Cd_2(4\text{-}TBA)_{10}(Bipy)_2]$ (Ln = Eu (**II**), Tb (**III**); 4-TBA is 4-(trifluoromethyl)benzoic acid anion), $[Cd(4\text{-}CBA)_2(H_2O)(Bipy)]$ (**IV**, 4-CBA is 4-cyanobenzoic acid anion), $[Cd(PFBA)_2(H_2O)(Bipy)]_n$ (**V**, PFBA is pentafluorobenzoic acid anion), and $[Cd_2(4\text{-}APFBA)_4(Bipy)_2] \cdot 4H_2O$ (**VI**, 4-ATFBA is 4-amino-2,3,5,6-tetrafluorobenzoic acid anion). The structures of new complexes **I**, **II**, **IV**, and **VI** are determined by X-ray structure analysis (CIF files CCDC nos. 1970348, 1970350, 1970347, and 1970351, respectively). The isostructural character of complexes **II** and **III** is confirmed by X-ray diffraction analysis. The structures and compositions of the series of isolated compounds **I**–**VI** are determined by the nature of substituents in the benzoate anion. The photoluminescence properties of compounds **II** and **III** are studied.

*Keywords:* cadmium, lanthanides, substituted benzoic acid, luminescence, X-ray structure analysis

**DOI:** 10.1134/S1070328420070076

## INTRODUCTION

The synthesis of heterometallic carboxylate complexes combining atoms of 3*d* metals or cadmium with atoms of rare-earth elements is related to solving a series of urgent scientific and practical problems. Heterometallic compounds of a specified composition, including the stoichiometric one, can be used as precursors for the production of various compositionally homogeneous disperse oxide materials [1].

The complexes with lanthanide atoms are studied as promising magnetic and luminescent materials [2, 3]. The polynuclear metallic frameworks formed in the composition of the molecular heterometallic compounds can be used as the beforehand prepared secondary blocks for metal-organic frameworks [4, 5]. The availability of a wide range of monocarboxylic acids makes it possible to prepare the heterometallic complexes, whose structures are determined by the nature of the anions, including the substituent at the carboxylate group, N-donor ligand, and the ion radii of the metal ions [6–8]. The extension of the range of the {Cd–Ln} complexes, the choice of the synthesis compositions, and an analysis of the structure, structure-determining factors, and physicochemical properties are inalienable tasks of inorganic chemistry. We used the synthesis procedures of the same type: the treatment of cadmium(II) and lanthanide(III) nitrates with potassium salt of benzoic acid derivatives and 2,2'-bipyridine (Bipy) in an ethanol solution. Only one parameter is varied in the presented system: the nature of substituents in the benzoate anion, which allows one to solve the problems indicated above and also to compare the reaction products and determine possible details of the synthesis of the target complexes.

**Table 1.** Weighed samples (g) of the reagents in the syntheses of complexes **I**–**VI** at the ratio Cd : Ln : $O_2CR$ : Bipy = 3 : 1 : 5 : 3

| Complex | $HO_2CR$ | $Cd(O_2CR)_2$ | | | $Ln(O_2CR)_3$ | | | Bipy |
|---|---|---|---|---|---|---|---|---|
| | | $Cd(NO_3)_2 \cdot 4H_2O$ | $HO_2CR$ | KOH | $Ln(NO_3)_2 \cdot xH_2O$ | $HO_2CR$ | KOH | |
| **I** | H(BA) | 0.01 | 0.063 | 0.036 | 0.049 | 0.040 | 0.018 | 0.051 |
| **II** | H(4-TBA) | 0.01 | 0.107 | 0.036 | 0.049 | 0.053 | 0.018 | 0.051 |
| **III** | H(4-TBA) | 0.01 | 0.107 | 0.036 | 0.050 | 0.036 | 0.018 | 0.051 |
| **IV** | H(4-CBA) | 0.01 | 0.076 | 0.036 | 0.049 | 0.038 | 0.018 | 0.051 |
| **V** | H(PFBA) | 0.01 | 0.109 | 0.036 | 0.049 | 0.055 | 0.018 | 0.051 |
| **VI** | H(4-ATFBA) | 0.01 | 0.123 | 0.036 | 0.049 | 0.062 | 0.018 | 0.051 |

In this study, we restricted our consideration by benzoic (H(BA)), 4-trifluoromethylbenzoic (H(4-TBA)), 4-cyanobenzoic (H(4-CBA)), 4-amino-2,3,5,6-tetrafluorobenzoic (H(4-ATFBA)), and pentafluorobenzoic (H(PFBA)) acids.

## EXPERIMENTAL

All procedures associated with the synthesis of new complexes were carried out in air using ethanol (reagent grade). The following reagents were used for the synthesis of new compounds: $Cd(NO_3)_2 \cdot 4H_2O$ (99+%, Acrosorganics), $Eu(NO_3)_3 \cdot 6H_2O$ (99.99%, Lankhit), $Tb(NO_3)_3 \cdot 6H_2O$ (99.99%, Lankhit), KOH (analytical grade), H(BA) (≥99.5%, ACS reagent), H(4-TBA) (98%, Acrosorganics), H(4-CBA) (99%, Acrosorganics), H(PFBA) (99%, P&MInvest), H(4-ATFBA) (98%, P&MInvest), and Bipy (99%, AlfaAesar).

The IR spectra of the compounds were recorded on a Spectrum 65 FTIR spectrophotometer (Perkin-Elmer) by the attenuated total internal reflection (ATR) mode in a frequency range of 4000–400 $cm^{-1}$. Luminescence spectra were measured on 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 measurements of the kinetic dependences of the luminescence decay. All spectra were corrected with allowance for the apparatus function of the instrument. Elemental analyses were carried out on a EuroEA 3000 CHNS analyzer (EuroVector). X-ray diffraction analysis (XRD) was conducted on a Bruker D8 Advance diffractometer ($CuK_\alpha$, $\lambda$ = 1.54060 Å, Ni filter, LYNXEYE detector, reflection geometry).

**Synthesis of $[Eu_2Cd_2(BA)_8(NO_3)_2(Bipy)_2]$ (I).** A solution of KBA (0.090 g, 0.649 mmol), which was prepared by the reaction of KOH (0.036 g, 0.649 mmol) and H(BA) (0.063 g, 0.649 mmol), in ethanol (10 mL) 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 15 min, and a white precipitate of $KNO_3$ was filtered off. The filtrate was added with a suspension obtained by the reaction of $Eu(NO_3)_3 \cdot 6H_2O$ (0.049 g, 0.108 mmol) and KBA (0.045 g, 0.325 mmol), which was prepared by the reaction of KOH (0.018 g, 0.325 mmol) and H(BA) (0.039 g, 0.325 mmol), in EtOH (10 mL). The reaction mixture was stirred at 70°C for 15 min, a white precipitate of $KNO_3$ was filtered off, a weighed sample of Bipy (0.051 g, 0.324 mmol) was added, and the mixture was stirred at 70°C until the white precipitate was dissolved. A colorless solution was kept at room temperature with slow evaporation. Colorless crystals suitable for X-ray structure analysis formed in 5 days were separated by decantation, washed with cold ethanol ($T \approx 5°C$), and dried in air. The yield of compound **I** was 0.078 g (27.4%) based on $Cd(NO_3)_2 \cdot 4H_2O$.

For $C_{80}H_{68}N_6O_{24}Cd_2Eu_2$

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 47.38 | H, 3.35 | N, 4.16 |
| Found, % | C, 46.88 | H, 3.33 | N, 4.30 |

IR (ATR), ν, $cm^{-1}$: 3389 m, 2973 w, 1594 m, 1545 m, 1491 s, 1475 m, 1439 s, 1392 s, 1317 m, 1291 s, 1176 s, 1156 m, 1071 s, 1040 s, 1019 m, 942 m, 879 m, 848 m, 814 m, 765 m, 716 s, 688 m, 676 m, 650 m, 628 w, 551 w, 427 m, 415 s.

**Synthesis of $[Eu_2Cd_2(4\text{-}TBA)_{10}(Bipy)_2]$ (II)** was carried out using the method similar to that for compound **I** using H(4-TBA) instead of H(BA) with the weighed samples indicated in Table 1. Colorless crystals suitable for X-ray structure analysis formed in 48 h were separated by decantation, washed with cold ethanol ($T \approx 5°C$), and dried in air. The yield of compound **II** was 0.235 g (61.3%) based on $Cd(NO_3)_2 \cdot 4H_2O$).

For $C_{100}H_{56}N_4O_{20}F_{30}Cd_2Eu_2$

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 43.92 | H, 2.05 | N, 2.05 |
| Found, % | C, 44.22 | H, 2.32 | N, 2.21 |

IR (ATR), ν, $cm^{-1}$: 2988 m, 1630 m, 1596 m, 1536 s, 1513 m, 1475 m, 1362 vs, 1316 vs, 1156 m, 1128 s, 1100 s, 1062 s, 1015 m, 868 s, 790 s, 783 s, 769 m, 757 m, 735 w, 710 s, 651 m, 629 w, 595 w, 539 w, 434 m, 419 m.

**Synthesis of $[Tb_2Cd_2(4\text{-}TBA)_{10}(Bipy)_2]$ (III)** was carried out by the method similar to that for compound **I** using H(4-TBA) instead of H(BA) and Tb nitrate as a source of lanthanide atoms with the weight samples indicated in Table 1. A white polycrystalline precipitate formed in 24 h was decanted, washed with cold ethanol ($T \approx 5°C$), and dried in air. The yield of compound **III** was 0.259 g (67.2%) based on $Cd(NO_3)_2 \cdot 4H_2O$.

For $C_{100}H_{56}N_4O_{20}F_{30}Cd_2Tb_2$

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 43.81 | H, 2.04 | N, 2.04 |
| Found, % | C, 44.10 | H, 2.17 | N, 2.05 |

IR (ATR), ν, $cm^{-1}$: 2991 w, 1633 s, 1592 m, 1535 s, 1517 m, 1474 s, 1359 s, 1316 vs, 1154 m, 1129 m, 1098 w, 1061 s, 1019 m, 864 m, 788 m, 785 m, 771 m, 757 m, 741 m, 711 s, 652 m, 627 m, 594 m, 541 m, 431 m, 422 m.

**Synthesis of $[Cd(4\text{-}CBA)_2(H_2O)(Bipy)]$ (IV)** was carried out by the method similar to that for compound **I** using H(4-CBA) instead of H(BA) with the weight samples indicated in Table 1. Colorless crystals suitable for X-ray structure analysis formed in 3 days were decanted, washed with cold ethanol ($T \approx 5°C$), and dried in air. The yield of compound **IV** was 0.062 g (37.8%) based on $Cd(NO_3)_2 \cdot 4H_2O$.

For $C_{26}H_{18}N_4O_5Cd$

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 53.89 | H, 3.13 | N, 9.67 |
| Found, % | C, 54.15 | H, 3.29 | N, 9.98 |

IR (ATR), ν, $cm^{-1}$: 3079 w, 2227 m, 1702 m, 1604 m, 1585 s, 1539 s, 1490 w, 1472 m, 1439 s, 1407 s, 1378 s, 1299 m, 1287 s, 1249 m, 1168 m, 1150 w, 1131 w, 1094 w, 1060 w, 1015 m, 976 w, 933 w, 862 s, 815 m, 768 s, 734 m, 693 m, 651 m, 628 w, 572 s, 542 s, 438 m, 421 w, 413 w.

**Synthesis of $[Cd(PFBA)_2(H_2O)(Bipy)]_n$ (V)** was carried out by the method similar to that for compound **I** using H(4-PFBA) instead of H(BA) with the weight samples indicated in Table 1. A colorless solution obtained in the reaction was placed in a round-bottom flask and kept at 5°C for 14 days. The formed colorless crystals suitable for X-ray structure analysis were decanted, washed with cold ethanol ($T \approx 5°C$), and dried in air. The yield of compound **V** was 0.112 g (57.3%) based on $Cd(NO_3)_2 \cdot 4H_2O$.

For $C_{24}H_{10}N_2O_5F_{10}Cd$

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 40.62 | H, 1.41 | N, 3.94 |
| Found, % | C, 41.19 | H, 1.39 | N, 3.83 |

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 $[Cd_2(4\text{-}APFBA)_4(Bipy)_2] \cdot 4H_2O$ (VI)** was carried out by the method similar to that for compound **I** using H(4-APFBA) instead of H(BA) with the weight samples indicated in Table 1. A colorless solution obtained in the reaction was kept at room temperature with slow evaporation for 9 days. The formed colorless crystals suitable for X-ray structure analysis were decanted, washed with cold ethanol ($T \approx 5°C$), and dried in air. The yield of compound **VI** was 0.076 g (37.6%) based on $Cd(NO_3)_2 \cdot 4H_2O$.

For $C_{48}H_{32}N_8O_{12}F_{16}Cd_2$

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 39.97 | H, 2.22 | N, 7.77 |
| Found, % | C, 39.68 | H, 2.09 | N, 7.61 |

IR (ATR), ν, $cm^{-1}$: 3411 m, 3188 w, 1662 m, 1567 s, 1526 m, 1487 s, 1441 m, 1374 s, 1248 w, 1175 m, 1126 m, 1099 w, 1061 m, 1017 w, 945 s, 806 m, 759 s, 746 s, 735 s, 650 m, 626 m, 575 w, 499 m, 446 m, 426 w, 414 m.

**X-ray structure analyses** of the single crystals of compounds **I**, **II**, **IV**, and **VI** were carried out on a Bruker Apex II diffractometer equipped with a CCD detector ($MoK_\alpha$, $\lambda = 0.71073$ Å, graphite monochromator) [9]. A semiempirical absorption correction was applied for all compounds using the SADABS program [10]. 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 by the riding model. The calculations were performed using the SHELX program package [11]. The geometry of the metal polyhedra was determined using the SHAPE 2.1 program [12, 13]. The crystallographic parameters and structure refinement details for compounds **I**, **II**, **IV**, and **VI** are presented in Table 2.

The coordinates of atoms and other parameters for compounds **I**, **II**, **IV**, and **VI** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1970348, 1970350, 1970347, and 1970351, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

**Table 2.** Crystallographic parameters and structure refinement details for compounds **I**, **II**, **IV**, and **VI**

| Parameter | I | II | IV | VI |
|---|---|---|---|---|
| $FW$ | 2026.16 | 2732.20 | 578.84 | 1441.61 |
| $T$, K | 120(2) | 120(2) | 150(2) | 296(2) |
| Crystal system | Triclinic | Triclinic | Monoclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P2/c$ | $P2_1/n$ |
| $a$, Å | 11.3382(5) | 15.6579(13) | 21.9699(10) | 15.6831(6) |
| $b$, Å | 13.8155(6) | 15.6751(13) | 8.6161(5) | 12.2957(4) |
| $c$, Å | 14.0949(6) | 21.493(2) | 12.2475(6) | 15.8547(6) |
| α, deg | 71.8130(10) | 76.123(2) | 90 | 90 |
| β, deg | 70.7460(10) | 77.701(2) | 92.4040(10) | 91.8000(10) |
| γ, deg | 81.1380(10) | 84.104(2) | 90 | 90 |
| $V$, Å$^3$ | 1977.0(2) | 4996.3(7) | 2316.3(2) | 3055.8(2) |
| $Z$ | 1 | 2 | 4 | 2 |
| $\rho_{calc}$, g cm$^{-3}$ | 1.702 | 1.816 | 1.660 | 1.567 |
| μ, mm$^{-1}$ | 2.176 | 1.786 | 0.990 | 0.805 |
| $\theta_{max}$, deg | 28.997 | 25.242 | 26.396 | 30.548 |
| $T_{min}/T_{max}$ | 0.658/0.780 | 0.673/0.842 | 0.673/0.745 | 0.645/0.746 |
| Number of measured reflections | 31800 | 76639 | 20739 | 37281 |
| Number of independent reflections | 10529 | 24056 | 4729 | 9332 |
| $R_{int}$ | 0.0377 | 0.0756 | 0.0418 | 0.0487 |
| Number of reflections with $I > 2\sigma(I)$ | 8849 | 17940 | 4348 | 7159 |
| Number of refined parameters | 999 | 9974 | 9875 | 9708 |
| GOOF | 1.024 | 1.042 | 1.076 | 1.034 |
| $R_1$ ($I > 2\sigma(I)$) | 0.0305 | 0.0695 | 0.0232 | 0.0632 |
| $wR_2$ ($I > 2\sigma(I)$) | 0.0753 | 0.1995 | 0.0544 | 0.1561 |
| $\Delta\rho_{min}/\Delta\rho_{max}$, e Å$^{-3}$ | –1.348/2.194 | –1.972/4.070 | –0.393/0.408 | –1.198/0.977 |

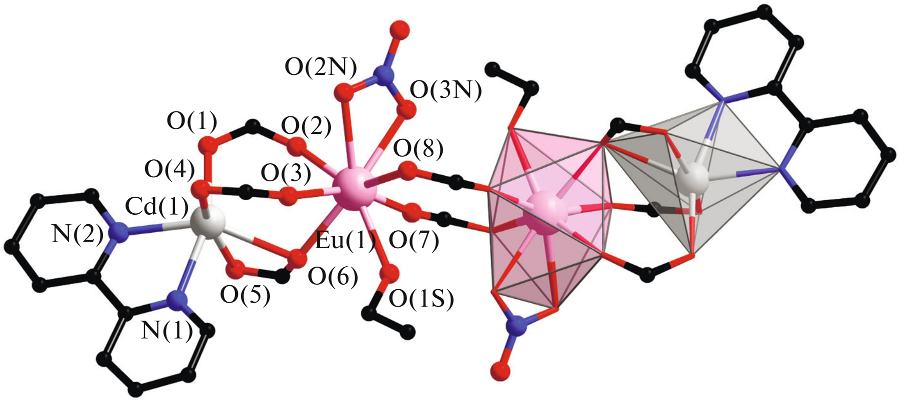
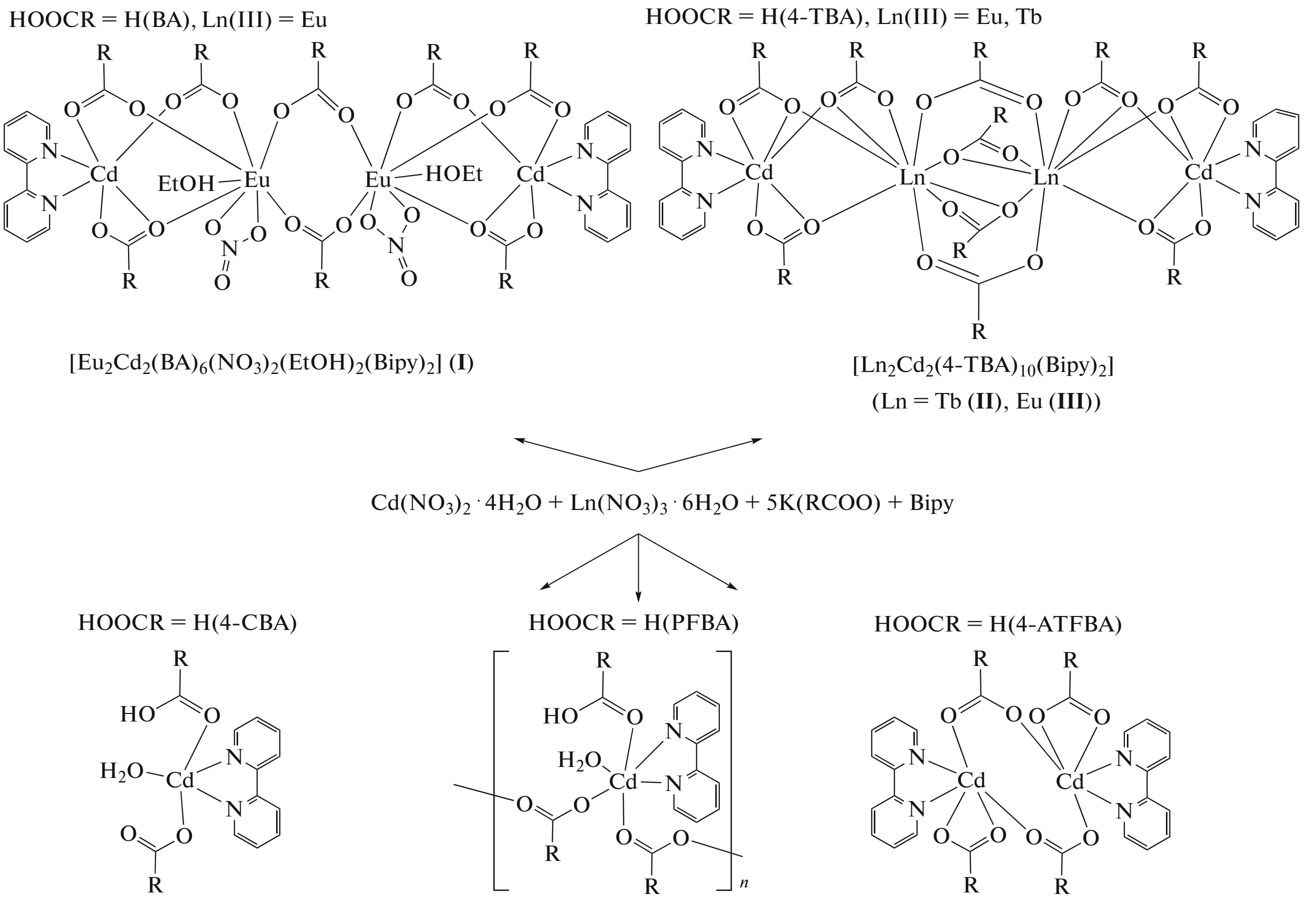


**Fig. 1.** Structure of complex **I** (substituents at the carboxylate group, hydrogen atoms, and solvate molecules are omitted).

## RESULTS AND DISCUSSION

Heterometallic complexes **I**–**VI** crystallize in the reactions of $Cd(NO_3)_2 \cdot 4H_2O$ and $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Eu, Tb) with potassium salts of acid H(BA) or its substituted derivatives (H(4-TBA), H(4-CBA), H(PFBA), or H(4-ATFBA) acids) in the presence of Bipy (ratio 1 : 1 : 5 : 1) in ethanol depending on the acid nature (Scheme 1).



$[Eu_2Cd_2(BA)_6(NO_3)_2(EtOH)_2(Bipy)_2]$ (**I**)

$[Ln_2Cd_2(4\text{-}TBA)_{10}(Bipy)_2]$ (Ln = Tb (**II**), Eu (**III**))

$[Cd(4\text{-}CBA)_2(Bipy)(H_2O)]$ (**IV**)

$[Cd(PFBA)_2(Bipy)(H_2O)]_n$ (**V**)

$[Cd_2(4\text{-}ATFBA)_4(Bipy)_2] \cdot 4H_2O$ (**VI**)

**Scheme 1.**

Compounds **I**–**III** with the BA and 4-TBA anions are tetranuclear complexes with the linear metallic framework {Cd...Ln...Ln...Cd} with different binding modes of the metal atoms between each other.

In the centrosymmetric molecule of complex **I**, two central Eu(1) atoms are bound to each other by two bridging carboxylate anions (Eu–O 2.242(2)–2.346(2), Eu(1)...Eu(1*A*) 4.865(4) Å). Each europium atom in the molecule is bound to the Cd(1) atom (angle Cd(1)Eu(1)Eu(1*A*) 156°) due to the coordination of one chelate bridging and two bridging carboxylate anions closing the chelate cycle on the Cd(1) atom (Eu–O 2.353(3)–2.433(2), Cd–O 2.208(3)–2.343(3), Cd(1)...Eu(1) 3.805(3) Å) (Fig. 1). Each cadmium atom builds up its octahedron environment ($CdO_4N_2$) by two N atoms of the chelate Bipy molecule (Cd–N 2.310(2), 2.331(3) Å). The Eu atom 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-bonded $NO_3$ anion (Eu–O 2.458(2)–2.540(3) Å). The initial inorganic salt is the source of $NO_3^-$.

In complex **II**, all atoms in the molecule are structurally nonequivalent. The geometry of the coordination environment of both central Eu atoms ($EuO_9$) corresponds to a one-capped square antiprism. The Eu(1) and Eu(2) atoms are linked by two bridging and two chelate bridging carboxylate anions (Eu–O 2.343(6)–2.584(5), Eu(1)...Eu(2) 3.964(7) Å) (Fig. 2a). In the Ln–Cd pairs, the metal atoms are bonded by two chelate bridging and one bridging or three chelate bridging carboxylate anions (Eu–O 2.317(7)–2.620(6), Cd–O 2.228(6)–2.722(6), Cd...Eu 3.672(7), 3.749(7) Å). The Cd atoms build up their environment ($CdO_{4/5}N_2$) to a distorted trigonal prism (Cd(1)–N 2.290(7), 2.362(9) Å) and a pentag-

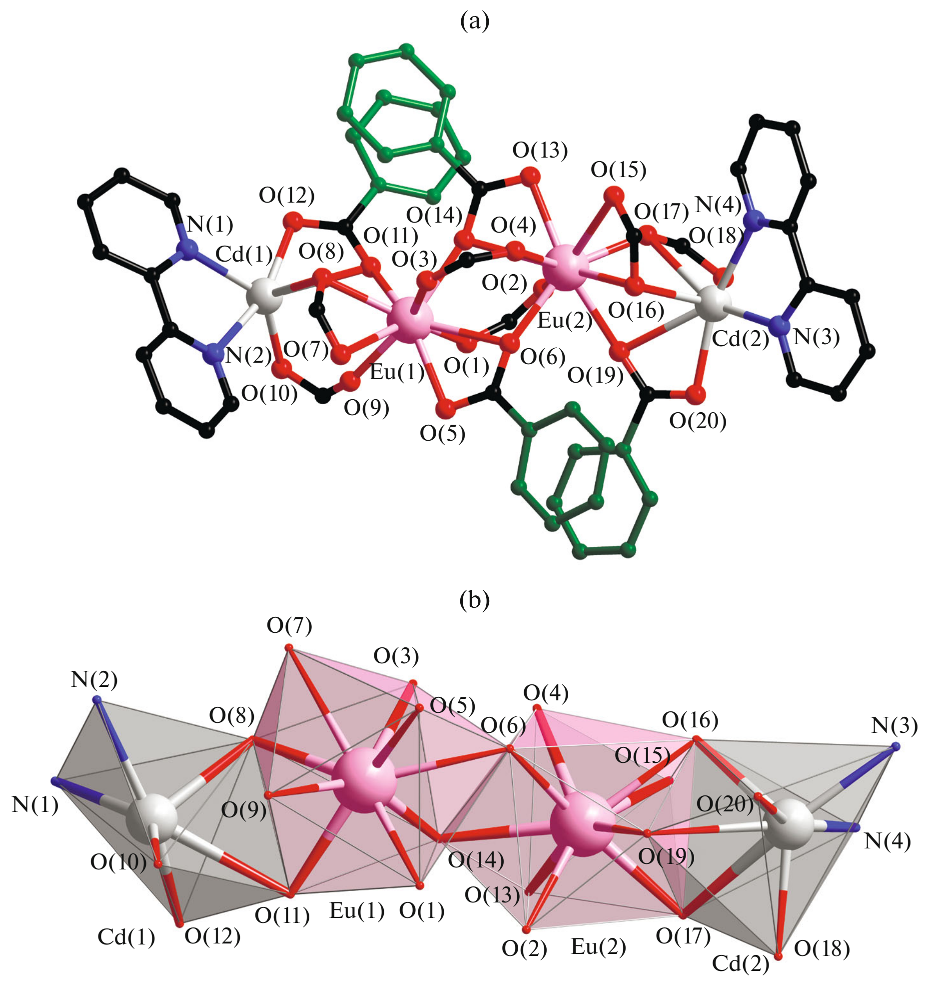


**Fig. 2.** (a) Structure of the molecule of complex **II** (substituents at the carboxylate group involved in the formation of intramolecular $\pi-\pi^*$ interactions are shown, and hydrogen atoms and solvate molecules are omitted) and (b) coordination polyhedra of the Cd and Eu ions in complex **II**.

onal bipyramid (Cd(2)–N 2.286(7), 2.387(9) Å) by the coordination of two N atoms of the Bipy molecules (Fig. 2b).

Complex **III** is isostructural to compound **II**, which was confirmed by the XRD data (Fig. 3). The crystal packing of the molecules also changes depending on the nature of carboxylic acid anions. The crystal of complex **I** exhibits supramolecular $\pi-\pi$ interactions due to the close to parallel orientation of the pyridyl fragments of the ligands of the adjacent molecules (the shortest distance between the planes of the cycles of the ligand ($d_{\text{pll}}-d_{\text{pl}}$), the distance between the centroids of the $C_5N$ fragments ($d_{\text{centr}}-d_{\text{centr}}$), and the dihedral angle between them ($\varphi$) are 3.30 Å, 3.72 Å, and 0.05°, respectively). Bipyridine also interacts with the BA aromatic cycle of the adjacent molecule of the complex (the distance between the centroids of the aromatic $C_5N$ and $C_6$ fragments and the dihedral angle

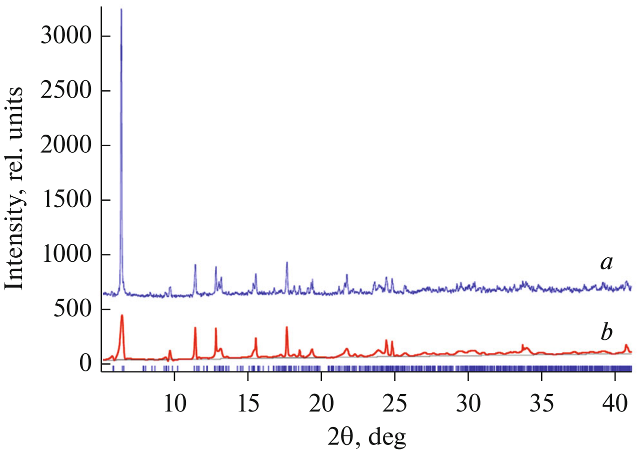


**Fig. 3.** Comparison of the (a) XRD pattern for complex **III** with (b) calculated (according to the X-ray structure analysis data) diffraction pattern for complex **II**.

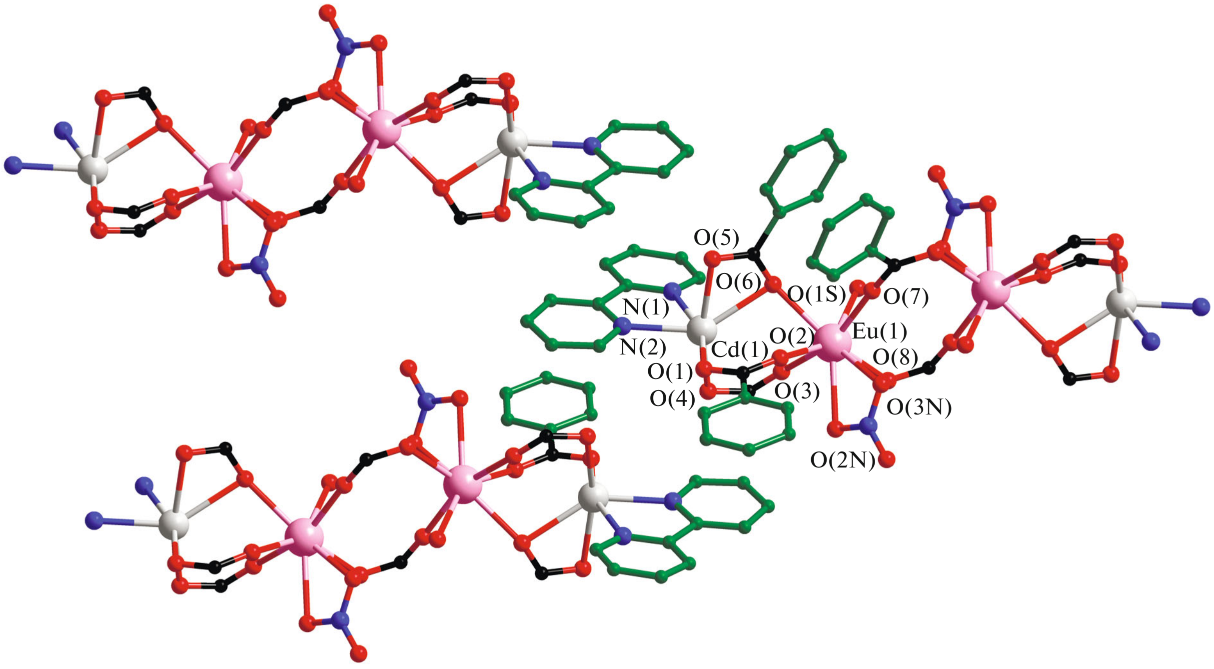


**Fig. 4.** Fragment of the crystal packing of complex **I**. The substituents at the carboxylate group and Bipy molecules involved in π–π* interactions are shown (hydrogen atoms and solvate molecules are omitted).

between then are 3.643 Å and 6.8°, respectively). Additional π–π interactions are observed between the BA anions of two adjacent molecules of compound **I** (the distance between the planes, the distance between the centroids of the $C_6$ fragments, and the dihedral angle between them are 3.39, 3.40 Å; 3.843, 3.830 Å; and 0.0°, 1.6°, respectively). The intramolecular hydrogen bond (O(1S)...O(3N) 2.745 Å) is formed between the OH group of the coordinated EtOH molecule and the O atom of the $NO_3$ anion (Fig. 4).

In the case of complex **II**, on the contrary, the molecules are isolated in the crystal and intramolecular π–π* interactions are observed only between two pairs of the 4-TBA anions ($d_{pl}$–$d_{pl}$ = 3.53, $d_{centr}$–$d_{centr}$ = 3.72 Å, φ = 4.61° and $d_{pl}$–$d_{pl}$ = 3.44, $d_{centr}$–$d_{centr}$ = 3.83 Å, φ = 6.81°, Fig. 2a).

The main distinction in the structures of the complexes is the character of the Eu atoms. For example, complex **I** contains two bridging carboxylate groups, whereas complex **II** contains two bridging and two chelate bridging carboxylate groups. The coordination polyhedra of the Eu atoms in complex **I** have one common vertex, whereas they are conjugated along the edge in complex **II**. This distinction is caused by the compositions of the complexes. In complex **I**, the compact $NO_3$ anions do not provide a sufficient shielding of the metal atom due to which its coordination environment is supplemented by the ethanol molecule, while the coordination environment of the Eu atom in complex **II** consists of nine O atoms of the carboxylate groups only. The average Ln–O bond elongates on going from the coordination number 8 to 9 (2.386 Å for **I**, 2.442 Å for **II**), which also characterizes the fact of increasing steric effects in the nearest environment of the metal ions.

Only several examples of the $\{Cd_2Ln_2\}$ complexes with anions of aromatic monocarboxylic acids are reported: they demonstrate the structures close to those of complexes **I** and **II** ($[Cd_2Ln_2(p\text{-Tol})_{10}(Phen)_2]$ (Ln = Nb, Pr, and Sm), $[Cd_2Ho_2(p\text{-ClBnz})_{10}(Phen)_2]$ [14] (Phen is 1,10-phenanthroline, H(*p*-Tol) is 4-methylbenzoic acid, and H(*p*-ClBnz) is 4-chlorobenzoic acid)). The heterometallic {CdEu} complex of benzoic acid and Phen ($[Cd_2Eu(BA)_7(Phen)_2]$), which, unlike complex **I**, forms the trinuclear metallic framework, was described [15]. The family of the {CdLn} complexes was supplemented by several examples of the binuclear, trinuclear, and pentanuclear compounds [14–18]. In the case of the Ln–3*d* complexes, the tetranuclear compounds of similar structures are presented more widely: Zn [15, 19, 20], Co [21–24], Ni [25, 26], and Mn [27].

In the case of using H(4-CBA), H(PFBA), or H(4-ATFBA) salts under the conditions similar to complexes **I**–**III**, no formation of heterometallic complexes was observed. The only isolated crystalline reaction products were homometallic coordination cadmium compounds **IV**–**VI**. However, the principal possibility for the formation of the heterometallic complexes in the solution should not be excluded because of their probable instability or high reactivity under the experimental conditions.

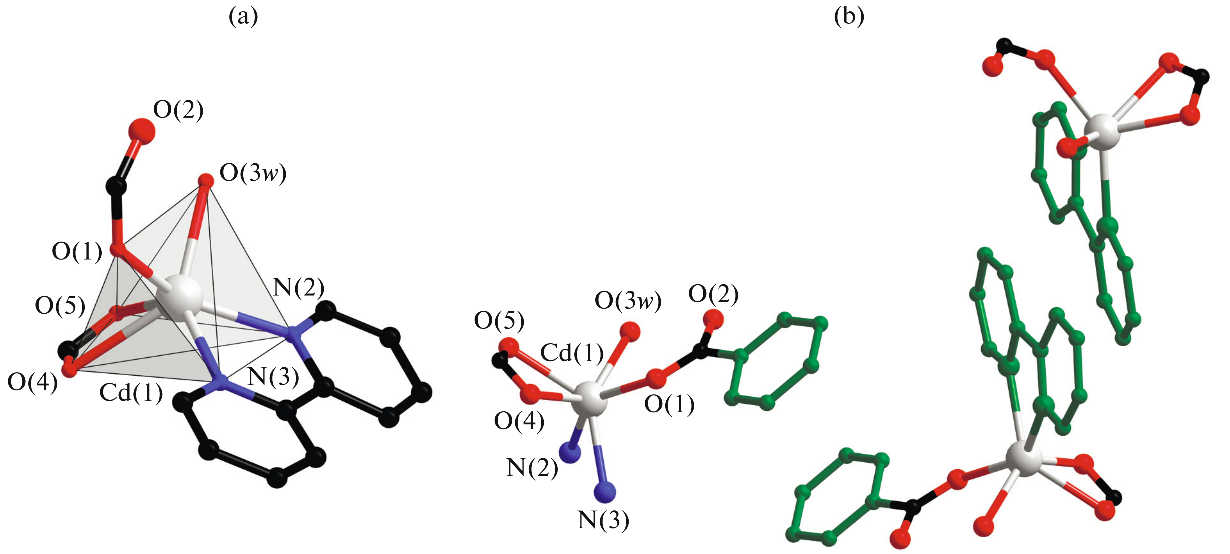


**Fig. 5.** (a) Structure of complex **IV** (substituents at the carboxylate group, hydrogen atoms, and solvate molecules are omitted) and (b) fragment of the crystal packing of complex **IV** (substituents at the carboxylate group and Bipy molecules involved in the formation of intramolecular π–π* interactions are shown, and hydrogen atoms and solvate molecules are omitted).

In the structure of mononuclear complex **IV** (Fig. 5a), the cadmium atom builds up its environment ($CdO_4N_2$) to a trigonal prism by the coordination of four O atoms of two 4-CBA anions bound via the chelate and monodentate modes (Cd–O 2.223(2)–2.459(2) Å) and of the water molecule (Cd–O 2.307(2) Å) and two N atoms of the Bipy molecule (Cd–N 2.303(2)–2.311(3) Å).

The packing of complex **IV** (Fig. 5b) exhibits the close to parallel orientation of the aromatic fragments of the N-donor ligands ($d_{centr}$–$d_{centr}$ = 3.57 Å and φ = 4.74°) and the aromatic fragments of the 4-CBA anions of the adjacent molecules of the complex ($d_{pl}$–$d_{pl}$ = 3.45 Å, $d_{centr}$–$d_{centr}$ = 3.67 Å, φ = 0.0°).

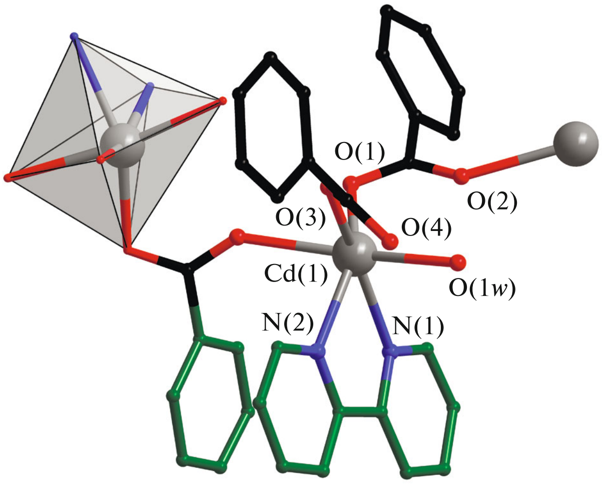


**Fig. 6.** Fragment of the polymer chain of complex **V** (substituents at the carboxylate group and Bipy molecules involved in the formation of intramolecular π–π* interactions are shown, and hydrogen and fluorine atoms and solvate molecules are omitted).

Complex **V** represents the known polymer [28] in which the structure of the elementary unit $\{Cd(H_2O)(O_2CR)_2(Bipy)\}$ resembles that of molecular complex **IV**, but the chelate carboxylate group accomplishes the bridging function to form a chain of the Cd atoms (Fig. 6). It should be mentioned that the polymeric structure is unusual, since the compounds $[Cd(H_2O)(O_2CR)_2(Bipy)]$ with monocarboxylic aromatic acid anions are presented by the mononuclear and binuclear molecular complexes only [29–34].

The authors [28] believe that the polymeric structure is stabilized due to π-stacking interactions, intermolecular hydrogen bonds, and weak C–H...F–C interactions. However, we have recently shown that the reaction of compound **V** carried out in a MeCN–EtOH medium using the ratio Cd : Ln = 3 : 1 makes it possible to avoid the formation of homometallic polymer **V** and to isolate the {$Cd_2Ln$} complex of the composition $[Cd_2Eu(4\text{-}CBA)_6(NO_3)(Bipy)_2]$ [17].

The use of potassium salt H(4-ATFBA), under the conditions similar to those of the preparation of complexes **I**–**V**, resulted in the formation of homometallic complex **VI**. In its structure, the Cd atoms form the centrosymmetric binuclear metallic framework due to the bridging coordination of two 4-ATFBA anions (Cd–O 2.252(2)–2.276(3) Å; Fig. 7). Each cadmium atom builds up its environment ($CdO_4N_2$) to a distorted octahedron by the coordination of two N atoms of Bipy (Cd–N 2.318(4), 2.367(4) Å) and two atoms of the carboxylate group bound via the chelate mode (Cd–O 2.321(3), 2.441(3) Å).

The crystal of complex **VI** contains intermolecular hydrogen bonds between the amino group and the oxygen atom of two 4-ATFBA anions of the adjacent molecules of the complex (N(3)...O(1) 2.893 Å). The π–π interactions ($d_{\mathrm{pl}}$–$d_{\mathrm{pl}}$ = 3.44, $d_{\mathrm{centr}}$–$d_{\mathrm{centr}}$ = 3.70 Å, φ = 0.29°) are observed between the aromatic Bipy fragments of the adjacent molecules of the complex to form a supramolecular chain along the *b* axis (Fig. 8).

The photophysical properties of complexes **II** and **III** containing lanthanide ions were studied for the solid samples at room temperature. Upon UV radiation, the samples demonstrate the metal-centered luminescence characteristic of europium(III) and terbium(III) ions, respectively. The narrow luminescence bands observed in the emission spectrum of complex **II** (Fig. 9a) with the maximum intensity at the wavelengths 580, 593, 617, 650, and 697 nm correspond to the $^5D_0 \to {}^7F_J$ transitions of the europium(III) complex, where $J$ = 0–4, respectively. A series of weak bands in a wavelength range of 520–560 nm is attributed to the radiation transitions from the higher excited state $^5D_1$ of the Eu$^{3+}$ ion. The $^5D_0 \to {}^7F_0$ transition in the luminescence spectrum is presented by the single symmetric band, indicating the same coordination environment of both europium(III) ions in the molecule. This is also confirmed by the one-exponential character of the luminescence decay of Eu$^{3+}$ in the studied complex ($\tau_{\mathrm{obs}}$ = 1.8 ms).

The ratio of integral intensities of the $^5D_0 \to {}^7F_2$ and $^5D_0 \to {}^7F_1$ transitions of the europium(III) ion often serves as an asymmetry measure of the environment of Eu$^{3+}$, since the $^5D_0 \to {}^7F_2$ transition is strictly forbidden in the presence of the inversion center. Therefore, the stronger the distortion of the local field symmetry of the europium(III) ion, the more intense the $^5D_0 \to {}^7F_1$ transition. The ratio $I(^5D_0 \to {}^7F_2)/I(^5D_0 \to {}^7F_1)$ for complex **II** is equal to 5.54, which is consistent with the absence of the inversion center of the coordination environment of Eu$^{3+}$.

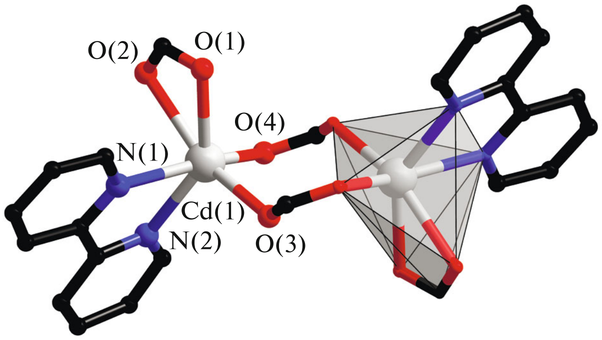


**Fig. 7.** Structure of complex **VI** (4-amino-2,3,5,6-tetrafluorophenyl substituents, hydrogen atoms, and solvate molecules are omitted).

The emission spectrum of complex **III** (Fig. 9b) contains narrow bands with intensity maxima at the wavelengths 490, 546, 585, and 622 nm corresponding to the transitions $^5D_4 \to {}^7F_J$, where $J$ = 6–3, respectively. The bands of the $^5D_4 \to {}^7F_J$ transitions ($J$ = 2–0) with maxima at 649, 668, and 680 nm, respectively, are much less intense.

The optical luminescence excitation spectra of complexes **II** and **III** are presented in Fig. 10. The broad bands assigned to the π → π* transitions of the ligands indicate the sensitization of luminescence of the lanthanide ions of the aromatic component of the complex (hereinafter, *d* block). The narrow lines are

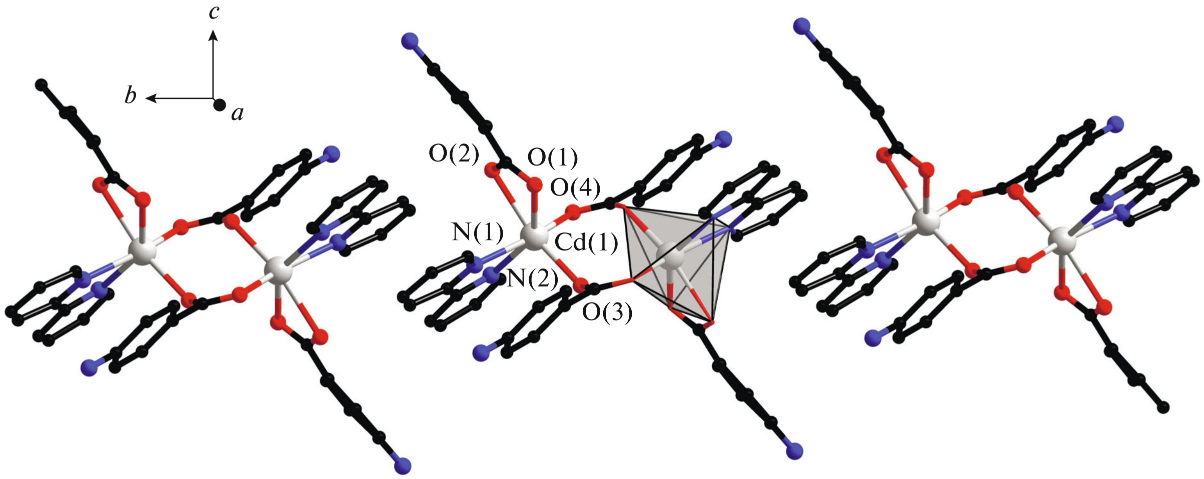


**Fig. 8.** Fragment of the crystal packing of molecules of complex **VI** (substituents at the carboxylate group and Bipy molecules involved in the formation of intramolecular π–π* interactions are shown, and hydrogen and fluorine atoms and solvate molecules are omitted).

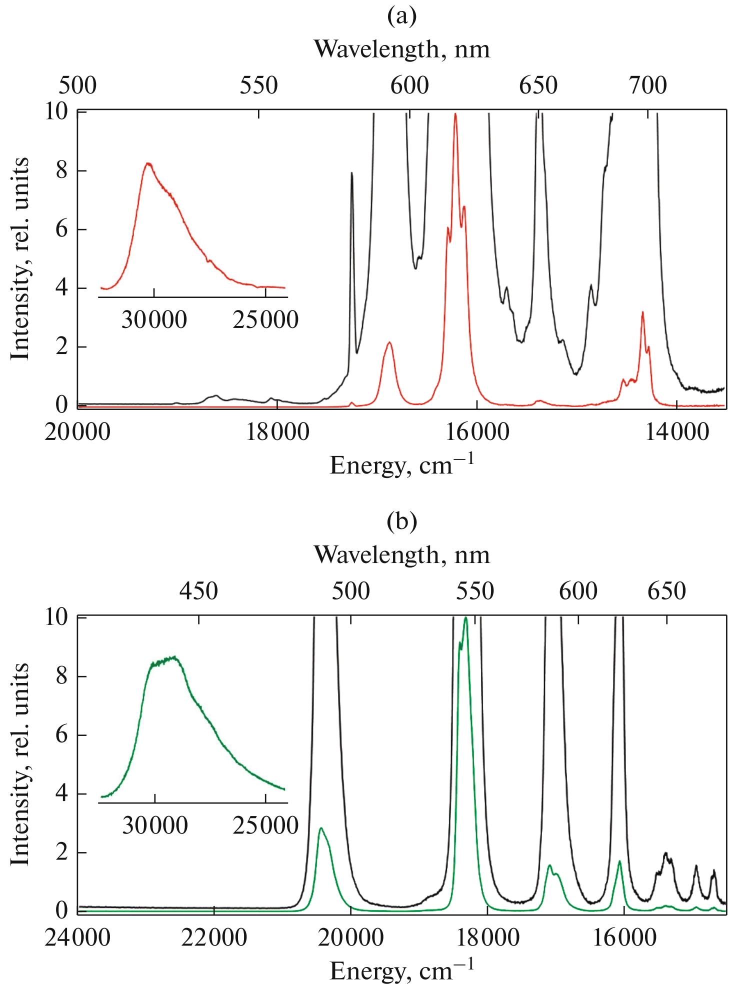


**Fig. 9.** Emission spectra of complexes (a) **II** and (b) **III** at $\lambda_{em}$ = 617 and 545 nm, respectively, at room temperature. Inset: fragment of the spectrum with the ligand-centered luminescence.

attributed to the *f*–*f* absorption of the corresponding lanthanide ions. As follows from the presented spectra, the excitation of the ions via the ligand in the case of the studied complexes is more efficient than the direct excitation of Ln$^{3+}$ and the pronounced "antenna effect" is observed.

Complexes **II** and **III** demonstrate a low quantum luminescence yield (13 and 7%, respectively). To reveal reasons for the low luminescence efficiency, complex **II** was studied in detail by the spectral and kinetic methods. The measurement of the luminescence decay showed a prolonged lifetime of the $^5D_0$ state of complex **II** (~1.8 ms), which is close to the lifetime of this state of the free europium(III) ion. The internal quantum yield was calculated by the equation $Q_{Eu}^{Eu} = \frac{\tau_{obs}}{\tau_R}$, where $\tau_{obs}$ is the characteristic lifetime of the $^5D_0$ state; $1/\tau_R = A_{rad} = A_{MD}\, n^3\, I_{tot}/I_{MD}$ is the probability of the radiation transition of Eu$^{3+}$ to the ground state; $A_{MD}$ is the radiative probability of the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$, which can be considered, in the first approximation, to be independent of the ligand environment and is equal to 14.65 s$^{-1}$; *n* is the refraction coefficient accepted by us to be 1.5; and $I_{tot}/I_{MD}$ is the ratio of the total integral luminescence intensity of the ion to the integral intensity of the $^5D_0 \rightarrow {}^7F_1$ transition [35]. The internal quantum yield of complex **II** is 81%, indicating the luminescence efficiency of the europim(III) ion in this matrix and the absence of luminescence quenching in the nearest environment of the ion, for example, the high-frequency oscillators O–H and C–H [36]. Therefore, the low absolute luminescence quantum yield is related to the inefficient energy transfer from the *d* block to the central ion. The low efficiency of energy transport is also indicated by broad bands in the wavelength range 310–440 nm in the luminescence spectra of complexes **II** and **III** (insets in Figs. 9 and 10, respectively) assigned to the radiation transitions of the *d* block to the ground state. The intensity of these bands

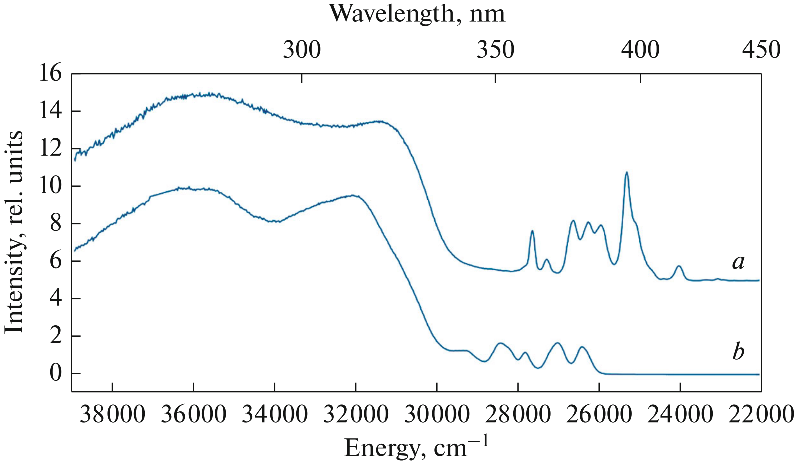


**Fig. 10.** Luminescence excitation spectra of complexes (a) **II** and (b) **III** at $\lambda_{exc}$ = 280 nm at room temperature.

with respect to the luminescence intensity of the lanthanide ion is ~2% for complex **II** and ~5% for complex **III**. A portion of the excitation energy is also lost to the nonradiative transitions of the ligands to the ground state that occur without energy transfer to the emission center.

Thus, we studied the influence of the nature of the substituent at the carboxylate group on the compositions and structures of the formed reaction products using the considered system. The heterometallic $\{Cd_2Ln_2\}$ complexes with anions of benzoic and 4-trifluoromethylbenzoic acids were isolated. The Cd complexes were obtained with anions of 4-cyanobenzoic, 4-amino-2,3,5,6-tetrafluorobenzoic, and pentafluorobenzoic acids. The synthesis conditions should be changed in order to isolate the $\{Cd_2Eu\}$ complex with the pentafluorobenzoic acid anion, which has been described previously. This indicates the possibility of the synthesis of the $\{Cd_2Ln_2\}$ complexes with anions of other acids as well. Complexes **II** and **III** are characterized by the metal-centered emission enhanced by the aromatic organic ligands. The low luminescence quantum yields for complexes **II** and **III** are related to a low-efficiency energy transfer from the ligand-antennas to the central ion.

## ACKNOWLEDGMENTS

The X-ray structure analyses (**IV** and **VI**), XRD, IR spectroscopy, and elemental analyses of the complexes were carried out on the equipment of the Center for Collective Use “Physical Methods of Investigation” at the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences) in terms of the state assignment of the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences) in the area of basic research. The structure determination for complexes **I** and **II** was supported by the Ministry of Science and Higher Education of the Russian Federation using the scientific equipment of the Center of Investigation of Structure of Molecules of the Nesmeyanov Institute of Organoelement Compounds (Russian Academy of Sciences). The authors are grateful to D.A. Makarov for help in the synthesis of compounds **IV** and **V**.

## FUNDING

Complex **I** was synthesized and studied in terms of the Russian Science Foundation (project no. 16-13-10537), the syntheses and studies of complexes **II**–**III** were supported by the Russian Foundation for Basic Research (project no. 18-29-04043), and the syntheses and studies of complexes **IV**–**VI** were conducted in terms of the state assignment of the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences) in the area of basic research. The study of the luminescence properties of complexes **II** and **III** was supported by the Russian Science Foundation (project no. 19-13-00272).

## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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*Translated by E. Yablonskaya*